KINETIC STUDIES ON THE NUCLEATION AND GROWTH OF SILICON VIA CHEMICAL VAPOUR DEPOSITION

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KINETIC STUDIES ON THE NUCLEATION AND GROWTH OF SILICON VIA CHEMICAL VAPOUR DEPOSITION

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR
IN DE WISKUNDE EN NATUURWETENSCHAPPEN
AAN DE KATHOLIEKE UNIVERSITEIT TE NIJMEGEN,
OP GEZAG VAN DE RECTOR MAGNIFICUS
PROF.DR. P.G.A.B. WIJDEVELD,
VOLGENS BESLUIT VAN HET COLLEGE VAN DECANEN
IN HET OPENBAAR TE VERDEDIGEN OP
VRIJDAG 27 FEBRUARI 1981 DES NAMIDDAGS TE 4.00 UUR

DOOR

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GEBOREN TE UDEN

Drukkerij Gema B.V. – Eindhoven

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ACKNOWLEDGEMENTS

All the experiments described in this thesis were carried out at Philips Research Laboratories, Eindhoven, The Netherlands. I would like to express my gratitude to the management of these laboratories for consenting the publication of these results in the present form.

Further I would like to thank all those who have contributed to this work in any way, in particular Mrs. C.W.T. Bulle and Mrs. G. v. Leeuwen for making the SEM and TEM photomicrographs. Mr. J. Goorissen and members of his group are thanked for valuable discussions and critical reading of the manuscript.

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The chapters II to IX have been published or are submitted to J. Electrochem. Soc., J. Crystal Growth, Recl. Trav. Chim. Pays-Bas and Philips Journal of Research.

Chapter II

The nucleation of CVD silicon on SiO_2 and Si_3N_4 substrates,

I the $\text{SiH}_4\text{-HCl-H}_2$ system at high temperatures

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Chapter IX

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CHAPTER I – INTRODUCTION

Monocrystalline silicon is of great importance in semiconductor technology in the manufacturing of bipolar and MOS (metal-oxide-semiconductor) devices and integrated circuits (IC). Thin polycrystalline silicon layers are also used extensively, for example as a gate material in MOS field effect transistors. These thin silicon layers are grown on various substrates under atmospheric or reduced total pressures by means of chemical vapour deposition (CVD technique). For this purpose a silicon-containing compound is added to a carrier gas, mostly hydrogen, and fed into the reactor, in which substrates are heated to the desired deposition temperature. The silicon-containing gases mostly used are silane (SiH_4) and the chlorosilanes (SiH_2Cl_2 , SiHCl_3 , SiCl_4).

In the growth of silicon two temperature regimes can be distinguished. At low temperatures ($T < 1000^\circ\text{C}$) the growth of silicon is limited by a chemical or surface-controlled process. Chemical reactions such as adsorption, desorption, surface diffusion and incorporation of silicon atoms into the lattice involve an activation energy. The reaction rates (r_s) of these activated processes increase exponentially with increasing temperature and can be described by the expression

$$r_s \propto \exp(-\Delta E/RT) \quad (1)$$

where ΔE is the activation energy for the process, R the gas constant and T the absolute temperature. For the growth of silicon from silane and the chlorosilanes ΔE is about 40 kcal/mole [1]. Going to higher temperature ($T > 1000^\circ\text{C}$) the surface reactions become so fast that the real rate-limiting step has to be found in the diffusion of the reactant towards the surface. If the growth rate is completely determined by gas phase diffusion only a weak temperature dependence of the growth rate of silicon can be expected as the diffusion coefficient of the reactant in the gas phase is approximately proportional to $T^{3/2}$.

$$r_d \propto T^{3/2} \quad (2)$$

In the simplest model of the growth of silicon the silicon-containing molecules are adsorbed on the surface, followed by a chemical reaction leading to silicon adatoms. According to Burton, Cabrera and Frank [2] these adatoms diffuse to steps and find a stable kink site position (terrace-ledge-kink model). In this model diffusion of adatoms is easily possible and the kink site is energetically the most attractive one because of the formation of two new silicon-silicon bonds. The growth of silicon is two-dimensional provided that repeatable atomic steps are present on the silicon surface, that the substrate temperature is high enough and that surface contaminants such as oxygen and carbon are absent [3]. On such a surface silicon growth proceeds by the lateral movement of the atomic steps. At lower temperatures the surface diffusion of silicon adatoms becomes more and more difficult and

silicon adatoms interact with each other before a stable kink site position has been reached. This results in the formation of three-dimensional nuclei between the steps, leading to polycrystalline silicon layers. On a perfect crystal face without steps, and for the growth of silicon on a foreign substrate, three-dimensional clusters can also be formed if the cohesive forces between the adatoms are stronger than the adhesive forces between adatoms and substrate atoms. If the temperature is still further decreased adatoms become almost immobile, resulting in the growth of amorphous layers. The transition between monocrystalline and polycrystalline growth and between polycrystalline and amorphous growth depends on the combination of growth temperature and growth rate, but also on the gas phase composition, as adsorption of different species on the surface could hamper surface diffusion of silicon adatoms. The purpose of the present study is to verify the general statements made above and to ascertain the rate-limiting steps between the various surface reactions.

The outline of this thesis is as follows. In chapter II and III the nucleation of silicon on silicon-oxide (SiO_2) and silicon-nitride (Si_3N_4) substrates is discussed for the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system at high and low temperatures, respectively. The experimental data are compared with existing nucleation theories and the size of the critical nucleus is calculated. In chapter IV the nucleation of silicon on SiO_2 and Si_3N_4 substrates is described for the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system and the data are compared with those described in chapters II and III.

The growth of silicon on silicon is discussed in chapter V ($\text{SiH}_4\text{-HCl-H}_2$ system), VI ($\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2\text{-HCl}$ system) and VII ($\text{SiH}_4\text{-H}_2\text{-N}_2$ system). The experimental data of these systems are mutually compared, and the outcome is a model in which the rate-determining reactions are selected between the different gas phase and surface reactions.

Chapter VIII gives a review of the experimental data described in chapters II to VII and also treats the role of surface adsorption on the growth rate. Chapter IX discusses the growth of silicon from silane in a cold wall apparatus, comparing the influence of total pressure with the influence of the addition of an inert gas. Thermodynamically this should give comparable results and differences are traced back to kinetic barriers present in the various reactions.

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CHAPTER II

THE NUCLEATION OF CVD SILICON ON SiO_2 AND Si_3N_4 SUBSTRATES

I. The SiH_4 -HCl- H_2 system at high temperatures

Abstract

The grain size in polycrystalline silicon layers is subject to various external conditions among which the initial nucleation of silicon on the substrate may play a decisive role. This article describes experiments with silicon on SiO_2 and Si_3N_4 substrates in the SiH_4 -HCl- H_2 system for temperatures between 925 ° and 1200 °C. The saturation cluster densities are determined as a function of gas phase composition and temperature and could be varied between $10^4 - 10^{11} \text{ cm}^{-2}$. The experimental results are compared with predictions of existing nucleation theories using analysis of the monomer silicon adatom concentration. In this way the nucleation can be described satisfactorily and approximate values for the size of the critical cluster can be derived.

1. Introduction

Polycrystalline silicon layers, which are grown by pyrolysis of silane, are widely used in the electronic industry, e.g. in the fabrication of MOS (Metal-Oxide-Silicon) field effect transistors and integrated circuits. The electrical properties of these layers closely depend on the size of the polysilicon grains in the layers [1]. It is not very well known how the grain size depends on the total number of nuclei and whether nucleation of new grains continues in the course of further growth.

Nucleation experiments with silicon on amorphous, polycrystalline and monocrystalline substrates have been reported [2–15], but attempts to make a more systematic study and quantitative evaluation of the results are relatively scarce. Joyce and Bradley [3] (pyrolysis of silane in vacuum) and Brooker and Unvala [4] (vacuum-evaporation) observed three-dimensional nuclei in the deposition of silicon on a monocrystalline silicon substrate. However, in a more recent article Joyce et al. [5] in collaboration with Charig and Skinner [6] showed that the initial growth becomes two-dimensional if surface contaminants such as C and O are removed by heat treatment up to 1300 °C in UHV. Nishizawa and co-workers [7] formed perfect $\{111\}$ facets on nearly $\{111\}$ oriented silicon substrates. By hydrogen reduction of SiCl_4 at 1200 °C nuclei in the form of pyramids are formed on the perfect $\{111\}$ facet, with a density depending on growth temperature and SiCl_4 concentration. Since these pyramids are distributed homogeneously on the facet and have a uniform size, the conclusion was drawn that they correspond to growth nuclei without lattice defects. Abrahams [8], Blank and Russell [9], Mercier [10], Bicknell et al. [11] and Cullen et al. [12] investigated nucleation processes of silicon on monocrystalline Al_2O_3 substrates. They observed three-dimensional islands. However, at temperatures higher than 800 °C, the Al_2O_3 surface reacts with the deposited silicon. High temperatures and relatively low silane pressures, or a silicon compound containing chlorine, favour this etching reaction.

Brown et al. [13] have reported a similar etching reaction for low silane input concentration on a monocrystalline quartz substrate. On amorphous and polycrystalline substrates, such as given by Si_3N_4 and SiO_2 , three-dimensional nuclei are observed as shown by Alexandrov et al. [14] (pyrolysis of silane on Si_3N_4 and SiO_2 substrates in vacuum) and Kamins and Cass [15] (pyrolysis of silane in an H_2 atmosphere on SiO_2 substrates). It has been shown that nucleation of silicon on a foreign substrate like SiO_2 or Si_3N_4 needs a higher supersaturation than nucleation on a clean silicon surface. This prompted studies on selective epitaxial growth of silicon on silicon slices partly coated with an oxide or nitride layer. Selective epitaxial growth of Si has been studied by Ogawa [16] on windows in Si_3N_4 layers ($\text{SiCl}_4\text{-H}_2$ system), by Ray-Choudhury [17] on windows in SiO_2 layers ($\text{SiCl}_4\text{-H}_2$ and $\text{SiH}_4\text{-H}_2$ systems), by Druminski [18] on windows in SiO_2 and Si_3N_4 layers ($\text{SiH}_4\text{-HCl-H}_2$ system) and by Sirtl and Seiter [19] on windows in SiO_2 layers ($\text{SiCl}_4\text{-Br}_2\text{-H}_2$ system). Ogawa et al. determined a critical SiCl_4 pressure for the nucleation on Si_3N_4 substrates as a function of growth temperature. In the $\text{SiH}_4\text{-H}_2$ system it was necessary to use a relatively high deposition temperature ($> 1200^\circ\text{C}$) in order to prevent growth on the SiO_2 mask. In the $\text{SiCl}_4\text{-H}_2$ system the SiO_2 was entirely removed for high SiCl_4 concentrations ($> 1200^\circ\text{C}$), while the Si_3N_4 film was not deteriorated at all for any growth condition. Sirtl and Seiter used Br_2 instead of HCl because the purity of Br_2 is much higher than that of HCl . The bromine added to the $\text{SiH}_4\text{-H}_2$ mixture is converted to HBr by the hydrogen, while thermodynamically HBr acts as HCl .

In order to obtain a more coherent picture of the nucleation of silicon as a function of gas phase composition and temperature a systematic experimental study was started to study nucleation and growth of silicon on SiO_2 and Si_3N_4 substrates. It was found that the total number of nuclei could be varied between $10^4\text{--}10^{11}\text{ cm}^{-2}$ by variation of temperature, input concentration of silane and by addition of small quantities of HCl to the carrier gas.

2. Experimental

Most of the nucleation experiments were performed in a horizontal epitaxial R.F. heated reactor, consisting of a rectangular water-cooled fused silica tube, provided with a pyrographite coated carbon susceptor covered with a thin layer of silicon. Nucleation of silicon was performed on silicon slices (2-inch wafers) covered with amorphous, 1500 Å thick LP-CVD SiO_2 and Si_3N_4 layers. The effective cross-section of the reactor was about 13 cm^2 . The gas system was provided with AFC 550 automatic flow controllers for the H_2 carrier gas and the SiH_4 source (5% SiH_4 in H_2). The flow rate of pure undiluted HCl was determined by a conventional Brooks flowmeter. Some experiments were performed in a horizontal air-cooled R.F. heated reactor. The system was also equipped with a mass flow-controller for HCl . The equipment is shown schematically in Figure 1.

Figure 1.
Schematic view of the equipment.

The carrier gas was purified of H_2O (< 1 p.p.m.) and O_2 (< 1 p.p.m.) with a A.S.M. gas purifier. Before each experiment the slices were cleaned by etching with 0.2 vol. % HCl in H_2 at about 1000°C for five minutes. After this the reactor was flushed with a stream of H_2 , while the substrate was brought to the desired nucleation temperature. During the nucleation experiment hydrogen loaded with SiH_4 and HCl was passed over the slices. To ensure stable gas flow conditions a room temperature gas velocity of about 50 cm/sec was chosen. Because of the rapid nucleation only short pulses of specific SiH_4 -HCl mixtures were often sufficient. It was found that reproducible results could be obtained with a constant HCl flow and a short additional pulse of SiH_4 gas. This procedure was followed throughout, including the experiments in which longer deposition times were used. The temperature of the slices was measured with an optical pyrometer focussed on the surface of an uncoated silicon slice; the readings were corrected for the emissivity of silicon and the absorption and reflection of the system. SEM and TEM photomicrographs were made from each slice in order to determine the morphology of the layer during the initial stage of deposition. These photomicrographs provided an easy means of measuring of the density of observed silicon islands.

3. Experimental results

3.1. Introduction

To study the initial stages of deposition of polycrystalline silicon on SiO_2 and Si_3N_4 substrates, we carried out a series of short depositions at different temperatures and different combinations of SiH_4 and HCl concentrations. For a constant substrate temperature and fixed SiH_4 and HCl concentrations the density of nuclei

was measured as a function of the time of growth. After an incubation period the density of Si clusters very quickly reached a saturation value with respect to exposure time where the exposure time is defined as the duration of the SiH_4 pulse in the mass flowcontroller. After this hardly any new clusters were formed. The existing clusters showed a very narrow size distribution. The initial nucleation took place in a short time, after which the clusters merely increased in size until coalescence occurred. Figure 2 gives a typical example for a constant ratio of SiH_4 and HCl at 1000°C and a SiO_2 substrate, where the nucleus density is plotted as a

Figure 2

The nucleus density as a function of the exposure time for $P_{\text{SiH}_4} = 8.8 \times 10^{-4}$ bar and $P_{\text{HCl}} = 4.4 \times 10^{-3}$ bar at 1000°C on a SiO_2 substrate

function of growth time. The corresponding SEM photomicrographs are shown in Figure 3. Up to 3 seconds no clusters were observed on SEM (Figure 3a) or TEM photomicrographs. In the case of TEM the detection limit is $150 \text{ \AA}$. A constant nucleus density is present between 6 and 25 seconds in which time the mean radius of the nuclei increases from 0.1 to $0.25 \text{ \mu m}$ (Figure 3b–e), after which coalescence occurs. It could be observed that the existing clusters show a narrow size distribution which supports the argument that the initial nucleation takes place in a very short period of time.

It was also observed that the time needed to reach the saturation density is shorter for a Si_3N_4 substrate than for a SiO_2 substrate, also these periods are longer for high HCl concentrations and low SiH_4 concentrations. Further these periods decrease with increasing temperature. It is found that, for the SiH_4 - HCl - H_2 system in the temperature range of 925 – 1200°C , this incubation time is of the order of 1 – 60 seconds.

Figure 3.
SEM pictures of the nucleus density for $PSiH_4 = 8.8 \times 10^{-4}$ bar and $PHCl = 4.4 \times 10^{-3}$ bar at 1000°C on a SiO_2 substrate as a function of the exposure time.

If we assume that the clusters are hemispherical, we can calculate the number of deposited atoms. With reference to Figure 3 it can be observed that the total deposited volume is small until coalescence is reached. After this the deposited volume increases linearly with time with the same slope as obtained on silicon substrates. In the latter case no incubation time is observed. This behaviour is an additional indication of the incomplete condensation in the early stages of nucleation and growth on the foreign substrates.

3.2. Nucleation on a SiO_2 substrate

The experimentally observed saturation densities of Si clusters are collected in Tables I and II. Figure 4 presents SEM photomicrographs for different input concentrations of SiH_4 and a SiO_2 substrate at 1000°C .

In Figure 5 the saturation density of Si clusters is plotted as a function of temperature for different input concentrations of SiH_4 and HCl on a SiO_2 substrate. It is apparent that the introduction of HCl reduces the number of nuclei and increases the temperature dependence of the formation process. It is also observed, but not shown here, that the nucleus density decreases at temperatures below 925°C . In a later publication this feature will be discussed. Further it was measured that at 1200°C the SiO_2 surface partly deteriorates when relatively low input concentrations of SiH_4 and long exposure times are used. It will be shown in the discussion that between 925° and 1200°C the experimental data on the saturation density of nuclei (N_s) as a function of temperature and gas phase compositions can be described by:

$$N_s = A \left\{ \frac{B^\circ P_{\text{SiH}_4}}{C^\circ P_{\text{HCl}}^2 + 1} \right\}^a \exp \frac{E}{kT},$$

where $C^\circ = 6 \times 10^6$ when P_{SiH_4} and P_{HCl} are expressed in bars. The exponent a and the activation energy E still depend on gas phase composition. In Figure 6 the saturation density of clusters at 1000°C is plotted as a function of $P_{\text{SiH}_4}/(6 \times 10^6 P_{\text{HCl}}^2 + 1)$. For SiH_4 the equilibrium vapour pressure (above which decomposition of SiH_4 can be expected) is $\sim 10^{-6}$ bar [20]. This value is nearly independent of temperature in the range of interest and in good agreement with the results given in Figure 6. From experiments as given in Figure 5 ($\log N_s$ vs $1/T$) for temperatures above 925°C an apparent activation energy can be obtained from the Arrhenius plot. The experimental values of E are given in Figure 7 as a function of the gas phase composition, the latter expressed as $P_{\text{SiH}_4}/(6 \times 10^6 P_{\text{HCl}}^2 + 1)$.

It is observed that at high supersaturations the activation energy comes to a limiting value of 1.9 eV. At lower supersaturations the activation energy increases, this behaviour is accompanied by a strong decrease in the number of nuclei.

PHCl (bar)	PSiH ₄ (bar)	1200 °C			1100 °C			1000 °C			925 °C		
		t (sec)	SiO ₂	Si ₃ N ₄	t (sec)	SiO ₂	Si ₃ N ₄	t (sec)	SiO ₂	Si ₃ N ₄	t (sec)	SiO ₂	Si ₃ N ₄
—	2.8x10 ⁻⁴	5	—	1.7x10 ⁹	8	—	2.7x10 ⁹	15	3x10 ⁹	7x10 ⁹	20	1.1x10 ⁹	1.6x10 ¹⁰
—	7.3x10 ⁻⁴	5	4.7x10 ⁸	2.2x10 ⁹	5	1.4x10 ⁹	3.9x10 ⁹	5	6x10 ⁹	1x10 ¹⁰	5	8x10 ⁹	2x10 ¹⁰
1.8x10 ⁻³	3.7x10 ⁻⁴	5	3.3x10 ⁶	—	10	1.3x10 ⁷	6.8x10 ⁸	15	1.2x10 ⁸	1x10 ⁹	30	3.2x10 ⁸	1.0x10 ⁸
1.8x10 ⁻³	7.3x10 ⁻⁴	5	2.2x10 ⁷	2.5x10 ⁸	5	6.1x10 ⁷	1.4x10 ⁹	5	3.9x10 ⁸	2.2x10 ⁹	5	1.5x10 ⁹	3.5x10 ⁹
1.8x10 ⁻³	2.6x10 ⁻³	3	6.7x10 ⁷	3.1x10 ⁸	3	2.8x10 ⁸	7x10 ⁸	5	8.5x10 ⁸	*	10	*	*
3.6x10 ⁻³	2.8x10 ⁻⁴	20	6x10 ³	1.0x10 ⁸	30	1.6x10 ⁴	1.0x10 ⁷	60	o	o	120	3x10 ³	o
3.6x10 ⁻³	7.3x10 ⁻⁴	5	3x10 ⁵	5.4x10 ⁷	5	9x10 ⁵	5.3x10 ⁸	5	7x10 ⁷	1.3x10 ⁹	15	7.2x10 ⁸	1.8x10 ⁹
3.6x10 ⁻³	1.4x10 ⁻³	5	1.4x10 ⁶	2.1x10 ⁸	10	7.9x10 ⁶	*	15	2.9x10 ⁸	*	25	9.5x10 ⁸	*
3.6x10 ⁻³	2.6x10 ⁻³	3	3.1x10 ⁷	1.1x10 ⁸	5	6.5x10 ⁷	*	8	6.1x10 ⁸	—	13	1.9x10 ⁹	*
5.5x10 ⁻³	7.3x10 ⁻⁴	5	8x10 ⁴	2.3x10 ⁷	30	2x10 ⁴	1x10 ⁸	30	3.0x10 ⁷	6.0x10 ⁸	30	2.5x10 ⁸	5x10 ⁸
7.2x10 ⁻³	7.3x10 ⁻⁴	5	3x10 ³	5.4x10 ⁷	60	8x10 ³	1.5x10 ⁷	30	9x10 ⁴	3x10 ⁶	240	2.4x10 ⁶	
7.2x10 ⁻³	1.4x10 ⁻³	5	6x10 ³	—	10	1.1x10 ⁵	1.4x10 ⁸	15	1.4x10 ⁷	5x10 ⁸	30	3.9x10 ⁸	1.9x10 ⁹

TABLE I

Saturation nucleus density (cm⁻²) for the SiH₄-HCl-H₂ system on SiO₂ and Si₃N₄ substrates between 1200 and 925 °C (water-cooled R.F. Reactor): * means coalescence takes place and o means no nucleation is observed. t is the exposure time.

P _{HCl} (bar)	P _{SiH₄} (bar)	t (sec)	substrate	
			SiO ₂	SiH ₄
—	1x10 ⁻⁵	370		2.7x10 ⁹
—	9x10 ⁻⁵	35	6.6x10 ⁸	1.7x10 ¹⁰
—	2.2x10 ⁻⁴	15	1.4x10 ⁹	1.4x10 ¹⁰ (*)
—	4.4x10 ⁻⁴	5	5.0x10 ⁹	2.8x10 ¹⁰
—	8.8x10 ⁻⁴	3	6.5x10 ⁹	4.0x10 ¹⁰
—	1.7x10 ⁻³	3	8x10 ⁹	*
4.4x10 ⁻⁴	8.8x10 ⁻⁴	5	2.5x10 ⁹	1.1x10 ¹⁰ (*)
8.8x10 ⁻⁴	8.8x10 ⁻⁴	5	1.6x10 ⁹	9.1x10 ⁹ (*)
1.3x10 ⁻³	8.8x10 ⁻⁴	5	8.0x10 ⁸	7.1x10 ⁹
2.2x10 ⁻³	8.8x10 ⁻⁴	5	3.8x10 ⁸	5.0x10 ⁹
4.4x10 ⁻³	8.8x10 ⁻⁴	10	8.0x10 ⁷	1.1x10 ⁹
6.6x10 ⁻³	8.8x10 ⁻⁴	30	9x10 ⁵	4.0x10 ⁷

TABLE II

Saturation nucleus densities (cm⁻²) for the SiH₄-HCl-H₂ system (air-cooled R F reactor) on SiO₂ and Si₃N₄ substrates at 1000 °C. t is the exposure time and * means that coalescence occurs.

3.3 Nucleation on a Si₃N₄ substrate, differences compared with a SiO₂ substrate

Tables I and II also present experimental data for the saturation densities of stable clusters in the SiH₄-HCl-H₂ system for Si₃N₄ substrates. From the Tables it can be observed that the saturation density of Si clusters is always larger for a Si₃N₄ substrate than for a SiO₂ substrate (other things being equal). This means that coalescence takes place much earlier on a Si₃N₄ substrate than on a SiO₂ substrate. In spite of the rapid nucleation and coalescence we were able to observe the saturation cluster density by choosing an appropriate exposure time. Figure 8 gives a plot of the saturation nucleus density for two different mixtures of SiH₄ and HCl as a function of temperature for both substrates. In the case of the Si₃N₄ substrate, too, the addition of HCl reduces the number of clusters and increases the temperature dependence of the saturation density, though to a smaller degree than for the SiO₂ substrate. The experimentally found expression for the saturation nucleus density (eq. 1) as a function of gas phase composition for the SiO₂ substrate can also be used for a Si₃N₄ substrate between 1200 – 925 °C, as will be shown in the discussion.

The nucleus density as a function of $P_{SiH_4}/(6 \times 10^6 P_{HCl}^2 + 1)$ for a Si₃N₄ substrate at 1000 °C is plotted in Figure 6. For temperatures above 925 °C an apparent

$X = 0 \quad t = 5 \text{ sec.}$

$X = 2.5 \quad t = 5 \text{ sec.}$

$X = 5.0 \quad t = 10 \text{ sec.}$

$X = 7.5 \quad t = 30 \text{ sec.}$

Figure 4.

SEM pictures of the nucleus densities for $PSiH_4 = 8.8 \times 10^{-4}$ bar and $PHCl = X \cdot PSiH_4$ (where $X = 0; 2.5; 5.0$ and 7.5) at 1000°C on a SiO_2 substrate. t is the exposure time.

Figure 5.

The saturation nucleus density as a function of the reciprocal temperature for different mixtures of SiH_4 and HCl on SiO_2 substrates.

Figure 6.

The saturation nucleus density of Si clusters on a SiO_2 and Si_3N_4 substrate at 1000°C for different input concentrations of SiH_4 and HCl (+, ⊕ only SiH_4 ; ○, ● mixture of SiH_4 and HCl).

Figure 7.

The relation between the activation energy for cluster formation and the input concentrations of SiH_4 and HCl for SiO_2 and Si_3N_4 substrates.

Figure 8.

The saturation cluster density of Si clusters as a function of temperature for two SiH_4 - HCl mixtures on SiO_2 and Si_3N_4 substrates ($\triangle, \blacktriangle P_{\text{SiH}_4} = 7.3 \times 10^{-4}$ bar and $P_{\text{HCl}} = 1.8 \times 10^{-3}$ bar $\square, \blacksquare P_{\text{SiH}_4} = 1.4 \times 10^{-3}$ bar and $P_{\text{HCl}} = 7.2 \times 10^{-3}$ bar

activation energy can be obtained from the Arrhenius plot ($\log N_s$ vs $1/T$) The experimental values of E for Si_3N_4 substrates are included in Figure 7 which also gives E values for SiO_2 substrates It is observed that with increasing supersaturation the activation energy decreases and this decrease is stronger for the SiO_2 substrate than for the Si_3N_4 substrate

4 Discussion

4.1 Nucleation theory

The growth of thin films on a substrate starts with the formation of small cap shaped clusters if the cohesive forces between the atoms in the cluster are greater than the adhesive forces between adsorbed atoms (adatoms) and the substrate The formation of the small clusters begins with the arrival of atoms or molecules from the vapour After adsorption, and perhaps chemical reaction, adatoms are formed on the surface These adatoms diffuse across the surface where, through statistical fluctuations in local concentration, they form small clusters of atoms which grow and decay by addition or loss of single atoms If the cluster exceeds a critical size (supercritical cluster) further growth becomes energetically favourable Clusters that are smaller than the critical size (subcritical) can decay

In the chemical thermodynamic approach we can write for the radius r^* of the critical cluster

$$r^* = \frac{2\delta v}{kT \ln p/p_e} \quad (2)$$

where δ is the surface free energy which is taken isotropic, v is the atomic volume and $kT \ln p/p_e$ is the supersaturation function giving the gain in free energy on crystallisation Using the experimental results we can give an estimation of r^* In Figure 6 the saturation density of Si clusters is plotted as a function of the gas phase composition This gives us the opportunity to calculate the supersaturation p/p_e , where $p_e \sim 10^{-6}$ bar is the equilibrium vapour pressure of SiH_4 Using equation (2) with $v = 2 \times 10^{-21} \text{ cm}^3$ and $\delta = 10^{-4} \text{ J/cm}^2$ [21] gives $r = 1.5 \text{ nm}$ for $p/p_e = 5$ and $r = 0.4 \text{ nm}$ for $p/p_e = 10^3$ This means that for high supersaturation the radius of the critical cluster approaches molecular dimensions, but in that case the thermodynamic interpretation of surface energies is no longer justified These difficulties are avoided when the nucleation process is treated by writing the partition function and potential energies for the adatoms and cluster as is done in the atomistic nucleation theory Walton [22], in an approximate treatment, considered the potential energy difference E_1 between 1 adatoms and a cluster of 1 atoms For the reaction on the surface

he found for the density of critical clusters n_1 if no stable clusters are present and $n_1 \gg n_1$,

$$\frac{n_1}{n_0} = C_1 \left(\frac{n_1}{n_0} \right)^1 \exp \frac{E_1}{kT} \quad (3)$$

where n_1 is the concentration of adatoms, n_0 is the number of surface sites, C_1 is a statistical weighting factor and E_1 is the heat of formation of the cluster consisting of 1 atoms. Equation (3) is generally used in the atomistic nucleation theories to find a general expression for the saturation density of stable clusters

The rate of formation of adatoms as a function of exposure time t and the incoming flux J_1 can be given by

$$\frac{dn_1}{dt} = J_1 - \frac{n_1}{\tau_{ev}} - \frac{n_1}{\tau_r} - \frac{n_1}{\tau_g} \quad (4)$$

where τ_{ev} is the mean residence time before evaporation, τ_r is the τ value if adatoms are removed by chemical reaction and τ_g is the τ value for the capture of adatoms by stable clusters. In the case of complete condensation the τ_{ev} and τ_r values are supposed to be so great that no desorption or etching of adatoms occurs. The adatom concentration increases with time until the diffusional flux has grown sufficiently to substantially reduce the value of n_1 . Evaporation or reaction come into play for incomplete condensation and the smallest τ values in the series determines the value of τ_s and therefore the value of n_1 giving

$$n_1 = J_1 \tau_s \text{ for } t \gg \tau_s \quad (5)$$

The surface concentration n_1 is attained before nucleation starts. As nucleation proceeds τ_s will decrease because adatoms also disappear by incorporation in stable clusters. Between the clusters the value of n_1 eventually drops below the initial steady state concentration, whereupon the production of new nuclei ceases. The maximum cluster density is one of the easily measurable quantities when the nucleation rate is too high to be measured. Following Venables [23] we can write for the formation rate of stable clusters

$$\frac{dn_x}{dt} = U_1 - U_c - U_m \quad (6)$$

where n_x is the density of stable clusters at the time t , U_1 is the nucleation rate and U_c and U_m are the rates at which stable clusters are lost due to coalescence and cluster mobility, respectively. In the $\text{SiH}_4\text{-HCl-H}_2$ system at temperatures between 925 °C and 1200 °C, n_x reaches a saturation value N_s long before coalescence

occurs (see Figure 2), hence $U_c \ll U_m$. Stowell's analysis of data on the nucleation of Au and Ag on alkali halide substrates shows that cluster mobility becomes important at temperatures above 400 °C [24]. Lewis [25] assumes that the detachment of peripheral atoms of hemispherical clusters determines the activation energy of the mobility process. In that case the activation energy for cluster diffusion is independent of cluster size, while the actual cluster mobility strongly depends on the size, viz, via a pre exponential entropy term. Masson et al [26] measured relatively large diffusion coefficients, which are probably caused by non-epitaxial orientation of the clusters. According to Behrndt [27] liquid nuclei, with consequently a relatively high surface mobility, are also possible at temperatures which are much lower than the melting point of the condensate. For the case where all stable clusters are mobile, at least initially until n_x saturates, Venables gives an expression describing the maximum cluster density N_s for incomplete condensation

$$\frac{N_s}{n_0} \cong \left(\frac{J}{n_0 \nu} \right)^{\frac{1+1}{2}} \exp \frac{(1+1)E_a + E_l + E_m - E_d}{2kT} \quad (7)$$

where E_a is the activation energy of desorption, E_x the activation energy for surface diffusion of mobile clusters, E_d the activation energy for surface diffusion of adatoms, n_0 the number of surface sites and ν the adatom vibration frequency, the other parameters have already been defined (eqs 3 and 5).

In the $\text{SiH}_4\text{-HCl-H}_2$ system there is an incubation period for the formation of a significant number of stable clusters and a non-linear increase of the deposited volume in the early state of growth (see section 3.1) which supports the arguments for incomplete condensation. The relation deduced by Venables (eq 7) can be compared with the experimentally found supersaturation with the help of eq 5 and the calculated adatom concentration (n_1) as given in eq A-16 of the appendix.

4.2 Adatom concentration and surface coverages

To arrive at an expression determining the adatom concentrations of Si on the substrates the main processes responsible for formation and removal are summarized in appendix A. It is concluded that the following steps may be important:

- a diffusion of silane towards the surface,
- b adsorption of silane, diffusion across the surface and chemical reaction (formation of adatoms),
- c etching reactions of HCl, H_2 and SiO_2 with silicon adatoms,
- d desorption of reaction products,
- e diffusion of reaction products away from the surface.

Since the value of the diffusion coefficient in the gas phase is rather insensitive to temperature (ideal gas $D \propto T^{3/2}$) the processes a and e will have a low activation energy.

In order to obtain realistic information about the concentration of adatoms and free surface sites some additional information may be helpful

- i. From nucleation experiments in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system at temperatures between 900° and 1100°C on SiO_2 and Si_3N_4 substrates [28] it is found that hydrogen strongly influences nucleation on SiO_2 substrates. In the case of Si_3N_4 substrates there is hardly any difference in saturation density between the results in H_2 or N_2 ambient
- ii. The saturation cluster density in the $\text{SiH}_2\text{Cl}_2\text{-N}_2$ system is equal for both substrates at temperatures between 925°C and 1100°C
- iii. From nucleation experiments in the $\text{SiH}_4\text{-H}_2$ system at temperatures between 900 and 600°C [28] we know that for SiO_2 substrates the saturation density decreases with decreasing temperature, whereas Si_3N_4 substrates show the opposite behaviour. The observations mentioned above suggest that the adsorption of hydrogen has a great influence on the nucleation kinetics, especially for the SiO_2 substrates. Under normal operating conditions ($925^\circ - 1200^\circ\text{C}$, $P_{\text{H}_2} \cong 1$ bar) it is thus likely that hydrogen adsorption will occur, but it is only below 900°C that hydrogen adsorption will influence nucleation on SiO_2 substrates by limiting the number of surface sites where SiH_4 adsorption may occur.

For the silicon adatom concentration on a SiO_2 substrate equation A-16 can be used. If hydrogen adsorption does not limit the number of surface sites and with $n_0 \gg [\text{SiH}_4^*], [\text{Cl}^*]$ one obtains

$$\frac{n_1}{n_0} = \frac{K_1 k_2 P_{\text{SiH}_4}}{(k_{-2} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_9)} \quad (8)$$

For nucleation on Si_3N_4 substrates also eq. A-16 can be used. In that case k_9 can be disregarded on thermodynamic grounds as reaction of Si with Si_3N_4 will be slow, also hydrogen adsorption is not rate-limiting. It is observed, moreover, that the number of stable clusters saturates at high concentrations and $[\text{SiH}_4^*]$ cannot be neglected. Therefore n_1 can be given as

$$\frac{n_1}{n_0} = \frac{K_1 k_2 P_{\text{SiH}_4}}{(k_{-2} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2) (1 + K_1 P_{\text{SiH}_4})} \quad (9)$$

For $P_{\text{HCl}} = 0$ and $K_1 P_{\text{SiH}_4} < 1$ the temperature dependence of n_1 is determined by $K_1 K_2$ which, in the temperature region of interest, is nearly independent of temperature. According to the JANAF Tables [20], $d(\ln K_p)/d(1/T) \cong 0$ around 1000°C .

4.3 Interpretation of results

In this section we compare the expression obtained by Venables (eq. 7) with the

results of the nucleation experiments in the $\text{SiH}_4\text{-HCl-H}_2$ system on SiO_2 and Si_3N_4 substrates in the temperature region of $925^\circ - 1200^\circ\text{C}$. Equation 7 can be modified by introducing $n_1 = J_1 \tau_s$, where n_1 is given by eq. (8) or (9) and τ_s is defined as $\tau_s = \nu^{-1} \exp E_a/kT$, E_a being the enthalpy of desorption and ν the adatom vibration frequency. The modified expression (eq. 7) then reads for SiO_2 substrates:

$$\frac{N_s}{n_0} \cong \left\{ \frac{K_1 k_2 P_{\text{SiH}_4}}{(k_{-2} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_9)} \right\}^{\frac{i+1}{2}} \exp \frac{E_i + E_m - E_d}{2kT} \quad (10)$$

It should be realized that the expression between curly brackets already presents a simplified version of a more complex expression. A possible activation energy from this relation has to be added to the exponential term. This, however, depends on which of the terms in the denominator prevails and whether HCl is present or not. In order to put eq. (10) into a form that permits evaluation of the experimental data we can write

$$N_s = A \left\{ \frac{B P_{\text{SiH}_4}}{C P_{\text{HCl}}^2 + 1} \right\}^{\frac{i+1}{2}} \exp \frac{E_i + E_m - E_d}{2kT} \quad (11)$$

in which A is a constant (equal to n_0)

$$B = \frac{K_1 k_2}{(k_{-2} P_{\text{H}_2}^2 + k_9)} = B^0 \exp \frac{-E_{r,1}}{kT} \quad (12)$$

$$C = \frac{K_6}{(k_{-2} P_{\text{H}_2}^2 + k_9)} = C^0 \exp \frac{-E_{r,2}}{kT} \quad (13)$$

The values of i , B and C thus depend on temperature and gas phase composition and will be different for nucleation on different substrates. For the SiO_2 substrate the constants A, B^0 and C^0 can be calculated as follows. From Figure 6 we know that, for pure SiH_4 , N_s is proportional to P_{SiH_4} . This means that $(i+1)/2 = 1$ for P_{SiH_4} ranging from 9×10^{-5} to 1.7×10^{-3} bar. Making use of the corresponding values of E (Figure 7) we find $AB^0 = 2 \times 10^5$. The mixture $P_{\text{SiH}_4} = 2.6 \times 10^{-3}$ bar and $P_{\text{HCl}} = 1.8 \times 10^{-3}$ bar gives a cluster density higher than the corresponding one for the lowest pure SiH_4 concentration. This leads to the conclusion that $(i+1)/2 = 1$ for this $\text{SiH}_4\text{-HCl}$ mixture as well. Inserting $AB^0 = 2 \times 10^5$, $(i+1)/2 = 1$ and $E = 1.9$ eV (the activation energy for this special $\text{SiH}_4\text{-HCl}$ mixture) in eq. (11) we obtain $C^0 = 6 \times 10^6$. The linear relationship $(i+1)/2 = 1$ between N_s and P_{SiH_4} for silane pressures between 9×10^{-5} and 1.7×10^{-3} bar leads to a critical cluster size of $i=1$. In

that case ($P_{\text{HCl}} = 0$) the experimentally found activation energy for cluster formation (E) becomes

$$E = \frac{1}{2}(E_i + E_m - E_d - 2E_{r,1}) = 1.9 \text{ eV} \quad (14)$$

As to the value of E_i , a cluster can be called stable when half of the possible bonds are formed between atoms in the cluster and between cluster and substrate [29]. For silicon, therefore two bonds have to be realized per silicon atom. In order to arrive at a relation between the binding energy E_i of a cluster of i atoms on SiO_2 and the Si-Si bond energy (E_b) a triangular lattice of oxygen atoms on the substrate is shown schematically in Figure 9. For amorphous SiO_2 a triangular lattice is acceptable because short-range order (regions of crystallinity 10 – 100 Å in size) may exist [30]. Amorphous SiO_2 forms a random three-dimensional network where each silicon atom is tetrahedrally surrounded by four oxygen atoms and each oxygen atom is bonded to two silicon atoms with an average Si-O distance of 1.62 Å, an average O-O distance of 2.65 Å and an average Si-Si distance of 3.00 Å [31]. At the surface, however, a silicon atom can be bonded in three different ways to the oxygen lattice. In the first place a Si atom can have a single bond to an oxygen atom (Si-adatom). Further a double and a triple bonding of a Si atom with the oxygen lattice is possible. The triple bonding, which is the most stable one, can

Figure 9.

Binding energies of atoms and clusters on a nearest-neighbour bond model of nucleation on a triangular oxygen lattice: a. single bonded, b. double bonded, c. triple bonded, d. critical cluster size $i = 1$, e. critical cluster size $i = 2$, f. critical cluster size $i = 3$.

be seen in Figure 9 ('c'). In this simple model a Si-Si bond is formed only when a Si atom ('a' in Figure 9) on the surface forms a bond with the triple-bonded Si atom (giving 'd' in Figure 9). In this case the critical cluster consists of one atom only (the triple-bonded Si atom belongs to the SiO_2 lattice). This model can be extended to clusters containing more than two Si atoms ('e' and 'f' in Figure 9 for $i = 2$ and $i = 3$), so that for the critical cluster it leads to an energy gain over the binding energy of one Si-Si bond

$$E_i \cong iE_{\text{Si-Si}} \quad (15)$$

For $i = 1$ and $E_{\text{Si-Si}} = 2 \text{ eV}$ [32] eq. (14) leads to

$$E_m - E_d - 2E_{r,1} = 1.8 \text{ eV} \quad (16)$$

If we compare the results for the Si_3N_4 substrate and the SiO_2 substrate in the temperature region $925^\circ - 1200^\circ\text{C}$ we see that the composition of the gas phase where nucleation is no longer observed (Figure 6) is almost the same for both substrates. This justifies the use of equation (11) for the saturation density on Si_3N_4 also. From Figure 7 we know that E is nearly constant at silane pressures between 5×10^{-5} and 10^{-3} bar. This means that the cluster size is constant in this region. From Figure 6 ($\log N_s$ vs $P_{\text{SiH}_4 \text{ eff}}$) it can be observed that in this particular region the tangent changes from 1 to $\frac{1}{2}$. At high supersaturation N_s probably saturates because the concentration of free surface sites is a function of the SiH_4 pressure (eq. 9). Thus, at silane pressures between 5×10^{-5} and 10^{-3} bar we have $i = 1$ and in that case E becomes

$$E = \frac{1}{2}(E_1 + E_m - E_d - 2E_{r,1}) = 1.2 \text{ eV} \quad (17)$$

With $E_{\text{Si-Si}} = 2 \text{ eV}$ [32] this gives

$$E_m - E_d - 2E_{r,1} = 0.4 \text{ eV} \quad (18)$$

Introducing $E_{r,1} \cong 0 \text{ eV}$ for Si_3N_4 (as discussed in section 4.2) into eq. (18) gives $E_m - E_d = 0.4 \text{ eV}$. Lewis expects $E_m \geq 2E_d$ [25], which then should give $E_m \cong 0.8 \text{ eV}$ and $E_d \cong 0.4 \text{ eV}$ as maximum values.

Coming back to the nucleation on SiO_2 substrates, we note that eq. (16) with $E_m - E_d = 0.4 \text{ eV}$, as obtained above, leads to $E_{r,1} = -0.7 \text{ eV}$. The difference between $E_{r,1}$ for SiO_2 (-0.7 eV) and $E_{r,1}$ for Si_3N_4 ($E_{r,1} \cong 0 \text{ eV}$) can be explained as being due to reactions with the substrate and the formation of SiO (k_9 in eq. 8), but for Si_3N_4 substrates this reaction is absent. This means that k_9 has an activation energy of 0.7 eV , and the formation of SiO is promoted by the presence of hydrogen. The reaction between a silicon adatom and the SiO_2 substrate can be described as

In this way the coverage of the substrate with the first silicon layer is impeded, the more so the higher the temperature, as found experimentally for SiO_2 substrates in hydrogen, where at 1200°C the SiO_2 surface partly deteriorates. If $6 \times 10^6 P_{\text{HCl}}^2 > 1$, the activation energy for cluster formation becomes

$$E = \frac{1}{2} [E_i + E_m - E_d - (i+1)(E_{r,1} - E_{r,2})]. \quad (20)$$

In the experiment on SiO_2 with $P_{\text{SiH}_4} = 2.6 \times 10^{-3}$ bar and $P_{\text{HCl}} = 1.8 \times 10^{-3}$ bar, where $i=1$ as discussed before, the activation energy equals that of pure silane (Figure 7). From this it can be expected that $E_{r,2}$ is small and can be disregarded in the first approximation. For low supersaturations the activation energy increases because of the increasing value of i and E_i . The highest value found for E_i of 6.2 eV with $E_m - E_d \cong 0.4$ eV, $E_{r,2} \cong 0$ and $E_{r,1} \cong -0.7$ eV and using eq. (15), gives a critical cluster with $i=4$. For Si_3N_4 the highest E value is $E \cong 2$ eV and a similar approach then leads to a critical cluster of $i = 2$.

5. Conclusions

In an attempt to understand and be able to monitor the crystallite size in polycrystalline silicon layers we have studied the nucleation of silicon on various substrates. Experiments on the nucleation of Si on SiO_2 and Si_3N_4 substrates are reported for the SiH_4 -HCl- H_2 system in the temperature range of $925^\circ - 1200^\circ\text{C}$. The differences and conformities between the two substrates are discussed. It is observed that the saturation nucleus density increases with decreasing temperature for both substrates. This effect, which is stronger for the SiO_2 than for the Si_3N_4 substrate, is attributed to the size and the formation energy of the initial critical cluster and to the reaction with the substrate, especially in the case of SiO_2 in which the H_2 ambient plays an important role. The introduction of HCl strongly reduces the nucleus density, resulting in an increased grain size in the polycrystalline material. The experimental results can be explained by the application of an expression as obtained by Venables, together with an analysis of the silicon adatom concentration on the substrate as a function of gas phase composition. It is found that the number of silicon atoms in the critical cluster varies between 1 and approximately 4 in the experimental range under discussion. It will be obvious that the values of the activation energies are open to criticism, because slightly different assumptions could change the picture. However, the impression remains that nucleation of silicon on SiO_2 and Si_3N_4 substrates at temperatures higher than 900°C can be explained semi-quantitatively on the basis of existing statistical nucleation theory supplemented by arguments of a chemical and kinetic nature.

Acknowledgements

The authors wish to thank Mrs C.W.T. Bulle and Mrs G. v. Leeuwen for the SEM and TEM photomicrographes and Mr. C.F.W. Flinsenberg for making available his water-cooled R.F. reactor.

APPENDIX: CALCULATION OF ADATOM CONCENTRATIONS

The main process responsible for nucleation and growth of silicon on a monocrystalline silicon substrate in the SiH_4 -HCl- H_2 system is described by Bloem and Giling [33]. Nucleation of silicon on a SiO_2 substrate will differ from that on a monocrystalline silicon substrate, but the processes which take place are approximately of the same nature.

- a. Supply of SiH_4 by means of gas phase diffusion:

$\text{SiH}_4 (b)$ is the concentration of SiH_4 in the bulk of the gas phase and $\text{SiH}_4 (g)$ the concentration of SiH_4 near the surface.

- b. Adsorption of SiH_4 on a free site on the surface (denoted by *):

- c. The reaction of SiH_4 at the surface:

- d. Adsorption of hydrogen, chlorine and SiCl_2 :

- e. Etching of adatoms by chlorine:

- f Growth of silicon by diffusion of Si adatoms on the surface and incorporation into a stable cluster

- g Evaporation of silicon adatoms

- h Reaction of Si adatoms with the substrate

- i Reaction of SiH₄ in the gas phase

Formation of silicon-containing compounds other than SiCl₂, such as SiH₂Cl₂, SiHCl₃ and SiCl₄, can be disregarded on the grounds of thermochemical data available in literature [34, 35]. In a steady-state situation the Si* and SiH₄* concentrations are constant, given by

$$n_1 = [\text{Si}^*] = \frac{k_1 [\text{SiH}_4^*]}{k_{-2} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_7 + k_8 + k_9} \quad \text{A-12}$$

$$[\text{SiH}_4^*] = \frac{k_1 P_{\text{SiH}_4 \text{ (g)}} [*] + k_{-2} n_1 P_{\text{H}_2}^2}{k_2 + k_{-1}} \quad \text{A-13}$$

In A-13 the second term in the numerator can be expected to be small compared with the first term, in which case

$$n_1 = \frac{k_1 k_2 [*] P_{\text{SiH}_4 \text{ (g)}}}{(k_2 + k_{-1}) (k_{-2} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_7 + k_8 + k_9)} \quad \text{A-14}$$

For nucleation of Si on a SiO₂ substrate in the SiH₄-HCl-H₂ system, several approximations can be made. We have seen that, after an incubation period, the nucleus density very quickly reached a saturation value. On the basis of these experiments it will be assumed that the time taken to attain the population of adatoms is short, so that n₁ reaches a constant value before nucleation occurs. Then

k_7 can be omitted until nucleation takes place. The existence of an incubation period further means that the reaction is surface-controlled and the greater part of the silane will desorb before reacting ($k_{-1} > k_2$). Because of the surface-controlled reaction, and provided gas phase nucleation can be left out of account, we can put $P_{SiH_4}(g) = P_{SiH_4}(s)$ during the induction period ($k_1 < k_a$). The presence of a carrier gas prevents evaporation ($k_8 < k_{-2} P_{H_2}^2$). The desorption of $SiCl_2$ in the initial stage before nucleation is not expected to be rate limiting, and therefore the surface coverage of $SiCl_2$ will be low and can be disregarded. In that case we can write for the concentration of free surface sites

$$[*] = n_0 - [SiH_4*] - [H*] - [Cl*] - n_1$$

where n_0 is the total number of sites at the surface. In adsorption equilibrium for every species an expression can be found as for $[H*]$, where eq. (A-4) leads to

$$[H*] = K_3 P_{H_2}^{1/2} [*], \quad K_3 = k_3/k_{-3}$$

For $n_1 \ll n_0$ this gives

$$[*] = \frac{n_0}{1 + K_1 P_{SiH_4} + K_3 P_{H_2}^{1/2} + K_4 P_{HCl}/P_{H_2}^{1/2}} \quad A-15$$

With the above approximation the steady state Si adatom concentration becomes

$$\frac{n_1}{n_0} = \frac{K_1 k_2 P_{SiH_4}}{(k_{-2} P_{H_2}^2 + k_6 P_{HCl}^2 + k_9)} \cdot \frac{1}{(1 + K_1 P_{SiH_4} + K_3 P_{H_2}^{1/2} + \frac{K_4 P_{HCl}}{P_{H_2}^{1/2}})} \quad A-16$$

In this equation the formation of silicon adatoms is governed by the equilibrium adsorption of SiH_4 (K_1), the rate of reaction of SiH_4 (k_2) and the total amount of free surface sites (as given by eq. A-15), divided by the ways in which adatoms are removed from the surface in the initial stages before the actual nucleation starts, i.e. etching by HCl and H_2 and reaction with the SiO_2 substrate (k_9)

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CHAPTER III

THE NUCLEATION OF CVD SILICON ON SiO_2 AND Si_3N_4 SUBSTRATES

III The SiH_4 -HCl- H_2 system at low temperatures

Abstract

The growth of polycrystalline silicon layers on SiO_2 and Si_3N_4 substrates can be hampered in the early stages of growth by the presence of different species adsorbed on the surface. In this article nucleation experiments with silicon on SiO_2 and Si_3N_4 are described in the SiH_4 - H_2 -HCl system at temperatures between 600 ° and 900 °C. In this temperature regime (and without HCl addition) the saturation nucleus density of silicon clusters on SiO_2 substrates shows a decrease in density with decreasing temperature, whereas on Si_3N_4 substrates the opposite occurs. Experiments with nitrogen as a carrier gas, however, give almost the same saturation nucleus densities of silicon clusters on SiO_2 and Si_3N_4 substrates. Additions of HCl to the SiH_4 - H_2 system produce a decrease in the nucleus saturation density on SiO_2 and Si_3N_4 substrates, and the density also decreases with decreasing temperatures below 900 °C. It is further shown that selective growth of silicon on partly coated silicon substrates becomes more difficult at lower growth temperatures. Adsorption of different surface species (H, Cl, SiCl_2 , and SiH_2) on SiO_2 and Si_3N_4 substrates is discussed and it is concluded that a strong adsorption of atomic hydrogen, notably on SiO_2 surfaces, may explain the difference in nucleus densities on SiO_2 and Si_3N_4 substrates at temperatures below 900 °C.

1 Introduction

In two preceding papers [1, 2] (referred to in the following as part I and part II) nucleation experiments are described on SiO_2 and Si_3N_4 substrates. Part I contains experimental data on the SiH_4 -HCl- H_2 system at temperatures between 925 ° and 1200 °C, while part II describes the nucleation behaviour in the SiH_2Cl_2 - H_2 - N_2 system at temperatures between 800 ° and 1100 °C. In parts I and II it was demonstrated that nucleation of silicon on a foreign substrate involves the presence of free silicon adatoms, acting as nucleation centres, whereas on a silicon substrate growth proceeds via the incorporation of adsorbed species at surface steps (SiH_2 , SiCl_2). As long as this layer growth is possible there is no need for separate nucleation between the steps, and therefore growth can already proceed at low supersaturations. This effect also explains the selective growth found under conditions of low supersaturations [3, 4]. It is not known in what way the nucleation of silicon proceeds at lower temperatures, where an increased surface adsorption could change the nucleation behaviour. For this reason nucleation and growth experiments were performed for the SiH_4 - H_2 -HCl system at temperatures between 600 ° and 900 °C, on SiO_2 and Si_3N_4 substrates.

2 Experimental and experimental results

The nucleation experiments were performed in a horizontal air-cooled, R.F. heated reactor. The experimental conditions have been described in parts I and II, but

some additional information is given below. The carrier gases hydrogen and nitrogen were purified to water and oxygen concentrations below 1 ppm. The flow rates of the carrier gases, silane (5% in hydrogen) and hydrogen chloride, both electronic grade, were controlled by means of automatic mass-flow controllers. The temperature was measured with the aid of a calibrated radiation pyrometer on an uncoated silicon slice. Silicon slices covered with an amorphous 1500 Å thick LPCVD layer of SiO_2 or Si_3N_4 were used as substrates. Because of the relatively high temperatures used and the small partial pressures of oxygen and water present it can be assumed that the Si_3N_4 surface is free of oxygen in contrast with Si_3N_4 which is exposed to air [5]. After the nucleation experiments SEM and TEM photomicrographs were used to count the density of the nuclei formed.

Just as in the $\text{SiH}_4\text{-HCl-H}_2$ system at high temperatures (part I), it is found that after an incubation period the density of stable clusters very quickly reaches a saturation density with respect to exposure time. This incubation period becomes longer with decreasing temperature and high hydrogen chloride concentrations combined with low silane concentrations. Furthermore, these periods are longer for SiO_2 substrates than for Si_3N_4 substrates, notably when hydrogen is the carrier gas. Figure 1 shows TEM photomicrographs for an input of 0.1 vol. % silane in hydrogen as a carrier gas at 800 °C on SiO_2 substrates and different exposure times. As noted before, the nucleus density of silicon clusters, after the incubation period, remains almost constant until coalescence occurs. In the following, therefore only saturation nucleus densities of silicon clusters (referred to as N_s) will be used. Figure 2 gives N_s values as a function of temperature on SiO_2 and Si_3N_4 substrates and an input of 0.1 vol. % silane in a hydrogen ambient. The experimental data at temperatures above 925 °C are discussed in part I and only given here for comparison. As will be noticed, N_s decreases with decreasing temperature, on SiO_2 substrates at temperatures below 900 °C, while at temperatures above 900 °C the opposite occurs. On Si_3N_4 substrates N_s varies only slightly with temperature; in the temperature region under discussion no maximum in N_s is observed. It was expected that hydrogen adsorption would strongly reduce the saturation nucleus density of silicon clusters, notably for SiO_2 substrates, in analogy with the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system (part II).

Such an affect is indeed observed: for 0.01 vol. % SiH_4 in hydrogen at 700 °C the nucleus density is extremely low and is estimated at 2×10^7 per cm^2 , whereas when nitrogen is the carrier gas (0.2 vol. % H_2 is present from the silane source, being 5 vol. % SiH_4 in H_2) the nucleus density rises to 1.2×10^{11} per cm^2 . The corresponding TEM photomicrograph for the SiO_2 substrate after an exposure time of 30 sec is shown in Figure 3. From the N_s values in hydrogen and nitrogen a variation of N_s proportional to $P_{\text{H}_2}^{-3/2}$ can be deduced. Figure 4 shows the influence of hydrogen pressure on N_s for Si_3N_4 substrates and an input of 0.01 vol. % SiH_4 . It can be observed that N_s decreases with increasing hydrogen pressure: by plotting N_s versus P_{H_2} a linear relationship can be obtained. Figure 5 gives N_s values on SiO_2 and Si_3N_4 substrates at 700 °C as a function of input concentrations of silane.

t = 60 sec.

t = 40 sec.

t = 20 sec.

Figure 1.

TEM photomicrographs of the nucleus density on a SiO_2 substrate for an input of 0.1 vol. % silane in hydrogen at 800°C as a function of the exposure time.

Figure 2.

The saturation density of silicon clusters (N_s) as a function of temperature for an input of 0.1 vol. % silane in hydrogen as a carrier gas on SiO_2 and Si_3N_4 substrates.

For the input concentrations used in these experiments, N_s is linearly proportional to the silane input pressure in a first approximation. Addition of HCl to the SiH_4 - H_2 mixtures greatly reduces the number of stable silicon clusters as can be seen from Figure 6. In this figure N_s is plotted as a function of the input concentration of HCl at 800 °C on SiO_2 substrates and for an input of 0.1 vol. % SiH_4 . For higher input concentrations of hydrogen chloride than those given in Figure 6 no nucleation is observed. Figure 7 shows the influence of the addition of various amounts of HCl to the SiH_4 - H_2 mixture on the density of nuclei as a function of temperature, both for SiO_2 and for Si_3N_4 substrates. At 900 °C N_s shows a distinct maximum, for both SiO_2 and Si_3N_4 substrates.

Another point appears from the observation that silicon layers can be grown selectively on partly oxide-coated or nitride-coated silicon slices [3, 4]. The selectivity is explained on the basis of a more difficult nucleation on foreign substrates. In figure 8 this selectivity is shown as a function of temperature for the

Figure 3.

TEM picture of the nucleus density for an input of 0.01 vol. % silane and 0.2 vol. % hydrogen in nitrogen as a carrier gas on a SiO_2 substrate at 700°C .

$\text{SiH}_4\text{-HCl-H}_2$ system in which the ratio $P_{\text{SiH}_4}/P_{\text{HCl}}^2$ is used as a measure of the supersaturation. Three regions can be distinguished: I no selective growth, II selective growth and III etching of the silicon slices. It will be seen that with decreasing temperatures the region where selective growth can take place becomes smaller, and at temperatures below 800°C the selectivity between silicon and SiO_2 or Si_3N_4 has disappeared.

3. Discussion

3.1 Introduction

In part I it was concluded that an expression given by Venables [6] could be used to characterize the saturation density of silicon clusters (N_s) in the present case where incomplete condensation has to be assumed. Venable's expression for the case of mobile clusters can be rewritten as

$$\frac{N_s}{n_o} \cong \left(\frac{n_1}{n_o} \right)^{\frac{i+1}{2}} \exp [(E_i + E_m - E_d)/2 kT] \quad (1)$$

Figure 4.

The saturation density of silicon clusters (N_s) for 0.01 vol. % silane and some hydrogen-nitrogen mixtures on Si_3N_4 substrates at 700°C .

where i is the number of atoms in the initial cluster, E_i the heat of formation of a cluster consisting of i atoms, E_m is the activation energy for surface diffusion of mobile clusters, E_d the activation energy for surface diffusion of adatoms, n_1 the concentration of adatoms per unit area and n_0 the total number of surface sites per unit area. If only small clusters are mobile at low temperatures equation (1) has to be replaced by

$$\frac{N_s}{n_0} \cong \left(\frac{n_1}{n_0} \right) \exp [(E_m - E_d)/2 kT] . \quad (2)$$

In the following section we give reaction schemes in order to arrive at expressions for n_1/n_0 .

Figure 5.

The saturation nucleus density on SiO_2 and Si_3N_4 substrates at $700^\circ C$ as a function of the input concentration of silane in a hydrogen ambient.

3.2 Interpretation of the results

In order to describe the nucleation experiments in the SiH_4 -HCl- H_2 system at temperatures below $900^\circ C$ it is necessary to consider a number of possible reactions that can take place at or near the surface. The reaction scheme as proposed for the SiH_4 -HCl- H_2 system at temperatures above $925^\circ C$ (part I) can be used with some additional assumptions concerning the species present on the surface. The reaction between silicon adatoms and SiO_2 can be neglected below $1000^\circ C$ [7].

If no HCl is present in the gas phase the following reaction schemes will be used:

- Gas phase dissociation of SiH_4 near the surface [8]

Figure 6.

N_s for SiO₂ substrates for an input of 0.1 vol. % silane and different input concentrations of hydrogen chlorine in hydrogen as a carrier gas at 800 °C.

b. Adsorption of SiH₂ on a free surface site (the latter denoted by *)

c. Adsorption of atomic hydrogen

d. Formation of silicon clusters

Figure 7.

The saturation nucleus density (N_s) as a function of temperature for two SiH_4 -HCl mixtures in hydrogen on SiO_2 and Si_3N_4 substrates ($\circ$, $\bullet$ 0.1 vol. % SiH_4 and 0.2 vol. % HCl; $\triangle$, $\blacktriangle$ 0.1 vol. % SiH_4 and 0.4 vol. % HCl).

The concentrations of the surface species $[\text{SiH}_4^*]$, $[\text{SiH}_3^*]$, $[\text{SiH}^*]$ and $[\text{Si}^*]$ are assumed to be small compared with the concentration of $[\text{SiH}_2^*]$, according to the experimental data concerning the growth of silicon on silicon in the SiH_4 - H_2 - N_2 system at 700°C [9]. As the SiO and the SiN bond strengths are strong compared with the Si-Si bonding (as discussed later), it is likely that nucleation on SiO_2 and Si_3N_4 substrates starts with the formation of these bonds. In a steady state situation the concentration of SiH_2 ad molecules reaches a constant value, which before formation of silicon clusters occurs can be expressed as

Figure 8.

The temperature dependence of selective growth of silicon on silicon slices partly coated with oxide or nitride as a function of temperature and supersaturation, expressed as $P_{\text{SiH}_4}/P_{\text{HCl}}^2$ in hydrogen as a carrier gas.

$$n_1 = [\text{SiH}_2^*] = \frac{K_1 K_2 P_{\text{SiH}_4} [*]}{P_{\text{H}_2}} \quad (8)$$

where $[*]$ is the concentration of free surface sites

$$[*] = n_0 - [\text{H}^*] - [\text{SiH}_2^*] - \dots \quad (9)$$

As will be discussed in the section on adsorption, hydrogen and silicon will be adsorbed preferentially at oxygen and nitrogen surface sites on SiO_2 and Si_3N_4 substrates, respectively. The expression as obtained by Venables (equation (1)) for N_s can be compared with the experimental data in the $\text{SiH}_4\text{-H}_2$ system on SiO_2 and Si_3N_4 substrates in the temperature range under discussion. Introducing equation (8) for n_1 in equation (1) gives

$$\frac{N_s}{n_0} \cong \left\{ \frac{K_1 K_2 P_{SiH_4} [\star]}{n_0 P_{H_2}} \right\}^{\frac{i+1}{2}} \exp [(E_i + E_m - E_d)/2 kT] . \quad (10)$$

In order to arrive at an expression describing the experimental data, the following remarks can be made:

- i. N_s is almost equal for SiO_2 and Si_3N_4 substrates in the SiH_4 - N_2 system at 700 °C, as discussed before.
Between 800 ° and 1100 °C the SiH_2Cl_2 - N_2 system showed the same behaviour (part II).
- ii. The saturation nucleus density of silicon clusters on Si_3N_4 substrates is in a first approximation inversely proportional to P_{H_2} ($N_s \propto P_{H_2}^{-1}$) (Figure 4).
In the case of SiO_2 substrates the hydrogen pressure is observed to have a stronger influence on N_s ($N_s \propto P_{H_2}^{-3/2}$). In part II it was concluded that adsorption of atomic hydrogen could explain the differences in N_s between SiO_2 and Si_3N_4 in the SiH_2Cl_2 - H_2 system ($N_s \propto P_{H_2}^{-1/2}$).
- iii. The saturation density of silicon clusters on SiO_2 and Si_3N_4 substrates is in a first approximation linearly proportional to the input concentration of silane (Figure 5).

The remarks made above lead to the following expression, describing N_s at a fixed temperature as a function of the gas phase composition

$$N_s = A \frac{P_{SiH_4}}{P_{H_2}} \times \frac{1}{(1 + K_3 P_{H_2}^{1/2})} \quad (11)$$

where A is a constant.

Comparison of this expression with the expression as given by equation (10) then leads to a critical cluster with $i = 1$ and SiH_2 as the predominant surface species. Further it can be concluded that under the experimental conditions the concentration of the surface species $[SiH_2 \star]$ is much smaller than the total number of surface sites (n_0) (equation (9)). This leads to $[\star] = n_0 - [H\star]$, which can be rewritten by using equation (5) to $[\star] = n_0 / (1 + K_3 P_{H_2}^{1/2})$. The differences in nucleation behaviour between SiO_2 and Si_3N_4 substrates at temperatures below 900 °C can be explained by a strong hydrogen adsorption on SiO_2 substrates ($K_3 P_{H_2}^{1/2} > 1$) and a weak adsorption of atomic hydrogen on Si_3N_4 substrates ($K_3 P_{H_2}^{1/2} < 1$). As will be discussed in the section on adsorption, this is due to a large difference in the bond strength between the NH and the OH bond.

If HCl is introduced to the $\text{SiH}_4\text{-H}_2$ system the following reactions are added to the reactions (a–d)

e. Attack of SiH_2^* by HCl

f. Desorption of SiCl_2

g. Adsorption of atomic chlorine

k. Formation of silicon clusters

If HCl is added to the system, almost all the SiH_2^* admolecules will be converted to SiCl_2^* , followed by desorption if no centers for growth are present [part I, 9]. Before silicon clusters are formed the steady state concentration of the SiH_2^* surface species can be given by

$$n_1 = [\text{SiH}_2^*] = \frac{K_1 k_2 P_{\text{SiH}_4} [*]}{P_{\text{H}_2} (k_{-2} + k_6 P_{\text{HCl}}^2)} \quad (17)$$

If silicon clusters are present, etching of these clusters also occurs. According to van der Putte et al. [10] this etch rate can be given by

$$R_{\text{etch}} = k_{\text{etch}} \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}} . \quad (18)$$

At an etch rate lower than the growth rate of silicon clusters this extra term has no influence on the total number of nuclei, but in the opposite case no nuclei will be formed. Inserting equation (17) into equation (1) leads to

$$\frac{N_s}{n_0} \cong \left\{ \frac{K_1 k_2 \text{PSiH}_4 [*]}{n_0 \text{PH}_2 (k_{-2} + k_6 \text{P}_{\text{HCl}}^2)} \right\}^{\frac{i+1}{2}} \exp [(E_i + E_m - E_d)/2 \text{ kT}] . \quad (19)$$

In part I an extensive discussion is devoted to experimental data on the SiH_4 -HCl- H_2 system on SiO_2 and Si_3N_4 substrates at temperatures above 925°C . From plots of $\log N_s$ versus $\log \text{PSiH}_4/\text{P}_{\text{HCl}}^2$ it was shown that, if the input concentrations of hydrogen chloride are not too high N_s is linearly proportional to $\text{PSiH}_4/\text{P}_{\text{HCl}}^2$, indicating that $i = 1$ and $[*]$ is constant at those temperatures. At higher HCl concentrations the initial cluster size changes from $i = 1$ to $i = 4$. At temperatures below 925°C , N_s decreases with decreasing temperatures, in contrast to the situation at higher temperatures where the opposite occurs (Figure 7). In order to interpret the experimental data below 900°C growth rate measurements for silicon on silicon in the SiH_4 -HCl- H_2 system are helpful [11]. At temperatures above 900°C the growth rate is gas phase diffusion-controlled and is relatively high compared with the etch rate given by the presence of HCl for not too high input concentrations of HCl. As discussed in part I, N_s is linearly proportional to $\text{PSiH}_4/\text{P}_{\text{HCl}}^2$ ($i = 1$) for $\text{PSiH}_4/\text{P}_{\text{HCl}}^2 > 50$ (p in bars) at temperatures above 925°C . At lower values of $\text{PSiH}_4/\text{P}_{\text{HCl}}^2$ the critical cluster size increases and for $\text{PSiH}_4/\text{P}_{\text{HCl}}^2 < 8$ no nucleation is observed at these temperatures. At temperatures below 900°C the growth rate of silicon on silicon is kinetically or surface-controlled in the SiH_4 - H_2 system and a strong decrease in the growth rate with decreasing temperatures is apparent. Addition of HCl to this system at temperatures below 900°C leads to an additional lowering of the growth rate as measured in the SiH_4 - H_2 system, due to the conversion of SiH_2 into SiCl_2 which easily desorbs [11]. At 800°C no nucleation is observed on SiO_2 and Si_3N_4 substrates for $\text{PSiH}_4/\text{P}_{\text{HCl}}^2 < 30$ (Figures 7 and 8 as will be discussed later in connection with selective growth). In the regime where the growth of silicon on silicon is surface-controlled ($T < 900^\circ\text{C}$) N_s is linearly proportional to $\text{PSiH}_4/\text{P}_{\text{HCl}}^2$ ($i = 1$) only for relatively high values of this parameter (> 100 as obtained from Figure 6). Or, in other words, when hydrogen chloride is added to a certain amount of silane the critical cluster size deviates from $i = 1$ for much smaller hydrogen chloride concentrations at 800°C than at temperatures above 900°C . This leads to a decrease in N_s , the term between the brackets in equation (10) being smaller than unity (n_1/n_0). A second possibility which could explain the decrease in N_s below 900°C as shown in Figure 7 for the SiH_4 -HCl- H_2 system is given by a strong adsorption of atomic chlorine. As will be discussed in the section on adsorption, chlorine will be preferentially adsorbed on the silicon surface atoms of the SiO_2 and Si_3N_4 substrates, but there is evidence that above 700°C the interaction between chlorine and the silicon surface atoms is only weak, leading to a small concentration of chlorine surface atoms ($[\text{Cl}*] \ll n_0$).

According to Figure 8 silicon can be grown selectively on silicon slices partly coated with oxide or nitride at temperatures above 800°C . As the growth of silicon on

silicon in the $\text{SiH}_4\text{-HCl-H}_2$ system can be given by $R = k_a P_{\text{SiH}_4} - k_b P_{\text{HCl}}^2$ leading to $R = 0$ for $P_{\text{SiH}_4}/P_{\text{HCl}}^2 = k_b/k_a$, this relation is used as a parameter in Figure 8. In the gas phase diffusion-controlled regime of the growth of silicon on silicon above 900°C , as discussed above, surface diffusion and incorporation of silicon at the atomic steps are relatively fast compared to the diffusion of reactants towards the surface. In the same temperature regime the nucleation of silicon on silicon is surface-controlled (part I), leading to desorption of SiCl_2 if no growth centres are present. Consequently a selective growth can become apparent.

At temperatures below 900°C the growth of silicon on silicon becomes surface-controlled, the reduction of SiCl_2 at the atomic steps being rate-limiting [9]. Nucleation of silicon on SiO_2 and Si_3N_4 in the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system below 900°C is also surface-controlled, as discussed before. At low temperatures, therefore, nucleation and growth are both limited by the reduction of SiCl_2 by hydrogen. This explains the loss of selectivity at lower temperatures in the Si-H-Cl system. According to Figure 2 some selectivity in the growth of silicon on SiO_2 and Si_3N_4 can also be expected in the $\text{SiH}_4\text{-H}_2$ system at low temperatures and low input concentrations of silane.

3.3 Adsorption on SiO_2 and Si_3N_4 substrates

In this section we discuss adsorption of H , Cl , SiH_2 and SiCl_2 in connection with the nucleation experiments on SiO_2 and Si_3N_4 substrates. We also give a comparison with adsorptions of the same compounds on silicon. The concentration of free surface sites on a SiO_2 substrate, $[*] = [*_{\text{Ox}}] + [*_{\text{Si}}]$ (where the subscripts ox and si refer to the surface atoms oxygen and silicon), can be given by

$$[*_{\text{Ox}}] = n_{\text{Ox}} - [\text{H}_{\text{Ox}}^*] - [\text{SiH}_2^*_{\text{Ox}}] - [\text{Cl}_{\text{Ox}}^*] - [\text{SiCl}_2^*_{\text{Ox}}] \quad (20)$$

$$[*_{\text{Si}}] = n_{\text{Si}} - [\text{H}_{\text{Si}}^*] - [\text{SiH}_2^*_{\text{Si}}] - [\text{Cl}_{\text{Si}}^*] - [\text{SiCl}_2^*_{\text{Si}}] \quad (21)$$

where $n_{\text{O}} = n_{\text{Ox}} + n_{\text{Si}}$ is the total number of surface sites per unit area. The concentration of free surface sites on Si_3N_4 can be given in a similar way. Making use of the equilibrium partial pressures of the various species in the gas phase, one can calculate the surface concentrations of the different compounds if values for the adsorption energies of these species are known [9]. If no direct measurements are available, these adsorption energies (E_a) can best be given by the dissociation energy (D) of the corresponding diatomic molecules. Table I gives accepted values for D , according to the JANAF tables [12] for most of the bonds.

D values for Si-O , O-Cl and N-Cl have been reported by Roberts and Caserio [13], who give average values for polyatomic molecules. Since, as far as the authors are aware, no dissociation energy for the single bond of Si-N is known, an estimate of $D_{\text{Si-N}}$ can be given by equating $D_{\text{Si-N}}/D_{\text{Si-O}} = D_{\text{C-N}}/D_{\text{C-O}}$. Using values for the single bonds derived from measurements on polyatomic molecules [13], this yields $D_{\text{Si-N}} = 92 \text{ kcal/mole}$ (Table I).

adsorbed atoms	Substrate atoms		
	Si	O	N
Si	70	108	92
H	70	102	83
Cl	90	52	46

TABLE I: Accepted adsorption energies in kcal/mole [12, 13].

Adsorption of monoatomic hydrogen

As discussed before, the nucleation experiments on SiO_2 and Si_3N_4 substrates indicate a strong adsorption of atomic hydrogen on SiO_2 and a weak adsorption on Si_3N_4 . According to Table I this could be due to the differences in bond strengths between OH and NH. It is therefore also to be expected that adsorption of atomic hydrogen on silicon will be relatively weak, leading to a small coverage with hydrogen atoms [9]. More evidence of a strong hydrogen adsorption on SiO_2 comes from the work of Morterra and Low [14] and of Lawrenko et al. [15]. Morterra and Low studied the reaction between porous silica and molecular hydrogen. They found that this silica reacts with molecular hydrogen. Infrared studies have shown that if molecular hydrogen reacts with porous SiO_2 at temperatures above 650°C , silanols (Si-OH) are formed while SiH groups are totally absent. Lawrenko et al. studied the adsorption of hydrogen on monocrystalline SiO_2 , Al_2O_3 and MgO . Measuring the weight losses of the samples by means of a microbalance they found that at temperatures below 900°C measurable quantities of hydrogen are adsorbed on the three substrates, indicating the formation of OH groups. They also observed that the adsorption is reversible. Stein and Wegener [16] found that CVD Si_3N_4 contains chemically bonded hydrogen. Annealing experiments showed that the SiH bonds are annealed out more easily than the NH bonds. It can therefore be concluded that adsorption of atomic hydrogen on SiO_2 substrates blocks adsorption sites, leading to a decrease in the saturation density of silicon clusters, whereas in the case of Si_3N_4 and silicon surfaces this adsorption is only weak.

Adsorption of atomic chlorine

According to Table I, chlorine does not adsorb preferentially on oxygen or nitrogen, and it may therefore be assumed that adsorption of chlorine on SiO_2 and Si_3N_4 can be treated as adsorption on the silicon surface atoms. Adsorption of atomic chlorine on silicon has been discussed previously in connection with growth

rate measurements of silicon on silicon [9] It was concluded there that at temperatures above 700 °C the fractional surface concentration of atomic chlorine is much smaller than unity, in agreement with evolution measurements reported by Miyamura et al [17]

Adsorption of SiH₂ and SiCl₂

Because of the relatively high values of DS_{I-N} and DS_{I-O} in contrast to DS_{I-Si} (Table I) it can be assumed that the surface species SiH₂ and SiCl₂ adsorb predominantly on top of oxygen or nitrogen atoms of the SiO₂ or Si₃N₄ substrates After adsorption of the first monolayer of silicon the surface mobility of further SiH₂ or SiCl₂ monomers will be enhanced This postulation could explain the similarity in nucleation densities on SiO₂ and Si₃N₄ with sapphire and spinel substrates as observed by Cullen and coworkers [18]

As discussed before, N_s is linearly proportional to the input concentration of silane on SiO₂ and Si₃N₄ substrates, indicating a small coverage of SiH₂ monomers As discussed previously, the surface concentrations of SiCl₂ on silicon in the SiH₄-HCl-H₂ systems are considered to be small [9] A strong adsorption of SiCl₂ on SiO₂ or Si₃N₄ substrates cannot be ruled out completely, but according to the experimental data as described in part II (the SiH₂Cl₂-H₂ system) the surface coverage of SiCl₂ is much smaller than that of atomic hydrogen, notably for SiO₂ substrates

4 Conclusions

In our study of the nucleation of silicon on SiO₂ and Si₃N₄ substrates at temperatures between 600 ° and 900 °C in the SiH₄-HCl-H₂ system, it was observed that the saturation nucleus density on SiO₂ substrates in the SiH₄-H₂ system shows a maximum at approximately 900 °C, whereas for Si₃N₄ substrates this density increases slightly with decreasing temperatures Addition of nitrogen to the SiH₄-H₂ systems produces a strong increase in the saturation density of silicon clusters, notably on SiO₂ substrates Analysis of the experimental data suggests that atomic hydrogen is strongly adsorbed because of the formation of OH bonds, whereas on Si₃N₄ substrates adsorption of atomic hydrogen leads to only small coverages. The introduction of HCl strongly reduces the nucleus density, notably at temperatures below 900 °C It is concluded that this additional reduction at temperatures below 900 °C is comparable with the decrease in growth rate in the case of silicon on silicon. The adsorption of H, Cl, SiCl₂ and SiH₂ on SiO₂ and Si₃N₄ substrates is discussed and compared with the adsorption of these species on silicon surfaces It is concluded that only adsorption of atomic hydrogen on SiO₂ is needed to explain the experimental results this adsorption blocks the adsorption sites, leading to a decrease in the saturation density of silicon clusters

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CHAPTER IV

THE NUCLEATION OF CVD SILICON ON SiO_2 AND Si_3N_4 SUBSTRATES

II The SiH_2Cl_2 - H_2 - N_2 system

Abstract

A description is given of nucleation experiments with silicon on SiO_2 and Si_3N_4 substrates in the SiH_2Cl_2 - H_2 - N_2 system, performed at temperatures between 800° and 1100°C . The saturation cluster densities were determined for different mixtures as a function of temperature and could be varied between 10^5 – 10^{10} cm^{-2} . A reaction scheme is proposed in which silicon adatoms reach a steady state concentration before nucleation occurs. Comparison of the experimental data with existing nucleation theories gives approximate values for the size of the critical cluster. A strong adsorption of atomic hydrogen, especially on SiO_2 surfaces, may explain the substantial differences in nucleation on SiO_2 and Si_3N_4 surfaces at temperatures below 1000°C .

1. Introduction

Polycrystalline silicon layers are finding extensive application in the fabrication of integrated circuits, e.g. as gate material in MOS (Metal-Oxide-Silicon) field effect transistors [1]. For this purpose CVD with SiH_4 as input gas is most widely used but chlorosilanes too, such as SiHCl_3 and SiCl_4 and recently SiH_2Cl_2 are becoming increasingly important as starting materials for the deposition of silicon layers [2]. Reports of nucleation experiments with silicon on amorphous, polycrystalline and monocrystalline substrates are relatively scarce. The present authors discuss such experiments in a previous paper dealing with nucleation of silicon on SiO_2 and Si_3N_4 substrates in the SiH_4 - HCl - H_2 system [3]. The present paper discusses nucleation in the SiH_2Cl_2 - H_2 - N_2 system on SiO_2 and Si_3N_4 substrates. The experimental results are described and compared with existing nucleation theories.

2. Experimental

The nucleation experiments were performed in a horizontal R.F. heated reactor, consisting of a rectangular air-cooled fused silica tube, provided with a pyrographite coated carbon susceptor covered with a thin layer of silicon. Nucleation of silicon was performed on silicon slices (wafer 0.5 inch square) covered with an amorphous 1500 Å thick LP-CVD SiO_2 or Si_3N_4 layer. The effective cross-section of the reactor tube was about 11 cm^2 . The gas system was provided with automatic mass flow controllers for the hydrogen and nitrogen carrier gas and the SiH_2Cl_2 source. Some experiments were performed with SiHCl_3 , in which case the input concentrations were controlled by passing a flow of hydrogen, monitored by means of an automatic mass flow controller, through a bubbler filled with SiHCl_3 at a constant temperature. The carrier gas was purified; both water vapour and oxygen concentrations were below 1 ppm. The slices were cleaned prior to a deposition experiment

in a $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ mixture followed by rinsing in water of ultra-high purity. After spin drying, the slices were further cleaned in the reactor tube with 0.2 vol. % HCl in hydrogen at 1000°C for five minutes. After this, the reactor was purged by a hydrogen flow, while the substrate temperature was brought to the desired nucleation temperature. Prior to deposition the reactor was flushed with the particular $\text{H}_2\text{-N}_2$ mixture, which is also used during the nucleation experiment for about five minutes. During the nucleation experiment the $\text{H}_2\text{-N}_2$ mixture loaded with SiH_2Cl_2 was passed over the slices. In order to obtain stable gas flow conditions a room temperature gas velocity of about 60 cm/sec was chosen. The temperature of the slices was measured with an optical pyrometer focussed on the surface of an uncoated silicon slice, and the values were corrected for the emissivity of silicon and the absorption and reflection of the system. After termination of the experiment the substrates were cooled without SiH_2Cl_2 addition and inspected at room temperature. The density of the nuclei formed was determined from either SEM or TEM photomicrographs.

3. Experimental results

3.1 Introduction

A series of short depositions was carried out with different concentrations of SiH_2Cl_2 in H_2 , N_2 or mixtures of H_2 and N_2 at temperatures between 800° and 1100°C . As in the $\text{SiH}_4\text{-HCl-H}_2$ system [3], it was found that after an incubation period the density of stable clusters very quickly reached a saturation density of nuclei with respect to exposure time. After this period the clusters merely increased in size until coalescence occurred. The existing clusters showed a very narrow size distribution, from which it may be concluded that the clusters are formed in a very short period of time.

3.2 Nucleation on a SiO_2 substrate

The experimentally observed saturation densities of Si clusters in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system have been collected in Table I. In Figure 1 the saturation densities of silicon clusters on SiO_2 substrates at 1000°C are plotted for 0.1 vol. % SiH_2Cl_2 for some $\text{H}_2\text{-N}_2$ mixtures, the latter expressed as $\text{PH}_2/(\text{PH}_2 + \text{PN}_2)$. The highest saturation density can be observed for pure nitrogen, while the introduction of hydrogen strongly reduces the saturation density of Si clusters on SiO_2 substrates. Figure 2 gives a plot of the saturation density of nuclei versus the reciprocal temperature in the temperature region $925^\circ - 1100^\circ\text{C}$ (with the exception of nitrogen, where results at 800°C are also given). For nitrogen the formation process is barely a function of temperature. If hydrogen is added to the mixture the temperature dependence of the formation process increases with increasing hydrogen concentrations. Figure 3 shows photomicrographs of nucleation on SiO_2 substrates at 1000°C , for an input concentration of 0.1 vol. % SiH_2Cl_2 in pure H_2 (a) and pure N_2 (b).

TABLE I. Saturation nucleus density (cm^{-2}) for the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system on SiO_2 substrates between 800° and 1100°C .
t is the exposure time.

Partial pressure (bar)			Temperature									
PSiH_2Cl_2	PH_2	PN_2	1100°C		1000°C		925°C		900°C		800°C	
			t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})
1×10^{-3}	1	—	10	4×10^8	10	5×10^7	120	8×10^6		—		—
2×10^{-3}	1	—	3	9×10^8	5	1.1×10^8	15	2.5×10^7		—		—
4×10^{-3}	1	—		—	5	1.8×10^8	15	5×10^7		—		—
1×10^{-3}	0.76	0.24		—	5	7×10^7		—		—		—
1×10^{-3}	0.44	0.56		—	5	4×10^8		—		—		—
1×10^{-3}	0.18	0.82	3	1.4×10^9	5	6×10^8	15	4×10^8		—		—
1×10^{-3}	0.03	0.97	3	4×10^9	5	3×10^9	15	2×10^9		—		—
2×10^{-4}	—	1		—	10	4×10^9		—		—		—
5×10^{-4}	—	1	5	1.1×10^{10}	5	1.1×10^{10}	30	1.2×10^{10}		—		—
1×10^{-3}	—	1	3	1.2×10^{10}	5	1.5×10^{10}		—	15	1.3×10^{10}	60	1.7×10^{10}

Figure 1.

The saturation nucleus density for some H_2 - N_2 mixtures and 0.1 vol. % SiH_2Cl_2 on SiO_2 and Si_3N_4 substrates at $1000^\circ C$.

It will be shown in section 4 that the experimental data on saturation densities of nuclei (N_s) on a SiO_2 substrate at $1100^\circ C$ as a function of gas phase composition can be described by

$$N_s = \frac{A P_{SiH_2Cl_2} (b)}{1 + B P_{H_2}^{1/2}} \quad (1)$$

where $P_{SiH_2Cl_2} (b)$ is the input concentration of SiH_2Cl_2 and A and B are constants. For $B P_{H_2}^{1/2} > 1$ a plot of $\log (N_s / P_{SiH_2Cl_2} (b))$ versus $\log (P_{H_2})$ should show a linear dependence, as indicated in Figure 4. For temperatures below $1100^\circ C$ the tangent in Figure 4 differs from $1/2$ for high hydrogen pressures. In this figure the points at P_{H_2} around 10^{-3} represent the saturation densities of nuclei for the SiH_2Cl_2 - N_2 system (no hydrogen added). As described in section 4, in a nitrogen medium SiH_2Cl_2 decomposes almost completely in the gas phase to

Figure 2.

The saturation nucleus density as a function of temperature on SiO_2 substrates for some H_2 - N_2 mixtures and 0.1 vol. % SiH_2Cl_2 .

SiCl_2 and H_2 . This means that an input concentration of 0.1 vol. % SiH_2Cl_2 gives $P_{\text{H}_2} \approx 10^{-3}$ bar.

3.3 Nucleation on a Si_3N_4 substrate: differences compared with a SiO_2 substrate

Table II gives the experimental data for the saturation densities of stable clusters on Si_3N_4 substrates in the SiH_2Cl_2 - H_2 - N_2 system. Figure 1 also shows saturation densities of silicon clusters for Si_3N_4 substrates as a function of $P_{\text{H}_2}/(P_{\text{H}_2} + P_{\text{N}_2})$ at 1000 °C. The difference between SiO_2 and Si_3N_4 substrates is remarkable. Introduction of hydrogen to the system reduces the saturation density of nuclei for the Si_3N_4 substrate, but for the SiO_2 substrate the variation is much stronger. In Figure 5 saturation densities of nuclei on Si_3N_4 substrates are given for 0.1 vol. % SiH_2Cl_2 in hydrogen and nitrogen as a function of temperature. As for the SiO_2 system (Figure 2) the experiments in hydrogen give the lowest density of nuclei and the strongest temperature dependence of the formation process. It appears that if

TABLE II. Saturation nucleus density (cm^{-2}) for the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system on Si_3N_4 substrates between 800° and 1100°C . t is the exposure time.

Partial pressure (bar)			Temperature							
$P_{\text{SiH}_2\text{Cl}_2}$	P_{H_2}	P_{N_2}	1100 °C		1000 °C		900 °C		800 °C	
			t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})	t (sec)	N_s (cm^{-2})
1×10^{-3}	1	—	5	6×10^9	10	4×10^9	15	1.4×10^9	120	7×10^8
1×10^{-3}	0.18	0.82		—	5	4×10^9		—		—
1×10^{-3}	0.03	0.97			5	7×10^9		—		—
5×10^{-4}	—	1	5	1.1×10^{10}	5	1.1×10^{10}		—		—
1×10^{-3}	—	1	3	1.1×10^{10}	5	1.2×10^{10}	15	1.6×10^{10}	60	1.7×10^{10}

Figure 3.

Photomicrographs of the nucleus density for 0.1 vol. % SiH_2Cl_2 in pure H_2 (a) and pure N_2 (b).

Figure 4.

The saturation nucleus density at 925 °C, 1000 °C and 1100 °C for different mixtures of $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$, expressed as $\log(N_s / P \text{SiH}_2\text{Cl}_2)$ versus $\log(P_{\text{H}_2})$ on SiO_2 substrates.

the hydrogen content is very low there is hardly any difference between a SiO_2 and Si_3N_4 substrate. The experimentally found expression for the saturation density of stable clusters (eq. 1) as a function of temperature and gas phase composition could also be used for Si_3N_4 substrates. In Figure 6 $\log(N_s / P \text{SiH}_2\text{Cl}_2)$ versus $\log(P_{\text{H}_2})$ is plotted at 1000 °C for Si on Si_3N_4 , giving a linear dependence between the two parameters. Further it can be observed that the tangent in this figure is smaller than $1/2$, indicating that the assumption $\text{BP}_{\text{H}_2}^{1/2} > 1$ is not acceptable in this case.

Figure 5.

The saturation nucleus density on Si_3N_4 substrates for 0.1 vol. % SiH_2Cl_2 in pure H_2 (+) and pure N_2 (o) as a function of temperature.

3.4 Nucleation of Si on SiO_2 and Si_3N_4 substrates: comparison of the SiH_2Cl_2 - H_2 system with other silicon-containing compounds in hydrogen

Figures 7 and 8 give saturation densities of silicon clusters for SiO_2 and Si_3N_4 substrates, respectively, as a function of temperature for SiH_4 [3], SiH_2Cl_2 and SiHCl_3 (all concentrations about 0.1 vol. %) in hydrogen as a carrier gas. The difference in the saturation nucleus density between SiH_4 and SiH_2Cl_2 as the silicon containing compounds for both substrates is remarkable. The saturation density of nuclei in the SiH_4 - H_2 system increases with decreasing temperatures, whereas for the other systems the opposite occurs. On SiO_2 substrates SiHCl_3 behaves in much the same way as SiH_2Cl_2 whereas on Si_3N_4 substrates this is only true at high temperatures (Figure 8). It was observed that the growth rate of silicon on silicon for a mixture of 0.1 vol. % SiH_4 and 0.2 vol. % HCl is almost equal to that of 0.1 vol. % SiH_2Cl_2 , both systems having hydrogen as a carrier gas and a temperature of 1000 °C [4]. It is therefore interesting to compare the saturation densities of nuclei on SiO_2 and Si_3N_4 substrates in the SiH_2Cl_2 - H_2 system with the results of nucleation experiments in the SiH_4 - HCl - H_2 system. In Figure 9 saturation densities of silicon clusters are given for SiO_2 and Si_3N_4 substrates as a function of temperature for

Figure 6.

$\log(N_s/PSiH_2Cl_2)$ versus $\log(PH_2)$ at $1000^\circ C$ for Si on Si_3N_4 .

0.1 vol. % SiH_2Cl_2 and a mixture of 0.1 vol. % SiH_4 and 0.2 vol. % HCl [4], both systems in a hydrogen medium. It can be observed on both substrates that for the $SiH_2Cl_2-H_2$ mixture the saturation density of nuclei decreases with decreasing temperature, whereas for the $SiH_4-HCl-H_2$ mixture the opposite occurs.

4. Discussion

4.1 Adatom concentration and surface coverage

In order to arrive at an expression describing the adatom concentration of silicon on the substrate it would be very helpful to have thermochemical data of the Si-H-N-Cl system. With this in view thermochemical data of the Si-H-Cl and Si-N-Cl systems have been calculated for $Cl/H_2 = 10^{-3}$ and $Cl/N_2 = 10^{-3}$, respectively, in the temperature range of 900 – 1400 K, using the procedure reported by Van der Putte et al. [5] (Figure 10). In equilibrium with solid silicon the most abundant species are H_2 , HCl , $SiCl_2$, SiH_2Cl_2 , $SiCl_4$ and $SiHCl_3$, in accordance with mass

Figure 7.

Saturation densities on SiO_2 substrates as a function of temperature for SiH_4 , SiH_2Cl_2 and SiHCl_3 (all concentrations about 0.1 vol %) in H_2 as a carrier gas.

spectrometric analysis results reported by Ban and Gilbert [6]. With the aid of the thermochemical data a number of reactions that can take place on or near the substrate are summarized in the Appendix. As discussed in the Appendix, reasonable assumptions could be made for the initial states of nucleation, leading to an expression for the silicon adatom concentration (A-15):

$$\frac{n_1}{n_0} = \frac{K_3 \text{PSiCl}_2}{k_B (1 + K_3 \text{PSiCl}_2 + K_{10} \text{P}_{\text{H}_2}^{1/2})} \quad (2)$$

Figure 8

Saturation densities on Si_3N_4 substrates for SiH_4 , SiH_2Cl_2 and SiHCl_3 in H_2 as a carrier gas (all concentrations about 0.1 vol %) as a function of temperature

The dissociation of SiH_2Cl_2 to SiCl_2 and H_2 (A-1) followed by a very strong adsorption of SiCl_2 compared to SiH_2Cl_2 plays an important role in obtaining this expression. The decomposition parameter α of reaction A-1 can be defined by

$$\begin{aligned} P_{\text{SiH}_2\text{Cl}_2} &= (1 - \alpha) P_{\text{SiH}_2\text{Cl}_2} \quad (\text{b}) \\ P_{\text{SiCl}_2} &= \alpha P_{\text{SiH}_2\text{Cl}_2} \quad (\text{b}) \end{aligned} \tag{3}$$

where $P_{\text{SiH}_2\text{Cl}_2} \quad (\text{b})$ is the input concentration of SiH_2Cl_2

If the equilibrium partial pressure of SiCl_2 is much higher than that of SiH_2Cl_2 it can be assumed that the decomposition of SiH_2Cl_2 into SiCl_2 and H_2 is almost complete ($\alpha \cong 1$) (Figure 10). For a H_2 - N_2 mixture we obtain, by introducing the decomposition parameter α into equation (2)

Figure 9.

Saturation nucleus densities on SiO_2 and Si_3N_4 substrates as a function of temperature for 0.1 vol. % SiH_2Cl_2 and a mixture of 0.1 vol. % SiH_4 and 0.2 vol. % HCl .

$$\frac{n_1}{n_0} = \frac{A \propto P_{\text{SiH}_2\text{Cl}_2}(b)}{(1 + K_3 \propto P_{\text{SiH}_2\text{Cl}_2}(b) + K_{10} P_{\text{H}_2}^{1/2})} \quad (4)$$

where $A = K_3/k_8$.

Equation (4) for the silicon adatom concentration can also be used if no H_2 is added deliberately. In that case P_{H_2} is given by the equilibrium partial pressure of H_2 (proportional to $\propto P_{\text{SiH}_2\text{Cl}_2}(b)$).

Figure 10

Thermodynamic data for the Si-H-Cl and the Si-H-Cl-N systems as a function of temperature and an input of 0.1 vol % HCl

4.2 Interpretation of results

4.2.1 The $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system

It was concluded that expressions given by Venables [3, 7] can be used to characterize the saturation density of stable clusters (N_s) in the present case where incomplete condensation of silicon has to be assumed. Because of the existence of an incubation period before the actual nucleation starts, it is thought probable that an equilibrium concentration of silicon adatoms can build up prior to the first nucleation. In this period therefore a strong uncomplete condensation regime applies. For this situation the relevant expression given by Venables can be re-written as

$$\frac{N_s}{n_0} \cong \left(\frac{n_1}{n_0} \right)^{\frac{i+1}{2}} \exp [(E_i + E_m - E_d)/2 kT] \quad (5)$$

where i is the number of atoms in the initial cluster, n_1 the monomer or adatom concentration and n_0 denotes the number of surface sites ($\cong 10^{14} \text{ cm}^{-2}$). E_i is the heat of formation of a cluster consisting of i atoms, E_m is the activation energy for surface diffusion of mobile clusters and E_d is the activation energy for surface diffusion of adatoms. As discussed in section 4.1, n_1/n_0 can be given as a first approximation by equation (4), leading to

$$\frac{n_1}{n_0} = \left\{ \frac{A \propto \text{PSiH}_2\text{Cl}_2(b)}{(1 + K_3 \propto \text{PSiH}_2\text{Cl}_2(b) + K_{10} P_{\text{H}_2}^{1/2})} \right\}^{\frac{i+1}{2}} \exp [(E_i + E_m - E_d)/2kT] \quad (6)$$

where A is a constant, α is the decomposition parameter and $\text{PSiH}_2\text{Cl}_2(b)$ is the input concentration of SiH_2Cl_2 , the other parameters being as defined before (equation (5)). Starting with the experiments done on SiO_2 substrates, it can be observed in Table I that N_s in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system is almost proportional to $\text{PSiH}_2\text{Cl}_2(b)$. It can thus be concluded that in eq. (6) $K_3 \propto \text{PSiH}_2\text{Cl}_2(b) < (1 + K_{10} P_{\text{H}_2}^{1/2})$, and moreover $i = 1$ for the temperature range between $925^\circ - 1100^\circ \text{C}$. If $i = 1$ for the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system, it is acceptable that in all other cases where the saturation nucleus density is higher one will also have $i = 1$. If furthermore $K_3 \propto \text{PSiH}_2\text{Cl}_2(b) < (1 + K_{10} P_{\text{H}_2}^{1/2})$ for all $\text{H}_2\text{-N}_2$ mixtures we obtain, from equation (6), for a fixed temperature

$$\frac{N_s}{n_0} = \frac{A \propto \text{PSiH}_2\text{Cl}_2(b)}{1 + K_{10} P_{\text{H}_2}^{1/2}} \quad (7)$$

The experimental data given in Figure 4 by plotting $\log (N_s/\text{PSiH}_2\text{Cl}_2(b))$ versus $\log (P_{\text{H}_2})$ can now be analysed. At 1100°C we observe a tangent which is almost $1/2$ for all $\text{H}_2\text{-N}_2$ mixtures, from which it may be concluded that adsorption of atomic hydrogen plays an important role in nucleation kinetics on SiO_2 substrates ($K_{10} P_{\text{H}_2}^{1/2} > 1$). Equation (7) can be used for the $\text{SiH}_2\text{Cl}_2\text{-N}_2$ system by introducing the equilibrium partial pressure of H_2 . This is done in Figure 4, and the results show that α is close to unity in accordance with the thermochemical data in Figure 10 ($P_{\text{H}_2} \cong \text{PSiH}_2\text{Cl}_2(b)$). At lower temperatures the tangent in Figure 4 is only $1/2$ for the lowest hydrogen pressures and the deviation from the slope $1/2$ is strongest at 925°C . Especially at the lower temperatures the assumption $K_{10} P_{\text{H}_2}^{1/2} > (1 + K_3 \propto \text{PSiH}_2\text{Cl}_2(b))$ remains acceptable. For SiO_2 substrates an additional decrease in N_s then has to be found in a lower value of α . At lower temperatures and the highest hydrogen pressures, therefore, hydrogen adsorption is no longer the

only factor that determines the saturation density. According to Figure 10, the dissociation of SiH_2Cl_2 into SiCl_2 and H_2 becomes more difficult under these experimental conditions, leading to the smaller value of α . If the decrease in saturation density is only caused by a decrease in α and if $\alpha \cong 1$ at 1000°C , we calculate an effective value of $\alpha = 10^{-2}$ at 925°C using Figure 4.

For the Si_3N_4 substrates equation (6) can also describe the experimental data given in Figures 1, 5 and 6. If we compare Figures 2 and 5, where the saturation nucleus density is plotted for hydrogen and nitrogen as a carrier gas, on SiO_2 and Si_3N_4 substrates, it can be observed that hydrogen adsorption on Si_3N_4 substrates could play a role but to a lesser degree than on SiO_2 substrates. By plotting $\log(N_s/\text{PSiH}_2\text{Cl}_2(b))$ versus $\log(\text{PH}_2)$ (Figure 6) we observe that the tangent in this figure is less than $1/2$ at 1000°C , leading to the conclusion that the assumption $K_{10}\text{PH}_2^{1/2} > (1+K_3 \alpha \text{PSiH}_2\text{Cl}_2(b))$ is not acceptable in this case, adsorption of SiCl_2 thus cannot be neglected.

It may be concluded that the difference in saturation nucleus densities between SiO_2 and Si_3N_4 substrates in a hydrogen medium is caused by strong adsorption of atomic hydrogen, especially on SiO_2 substrates. According to the JANAF tables [8] the OH bond energy is stronger than the NH bond by about 20 kcal/mole. This difference in bond energy is sufficient to explain the experimental data.

4.2.2 Comparison between different silicon-containing compounds in a H_2 medium

Figures 7 and 8 give saturation densities of silicon clusters for SiO_2 and Si_3N_4 substrates, respectively for SiH_4 , SiH_2Cl_2 and SiHCl_3 (all concentrations about 0.1 vol. %) in hydrogen as a carrier gas. If we start with the SiO_2 substrate a remarkable difference between the $\text{SiH}_4\text{-H}_2$ and the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system is observed. As discussed in section 4.2.1., the presence of hydrogen hampers the dissociation of SiH_2Cl_2 , and moreover adsorption of atomic hydrogen on SiO_2 blocks the adsorption for silicon species, as a consequence of which the saturation density decreases with decreasing temperature. In the $\text{SiH}_4\text{-H}_2$ system, hydrogen adsorption does not determine nucleation kinetics in the temperature range under discussion. At temperatures below 900°C hydrogen adsorption also becomes important for SiH_4 on SiO_2 substrates, which results in a decrease of the saturation density with decreasing temperatures for the $\text{SiH}_4\text{-H}_2$ system as well [3]. The $\text{SiHCl}_3\text{-H}_2$ system behaves like the SiH_2Cl_2 system, but shows a lower saturation nucleus density than the former system. Nucleation is more difficult than for the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system, due to a smaller decomposition parameter. For Si_3N_4 substrates the difference between the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system and the $\text{SiH}_4\text{-H}_2$ system is smaller than for the SiO_2 substrates (Figure 8). This can be understood because we have seen that hydrogen adsorption plays a less important role on Si_3N_4 substrates in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system, and in the $\text{SiH}_4\text{-H}_2$ system hydrogen adsorption does not come into play. The strong decrease of the saturation density at temperatures

below 1000 °C in the $\text{SiHCl}_3\text{-H}_2$ system also has to be explained by a decrease of the SiCl_2 concentration in the gas phase.

Introduction of HCl to the $\text{SiH}_4\text{-H}_2$ system decreases the saturation nucleus density, but down to 900 °C this density still increases with decreasing temperature (Figure 9). In the $\text{SiH}_4\text{-HCl-H}_2$ system etching of Si adatoms by HCl occurs, whereas in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system as discussed in the Appendix, hardly any free HCl is present before the onset of nucleation. The greater critical cluster size, which varies from 1 to approximately 4 for the $\text{SiH}_4\text{-HCl-H}_2$ system, could also be explained in terms of the etching of Si adatoms by HCl giving SiCl_2 [3]. The difference in nucleation on SiO_2 and Si_3N_4 substrates in the $\text{SiH}_4\text{-HCl-H}_2$ and SiH_2Cl_2 systems are ultimately traced back to the difference in the steady state concentration of silicon adatoms on the substrates prior to the actual nucleation.

Conclusions

In an attempt to understand and be able to monitor the crystallite size of polycrystalline silicon layers we have studied the nucleation of silicon on various substrates for different silicon-containing compounds as a function of gas phase composition and temperature. Experiments with nucleation of silicon on SiO_2 and Si_3N_4 substrates were reported for the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system in the temperature range of 800 ° – 1100 °C. The differences and conformities between the $\text{SiH}_4\text{-H}_2\text{-HCl}$, $\text{SiHCl}_3\text{-H}_2$ and the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ systems were also discussed. As far as the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system is concerned it is observed that the saturation nucleus densities on SiO_2 and Si_3N_4 substrates are almost the same for nitrogen as a carrier gas, and these densities are barely a function of temperature. Introduction of hydrogen strongly reduces the saturation nucleus density and this decrease is much stronger for SiO_2 than for Si_3N_4 substrates, resulting in a decrease of the saturation nucleus density with decreasing temperatures. Further the temperature dependence of the formation process increases with increasing hydrogen pressures. The experimental data can be explained from an analysis of the silicon adatom concentration on the surface as a function of gas phase composition and temperature. Application of an expression for the saturation nucleus density as obtained by Venables gives an indication of the size of the critical cluster, which seems to be 1 for all SiH_2Cl_2 mixtures under discussion. The differences between the $\text{SiH}_4\text{-H}_2\text{-HCl}$, the $\text{SiH}_4\text{-H}_2$, the $\text{SiHCl}_3\text{-H}_2$ and the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ systems are remarkable. For SiHCl_3 and SiH_2Cl_2 the saturation density of silicon clusters decreases with decreasing temperature, whereas for the $\text{SiH}_4\text{-HCl-H}_2$ and $\text{SiH}_4\text{-H}_2$ systems the opposite occurs. Formation of SiCl_2 by dissociation of SiH_2Cl_2 or SiHCl_3 becomes more difficult at decreasing temperatures, leading to a smaller steady state concentration of silicon adatoms at lower temperatures.

Acknowledgements

The authors wish to thank H. Haanstra and members of his group for the SEM and TEM photomicrographs.

APPENDIX:

REACTION SCHEME FOR THE SiH_2Cl_2 - H_2 - N_2 SYSTEM

According to the thermochemical data in Figure 10 the main processes which take place on or near the surface can be summarized as follows:

- a. Supply of SiH_2Cl_2 by means of gas phase diffusion:

$\text{SiH}_2\text{Cl}_2 (b)$ is the input concentration of SiH_2Cl_2 and $\text{SiH}_2\text{Cl}_2 (g)$ is the concentration of SiH_2Cl_2 near the surface.

- b. Dissociation of SiH_2Cl_2 in the gas phase:

- c. Adsorption of SiH_2Cl_2 and SiCl_2 on a free surface site (denoted by $*$) and dissociation of $\text{SiH}_2\text{Cl}_2 *$:

- d. Formation of Si adatoms on the surface:

e. Formation of stable silicon clusters by diffusion of Si adatoms on the surface:

f. Reaction of Si adatoms with hydrogen:

g. Adsorption of hydrogen and chlorine:

Formation of chlorosilanes other than SiCl_2 , such as SiHCl_3 and SiCl_4 , can be left out of consideration, at least in the initial stage of nucleation, where practically no HCl is present. The notation (g) will only be used when comparison with bulk values of the vapour pressure is made.

The total number of reactions can be decreased by judging the various parameters in view of experimental results and thermochemical data. The following assumptions can be made.

- Because hardly any HCl is present in the initial stage of nucleation, the back reaction k_{-5} and k_{-6} can be neglected and also $[\text{Cl}^*]$ can be treated as small.
- Nucleation and growth experiments in the $\text{SiH}_4\text{-HCl-H}_2$ system lead to the conclusion that silicon adatoms $[\text{Si}^*]$ are needed to arrive at nucleation [3].
- Gas phase dissociation of SiH_2Cl_2 to SiCl_2 and H_2 occurs at temperatures above 800°C . This is according to Smith and Sedgwick [9] who performed in situ measurements using inelastic light scattering and obtained spectra of SiCl_2 in a R.F. heated reactor in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system.
- The nucleation starts via the adsorption of SiCl_2 or via adsorption of SiH_2Cl_2 . In order to discriminate between adsorption of SiH_2Cl_2 and SiCl_2 we have to notice that SiH_2Cl_2 is a fully coordinated molecule with four atoms bonded in a tetrahedral configuration. If SiH_2Cl_2 adsorbs without dissociation, then a peripheral hydrogen or chlorine atom has to come into contact with the surface. In the non-linear SiCl_2 molecule the silicon atom is not sterically blocked from the surface of the substrate, and the presence of the unbonded electrons on the silicon greatly enhances its adsorption by interaction with the dangling bonds on

the surface [10]. It can therefore be concluded that the adsorption energy of SiH_2Cl_2 is much smaller than that of SiCl_2 . This means that (A-2), (A-4) and (A-5) can be left out of consideration. With the above approximations the steady state concentrations of $[\text{Si}^*]$ and $[\text{SiCl}_2^*]$ will be given by

$$n_1 = [\text{Si}^*] = \frac{k_6 [\text{SiCl}_2^*] P_{\text{H}_2} + k_{-8} [\text{SiH}_2^*]}{k_7 + k_8 P_{\text{H}_2}} \quad \text{A-11}$$

$$[\text{SiCl}_2^*] = \frac{k_3 P_{\text{SiCl}_2} [*]}{k_{-3} + k_6 P_{\text{H}_2}} \quad \text{A-12}$$

As for the $\text{SiH}_4\text{-HCl-H}_2$ system [3] the nucleus density very quickly reaches a saturation density, with respect to exposure time, after an incubation period. On the basis of these experiments it was assumed that the time needed to attain the population of adatoms is small, giving a constant value of n_1 before nucleation occurs. This means that k_7 can be omitted until nucleation takes place. The second term in the nominator, the indirect formation of Si^* , can be assumed to be small compared to the first term and can be neglected. The silicon adatom concentration will be much smaller than the concentration of adsorbed SiCl_2 molecules, therefore it can be assumed that $k_{-3} > k_6 P_{\text{H}_2}$. With these approximations one obtains

$$n_1 = \frac{k_6 K_3 P_{\text{SiCl}_2} [*]}{k_8} \quad \text{A-13}$$

For the concentration of free surface sites we can write

$$[*] = n_0 - [\text{Si}^*] - [\text{SiCl}_2^*] - [\text{H}^*] - [\text{SiH}_2^*]$$

where n_0 is the total number of sites per unit area

With $[\text{H}^*] = K_{10} P_{\text{H}_2}^{1/2} [*]$, $K_{10} = k_{10}/k_{-10}$, $[\text{SiCl}_2^*] = K_3 P_{\text{SiCl}_2} [*]$, $K_3 = k_3/k_{-3}$ and $[\text{Si}^*]$, $[\text{SiH}_2^*] \ll [\text{SiCl}_2^*]$, this leads to

$$[*] = \frac{n_0}{(1 + K_3 P_{\text{SiCl}_2} + K_{10} P_{\text{H}_2}^{1/2})} \quad \text{A-14}$$

The silicon adatom concentration can now be given by

$$\frac{n_1}{n_0} = \frac{K_3 k_6 P_{\text{SiCl}_2}}{k_8 (1 + K_3 P_{\text{SiCl}_2} + K_{10} P_{\text{H}_2}^{1/2})} \quad \text{A-15}$$

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CHAPTER V

RATE-DETERMINING REACTIONS AND SURFACE SPECIES IN CVD OF SILICON

1 The SiH_4 -HCl- H_2 system

Summary

CVD of silicon from 0.1 volume percent SiH_4 in hydrogen shows a growth rate that does not change significantly on addition of 0.4% HCl to the gas phase for growth temperatures above 1000 °C. Below 1000 °C, however, this addition causes a vastly reduced growth rate compared to the growth from SiH_4 alone. This behaviour produces experimental information on the possible rate-limiting steps in the lower temperature region. It is concluded that, for SiH_4 without HCl, surface diffusion of silicon-containing species and the incorporation on steps on the surface constitutes the rate-determining reaction. At lower temperatures the concentrations of these species increase far above the equilibrium values. The introduction of HCl then changes the adatoms (Si and SiH_2) into SiCl_2 , subsequent desorption of SiCl_2 is responsible for the reduction in growth rate. The mechanism is discussed in terms of recent calculations reported by Chernov et al. [2] on the adsorption of different species on the silicon surface.

1. Introduction

In CVD of silicon for the production of monocrystalline silicon layers on silicon substrates the quality of the resulting layers is of prime importance. In order to achieve a deposit of higher quality deposition temperatures above 1050 °C are generally used. Under these circumstances the surface reactions are sufficiently rapid and it is the supply of reactants that determines the growth rate via gas phase diffusion. Hydrogen is preferred as a carrier gas, to bring about the reduction of silicon halides, to reduce homogeneous gas phase nucleation of SiH_4 and to minimize the undesired effects of oxygen on nucleation and growth. This high-temperature regime has been the subject of much study, and reasonable models are available to explain the growth rate in this regime [1]. As to the situation at temperatures below 900 – 1000 °C there is less confidence in our knowledge, and speculative models are used to describe the growth, which is controlled by surface reactions of unknown origin. Recently, Chernov et al. [2] calculated the adsorption energy of H, Cl, SiCl_2 and other species that could be present on the silicon surface. They found an extremely high surface coverage of especially H and Cl (~99%), because of their high energy of adsorption of 71.4 and about 100 kcal/mole respectively. It was stressed by Chernov [2] that this high surface coverage could hamper the diffusion of adatoms on the silicon surface. The influence of this adsorption on crystal growth could be one of the reasons why layers grown below 900 °C in a hydrogen ambient tend to become polycrystalline whereas in a He ambient or at reduced pressures still monocrystalline layers can be produced. This is the more so at UHV conditions where the growth of monocrystalline layers is still possible at appreciably lower temperatures [3]. In these UHV systems not only

hydrogen adsorption is minimized, it is also much easier to control the presence of oxide on the silicon surface. The reason is found in the extremely low background oxygen and water vapour pressures possible at UHV conditions.

Experiments were therefore planned to obtain information on the low temperature growth kinetics, mainly by studying growth and etching in the SiH_4 -HCl system. It will be shown in the present study that experiments at lower temperatures give indications on the specific surface reaction responsible for the reduced growth rate below 1000°C .

2 Experimental results

It has been shown [4] that, at high temperatures where chemical equilibrium at the silicon surface can be expected, growth by SiH_4 and etching by HCl can be taken to proceed independently of each other. The growth rate could be given as

$$R = k_a P_{\text{SiH}_4} - k_b P_{\text{HCl}}^2 \quad (1)$$

The quadratic term in P_{HCl} is caused by the main reaction product being SiCl_2 and the circumstances that only a fraction of the HCl that is present reacts to form SiCl_2 . It has been shown by Van der Putte et al. [5] that the etching of silicon proceeds via the attack by HCl on surface steps and the subsequent diffusion and desorption of SiCl_2 molecules. The experimental evidence shows that 0.1 volume percent SiH_4 in hydrogen shows a growth rate of about $0.3 \mu\text{m}/\text{min}$ at 1000°C , whereas 0.4% HCl in hydrogen gives an etch rate of only $0.02 \mu\text{m}/\text{min}$ at 1000°C . For a mixture with an input concentration of silane of 0.1% and a fourfold HCl concentration (resembling the input of SiCl_4 in hydrogen) the growth rate at 1000°C within a few percent equals the growth rate given by SiH_4 alone. It was assumed at that time that these results could be extrapolated to temperatures below 900°C [6]. The present experiments were performed in a conventional air cooled, RF-heated fused silica reactor. The silicon slices were heated on a SiC coated graphite susceptor. A typical gas flow rate of $60 \text{ cm}^3/\text{sec}$ was used in order to obtain stable laminar flow conditions. The hydrogen carrier gas was purified by means of a conventional gas purifier to a water and oxygen content below 1 ppm. The carrier gas as well as the reactants (electronic grade HCl and 5% SiH_4 in H_2) were introduced via automatic flow controllers. Growth and etch rates were determined by means of IR interference measurements on grown layers or from the decrease in thickness of layers with accurately known thickness. Temperature measurements were done by optical pyrometry using the surface temperature of silicon slices, after correction for the emissivity of silicon and the absorption of the reactor wall. Prior to the growth or etching experiments the silicon wafers were treated at 1100°C for 3 minutes with 0.4% HCl in H_2 to remove $0.05 \mu\text{m}$ from the surface. Firstly the growth rate of silicon as a function of temperature was re-measured for an input concentration of SiH_4 of 0.1 volume percent with hydrogen

Figure 1.

Growth rate given by a mixture of 0.1% SiH_4 and 0.4% HCl in hydrogen as a function of temperature, compared with the growth rate shown by silane without HCl addition, the drawn curve for SiH_4 according to Van den Brekel [7], the data points are from the present study.

as carrier gas. Figure 1 gives the result, which is in accordance with the result of previous investigations [1, 7], showing the high temperature region where growth is limited by the supply of reactant via gas phase diffusion, and below 900 °C the decrease in growth rate because of the onset of a rate-limiting surface reaction of unknown origin. The results given in Figure 1 for SiH_4 are exactly comparable to those of Van den Brekel [7] measured at the centre part of the susceptor. The upper curve of fig. 1 is according to ref. 7, the data points are from the present study. Figure 2 shows the etch rate of silicon given by 0.4 and 1.0 volume percent HCl in hydrogen as a function of temperature. Here, too, the etch rate is temperature-independent until well below 900 °C where a strong decrease is observed. This has been reported before [8, 9]. It was noticed that, even at the lowest temperatures (800 °C), no incubation time for the etch rate could be observed. Figure 3 shows the etch rate of silicon at 1000 °C as a function of the input concentration of HCl , confirming the variation of the etch rate with P_{HCl}^2 . A mixture of SiH_4 (0.1%) and HCl (0.4%) gives the result shown in the lower curve of figure 1. Down to 900 °C the small difference is equal to the etch rate given by HCl alone (see eq. 1). Below 900 °C, however, the growth rate falls off rapidly. The difference

Figure 2.

The etch rate of silicon in hydrogen with 0.4 and 0.1 volume percent HCl as a function of temperature.

Figure 3.

The etch rate of silicon at 1000°C as a function of the input concentration of HCl with hydrogen as the carrier gas.

Figure 4.

The difference in growth rate shown by 0.1% SiH_4 and that of a mixture of 0.1% SiH_4 and 0.4% HCl can be interpreted as an apparent etch rate of HCl . This apparent etch rate is shown in the upper curve and is compared with the etch rate of HCl alone as given in figure 2.

between the upper and lower curve in figure 1 reflects the influence of the addition of HCl and can be interpreted as an etch rate. This etch rate, however, is much greater than the etch rate given by the same concentration of HCl without SiH_4 being present. In figure 4 the apparent etch rate of HCl in the mixture is given, calculated from the difference in the curve for SiH_4 and for $\text{SiH}_4 + 4 \text{HCl}$. The difference curve below 900 °C shows an etch rate appreciably higher than that given by HCl alone (lower curve). Figure 5 shows the temperature dependence of the growth rate for 0.1, 0.2 and 0.4 volume percent of SiH_4 mixed with 0.4 volume percent of HCl . For all silane concentrations a rapid decrease in growth rate below 900 °C is observed.

In order to study the influence of the amount of HCl in the mixture, experiments were done with 0.1 % silane and increasing amounts of HCl at temperatures of 1000 °C, 900 °C and 800 °C. The results are given in figure 6. The curve at 1000 °C shows the behaviour given in eq. (1): $R = k_a P_{\text{SiH}_4} - k_b P_{\text{HCl}}^2$. At 900 °C, however, the first addition of HCl gives rise to a rapid initial decrease in growth rate

Figure 5.

Temperature dependence of the growth rate of mixtures of SiH_4 and 0.4% HCl , for SiH_4 input concentrations of 0.1, 0.2 and 0.4 volume % in hydrogen.

followed by a slower fall-off at a lower level. This effect is even better perceivable at 800°C . Plotting the growth rate of SiH_4 - HCl mixtures for constant P_{SiH_4} as a function of P_{HCl}^2 one obtains the results given in figure 7, confirming the rapid decrease of the growth rate on the first addition of small amounts of HCl and indicating a subsequent reduction in growth rate proportional to P_{HCl}^2 . The same kind of experiments for other silane input concentrations show the same behaviour. This is shown in figure 8 and figure 9 for growth rates at 900 and 800°C respectively as a function of P_{HCl}^2 . In all cases an initial decrease in growth rate is observed followed by a slower fall off proportional to P_{HCl}^2 . The decrease in growth rate appears to be proportional to the input concentration of P_{SiH_4} , or, in other words both the initial growth rate without HCl and the growth rate after the rapid initial decrease are proportional to P_{SiH_4} . The resulting growth rate after introduction of HCl can be extrapolated to $P_{\text{HCl}} = 0$, this value (R_2) is plotted in figure 10 as a function of P_{SiH_4} together with the growth rate without HCl (R_1).

Figure 6.

Growth rates shown by mixtures of 0.1 vol. % SiH_4 and increasing amounts of HCl at 1000, 900 and 800 °C.

Figure 7.

The growth rate shown by mixtures of 0.1 vol. % SiH_4 and HCl plotted as a function of ρ_{HCl}^2

Figure 8.

Growth rates at 900 °C for 0.05, 0.1, 0.2 and 0.4 volume % SiH_4 as a function of the HCl concentrations, plotted as P_{HCl}^2

The ratio R_2/R_1 is about 0.8 at 900 °C and 0.25 at 800 °C. The growth rate for R_2 thus can be expressed as

$$R_2 = k_c P_{SiH_4} - k_b P_{HCl}^2$$

The etching term $k_b P_{HCl}^2$ is nearly equal to the etch rate of silicon by HCl alone (figure 2).

3. Discussion

In the high temperature regime above 1000 °C the silicon surface can be assumed to be in local chemical equilibrium with the gas phase in contact with that surface. Surface adatoms and adsorbed molecules are present, moving over the surface until they are incorporated in the lattice at specific sites. According to the crystal growth theory given by Burton, Cabrera and Frank [10], steps on the surface provide the sinks for the moving adatoms and this surface diffusion is the slowest step on the

Figure 9.

Growth rates at 800°C for 0.1, 0.2 and 0.4 % SiH_4 in hydrogen as a function of P_{HCl}^2

surface. The adatoms and molecules that can be visualized as present on the surface, are SiH_2^* , Si^* and SiCl_2^* . The asterisks denote that we are dealing with adsorbed species not yet incorporated into the crystal lattice. This incorporation proceeds via surface diffusion, incorporation on the steps and subsequent removal of H and Cl atoms by chemical reactions. At high temperatures ($T > 1000^\circ\text{C}$) these surface processes occur so easily that the transport of reactants from the gas phase becomes the rate-determining step. At temperatures below 1000°C the surface kinetics become slower and gas phase diffusion no longer constitutes the slowest step. According to Chernov [2] the surface diffusion coefficient of adatoms (D_s) is given by

Figure 10.

The growth rate of silicon as a function of input concentration of silane at 800 ° and 900 °C. R_1 shows the growth rate for SiH_4 without HCl , R_2 is the growth rate in the presence of HCl , extrapolated to $P_{\text{HCl}} = 0$. $R_1 = R_{\text{Si}}$; $R_2 = R_{\text{SiCl}_2}$.

$$D_s = D_s^0 \theta \exp(-E_D/kT) \quad (2)$$

in which E_D is the activation energy for diffusion, D_s^0 is a constant and θ is the fraction of free surface sites needed to make surface diffusion possible. Chernov also made it clear that especially adsorption of HCl is important. Around 1000 °C at least 99% of the surface sites could be filled with atomic hydrogen or chlorine. It seems probable, therefore, that the diffusion of adatoms is the main rate-limiting step in the growth of silicon at lower temperatures. Experiments done by Van der Putte et al. [5] showed that in the case of etching with HCl the diffusion of SiCl_2 away from the steps where it has been formed constitutes the rate-limiting reaction. Nucleation experiments [11, 12] also are explained on the basis of surface diffusion of adatoms. Returning to the experiments cited above, we note that the temperature independent etch rate given in figure 2 is in accordance with the analysis reported by Van der Putte for $T > 900^\circ\text{C}$. The sharp decrease at temperatures below 900 °C can be caused by the influence of trace amounts of oxygen and water vapour. The results of Rijks et al. [9] clearly show that SiO_2 can be formed on the surface, effectively hampering the etching reaction. At 900 °C already 0.2 ppm of

Figure 11.

Schematic representation of the growth rate of silicon via Si^* and SiCl_2^* (R_{Si} and R_{SiCl_2}) as a function of P_{HCl} .

The total growth rate is composed of the sum of R_{Si} and R_{SiCl_2} minus the etch rate given by HCl .

oxygen or water vapor in H_2 or in N_2 is sufficient to create a stable SiO_2 phase, well within the range of gas purity in the present system. In figure 7 it is seen that etching is still possible in the SiH_4 - HCl - H_2 system. The reduction in growth rate at 800 and 900 °C gives the same slope of R vs. P_{HCl}^2 after the initial rapid decrease in growth rate. The influence of trace amounts of oxygen or water vapour is thus apparently reduced, probably by a gas phase reaction between SiH_4 and oxygen.

The growth of silicon from silane (figure 1) is in good agreement with earlier observations: below 900 °C surface reactions become rate-determining. The mixture of $\text{SiH}_4 + 4 \text{HCl}$ however, shows an appreciably lower growth rate below 900 °C. The reduction of the growth rate in this region will be dependent on the surface reactions that occur in the kinetic region. Figure 4 shows that indeed the start of the kinetic region coincides with the reduction in growth rate, which further decreases with decreasing temperature, as it can not surpass the growth rate of pure SiH_4 at the same temperature.

In a more detailed discussion of the process, the distinction between the high and low temperature regimes has to be stressed. The high temperature behaviour gives a growth rate (eq. 1) composed of a growth term and an etching term. In the growth term diffusion of SiH_4 from the bulk of the gas phase (b) towards the surface is the main kinetic barrier

The addition (g) denotes the concentration near the silicon surface. The etching term in eq. (1) is caused by the etching of silicon by HCl on steps present on the surface via the overall reaction

A surface catalyzed gas phase reaction can be given as:

At the higher temperatures SiCl_2 is the main reaction product [5], going to lower temperatures also the presence of SiHCl_3 has to be considered. The fully coordinated species as SiH_4 , SiHCl_3 , and SiCl_4 have low adsorption energies compared with Si^* , SiCl_2^* and SiH_2^* [2], this will influence the adsorption-desorption equilibria and the various surface reactions. In the present experiments it is not possible to separate the contribution of Si^* and SiH_2^* . According to Chernov they have nearly equal adsorption energies and could have nearly equal concentrations in a hydrogen ambient. Therefore in the following only Si^* will be considered in the calculations. The main rate-limiting reaction has to be found between the various surface reactions like the adsorption of silane, the chemical reaction to form adatoms, the diffusion of surface species to reactive sites and the incorporation of silicon on the steps. As discussed above, the rate-limiting step can best be correlated with the surface diffusion and the incorporation at the atomic steps of the adatoms. In both cases the steady state concentrations of Si^* and SiCl_2^* will be increased. As Si^* is a reactive species, addition of HCl will reduce its concentrations converting it to SiCl_2^* . It has to be realised that, whatever the surface species present, the growth rate will be the same when a condition of complete condensation prevails. When SiCl_2^* is present at the surface and the incorporation reaction is the rate determining step, then the SiCl_2^* concentration between the steps will be increased. This supersaturation will promote the desorption of SiCl_2 and the formation of SiHCl_3 by reaction of SiCl_2 with HCl. The occurrence of these alternative reactions is the reason for a reduction in growth rate. A number of surface reactions and the steady state concentrations of Si^* and SiCl_2^* are given in the Appendix, where also general expressions for the growth of silicon are calculated in terms of the input concentrations of HCl and SiH_4 and of the rate constants of the various surface reactions. A comparison of the experimentally found relations and the theoretical

expression for the growth rates gives rise to the following points

- i The first observation concerns the main surface species present In a system without HCl silicon adatoms are formed, incorporation of Si^* at the surface steps constitutes the layer growth of silicon On the addition of HCl the results can only be explained for SiCl_2^* as the predominant surface species The introduction of some HCl already decreases the concentration of Si^* (and SiH_2^*) to insignificant amounts and diffusion and incorporation via SiCl_2^* has to take over (see figure 11)
- ii The desorption rate of SiCl_2 causes the reduction of the growth rate as a consequence of HCl addition
- iii From the present experiments it has to be concluded that the introduction of HCl at temperatures below 900°C leads to an increased concentration of surface species (SiCl_2^*) The rate-determining step therefore has to be found at the end of the chain of reactions These are the diffusion and incorporation of SiCl_2 at surface steps together with the chemical reaction needed to remove Cl atoms from the step site Additional information is needed to decide between these possibilities
- iv It has been shown that especially at lower temperatures, nucleation becomes difficult as soon as some HCl is present, nucleation experiments [12] indicate that Si^* adatoms are needed to come to nucleation In addition it was found that, under conditions where such a nucleation on a foreign surface or on a perfect silicon facet meets with difficulties, growth of silicon on a stepped silicon substrate still remains possible This experimental result can now be explained by the possibility of growth via SiCl_2 in the latter case, the reaction is more readily achieved at an atomic step than from an isolated SiCl_2 molecule adsorbed on the silicon surface between the steps
- v The general picture obtained is that of a predominant occurrence of SiCl_2 on the silicon surface as soon as some HCl is present in the gas phase In this respect the growth of silicon as described here and the etching of silicon by HCl as described in ref 5 show a perfect match In both cases diffusion and reaction of SiCl_2^* is the rate-limiting step The perfect analogy is also present in the morphology and the defects introduced on growth or etching [13, 14, 15]

4 Conclusion

The growth and etching of silicon in CVD has been studied and a comparison with recent nucleation studies leads to a consistent picture of the atomic processes during nucleation and growth of silicon

In the nucleation experiments it was ascertained that silicon adatoms (Si^*) are responsible for the initial nucleation of silicon on foreign substrates

The present experiments on the growth of silicon on silicon substrates shows that, at temperatures below 900°C , the main surface species responsible for growth is SiCl_2^* , as soon as some HCl is present in the gas phase because Si^* rapidly reacts to form SiCl_2^* . Growth now has to proceed via SiCl_2^* , thus appears to be only possible on a silicon surface provided with atomic steps, on a foreign surface the nucleation barrier is more difficult to surpass. SiCl_2^* diffuses over the silicon surface and is incorporated at steps on the surface after which the Cl atoms have to desorb in order to give a positive growth rate. At higher temperatures above 1000°C the surface reactions become so rapid that the supply of reactants by gas phase diffusion becomes rate-limiting.

APPENDIX

a The following reactions can be distinguished

1. Gas phase transport of SiH_4 and HCl from the bulk of the gas phase (b) to the region near the silicon surface (g)

2. Adsorption reactions

(* denotes a free surface site)

3. Surface reactions

4. The incorporation of silicon into the lattice, represented by the surface diffusion of Si^* and SiCl_2^* to the atomic steps and the incorporation reaction at the step.

The fraction of free surface sites (θ) follows from

$$1 = \theta + [\text{H}^*] + [\text{Cl}^*] + [\text{SiCl}_2^*] +$$

with eq (4), (5) and (7) this leads to

$$\theta = \frac{1}{1 + K_9 P_{\text{H}_2}^{1/2} + K_4 P_{\text{HCl}}/P_{\text{H}_2}^{1/2} + K_7 P_{\text{SiCl}_2}} \quad (\text{A } 13)$$

where $k_4/k_{-4} = K_4$ etc

In the following the notation (g) will only be used when comparison with bulk values of the vapour pressures is made

In a steady state situation it is possible to calculate the Si^* and SiCl_2^* concentrations by equating all the ways to produce and to eliminate these species. This gives for Si^*

$$\begin{aligned} \frac{d[\text{Si}^*]}{dt} = 0 = & k_3 P_{\text{SiH}_4} \theta + k_{-6} [\text{SiCl}_2^*] P_{\text{H}_2} + k_{-9} [\text{Si(st)}] - [\text{Si}^*] (k_{-3} P_{\text{H}_2}^2 + \\ & + k_6 P_{\text{HCl}}^2 + k_9) \end{aligned}$$

The rate constants k_{-6} and k_{-9} (the reverse reactions of k_6 and k_9) are expected to be small, thus

$$[\text{Si}^*] = \frac{k_3 P_{\text{SiH}_4} \cdot \theta}{(k_{-3} P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_9)} \quad (\text{A } 14)$$

Equilibrium between solid silicon and hydrogen gas gives a value of P_{SiH_4} near to 10^{-6} bar at temperatures between 700 and 1100 °C [12]. In the kinetic region $P_{\text{SiH}_4} \text{ (g)} \approx P_{\text{SiH}_4} \text{ (b)}$ this means that the surface concentration of Si^* can be a factor of 1000 higher than the equilibrium value for an input concentration of SiH_4 of 10^{-3} bar (0.1 volume percent of SiH_4 in H_2) as used in the present experiments

In the presence of HCl the term $k_6 P_{\text{HCl}}^2$ will soon dominate leading to

$$[\text{Si}^*] = \frac{k_3 P_{\text{SiH}_4} \cdot \theta}{k_6 P_{\text{HCl}}^2} \quad (\text{A-15})$$

Along the same lines for SiCl_2^* we find

$$[\text{SiCl}_2^*] = \frac{k_6 [\text{Si}^*] P_{\text{HCl}}^2 + k_7 P_{\text{SiCl}_2} \cdot \theta + k_{11} [\text{SiCl}_2 (\text{st})]}{k_7 + k_6 P_{\text{H}_2} + k_8 P_{\text{HCl}} + k_{11}}, \quad (\text{A-16})$$

for small values of k_{11} , k_{11} and P_{SiCl_2} we obtain, using A-15,

$$[\text{SiCl}_2^*] = \frac{k_3 P_{\text{SiH}_4} \cdot \theta}{k_7 + k_8 P_{\text{HCl}} + k_{11}} \quad (\text{A-17})$$

For $\text{Si} (\text{st})$ we have

$$[\text{Si} (\text{st})] = \frac{k_9 [\text{Si}^*]}{k_{10} + k_9}. \quad (\text{A-18})$$

In the present experiments it is not possible to discriminate between k_9 and k_{10} , it will be assumed that k_{10} is large, thus

$$[\text{Si} (\text{st})] = k_9 [\text{Si}^*] / k_{10} \quad (\text{A-19})$$

For $\text{SiCl}_2 (\text{st})$ we find

$$[\text{SiCl}_2 (\text{st})] = \frac{k_{11} [\text{SiCl}_2^*]}{k_{11} + k_{12} P_{\text{H}_2}} \quad (\text{A-20})$$

Growth via Si^* is now found from

$$R_{\text{Si}} = k_{10} [\text{Si} (\text{st})] = \frac{k_9 k_3 P_{\text{SiH}_4} \cdot \theta}{(k_3 P_{\text{H}_2}^2 + k_6 P_{\text{HCl}}^2 + k_9)}$$

Without HCl we could have (k_9 large)

$$R_{\text{Si}} = k_3 P_{\text{SiH}_4} \cdot \theta \quad (\text{A-21})$$

In the presence of HCl then

$$R_{\text{Si}} = \frac{k_9 k_3 \cdot P_{\text{SiH}_4} \cdot \theta}{k_6 P_{\text{HCl}}^2} \quad (\text{A-22})$$

In that case the route via eq. (A-12) becomes possible leading to the chemical reaction of SiCl_2 with H_2 at the steps giving

$$R_{\text{SiCl}_2} = k_{12} P_{\text{H}_2} [\text{SiCl}_2 (\text{st})] = \frac{k_{12} P_{\text{H}_2} k_{11} k_3 P_{\text{SiH}_4} \cdot \theta}{(k_{12} P_{\text{H}_2} + k_{11}) (k_7 + k_8 P_{\text{HCl}} + k_{11})},$$

For a slow desorption of SiCl_2 from the steps (small value of k_{11}) we have a growth reaction limited by surface diffusion of SiCl_2

$$R_{\text{SiCl}_2} = \frac{k_{11} k_3 P_{\text{SiH}_4} \cdot \theta}{(k_7 + k_8 P_{\text{HCl}} + k_{11})}. \quad (\text{A-23})$$

A slow chemical reaction ($k_{12} P_{\text{H}_2} < k_{11}$) leads to

$$R_{\text{SiCl}_2} = \frac{k_{12} P_{\text{H}_2} \cdot k_{11} k_3 P_{\text{SiH}_4} \cdot \theta}{(k_7 + k_8 P_{\text{HCl}} + k_{11})}. \quad (\text{A-24})$$

Additional experiments are needed to discriminate between (A-23) and (A-24). Both reactions lead to an increased SiCl_2^* concentration between the steps. The foregoing expressions have to be compared with the experimentally observed behaviour of a rapid decrease in growth rate on the introduction of HCl followed by a relation of the type

$$R_2 = k_c P_{\text{SiH}_4} - k_b P_{\text{HCl}}^2$$

The initial decrease can be explained by the growth rate via Si^* , rapidly decreasing with increasing HCl concentration (A-22). The growth then remains via the SiCl_2 route, the negative term in P_{HCl}^2 describes the etching on the steps. We obtain then

$$R_{\text{SiCl}_2} = \frac{k_{12} P_{\text{H}_2}}{(k_{11} + k_{12} P_{\text{H}_2})} \cdot \frac{k_{11} k_3 P_{\text{SiH}_4} \cdot \theta}{(k_{11} + k_8 P_{\text{HCl}} + k_7)} - k_b \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}}. \quad (\text{A-25})$$

In (A-23 and A-24) the expected growth rate via SiCl_2 is given. Comparison with the experimental growth rate equation shows that k_8 has to be small, the main desorption process has to be correlated with k_7 .

In order to come to the origin of the initial rapid decrease in growth rate on the introduction of HCl , the growth via Si^* , (A-21) has to be compared with the growth via SiCl_2^* , e.g. via eq. (A-23)

$$\frac{R_{\text{SiCl}_2}}{R_{\text{Si}}} = \frac{k_{11}}{k_{11} + k_7} \cdot \frac{\theta_{\text{Cl}}}{\theta_{\text{H}}}.$$

The value of θ could be different in H_2 and $H_2 + HCl$ as the heat of adsorption of Cl is higher than that of H.

Between Cl adatoms repulsive forces are present however, which is not the case for H [2]. Because of the repulsive effect the heat of adsorption of Cl and H come close to each other. In a first approximation it is therefore assumed that the value of θ is not greatly different when we compare a H_2 ambient to $H_2 + HCl$.

The ratio of growth rates expected via $SiCl_2^*$ and Si^* then becomes

$$\frac{R_{SiCl_2}}{R_{Si}} = \frac{k_{11}}{k_{11} + k_7}.$$

It is seen that, for comparable values of θ_{Cl} and θ_H , the desorption of $SiCl_2$ via k_7 is the main reason for the decrease in growth rate on introduction of HCl .

At high temperatures the surface diffusion term (k_{11}) is so large that the growth rate is the same via the two routes.

At lower temperatures the value of k_{11} decreases, the increased adatom concentration between the steps then promotes the desorption.

The temperature dependence of the ratio R_{SiCl_2}/R_{Si} is governed by the activation energies for surface diffusion of $SiCl_2$ compared with the heat of desorption of $SiCl_2$. The diffusion of $SiCl_2$ depends on the activation energy for diffusion of $SiCl_2$ plus the activation energy to break the Si-H bond needed to create a vacant surface site (eq. 2). k_7 depends on the heat of adsorption of $SiCl_2$. The ratio R_{SiCl_2}/R_{Si} then has an activation energy

$$E_R = E_{11} - E_7 = E_{diff.SiCl_2} + E_{des.H} - E_{des.SiCl_2}$$

From the experiments (figure 10) E_R can be calculated to be close to 30 kcal/mole. As the heats of desorption of H and $SiCl_2$ are nearly equal and $E_{(diff.SiCl_2)} = 32$ kcal/mole according to Van der Putte et al [13] the present effect shows the right order of magnitude.

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CHAPTER VI

RATE-DETERMINING REACTIONS AND SURFACE SPECIES IN CVD OF SILICON

II The SiH_2Cl_2 - H_2 - N_2 -HCl system

Summary

The growth rate of CVD silicon from SiH_2Cl_2 -nitrogen-hydrogen mixtures is found to be a linear function of the partial pressure of hydrogen at temperatures between 800 ° and 1000 °C. At temperatures below 900 °C, the SiH_2Cl_2 - N_2 system shows a saturation in growth rate for input concentrations above 0.5 volume percent. This is at variance with the SiH_2Cl_2 - N_2 system, which shows a linear dependence between the growth rate and the input concentration of SiH_2Cl_2 at 800 °C. Addition of HCl to the SiH_2Cl_2 - H_2 system reduces the growth rate at temperatures below 1000 °C due to the formation of SiHCl_3 in the gas phase. The formation of SiHCl_3 is directly related to the dissociation of SiH_2Cl_2 in the gas phase into SiCl_2 and H_2 . It is concluded that in a Si-H-N-Cl system the surface concentration of SiCl_2 is always much larger than the Si adatom concentration. The reduction of SiCl_2 at step sites is proposed to be the rate-limiting reaction, leading to a surface concentration of SiCl_2 far above the equilibrium concentration and favouring desorption of SiCl_2 . The high SiCl_2 concentration accounts for the saturation in growth rate as a function of input concentration of SiH_2Cl_2 in hydrogen; the linear increase in growth rate when nitrogen is used as a carrier gas can also be explained along these lines.

1. Introduction

In a previous paper [1] (referred to as part I in the following) the rate-determining reactions in the SiH_4 -HCl- H_2 system were described at temperatures below 1000 °C. It was demonstrated there that SiCl_2 is the main surface species in a Si-Cl-H system. It was concluded that candidates for the rate-determining surface reactions below 1000 °C could be either the surface diffusion of SiCl_2 to atomic steps or the chemical reaction at the silicon step to remove the chlorine atoms from the attached SiCl_2 molecules. No preference could be given between these possibilities based on the data available at that time. The present paper reports on additional experiments directed at resolving this dilemma, for which purpose the chlorosilanes can be used. Dichlorosilane was selected because unlike other homologues, it decomposes without hydrogen addition. As a consequence, the kinetics of decomposition can be studied with and without either hydrogen or hydrogen chloride being present in the gas phase, thus providing information on rate-limiting steps.

2. Experimental

The experiments were performed in a horizontal air-cooled R.F. heated reactor. Most of the experimental conditions have been described in part I, but some additional information is given below. The gas system was provided with automatic mass-flow controllers for the carrier gases hydrogen and nitrogen and the reactants SiH_2Cl_2 and HCl (both electronic grade). The carrier gases were purified to bring

water and oxygen concentrations below 1 ppm. Monocrystalline silicon slices, covered with a 1500 Å thick LPCVD Si_3N_4 layer, were used as substrates. In order to avoid nucleation difficulties [2] the substrates were covered prior to deposition with a thin polycrystalline silicon layer (about 1000 Å), using 0.1 vol % SiH_4 in hydrogen for 20 seconds at 1000 °C.

The growth rate of silicon on silicon as a function of temperature from SiH_2Cl_2 in hydrogen shows a kinetically controlled regime at temperatures below 1000 °C and a gas phase diffusion-controlled regime above this temperature [3]. The experiments reported in this paper relate to the kinetically controlled temperature region. Figure 1 shows the growth rate of silicon at an input concentration of 0.4 vol. % SiH_2Cl_2 for different mixtures of hydrogen and nitrogen at 800, 900 and 1000 °C. As can be seen, the growth rate depends linearly on the partial pressure of hydrogen. The growth rate as a function of the input concentration of SiH_2Cl_2 in a hydrogen atmosphere is given in Figure 2 at temperatures between 800 °

Figure 1.

Growth rate versus the content of H_2 of mixtures of $\text{H}_2\text{-N}_2\text{-SiH}_2\text{Cl}_2$, for 0.4 vol. % SiH_2Cl_2 at 800, 900 and 1000 °C.

Figure 2.

Growth rate as a function of input concentration of SiH_2Cl_2 at 800, 900 and 1000 °C in a H_2 ambient.

Figure 3.

The growth in a N_2 atmosphere at 800, 900 and 1000 °C as a function of the input concentrations of SiH_2Cl_2 .

Figure 4.

Influence of addition of HCl on the growth rate of 0.1 vol. % SiH_2Cl_2 in H_2 at 900 and 1000 °C.

and 1000 °C. It can be observed from Figure 2 that the growth rate deviates from linearity, notably at the lowest temperatures. Figure 3 gives the growth rate as a function of the input concentration of SiH_2Cl_2 in nitrogen. Contrary to the experimental data of Figure 2, there is no saturation effect observable at 800 °C, while at temperatures above 800 °C the growth rate becomes non-linear. Addition of HCl to the SiH_2Cl_2 - H_2 system results in a growth rate behaviour as shown in Figures 4 and 5. Figure 4 gives data for the growth rate as a function of HCl added to 0.1 vol. % SiH_2Cl_2 at 900 and 1000 °C. At 1000 °C the decrease in the growth rate is almost a quadratic function of the input concentration of HCl while at 900 °C addition of HCl gives rise to a decrease in the growth rate, which is almost linear with p_{HCl} . This linear relation between the growth rate of silicon and the input concentration of hydrogen chloride can also be observed in Figure 5, which gives the results of experiments performed with 0.4 vol. % SiH_2Cl_2 at 800 and 900 °C. The addition of HCl to the SiH_2Cl_2 - N_2 system at 800, 900 and 1000 °C

Figure 5.

The growth rate of 0.4 vol. % SiH_2Cl_2 at 800 and 900°C as a function of the input concentration of HCl in hydrogen as a carrier gas.

shows the results as given in Figure 6. In this temperature range and for an input of 0.1 vol. % SiH_2Cl_2 the growth rate varies linearly with the input concentration of HCl . The slopes of these lines decrease with decreasing temperature.

3. Discussion

3.1 Introduction

In order to arrive at an expression that describes the growth rate of silicon in the SiH_2Cl_2 - H_2 - HCl system it is necessary to consider a number of possible reactions that can take place on or near the surface. These are summarized in the Appendix. The following steps should be considered:

- Supply of SiH_2Cl_2 through gas phase diffusion.
- Gas phase reactions, such as dissociation of SiH_2Cl_2 into SiCl_2 and H_2 and formation of SiHCl_3 .

Figure 6.

Growth rate as a function of increasing amounts of HCl in mixtures of 1.0 vol. % SiH_2Cl_2 in N_2 at 800, 900 and 1000 °C.

c. Adsorption of different species on the surface, such as SiCl_2 , chlorine and hydrogen .

d. Surface reactions followed by incorporation of silicon at the steps.

For the silicon growth rate the following expression is found (by introducing A-19 and A-20 into A-18):

$$R \approx \frac{k_4 k_{14} k_{15} P_{\text{H}_2} P_{\text{SiCl}_2} \theta}{(k_{-4} + k_{14}) (k_{-14} + k_{15} P_{\text{H}_2})} - \frac{K_e P_{\text{HCl}}^2}{P_{\text{H}_2}} \quad (1)$$

with the fraction of free surface sites θ given by equation (A-22):

$$\theta = \frac{1}{1 + K_4 P_{\text{SiCl}_2} + K_5 P_{\text{HCl}} / P_{\text{H}_2}^{1/2} + K_6 P_{\text{H}_2}^{1/2}} .$$

The first term of equation (1) describes the growth via reduction of SiCl_2 species adsorbed on step sites of the silicon surface. The negative term stems from etching reactions caused by gaseous hydrogen chloride. With the aid of the assumptions made in the Appendix rate-limiting reactions can be classified. In Table I these rate-limiting reactions are given in the case that no HCl is added and assuming complete gas phase dissociation of SiH_2Cl_2 into SiCl_2 and H_2 . Comparison with the experimental results indicates that e is the most probable rate-limiting reaction in which θ is constant over a wide range of experimental conditions. The assumptions made in order to obtain equation (1) and Table I will be discussed in the following sections.

TABLE I

Possible rate-limiting reactions for the growth of silicon from SiH_2Cl_2 in H_2 - N_2 mixtures. Complete dissociation of SiH_2Cl_2 into SiCl_2 and H_2 is assumed and the reactions, as given in the Appendix are used. R_i gives an expression for the growth rate when the corresponding reaction is rate-limiting. $P_{\text{SiH}_2\text{Cl}_2}^0$ is the input concentration of SiH_2Cl_2 .

Reaction	R_i for i as rate-limiting reaction
a gas phase diffusion (eq (A-0))	$R_a = k_a P_{\text{SiH}_2\text{Cl}_2}^0$
b gas phase dissociation of SiH_2Cl_2 (eq (A-1))	$R_b = k_b P_{\text{SiH}_2\text{Cl}_2}^0$
c adsorption of SiCl_2 (eq (A-4))	$R_c = k_c P_{\text{SiH}_2\text{Cl}_2}^0 \theta$
d incorporation of SiCl_2 at an atomic step (eq (A-14))	$R_d = k_d P_{\text{SiH}_2\text{Cl}_2}^0 \theta$
e reduction of SiCl_2 at an atomic step (eq (A-15))	$R_e = k_e P_{\text{H}_2} P_{\text{SiH}_2\text{Cl}_2}^0 \theta$

The experimental growth rate is given by

$$R_{\text{exp}} = k_{\text{exp}} P_{\text{H}_2} P_{\text{SiH}_2\text{Cl}_2}^0 \quad (\text{eq (6)})$$

3.2 Interpretation of results

3.2.1 The SiH_2Cl_2 - H_2 - N_2 -HCl system

For the silicon growth rate (R) equation (1) can be used. For not too high input concentrations of SiH_2Cl_2 , and without deliberate addition of HCl, as discussed

later, all terms containing PHCl can be neglected. This approximation leads to

$$R = \frac{k_4 k_{14} k_{15} P_{\text{H}_2} P_{\text{SiCl}_2}}{(k_{-4} + k_{14})(k_{-14} + k_{15} P_{\text{H}_2})} \times \frac{1}{(1 + K_4 P_{\text{SiCl}_2} + K_6 P_{\text{H}_2}^{1/2})} \quad (2)$$

In the surface-controlled regime of the growth ($T < 1000^\circ\text{C}$) it is convenient to introduce the decomposition parameter (α) for the gas phase reaction of SiH_2Cl_2 (A-1)

in which $P_{\text{SiH}_2\text{Cl}_2} = (1 - \alpha) P_{\text{SiH}_2\text{Cl}_2}^0$

$$P_{\text{SiCl}_2} = \alpha P_{\text{SiH}_2\text{Cl}_2}^0$$

if no extra hydrogen is added

$$P_{\text{H}_2} = \alpha P_{\text{SiH}_2\text{Cl}_2}^0$$

$P_{\text{SiH}_2\text{Cl}_2}^0$ is the input concentration of SiH_2Cl_2

Figure 7

Thermochemical data for the Si-H-Cl and the Si-N-H-Cl systems at 727 and 1027 °C and an input of 0.4 vol % SiH_2Cl_2

Figure 8.

Thermochemical data for the Si-H-Cl and the Si-H-N-Cl systems as a function of temperature and an input of 0.1 vol. % HCl.

In order to give an estimate of α thermochemical data on the Si-H-N-Cl system as a function of gas phase composition and temperature are given in Figures 7 and 8. The procedure reported by Van der Putte et al [4] was used. The most abundant species are depicted in Figure 7 as a function of the composition of the hydrogen-nitrogen mixture at 727 ° and 1027 °C and an input of 0.4 vol. % SiH₂Cl₂, and in Figure 8 as a function of temperature in hydrogen and nitrogen and an input of 0.1 vol. % HCl. From these thermodynamic data it can be deduced that the α values are in general close to unity for the gas phase decomposition of SiH₂Cl₂ both in nitrogen and in hydrogen. At low temperatures in hydrogen, however, the value of α becomes appreciably smaller. This follows from the equilibrium constant K_1 and equation (3):

$$K_1 = \frac{P_{\text{SiCl}_2} P_{\text{H}_2}}{P_{\text{SiH}_2\text{Cl}_2}} = \frac{\alpha P_{\text{H}_2}}{(1-\alpha)}$$

$$\text{thus } \alpha = \frac{K_1}{K_1 + P_{H_2}} \quad (4)$$

According to the thermochemical data [5] the value of K_1 is 6 l at 1000 °C and 6×10^{-2} at 700 °C. At the lower temperatures α can best be considered equal to K_1/P_{H_2} in contrast to the situation at higher temperatures or the situation where P_{H_2} is small (inert gas or reduced pressure) giving $\alpha = 1$.

For the growth rate of silicon in a hydrogen ambient it follows from equations (2), (3) and (4) that

$$R = \frac{k_4 k_{14} k_{15} P_{H_2} P_{SiH_2Cl_2}^0 \alpha}{(k_{-4} + k_{14}) (k_{-14} + k_{15} P_{H_2}) (1 + K_4 \alpha P_{SiH_2Cl_2}^0 + K_6 P_{H_2}^{1/2})} \quad (5)$$

According to Figure 1 the experimentally found growth rate can be expressed as

$$R_{exp} = K_{exp} P_{H_2} P_{SiH_2Cl_2}^0 \quad (6)$$

Comparison of equations (5) and (6) leads to the following conclusions. For relatively low input concentrations of SiH_2Cl_2 and α close to unity (above 900 °C, according to equation (4) and thermochemical data at those temperatures) it may be concluded that $k_{-14} > k_{15} P_{H_2}$ and $K_4 \alpha P_{SiH_2Cl_2}^0 + K_6 P_{H_2}^{1/2} < 1$. According to Figure 1 at 800 °C the growth rate found is nearly independent of the presence of hydrogen. This point can be understood from the smaller values of α (equation (4)) at these lower temperatures ($\alpha = K_1/P_{H_2}$) in combination with $k_{-14} > k_{15} P_{H_2}$ and $K_4 \alpha P_{SiH_2Cl_2}^0 + K_6 P_{H_2}^{1/2} < 1$. In this way the influence of hydrogen on the reduction of $SiCl_2$ is counteracted by its influence on the decomposition of SiH_2Cl_2 to form $SiCl_2$. In conclusion it can be said that k_{-14} has to be larger than $k_{15} P_{H_2}$, which means that the chemical reaction at the steps constitutes the slowest and rate determining step in the chain of reactions. Also interesting is the conclusion that $K_6 P_{H_2}^{1/2}$ has to be smaller than unity, which leads to a smaller surface concentration of monoatomic hydrogen than postulated by Chernov [6]. Equation (5) indicates that saturation of the growth rate as a function of the input concentration of SiH_2Cl_2 can be expected if $K_4 \alpha P_{SiH_2Cl_2}^0$ is greater than $(1 + K_6 P_{H_2}^{1/2})$. This is seen to be the case in Figure 2 at the lower temperature, indicating that the adsorption of $SiCl_2$ on the silicon surface is much more pronounced than the adsorption of monoatomic hydrogen.

The experiments given in Figure 3 (growth in nitrogen) show a nearly linear variation of the growth rate with increasing input concentration of SiH_2Cl_2 at 800 °C. Saturation does not occur as it does in hydrogen (Figure 2). In the

$\text{SiH}_2\text{Cl}_2\text{-N}_2$ system this can readily be explained with the aid of equation (2) Again $k_{15} P_{\text{H}_2} < k_{14}$ and $K_6 P_{\text{H}_2}^{1/2} < K_4 P_{\text{SiCl}_2}$ is assumed Now according to equation (3), P_{H_2} is equal to $\alpha P_{\text{SiH}_2\text{Cl}_2}^0$ and equation (2) becomes

$$R = \frac{k_4 k_{14} k_{15} [P_{\text{SiH}_2\text{Cl}_2}^0]^2 \alpha^2}{(k_{14} + k_{15}) (1 + K_4 \alpha P_{\text{SiH}_2\text{Cl}_2}^0)} \quad (7)$$

The linear growth rate observed at 800 °C can be explained if $K_4 \alpha P_{\text{SiH}_2\text{Cl}_2}^0$ is larger than unity, again indicating a strong adsorption of SiCl_2 on the silicon surface At temperatures above 800 °C there is a gradual change to the situation above 1000 °C where the supply of reactants from the gas phase determines the growth rate At the higher growth rates more HCl is formed as a reaction product Notably at higher input concentrations of SiH_2Cl_2 , therefore, the full equation (1) has to be considered, leading to a lowering of the growth rate and a deviation from linearity because of the back-etching effect of hydrogen chloride As the etching is proportional to $P_{\text{HCl}}^2/P_{\text{H}_2}$ [4] increased etch rates are found in an inert medium with a low value of P_{H_2} Indeed, for the $\text{SiH}_2\text{Cl}_2\text{-N}_2$ system the deviation from linearity is much larger than for the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system (Figures 2 and 3 at 1000 °C)

In the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system a deviation from linearity in the growth rate of silicon can be expected for high input concentrations of SiH_2Cl_2 , as observed by Robinson and Goldsmith [7]

Experimentally the growth rate depends strongly on the partial pressure of hydrogen In order to find out whether the type of inert gas influences the growth rate, we performed a growth experiment at 1000 °C in helium as a carrier gas and an input of 0.4 vol % SiH_2Cl_2 With this mixture the growth rate is 0.24 $\mu\text{m}/\text{min}$ With nitrogen as a carrier gas, the growth rate at otherwise similar conditions, was 0.20 $\mu\text{m}/\text{min}$ The conclusion is therefore that the growth rate is not determined by the hydrodynamics of the gas flow but by chemical reactions at the surface

3.2.2 The $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-HCl}$ system

The experimental data on the addition of HCl to the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system are given in Figures 4 and 5 These figures show the growth rate for two input concentrations of SiH_2Cl_2 at temperatures between 800 and 1000 °C Comparison of these data with those of the $\text{SiH}_4\text{-HCl-H}_2$ system (part I) leads to the following conclusions

At 1000 °C in the diffusion limited high temperature regime the $\text{SiH}_4\text{-H}_2\text{-HCl}$ and the $\text{SiH}_2\text{Cl}_2\text{-HCl-H}_2$ systems show a nearly similar behaviour The surface processes occur easily and the supply of reactants from the gas phase determines the combined effect of growth and etching Closer inspection, however, shows a larger

decrease in growth rate for the SiH_2Cl_2 system, compared to the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system at 1000°C . Another term, linear in P_{HCl} has to be added

At temperatures below 1000°C surface reactions constitute the rate-limiting step and typical differences between the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-HCl}$ system and the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system show up. At 800 and 900°C the addition of HCl to $\text{SiH}_4\text{-H}_2$ causes a rapid decrease in growth rate and this decrease is proportional to P_{HCl}^2 . The rapid initial decrease is followed by a slower decrease in growth rate, which is also proportional to P_{HCl}^2 (part I). In the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-HCl}$ system a linear dependence is found between the decrease in growth rate and the amount of HCl added (Figures 4 and 5). In the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system the rapid decrease in growth rate is explained in terms of the conversion of the reactive Si or SiH_2 surface species into SiCl_2 on the addition of small amounts of HCl (part I). The absence of a rapid initial decrease in growth rate in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-HCl}$ system leads to the conclusion that the concentration of Si is small compared to the concentration of SiCl_2 adsorbed on the surface. Even without the addition of HCl , the main mobile species on the surface is expected to be the SiCl_2 molecule. The linear decrease in growth rate with input concentration of HCl at temperatures below 1000°C is supposed to be caused by the formation of SiHCl_3 in the gas phase (reaction A-1, A-2)

Since SiH_2Cl_2 readily dissociates into SiCl_2 and H_2 the formation of SiHCl_3 from SiCl_2 and HCl in the gas phase has to be expected at the lower temperatures in hydrogen, as may be seen from Figures 7 and 8. Combination of equation (A-1) and (A-2) leads to

$$P_{\text{SiCl}_2} = \frac{k_1 P_{\text{SiH}_2\text{Cl}_2}}{k_2 P_{\text{HCl}} + k_{-1} P_{\text{H}_2}} \quad (8)$$

Inserting this equation into equation (1) we obtain an expression describing the growth rate. Addition of HCl will lower the partial pressure of SiCl_2 and consequently cause a linear decrease in the growth rate. The term $K_e P_{\text{HCl}}^2 / P_{\text{H}_2}$ in equation (1) is of minor importance under the experimental conditions, according to measured etch rates of silicon by HCl in hydrogen (part I). The formation of SiHCl_3 did not play any role in the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system. In that case SiCl_2 is a reaction product of the surface reactions between silicon and hydrogen chloride. The concentration of SiCl_2 in the gas phase is small and, according to Van der Putte et al. [4], desorption of SiCl_2 is not rate-limiting. These circumstances

guarantee that possible gas phase reactions will not influence the growth rate in the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system

Formation of SiCl_4 as a reaction product is also possible according to the thermochemical data as shown in Figures 7 and 8. From the experimental results, however, no evidence can be obtained that formation of SiCl_4 contributes to the growth of silicon. The reason for this is that SiCl_4 has to be formed on the surface via additional, rather complicated reactions and it is therefore understandable that the resulting SiCl_4 concentration remains small, in accordance with mass spectrometric analysis performed by Ban and Gilbert [8].

3.2.3 The $\text{SiH}_2\text{Cl}_2\text{-N}_2\text{-HCl}$ system

Figure 6 gives the growth rate for an input concentration of 1.0 vol % SiH_2Cl_2 and increasing amounts of HCl at 800, 900 and 1000 °C. At all three temperatures the growth rate depends linearly on the HCl input concentration but this effect decreases with decreasing temperature.

The experiments described so far all show gas phase diffusion-limited growth rates at temperatures of 1000 °C and above. This is also expected in the $\text{SiH}_2\text{Cl}_2\text{-N}_2$ system. Still on addition of HCl, a linear decrease in the growth rate with increasing values of P_{HCl} is found at 1000 °C (Figure 6). According to Van der Putte et al [4] the etch rate of silicon by HCl is proportional to the equilibrium concentration of SiCl_2 on the surface, being proportional to $P_{\text{HCl}}^2/P_{\text{H}_2}$. In the present case no extra hydrogen is added to the gas mixture. The etching is described by

The overall reaction shows that P_{SiCl_2} will be nearly equal to P_{H_2} in an inert ambient and P_{SiCl_2} and P_{H_2} will both be proportional to $K_a^{1/2} P_{\text{HCl}}$, leading to an etch rate in an inert gas proportional to P_{HCl} , in agreement with experimental data [4-9]. The growth rate of silicon can now be given by equation (1) by introducing equation (7) for the first term and $K_e P_{\text{HCl}}$ for the second term. At temperatures below 1000 °C, Figure 6 shows a linear decrease in growth rate for increasing input values of HCl, the same as found at 1000 °C. The slopes of the lines become less steep going to lower temperatures. This effect can be attributed to a lower etch rate at lower temperatures. Etching experiments with silicon etched by 0.2 vol % HCl in nitrogen showed etch rates of 0.20, 0.12 and 0.07 $\mu\text{m}/\text{min}$ at temperatures of 1100, 1000 and 900 °C respectively [9]. These etch rates are sufficient to explain the decrease in growth rate found experimentally in the presence of SiH_2Cl_2 . Formation of SiHCl_3 in the gas phase cannot be excluded but is not directly apparent from the experimental data. In this connection Figures 7 and 8 show that in an inert ambient the concentration of SiHCl_3 is indeed relatively low.

4 Conclusion

In an attempt to understand the nature of the slowest step in the growth of silicon on silicon we have studied the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2\text{-HCl}$ system, comparing the experimental data with those obtained on the $\text{SiH}_4\text{-HCl-H}_2$ system. The experiments on the latter system led to the conclusion that the incorporation of silicon at surface steps or the diffusion of SiCl_2 on the silicon surface is the slowest step in the chain, but no choice could be made between them. By measuring the growth rate, for a constant input concentration of SiH_2Cl_2 at temperatures between 800 and 1000 °C, as a function of the composition of H_2 and N_2 in the gas-mixture we were able to show that the incorporation of silicon at the step determines the growth rate. Further we could explain the observation that the growth rate of silicon at low temperatures (< 900 °C) saturates in a hydrogen medium, and not in a nitrogen medium (800 °C), as a function of the input concentration of SiH_2Cl_2 . Introduction of HCl to the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system shows that SiHCl_3 is formed in the gas phase and it also confirms that the Si adatom concentration is always small compared with the SiCl_2 surface concentration in the Si-H-N-Cl system. As a consequence of the conclusion that equation (A-15) constitutes the rate-limiting reaction it follows that the foregoing reactions lead to a quasi equilibrium concentration of surface species. The surface concentration of SiCl_2^* and $\text{SiCl}_2(\text{st})$ therefore reflect the supersaturation in the gas phase, no large additional enhancement is expected.

Acknowledgement

The authors wish to thank Dr. L. J. Giling for help with the thermochemical calculations and Mr. J. Goonssen for the critical reading of the manuscript.

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APPENDIX

The following reactions can be distinguished:

a. Supply of SiH_2Cl_2

$\text{SiH}_2\text{Cl}_2 \text{ (b)}$ is the input concentration of SiH_2Cl_2 and $\text{SiH}_2\text{Cl}_2 \text{ (g)}$ the concentration of SiH_2Cl_2 near the silicon surface.

b. Gas phase reactions

c. Adsorption (* denotes a free surface site)

d. Surface reactions

e Growth reactions

((st) denotes a position at an atomic step on the surface, Si(cr) means that the silicon has found a stable position as part of the crystal)

In the following the notation (g) will only be used when comparison with bulk values of the vapour pressure is made (e.g. $P_{\text{SiH}_2\text{Cl}_2} = P_{\text{SiH}_2\text{Cl}_2} (\text{g})$). In order to simplify the total number of expressions it is possible to judge the weight of the various parameters using the experimental results and the thermochemical data given in Figures 7 and 8. As discussed in section 3.2, comparison of the SiH_2Cl_2 - H_2 - N_2 - HCl system with the SiH_4 - HCl - H_2 system (part I) leads to the following conclusions

- i In a Si-H-N-Cl system the concentration of Si^* is always much smaller than the concentration of SiCl_2^* . This means that in a first approximation (A-7), (A-9), (A-12) and (A-13) can be neglected
- ii Formation of SiHCl_3 (reaction (A-10)) and SiCl_4 (reaction (A-11)), which both take place on the silicon surface, can be left out of account. Under the operating conditions SiHCl_3 will only be formed in the gas phase (equation (A-2)).

Two growth routes can be distinguished, one via PSiCl_2 and the other via PSiH_2Cl_2 . In order to discriminate between these two routes the following remarks are helpful. According to Chernov [6] the fully coordinated SiH_2Cl_2 molecule has a low adsorption energy compared with that of the non-linear SiCl_2 molecule. The adsorption of SiCl_2 is greatly enhanced by the presence of residual unbonded electrons on the silicon atom in this molecule which can interact with the dangling bonds on the surface. It is therefore likely that the reaction starts with the adsorption of SiCl_2 (equation (A-4)) if SiCl_2 is formed by dissociation of SiH_2Cl_2 . This is the case according to thermochemical data (Figures 7 and 8) and experiments reported by Smith and Sedgwick [10], who measured SiCl_2 with an inelastic light scattering method in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system. This means that K_3 and K_8 are also small, so that the corresponding reactions A-3 and A-8 can be neglected.

The concentrations of the various species on the surface, using the reactions given above and introducing the concept of a steady-state situation, can now be given. With the above approximations the steady-state concentration of $[\text{SiCl}_2^*]$ and $[\text{SiCl}_2(\text{st})]$ will be given by

$$[\text{SiCl}_2^*] = \frac{k_4 \theta \text{PSiCl}_2 + k_{-14} [\text{SiCl}_2(\text{st})]}{k_{-4} + k_{14}} \quad \text{A-16}$$

$$[\text{SiCl}_2(\text{st})] = \frac{k_{14} [\text{SiCl}_2^*] + k_{-15} \text{P}_{\text{HCl}}^2}{k_{-14} + k_{15} \text{P}_{\text{H}_2}} \quad \text{A-17}$$

As described in part I for the $\text{SiH}_4\text{-HCl-H}_2$ system, it can be assumed that the growth and etching of silicon can be treated as being independent of each other

$$R = R_{\text{growth}} - R_{\text{etch}} \quad \text{A-18}$$

For a positive growth rate the reactions k_{-14} and k_{-15} can be neglected compared with reaction k_4 and k_{14} respectively in the numerator of equations (A-16) and (A-17), leading to

$$R_{\text{growth}} = k_{15} \text{P}_{\text{H}_2} [\text{SiCl}_2(\text{st})] = \frac{k_4 k_{14} k_{15} \text{P}_{\text{H}_2} \text{PSiCl}_2 \theta}{(k_{-4} + k_{14}) (k_{-14} + k_{15} \text{P}_{\text{H}_2})} \quad \text{A-19}$$

The term R_{etch} in (A-18) has been given by Van der Putte et al [4]. According to these authors, who measured etch rates of silicon by HCl in hydrogen and argon, R_{etch} can be given by

$$R_{\text{etch}} = \frac{K_e \text{P}_{\text{HCl}}^2}{\text{P}_{\text{H}_2}} \quad \text{A-20}$$

where P_{HCl} and P_{H_2} are equilibrium values and K_e is a constant.

The sum of the fractions of free and occupied surface sites gives

$$1 = \theta + [H^*] + [Cl^*] + [SiCl_2^*] + \dots \quad A-21$$

$$\text{With } [H^*] = K_6 P_{H_2}^{1/2} \theta, [Cl^*] = K_5 P_{HCl} \theta / P_{H_2}^{1/2}$$

$$\text{and } [SiCl_2^*] = K_4 P_{SiCl_2} \theta \text{ we obtain}$$

$$\theta = \frac{1}{(1 + K_4 P_{SiCl_2} + K_5 P_{HCl} / P_{H_2}^{1/2} + K_6 P_{H_2}^{1/2})} \quad A-22$$

Here $k_6/k_{-6} = K_6$ etc.

CHAPTER VII

RATE-DETERMINING REACTIONS AND SURFACE SPECIES IN CVD OF SILICON

III The $\text{SiH}_4\text{-H}_2\text{-N}_2$ system

Summary

At a temperature of 700°C the growth rate of silicon in the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system is found to be inversely proportional to the partial pressure of hydrogen and linearly proportional to the input concentration of silane (up to 0.4 vol %). Analysis of the experimental data shows that SiH_2 is the most abundant surface species and hydrogen adsorption does not influence the growth rate. Addition of hydrogen chloride to the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system results in a reduction of the growth rate, due to the conversion of SiH_2 into SiCl . This reduction in the growth rate is most pronounced in an inert medium. Adsorption on the silicon surface is discussed and it is concluded that H , Cl , SiCl and SiH_2 are present as surface species among which, however, hydrogen and chlorine are only of minor importance.

1. Introduction

Polycrystalline silicon layers, which are widely used in the electronics industry [1], are usually grown by pyrolysis of silane under atmospheric pressure (CVD) or reduced pressure (LPCVD). In both systems hydrogen or an inert gas can be used as a carrier gas. It is known that at temperatures below 800°C the growth rate of silicon in an inert medium is much higher than in hydrogen [2, 3, 4]. Bryant [2] discussed experimental data given by several authors for the growth rate of silicon from silane in hydrogen or in an inert medium. Plotting different authors' measurements in a single figure and analysing the results, Bryant concluded that hydrogen desorption controlled the reaction around 700°C if an inert gas was used as a carrier gas. In a hydrogen medium the chemical reaction on the surface was thought to be rate-limiting. The procedure followed by Bryant could lead to erroneous conclusions, however, the picture could be distorted because of differences in experimental conditions, as will be discussed later.

Relatively little has been published on the growth rate of silicon using mixtures of hydrogen and inert gases or reduced pressures of hydrogen. Yasuda et al. [3] measured growth rates of silicon given by 0.05 vol % silane in mixtures of argon and hydrogen (pure argon, $\text{Ar:H}_2 = 75:25$ and $\text{Ar:H}_2 = 50:50$) at temperatures between 600 and 800°C . From these experimental results a growth rate proportional to $P_{\text{H}_2}^{-1}$ can be deduced. Duchemin et al. [4] measured growth rates of silicon for different silicon-containing compounds at reduced pressures in a hydrogen ambient and temperatures between 800 and 1050°C . From indirect experiments they found a $P_{\text{H}_2}^{-1/2}$ dependence at low hydrogen pressures while at higher hydrogen pressures the growth rate of silicon becomes inversely proportional to the hydrogen pressure ($R \propto P_{\text{H}_2}^{-1}$). At 1025°C Manasevit [5] measured the growth rate of silicon from 2.5 vol % silane in a hydrogen – helium mixture. For

hydrogen concentrations up to 30% he found a growth rate proportional to the hydrogen pressure ($R \propto P_{H_2}$) and observed a saturation in the growth rate at higher hydrogen concentrations. However, in Manasevits' experiments the walls of the reactor became heavily contaminated caused by gas phase nucleation. Thermo diffusion in a cold wall apparatus leads to deposit of clusters on the cold walls, reducing the apparent growth rate on the heated silicon slice. Therefore these experimental results cannot be considered to be representative for the silicon growth but merely reflect a lower gas phase nucleation in a hydrogen ambient [6].

We have carried out systematic experiments with silane in mixtures of hydrogen and nitrogen at 700 °C. This could give more information about surface species and rate-limiting steps in the growth of silicon. In this paper adsorption of different species is considered in connection with two foregoing papers [7-8] where rate-determining reactions are described in the SiH_4 - H_2 -HCl system and the SiH_2Cl_2 - H_2 - N_2 -HCl system, respectively (referred to as part I and part II in the following). In addition we study the influence of the addition of HCl to the SiH_4 - H_2 - N_2 mixture.

2 Experimental

A horizontal air-cooled RF heated reactor was used for the experiments. The carrier gases hydrogen and nitrogen were purified to a water and oxygen concentration below 1 ppm. The silane and hydrogen chloride used were both electronic grade. For all gases automatic gas flow controllers were used. The temperature was measured on a silicon slice by means of a calibrated radiation thermometer. The rest of the experimental conditions were as described in part I and part II [7-8].

Figure 1 shows the growth rate of silicon at 700 °C for an input concentration of 0.2 vol % SiH_4 and different mixtures of hydrogen and nitrogen, the latter expressed as $P_{H_2}/(P_{H_2} + P_{N_2})$. It can be observed that the growth rate strongly decreases when small amounts of hydrogen are added to the silane-nitrogen mixture. The experimental data, in this figure, can be described by an expression in which the growth rate of silicon on silicon at 700 °C is inversely proportional to the hydrogen pressure:

$$R_{exp} = \frac{A P_{SiH_4}^0}{1 + B P_{H_2}} \quad (1)$$

where $P_{SiH_4}^0$ is the input concentration of silane, P_{H_2} the hydrogen pressure while A and B are constants. According to equation (1) ($P_{SiH_4}^0/R$) plotted versus P_{H_2} should give a straight line relationship. This is shown to be the case in Figure 2 for different input concentrations of silane at 700 °C. Figure 3 gives the growth rate of silicon on silicon at 700 °C as a function of the input concentration of silane up to

Figure 1.

The growth rate of silicon at 700 °C, for 0.2 vol % SiH₄ and different hydrogen-nitrogen mixtures.

0.4 vol. % and different combinations of hydrogen and nitrogen as a carrier gas. A linear relation between the growth rate and the input concentrations of silane can be observed for hydrogen and the hydrogen-nitrogen mixture. In nitrogen as a carrier gas the deviation from linearity is caused by gas phase nucleation, as evidenced by a contamination of the reactor walls for an input concentration exceeding 0.2 vol. % of silane. In all other cases gas phase nucleation can be neglected. Van der Meer [9] also found a linear dependence between the growth rate of silicon and the input concentration of silane (up to 1.0 vol. %) in hydrogen as a carrier gas and temperatures between 600 and 800 °C. In Figure 4 the growth rate is given as a function of the input concentration of silane at 700 °C in inert gases, as given by Adamczewska and Budzynski [10], Wells et al. [11] and Seto [12]. The experimental results of Wells and Seto formed the basis of Bryant's analysis [2]. The log-log plot of these data gives a slope equal to 0.5, leading to the conclusion that desorption of hydrogen is rate-limiting if an inert gas is used as a carrier gas. However, log-log plots of the experimental data of Adamczewska

Figure 2.

The growth rate of silicon on silicon at 700 °C for different mixtures of $\text{SiH}_4\text{-H}_2\text{-N}_2$, expressed as (P_{SiH_4}/R) versus (P_{H_2}) : $\circ$ 0.1 vol. % SiH_4 ; $+$ 0.2 vol. % SiH_4 and $\blacktriangle$ 0.4 vol. % SiH_4 .

and our results gives, for low input concentrations of silane a linear dependence between the growth rate and the input concentration of silane. The large discrepancy between these results and those of Wells and Seto could be explained by a low Peclet number for small linear gas velocities, as indicated in Figure 4, leading to depletion of silane in the gas phase and a deviation from linearity in the growth rate as a function of the input concentration of silane. The addition of HCl to the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system results in a strong decrease in the growth rate, as shown in Figure 5. In this figure growth rates are given as a function of P_{HCl}^2 for an input concentration of 0.2 vol. % SiH_4 in a mixture of hydrogen and nitrogen (4% hydrogen) and in a hydrogen ambient at 700 °C. It can be observed that the initial decrease in growth rate is strongest for the lower hydrogen concentration. There is a typical difference in growth rate after the rapid initial decrease on addition of HCl; the growth rate remains higher at a low hydrogen concentration in the carrier gas.

Figure 3.

The growth rate at 700°C for silane concentrations up to 0.4 vol. % and different mixtures of carrier gases.

Figure 4.

The growth rate of silicon at 700°C from silane in an inert ambient: + this work, o ref. 10, ▲ ref. 11, • ref. 12.

Figure 5.

Growth rate as shown by 0.2 vol. % SiH_4 in hydrogen and a mixture of hydrogen and nitrogen and increasing amounts of HCl at 700 °C.

3. Discussion

3.1 Reaction scheme for the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system

In order to arrive at an expression describing the growth of silicon on silicon in the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system, the reaction scheme as proposed in the Appendix of part I [7] will be followed with some additional assumptions concerning the species present on the silicon surface. The following steps could be taken into account:

- a. Gas phase diffusion towards the surface

(b) refers to bulk concentrations and (g) to concentrations near the surface.

b. Decomposition of silane near the surface

c. Chemisorption of a SiH_n compound on a free surface site (denoted by $*$)

d. Surface diffusion of SiH_n^* to an atomic step

e. Attachment on a free step site (denoted by $*_s$)

f. Incorporation by desorption of hydrogen

Adsorption of atomic hydrogen can be described as:

The fraction of free surface sites θ and free step sites θ_{st} can be given by

$$\theta = 1 - [\text{H}^*] - [\text{SiH}_n^*] \quad (10)$$

$$\theta_{st} = 1 - [\text{H}^*_s]$$

There is a difference between both terms in (10) as SiH_n adsorbed on a step site cannot be distinguished from n adsorbed H atoms. If equilibrium conditions are assumed for the adsorption of atomic hydrogen, and if the adsorption is dominant θ and θ_{st} can be given as

$$\theta = \frac{1}{1 + K_7 P_{\text{H}_2}^{1/2}} \quad (11)$$

$$\theta_{\text{st}} = \frac{1}{1 + K_8 P_{\text{H}_2}^{1/2}}$$

It is assumed that nucleation on the silicon surface is not a problem, such that sufficient step sites are present on a real surface. One of the reactions (2)–(7) is then rate-limiting, the reactions preceding the slowest reaction are assumed to be in equilibrium, while the reactions after the slowest step are fast. These rate-limiting reactions are collected in Table I, where it is assumed that equilibrium conditions exist for hydrogen adsorption. Expressions for the growth rate are given corresponding to the specific rate-limiting reaction.

Comparison with experiment

The experimental data as given in Fig. 1, 2 and 3 can be described by equation (1)

$$R_{\text{exp}} = \frac{A P_{\text{SiH}_4}^0}{1 + B P_{\text{H}_2}}$$

This expression has to be compared with the rate limiting reactions as given by R_a – R_f (Table 1). From this table it can be deduced that in the SiH_4 – H_2 – N_2 system rate limitation by gas phase diffusion of silane towards the surface (R_a and gas phase dissociation of SiH_4 (R_b)) cannot explain the experimental data. The rate-limiting reactions have to be found in one of the surface reactions c to f. Two solutions can be distinguished, depending on the magnitude of the hydrogen adsorption on the silicon surface.

- i For a strong hydrogen adsorption $[(\theta, \theta_{\text{st}} \ll 1), ([\text{H}^*], [\text{H}^*_{\text{s}}] \cong 1)]$ the fraction of free surface sites and step sites can be given by $\theta = 1/K_7 P_{\text{H}_2}^{1/2}$ and $\theta_{\text{st}} = 1/K_8 P_{\text{H}_2}^{1/2}$, as obtained by using equation (11). The experimental results then lead to a value of n equal to four, giving SiH_4 as the main silicon-containing surface species. When for statistical reasons only one θ has to be included then $n=3$, leading to SiH_3 as the most important silicon-containing surface species.
- ii For a moderate hydrogen adsorption the values of θ and θ_{st} are close to unity $[(\theta, \theta_{\text{st}} \cong 1), ([\text{H}^*], [\text{H}^*_{\text{s}}] \ll 1)]$ and n becomes equal to 2, indicating SiH_2 as the most important surface species, both in hydrogen as well as in a nitrogen ambient.

TABLE I

Rate-limiting reactions for the growth of silicon from silane, according to the equations (2–7). The growth rate R_i corresponds to these rate-limiting reactions. $P_{\text{SiH}_4}^0$ denotes the input partial pressure of silane.

Reaction	R_i for i as rate-limiting reaction
a. gas phase diffusion (eq. (2))	$R_a = k_a P_{\text{SiH}_4}^0$
b. gas phase dissociation (eq. (3))	$R_b = k_b P_{\text{SiH}_4}^0$
c. chemisorption (eq. (4))	$R_c = k_c P_{\text{SiH}_4}^0 \theta / (P_{\text{H}_2})^{(4-n)/2}$
d. surface diffusion* (eq. (5))	$R_d = k_d P_{\text{SiH}_4}^0 \theta^2 / (P_{\text{H}_2})^{(4-n)/2}$
e. step incorporation (eq. (6))	$R_e = k_e P_{\text{SiH}_4}^0 \theta \cdot \theta_{\text{st}} / (P_{\text{H}_2})^{(4-n)/2}$
f. silicon formation (eq. (7))	$R_f = k_f P_{\text{SiH}_4}^0 \theta \cdot \theta_{\text{st}} / (P_{\text{H}_2})^{(4-n)/2}$

* For a directional diffusion a BCF expression can be used. Diffusion limited by surface adsorption then leads to

$$R_d = k_d P_{\text{SiH}_4} \cdot \theta^{3/2} / P_{\text{H}_2}^{(4-n)/2}$$

As will be discussed in the section on adsorption, the concentration of adsorbed atomic hydrogen is thought to be small and therefore SiH_2 is considered to be the most abundant silicon-containing species on the surface. The great difference in adsorption probabilities between the full coordinated SiH_4 molecule and the non-linear SiH_2 molecule [13] and single-pulse shock tube experiments of Newman et al. [14], in which H_2 and SiH_2 are formed when SiH_4 decomposes, leads to the same conclusions. Formation of SiH_3 can be eliminated, as the single bond rupture process, $\text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H}$ needs a high activation energy (93 Kcal/mole [14]) compared to molecular hydrogen elimination from silane. As can be observed in Fig. 3, the growth rate of silicon on silicon in the $\text{SiH}_4\text{-N}_2$ system is linearly proportional to the input concentration of silane for relatively low input concentrations. For concentrations above 0.2 vol. % the reactor becomes contaminated because of gas phase nucleation, leading to a deviation from linearity of the growth rate as a function of the input concentration of silane. Under the above-mentioned conditions the growth rates obtained in nitrogen are so high that gas phase diffusion can be assumed to be rate-limiting (R_a) even at 700 °C.

3.2 The $\text{SiH}_4\text{-H}_2\text{-N}_2$ system

The addition of HCl to the $\text{SiH}_4\text{-H}_2$ system at temperatures between 800 and 1000 °C has been described in part I [7]. At a temperature below 900 °C a rapid decrease in growth rate was observed, proportional to P_{HCl}^2 , when small amounts of HCl were added, followed by a much smaller decrease in the growth rate, also proportional to P_{HCl}^2 . The same behaviour can be observed in the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system. This can be seen in Figure 5, which shows the influence of the addition of HCl on the growth rate of silicon for an input concentration of 0.2 vol % SiH_4 and 4 vol % H_2 in nitrogen at 700 °C (growth rate versus P_{HCl}^2). This figure also gives the growth rate at 700 °C for an input concentration of 0.2 vol % SiH_4 in a hydrogen ambient. In order to discuss the influence of the addition of HCl to the system some additional remarks have to be made. Besides the reactions (a–f) the following steps can be distinguished after addition of HCl to the system

f Conversion of SiH_2^* into SiCl_2^*

h Surface diffusion of SiCl_2^*

i Incorporation on a free step site

j Reduction of SiCl_2 at the step site

k Desorption of SiCl_2

l Formation of SiH_2Cl_2

m Adsorption of chlorine

If $[\text{H}^*, \text{H}^*_{\text{s}}] \ll 1$ and $[\text{SiH}_2^*] \ll 1$, as discussed before, the fraction of free surface sites θ and free step sites θ_{st} can now be given by

$$\theta = 1 - [\text{Cl}^*] - [\text{SiCl}_2^*] \quad (20)$$

$$\theta_{\text{st}} = 1 - [\text{Cl}^*_{\text{s}}] .$$

As discussed in part II [8], the rate-limiting reaction has to be found in the reduction of SiCl_2 at the step site ($k_{12} P_{\text{H}_2} < k_{-11}$). After conversion of SiH_2 into SiCl_2 (equation (12)), further addition of HCl leads to attack of the silicon lattice itself. According to Van der Putte et al [15] and discussed in part II, this etch rate can be given as

$$R_{\text{etch}} = k_{\text{etch}} P_{\text{HCl}}^2 / P_{\text{H}_2} . \quad (21)$$

The resulting growth rate, after the initial decrease, can now be given as

$$R = k_{12} P_{\text{H}_2} [\text{SiCl}_2^{**}_{\text{s}}] - k_{\text{etch}} P_{\text{HCl}}^2 / P_{\text{H}_2} \quad (22)$$

where $k_{12} P_{\text{H}_2} [\text{SiCl}_2^{**}_{\text{s}}] = R_{\text{SiCl}_2}$, as defined in part I. The steady state concentration of $[\text{SiCl}_2^{**}_{\text{s}}]$ can be described in a similar way as described in part I, leading with $k_{12} P_{\text{H}_2} < k_{-11}$ to

$$R = \frac{K_1 k_2 k_3 k_4 k_{11} k_{12} P_{\text{H}_2} P_{\text{HCl}}^2 P_{\text{SiH}_4}^0 \theta \theta_{\text{st}}}{(k_{-2} P_{\text{H}_2} + k_3 \theta) (k_9 P_{\text{HCl}}^2 + k_{-3}) (k_{11} \theta_{\text{st}} + k_{-9} P_{\text{H}_2}^2 + k_{13} + k_{14} P_{\text{H}_2})} - k_{\text{etch}} \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}} . \quad (23)$$

The experimental data as given in Figure 5 can now be compared with this expression. R_{SiCl_2} can be considered to be independent of P_{HCl} as the reduction in growth rate on further addition of HCl equals the expected etch rate with HCl only. According to Figure 5, $R_{\text{SiCl}_2} = 0.042 \mu\text{m/min}$ for an input of 0.2 vol. % SiH_4 in a carrier gas containing 4 vol. % hydrogen at 700°C . In hydrogen as a carrier gas the initial reduction of the growth rate is less steep than for the H_2/N_2 mixture, due to a less complete conversion of SiH_2^* into SiCl_2^* for the HCl input concentration used (equation 12). Therefore $R_{\text{SiCl}_2}(700^\circ\text{C})$ for this mixture cannot be obtained from Figure 5 and an indirect way is necessary. In part I [7] values of R_{SiCl_2} are given for an input of 0.2 vol. % SiH_4 in hydrogen as a carrier gas at 800°C and 900°C , being 0.030 and $0.34 \mu\text{m/min}$ respectively. $R_{\text{SiCl}_2}(700^\circ\text{C})$ can now be calculated by assuming a $1/T$ behaviour leading to $0.0017 \mu\text{m/min}$. The values of R_{SiCl_2} at 700°C for $P_{\text{H}_2} = 1$ bar and $P_{\text{H}_2} = 0.04$ bar are thus shown to be proportional to $P_{\text{H}_2}^{-1}$. The experimental growth rate after the initial decrease can now be given by

$$R = k_{\text{SiCl}_2} \frac{P_{\text{SiH}_4}^0}{P_{\text{H}_2}} - k_{\text{etch}} \frac{P_{\text{HCl}}^2}{P_{\text{H}_2}} \quad (24)$$

Comparison of this equation with the expression as given by equation (23) leads to the following solutions depending on the magnitude of chlorine adsorption

- I For a strong chlorine adsorption, and chlorine being the most abundant surface species, the concentrations of free surface sites θ and free step sites θ_{st} can be given by

$$\theta = \frac{P_{\text{H}_2}^{1/2}}{K_{13} P_{\text{HCl}}}, \quad \theta_{\text{st}} = \frac{P_{\text{H}_2}^{1/2}}{K_{14} P_{\text{HCl}}} \quad (25)$$

For strong chlorine adsorption the value θ and θ_{st} in equation (25) is introduced in equation (23), giving the disappearance of the P_{HCl}^2 term and the introduction of $P_{\text{H}_2}^2$ in the numerator of the first term (R_{SiCl_2}).

The experimental data then suggests a model I in which $k_9 P_{\text{H}_2}^2 > (k_{11} \theta_{\text{st}} + k_{13} + k_{14} P_{\text{H}_2})$, $k_9 P_{\text{HCl}}^2 < k_{-3}$ and $k_{-2} P_{\text{H}_2}^2 > k_3 \theta$, in order to arrive at the result of equation (24).

For θ and θ_{st} values close to unity two solutions are possible, in both cases $k_9 P_{\text{HCl}}^2 > k_{-3}$ has to be assumed

II If $k_{-2} P_{\text{H}_2} < k_3 \theta$ then $k_9 P_{\text{H}_2}^2 > (k_{11} \theta_{\text{st}} + k_{13} + k_{14} P_{\text{H}_2})$

III If $k_{-2} P_{\text{H}_2} > k_3 \theta$ then $k_{14} P_{\text{H}_2} > (k_9 P_{\text{H}_2}^2 + k_{11} \theta_{\text{st}} + k_{13})$

As will be discussed in the section on adsorption, the fractional surface concentration of chlorine is assumed to be small compared to unity at temperatures above 700 °C, excluding model I. In order to discriminate between models II and III it can be mentioned that assumptions made in model II are less probable because a relatively high value of $k_{-9} P_{H_2}^2$ is needed and formation of SiH_2Cl_2 is more likely than reduction of $SiCl_2$ to SiH_2 . Because the rate-limiting step has to be found in the reduction of $SiCl_2$ on the step (equation (15)) a surface concentration of $SiCl_2$ much higher than the equilibrium concentration can be expected. This leads to a desorption of $SiCl_2$ or, according to thermodynamic data at 700 °C of the Si-H-N-Cl system (part II), to formation of SiH_2Cl_2 (equation (17)).

The experimental data can therefore best be described by model III, giving

$$R = \frac{K_1 K_2 K_3 K_{11} k_{12} P_{SiH_4}^0}{k_{14} P_{H_2}} - k_{etch} \frac{P_{HCl}^2}{P_{H_2}} \quad (26)$$

Finally, according to equation (20) a strong adsorption of $SiCl_2$ should lead to a small value of θ notably for the lowest hydrogen pressures, in contradiction with the experimental data as given in Figure 5. This point will be further discussed in the following section on adsorption.

3.3 Adsorption on the silicon surface

In this section the adsorption of H, Cl, $SiCl_2$ and SiH_2 will be discussed, because these species are considered to be the most important representatives on the silicon surface. At the start of the present series of experiments we expected to find a strong influence of the adsorption of monoatomic hydrogen and chlorine on the growth rate of silicon, as suggested by Chernov [13]. The fraction of free surface sites can be given by

$$\theta = 1 - \theta_H - \theta_{Cl} - \theta_{SiH_2} - \theta_{SiCl_2} \quad (26)$$

and an analogous expression can be given for the fraction of free step sites, with the remark that $SiCl_2^*$ and SiH_2^* adsorbed on a step cannot be distinguished from adsorbed H^* and Cl^* atoms. In adsorption equilibrium an expression can be found for every species as for θ_H [16]

$$\theta_H = \frac{k_H P_H}{1 + \sum_u k_u P_u} \quad u = H, Cl, SiCl_2, SiH_2 \quad (27)$$

$$\text{with } k_u = \frac{\exp [E_{a,u}/kT]}{n_0 \nu_u \sqrt{2\pi m_u kT}}$$

where P_u is the partial pressure of species u in the gas phase, m_u the mass of the adsorbed molecule, k is Boltzmann's constant, T the absolute temperature, $E_{a,u}$ the heat of adsorption of u , ν_u the stretching vibration of the Si-U bond and n_0 is the total number of surface sites per unit area. In a first approximation ν_u is inversely proportional to the square root of the molecular mass of the adsorbed atom or molecule, which leads to

$$\frac{\theta_H}{\theta_u} = \frac{P_H}{P_u} \exp(E_{a,H} - E_{a,u})/kT \quad (28)$$

where $u = H, Cl, SiCl_2$ or SiH_2 . Using this equation relative surface concentrations of the various adsorbing species can be calculated if values for E_a and P_u are available. The partial pressures can be obtained from thermochemical data for the Si-H-N-Cl system, as given in part II. The heat of adsorption E_a is normally taken to be nearly equal to the dissociation energies (D) or bond strengths of the corresponding diatomic molecules ($SiH, SiCl, Si_2$). The JANAF tables recommend values of 90 ± 15 kcal/mole for $DSiCl$, 70 kcal/mole for $DSiH$ and 73 kcal/mole for DSi_2 [17]. Recently Farber and Srivastava [18] have used Knudsen effusion mass spectroscopy to study the reaction between $SiCl_4$ (g) and solid or liquid silicon. From the experimental results they deduced for $SiCl$ a dissociation energy of 88.6 ± 0.6 kcal/mole. In the following we will accept a value of 90 kcal/mole for the heat of adsorption of chlorine, and take 70 kcal/mole for the adsorption of atomic hydrogen.

Adsorption of monoatomic hydrogen

As discussed before, the growth rate of silicon in the SiH_4 - H_2 - N_2 system is proportional to $P_{H_2}^{-1}$. This could be explained by a small surface concentration of atomic hydrogen if SiH_2 is the most abundant species on the surface, or by a concentration of free surface sites proportional to $P_{H_2}^{-1/2}$ combined with SiH_4 as the most important silicon-containing surface species.

Evidence for the importance of H^* comes from nucleation experiments in the SiH_4 system [19] and the SiH_2Cl_2 system [20]. Below $1100^\circ C$ the nucleation on SiO_2 substrates in the latter system strongly depends on the hydrogen content of the gas phase. The density of nuclei varied proportionally with $P_{H_2}^{-1/2}$, as expected for the adsorption of atomic hydrogen on the SiO_2 substrate blocking adsorption sites. In the SiH_4 system the same behaviour was observed, but only at temperatures below $900^\circ C$. For the Si_3N_4 substrates, hydrogen adsorption also reduces the nucleus density, but this effect is much less pronounced than for the SiO_2 substrates. According to the JANAF tables [17] the bond strength between oxygen and hydrogen is 102 kcal/mole, between nitrogen and hydrogen 83 kcal/mole, while for the Si-H bond 70 kcal/mole is reported. The same sequence can be

expected to apply to the heats of adsorption of hydrogen on oxides, nitrides and silicon. The nucleation results may then be compared with the results of the growth experiments, and the adsorption of atomic hydrogen on silicon can be neglected above 700 °C. Another indication is found from the properties of amorphous hydrogenated silicon films [21]. In these materials ($=\text{SiH}_2$) and ($\equiv\text{SiH}$) centers are found when amorphous silicon is prepared from silane in a glow discharge or by sputtering of silicon in the presence of hydrogen at temperatures below 300 °C. Annealing of these materials above 300 °C gives evolution of H_2 (one peak near 375 °C due to the decomposition of ($=\text{SiH}_2$) and the other around 600 °C, associated with the decomposition of ($\equiv\text{SiH}$)). It is therefore to be expected in the CVD of silicon, too, that the surface concentrations of atomic hydrogen (H^*) will be small. At low temperatures the dissociation of hydrogen is too difficult and at temperatures above 600 °C the SiH bonds decompose easily.

Adsorption of SiH_2

Adamczewska and Budzynski [10] observed a saturation in the growth rate from SiH_4 at 500 °C with nitrogen as a carrier gas. Under reduced pressures and at 625 °C the same behaviour was observed by Van den Brekel and Bollen [22]. Under these circumstances, therefore, a high SiH_2 surface concentration could be expected. In the present series of experiments at 700 °C, however, no saturation in the growth rate is observed for input concentrations up to 0.4 vol. %, leading to the conclusion that under those circumstances θ_{SiH_2} is much smaller than unity. As discussed before, the deviation from linearity in nitrogen as a carrier gas (Figure 3) can be explained by gas phase nucleation of silane.

Adsorption of atomic chlorine

In the Si-H-N-Cl system SiH_2 will be converted into SiCl_2 , as previously discussed, and in this case, too, adsorption of chlorine comes into play. Most interesting in this respect is the reduction in growth rate in the $\text{SiH}_4\text{-HCl-H}_2\text{-N}_2$ system, where the first addition of HCl gives a strong reduction in growth rate (part I and Figure 5). This reduction could be caused by a strong adsorption of chlorine and subsequent reduction of adsorption possibilities for silane (model I). The experimental data in the $\text{SiH}_4\text{-H}_2\text{-N}_2\text{-HCl}$ system as well as in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-HCl}$ system (part II) [8] can be explained readily without resorting to chlorine adsorption. Evidence for a fractional chlorine surface concentration much smaller than unity, at least at temperatures above 700 °C, comes from the work of Miyamura et al. [23], who studied the adsorption of HCl on thermally cleaned Si (111) surfaces by Auger electron spectroscopy, electron energy loss spectroscopy, electron impact desorption and work-function change measurements. Equation (28) can be used to calculate the relative concentrations of Cl^* and H^* . With a SiH bond strength of 70 kcal/mole and realistic values of P_{H} and P_{Cl} at 700 °C it is found that a decrease in the heat of adsorption of chlorine of 10 kcal/mole is sufficient to obtain a con-

centration of chlorine smaller than the concentration of atomic hydrogen. A heat of adsorption of 90 kcal/mole for chlorine seems therefore to be too high when compared with the adsorption energy of atomic hydrogen (70 kcal/mole).

Adsorption of SiCl_2

As discussed in part II [8], a strong adsorption of SiCl_2 has to be assumed in order to explain the experimental data on growth of silicon from SiH_2Cl_2 both in hydrogen and in nitrogen. The saturation in the growth rate in the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system at 800 °C shows that the concentration of SiCl_2 molecules on the surface is much higher than the atomic hydrogen concentration. Using equation (28) a minimum heat of adsorption of SiCl_2 can be calculated by putting $\theta_{\text{SiCl}_2} = \theta_{\text{H}}$. In the growth via SiH_2Cl_2 in nitrogen as a carrier gas, the value of P_{SiCl_2} is nearly equal to the input concentration of SiH_2Cl_2 . It can be calculated that a heat of adsorption for SiCl_2 on silicon higher than 30 kcal/mole is sufficient to give an appreciable concentration of SiCl_2 . * This value is quite reasonable, but it has to be pointed out that desorption of SiCl_2 is found to occur after conversion of SiH_2 into SiCl_2 . We therefore expect $E_{\text{SiCl}_2} < E_{\text{SiH}_2} \cong E_{\text{Si}}$. In the $\text{SiH}_4\text{-HCl-H}_2\text{-N}_2$ system the value of P_{SiCl_2} is always smaller than the equilibrium concentration of SiCl_2 . Therefore in this $\text{SiH}_4\text{-H}_2\text{-N}_2\text{-HCl}$ system a surface concentration of SiCl_2 can be expected to be much smaller than in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system for equal input concentrations, other things being equal, as evidenced by the results in Figure 5.

4 Conclusions

The growth of silicon on silicon has been studied at 700 °C in the $\text{SiH}_4\text{-H}_2\text{-N}_2\text{-HCl}$ system. Without addition of HCl the highest growth rates are obtained when nitrogen is used as a carrier gas. Addition of hydrogen to the $\text{SiH}_4\text{-N}_2$ system leads to a reduction in the growth rate, which is inversely proportional to the hydrogen pressure. Analysis of the experimental data leads to the conclusion that the equilibrium reaction, $\text{SiH}_4 = \text{SiH}_2 + \text{H}_2$, plays a dominant role. The rate-limiting step has to be found between subsequent surface reactions. The adsorption of atomic hydrogen at surface sites or step sites can be assumed to be of minor importance. A fraction of free surface sites close to unity gives the best fit with the experimental data. This observation is in agreement with hydrogen evolution measurements in amorphous hydrogenated silicon [21]. Addition of HCl to the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system gives a strong decrease in growth rate, due to conversion of SiH_2 into SiCl_2 . In nitrogen-hydrogen mixtures this reduction in the growth rate is larger than in the $\text{SiH}_4\text{-H}_2$ system. The adsorption of H, Cl, SiCl_2 and SiH_2 has been discussed using the experimental data of the $\text{SiH}_4\text{-H}_2\text{-N}_2\text{-HCl}$ system and the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2\text{-HCl}$ system. It is concluded that a high surface concentration of SiCl_2 can be expected, notably in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system. Chlorine adsorption cannot be excluded completely, but there are strong indications that chlorine ad-

sorption does not have a major influence on the kinetics of the growth of silicon on silicon. It has to be expected that the crystallinity of the grown layer is disturbed by small surface coverage of hydrogen and chlorine, the growth rate however remains the same whether monocrystalline or polycrystalline material is formed.

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CHAPTER VIII

KINETIC STUDIES ON THE NUCLEATION AND GROWTH OF SILICON VIA CHEMICAL VAPOUR DEPOSITION

Abstract

Chemical vapour deposition (CVD) of silicon on various substrates is a well-known technique in semiconductor technology

An experimental study has been made of the nucleation of silicon on SiO_2 and Si_3N_4 substrates together with a search for rate-limiting steps in the growth of silicon from silane (SiH_4) and chlorosilanes

Analysis of the experimental data shows that the nucleation depends on the concentration of silicon adatoms on the surface, (Si^*). After formation of stable nuclei and coalescence of the growing domains, further growth of silicon on silicon proceeds

For the growth of silicon via silane the rate-limiting reaction could not be indicated exactly, addition of some HCl results in a rapid change of the surface species into SiCl_2^* , indicating that the rate-limiting step has to be found at the end of the chain of surface reactions. This conclusion is confirmed by experiments with an input of SiH_2Cl_2 , in which case the SiCl_2^* surface species predominates. Reduction to silicon is then found to be the rate-limiting reaction. The reduction or desorption of chlorine probably takes place at specific sites on the surface, such as atomic surface steps where an adsorbed SiCl_2 molecule can form a second silicon-silicon bond.

The adsorption of monoatomic hydrogen and chlorine on the silicon surface has been analysed and the conclusion is drawn that these surface species are not present in a sufficient concentration to turn the initial adsorption or the surface diffusion of silicon-containing compounds into rate-limiting reactions.

1 Introduction

The chemical vapour deposition of silicon is widely used in semiconductor technology for the growth of monocrystalline, polycrystalline or amorphous silicon layers.

Monocrystalline layers are grown on monocrystalline substrates in the production of bipolar and MOS (metal-oxide-semiconductor) devices and integrated circuits. Polycrystalline silicon is mostly used as gate material in MOS transistors. Amorphous silicon has attracted attention as a possible base material for solar cells.

In the growth of silicon from the vapour phase via CVD gaseous silicon compounds such as silane (SiH_4) and the chlorosilanes SiH_2Cl_2 , SiHCl_3 and SiCl_4 are used. Hydrogen mostly performs the dual function of reducing agent and carrier gas.

A typical apparatus used for the production of monocrystalline (so-called epitaxial)

layers on monocrystalline substrates (silicon, sapphire or spinel) is shown in figure 1.

Figure 1.

A horizontal CVD reactor. An RF field is used to heat the graphite susceptor and the silicon wafers to the desired temperature.

A high frequency generator is used to heat the graphite susceptor. On the susceptor the substrate slices are positioned and the carrier gas mixed with a small concentration of silane or chlorosilane is passed over the slices.

At temperatures above 1000°C monocrystalline layers can be grown at a rate of around $1\text{ }\mu\text{m/min}$. In the cold-wall apparatus of figure 1 a temperature difference exists in the gas phase between the heated susceptor and the cold wall. As the viscosity of the gas increases with increasing temperature a boundary layer is developed; diffusion of silicon containing compounds through this boundary layer now determines the growth rate of the layer. The growth rate as a function of temperature for a constant input concentration of silane in hydrogen is depicted in figure 2. It is seen that at temperatures above 1000°C the growth rate is hardly temperature-dependent as one would expect for a growth rate determined by the supply of reactant. The diffusion coefficients in the gas phase depend only slightly on temperature, thus explaining the growth behaviour in region 1 of figure 2.

At high growth temperatures the surface reactions are rapid and chemical equilibrium can be established at the silicon surface. These surface reactions, however, do not always lead to growth of a silicon layer. This is shown in figure 3 for the case of SiCl_4 as silicon compound.

It is seen that initially the growth rate increases linearly with increasing input concentration of SiCl_4 ; it then goes through a maximum, and at very high input concentrations, around 20 volume percent, the growth rate decreases to zero again.

Figure 2.

Silicon growth rate as a function of temperature for a silane concentration of 0.1 volume percent in hydrogen. The low and high temperature regions are clearly visible.

Figure 3.

The growth rate of silicon as a function of input concentration of SiCl_4 in hydrogen as a carrier gas.

This behaviour can be explained on the basis of thermodynamic equilibrium between two competing reactions:

At higher input concentrations the second reaction is dominant giving the result shown in figure 3. For SiH_2Cl_2 and SiHCl_3 the reduction in growth rate on increasing the input concentration is much smaller; no maximum in the growth rate versus concentration is found, only a deviation from linearity is observed [1].

Going to lower growth temperatures (region 2 in figure 2) a much stronger temperature dependence of the growth rate is found and surface reactions are thought to limit the growth. In such a situation the surface concentration of silicon species no longer corresponds to a chemical equilibrium. High surface concentrations of species occur, waiting for the next step in the chain of reactions. It can be visualized that such a sequence could consist of the following elements:

1. supply of reactant by gas phase diffusion,
2. adsorption of silicon compounds on the surface,
3. chemical reaction to form stable surface species,
4. surface diffusion to a suitable surface site,
5. incorporation of silicon in the lattice,
6. surface diffusion of reaction products,
7. desorption of reaction products,
8. gas phase diffusion of products away from the interface.

The first step constitutes the rate-limiting reaction at high temperature, as discussed previously.

In the etching of silicon by gaseous HCl it has been shown by Van der Putte [2] that the rate-determining reaction is given by 6. and 8., the reaction product being SiCl_2 .

It has been suggested by Chernov [3] that adsorption of monoatomic hydrogen and chlorine are of great importance. He calculated a dense population of H and Cl atoms (denoted H^* and Cl^*) under equilibrium conditions, even at temperatures above 1000°C . These adatoms could hamper the adsorption of silanes on the surface, and also could slow down the surface diffusion of reaction species towards specific surface sites. We will come back to this point and conclude that the equilibrium adsorption of H^* and Cl^* is of less importance.

Points 1. to 8. mentioned above are the result of theoretical work done by Kossel and Stranski, and later extended by Burton, Cabrera and Frank [4]. A schematic representation is given in figure 4. It can be thought that molecules adsorb on the

Figure 4.

Surface model with adatoms (A), atoms on atomic steps (ledge position B) and the stable kink position (C). (terrace-ledge-kink model) [4].

surface, followed by a chemical reaction to produce silicon adatoms that diffuse to a step and find a stable position on a so-called kink site. In this concept a kink site is energetically more attractive than an adatom position and diffusion is easily possible on the low-index perfect lattice plane between the steps.

At somewhat lower temperatures the surface diffusion of the adatoms becomes more difficult and nucleation of new centres between the steps becomes possible when the cohesive forces between the adatoms are stronger than the adhesive forces between adatom and substrate. This leads to less perfect growth and eventually to the growth of a polycrystalline layer. At still lower temperatures surface diffusion is so slow that an adatom has not yet diffused away before the next one arrives at the same lattice site. This leads to the formation of an amorphous layer, in which only short range interactions are present; reheating at higher temperatures can bring the layer to recrystallization [5].

The nucleation of silicon on a silicon substrate has mainly been studied in ultra high vacuum (10^{-10} torr) [6]. The surface has to be heated above 1250°C in order to be cleaned and a slight misorientation is preferred in order to promote the formation of a well-defined array of atomic steps. It has been shown [7] that on such a surface the lateral movement of the steps brings about the layer growth. In the growth of monocrystalline layers, therefore, a misorientation of about 3 degrees from the (111) orientation in the direction of the nearest (110) is generally used to optimise the growth of defect-free layers. Three degrees misorientation corresponds to an average step separation of about 20 lattice parameters. At temperatures below 1000°C polycrystalline growth is observed for growth at atmospheric pressure,

whereas amorphous growth is found below 700°C . The change in growth habit depends on the growth rate and on the ambient pressure, low growth rates and reduced pressures allowing lower transition temperatures. Nucleation of silicon on monocrystalline sapphire and spinel substrates has been studied by Abrahams and Blanc [8] and by Cullen [9]. They demonstrated that the first nucleation leads to small islands that grow out until coalescence occurs. Kamins [10] reported that growth of silicon on amorphous SiO_2 shows an incubation time that depends on temperature and silane input concentration. The growth of silicon on amorphous SiO_2 and Si_3N_4 layers onto silicon slices is an important process in the semiconductor industry, leading to polycrystalline layers of high resistivity. The grain size of the polycrystalline layer is the main parameter that determines the electrical resistivity. The grain size in turn depends on the nucleation and growth conditions. Since the kinetics of growth between 700 and 1000°C and the nucleation of silicon on a foreign substrate as SiO_2 and Si_3N_4 are both unknown, a systematic study has been initiated in order to explore this area.

2 Nucleation of silicon on SiO_2 and Si_3N_4 substrates

From nucleation experiments with silicon on a foreign substrate it has been deduced [11] that nucleation is preceded by the formation of a steady state concentration of monomers, dependent on the rate of adsorption and the rates of desorption or chemical reaction. The following step is the formation of silicon clusters on the surface that grow and decay until a critical size is exceeded (the critical cluster), when these clusters begin to grow by attracting neighbouring adatoms. This process can proceed so fast that the surface concentration of silicon adatoms between the growing nuclei becomes depleted, preventing further nucleation [12]. This type of behaviour is illustrated in figure 5, which gives a picture of

Figure 5

The density of stable nuclei on a SiO_2 substrate as a function of the exposure time at 1000°C ($P_{\text{SiH}_4} = 10^{-3}$, $P_{\text{HCl}} = 5 \times 10^{-3}$ in hydrogen at atmospheric pressure)

the number of nuclei formed on a silicon-oxide surface as a function of the time of deposition. To this end silicon slices were covered with a thin layer of SiO_2 or Si_3N_4 via deposition from the gas phase at reduced pressure. In the epitaxial apparatus shown in figure 1 the slices were heated to the desired temperature and a short pulse of silane or silane-HCl mixtures was introduced into the apparatus. The length of the pulse is the deposition time given in figure 5. After cooling down, the slices were examined in an electron microscope (SEM and TEM). For short pulses no nucleation is observed; after this incubation time the number of stable clusters suddenly increases to a constant value. For longer pulses the number of nuclei remains the same, the nuclei merely growing out to a larger size. Eventually, the clusters overlap and coalescence causes a decrease in the number of nuclei counted per surface area. The nucleation rate after the incubation time is so high that it cannot be determined and therefore the steady state number of nuclei (n_s) has been further studied as a function of temperature and gas phase composition. Figures 6 and 7 show some results as regards the concentration of stable nuclei as a function of the HCl content for a constant silane concentration. As outlined by Claassen [11] the nucleation process can be described by an expression given by Venables [12, 13]. In the case of incomplete condensation with a high mobility of adatoms and small clusters the maximum density of stable nuclei n_s is given as

$$n_s = C n_1 \frac{i+1}{2} \exp \frac{E_i + E_x - E_d}{kT} \quad (2.1)$$

where C is a statistical weighting factor, n_1 is the concentration of adatoms on the surface, i is the number of atoms in a critical cluster, E_i is the heat of formation of a cluster consisting of i atoms, E_x is the energy for surface diffusion of mobile clusters, and E_d is the energy for surface diffusion of adatoms. In equation (2.1) the concentration of adatoms (n_1) is used, the value of which depends on the supersaturation in the gas phase. An expression for n_1 can be obtained when the formation of adatoms is conceived of as a sequence of successive steps [11]. A simplified scheme is given here that will be supplemented in subsequent sections.

i adsorption of silane on a free site (*):

ii the reaction of silane, creating adatoms

Figure 6.

Nucleus density from mixtures of SiH₄ and HCl for 0.1 volume percent of silane. X denotes the ratio of the input concentration of HCl and SiH₄, ($X = P_{\text{HCl}}/P_{\text{SiH}_4}$). The exposure time is chosen long enough for a constant number of nuclei to be reached.

Figure 7.

The saturation nucleus density of silicon clusters on SiO_2 as a function of the reciprocal temperature for different mixtures of SiH_4 and HCl .

iii the etching of adatoms

Reactions with the substrate and the adsorption of species other than silane have been left out of account. In the steady state where $dn_1/dt = 0$, the adatom concentration $[\text{Si}^*] = n_1$ is given by

$$n_1 = \frac{k_1 k_2 P_{\text{SiH}_4} [*]}{k_{-2} P_{\text{H}_2}^2 + k_3 P_{\text{HCl}}^2} . \quad (2.5)$$

For a fraction of free adsorption sites close to unity and $P_{\text{H}_2} = 1$ at atmospheric pressure, eq. (2.5) reduces to

$$n_1 = \frac{k' P_{\text{SiH}_4}}{1 + k'' P_{\text{HCl}}^2} . \quad (2.6)$$

Eq (2.1) now reads

$$n_s = C \left(\frac{k' P_{\text{SiH}_4}}{1 + k'' P_{\text{HCl}}^2} \right)^{\frac{i+1}{2}} \exp \frac{E_i + E_x - E_d}{kT} \quad (2.7)$$

In figure 8 experimental nucleation densities are given for various combinations of PSiH_4 and PHCl . The results can very well be described by

$$n_s \propto \frac{P_{\text{SiH}_4}}{1 + 6 \times 10^6 \cdot P_{\text{HCl}}^2} \quad (2.8)$$

Figure 8.

The saturation nucleus density of silicon clusters at 1000 °C for different input concentrations of SiH_4 with and without HCl .

Inspection of figure 8 shows that, for higher values of $P_{\text{SiH}_4}/P_{\text{HCl}}^2$, the slope of n_s versus supersaturation is equal to unity. According to eq. (2.7) the slope is given by $(1 + i)/2$, and hence i equals unity, or, the critical cluster consists of one atom. For lower supersaturations the value of n_s decreases rapidly, and values of i up to 4 are then calculated from the experimental data.

Going to lower temperatures typical differences become visible between the con-

centrations of stable nuclei formed on SiO_2 and Si_3N_4 substrates. For hydrogen as a carrier gas the nucleus density on SiO_2 becomes much smaller than on Si_3N_4 (figure 9), in nitrogen the densities are nearly equal on these two substrates. This observation suggests that by adsorption of monoatomic hydrogen the adsorption sites for silane are blocked on the SiO_2 surface. This appears not to be the case on the silicon nitride surface, in which connection it is interesting to note that the O-H and N-H bond strengths are 102 and 83 kcal/mole respectively. This difference is large enough to explain the experimental results providing that the heat of adsorption of the main silicon species is greater than 83 kcal/mole.

It has also been shown in the nucleation experiments that the stable nucleus density could be varied between 10^5 and 10^{11} per cm^2 resulting in polycrystalline layers with a corresponding number of grains. After coalescence of the growing nuclei these grains are seen to grow in a columnar fashion. On a monocrystalline substrate like sapphire and spinel a comparable number of nuclei is formed. In that case the nuclei are not randomly oriented, as they are on an amorphous substrate, and reasonably crystalline layers can be formed [8, 9].

Figure 9

The steady state nucleus densities on SiO_2 and Si_3N_4 substrates in hydrogen as a carrier gas. At the lower temperatures hydrogen adsorption on SiO_2 hampers the nucleation.

3 Growth of silicon on silicon

A number of recent experiments will now be discussed that give some insight into the kinetics of the growth of silicon from silane and the chlorosilanes at temperatures between 700 and 1000 °C. In order to facilitate the discussion a generalised scheme will be presented first in which the essential steps in the growth from silane and chlorosilanes are formulated in a way that permits a close comparison

3.1 General scheme for the growth of silicon

As a result of the experiments it is believed that gas phase reactions close to the silicon surface are important. Two main reaction products are of interest, i.e. SiH_2 and SiCl_2 , formed according to

and

The gas phase reactions are followed by adsorption of the SiH_2 and SiCl_2 species on the silicon surface. A free surface site is denoted as *, giving

The adsorbed species diffuse over the silicon surface until a site is reached where a second silicon-silicon bond can be formed, e.g. a free site at an atomic step on the surface. We then have

Next comes the rate-limiting reaction given by the release of the adsorbed H and Cl atoms, resulting in

In the following the considerations leading to this general scheme will be presented.

3.2 Growth from silane

The growth of polycrystalline silicon films has been studied at atmospheric pressure in a carrier gas consisting of various mixtures of hydrogen and nitrogen [14]. Care has been taken to use silane concentrations low enough to be sure that no gas phase nucleation occurs [15]. A typical result is shown in figure 10, where it can be seen that the growth rate is high in inert gas and lowest in pure hydrogen. For all experi-

Figure 10.

The growth rate of silicon at 700 °C as a function of the hydrogen content in the gas phase with silane (SiH_4) as silicon source material.

Reaction		Growth rate from RLR	
		with $\theta = 1, n = 2$	
adsorption	$\text{SiH}_4 + * \rightleftharpoons \text{SiH}_4^*$	$R_1 = k_1 P_{\text{SiH}_4} \cdot \theta$	$R_1 = k_1 P_{\text{SiH}_4}$
chemical reaction	$\text{SiH}_4^* \rightleftharpoons \text{SiH}_n^* + \frac{4-n}{2} \text{H}_2$	$R_2 = k_2 \cdot P_{\text{SiH}_4} \cdot \theta$	$R_2 = k_2 P_{\text{SiH}_4}$
surface diffusion	$\text{SiH}_n^* + * \rightleftharpoons \text{SiH}_n^* + *$	$R_3 = k_3 \cdot \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}^{(4-n)/2}} \cdot \theta^2$	$R_3 = k_3 \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}}$
step attachment	$\text{SiH}_n^* + * (\text{st}) \rightleftharpoons \text{SiH}_n^{**}$	$R_4 = k_4 \cdot \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}^{(4-n)/2}} \cdot \theta \cdot \theta_{\text{st}}$	$R_4 = k_4 \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}}$
release of H_2	$\text{SiH}_n^{**} \rightleftharpoons \text{Si}(\text{cr}) + \frac{n}{2} \text{H}_2$	$R_5 = k_5 \cdot \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}^{(4-n)/2}} \cdot \theta \cdot \theta_{\text{st}}$	$R_5 = k_5 \frac{P_{\text{SiH}_4}}{P_{\text{H}_2}}$

TABLE I

Reaction path for the growth of silicon from silane. The last column gives an expression for the growth rate when the corresponding reaction is rate-limiting (RLR). The fraction of free surface and step sites is denoted by θ and θ_{st} respectively. For hydrogen adsorption

$$\theta = 1/(1 + k_{\text{H}} P_{\text{H}_2}^{1/2}).$$

ments the growth rate can fairly well be expressed as a function of the input pressures of silane and hydrogen

$$R = \frac{k_a P_{\text{SiH}_4}}{1 + k_b P_{\text{H}_2}} \approx \frac{k_a P_{\text{SiH}_4}}{k_b P_{\text{H}_2}} \quad (3.5)$$

The experimental result of eq (3.5) is of extreme importance in the interpretation of the silicon growth rate. In Table I possible reactions of silane are given, together with an expression for the growth rate when that specific reaction is rate-limiting. The adsorption of a fully coordinated compound like SiH_4 is rather improbable because of the low heat of adsorption. Formally, however, SiH_4 adsorption can be accepted as a precursor to the adsorption of other Si-H molecules. It is also possible, by combination of eq 1 and eq 2 in Table I, to describe a dissociative adsorption. It has been suggested [16] that adsorption of monoatomic hydrogen hampers the growth at lower temperatures, thereby blocking sites for the adsorption of silane via the reaction

The asterisk denotes a free surface site and H^* stands for an adsorbed hydrogen atom. From eq (3.6) follows the fraction of free surface sites (θ) in the case of predominant hydrogen adsorption, given by

$$[\text{H}^*] = K_H P_{\text{H}_2}^{1/2} [*] \quad (3.7a)$$

and

$$[*] = \theta = 1/(1 + K_H P_{\text{H}_2}^{1/2}) \quad (3.7b)$$

From Table I it can be deduced that an experimental result as given in eq 3.5 points to a value of $n = 2$ with $\theta = 1$ or $n = 4$ when $\theta = 1/K_H P_{\text{H}_2}^{1/2}$. Most probable is $n = 2$ with SiH_2^* as surface species, leading to the conclusion that surface adsorption of hydrogen does not result in a complete surface coverage. It is also clear from Table I that adsorption of silane cannot explain the experimental results. The actual rate-limiting step has to be found amongst the surface diffusion, step attachment and release of hydrogen. Different hydrogen partial pressures will give different amounts of SiH_2^* , leading to a higher growth rate in an inert gas, and the same effect is expected for growth under reduced pressures where the value of P_{H_2} is equally reduced. Indications of a variation of growth rate with $P_{\text{H}_2}^{-1}$ have also been found by Yasuda [17]. At high growth temperatures Manasevit [18] found a growth rate proportional to P_{H_2} . In his experiments, however, the gas phase concentration of silane was so high that gas phase decomposition predominates via

(3.8)

In a hydrogen ambient the formation of free SiH_2 is hampered giving a smaller rate of deposition of polymers on the reactor wall and thus a higher growth rate on the substrate. The present experiments on the growth of silane indicate that SiH_2 could be a predominant surface species. A conclusive indication of the nature of the rate-limiting reaction can not be given from these experiments alone. Further insight might be gained from additional experiments. The first to be discussed is the system in which some HCl gas is mixed with silane in a hydrogen ambient.

3.3 Growth from SiH_4 plus HCl

It has been shown previously by Van der Putte et al. [2] that gaseous hydrogen chloride etches silicon, the main reaction being

Van der Putte et al. have studied the etching reaction in some detail, the etch rate is found to be proportional to the amount of SiCl_2 formed and can be expressed as

$$R_{\text{etch}} = k_c P_{\text{HCl}}^2 / P_{\text{H}_2}. \quad (3.9)$$

The etch rate therefore is fast in inert ambients and slows down in hydrogen as a carrier gas.

The addition of a small amount of HCl to silane has been used in order to prevent the gas phase nucleation of silane [1]. At temperatures above 1000°C mixtures of 0.1 volume percent SiH_4 and 0.4 volume percent HCl show a silicon growth rate of $0.3 \mu\text{m}/\text{min}$, almost equal to that shown by silane. The etch rate given by 0.4 volume percent HCl in hydrogen is small ($0.02 \mu\text{m}/\text{min}$). For growth temperatures exceeding 1000°C it has been demonstrated that growth via silane and etching via HCl occur simultaneously and independent of each other on the silicon surface. Going to lower growth temperatures figure 2 shows that surface reactions begin to hamper the growth rate, but the etch rate remains more or less constant. It could be expected that the sum of eqs. (3.9) and (3.5) would represent the outcome of a combined growth and etching behaviour, even at temperatures below 900°C . Experimentally, however, it is found that below 900°C an enormous reduction in growth rate appears [19]. This behaviour is interesting as it points to specific surface reactions that occur in the kinetically controlled regime. Figure 11 gives some results. A strong reduction in growth rate is apparent. This reduction depends on the amount of HCl added. Figure 12 shows that there is a drastic decrease in growth rate on the first addition of HCl (shown to be proportional to

Figure 11.

Growth rate given by a mixture of 0.1 volume percent silane and 0.4 volume percent HCl in hydrogen as a function of temperature, compared with the growth rate given by SiH_4 without HCl addition.

P_{HCl}^2 followed by a slower decrease in growth rate. This decrease is also proportional to P_{HCl}^2 . The decrease in growth rate when interpreted as an etch rate is such as expected from eq. (3.9). It was concluded that the decrease in growth rate is to be explained by the attack of Si^* and SiH_2^* surface species by HCl, leading to the formation of SiCl_2 as the main adsorbed surface species in a new steady state situation. The explanation of the reduced growth rate can then be given on the basis of an analysis of the possible rate-limiting reactions. When the rate-limiting step is at the end of the chain of reactions, an increased concentration of Si^* and SiH_2^* then builds up. The supersaturation can be a factor of 10^3 for an input concentration of silane of 10^{-3} and a calculated equilibrium concentration of 10^{-6} bar for silicon in contact with hydrogen at temperatures around 1000°C [20]. In this situation HCl is able to attack these reactive species, giving SiCl_2^* on the surface. Desorption of SiCl_2 is readily possible under the conditions of increased surface concentration, leading to the observed decrease in growth rate. This new situation is established on the first addition of HCl; any further increase in HCl content cannot increase the SiCl_2 concentration other than via the normal etching of bulk silicon atoms (eq. 3.9).

Figure 12.

The growth rate shown by mixtures of 0.1 volume percent silane and various amounts of HCl, plotted as a function of P_{HCl}^2 .

A reduction in growth rate by the introduction of HCl can also be explained by adsorption of chlorine on the silicon surface

The chlorine content would reduce the number of free surface sites and thus make the adsorption of silane more difficult. There are two points that make this explanation less attractive. The first is that the reduction in growth rate is then expected to be proportional to P_{HCl} , whereas in practice a reduction proportional to P_{HCl}^2 is found. The other point is the new level in growth rate obtained after the first intro-

Figure 13

The growth rate of silicon from SiH_2Cl_2 as a function of the addition of HCl

duction of HCl , which cannot be explained simply on the basis of chlorine adsorption. Therefore, the chemical reaction is favoured in which the original surface species are converted into SiCl_2^* . In this way the experiments in the SiH_4 - HCl system shed new light on the kinetics, but still no conclusion can be drawn on the nature of the rate-limiting step. Experiments with SiH_2Cl_2 will therefore be interesting, the question being to what extent SiCl_2^* will already be present without HCl addition.

3.4 Growth via SiH_2Cl_2

According to thermochemical data [20] and confirmed by experiment [21] it is to be supposed that the following equilibrium already exists in the gas phase

Figure 14.

The growth rate of silicon from SiH_2Cl_2 as a function of hydrogen content of the carrier gas with the growth temperature as a parameter.

It can be shown that for the dissociation of eq. (3.11) we have

$$p_{\text{SiCl}_2} = \frac{k_d}{k_d + p_{\text{H}_2}} \cdot p_{\text{SiH}_2\text{Cl}_2}^0$$

At 1000 °C, k_d is equal to 6.1, and $k_d = 6.6 \times 10^{-2}$ at 700 °C [20] The dissociation is therefore almost complete in an inert gas ambient, but in hydrogen at lower temperatures only a partial dissociation is expected, giving

$$p_{\text{SiCl}_2} = p_{\text{SiH}_2\text{Cl}_2}^0 / p_{\text{H}_2}$$

Figure 15

The growth rate of silicon from SiH_2Cl_2 as a function of the input concentration of SiH_2Cl_2 in H_2

Our experiments (figure 13) on the growth of silicon from SiH_2Cl_2 showed that addition of HCl does not give an abrupt decrease in growth rate as found for $\text{SiH}_4\text{-HCl}$. In view of the previous section the main conclusion has to be that the dominating silicon-containing surface species will be SiCl_2^* . The growth via SiH_2Cl_2 has further been studied in mixtures of hydrogen and nitrogen for temperatures between 800 and 1000°C . Some results are given in figure 14 [22]. It is found that the highest growth rates are observed in a hydrogen ambient, especially at higher temperatures. Moreover the growth rate as a function of input concentration of SiH_2Cl_2 shows a saturation behaviour as depicted in figure 15. This kind of saturation is also found in the $\text{SiH}_4\text{-N}_2$ system at growth temperatures below 700°C [23]. The saturation in growth rate points to a Langmuir type of adsorption, causing a saturation in growth rate at higher input concentrations. Adsorption of SiH_2Cl_2 as a fully coordinated compound is less probable than adsorption of SiCl_2 . It is therefore assumed that SiCl_2 formed in the gas phase (eqs 3.2, 3.11) is adsorbed on the silicon surface. For a nearly complete dissociation P_{SiCl_2} is nearly equal to input concentration of SiH_2Cl_2 ($P_{\text{SiH}_2\text{Cl}_2}^0$). The adsorbed SiCl_2 diffuses over the surface and at a step site chlorine is desorbed, according to the reaction

When reaction (3 12) represents the rate-limiting reaction the growth rate can be calculated analogous to the results given in Table I as being

$$R_{gr} = k_e [\text{SiCl}_2 (\text{step})] P_{\text{H}_2} \\ = k_f P_{\text{SiH}_2\text{Cl}_2}^0 P_{\text{H}_2} \theta \theta_{st} \frac{k_d}{k_d + P_{\text{H}_2}} \quad (3 13)$$

This result can be compared with the experimental data shown in figure 14, it can be concluded that a good correlation is obtained for values of θ and θ_{st} close to unity. For high input concentrations of SiH_2Cl_2 and at low temperatures a deviation from (3 13) is observed (figure 15). The fraction of free surface sites is no longer equal to unity, and we have for θ and θ_{st}

$$\theta = 1 - [\text{H}^*] - [\text{Cl}^*] - [\text{SiCl}_2^*] -$$

$$\theta_{st} = 1 - [\text{H}^*] - [\text{Cl}^*]$$

The difference in the expressions for θ and θ_{st} is explained by the circumstance that, on a one-dimensional step, no distinction can be made between an adsorbed SiCl_2 molecule and a pair of adsorbed chlorine atoms. The same applies to SiH_2 adsorption versus adsorption of two hydrogen atoms on a step. The experimental results shown in figure 15 can be readily explained by the assumption of an important surface adsorption of SiCl_2 between the steps, combined with a minor surface coverage by adsorbed hydrogen and chlorine atoms. The adsorption of SiCl_2 can be accounted for by the use of an expression such as eq (3 7). With $P_{\text{SiCl}_2} = P_{\text{SiH}_2\text{Cl}_2}^0$ we then obtain from eq (3 13) the final expression describing the growth of silicon from dichlorosilane in the surface controlled mode of growth

$$R_{gr} = \frac{k_f P_{\text{SiH}_2\text{Cl}_2}^0 P_{\text{H}_2}}{1 + k_g P_{\text{SiH}_2\text{Cl}_2}^0} \quad (3 14)$$

From the present experiments it may be concluded that the rate-limiting reaction in the growth of silicon from dichlorosilane has been located at the reduction of SiCl_2 at specific sites where silicon is incorporated in the crystal lattice. An adsorbed SiCl_2 molecule can be considered to have one Si-Si bond, the formation of a second Si-Si bond at a step site can then be the decisive reaction in the incorporation of a new silicon atom into the lattice. Additionally, strong supersaturations of SiCl_2 on the surface are found in accordance with the high value of P_{SiCl_2} expected in the gas phase and caused by gas phase dissociation of SiH_2Cl_2 .

Figure 16

The growth rate of silicon from SiHCl_3 as a function of the input concentration of SiHCl_3 [25]

3.5 Growth from SiHCl_3

Experiments with the growth of silicon from SiHCl_3 at lower temperatures show a saturation behaviour [24] as shown in figure 16. In this system it can also be supposed that SiCl_2^* is the main surface species. The rate-limiting reaction will again be the reduction of SiCl_2 at step sites. Saturation of the growth rate at lower temperatures reflects the increased SiCl_2^* concentration waiting for reduction at the step sites. In the foregoing sections arguments have been given that led to the general scheme of section 3.1. The results presented indicate that a complete coverage of the silicon surface with H^* or Cl^* is not in agreement with the experimental evidence. Further discussion of this point will be given in the next section.

4 Adsorption on the silicon surface

From the experimental results obtained so far a direct indication of a rate-determining surface adsorption is obtained only for SiCl_2^* at high gas phase concentrations of SiCl_2 (SiH_2Cl_2 system).

Desorption of Cl^* and H^* is found to involve important, even rate-limiting steps, indicating that the corresponding concentrations are higher than normal. No indications are found, however, to suggest a high equilibrium surface coverage by H^* and Cl^* species.

This finding is in contradiction with the equilibrium calculations of Chernov et al [3], who supposed the heat of adsorption of monoatomic hydrogen and chlorine on the silicon surface to be equal to the heat of dissociation of the gaseous diatomic molecules SiH and SiCl . The heats of adsorption of SiCl_2 and SiH_2 were taken to be nearly equal to the Si-Si bond strength. With a Langmuir type of adsorption a complete surface coverage with H^* is then calculated for silicon in hydrogen even at 1200°C , in the presence of HCl large quantities of Cl^* are present too. Under equilibrium conditions the partial pressure of SiCl_2 is low and so too therefore is the quantity of SiCl_2^* .

From the nucleation experiments described in section 2 a clear indication of hydrogen adsorption on SiO_2 is found for the $\text{SiH}_4\text{-H}_2$ system below 900°C . The OH bond strength is 102 kcal/mole . Adsorption of hydrogen on Si_3N_4 has a minor influence on the nucleation of silicon, in accordance with the N-H bond strength of 83 kcal/mole . The SiH bond strength of 70 kcal/mole is still lower and the coverage of silicon by hydrogen could thus be less important. Another indication is given by the hydrogen content of amorphous silicon when prepared below 300°C in a hydrogen plasma. Via infrared absorption measurements SiH_2 and SiH bonds appear to be present. On annealing the first adsorption (SiH_2) disappears at 375°C , the Si-H bonds decompose below 600°C [25].

The hydrogen release is confirmed by other quantitative methods [26] as well. This evidence, together with the observation that the temperature dependence of the growth rate of silicon below 1000°C ($\approx 1.6\text{ eV}$) is nearly the same in hydrogen as in nitrogen and also under reduced pressure [27], leads to the conclusion that a complete coverage of hydrogen under all these conditions is improbable. The number of hydrogen adatoms can be calculated in adsorption equilibrium. The number of hydrogen atoms impinging on the silicon surface (R_H) is given by

$$R_H = \frac{P_H}{(2\pi m_H kT)^{1/2}} \text{ cm}^{-2} \text{ sec}^{-1} \quad (4.1)$$

where P_H is the partial pressure of monoatomic hydrogen, m_H is the atomic mass of hydrogen, k is Boltzmann's constant and T the temperature in K . The number of hydrogen atoms desorbing is found from

$$n_{\text{des}} = n_H \nu \exp\left(-\frac{E_{\text{des}}}{kT}\right) \quad (4.2)$$

where n_H is the surface concentration of adsorbed atoms, ν is the vibration frequency of the Si-H bond, and E_{des} is the heat of desorption of the adsorbed atom.

Assuming a sticking probability of unity, in the steady state $n_{\text{des}} = R_{\text{H}}$, so that the value of n_{H} comes to

$$n_{\text{H}} = \frac{P_{\text{H}}}{(2\pi m_{\text{H}} kT)^{1/2} \nu} \exp \frac{E_{\text{des}}}{kT} \quad (4.3)$$

In the gas phase an equilibrium between H_2 molecules and H atoms is present, leading to

$$P_{\text{H}} = K_{\text{H}_2} P_{\text{H}_2}^{1/2} = K_{\text{H}_2}^0 P_{\text{H}_2}^{1/2} \exp \left(- \frac{E_{\text{diss}}}{kT} \right) \quad (4.4)$$

K_{H_2} is given in the thermochemical tables and contains the temperature dependent term in which the dissociation energy of H_2 is denoted as E_{diss} . For a small coverage the number of adsorbed hydrogen atoms can thus be given as

$$\begin{aligned} n_{\text{H}} &= \frac{K_{\text{H}_2}^0 P_{\text{H}_2}^{1/2}}{(2\pi m_{\text{H}} kT)^{1/2} \nu} \exp \frac{E_{\text{des}} - E_{\text{diss}}}{kT} \\ &= K_{\text{H}} P_{\text{H}_2}^{1/2} \end{aligned} \quad (4.5)$$

For higher densities of adsorbed hydrogen, the formulation given in eqs (3.6) and (3.7) leads to the following expression in which K_{H} is the same as given in eq (4.5)

$$n_{\text{H}} = \frac{K_{\text{H}} P_{\text{H}_2}^{1/2}}{1 + K_{\text{H}} P_{\text{H}_2}^{1/2}} \quad (4.6)$$

The value of E_{diss} is 2.24 eV, the magnitude of E_{des} is estimated to be equal to the heat of dissociation of the Si-H gaseous dimer, being 3.1 eV. This estimate has been used by Chernov and via eq (4.6) a complete surface coverage is found at temperatures of 1000 °C to 1200 °C. In order, however, to explain the experimental evidence in the kinetics of the growth of silicon a lower value for the heat of adsorption of hydrogen on silicon has to be assumed. A comparable dilemma exists in the heat of adsorption of silicon on silicon, generally a value of about 2 eV is accepted equal to half the heat of vapourisation of silicon (107 kcal/mole or 4.6 eV) whereas the heat of dissociation of the Si-Si gaseous dimer amounts to 3 eV (76 kcal/mole). The adsorption of chlorine on the silicon surface can be treated along similar lines as for hydrogen. The gas phase reaction of HCl to give chlorine and hydrogen is used to calculate P_{Cl} . For chlorine a Si-Cl bond strength of 90 ± 15 kcal/mole is given [28], whereas recent measurements reported by Farber [28] gave a value of 89 kcal/mole. The dissociation energy of HCl to give chlorine and hydrogen is 46 kcal/mole. The resulting heat of reaction and adsorption comes to

43 kcal/mole (1.9 eV). It is pointed out by Chernov [3] that at a higher surface coverage chlorine adatoms will undergo strong interactive repulsive forces, reducing the adsorption energy to values close to that of the Si-H bond. Therefore for chlorine adsorption too, no high coverage need be present.

The adsorption of SiCl_2 from the gas phase depends on the value of P_{SiCl_2} and the adsorption energy. In the growth via SiH_2Cl_2 , the value of P_{SiCl_2} is nearly equal to the input pressure of SiH_2Cl_2 . A heat of adsorption of 40 kcal/mole (1.8 eV) is sufficient to explain a complete coverage.

The addition of HCl to SiH_4 is shown to convert the surface species into SiCl_2^* . A lower growth rate under these circumstances is to be explained by a desorption of SiCl_2 . This indicates a heat of desorption of SiCl_2 lower than that of silicon or SiH_2 , which is not improbable.

The adsorption of surface species on silicon, therefore, appears to be limited under real growth conditions to the presence of silicon-containing species with Cl^* and H^* being present in amounts that do not hamper the adsorption or surface diffusion of silicon-containing species to any measureable extent. This means that for the fraction of free surface sites, θ a value near unity can be chosen. Only at lower temperatures can this change, as found in the SiH_2Cl_2 system. Furthermore the observation that polycrystalline silicon is formed under reduced pressures at 625 °C whereas amorphous silicon is produced in a hydrogen ambient, gives an indication that below 700 °C the surface mobility is hampered seriously in a hydrogen ambient.

5. Conclusion

The nucleation and growth of silicon has been studied at atmospheric pressure and temperatures between 800 and 1000 °C, being a temperature region in which growth of polycrystalline silicon is normally performed. Below 700 °C the growth of amorphous material is observed in hydrogen at atmospheric pressure. The nucleation of silicon on a foreign substrate such as SiO_2 and Si_3N_4 is shown to proceed via silicon adatoms formed on the surface. A critical cluster of a few atoms is found to be sufficient to give a stable nucleus that grows out until coalescence of the grains leads to a further growth of silicon on silicon.

For the growth of silicon from silane (SiH_4) it has been deduced that the rate-limiting reaction is not the adsorption of silane or a chemical reaction to give SiH_2 but is probably found in the diffusion of SiH_2 on the surface or the incorporation of SiH_2 units on atomic surface steps, after which desorption of hydrogen follows. In the presence of some HCl in the gas phase all surface species are converted into SiCl_2 . The SiCl_2 adatoms are stabilised by the formation of a second Si-Si bond. The subsequent desorption of chlorine atoms constitutes the rate-limiting reaction for further growth via the addition of new SiCl_2 units. The experimental evidence

cannot be explained by a strong adsorption of monoatomic hydrogen on the silicon surface. The conclusion is drawn that the adsorption energy of H^* on the silicon surface is appreciably lower than the heat of dissociation of the gaseous diatomic Si-H molecule. The influence of the addition of HCl has been explained by the formation of $SiCl_2$ at the cost of Si and SiH_2 as surface species. Saturation in the growth rate as a function of input concentration of SiH_2Cl_2 is also explained in terms of $SiCl_2$ adsorption. The evidence could also be explained by chlorine adsorption and a rate-limiting reaction for growth given by the surface diffusion of $SiCl_2$ hampered by adsorbed chlorine atoms (compare eq. 4 in Table I). The constant level in growth rate after introduction of HCl in the SiH_4 - H_2 system (figure 12), the absence of a sudden drop in growth rate on the introduction of HCl in the SiH_2Cl_2 - H_2 system (figure 13) and the saturation in growth rate for higher values of $P_{SiH_2Cl_2}$ (figure 15), where only small values of P_{HCl} are present, lead to the additional conclusion that the experimental evidence is most readily explained by a small surface coverage by chlorine in the systems used and at temperatures above 700 °C.

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CHAPTER IX

THE GROWTH OF SILICON FROM SILANE IN COLD WALL CVD SYSTEMS

Abstract

The authors discuss the growth of silicon from silane as a function of substrate temperature and hydrogen partial pressure in cold wall CVD systems at different total pressures. At high temperatures the growth rate is determined by gas phase diffusion of the silicon compound towards the surface. In this regime and at atmospheric pressure the growth rates of silicon for the $\text{SiH}_4\text{-H}_2$ and the SiH_4 -inert gas system are almost the same. Reducing the total pressure initially increases the growth rate, which is then inversely proportional to the total pressure, while at pressures below 0.1 bar the growth rate is less than in inverse proportion to the total pressure, owing to the influence of the steep temperature gradients on the diffusional behaviour of the reactants at these low pressures in a cold wall apparatus.

At low temperatures the growth rate is controlled by surface reactions and is inversely proportional to the hydrogen pressure and proportional to the silane input concentration. In this regime the growth rate of silicon increases exponentially with increasing temperature and the apparent activation energy is in a first approximation independent of the total pressure and of the partial pressure of hydrogen. It is stressed that at high temperatures the physical influence of the total pressure determines the growth rate, whereas at lower temperatures ($< 1000^\circ\text{C}$) it is the hydrogen partial pressure that exerts a chemical influence on the growth rate.

1. Introduction

The temperature dependence of the growth rate of silicon from silane in hydrogen at atmospheric pressure has two temperature regimes [1], as shown schematically in Figure 1. According to Van den Brekel [2] the local growth rate of silane in hydrogen as a carrier gas as a function of temperature in a horizontal cold wall reactor can best be given by the expression

$$G(X) = \frac{A P_0}{T_s(R_1 + R_2)} \exp \left[\frac{-T_0 X}{V_0 T_s b(R_1 + R_2)} \right] \quad (1)$$

where $G(X)$ is the growth rate of silicon along the X -axis, A is a reactor constant, P_0 the input pressure of the reactant, T_s the substrate temperature, T_0 the room temperature, V_0 the mean gas velocity at room temperature and b the free height above the susceptor. R_1 and R_2 are the diffusion and transfer resistances, which can be given by

$$R_1 = \frac{\delta T_0^2 \ln(T_s/T_b)}{D_{12} T_s (T_s - T_b)} \quad (2)$$

and

$$R_2 = \frac{1}{k_d} \quad (3)$$

where δ is the thickness of the diffusion boundary layer, D_{12} the binary diffusion coefficient of the reactant in the carrier gas at room temperature, T_b the bulk gas temperature and k_d a mass transfer coefficient. At relatively low temperatures k_d is so small that hardly any concentration gradient is present over the boundary layer and along the susceptor. Under these conditions ($R_2 \gg R_1$) and with $k_d = k_d^0 \exp(-\Delta E/RT)$, equation (1) can be transformed into

$$G(X) = G_0 \exp(-\Delta E/RT) \quad (4)$$

where $G_0 = AP_0 k_d^0 / T_s$ is a pre-exponential factor and ΔE an apparent activation energy which is about 37 kcal/mole for silane in hydrogen at atmospheric pressure [1]. Going to higher temperatures the surface reactions become so fast that the gas phase diffusion of silane towards the surface becomes the real limiting step ($R_1 \gg R_2$). This leads to

$$G(X) = \frac{B D_{12} P_0}{\delta} \exp\left(\frac{-C X D_{12}}{\delta}\right) \quad (5)$$

where B and C are constants at a fixed temperature. At high temperatures the growth rate of silicon for $X = 0$ is only a weak function of temperature, because the diffusion coefficient is approximately proportional to $T^{3/2}$ and B/δ is almost independent of temperature. The exponential term of equation (5) describes the decrease of the growth rate of silicon along the susceptor due to the depletion of silane in the gas phase. It should be noted that in the intermediate regime ($R_1 \cong R_2$) the temperature dependence of the silicon growth rate gradually changes from about $T^{3/2}$ ($\cong 5$ kcal/mole at 1000 °C) to about 37 kcal/mole.

Both at reduced total pressure and in inert ambients at atmospheric pressure the apparent activation energy ΔE (equation (4)) is about 37 kcal/mole, as will be discussed below. However, the position of the knee in the curve of growth rate versus $1/T$ (Fig. 1) depends on the partial pressure of hydrogen and on the total pressure. According to Van den Brekel the position of this knee is defined by the condition that

$$R_1 = R_2 \quad (6)$$

In the following sections the growth of silicon from silane is reviewed and some new results are presented. Emphasis is placed on the influence of the hydrogen pressure on the growth rate. It is assumed that equation (1) is also valid for inert ambients at atmospheric pressures and under reduced pressures.

2. Growth from silane

2.1 Comparison of the silicon growth rate as a function of hydrogen content of the carrier gas at atmospheric pressure.

As described before, the growth rate of silicon at temperatures below the knee in the curve of the growth rate versus $1/T$ (Fig. 1) is limited by the chemical kinetics on the silicon surface. In this regime the growth rate can be given by equation (4) in

Figure 1.

The growth rate of silicon as obtained in a chemical vapour-deposition process, schematically given as a function of temperature for a constant input concentration of silane in hydrogen as a carrier gas.

which according to Bryant [3] the apparent activation energy is almost independent of the hydrogen pressure, provided that no gas phase nucleation and growth rate saturation effects are present. It was further observed that the position of the knee in the curve of the silicon growth rate versus $1/T$ (Fig. 1) is positioned about 200° lower for inert carrier gases than for a hydrogen ambient, while at lower temperatures the growth rates are much higher in an inert ambient than in hydrogen. According to Claassen and Bloem [4] the growth rate of silicon at 700°C strongly decreases when small amounts of hydrogen are added to a silane-nitrogen mixture. The experimental data could be described by: $G = F P_{\text{O}} / (1 + H P_{\text{H}_2})$, where P_{O} is the input pressure of silane, P_{H_2} the partial pressure of hydrogen and F and H are constants at 700°C . Since the apparent activation energy (ΔE) is almost independent of the partial pressure of hydrogen in the surface-controlled regime of the silicon growth, the growth rate can be expressed as

$$G = \frac{F^0 P_0}{1 + H P_{H_2}} \exp(-\Delta E/RT). \quad (7)$$

When the experimental data for the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system at 700°C are used [4] the constants F and H can be calculated by plotting $1/G$ versus P_{H_2} . In Fig. 2 the growth rate of silicon for 2×10^{-3} bar silane and different hydrogen mixtures is plotted as a function of the hydrogen pressure. When the pressure is expressed in bars $F = 1.7 \times 10^2 \mu\text{m}(\text{min} \cdot \text{bar})^{-1}$ and $H = 12 \text{ bar}^{-1}$. At relatively high hydrogen pressures the growth is inversely proportional to the hydrogen pressure ($G \propto P_{H_2}^{-1}$) while at lower hydrogen pressures the tangent gradually changes to zero.

Figure 2.

The influence of the hydrogen pressure on the silicon growth rate at 700°C and an input of 2×10^{-3} bar silane.

At higher temperatures the gas phase diffusion of the reactant towards the surfaces determines the growth rate; differences in silicon growth rates for the $\text{SiH}_4\text{-H}_2$ system and the $\text{SiH}_4\text{-inert gas}$ system then become smaller, as can be seen in Fig. 3. In this figure the growth rate of silicon is plotted for an input of 0.1 vol. % silane at 1000°C in hydrogen-helium and hydrogen-nitrogen mixtures. In the case of the $\text{SiH}_4\text{-He}$ system the growth rate of silicon is almost independent of the hydrogen-helium ratio (for not too small pressures of hydrogen). At small hydrogen concentrations gas phase nucleation comes into play, leading to a heavily contaminated reactor wall and a decrease in the growth rate on the heated susceptor. This behaviour could be explained by the occurrence of the following gas phase reactions (5):

Figure 3.

The growth rate of silicon at 1000°C for $P_{\text{SiH}_4} = 10^{-3}$ bar silane.

(8)

The formation of polymers of silane can therefore be expected at relatively low hydrogen partial pressures. In a cold wall apparatus the clusters formed in the gas phase are transported to the cold walls by the process of thermodiffusion. The apparent growth rate is then reduced because of the lower monomer silane concentration in the gas phase. In the case of the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system it can be observed from Fig. 3 that the growth rate first decreases linearly with decreasing hydrogen content of the carrier gas until the growth rate saturates or even increases. At still lower hydrogen pressures gas phase nucleation is also observed, consequently leading to lower growth rates. As discussed before, the growth rate of silicon depends on the ratio D_{12}/δ if the growth rate is controlled by gas phase diffusion of the reactant towards the surface.

According to Berkman et al. [6] the diffusion coefficient of reactant (1) in carrier gas (2) can be calculated for this binary system from

$$D_{12} = 2.628 \times 10^{-19} \frac{[T^{3/2} (1/M_1 + 1/M_2)]^{1/2}}{P \sigma_{12}^2 \Omega_{12}} \quad (9)$$

where M_1 and M_2 are the molecular weights of the reactant and the carrier gas, P is the total pressure, Ω_{12} the collision integral and σ_{12} a force constant. The Ω_{12} and σ_{12} values can be calculated from the critical temperatures and pressures [7]. Berkman et al. [6] also give an expression for the thickness of the diffusion boundary layer ($\delta(X)$) in a horizontal reactor, which reads

$$\delta(X) = 1.23 \left(\frac{D_T X}{V_T} \right)^{1/2} - \frac{0.56}{b} \left(\frac{D_T X}{V_T} \right) - \frac{0.077}{b^2} \left(\frac{D_T X}{V_T} \right)^{3/2} \quad (10)$$

where D_T is the self-diffusion coefficient of the carrier gas at an average temperature T , X is an arbitrary point along the susceptor, V_T an average gas velocity and b the free height between the top of the susceptor and the tube wall. The self-diffusion coefficient of the carrier gas at room temperature (D_T) can be given by

$$D_T = 2.628 \times 10^{-19} \frac{[T^3 / M_2]^{1/2}}{P \sigma_2} \quad (11)$$

In order to interpret the experimental data, as given in Fig. 3, D_{12} and $\delta(X)$ values are calculated using the equations (9, 10, 11) at a mean temperature T_A in a similar way as described by Berkman et al. [6]. In Table 1 these values are given under the operating conditions used [8] ($b = 1.5$ cm, $X = 10, 20$ and 30 cm, a substrate temperature of 1000°C and a room temperature gas velocity of 60 cm/sec). The experimental data given in Fig. 3 are for $X = 20$ cm (middle of the susceptor).

TABLE 1

Calculated values for D_{12} of silane and $\delta(X)$ with $X = 10, 20$ and 30 cm for the carrier gases hydrogen, helium and nitrogen and a substrate temperature of 1000°C .

	$\delta(X)$ cm			D_{12} (cm ² /sec)
	10	20	30	
H ₂	0.72	0.85	0.90	4,6
He	0.69	0.84	0.89	4,2
N ₂	0.35	0.48	0.55	1,2

From Table 1 it can be observed that δ reaches an almost constant value of approximately $b/2$ very near the leading edge of the hot susceptor for the carrier gases helium and hydrogen, whereas for nitrogen the diffusion boundary layer is not fully developed along the susceptor. It can further be observed that the ratio D_{12}/δ for the gases helium and hydrogen are of comparable magnitude, giving approximately

the same growth rate of silicon, in agreement with the experimental data given in Fig. 3. For nitrogen the D_{12}/δ value is smaller than for helium and nitrogen and the observed decrease in the growth rate with decreasing hydrogen contents for the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system can be explained in this way. For high nitrogen contents the laminar flow breaks up into a thin stagnant layer covered by a turbulent flow region, as observed by Giling et al. [9]. This may explain an increase in growth rate for low hydrogen contents. Under the experimental conditions as given in Fig. 3 we further observed a small decrease in growth rate along the susceptor. This decrease in the growth rate of silicon is independent of the hydrogen-helium ratio, while for the hydrogen-nitrogen mixture this depletion increases going to lower hydrogen contents. This effect can be explained by an increase of the thickness of the boundary layer along the susceptor, which is strongest for hydrogen-nitrogen mixtures with the lowest concentration of hydrogen (Table 1).

2.2 Reduced pressures

As explained in the introduction, it will be assumed that the growth of silicon from silane at reduced pressures can also be described by equation (1). In the surface-controlled regime of the growth of silicon ($R_2 \gg R_1$) equation (4) can then be used:

$$G = G_0 \exp(-\Delta E/RT).$$

At reduced pressures, with or without hydrogen as a carrier gas, apparent activation energies (ΔE) of about 37 kcal/mole are reported by Joyce et al. [10] and Hottier et al. [11]. According to Van den Brekel and Bollen [12] the growth rate of silicon is independent of the carrier gases hydrogen or nitrogen (the silane pressure being equal) at 625 °C and a total pressure of about 10^{-3} bar, in agreement with the curve in Fig. 2, where it is shown that the growth rate of silicon becomes independent of the partial pressure of hydrogen below $P_{\text{H}_2} = 10^{-2}$ bar. Going to higher temperatures the surface reactions become so fast that the temperature dependence of the growth rate deviates from the reported ΔE values and at relatively high temperatures the diffusion of silane towards the silicon surface controls the growth rate. In this regime high growth rates can be expected compared with those at atmospheric pressure (the partial pressure of silane being equal) as the diffusion coefficient D_{12} is inversely proportional to the total pressure (equation (9)) and the thickness of the diffusion boundary layer may be assumed to be nearly constant. The thickness of the diffusion boundary layer is independent of the total pressure under the condition that the linear gas velocity is inversely proportional to the total pressure, as will be discussed below, considering that D_T , the self-diffusion coefficient of the carrier gas, is also inversely proportional to the total pressure (equations (10) and (11)). In reality, however, as experienced by Duchemin et al. [13] these high growth rates, notably below a total pressure of 10^{-1} bar, are not obtained.

These authors studied the growth of silicon for the $\text{SiH}_4\text{-H}_2$ system at temperatures between 700 and 1050 °C and at total pressures between 1.3×10^{-2} and 1 bar. In all their experiments a hydrogen flow of 18 litres/min and a silane molar ratio below 3×10^{-3} was used. In order to obtain a constant silane pressure at different total pressures and a constant flow (measured at room temperature and atmospheric pressure) the pumping rate is adjusted, leading to a gas velocity inversely proportional to the total pressure ($V \propto P_{\text{tot}}^{-1}$).

From their growth rate measurements Duchemin et al. recalculated the growth rates of silicon as a function of the hydrogen pressure for a fixed partial pressure of silane, using the experimental evidence that for a fixed hydrogen pressure the growth rate is linearly proportional to the silane input pressure. At temperatures between 930 and 1050 °C and pressures above 10^{-1} bar the growth rate is roughly inversely proportional to the hydrogen pressure ($G \propto P_{\text{H}_2}^{-1}$), whereas at pressures below 10^{-1} bar a ($G \propto P_{\text{H}_2}^{-1/2}$) dependence is found. The $G \propto P_{\text{H}_2}^{-1}$ behaviour is explained by Duchemin and co-workers as being due to a gas phase diffusion-controlled reaction and could therefore be replaced by $G \propto P_{\text{tot}}^{-1}$, in agreement with equations (9) and (5). It was also found that in this regime the growth rate is almost independent of temperature, again indicating a gas phase diffusion-limited process. According to Duchemin et al. the $G \propto P_{\text{H}_2}^{-1/2}$ behaviour is caused by the onset of a surface-controlled reaction in which hydrogen adsorption plays an important role. In order to discriminate between a gas phase diffusion-controlled process and a kinetically or surface-limited growth at pressures below 10^{-1} bar the following points could be important:

- i For the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system at 990 °C Duchemin et al. [13] found the same pressure regimes as for the $\text{SiH}_4\text{-H}_2$ system ($G \propto P_{\text{H}_2}^{-1/2}$) below 5×10^{-2} bar and $G \propto P_{\text{H}_2}^{-1}$ above 5×10^{-2} bar. However, according to growth rate measurements on the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system at atmospheric pressures and temperatures below 1000 °C [14], the growth rate in the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system is proportional to the hydrogen pressures ($G \propto P_{\text{H}_2}$), which is explained by the surface reaction, $\text{SiCl}_2 + \text{H}_2 \rightarrow \text{Si}(\text{cr}) + 2 \text{HCl}$. The experimental data of Duchemin give $G \propto P_{\text{H}_2}^{-1}$, as expected for a gas phase diffusion-limited reaction rate.
- ii From the growth rate measurements Duchemin et al. deduced an activation energy of 15 kcal/mole at temperatures between 750 and 1050 °C, which seems somewhat too high for a gas phase diffusion-limited process. However, Hottier [11] measured a temperature dependence between 850 and 1150 °C of 10 kcal/mole, whereas between 600 and 850 °C 40 kcal/mole was reported. In the high temperature regime above 900 °C Origirima et al. [15] reported 11 kcal/mole for the $\text{SiH}_4\text{-H}_2$ system at atmospheric pressure.

These two points suggest that the growth rate for the $\text{SiH}_4\text{-H}_2$ system at temperatures above 850 °C is diffusion-limited even at a total pressure below 10^{-1} bar and therefore $P_{\text{H}_2}^{-1/2}$ can better be given as $P_{\text{tot}}^{-1/2}$. It can now be postulated that the growth rate of silicon at temperatures exceeding 850 °C is controlled by the supply

of the reactant through the gas phase ($R_1 \gg R_2$) in equation (1)). Under the experimental conditions as used by Duchemin et al. ($V \propto P_{\text{tot}}^{-1}$), the thickness of the diffusion boundary layer can be assumed to be constant, as discussed above, and the growth rate at reduced pressures $G(X)_P$ can be given by

$$G(X)_P = \frac{\beta G(X)_{P=1 \text{ bar}}}{P} \quad (12)$$

where $G(X)_{P=1 \text{ bar}}$ is the growth rate at atmospheric pressure (equation (5)) and β is a correction factor due to differences in temperature gradients in the gas phase perpendicular to the surface, as will be discussed below. As Duchemin et al. [13] and Hottier et al. [11] used a horizontal cold wall reactor, it can be assumed that the temperature of the tube wall is higher at atmospheric pressure than at reduced pressure because of the reduced thermal conductivity of the carrier gas. This fact is in agreement with the observation of Duchemin et al. that the temperature difference between susceptor and substrate becomes higher when the total pressure is reduced (at a total pressure of about 10^{-2} bar a temperature difference of about 140°C was measured), whereas at atmospheric pressure this temperature difference is of the order of 20°C . If the mean gas temperature decreases the ratio D_{12}/δ also decreases as the diffusion coefficients D_{12} and D_T are almost quadratic functions of temperature, whereas the gas velocity V_T is linearly proportional to the temperature. According to Berkman et al. [6] the average temperature T_A in the region of laminar flow can be given by:

$$T_A = 1/4 (T_s + T_b) \quad (13)$$

where T_s is the substrate temperature and T_b the bulk gas temperature which is approximately equal to the wall temperature. As T_b , and therefore T_A as well, will depend on the total pressure, in a first approximation a linear dependence can be assumed.

$$T_A = T_A^1 - L/P \quad (14)$$

where L is a constant, P the total pressure and $T_A^1 = 625^\circ\text{C}$ at atmospheric pressure in hydrogen [2]. Using the experimental data of Duchemin et al. as given above and the assumption that in their experiments the effective cross-section was 10 cm^2 and the free height above the susceptor (b) was 2 cm , the growth rate can be calculated as a function of the total pressure. These growth rates are given in Fig. 4, disregarding thermodiffusion ($\alpha = 0$) for T_s equal to 1000°C and assuming that T_b at room temperature and at total pressures below 10^{-3} bar leads to $T_A = 270^\circ\text{C}$ (equation (13)) and $L = 0.36 \text{ deg. bar}^{-1}$. Because of the steep temperature gradient, which is a function of total pressure, the influence of thermodiffusion cannot be left out of account [1]. Fig. 4 therefore gives the growth rate with the

Figure 4.

The calculated growth rate of silicon as a function of the total pressure for a substrate temperature of 1000 °C and for the thermodiffusion factors $\alpha = 0$ and $\alpha = 1$ in a cold wall apparatus.

thermodiffusion factor $\alpha = 1$. As can be observed from Fig. 4, the growth rates deviate from linearity ($\beta < 1$) with decreasing total pressure, notably when thermodiffusion is taken into account. The experimental data of Duchemin can therefore be fitted by introduction of thermal gas conductivity and thermodiffusion in the expression for the gas phase diffusion-limited growth of silicon.

2.3 Comparison between the growth rate of silicon at atmospheric pressures and at reduced pressures

In the previous section we have discussed the growth rate of silicon from silane in hydrogen and inert carrier gases, both at atmospheric pressures and at reduced pressures. In this section figures are constructed in which the growth rate of silicon is plotted as a function of temperature using the experimental data as given in the previous sections. Figure 5 gives the growth rate of silicon as a function of temperature for silane ($\text{PSiH}_4 = 10^{-3}$ bar) in hydrogen at atmospheric pressure according to experimental data as described by Bloem and Claassen [8] and for equal concentrations of silane in inert ambients at atmospheric pressure. The curve for inert ambients is plotted using the experimental evidence that the growth rate of silicon for temperatures exceeding 1000 °C is almost independent of the carrier gas (Fig. 3)

Figure 5.

The growth rate of silicon as a function of temperature from silane ($P_{\text{SiH}_4} = 10^{-3}$ bar) at atmospheric pressure in hydrogen and inert carrier gases.

and that at temperatures below 1000 °C the growth rate of silicon is much higher in inert ambients than in a hydrogen atmosphere (Fig. 2). The growth rate of silicon for the $\text{SiH}_4\text{-H}_2$ system below 900 °C and for the $\text{SiH}_4\text{-inert gas}$ system below about 700 °C (both at atmospheric pressure) can be expressed by equation (4) in which the apparent activation energy is about 37 kcal/mole for both systems. It should be noted that slightly smaller values can be found, notably in an inert carrier gas, because of gas phase nucleation when too high input concentrations of silane are used.

As discussed before, the position of the knee in the growth rate versus $1/T$ curve is defined by $R_1 = R_2$, where $R_1 \propto \delta/D_{12}$ and $R_2 = 1/k_d$ (equations (2), (3) and (6)). Van den Brekel [2] defined the CVD number (or Sherwood number) as

$$\text{CVD} = \frac{R_1}{R_2} \propto \frac{k_d \delta}{D_{12}}. \quad (15)$$

At atmospheric pressure the CVD number becomes smaller when hydrogen is used instead of an inert carrier gas because, according to equation (7) we find $k_d = k_d^0/(1 + HP_{\text{H}_2})$, and consequently the position of the knee shifts to higher temperatures with increasing values of P_{H_2} .

At reduced pressures, with or without hydrogen, an apparent activation energy of about 37 kcal/mole has also been reported for the surface-controlled growth rate, as previously discussed. Further the reported growth rates of silicon in the low-temperature regime for inert ambients at atmospheric pressure are comparable with those at reduced pressure, provided that $P_{H_2} \leq 10^{-2}$ bar (Fig. 2). Using the data given above, a figure can be constructed in which the growth rate of silicon is plotted versus $1/T$ for $PSiH_4 = 10^{-3}$ bar and different total pressures (Fig. 6). In this figure the low-temperature growth rate curves are seen to be almost equal for silane in an atmospheric inert ambient (P_c) and at reduced pressures (P_a and P_b , where $P_a < P_b$).

Figure 6.

The growth rate of silicon as a function of temperature at reduced total pressures and in inert ambients at atmospheric pressure. ($P_c = 1$ bar; $P_a < P_b < P_c$).

At higher temperatures the growth rate is higher at reduced pressures as diffusion of the reactant becomes easier at reduced pressures. As discussed earlier, a $G \propto P_{tot}^{-1}$ behaviour could be expected, but a deviation from this relation occurs in cold wall systems due to the influence of steep temperature gradients on the diffusional behaviour of the reactants. It can further be seen from Fig. 6 that the position of the knee in the growth rate versus $1/T$ curve shifts to higher temperatures with decreasing total pressures. In an inert gas ambient with a partial pressure of hydrogen below 10^{-2} bar (Fig. 2) the position of the knee shifts to higher temperatures when the total pressure is reduced because the CVD number (equation (15)) becomes smaller at these low pressures ($R_1 \propto 1/D_{12} \propto P_{tot}$, equations (2) and (9)). This

conclusion is in agreement with experimental data reported by Joyce et al. [10], who found a knee in the growth versus $1/T$ curve at about 1050°C when an input of about 10^{-3} bar silane was used without a carrier gas.

Figure 7.

A combination of Figures 5 and 6, giving the growth of silicon from 10^{-3} bar of silane as a function of temperature for different carrier gases (H_2 or inert gas) and total pressures.

Fig. 7 combines Figures 5 and 6 and gives the growth rate of silicon for $\text{PSiH}_4 = 10^{-3}$ bar in hydrogen and inert ambients (both at atmospheric pressure) and for a reduced pressure of 10^{-2} bar. It should be noted that Figures 5, 6 and 7 are plotted schematically. At high input concentrations of silane, notably in inert ambients, homogeneous gas phase nucleation will probably reduce the expected growth rate.

3. Temperature dependence of the growth rate

In the low temperature regime the growth rate is determined by surface reactions and can be given by equation (4), in which the apparent activation energy is, in a first approximation, independent of the total pressure and independent of the partial pressure of hydrogen. According to recent experiments, a generalized scheme may be present for the growth rate of silicon in the surface-controlled regime from silane [4, 8]. In this scheme gas phase and surface reactions are postulated with SiH_2 as the main silicon-containing surface species:

a. Gaseous reactions

b. Adsorption on a free surface site (*)

c. Surface diffusion and incorporation at a free step site (* (step))

d. The rate-limiting reaction can be found in the release of hydrogen

Assuming that k_4 is rate-limiting [4] the growth rate and its temperature dependence can be given by

$$\begin{aligned} G &= k_4 [\text{SiH}_2^{**}] \\ &= k_4^0 [\text{SiH}_2^{**}] \exp(-\epsilon_4 / RT) . \end{aligned} \quad (20)$$

In a steady-state situation the concentrations of SiH_2 species in the gas phase and on the surface can be calculated [4, 8]. For a positive growth rate the reactions k_{-2} and k_{-3} can be neglected compared with the reactions k_1 and k_2 respectively. This leads to

$$[\text{SiH}_2^{**}] = \frac{k_1 P_{\text{SiH}_4}}{(k_{-1} P_{\text{H}_2} + k_2 [*])} \times \frac{k_2 [*]}{(k_{-2} + k_3 [* (\text{step})])} \times \frac{(k_3 [* (\text{step})])}{(k_{-3} + k_4)} . \quad (21)$$

With a fraction of free surface sites and free step sites equal to unity and with $k_4 < k_{-3}$ and $k_3 < k_{-2}$ [4, 8] equation (21) can be transformed to

$$[\text{SiH}_2^{**}] = \frac{K_1 K_2 K_3 P_{\text{SiH}_4}}{[P_{\text{H}_2} + (k_2/k_{-1})]} . \quad (22)$$

Using $K_1 = K_1^0 \exp(-E_1/RT)$ equation (20) then reads

$$G = K_1^0 K_2^0 K_3^0 k_4^0 \frac{P_{\text{SiH}_4}}{[P_{\text{H}_2} + (k_2/k_{-1})]} \exp(-\Delta E/RT). \quad (23)$$

Using hydrogen as a carrier gas ($P_{\text{H}_2} > k_2/k_{-1}$ (Fig. 2)) we find

$$\Delta E = E_1 + E_2 + E_3 + \epsilon_4. \quad (24)$$

At reduced pressures, or with inert carrier gases the same activation energy is found by experiment (Figures 5 to 7). In the present model this points to a small temperature dependence of k_2/k_{-1} . An evaluation of ΔE will now be given, based on the reaction scheme given above. For the $\text{SiH}_4\text{-H}_2$ system the heat of reaction (E_1) for the gas phase reaction, as given by equation (16), has been determined by Newman et al. [5], using single-pulse shock tube data ($E_1 = 52$ kcal/mole). It can furthermore be postulated that the heat of adsorption of SiH_2 on the silicon surface is close to that of silicon itself [16], leading to $E_2 \cong E_3 \cong -73$ kcal/mole, being the energy gain when a Si-Si bond is formed [4]. With $\Delta E = 37$ kcal/mole, ϵ_4 can be calculated from equation (24). This yields $\epsilon_4 = 130$ kcal/mole, which is close to the energy needed to break two SiH bonds [4]. The model presented for the growth of silicon from silane thus leads to a reasonable explanation of the activation energy in the low temperature growth of silicon.

4 Conclusion

The growth rate of silicon in the gas phase diffusion-controlled regime of the high temperature growth is determined by the total pressure and the input concentration of silane but not by the kind of carrier gas used. In this regime the growth rate is found to be linearly proportional to the input concentration of silane and inversely proportional to the total pressure. It is concluded that steep temperature gradients, notably at pressures below 10^{-1} bar, give rise to a decrease in growth rate and therefore a deviation from the $G \propto P_{\text{tot}}^{-1}$ behaviour can be expected. At lower temperatures, surface reactions control the growth rate, and for the SiH_4 system the influence of the hydrogen pressure on the growth rate becomes apparent ($G \propto P_{\text{H}_2}^{-1}$). The temperature dependence of the growth rate is found to be about 37 kcal/mole, independent of the total pressure or the hydrogen pressure.

In general it can be said that great differences between growth rate results at reduced pressures and in systems diluted with inert gas only exist at high temperatures, where gas phase diffusion limits the growth rate. At lower temperatures, where the growth rate is determined by surface reactions, growth rates are comparable for equal silane concentrations in inert gas or at reduced pressure, provided the hydrogen pressure is below 10^{-2} bar.

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SUMMARY

Polycrystalline silicon layers are widely used in the electronics industry. The electrical properties of these layers closely depend on the size of the polysilicon grains in the layers. The experimental study on the nucleation of silicon on SiO_2 and Si_3N_4 substrates shows that the grain size of the polysilicon layers is subject to various external conditions, among which the initial nucleation of silicon on the substrate plays a decisive role. The nucleation of silicon was studied at atmospheric pressure and at temperatures between 600 and 1200 °C for the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system (chapters II and III) and between 800 and 1100 °C for the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ system (chapter IV). The saturation cluster densities were determined as a function of gas phase composition and temperature and can be varied between $10^4 - 10^{11} \text{ cm}^{-2}$. It is shown that the nucleation of silicon proceeds via the formation of SiH_2 monomers on the surface. Addition of hydrogen chloride to the system produces a strong decrease in SiH_2 concentration due to the conversion of SiH_2 into SiCl_2 , and consequently the saturation nucleus density (N_s) decreases ($N_s \propto P_{\text{SiH}_4} / P_{\text{HCl}}^2$, where P denotes the input pressure). It is further shown that a strong hydrogen adsorption exists notably on SiO_2 substrates, which may explain the substantial differences in nucleation on SiO_2 and Si_3N_4 substrates at temperatures below 1000 °C. The nucleation experiments can be described satisfactorily by comparing the experimental data with predictions of existing nucleation theories using analysis of the silicon adatom (or SiH_2 monomer) concentration. In this way approximate values are derived for the size of the critical cluster and values between 1 and 4 atomic units are obtained.

Chapters V to VII deal with the growth of polycrystalline silicon for the $\text{SiH}_4\text{-H}_2\text{-HCl}$ system, the $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2\text{-HCl}$ system and the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system. In the kinetically controlled regime of silicon growth in the $\text{SiH}_4\text{-H}_2\text{-N}_2$ system it is found that the growth rate is linearly proportional to the input concentration of silane and inversely proportional to the partial pressure of hydrogen. Analysis of the experimental data shows that hydrogen adsorption does not influence the growth rate, SiH_2 being the most abundant surface species. Addition of hydrogen chloride to this system results in a strong decrease in growth rate, due to the conversion of SiH_2 into SiCl_2 . The reduction of SiCl_2 at step sites is proposed to be the rate-limiting step, leading to a surface concentration of SiCl_2 far above the equilibrium concentration and favouring desorption of SiCl_2 . Going to higher temperatures the surface reactions become so fast that gas phase diffusion of the reactant towards the surface becomes the rate-limiting step. It is shown that in this regime the growth rate is almost independent of the carrier gas used at atmospheric pressure. At reduced pressures the growth rate of silicon first increases in inverse proportion to the total pressure while at total pressures below 0.1 bar the growth rate deviates from the $R \propto P_{\text{tot}}^{-1}$ behaviour, due to increasing temperature gradients in the gas phase which tend to slow down the gas phase diffusion of reactants towards the growing interface. In the growth of silicon from SiH_2Cl_2 the dissocia-

tion of this compound into SiCl_2 and H_2 plays an important role. Addition of HCl to the $\text{SiH}_2\text{Cl}_2\text{-H}_2$ system reduces the growth rate because the gas phase dissociation of SiH_2Cl_2 is followed by formation of SiHCl_3 . It is concluded that a strong adsorption of atomic hydrogen and chlorine is not needed to explain the experimental evidence, whereas adsorption of SiH_2 and SiCl_2 has been found to reduce the growth rate at lower temperatures.

In chapter VIII a review is given of the experimental data presented in chapters II to VII.

In chapter IX it is pointed out that it is only at high temperatures, where gas phase diffusion limits the growth rate, that great differences exist between growth rate results at reduced pressures and in systems diluted with inert gas. In the low temperature region, where surface reactions are predominant, it is found that the growth rates are comparable for the two systems.

SAMENVATTING

Polycrystallijne silicium lagen worden uitgebreid toegepast in de elektronische industrie. De elektrische eigenschappen van deze lagen hangen onder andere af van de grootte van de polysilicium korrels in de lagen. Een experimentele studie waarbij de kiemvorming van silicium op SiO_2 en Si_3N_4 wordt onderzocht toont aan dat de grootte van polysilicium korrels sterk afhangt van de allereerste aanleg van silicium-atomen op de verschillende substraten. De kiemvorming van silicium is bestudeerd bij atmosferische druk en voor temperaturen tussen 600 en 1200 °C voor het $\text{SiH}_4\text{-HCl-H}_2$ systeem (hoofdstukken II en III) en tussen 800 en 1100 °C voor het $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2$ systeem (hoofdstuk IV). De verzadigingsdichtheid aan silicium kiemen is bepaald als functie van de gasfase samenstelling en de temperatuur en kan worden gevarieerd tussen $10^4 - 10^{11} \text{ cm}^{-2}$. Het is aangetoond dat de kiemvorming van silicium plaatsvindt door vorming van SiH_2 monomeren op het oppervlak. Toevoeging van zoutzuurgas aan het systeem verlaagt de SiH_2 oppervlakteconcentratie doordat SiH_2 wordt omgezet in SiCl_2 en als gevolg hiervan daalt de verzadigingsdichtheid aan silicium kiemen (N_s) ($N_s \propto P\text{SiH}_4/P_{\text{HCl}}^2$, waarbij P de partiaal druk voorstelt). Het is verder aangetoond dat atomaire waterstof sterk adsorbeert met name op SiO_2 substraten, en dat de verschillen in kiemvormingsgedrag op SiO_2 en Si_3N_4 voor temperaturen beneden 1000 °C hierop kunnen worden teruggevoerd. De kiemvormingsexperimenten kunnen goed worden beschreven met bestaande atomistische kiemvormingstheorieën en een vergelyk tussen theorie en experiment leidt tot een kritieke kiemgrootte tussen de 1 en 4 atomaire eenheden

In de hoofdstukken V tot en met VII wordt het groeiproces van silicium beschreven uitgaande van het $\text{SiH}_4\text{-H}_2\text{-HCl}$ systeem, het $\text{SiH}_2\text{Cl}_2\text{-H}_2\text{-N}_2\text{-HCl}$ systeem en het $\text{SiH}_4\text{-H}_2\text{-N}_2$ systeem. Het is aangetoond dat voor het $\text{SiH}_4\text{-H}_2\text{-N}_2$ systeem de groeisnelheid lineair evenredig is met de silaan concentratie en omgekeerd evenredig met de partiaal druk van het waterstofgas in het temperatuurgebied waar de groeisnelheid van silicium kinetisch is bepaald. Een analyse van de experimentele resultaten toont aan dat adsorptie van atomaire waterstof op het silicium oppervlak de groeisnelheid niet beïnvloedt en dat SiH_2 de meest belangrijke siliciumhoudende verbinding op het oppervlak is. De toevoeging van zoutzuurgas aan dit systeem resulteert in een sterke daling van de groeisnelheid hetgeen wordt veroorzaakt door de omzetting van SiH_2 , met behulp van het zoutzuurgas (HCl), in SiCl_2 . De reductie van SiCl_2 aan een atomaire stap is mogelijk de snelheidsbepalende stap, hetgeen leidt tot een SiCl_2 oppervlakteconcentratie welke veel groter is dan de evenwichtsconcentratie en desorptie van SiCl_2 is dan ook te verwachten. Bij hogere temperaturen worden de oppervlakte reacties zo snel dat de werkelijke snelheidsbepalende stap kan worden gevonden in de gasfase diffusie van de reactanten naar het silicium oppervlak. Ook wordt aangetoond dat in dit gebied de groeisnelheid in eerste benadering onafhankelijk is van het gebruikte dragergas bij atmosferische druk. Bij een verlaagde totaal druk neemt de groeisnelheid van silicium eerst toe (omgekeerd evenredig met de totaal druk) terwijl voor totaal drukken beneden 0.1 bar de groei-

snelheid afwijkt van het $R \propto P_{\text{tot}}^{-1}$ gedrag doordat steilere temperatuursgradienten de gasfase diffusie van de reactanten naar het oppervlak bemoeilijken. Bij de groei van silicium uitgaande van SiH_2Cl_2 speelt de gasfase ontleding van deze verbinding in SiCl_2 en H_2 een belangrijke rol. De toevoeging van HCl aan het $\text{SiH}_2\text{Cl}_2\text{-H}_2$ systeem heeft een verlaging van de groeisnelheid van silicium tot gevolg doordat HCl tezamen met SiCl_2 SiHCl_3 vormt. De conclusie wordt getrokken dat een sterke adsorptie van atomair waterstof en chloor niet nodig is om de experimenten te verklaren maar dat adsorptie van SiH_2 en SiCl_2 wel kan leiden tot een verlaging van de groeisnelheid, met name bij relatief lage temperaturen.

In hoofdstuk VIII wordt een overzicht gegeven van de experimentele resultaten zoals beschreven in de hoofdstukken II tot en met VII.

In hoofdstuk IX wordt benadrukt dat bij hogere temperaturen waarbij gasfase diffusie de groeisnelheid bepaalt, er een groot verschil bestaat tussen groeisnelheden zoals verkregen bij verlaagde totaal druk en het systeem bij atmosferische druk waarbij een inert gas als dragergas werd gebruikt. In het lage temperatuur gebied, waar oppervlakte reacties de groeisnelheid bepalen, is gevonden dat de groeisnelheid voor beide systemen van gelijke grootte is.

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STELLINGEN

bij het proefschrift

**“KINETIC STUDIES ON THE NUCLEATION AND GROWTH
OF SILICON VIA CHEMICAL VAPOUR DEPOSITION”**

W.A.P. Claassen

27 februari 1981

- 1 De experimentele gegevens betreffende de chemisorptie van waterstof op silicium zoals gerapporteerd door Sakurai en Hagstrum, worden door Hottier en Cadoret verkeerd geïnterpreteerd

T Sakurai en H D Hagstrum, *J Vac Sci Techn* **13**, 807 (1976)

F Hottier en R Cadoret, *ICCG 6*, Moscow, 1980

- 2 Dat de decompositiegraad van SiH_4 in de gasfase mogelijk wordt verlaagd door toevoeging van N_2O , zoals wordt beweerd door Knolle et al, is hoogst onwaarschijnlijk

W R Knolle, H R Maxwell, Jr en R E Benenson, *J Appl Phys* **51**, 4385 (1980)

- 3 De zuiver geometrische modellen voor de fluctuerende mikroskopische groeisnelheid bij kristalgroei uit de smelt, zoals die zijn voorgesteld door Morizane et al en door Barthel en Jursch, voeren door het verwaarlozen van het transport van stollingswarmte tot onjuiste uitdrukkingen voor de fluctuatieamplitude van deze groeisnelheid

K Morizane, A F Witt, en H C Gatos, *J Electrochem Soc* **114**, 738 (1967)

J Barthel en M Jursch, *Kristall und Technik*, **8**, 199 (1973)

- 4 De berekening van Chernov en Rusaikin dat een silicium oppervlak, in evenwicht met een waterstof waterstofchloride gasmengsel, bij temperaturen boven 1000 °C, nagenoeg geheel bedekt is met atomaire waterstof en chloor is in tegenspraak met experimentele gegevens

A A Chernov en M P Rusaikin, *J Crystal Growth* **45**, 73 (1978)

Dit proefschrift, hoofdstuk VII

- 5 Het model, voor de overgang van smektsch naar nematisch vloeibaar kristallijn gedrag, gebaseerd op metingen van de elastische constanten van de homologe reeks 4,4'-di (n-alkoxy) azoxybenzenen, zoals voorgesteld door Gruler, is aan bedenkingen onderhevig

H Gruler, *Z Naturforsch* **28a**, 474 (1973)

W H de Jeu en W.A P Claassen, *J Chem Phys* **67**, 3705 (1977)

- 6 Het bepalen van absolute hoeveelheden adsorbaat door vergelijking van piekhoogten in Auger spectra, gemeten met verschillende soorten analysatoren, kan aanleiding geven tot aanzienlijke fouten

I Solymori en J Kiss, *Proc ICSS IV and ECOSS III Cannes* 1980

- 7 In tegenstelling tot wat gebruikelijk is in de elektronische industrie wordt in de landbouw de opbrengst aan consumeerbare chips per plak verhoogd door het toevoegen van alkalimetalen aan SiO_2

8. Het woord “milieuvriendelijk”, dat vaak in advertenties gebruikt wordt in de uitdrukking “milieuvriendelijk produkt”, is misleidend.
9. Het is bij innovatie van produkten uiterst gevaarlijk om de opmerking “als dat zo eenvoudig was, zou het al lang uitgevonden zijn” te plaatsen.