TEMPERATURE DEPENDENCE OF SILICON DOPING OF GaAs BY SiH_4 AND Si_2H_6 IN ATMOSPHERIC PRESSURE METALORGANIC CHEMICAL VAPOUR DEPOSITION

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The temperature dependence of silicon doping in the metalorganic chemical vapour deposition process has been investigated in the temperature range 550 to 800 °C using silane (SiH_4) and disilane (Si_2H_6). The experiments have been carried out at atmospheric H_2 pressure in a long horizontal reactor. The silicon doping process with both silicon precursors appears to be strongly temperature dependent, with apparent activation energies E_{act} of 51.4 ± 5.8 kcal/mol (2.2 ± 0.3 eV) for silane and 45.5 ± 4 kcal/mol (2.0 ± 0.2 eV) for the doping process with disilane. A thorough analysis is given of the rate determining step in both cases based on the presence of a chemical boundary layer.

1. Introduction

The development of III/V devices requires well-defined doping profiles and high quality materials and interfaces. So, among other demands, there is a great need for suitable n- and p-type dopants. One of the most commonly used n-type dopants is silicon [1–4,7]. In principle there are two sources available for the silicon doping, viz. silane (SiH_4) and disilane (Si_2H_6).

In spite of the general applicability of silane as an n-type doping source (at least for metalorganic chemical vapour deposition (MOCVD) purposes) there is not much agreement upon the temperature dependence of the incorporation of silicon from silane in the literature. The apparent activation energies vary from 27 to 40 kcal/mole (1.2–1.8 eV) [1,5–8]. However, all these experiments are performed under different experimental conditions so that a comparison between these results is nearly impossible.

In contrast with silane (SiH_4) disilane (Si_2H_6) appears to be more suitable as a dopant source because of its claimed temperature independence

[1]. When temperature gradients are present over the wafer and for certain reactor geometries (as will be shown later) it should be possible with disilane, at least in theory, to dope the epilayers more uniformly over larger areas than with silane.

2. Experimental

In our experiments we have investigated the temperature dependence of the silicon incorporation in GaAs using silane and disilane. We have performed our experiments in a long horizontal reactor at atmospheric pressure [9]. This reactor allows flow and temperature gradients to become fully developed. So it is in principle possible to calculate the temperature gradient and mass fluxes in our reactor.

We have used arsine (AsH_3) and trimethyl gallium (TMG) to accomplish the GaAs growth. All the epitaxial layers were grown on (100) $\xrightarrow{2°}$ (110) GaAs substrates. The silane and disilane used were diluted gases of 100 ppm in hydrogen and in nitrogen respectively. We have utilized a partial pressure of silane of 4×10^{-8} bar and a partial pressure of disilane of 3.8×10^{-8} bar. Hydrogen was used as a carrier gas at 1 bar. The

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mean gas flow rate at the entrance of the reactor was about 7 cm/s. All the experiments were carried out under a V/III ratio of 20. The growth temperature was varied from 550°C to 800°C. The growth rate varied, depending on the position in the reactor and on the growth temperature, from 0.03 to 0.15 μm/min.

The temperature was determined by measuring the substrate temperature using a calibrated pyrometer. The electrical characterization was performed using Hall–Van der Pauw measurements and C-V measurements using a C-V profiler. All these electrical measurements were carried out at room temperature.

3. Results and discussion

In fig. 1 the results of the silane doping experiments are given. In this figure we have plotted the electron concentration as a function of the reciprocal temperature (range measured 550–800°C). The electron concentration, and thus probably also the silicon incorporation, shows Arrhenius-type behaviour with an apparent activa-
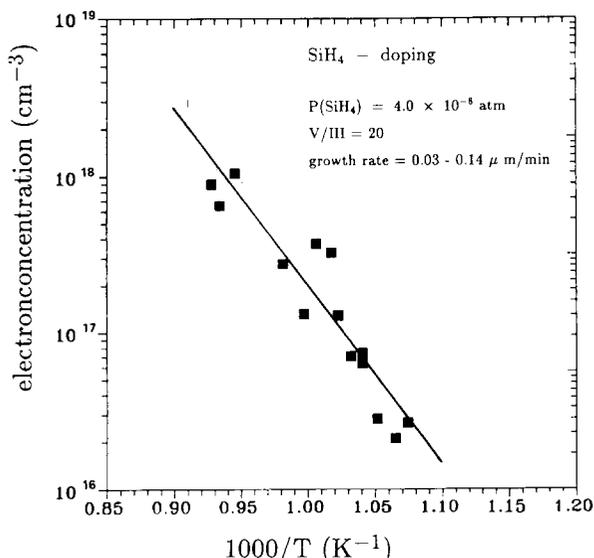

Fig. 2. Disilane (Si_2H_6) doping of GaAs ($P_{Si_2H_6} = 3.8 \times 10^{-8}$ bar) Dependence of the electron concentration (300 K, Hall–Van der Pauw) on the growth temperature. The solid line indicates the best fit. $P_{H_2} = 1$ bar.
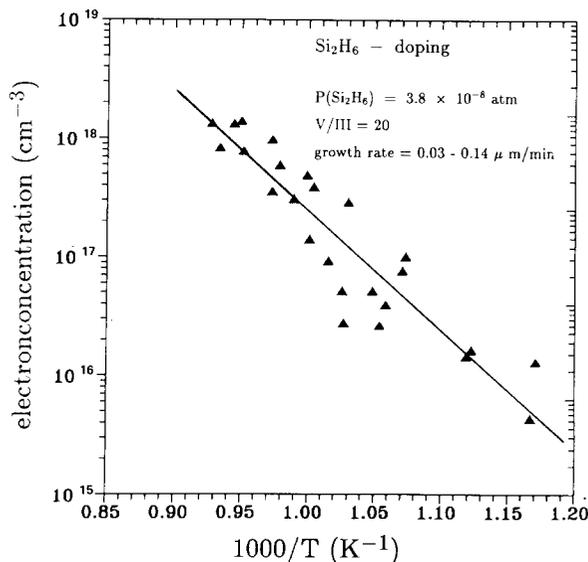
tion energy E_{act} of 51.4 ± 5.8 kcal/mol (2.2 ± 0.3 eV). This value is significantly higher (about a factor of 2) than those reported in the literature [1,5,6].

The experiments with disilane have been performed over a wider temperature range, especially to lower temperatures. At the high temperature side, the experiments also cover the region where the growth rate itself falls off due to desorption of the Ga growth species. In fig. 2 the results of disilane doping experiments are plotted. Again the electron concentration (incorporated silicon) shows Arrhenius-type behaviour with an apparent activation energy E_{act} of 45.5 ± 4 kcal/mol (2.0 ± 0.2 eV). This is an even more striking result than the one obtained by the silane doping considering the results of Kuech et al. [1] or of Shimazu et al. [8] who found that the doping with disilane is a thermally non activated process.

At first sight one would say that our doping experiments with silane and disilane are in complete disagreement with the results one can find in the literature [1,5,6]. Still all results can be explained in a logical way – even the zero activation energy of Kuech et al. and our value of 45.5

Fig. 1. Silane (SiH_4) doping of GaAs ($P_{SiH_4} = 4 \times 10^{-8}$ bar) Dependence of the electron concentration (300 K, Hall–Van der Pauw) on the growth temperature. The solid line indicates the best fit. $P_{H_2} = 1$ bar.

kcal/mol for the disilane process – when one takes into account the different conditions under which all these incorporation processes have been studied. In particular one has to consider the influence of the parameters: total pressure, partial pressure of hydrogen, length of the susceptor (i.e. boundary layer or not) and of course the trivial point of the type of reactor (vertical or horizontal). It is worthwhile to remember that we have performed our experiments in a regime of fully developed temperature and flow profiles in H_2 at atmospheric pressures, in contrast to the quoted authors where the experiments were performed in reactors where a physical boundary layer regime exists although they worked at lower pressures [1,5,6]. This is basicly the reason for the different results which have been obtained in the various studies.

In order to explain the results presented in figs. 1 and 2, one has to consider the following reactions:

$$SiH_4 \rightarrow SiH_2 + H_2, \tag{1}$$

$$SiH_2 + H_2 \rightarrow SiH_4, \tag{2}$$

$$Si_2H_6 \rightarrow SiH_4 + SiH_2, \tag{3}$$

$$SiH_4 + SiH_2 \rightarrow Si_2H_6. \tag{4}$$

Gas phase decomposition of silane (1) and disilane (3) are highly activated reactions with an activation energy of about 50 kcal/mol [10]. The formation of silane from hydrogen and SiH_2 (2) is very fast and hardly activated. The result is, that at a H_2 pressure of 1 bar, the equilibrium concentration of SiH_2 is very low (fig. 3).

3.2. SiH_4 doping

Assuming that SiH_2 is the species that will adsorb on the growing surface and will be incorporated, one can imagine that the SiH_2 concentration will determine the silicon incorporation rate. We can exclude diffusion limitation of SiH_4 itself because in that case we would have found hardly any temperature dependence for this type of process. In addition in our experiments the doping concentration of silicon appears to be inversely proportional to the growth rate which also points
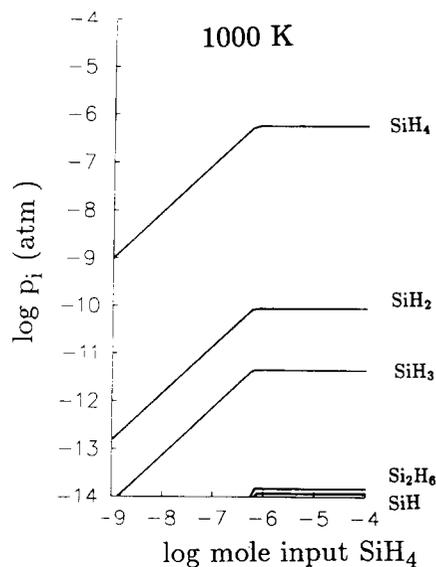
Fig. 3. Equilibrium partial pressures of the most important silicon species as a function of the input concentration (molar fraction) of SiH_4 at 1000 K. $P_{H_2} = 1$ bar.

to a kinetic limitation [11]. The decomposition of SiH_4 will take place in the chemical boundary layer which is in most cases a window in which a chemical reaction will occur [12]. However, in this special case an equilibrium is present, so one can refer to this region as a chemical equilibrium zone. This zone, due the high activation energy for the decomposition, is very thin [11]. From the results of the gas phase equilibrium calculations as given in fig. 3 [11], we may conclude that the SiH_2 concentration only will be a very small fraction of the SiH_4 concentration at that temperature (1000 K) and that virtually all silane will remain undecomposed. This also explains why there are no depletion effects as observed for this doping process [11].

From our experiments we must conclude that the doping with SiH_4 is determined by kinetics and not by diffusion. Most probably the gas phase decomposition of SiH_4, reaction (1), will be the rate limiting step in the growth process, as this can explain the apparent activation energy observed in our experiments (fig. 1). The concentration profiles of SiH_4 and SiH_2 inside and outside the chemical boundary layer are depicted in fig. 4. It is seen that inside the chemical boundary layer the

SiH$_4$ – doping

SiH$_4$

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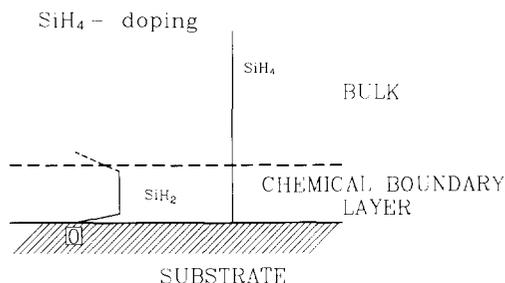
CHEMICAL BOUNDARY LAYER

SiH$_2$

SUBSTRATE

Fig. 4. Sketched partial pressures profiles in the case of SiH$_4$ doping. Thermal diffusion effects are not taken in to account. $P_{H_2} = 1$ bar. The figure is not on scale.

Si$_2$H$_6$ doping

SiH$_4$

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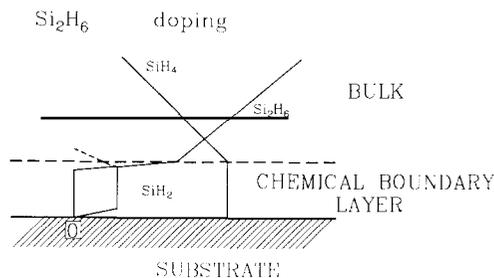Si$_2$H$_6$

CHEMICAL BOUNDARY LAYER

SiH$_2$

SUBSTRATE

Fig. 5. Sketched partial pressures profiles in the case of Si$_2$H$_6$ doping. Thermal diffusion effects are not taken in to account. $P_{H_2} = 1$ bar. The figure is not on scale.

silicon subsystem is in near equilibrium as the SiH$_2$ concentration is constant over the main part of this layer. The chemical decomposition of silane in the very thin layer close to the substrate, which is about 30 μm thick, followed by the diffusion of SiH$_2$ to the surface, is responsible for the observed kinetic behaviour. This will be explained below.

3.2. Si$_2$H$_6$ doping

In the case of Si$_2$H$_6$ one has to consider in addition reactions (3) and (4). Although the decomposition of Si$_2$H$_6$ (reaction (3)) has about the same apparent activation energy as the decomposition of SiH$_4$ [10], the rate of reaction (3) is much higher than the rate of reaction (1) due to the high value of the pre-exponential factor [10], so that at all the growth temperatures used in this study nearly all the Si$_2$H$_6$ is decomposed into SiH$_4$ and SiH$_2$. At a H$_2$ pressure of 1 bar, the total decomposition of Si$_2$H$_6$ occurs at the top of the chemical boundary layer. The back reaction, i.e. the formation of Si$_2$H$_6$ from SiH$_4$ and SiH$_2$ (reaction (4)), can be neglected because of the very low reaction rates due to the low concentration of silicon containing species as compared to the high hydrogen concentration in the reactor. So one can really say that at the growth temperatures all the Si$_2$H$_6$ is decomposed. The chemical situation for this case is depicted in fig. 5, in which the concentration profiles are sketched inside and outside the chemical boundary layer.

The Si$_2$H$_6$ concentration declines from the input value to zero at the top of the chemical boundary layer. Here all Si$_2$H$_6$ is decomposed into SiH$_2$ and SiH$_4$. The diffusion length of the

SiH$_2$ radical in H$_2$ is given by $(D/k_2 P_{H_2})^{1/2}$, where k_2 is the rate constant of the reaction of H$_2$ with SiH$_2$ (reaction (2)) and D is the diffusion coefficient of SiH$_2$ at the growth temperature. The value of this diffusion length is much smaller than the width of the chemical boundary layer and is in the order of 30 μm [10]. Inside the boundary layer virtually all SiH$_2$ has reacted with H$_2$ to SiH$_4$, only a very minor fraction of SiH$_2$, as determined by the SiH$_4 \rightleftharpoons$ SiH$_2$ + H$_2$ equilibrium (fig. 3), will be present in a constant concentration over the main part of the chemical boundary layer. Close to the surface the SiH$_2$ concentration falls off to zero again because of the incorporation in the GaAs lattice. The SiH$_4$ concentration is almost constant over the boundary layer, at least for positions beyond the entrance region.

The observed kinetic behaviour can be attributed in the first place to the chemistry coupled to diffusion in the very small region of 30 μm inside the gas phase, i.e. the decomposition of SiH$_4$ to SiH$_2$ coupled to diffusion of SiH$_2$ to the surface, which as rate limiting step leads to the incorporation rate r_d:

$$r_d = k_1[\text{SiH}_4](D/k_2 P_{H_2})^{1/2},$$

which can be written as

$$r_d = \frac{D}{(D/k_2 P_{H_2})^{1/2}} \frac{k_1}{k_2} \frac{[\text{SiH}_4]}{P_{H_2}} = \frac{D}{\delta} \frac{k_1}{k_2} \frac{[\text{SiH}_4]}{P_{H_2}}$$

$$= \frac{D}{\delta}[\text{SiH}_2],$$

where k_1 is the reaction constant of the decom-

position of SiH$_4$ [12]. This relation clearly reveals that diffusion of the SiH$_2$ molecule is responsible for the rate limiting step. The activation energy is determined by the product $k_1(D/k_2)^{1/2}$. As the temperature dependence of the factor $(D/k_2)^{1/2}$ is about zero, the final activation energy is determined by k_1, i.e. the decomposition of silane.

In the second place the adsorption process itself can be rate limiting. The rate r_a for this process is given by

$$r_a = k_{ads} K \frac{[SiH_4]}{P_{H_2}} \Theta *,$$

where K is the equilibrium constant for the silane decomposition and $\Theta *$ is the amount of free adsorption sites. Here the Arrhenius energy is determined by the temperature dependence of the product $k_{ads} K$. As the activation energy for the adsorption process will be about zero, the enthalpy ΔH for the silane decomposition will determine the kinetic process. As $\Delta H \approx E_{act}$ (reaction (2)) no distinction can be made at this point between these two processes. A calculation of the magnitude of the rate of adsorption, with data from refs. [10] and [13], clearly reveals that this process is at least one order of magnitude faster than the decomposition in the gas phase however. So the conclusion is that actually the formation of SiH$_2$ radicals followed by their diffusion to the surface is the rate limiting step in this case.

From both studies presented above, i.e. the doping of GaAs by SiH$_4$ and Si$_2$H$_6$, the same step appeared to be rate limiting, viz. the production of SiH$_2$ radicals close to the substrate followed by their diffusion to the surface. Consequently, in both cases the same activation energy should be observed, viz. about 50 kcal/mol, which is the activation energy for the decomposition of silane.

The observed values of 51.4 ± 5.8 and 45 ± 4 kcal/mol for the decomposition of silane and disilane respectively, deserve a closer analysis, especially because these values also include the temperature dependence of the growth rate itself. It will be shown in a subsequent paper [14] that when the proper corrections are taken into account both corrected values come close to the theoretical value. In this coming paper also a thorough analysis will be given for the pressure dependence of the activation energy.

3.3. Si$_2$H$_6$ doping in small reactor cells

The total decomposition of Si$_2$H$_6$ at the top of the chemical boundary layer results in a relatively high concentration of SiH$_2$ radicals, which – when they are produced close enough to the crystal surface, i.e. within a distance smaller than their diffusion lengths – will give rise to a very high efficiency of the dopant incorporation process. This is the case for studies performed at 0.03 to 1 bar H$_2$ pressure on small susceptors which have a thin physical boundary layer for flow and temperature. In this situation the incorporation seemingly is also temperature independent because the reaction is already for 100% completed at relatively low temperatures due to the high value of the pre-exponential factor for this decomposition reaction (note that the actual activation energy for the decomposition of Si$_2$H$_6$ is about as large as that of the decomposition of SiH$_4$ [10]). When the SiH$_2$ radicals are not producted from Si$_2$H$_6$ within reaching length of the crystal surface, quite a different situation is created, because now the very fast reaction of SiH$_2$ with H$_2$ will take place (this determines the actual diffusion length), resulting in the formation of SiH$_4$. This situation is predicted to take place in reactors where the flow and temperature profiles are fully developed together with high H$_2$ pressures.

4. Conclusion

Concluding, we can say that doping with SiH$_4$ is a kinetically determined process, and for growing larger and uniform layers one has to be able to control the temperature within a few degrees. The doping with Si$_2$H$_6$ at 1 bar hydrogen pressure is a similar process and will cause the same troubles.

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