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SURFACE MORPHOLOGY OF SI(111) IN ALKALINE ETCHING SOLUTIONS

een wetenschappelijke proeve op het gebied van de Natuurwetenschappen, Wiskunde en Informatica

Proefschrift

ter verkrijging van de graad van doctor aan de Radboud Universiteit Nijmegen, op gezag van de rector magnificus prof. mr. S.C.J.J. Kortmann, volgens besluit van het college van decanen in het openbaar te verdedigen op dinsdag 31 mei 2011 om 15:30 uur precies

door

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geboren op 9 januari 1973 te Vroomshoop
This research was financially supported by the Dutch Technology Foundation STW. Project number TPC-5990.

Cover image: Microscopic image of a Si(111) surface after etching (front cover). Various etching results combined with Lichtfigur reflections (back cover).

Cover design by: Ismail Shah

Printed by: Ridderprint BV

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Chapter 1

Introduction

1.1 Silicon

Silicon makes up 25.7% of the Earth’s crust and is the second most abundant element on Earth, after oxygen. Although prominently present, pure silicon crystals are rarely found in nature. Silicon is usually found in the form of silicon dioxide (also known as silica), and silicate. Silica occurs in minerals consisting of (practically) pure crystalline silicon dioxide in different forms, e.g. sand, quartz, rock crystal, jasper and opal. Silicon also occurs as silicates, which are minerals containing silicon, oxygen and one or more additional elements. These minerals occur in clay, sand and various types of rock such as granite and sandstone [1]. In marine life silicon compounds are sometimes used by micro organisms to form skeletons. Silicon has properties comparable to carbon, however, it is incapable of forming double bonds, making it less likely to be used as the chemical base for life, in comparison to carbon [2]. Due to its wide applicability, silicon, like carbon, is a very versatile and intriguing element.

Despite its abundance, it took a while to discover the pure element silicon. The word ‘Silicon’ is derived from the Latin word silex, which means fire stone, which normally consists of quartz (SiO₂). Silicon was first identified by Lavoisier in 1787 as a component of this silex. It was Berzelius in 1823, who successfully obtained amorphous silicon by treating potassium fluorosilicate with potassium. Eventually, it was Deville in 1854 who first obtained regular crystalline silicon. The difficulty of obtaining pure silicon lies in the high reactivity of the element, as pure silicon will react with almost anything, as already observed in the protecting native oxide layers on top of silicon wafers due to immediate reaction with oxygen in air.
Silicon crystals for both Micro Electro Mechanical Systems and IC industry are needed with extreme degrees of perfection. The starting material is silicon dioxide, SiO$_2$. Through reduction of the SiO$_2$ in a furnace, using carbon as a reducing agent and sufficient energy to achieve the necessary high temperatures, polycrystalline silicon is produced. This metallurgical grade silicon is further purified in three steps. First, the silicon is converted into SiHCl$_3$ (trichlorosilane), a liquid with a boiling point of 31.8°C, which is then distilled to extreme purity. The high purity silicon is produced by reduction of SiHCl$_3$ into silicon in a hydrogen ambient at high temperatures. The now obtained ultrapure poly-silicon, doped to the desired level, needs to be converted into a single crystal.

The increasing use of silicon in integrated circuits, micro mechanics and later on in solar cells and porous silicon, has lead to the rapid development of silicon crystal growth technology. The main driving force was the cost reduction in the device industry that led to the diameter race, currently standing at 300 mm wafer diameter, with an outlook at 450 mm diameter. An important aspect of the silicon growth technology is the understanding of the most relevant bulk defects and their behavior in device processes. In particular, interest is focussed on the aggregation of vacancies resulting in the formation of micro voids, that are increasingly harmful to device performance with shrinking design rules. Another trend in growth technologies is to produce silicon for solar cells using simplified ingot techniques resulting in significantly higher impurity levels.

Crystal growth from liquid silicon contains some challenges. There will always be some dissolved SiO$_2$ and therefore oxygen in the liquid silicon. Doping is used to improve conductivity, which is essential for integrated circuits or devices to work. Another aspect is the larger solubility of impurity atoms in the melt compared to the solid. The crystal will become ‘cleaner’ than the liquid. The segregation coefficient $k_{seg}$ gives the ratio of the concentration of impurity atoms in the growing crystal and that of the melt. It is usually much lower than one, because impurity atoms have a preference to stay in the melt. As a consequence, the distribution of impurities, including the dopants and oxygen, will change along the length of a crystal, so a homogeneous doping profile is difficult to achieve. The main reason to use As, P, and B as dopants, is their segregation coefficient being close to one, which assures a more or less homogeneous distribution during crystal growth [3].

Two main growth technologies are applied, the classical Czochralski (CZ) method, which covers the majority of the market share and the floating (FZ) zone technique, more used for niche products like power and high frequency devices. The Czochralski method, invented by the Polish scientist J. Czochralski
1.1 Silicon

Figure 1.1: The raw silicon can be purified and crystallized and then applied in different applications.

in 1916 [4, 5], is the method of choice for high volume production of ultrapure silicon single crystals. Essentially, a crystal is ‘pulled’ from a vessel containing molten silicon by dipping a seed crystal into the liquid and then slowly withdrawing it, keeping the surface temperature of the melt just above the melting point. The pulling rate (usually a few mm/min) and the temperature profile determine the crystal diameter. The major challenge is to get rid of the heat of crystallization, and to control other factors like defects, voids and dopant concentration, which determine the quality and homogeneity [6].

In the float zone method an RF coil is used to produce a locally melted zone in the polycrystalline rod that is dragged from one end to the other. A seed crystal is used at one end in order to start the single crystal growth. The molten zone carries the impurities away with it and hence reduces impurity concentration. The end result is a high purity material unmatched by most of the other ‘high purity’ materials. The dimensions of float-zone wafers are generally less than 150 mm due to the surface tension limitations during growth.
From the rod-like silicon boule, wafers must be cut to exceedingly tight geometric specifications with respect to diameter, thickness, flatness and crystallographic orientation. Other important wafer specifications are the n or p dopant used (P, As or B) and resistivity. After the rough cutting process the silicon wafers are polished to obtain a surface with a smoothness down to the nanometer scale. The final polishing and cleaning steps are done in a cleanroom, after which the wafers are ready for further processing. The focus in this thesis, however, will be on the surface morphology during and after etching these crystals in alkaline solutions for several applications.

1.1.1 Applications

Besides the use of silicon in steel (hence the name metallurgical grade), the first and major application of silicon is within the field of IC technology. Since the invention of the first transistor, the applicability and availability of silicon compared to germanium was quickly recognized and resulted in the advancement of silicon processing technologies. The main driving force for using silicon has been as a platform for integrated circuits. These microelectronic devices are built in and on top of the silicon wafer. The wafers undergo a variety of processing steps such as deposition, doping, ion implantation, wet or dry etching, photolithographic patterning and chemical mechanical polishing [7]. Compared to vacuum tubes, the modern day integrated circuit has enabled an enormous downsizing of electronic equipment. This resulted in the easy and cheap availability of electronic devices, the cornerstone of modern day information driven society. Downsizing the scale of the devices is an ongoing process driven by further cost reduction and device performance improvement.

Porous Silicon has emerged as a totally new kind of material. The formation of pores in silicon has found increased interest for many potential applications since the discovery of the unexpected optical properties of this material in 1990 [8]. Very soon new properties and applications of micro porous silicon followed [9, 10]. It is electrochemically made from single-crystalline Si and comes in many variants. Possible uses are electrodes for fuel cells, very special optical and X-ray filters, bio chips, fuses for airbags, ‘normal’ bio sensors and special actuators. Besides, through electrochemistry, porous silicon can also be produced by thermal oxidation of silicon at a temperature above 1000°C to promote full oxidation of silicon, as well as by etching the silicon in concentrated acidic solutions containing HF and HNO₃.

Ultra pure silicon crystals are intended for use as the new standard to replace the Platinum standard of the SI System [11]. In this approach, known as
1.1 Silicon

the Avogadro project, the kilogram would be defined as a softball-size (93.6 mm diameter) sphere of silicon atoms. Silicon is used because of its well-known crystal structure, stability, and its relative ease of use. The volume is determined from the measurement of the silicon sphere’s diameter and roundness. Accurate measurement of the mass then allows the density to be derived. With its average atomic mass and atomic spacing known, the required sphere diameter follows and can be shaped and polished with sufficient precision into a target mass of one kilogram.

The sun irradiates roughly 10000 times more energy per year than the annual consumption by mankind, making solar energy an interesting alternative energy source. While there are solar cells made from other semiconducting materials, the overwhelming majority of solar cells currently producing power are made from silicon. The main arguments are processing costs and introduction of cheap solar panels. As a result, a variety of processing approaches is currently competing with each other. Solar cell substrates are essentially made in the same way as wafers for IC industry, except that quality standards are more relaxed and wafers are much thinner. Therefore they are significantly cheaper. A different approach to solar cell production is wafers of poly-crystalline silicon with preferably large grains, also referred to as multi-crystalline silicon. The advantage of this material is the lower production cost. However, the cell efficiency is lower compared to mono-crystalline silicon. Surface roughness plays an important role in silicon solar cells. Micro pyramids on anisotropically etched silicon (100) surfaces reflect incoming light at a different angle than the smooth surface, causing a reduced outbound reflectivity [12] of the incoming light. As a result more light is collected in the solar cell, which increases the cell efficiency.

1.1.2 Application for MEMS

Microelectromechanical systems (MEMS) are very small components with sizes in the micrometer range. Usually they consist of a microprocessor and several components that perform a specific task, such as a micro sensor. The potential of these very small machines or systems was recognized long before the technology existed to make them [13]. These small devices became practical once they could be produced using modified semiconductor manufacturing technologies, normally used to make smaller sized integrated circuits.

There are different approaches to produce these sensors. Bulk micromachining is the oldest method producing MEMS. The whole thickness of a silicon wafer is used for building the micro-mechanical structures. Surface micromachining uses layers deposited on the surface of a substrate as the structural
Introduction

materials, rather than using the substrate itself. It was introduced to better integrate micromachining of silicon with integrated circuit technology on the same wafer. Silicon is machined using various etching processes, preferably wet chemical etching for its comparably low costs.

Both bulk and surface silicon micromachining are used in the industrial production of sensors, ink-jet nozzles, and other devices. But in many cases the distinction between both approaches has diminished. A new etching technology, deep reactive ion etching, has made it possible to combine bulk micromachining with comb structures and in-plane operation typical of surface micromachining.

Figure 1.2: Some examples of how silica-based micro shells can act as tiny machines in future MEMS devices (Image from reference [14]).

MEMS is very versatile and the applications of this technique are manifold [15]. Inkjet printers use piezoelectrics or thermal bubble ejection to deposit ink on paper. Accelerometers are used in modern cars for a large number of purposes including airbag deployment in collisions. In the field of data communication MEMS devices are used in optical switching components for data alignment. In the field of medical and health related technologies their applications range from disposable blood pressure sensors to Bio-MEMS applications and Lab-On-Chip.

Wet chemistry is used to obtain the highly structured features and it is within the wet-chemical etching techniques that reproducibility remains an is-
1.2 Wet chemical etching of silicon

Etching is a long-established technique used to decorate metals or by artists in print making. The main purpose of etching is to remove parts of a material. If performed in a selective and controlled manner it can be used to produce devices; the challenge remains to do this with high reproducibility. Both dry and wet-chemical etching methods are widely used in the field of IC and MEMS manufacturing. Chemical dissolution of silicon can be performed in liquid as well as in gaseous media. The latter is widely used in semiconductor manufacturing and is also known as dry etching or reactive ion etching (RIE). Wet chemical etching techniques are widely used in texturizing silicon [17], mainly as these methods are relatively cheap.

Etching can be isotropic or anisotropic in nature. This is determined by the kinetics of the surface reaction and mass transport of reactants or reaction products in the solution. If the etching is limited by hydrodynamics, i.e. the surface reaction is fast, the etch rate is not sensitive to crystal orientation or surface condition. As a result, the etching will be isotropic in nature [15]. Normally this is observed with acidic etching of silicon, using HF. On the other hand, if the etching is determined by the kinetics of the surface reaction, different crystallographic planes may have highly different etch rates. Prolonged etching will then reveal the slowest etching facets or planes. Wet chemical etching for devices is frequently performed in alkaline solutions and has been investigated for several decades. Despite the intensive research the actual etching mechanism and resulting etch anisotropy in alkaline solutions is still not well understood. Effects like unexpected anisotropy, the influence of reaction products or electrochemical interactions are important factors in obtaining control over the surface morphology and chemistry.

Wet etching has become a key technology for the fabrication of miniature sensors and other microsystems. When downsizing the scale to nanometer levels, this precision technology is still insufficient for many applications, which prevents it from being used in different fields.
1.2.1 Control and Reliability

Problems associated with the reproducibility of the etch rate, emergence of defects, surface finish and roughness of features, cause lack of control during etching. These problems are related to the interaction of the solid surface with the etching solutions.

Anisotropic wet-chemical etching of silicon has been extensively investigated for various solutions, such as potassium hydroxide (KOH), tetramethyl ammonium hydroxide (TMAH) and ammonium fluoride (NH₄F). These solutions dissolve the \{100\} and \{110\} planes much faster than the \{111\} plane [18]. The etch rates of silicon, especially the aspect ratio of the \{100\} and \{110\} planes versus the \{111\} planes, are of significant technological importance [16, 19, 20] in obtaining control of alkaline etching of silicon for MEMS applications. Therefore, they have received great interest for many years and measuring them accurately has been a key factor in understanding the observed aspect ratios. This ratio is influenced by the purity of the KOH, additives, temperature and many other factors. In this study we focus on the important silicon \{111\} surfaces.

1.2.2 Etch rate measurements

A variety of methods has been developed to investigate the etching of different silicon planes, e.g. hemispherical etching or wagon wheel etching. Both approaches allow for the simultaneous measurement of etch rates for a wide range of crystal orientations. These methods, however, have a number of disadvantages: they are not simple and analysis of the results is extensive. More importantly the etching conditions differ from those used for device fabrication, e.g. sample geometry, hydrodynamics, gas evolution and possible galvanic interaction between facets may influence the determination of etch rate and morphology [21]. The most important disadvantage of these methods is the difficult determination of the real \{111\} etch rate, as this face rapidly makes way for slightly misoriented faces upon continued etching. This can be partially overcome by using the offset trench pattern [22].

Masking a wafer of a given orientation and, after etching, determining the etched depth with a profilometer is another approach. In addition, examination of the sample after cleavage with optical microscopy or Scanning Electron Microscopy (SEM) can give information about etch rates of other orientations, which are obtained via underetching [23, 24]. Since measurement of etch rates as a function of crystal orientation requires a number of separate experiments, this approach is tedious, especially if one wishes to screen a wide range of experimental conditions. Steinsland et al. studied the KOH etching of the three
important crystallographic orientations of silicon, i.e. (100), (110), and (111) using interferometry and developed a simulation model [25, 26]. However, surface roughness and gas evolution were recognized as being troublesome with this approach. An experimentally more challenging and less reproducible way of determining etch rates is by using in-situ STM observation. Although very accurate, this method only provides information on a nanoscale level which does not necessarily represent microscopic and macroscopic surface properties [27]. The effective measurement of Si(111) etch rates thus remains difficult, as many factors influence the true etch rate of the Si(111) plane. To accurately determine these etch rates is the key factor for obtaining reproducibility in the aspect ratio.

1.2.3 Dopant, alkaline concentration and temperature

The degree of anisotropy (= etch rate selectivity between different crystal planes), the absolute etch rates, and the uniformity of etching depend on the etching temperature, defects and impurities in the silicon crystal, impurities (e.g. metal ions) in the etchant, and the concentration of silicon atoms already etched. The doping concentration of the silicon to be etched also strongly impacts on the etching. The commonly used boron doped silicon forms a borosilicate glass layer on the surface during etching, which acts as an etch stop if the boron doping concentration is high. In addition, high boron concentrations induce the shrinking of a space charge layer on the silicon surface, which in turn leads to the fast recombination of electrons injected into the conduction band making them no longer available for the reduction of water [16].

Contrary to acidic etching of silicon with mixtures of HF and HNO₃, which involves an exothermic reaction and thus requires cooling to avoid fast removal rates, the alkaline etching of silicon is endothermic in nature and thus needs elevated temperatures to achieve sufficient removal rates. Both temperature and KOH concentration have a strong influence on the etched surface morphology [28, 29, 30]. In addition, the aspect ratio of the different planes can change significantly for different concentrations [31]. At higher temperatures more surface roughening is observed and at lower alkaline concentrations surface kinetic effects are observed, resulting in e.g. micro-pyramid formation on silicon (100) surfaces. Surface roughening is observed in many applications and this strongly reduces the usability and reproducibility. To further improve the roughness induced by etching, a variety of additives is used to influence the etching process.
1.2.4 Additives

Additives have been used in MEMS processing to improve surface morphology after etching. The effect of organic additives in the KOH solution has been extensively studied. It was found that some additives generate similar effects on surface morphology during etching.

Isopropanol

Isopropanol (IPA) is the best known additive to influence etch rate and surface morphology. It is known for its moderating effect and numerous investigations with IPA as an additive to alkaline etchants have been performed [32, 33, 34, 35, 36]. Despite improving surface quality and changing the anisotropy ratio [37], the origin of the effect of IPA is not fully clear. One hypothesis is that IPA is chemically bonded to the silicon surface during etching [35], which leads to a pentavalent transition state via deprotonation of the hydroxy-group [38]. The morphological effects of IPA on silicon etching are then attributed to the slow etching of this pentavalent silicon isopropoxy species. However, from $^{29}$Si-nuclear magnetic resonance measurements no difference in etch products was observed for H$_2$O/OH$^-$ or H$_2$O/OH$^-$/IPA systems [39]. This observation makes it likely that IPA is not chemically involved in the etching process, but acts as a moderator rather than blocking or enhancing the etch rate [40]. Therefore, a more likely explanation for the observed effects of IPA is given by the reduction in surface tension [41] or solvation of the etchant upon addition. This implies that the additive changes the rate of diffusion of either etch products to the bulk solvent or the diffusion of etchant from the bulk solvent to the silicon surface and thus lowers the etch rate.

Other additives

Other examples of additives are different hydroxides [43], alcohol additives [44], other etching compounds and surfactants or strong oxidizing agents in electrochemical etch systems. Some of the additives may form ions in alkaline solutions. This has lead to different hypotheses for their action. One explanation is adsorption (either physical or chemical) of the ions at the silicon surface. As etching is done in highly alkaline environments, an alcohol becomes partially deprotonated and forms an equilibrium with the alkoxide ion. Although the equilibrium strongly favors the alcohol, a small amount of alkoxide is present in the etching mixture. From organosilicon chemistry, nucleophilic displacement of hydrogen from silicon compounds by alkoxide ions occurs rapidly and is sug-
1.2 Wet chemical etching of silicon

gested to occur at the silicon surface during etching [45]. An alternative model, not based on ions, assumes that nucleophilic attack by the oxygen lone pair of the alcohol to the silicon surface takes place. Removal of dihydrogen leads to an overall reaction in which oxidative addition of the alcohol takes place [46]. This again could lead to a change in etch rate for the fast etching positions. Small concentrations of metal impurities can strongly influence the etching of silicon [47, 48]. As a result, the surface morphology of silicon (111) changes under these different etching conditions. Even dissolved gasses can affect the etch rate. Other influences, but more difficult to control, are oxygen precipitates in the silicon and etch bath hydrodynamics.

The composition of the etching solution in time is of high importance for understanding the chemistry at the surface. During etching the composition changes and the presence of silicate reaction products can locally alter the etch rate and thus change surface morphology. The chemistry of silicate reaction products is complex. The formed small particles of silicic acid are capable of polymerization, specifically at higher pH values [49]. Reduced solubility of silicate reaction products and increased turbidity at lower alkaline concentrations is observed [50, 51]. These factors combined with the observed formation of waterglass [52] and the absence of additives in the reaction products [39] further confirm the complex chemistry involved in silicon dissolution.

1.2.5 Etching mechanism

The etching of crystalline silicon at Open Circuit Conditions (OCP) in KOH solutions is a very complicated process [16]. As many factors can influence the etch rate, the following overall reaction is generally accepted in literature:

$$\text{Si} + 2 \text{H}_2\text{O} + 2 \text{OH}^- \rightarrow \text{SiO}_2(\text{OH})_2^- + 2 \text{H}_2 \uparrow$$  \hspace{1cm} (1.1)

The simplicity of the overall reaction masks the complexity of the etching mechanism. A hydrogen terminated silicon atom at the surface is oxidized to a hydroxide terminated silicon, through a pentavalent intermediate step [53] and under formation of hydrogen gas (see figure 1.4). Then the hydroxide present in the etching solution will enable the second step, acting merely as a catalyst. In the second step water attacks the silicon hydroxide surface bond under the formation of a silicate complex, which will dissolve into the solution, leaving a new hydrogen terminated silicon surface site available for dissolution (see figure 1.5). The overall etch rate is dependent on the hydroxide concentration [16]. This gives rise to the conclusion that the oxidation step is rate determining and
the transitional state strongly determines the etch rate. This general description does not include factors like specific surface site reactivity and is therefore insufficient to describe all surface evolutions accurately.

To obtain a better understanding of the surface evolution, different specific surface sites are distinguished [54] and simulations are used to evaluate them. These simulation methods are based on kinetic Monte Carlo [55, 34] or Cellular Automation techniques [56]. Wind et al. [34] used a simple step flow model to describe the anisotropy of the etch rate in the vicinity of the \{111\} face and this model describes the formation of step bunches during etching. The actual etch rate however, is much better described by using specific removal rates for the different surface sites. The accuracy of these models relies on the correct description of the properties of each surface site, their neighbouring atoms and even second nearest neighbours. Other factors influencing etching are electrostatic interactions and steric hindrance of the reaction components [53, 57]. In these models the different positions for etching are systematically identified and compared [58]. An experimental way to describe etch rates and influences on it, is provided by others [59]. These models are based on an analytical breakdown of the etch conditions and are used to describe the evolution of the experimentally observed etch rates.

1.2.6 Electrochemistry

Electrochemistry influences the etch rate and substrate conditions to a large extent [21, 60]. The previously mentioned and simplified mechanism is based on electroless etching at open circuit potential $U_{\text{oc}}$, while both an electrochemical and an chemical pathway are involved in the dissolution reaction (see figures 1.4 and 1.5). In fact, it was shown [61, 62] that reaction intermediates are formed during chemical etching under open circuit potential, from which electrons can be injected into the conduction band. Using this phenomenon the shapes of recorded voltammograms provide insight in the chemical reaction mechanism [63] (see figure 1.3).

The two-fold reaction scheme of a likely approach towards the influence of applied potential on the dissolution chemistry is described in figures 1.4 and 1.5. In horizontal direction the chemical pathway is depicted and the vertical direction describes the electrochemical path. The anisotropic etching can be represented by this simplified scheme. However, it eludes the underlying interactions of the surface sites and reaction intermediates. In more recent work the role of intermediates and their effect on both the chemical and electrochemical pathway has been extensively investigated [64]. The influence of electrochem-
1.2 Wet chemical etching of silicon

Figure 1.3: Voltammograms for n- and p-type Si-(100) measured in the dark in a 5.0 M KOH solution at 60°C. The potential was scanned from negative to positive at a rate of 10 mV/s. (b) Schematic representation of the n-type Si - solution interface. Due to the chemical etching reactions at the surface of silicon, activated reaction intermediates are produced with energy levels high in the bandgap (these energy levels are depicted schematically by the rectangle at the interface). When a sufficiently positive potential is applied, electrons, injected from these states into the conduction band, give rise to an anodic current in the external circuit (Figures from reference [64]).

Figure 1.4: Reaction Scheme 1, showing the first step of the dissolution mechanism of silicon. The intermediate is denoted by I and the electrochemical pathway is depicted by route 1c.
Introduction

The intermediate is depicted by II and the electrochemical steps are depicted by routes 2c and 2d.

Figure 1.5: Reaction scheme 2 showing the second step of the dissolution mechanism of silicon. The intermediate is depicted by II and the electrochemical steps are depicted by routes 2c and 2d.

istry on the etching of silicon is also elaborated using a kinematic wave analysis to ascribe observed electrochemical interactions to crystal surface site reactivity [22]. At potentials more positive than the OCP, the surface oxidizes and the hydrogen terminated surface changes to a hydroxyl terminated and eventually forming an oxide terminated surface. At the surface, due to the different reactivity of the surface sites (kinks and steps), a change of morphology can be expected. The observation of this surface morphology provides information on the overall etching mechanism, besides the determination of actual etch rates.

1.3 Surface characterization

In this thesis two of the techniques used to study the etched samples are Differential Interference Contrast Microscopy (DICM) and Phase Shifting Interferometry (PSI). Both techniques are very suitable for observing small height differences and shallow pit angles on a surface and can be used to determine pit
1.3 Surface characterization

densities. Complementary to the qualitative DICM, PSI is capable to quantify pit shapes and angles. The drawback of both techniques, however, is the difficulty to get an average picture of an etched surface. In order to quantify the changes in average pit morphology, the Lichtfigur technique is introduced. The concept of the Lichtfigur technique is based on the average reflection of a laser beam from a multitude of etch pits. As the etch pit morphology changes in time and with the use of additives, this technique provides an easy and quantifiable method for the analysis of average pit shape and surface morphology changes. Besides macroscopic observation, a closer look at the atomistic level has been made to study the surface ordering during etching, using surface X-Ray diffraction.

1.3.1 Microscopic Observation

Optical microscopy is used to observe etch patterns and all kinds of features on the crystal surface. When reflected from a surface, a light wave will show phase variations as a result of small height differences present on the crystal. To allow for observation of these small phase differences they have to be translated into intensity differences. The most commonly used way of doing this is differential interference contrast microscopy (DICM) according to the Nomarski principle.

![Diagrams showing interference image and examples of differential interference contrast microscopy](image)

Figure 1.6: Principle and examples of differential interference contrast microscopy.
The principle of this DICM technique is schematized in figure 1.6. An incident light beam is reflected from a surface with a step of height $h$. The reflected beam passes an optical device that splits it into two coherent waves of equal intensity, which are shifted over a small lateral distance $\Delta$ (roughly 1 $\mu$m) and over an adjustable distance $\delta$ along the optical axis. In the region $\Delta$ near the step, the phase difference between both waves is $4\pi h / \lambda + \delta$, which differs from the value $\delta$ elsewhere. By interference of the two waves a step becomes visible as a line of different intensity in the microscope image. The method, which is capable of detecting step heights as low as 1 nm, gives only qualitative information, but it is very useful for both in-situ and ex-situ surface observations.

White light interferometry is certainly not new, but combining white light interferometry techniques with modern electronics, computers, and software has resulted in Phase Shifting Interferometry (PSI), which is an extremely powerful quantitative measurement tool. Mainly the high accuracy in combination with the rapid measurement, even with low contrast fringes, makes it a very useful tool in measuring small height differences on large surface areas [65]. The largest drawback of interferometry is its sensitivity to vibrations, demanding special setups to minimize this effect. Complementary to DICM, actual height profiles and height differences can be accurately measured down to nanometer scale using PSI.

1.3.2 Lichtfigur Analysis

The Lichtfigur method was used as a technique that complements the direct optical observation of etched surfaces. This method has been developed in the 19th century and several researchers used it [66, 67] to identify point groups from the reflection patterns of etched surfaces. In the 1920’s it was extensively used to study the etching behavior of natural minerals [68]. The method was further refined by using photography and goniometry to determine the indices of the reflected surface planes [69]. More recently, the method was applied to study the morphology of silicon and germanium surfaces [70] and to determine the orientation of single crystal rods.

The principle of the Lichtfigur technique is beautiful in its simplicity. A parallel beam of (laser)light is reflected from an etched crystal surface and projected onto a screen, revealing all orientations on the crystal surface after etching (see figure 1.7). The reflection from a set of flat surfaces will result in point shaped reflections, the presence of a continuous range of reflections in-between the points indicates the presence of curved vicinal planes on the etched
1.3 Surface characterization

![Diagram of Lichtfigur technique](image)

**Figure 1.7:** The Lichtfigur technique is used to investigate etch pits on the etched silicon samples. (a) Laser light is reflected from the etched sample and via a beam splitter projected onto a plane. This projection is called the Lichtfigur and the resulting picture is used to determine the average etch pit geometry. (b) The experimental setup as used in the measurements.

Crystal. The greatest advantage of the Lichtfigur method is the ability to represent in one single projection the distribution of all orientations of the etched surface. This makes the method extremely useful in the field of mineralogy and etch pit characterization, since one projection depicts all information.

1.3.3 X-Ray Diffraction of interfaces

A multitude of techniques are available to characterize the atomic structure of the surfaces of semiconducting materials. Amongst them the Surface X-ray diffraction technique (SXRD) is very suitable for the structure determination of the interface between a crystal surface and solution [71] by using intense X-Ray beams available from synchrotron radiation sources (see figure 1.8). Initially developed to study surfaces in vacuum, the SXRD technique is nowadays also used to investigate solid-liquid interfaces. As the number of atomic scatter centres at the surface is orders of magnitude smaller than in the bulk, a very high intensity of radiation is needed in order to detect the weak signal from
the surface. Second to that, a good signal to noise ratio is required to detect the weak surface signal. To achieve a good signal from the surface, surface smoothness has to be achieved at an atomic level and the geometry has to be optimized to reduce the X-Ray absorption by the liquid on top of the crystal.

![Figure 1.8: (a) A view of the scattering geometry used in surface diffraction scattering experiments. The incoming x-ray beam on the sample has a wave vector \( \mathbf{k}_i \) and an incidence angle \( \beta_{\text{in}} \) with respect to the plane of the surface. The scattered radiation is observed in the direction of the vector \( \mathbf{k}_f \) defined by the detector position. (b) The position in reciprocal space is given by the momentum transfer vector \( \mathbf{q} \), i.e. the difference between the vectors \( \mathbf{k}_i \) and \( \mathbf{k}_f \). The intensity at a specific point \((hkl)\) is integrated by rotating the sample about the surface normal in a rocking scan (Figures adjusted from reference [72]).](image)

The two-dimensional nature of the surface results in rods of X-Ray diffraction intensity, the so-called Crystal Truncation Rods (CTRs) \([73, 74]\), whereas three-dimensional diffraction from the bulk leads to spots of high intensity, the so-called Bragg peaks. These Bragg peaks are denoted with three integer indices \((hkl)\) and correspond to lattice points in reciprocal space. The information about the surface structure is found in a CTR at the positions between the Bragg peaks, where the diffracted intensity mainly originates from the surface. The central \((00)\) rod, also known as specular rod, provides information on the thickness of the solid and liquid layers adjacent to the surface. The method is based on integrating the measured intensity profiles. After corrections, the interface structure can be derived by fitting models to the experimental data using least squares methods.
1.4 Thesis outline

In this thesis we investigate the surface morphology of silicon under alkaline etching conditions. We pay special attention to the effects of additives, electrochemical control and reaction products on the etching of silicon in aqueous alkaline solutions. Our focus has been directed towards the morphology and atomic scale structure of the \{111\} faces. For this purpose we prepared samples from single crystal silicon-(111) wafers. After etching the samples were studied using optical microscopy, phase shifting interferometry, Lichtfigur analysis and surface X-ray diffraction.

After this introduction, the second chapter discusses the etching mechanism itself and the role of additives and reaction products on the surface morphology. We observed an autocatalytic behavior of the reaction products, locally enhancing the etch rate, leading to the formation of etch pits, which are not related to any crystal imperfections of the silicon lattice.

Chapter three introduces the Lichtfigur technique and compares it with the optical techniques of differential interference contrast microscopy and white light phase shifting interferometry. The Lichtfigur method turns out to provide an easy tool to compare the average pit morphology on etched surfaces. The role of the additive IPA is studied and it has been experimentally shown that in absence of water no etching occurs, implying the essential contribution of water in the etch reaction.

In chapter four we discuss the influence of different additives on alkaline etching, applying both the Lichtfigur technique and optical microscopy. The pit shapes significantly alter under addition of different types of protic, aprotic and ionic additives. The change of pit morphology cannot be directly related to the structure and properties of the additive, rather the additives act as an anti-solvent at the etched surface.

Chapter five takes a closer look at the silicon-etchant solution interface. In this we use the surface X-Ray diffraction technique to study to interface and surface interactions under etching conditions. We experimentally achieved a suitable \textit{in-situ} preparation technique to obtain nearly atomically flat \{111\} silicon surfaces under etching conditions and observed subtle but significant surface relaxation in the topmost layer and differences in surface roughness when using different etching solutions. Moreover we found the first water to be laterally highly ordered to the surface by van der Waals forces. The oxidation of the surface occurs through Birth and Spread of small oxide islands on the surface.

In chapter six the absolute etch rate of silicon (111) during wet chemical
etching in aqueous KOH solution has been investigated with optical interferom-
etry, using masked samples. The etch rate is constant in time and independent
of alkaline concentration for higher alkaline concentrations; at lower alkaline
concentrations the etch rate decreases. Addition of isopropanol does not sig­
nificantly alter the absolute etch rate. The relatively high activation energy
of the etching reaction indicates that the reaction is determined by reaction
kinetics and not by transport limitations. In all cases the surfaces are covered
by shallow etch pits, not related to defects in the crystal. This implies that the
actual factor that determines the etch rate is the 2D nucleation of new vacancy
islands at the bottom of these pits. This process is likely catalyzed by a local
accumulation of reaction products.

In the seventh and final chapter we use voltammetry and Lichtfigur analysis
to in-situ investigate the morphological changes of etched silicon \{111\} under
differently applied electrochemical potentials. A reverse of pit morphology is
observed when this potential is shifted from cathodically to an anodically ap­
plied potential.
References


REFERENCES


REFERENCES

Chapter 2

Wet chemical etching of silicon \{111\}: Autocatalysis in pit formation

\footnote{Accuracy and reproducibility of etching is essential to obtain the smallest scale devices in silicon. The present study focuses on the etching of silicon \{111\}, the slowest etching face, using different aqueous solutions of KOH. In all cases shallow, point bottomed etch pits are formed. It was found that etchant concentration, temperature, transport limitation and addition of Isopropyl Alcohol (IPA) change the number density and morphology of the pits to a large extent. Sirtl delineation etching proved that the pits are not related to dislocations or stacking faults in the crystals. We propose that etch pit formation is autocatalytic in nature and is triggered by accumulation of reaction products at the bottom of the pits, locally enhancing the downward etch rate. This autocatalytic process also explains the formation of the concave shaped pits, obtained after etching in KOH solution with IPA additive.}

\footnote{Published in Journal of Electrochemical Society \textbf{155} (2008), J55.}
2.1 Introduction

Anisotropic wet chemical etching of silicon single crystals is an extensively used process in the production of Micro Electro Mechanical Systems (MEMS). The applications of this technique are manifold and include micro pumps, sieves and reactors [1, 2, 3]. The etching process itself, however, is only understood and controlled to a limited extent. If control can be improved down to the nanometer scale, a wide range of new applications becomes possible; for instance, nano structures can be grown on atomically flat surfaces. Improvement in accuracy and reproducibility of etching requires knowledge of the physical chemistry of the etching process. Many of the influences on etching (e.g. chemical and physical parameters like etchant composition, additives, contaminants and electrochemical potential) are not fully understood yet. Other studies have focused on etching of wagon-wheel patterns [4, 5]. Although this technique provides relevant information on the whole crystallographic range of etching, it does not provide reliable data on the etching of silicon \{111\}. Therefore, in order to increase the reliability and usability of wet chemical etching, the specific influences of these parameters on the silicon \{111\} crystal plane have to be investigated in detail.

A widely used anisotropic etching solution for silicon is aqueous potassium hydroxide (KOH). The etch rate is known to be dependent on the presence of defects in the silicon [6], such as dislocations, stacking faults and clusters of aggregated point defects. Further, it is affected by alcoholic moderators [7, 8, 9, 10, 11, 12, 13], such as isopropyl alcohol (IPA) [12], as well as by transport limitation of reactant and reaction products [4, 14]. The silicon etch rate and its anisotropy show a strong dependence on KOH concentration and temperature. The question that now arises is, what is the relative influence of crystal defects, etchant properties and transport on the surface morphology and etch rate?

The present study focuses on the etching of silicon \{111\} using different etchant mixtures of aqueous KOH and IPA. Control of silicon \{111\} etching is particularly important for obtaining a maximum anisotropy ratio in wet-chemical etching, because this ratio depends strongly on the etch rate of the slowly etching \{111\} face. Adding IPA or hampering transport of reactants to and reaction products from the surface leads to the development of a high density of triangular etch pits. In the case of pure KOH etching without transport restrictions a relatively low number of rounded pits is formed. These very different surface patterns are examined using Differential Interference Contrast Microscopy (DICM) and Atomic Force Microscopy (AFM). Sirtl [15, 16] delin-
2.2 Experimental

2.2.1 Silicon etching

The samples investigated were cut from polished p-type silicon \{111\} wafers. The silicon used was as-grown and not subjected to any further heat treatment. Samples were cleaned using HNO_3 69% for 15 minutes to remove organic contaminants, followed by rinsing in high-ohmic ultrapure water. Diluted HF (5% in water) was used to remove the native oxide layer, followed by a rinse in high-ohmic ultrapure water. Although the SiO_2 etch rate is sufficiently fast in concentrated KOH solutions at elevated temperatures to remove the native oxide layer without affecting the overall etch rate of the silicon [17], all samples were pretreated with HF to give all samples the same starting conditions.

After cleaning, the samples were placed in a Teflon beaker, containing a 100 ml KOH or KOH / IPA solution. The etchant underwent no further treatment, like degassing of oxygen. Then, the beaker was sealed with parafilm to avoid evaporation. All the samples were etched for 20 hours at 30 or at 60°C in duplo by placing the beakers in a thermostatic bath with an accuracy of 0.1°C. Standard aqueous KOH (Merck, purified agent) solutions were used in two concentrations of 0.5 M and 5.0 M. In half of the experiments, the standard solution was used; in the remaining experiments IPA (Merck, VLSI) was added to the solution at a concentration of 6.5 wt % (= 1.0 M) relative to water. To obtain well-defined surface patterns, etching was stopped abruptly prior to microscopic examination. For this purpose, after separation from the etching solution, the samples were rinsed with ultrapure water and subsequently immersed in concentrated sulfuric acid (98%) for at least 10 minutes to stop the alkaline etching. After this, the specimens were again rinsed in ultrapure water and dried in a flow of nitrogen.

2.2.2 Defect characterization by preferential etching

In first instance, the nature of the etch pits obtained after KOH and KOH / IPA etching was investigated using a dislocation-revealing etchant. Yang [16] delineation etches are, in principle, a method to map the end points of dislocations.
at the silicon surface, but contrary to former experiments [6], neither dislocations nor stacking faults could be revealed. Therefore, we used the Siril [15, 16] delineation etch instead. This has proven to be a simple and fast technique that is especially powerful for imaging the outcrops of defects at silicon \{111\} surfaces, as a result of its stronger oxidizing and etching power. The etching solution consists of CrO₃, HF and H₂O. Prior to etching, 48% HF in water was added in a one-to-one volume ratio to a 5.0 M CrO₃ stock solution in water. The samples were immersed in this liquid for 10 minutes. After separation from the solution, the silicon crystals were rinsed in water and dried. In this way, clear surface patterns related to dislocations and stacking faults were obtained. These patterns were compared with etch-pit patterns obtained after the KOH etching.

### 2.2.3 Surface observation

The etch patterns obtained were examined using DICM in reflection mode. By this optical method, shallow features and very small differences in inclination can be revealed. AFM (Digital Dimension 3100) in contact mode was used for high magnification views and slope measurements. Both height and deflection images were recorded using Si₃N₄ cantilevers. We verified by focusing the optical microscope and by using AFM that the observed patterns comprise of shallow etch pits in all cases.

### 2.3 Formation of etch pits in pure KOH solutions

The silicon samples were placed horizontally on the bottom of the Teflon beakers. Under all etch conditions shallow etch pits were formed, but of different shapes and number densities. An overview of the observed etch pits is given in Table 2.1 under ‘Pure KOH’. Standard alkaline etching in KOH,(5 M and 60°C) yields surfaces with numerous large, more-or-less rounded pits which are point-bottomed (figure 2.1a). The AFM scan (figure 2.1b) shows the etch pits to be rounded-triangular in shape, and to consist of steps roughly parallel to \(<110>\) and sloping down towards the \(<112>\) direction. This indicates (mainly) monohydride step termination [18]. Although the slope of the etch pits looks rather steep in the images, the AFM analysis reveals them to be at most 2.5°.

As listed in Table 2.1, the KOH concentration has a substantial effect on the etch-pit density and shape. For both temperatures, the etch-pit density increases when the KOH concentration is decreased. At the same time, the pits become more triangular and are bounded by \(<112>\) steps (see figure 2.1c).
2.4 Autocatalysis

Table 2.1: Overview of densities and shapes of etch pits obtained at different conditions

<table>
<thead>
<tr>
<th>Solution</th>
<th>T (°C)</th>
<th>KOH (M)</th>
<th>Pit Density (1/ mm²)</th>
<th>Pit Shape</th>
<th>Fig.</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>60</td>
<td>5</td>
<td>3</td>
<td>Large round pits</td>
<td>fig. 2.1a, 2.1b</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.5</td>
<td>2500</td>
<td>Triangular pits</td>
<td>fig. 2.1c</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>2000</td>
<td>Round pits,</td>
<td>fig. 2.1d</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.5</td>
<td></td>
<td>Round to triangular pits</td>
<td></td>
</tr>
<tr>
<td>KOH Transport</td>
<td>60</td>
<td>5</td>
<td>1200</td>
<td>Small Triangular pits</td>
<td>fig. 2.5</td>
</tr>
<tr>
<td>limited</td>
<td>60</td>
<td>0.5</td>
<td>7500</td>
<td>Small Triangular pits</td>
<td></td>
</tr>
<tr>
<td>KOH with 20 g/l Si dissolved in solution</td>
<td>60</td>
<td>5</td>
<td>100</td>
<td>Triangular</td>
<td>fig. 2.4, 2.6a</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>2100</td>
<td>Round to triangular</td>
<td></td>
</tr>
<tr>
<td>KOH with 6.5 wt% IPA added to solution</td>
<td>60</td>
<td>5</td>
<td>100</td>
<td>Round to triangular</td>
<td>fig. 2.4, 2.6a</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.5</td>
<td>5900</td>
<td>Triangular pits</td>
<td>fig. 2.6b, 2.7</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>5</td>
<td>250</td>
<td>Hexagonal-like pits</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.5</td>
<td>62500</td>
<td>Triangular pits</td>
<td></td>
</tr>
</tbody>
</table>

The pits formed in a 5 M KOH solution at both temperatures are more-or-less circular.

The effect of temperature is less straightforward. For 5 M KOH, lowering the temperature from 60 to 30°C leads to an increase in pit density, whereas a decrease was found for 0.5 M KOH. However, the effect of temperature is less than the effect of changing KOH concentration. The pit shape is hardly affected by temperature change.

2.4 Autocatalysis

2.4.1 Defect delineation by Sirtl etch

The etch pits obtained after KOH etching always have a point-bottomed nature. In most cases reported in literature [19], such pits are related to extended
Figure 2.1: Surface morphologies of silicon {111} etched in aqueous solutions of pure KOH: (a) DICM, 5 M KOH at 60°C; (b) Deflection AFM image, 5 M KOH at 60°C; (c) DICM, 0.5 M KOH at 60°C; (d) DICM, 0.5 M KOH at 30°C.

defects, such as dislocations or stacking faults, outcropping at the surface. The Sirtl etch [15] is used to examine the density of the defects. Delineating clean and KOH etched silicon (111) surfaces by the Sirtl etch only reveals a very low density of defects ($< 1/\text{mm}^2$).

Figure 2.2 shows that the defect density is several orders of magnitude smaller than the density of pits formed after alkaline etching in KOH solution. This proves that in the present case etch-pit formation is not induced by the presence of extended defects. A connection between pits and dislocations would also cause a problem in explaining the huge differences in pit density for different etchant concentrations, temperatures and other conditions as summarized in Table 2.1, as all of the silicon wafers used were from the same batch.

Another possible explanation for the multitude of etch pits and their distinct shape could be point defects in the crystal. However, this group of defects
2.4 Autocatalysis

Figure 2.2: Clean (a) and (b) KOH etched Si \{111\} surface after Sirtl etch demonstrating the very low defect density of the silicon crystal as compared to the large number of etch pits obtained after alkaline etching. The inset shows intentionally introduced dislocation Sirtl etch pits typical of Si \{111\}. These are absent in the KOH etched surface.

cannot explain the formation of the point bottomed etch pits. If the stress field around a point defect causes an increased vertical etching at the pit bottom, this process stops after dissolution of this defect, and an expanding but flat-bottomed etch pit is left. Moreover, such pits are expected to be shallow - only a few nanometers deep. Therefore, the presence of individual substitutional oxygen impurity atoms, vacancies, or vacancy clusters cannot provide an explanation of the formation of the point-bottomed pits upon KOH etching.

Nijdam et al. \[6\] observed a low density of etch pits after alkaline etching in KOH solution. These etch pits were related to stacking faults and dislocations by using a Yang etch. However, we observed a high pit density, not related to defects. This difference is explained by the different defect structure of the samples. Nijdam et al. applied a heat-treatment to the samples, which leads to reordering of dispersed oxygen and vacancies in the crystals, resulting in the development of stacking faults and dislocations \[20\]. Our specimens were not subjected to a heat-treatment, so reordering or migration of point defects did not take place and no extended defects were formed. If many dislocations or stacking faults are present in the crystals, we expect that this leads to faster etching and thus steeper etch pits, which ‘overrun’ those not related to defects.

2.4.2 Autocatalytic etching

The question now arises: How are the many point-bottomed etch pits formed in absence of a central defect? The DICM and AFM topographs show that the
{111} Si face etches by a layer-by-layer mechanism involving steps; the surface is not rough. This implies that the removal of the double- and triple-bonded silicon atoms at the step positions proceeds much faster than the removal of the triple bonded atoms at the terraces in between the steps (see figure 2.3). However, preferential etching appears to happen on the pit bottom, where the silicon atoms are also triple-bonded like those at the terraces.

A closer look at the bottoms of the pits obtained after KOH etching, using AFM, reveals some debris in a number of cases. An example is shown in figure 2.4. As this material did not dissolve in water or sulfuric acid, we conclude that this material is composed of silicate reaction products. This observation suggests that pit formation is promoted by a local accumulation of silicate reaction products, which speed up vertical etching at the pit bottom. An increase of silicon reaction rate promoted by reaction products has previously been suggested by Garcia et al. [14], but these authors suggested water glass as the relevant reaction product.

Reaction products, like silicate colloid particles, have also been used to explain the formation of etch pyramids on the Si-(100) surface [21]. On this surface with an etch rate that is about 100 times faster than of the (111) face, the reaction products reduce the etch rate, rather than enhancing it. On the Si-(100) surface, the proposed mechanism of pyramid formation is through locally blocking the transport of etchant towards the pyramid tops. On the slow etching silicon {111} surfaces, however, the hampering of transport by such colloid particles can be neglected compared to their catalytic action, and point-bottomed pits instead of pyramids are formed.

2.5 Influence of Reaction Products

We can test our autocatalysis hypothesis by varying the etching conditions in ways that should affect the presence of reaction products. The first test is the observed dependence of the etch pit density on the pure KOH concentration as discussed above. The etch products, which are silicic-acid-like, dissolve easier in stronger alkaline solutions [22], and thus we expect an increased density of pits for lower KOH concentrations, as indeed observed.

2.5.1 Mass transport

To investigate the effects of mass transport, we first change the transport of reaction products from the crystal surface with respect to the supply of reactants toward the surface. A simple way to realize this is to perform experiments
2.5 **Influence of Reaction Products**

**Figure 2.3:** Structure of a \( <112 > \) step on \{111\} silicon, showing kink (\( P_k \)), step (\( P_{st} \)) and terrace (\( P_t \)) positions.

**Figure 2.4:** AFM deflection image of a Si \{111\} surface after etching in 5 M KOH, 6 wt% IPA added. Collections of reaction products are visible at the bottom of the etch pits.

with and without stirring the KOH solution. Stirring enhances the reactant concentration and this should increase the etch rate. The etch rate, however, is observed to decrease with stirring. Also the pit density decreases. Both observations are explained by the fact that stirring removes reaction products from the crystal surface more rapidly and thus reduces their autocatalytic action in etching and pit formation.

Next we minimize the mass transport. This is realized by placing the silicon plates in a Teflon holder with a narrow opening, resulting in diffusion-limited transport to and from the surface. As both the concentration and the diffusion constant of \( K^+ \) and \( OH^- \) are expected to be larger than that of the reaction products, this hindrance of mass transport (diffusion limited) should lead to an increased accumulation of reaction products at the silicon surface and thus to an increasing pit density. The surface obtained after transport-limited etching shows indeed a high density of small triangular etch pits for the 5 as well as the 0.5 M KOH solutions. For the 5 M KOH solution at 60°C the pit density increased by a factor of 300 as compared to the case without transport limitation, see figure 2.5 and Table 2.1. This agrees with the autocatalysis hypothesis for pit formation.

By introducing transport limitations, the resulting etch pits have obtained a triangular shape with straight edges, unlike the rounded shapes in freely flowing alkaline solutions. The orientation of the etch pits did not change, so the steps
remain $<112>$ type as indicated in figure 2.3. All pits are point-bottomed and have a slope of about 2.5°. At a lower KOH concentration in alkaline solutions without transport hampering, triangular pits are obtained as well. In both cases the etch process proceeds at lower driving force, as a consequence of the lower alkaline concentration, thus making the process less prone to step roughening, as detailed in section 2.6. This explains the more triangular shape of the etch pits.

Figure 2.5: Silicon $\{111\}$ surface after transport limited etching in 5 M KOH at 60°C. (DICM)

2.5.2 Addition of silicate reaction products

Another approach to testing the autocatalysis hypothesis for pit formation is by deliberately adding reaction products to the KOH etching solution. To mimic the effect of etch products in a KOH solution, we performed etching experiments with dissolved silicon in the liquid. Etchant was prepared by dissolving $\approx 20$ g/l ground silicon in 5 M KOH. Alkalinity measurement showed that the pH definitely exceeds 14, which is the limit of the pH measurement method used in this study, so dissolving silicon did not affect the OH$^-$ concentration to a large extent. The OH$^-$ ion only acts as a catalyst in the silicon etching reaction [23]. This etchant was then used as in the normal experiments. At 60°C and 5 M KOH the pit density increased with roughly a factor 30 when the silicate was added (See Table 2.1). At 30°C and 5 M KOH solution, this increase was even more, about 80 times greater. Unfortunately, the measurement of absolute etch rates by weighting was not possible for these specimens, as the amount of material removed from the sides of the crystal plates, not bounded by slowly etching $\{111\}$ faces, is several times more than the material removed from the slowly etching top and bottom faces. Thickness measurements also did not
2.5 Influence of Reaction Products

give useful results, as the back side of the crystal wafers was not polished and therefore generated unreliable data. Preliminary measurements of absolute etch rates of SiN masked Si(111) samples in clean and in silicate containing solutions showed some decrease in etch rate for the solution with silicates, but a large increase in the number of etch pits [24]. This indicates that adding silicate reaction products does not increase the activity of the individual autocatalytic aggregates, but only increases their number, leading to a higher density of etch pits. In other words, they act in parallel.

The above experiments show that the reaction products of silicon etching play an important role in pit formation and thus this experiment gives additional support to the autocatalysis hypothesis. As the fine details of the general mechanism of KOH etching are not yet fully understood, elaborating on the mechanism of the autocatalytic process remains speculative. We think that the OH\(^-\) groups of the accumulated reaction products compete with the OH\(^-\) in the solution in attacking the triple bonded Si atoms at the bottom of the pits and thus promote vertical etching.

2.5.3 Addition of Isopropyl Alcohol (IPA)

Besides, changing mass transport and adding reaction products to the KOH solution, additives in solution can influence the etching process at the crystal surface as well. A well-known additive in aqueous KOH solutions is IPA. The addition of IPA to the aqueous KOH solutions increases the pit density to a large extent (figure 2.6). Adding 1 M IPA to 5 M KOH at 60\(^\circ\)C gives a \(\approx 33\) times increase, whereas for the 0.5 M KOH solution the pit density becomes \(\approx 3\) times higher.

The effects of adding IPA are similar to those upon increasing the amount of reaction products at the silicon surface by transport limitation or adding silicates to the solution. In both cases, the number density of the pits increases and their shape becomes more triangular. We expect that adding IPA affects the solvation of the silicate reaction products and thus reduces their solubility in the KOH solution, in which the IPA acts as an antisolvent for reaction products. This causes more reaction products to stick at the crystal surface, which leads to enhanced pit formation through the autocatalytic mechanism as compared to the standard alkaline solutions.
Figure 2.6: DICM images of silicon {111} surface after KOH etching with 1 M IPA added at 60°C: (a) 5 M KOH; (b) 0.5 M KOH.

2.6 Pit Shapes

2.6.1 No or silicate additives

The shape of an etch pit is determined by the anisotropy of the step propagation velocity on the {111} surfaces. Straight or rounded steps bound all pits observed in this study, with an average downward slope towards <112>. As elaborated on in Refs. [25] and [26], the anisotropy in step velocity is determined by the relative probabilities of removal of a double bonded silicon atom at a kink site ($P_k$ in figure 2.3) and a triple bonded silicon atom at a step site ($P_{st}$) of such a $<112>$ step. If $P_k \approx P_{st}$, then the kink density is high and there is no tendency for a step to straighten. In this case, rounded, convex-shaped pits are formed, as is observed for etching in pure KOH solutions at high concentrations. If $P_k \gg P_{st}$, which implies a quick removal of kinks, then the kink density becomes low and the step straightens; thus, well-faceted pits bound by straight edges are formed. This was observed for etching in solutions with low alkaline concentration, in solutions containing silicate reaction products, and for transport-limited etching. The reaction products tend to increase the ratio $P_k/P_{st}$, i.e., slow down $P_{st}$ with respect to $P_k$, for example, by steric hindrance of the attacking $\text{H}_2\text{O}/\text{OH}^-$. This oxidizing step is rate determining in the reaction mechanism [27]. A second possible explanation for the increase of $P_k/P_{st}$ is a reduction in driving force for etching. Then a larger difference in removal rate of surface atoms with a different number of back-bonds is expected.
2.6 Pit Shapes

2.6.2 Addition of IPA

The addition of IPA to the etchant solution alters the surface morphology of the etched silicon significantly. It increases the pit density to a large extent, and the shape of the pits becomes more triangular. For the 5 M KOH solutions the change in pit shape is significant, but less pronounced. However, an effect is clearly visible for the 0.5 M KOH solutions (figure 2.6b), which indicates that here \( P_K \gg P_{st} \). The effects of adding IPA are similar to those upon increasing the amount of reaction products at the crystal surface by the methods described in section 2.5.

![Figure 2.7: Concave shaped pits obtained after etching in 0.5 M KOH at 60°C with 1 M IPA added: (a) AFM deflection image; (b) Schematic drawing of step pattern with velocity sources \( V_{\text{corner}} \) indicated.](image)

Detailed AFM scans of the triangular pits formed in 0.5 M KOH solutions at 60°C with IPA added reveals concave step patterns. An example of such a pit as well as a schematic drawing is given in figure 2.7. This concave pit shape is rather unexpected, as the dynamic Gibbs-Wulff construction of expanding closed loop step patterns only allows the development of convex or straight, i.e., polygonized, shapes. Anisotropy in step velocity cannot explain the formation of concave step patterns in an etch pit.

The concave shape however, can very well be explained by the introduction of a so-called ‘velocity source’ [28], due to which the etch velocity of a corner point of a pit becomes larger than twice the step velocity in a \(<112>\) direction (see figure 2.7). Previously, concave-shaped growth spirals observed on (0001)
SiC crystals have been explained by the occurrence of step interlacing [28, 29]. At the corners of these polygonized spirals, higher steps split into lower ones, which advance faster. This increased step speed, which is a velocity source ‘pulling’ at the spiral corners, leads to the observed concave step patterns. However, interlacing cannot explain the concave step patterns in the present case, because no screw axis or glide plane is available perpendicular to the Si \( \{111\} \) plane [30]. A possible explanation is given by a preferential formation of kinks in the vicinity of the step corners as depicted in figure 2.8. This implies that the etch probability of a triple bonded Si atom at a step, \( P_{st} \), is largest near the corners of the step patterns, which is likely caused by the accumulation of reaction products conglomerating in the vicinity of two steps close together. These reaction products can thus locally increase the etch rate, in a similar way as already elaborated for the pit bottoms. At the pit bottoms three steps are joined, giving three step corners in close proximity. In this case even more reaction products accumulate than at the single step corners. This facilitates the removal of triple-bonded Si atoms at the pit bottom, which are more strongly bonded than those at the step edges [25]. As a result, point-bottomed pits develop by autocatalytic etching.

2.7 Conclusions

Alkaline etching of Si \( \{111\} \) in both pure KOH and KOH/IPA solutions leads to the formation of many etch pits. The number and shape of the pits varies strongly with concentration, temperature, presence of additive IPA and transport of KOH to and etch products from the crystal surface.

Sirtl etching showed unambiguously that these etch pits are not related to extended defects, like dislocations and stacking faults in the crystal. All the etch pits have a point-bottomed shape, which also excludes point defects from influencing the etching mechanism. The preferential etch at the pit bottoms can
be explained by an autocatalytic process, in which an increased concentration of reaction products at the pit bottoms locally enhances the vertical etch rate. This locally enhanced etching was also observed at corners of etch pits obtained after KOH / IPA etching, leading to the formation of concave etch pits.

This autocatalytic etching is highly relevant for MEMS technology, since pit formation increases the etch rate of the Si \{111\} plane and therefore strongly decreases the anisotropy ratio, \( R_{\text{Si}(100)} / R_{\text{Si}(111)} \). Elimination of this process can lead to significant improvement of the silicon wet chemical etch technique. Applying potentiostatic control during etching and choosing optimal hydrodynamic conditions (e.g. stirring and ultrasonic bath) may provide better control over this autocatalytic process.
References


Chapter 3

Wet chemical etching of silicon \{111\}: etch pit analysis by the Lichtfigur method

1 The Lichtfigur method is introduced to determine the average pit morphology of etched silicon surfaces. It is an effective method in surface analysis complementary to optical microscopy. The surface morphology of silicon \{111\} after wet chemical etching in aqueous KOH solution has been investigated by this technique. The morphology does not change significantly in pure KOH solutions as a function of time. In solutions containing additive isopropanol, however, the etch pits evolve from circular to triangular, with a final shape that depends on the isopropanol concentration. It has been experimentally proven that the IPA additive does not participate in the etching reaction and no etching occurs in the absence of water, which implies that OH\(^-\) only serves as a catalyst.

1 Published in Journal of Crystal Growth, 311 (2009), 1371.
3.1 Introduction

Anisotropic wet chemical etching of silicon crystals is an extensively used process in the manufacturing of Micro Electro Mechanical Systems (MEMS) [1]. The process is based on the significant difference in etch rate between the \( \{100\} \) and \( \{110\} \) faces vs the \( \{111\} \) faces of the silicon crystal. As a result, complex structures can be etched in a silicon crystal. This difference in etch rate between the different crystallographic orientations of silicon during etching is also known as the anisotropy ratio. It can be controlled by using a proper etchant as well as by application of a suitable additive to the etching solution [2, 3, 4, 5].

A well-known anisotropic wet chemical etching solution for silicon is aqueous potassium hydroxide (KOH). To improve applicability of wet chemical etching, it is necessary to control the process at a sub-microscopic level. Unfortunately, the current understanding of the etching process is insufficient to master the etching at such scales. Ideally, a flat surface should be obtained, but the surface is roughened by etch hillocks (pyramids), etch pits and, at a smaller scale, steps and kinks. Numerous studies have been devoted to understand and control the roughness of the fast etching \( \{100\} \) faces [6, 7]. The surface roughness of this face after etching was investigated using different purity grades of \( \text{H}_2\text{O} \) and KOH, different organic additives, such as isopropanol (IPA), or by dissolving oxygen or nitrogen gas in the etchant solution. All these parameters were found to influence the roughness strongly. Compared to Si-\( \{100\} \), the roughness of the \( \{111\} \) faces received less attention. The major source of roughness on KOH etched Si-\( \{111\} \) surfaces is the formation of shallow etch pits. From a previous study [8], we concluded that these pits are not related to crystal defects, but are probably formed by an autocatalytic process in which silicate reaction products promote downward etching at the pit bottoms.

The present study focuses on the shape of etch pits on Si-\( \{111\} \) using standard KOH solutions [9] and mixtures with IPA. Both the time evolution and the influence of IPA concentrations are studied. Optical differential interference contrast microscopy (DICM) and phase shifting interferometry (PSI) provide quantitative information on the morphology of individual pits. The drawback of these techniques, however, is the difficulty to get an average picture of an etched surface. Therefore, we applied the ‘Lichtfigur’ technique to gather information on the average shape of the etch pits. This classical optical method for mapping the distribution of slopes on a crystal surface was first introduced by Brewster in 1837 [10]. The Lichtfigur technique was intensively used for the investigation of etch pit patterns on mineral crystals in the second part of the 19th century and the first part of the 20th century, but at the present day it is somewhat
neglected. The Lichtfigur technique is based on the reflections of a parallel beam of light from a multitude of etch pits on a crystal surface. We will show that the Lichtfigur method is an effective method for determining averaged pit morphologies and is complementary to modern optical microscopic techniques, such as DICM and PSI. Using a combination of these techniques, information on the etching mechanism of alkaline etching of Si-(111) is obtained.

### 3.2 Specimen preparation and characterization

The samples with a surface area of 2 - 4 cm² were cut from p-type silicon (111) wafers (Okmetic, Cz, Boron doped, resistivity 5-10 Ω·cm, diameter 100±0.5 mm, thickness 525 ± 25 μm, miscut < 0.5°). The silicon used was as-grown and not subjected to any further heat treatment. The samples were cleaned using HNO₃ 69 % for 15 minutes to remove organic contaminants, followed by rinsing in ultrapure water. Diluted HF (5 % in H₂O) was used to remove the native oxide layer on the silicon, followed by rinse in ultrapure water. All samples were pretreated with HF to give all samples the same starting conditions. After cleaning, the samples were placed in a Teflon beaker, containing 100 ml of aqueous KOH solution or aqueous KOH solution with IPA added, which was sealed to avoid evaporation. All the samples were etched at 60°C in duplo by placing the beakers in a thermostatic bath (Heko) with an accuracy of 0.1°C. Standard aqueous KOH of 2.0 M concentration (Merck, p.a.) solutions were used. To investigate the effect of IPA, time evolution of the surface pattern was observed for both the standard solution and for solutions in which IPA (Merck, VSLI) was added at a concentration of 6.5 wt% relative to water (equal to 1 M IPA). Etching times ranged from 5 minutes to several tens of hours. To determine the influence of IPA concentration on pit shape, experiments with IPA concentrations increasing from 0% to 100% were performed. Here the etching time was kept at 20 hours for all runs.

Preparing an alkaline solution in 100 % IPA needs a special preparation, since alkali hydroxides are hygroscopic and always contain some water. For the water-free etching experiments, the solution was prepared via the reaction of potassium hydride (KH) and H₂O in IPA under formation of KOH + H₂. This preparation was done under Schlenk conditions: under constant N₂ or Ar-flow a KH oil emulsion (30 % weight, Acros), was sucked dry and washed with n-hexane several times (4 - 6 times). Isopropanol was put in a flask, and under N₂-flow, the dried KH was dissolved in IPA. After stabilization, H₂O was added to this solution in the appropriate stoichiometric ratio. To minimize any impurity effects, the solution was settled and decanted to remove any left over
solid deposits. The etching experiments (20 hours in 80 ml solution at 30°C) were performed under constant N₂-flow to prevent any water from entering the system. Two runs were carried out in duplo to investigate the influence of water: the first one using a water free solution, the second one using a solution containing 1% w/w water.

To obtain well-defined surface patterns, the etching reaction was quenched by immersion of the silicon specimens in diluted sulfuric acid (roughly 10%) for 10 minutes prior to microscopic examination. After this, the specimens were rinsed again in ultrapure water and dried in a flow of dry nitrogen.

The etch patterns obtained were examined using DICM, PSI and the Lichtfigur method. DICM and PSI were used to image and measure, respectively, the morphology of individual etch pits. The DICM used was a Zeiss Axioplan 2 microscope, the PSI used was a Wyko NT1100 white light optical profiler. Apart from mapping individual pits, DICM and PSI were also used to verify the applicability of the Lichtfigur method, as is discussed below.

### 3.3 The Lichtfigur method

#### 3.3.1 Principle and set-up

In contrast to the analysis of individual etch pits, the Lichtfigur method is ideal to study the average distribution of pit slopes. The Lichtfigur method is an old and simple technique to investigate the symmetry of crystal faces or etch pit geometry [11]. In this method a parallel beam of light is directed to a surface and the reflected beams of light are projected on a screen (see figure 3.1).

From geometrical analysis and assuming shallow inclinations, it follows that for a given position \((x,y)\) on the surface \(z(x,y)\), the reflected beams hits the screen at coordinates

\[
(X, Y) \approx -2 h \left( \frac{\partial z(x, y)}{\partial x}, \frac{\partial z(x, y)}{\partial y} \right) = -2 h \nabla z(x, y),
\]

(3.1)

with \(h\) the surface to screen distance. So, if the incident beam is one or several orders of magnitude wider than the individual surface features, a two-dimensional frequency distribution of surface slopes \(\nabla z(x, y)\) is mapped. In other words, the intensity of the light on screen position \((X, Y)\) is proportional to the number of occurrences of \(\nabla z(x, y)\) on the investigated surface. For example, if the surface is covered by well-defined triangular etch pits, with planar side walls of identical slope, only three discrete values of \(\nabla z(x, y)\) exist, which are mapped as three points on the screen. For cone-shaped, round pits a circu-
3.3 The Lichtfigur method

The Lichtfigur method

Figure 3.1: Schematic drawing of the Lichtfigur principle. The light is transmitted through a hole in the screen, reflected from the surface and then projected on the screen.

Figure 3.2: Experimental set-up used in this study.

3.3.2 Application to etched Si-(111) surfaces

The shape of the pits formed after KOH etching provides information on the mechanism of the Si-(111) etching process. The pit shapes observed range from triangular, bounded by straight steps parallel to the three symmetrically equivalent $< 2\bar{1}1 >$ directions on the Si-(111) surface, to circular and thus comply with the $3\bar{m}1$ 2D point group of the Si-(111) surface. The straight steps propagate towards the $[2\bar{1}1]$ and the two other symmetrically equivalent directions on Si-(111), i.e. are mono-hydride steps. This means that each atom in the step is triply bonded to the crystal surface and has only one dangling bond, which is saturated by a hydrogen atom [12, 13, 14]. As a measure for pit triangularity we here introduce a parameter $R_{ab} = a/b$, where $a$ is the distance, projected on the (111) plane, between the pit center and the pit edges $< 2\bar{1}1 >$,
Figure 3.2: The Lichtfigur technique is used to investigate etch pits on the etched silicon samples. (a) Laser light is reflected from the etched sample and via a beam splitter projected onto a plane. This projection is called the Lichtfigur and the resulting picture is used to determine the average etch pit geometry. (b) The experimental setup as used in the measurements.

while \( b \) represents the projection of the distance between the pit center and the pit corners opposite to the just-mentioned edges (figures 3.3 and 3.4). For shallow pits \( R_{ab} \) is inversely proportional to the slopes in the directions, i.e. \( R_{ab} = \frac{2}{\alpha} \). A circular pit has an \( R_{ab} \) of 1. For lower \( R_{ab} \) the pits are less convex, until \( R_{ab} = 0.5 \), at which value they are perfectly triangular. For \( R_{ab} < 0.5 \) the pits are concave.

Pit morphology and \( R_{ab} \) are related to each other [14], as the pit shapes observed with microscopy show a relative radius of curvature \( \kappa \), and the Licht-
3.3 The Lichtfigur method

figur analysis provides a property $R_{ab}$, which is geometrically related to $\kappa$. The relative radius of curvature of mono-hydride steps propagating in the [211] direction, $\kappa$, is defined as the ratio of the radius of steps propagating in this direction divided by their distance from the pit center (see Figure 3.3). By considering the curved step patterns or pit sides as circle segments with radius, $r_{pit}$, intersecting each other at the corner points of the pits, a geometrical analysis shows that

$$\kappa = \frac{r_{pit}}{a} = \left(2R_{ab}^2 - R_{ab}\right)^{-1}.$$  \hspace{1cm} (3.2)

Going from circular to perfectly triangular step (pit) patterns, $\kappa$ increases from 1 to $\infty$. For concave patterns $\kappa$ is negative. The dimensionless radius $\kappa$ gives information on the relative removal rate, $P_{st}$, of the triple-bonded atoms in the mono-hydride steps propagating towards the [211] directions and of the double bonded atoms at the kink positions of these steps, $P_k$. As elaborated in the previous work [14], an increased $\kappa$ indicates a larger ratio $P_k/P_{st}$. For negative $\kappa$, the 'velocity sources' induced by autocatalytic processes, operate at the vertices of the pits, locally creating additional kinks, which makes the etch pits concave in shape [8].

$R_{ab}$ can be readily obtained from the Lichtfigur pattern (see Figure 3.4), as $R_{ab} \approx \beta/\alpha = 2h\beta/2h\alpha \approx b'/a'$, for shallow pit slopes. Here $h \gg a$ and $b$ is the distance between crystal surface and projection screen, and $a'$ and $b'$ are the outer dimensions of the Lichtfigur image in the appropriate <211> and <211> directions. Figure 3.5 displays a number of observed Lichtfigur patterns for different pit shapes with different $R_{ab}$ values. If the pit slopes

![Figure 3.3: Schematic drawing of top and side view of an etch pit.](image)
are constant going from pit center to periphery and do not differ for different pits of the ensemble, the Lichtfigur pattern is expected to consist of three isolated points or circle segments. However, the continuous range of reflections embedded in the pattern indicates a range of pit slopes. Using phase shifting interferometry, the planes of the etch pits were analyzed and turned out to have constant slopes in each direction. So, the spread in the Lichtfigur pattern is mainly due to a spread in slopes of different pits. Some scattering effects may play a role as well.

3.4 Lichtfigur versus optical microscopy

To verify the applicability, merits and disadvantages of the Lichtfigur method, the $R_{ab}$ values obtained by this technique are compared with measurements by DICM and PSI. By using PSI a limited number of pits are selected and measured. By using DICM several representative pits with slightly bunched step patterns as markers are selected on each specimen crystal. As shown in figure 3.6, $R_{ab}$ can be measured straightforwardly from the bunched patterns.

In contrast to the easy and rapid Lichtfigur method, PSI is quite elaborate and only a few pits can be measured. DICM only works for pits with bunched step patterns, as the bunches are needed to measure the pit distances. Results obtained by the three methods for Si-(111) surfaces etched in KOH solutions with and without IPA added, are summarized as a function of time in figure
3.4 LICHTFIGUR VERSUS OPTICAL MICROSCOPY

![Lichtfigur patterns](image)

**Figure 3.5:** Lichtfigur patterns obtained from etch pit ensembles on etched Si-(111) surfaces. Top row: Lichtfigur images for different $R_{ab}$ values; bottom row: schematic representation of corresponding pit shapes.

![Pit curvature determination](image)

**Figure 3.6:** Determination of the pit curvature using optical microscopy. The bunches provide an accurate way to measure the relative step velocities.

3.7.

For the pure 2 M KOH solution the pits remain rounded ($R_{ab} \approx 0.85$), regardless of etching time. No significant difference in $R_{ab}$ values determined by the Lichtfigur and the PSI methods is found. The formation of circular pits is confirmed by DICM as shown in figure 3.8. In solutions with 1 M IPA added, the average value of $R_{ab}$ rapidly decreases after an initial etching period of about 250 minutes from $\approx 1$ to 0.4 - 0.5 and
Figure 3.7: Lichtfigur vs PSI and DICM measurements of $R_{ab}$ as a function of time for specimens etched in 2 M KOH solutions (left) and 2 M KOH with 1 M IPA added (right).

Figure 3.8: DICM images showing the surface morphology of Si-(111) specimens etched in 2 M KOH solutions at 60°C for 240 minutes (left) and 1080 minutes (right). In both cases only circular etch pits are visible.

then remains constant for the period that follows. This readily follows from the Lichtfigur and the DICM measurements as presented in figure 3.7. DICM micrographs displaying the change from rounded to triangular pit shape are shown in figure 3.9.

The PSI measurements show a large scatter, which indicates a considerable spread in pit shapes. The DICM and Lichtfigur measurements, based on a representative selection of individual pits and average values respectively, show close agreement. From the above it is clear that the Lichtfigur method provides a rapid and reliable way to gather information on average pit morphology.
3.5 Influence of time and IPA concentration on Si-(111) etching

Figure 3.9: DICM images of the surface morphology of Si-(111) specimens etched in 2 M KOH solutions with 1 M IPA added at 60 °C for 250 minutes (left), 1200 minutes (middle) and 2500 minutes (right). Going from left to right the etch pit shape changes from circular to triangular.

3.5 Influence of time and IPA concentration on Si-(111) etching

Figure 3.10 (left) displays the $R_{ab}$ values of Si-(111) surfaces etched at 60°C in 2 M KOH solutions with and without IPA added as a function of time. The etch pit morphology obtained in the KOH solution without IPA does not significantly alter in time. The average pit shape, $R_{ab}$, varies between 0.85 and 0.95. This corresponds to a relative step curvature $\kappa$ ranging from 1.2 to 1.7 and indicates that the relative rates of kink and step removal do not differ much. Adding IPA results in a completely different etching behavior. Starting from $R_{ab} \approx 0.95$ the triangularity drastically increases after roughly 250 minutes of etching and $R_{ab}$ attains a value of 0.4 - 0.5 after a period of 1000 minutes, which remains unaltered upon further etching.

As elucidated in reference[14], the increase of $\kappa$ upon adding IPA is explained by a large increase of the $P_k/P_{st}$ ratio, due to a decrease in the removal rate, $P_{st}$, of the step site atoms. This reduction of removal rate is attributed to the presence of an IPA enriched adsorption layer with a reduced OH\textsuperscript{-} concentration and an increased amount of reaction products. The time dependent evolution of pit shape from rounded to triangular, i.e. from $P_k/P_{st} \approx 1$ to very large, indicates that the development of such a layer needs some time before a stationary situation is obtained. The formation of a surface layer enriched with heavier reaction products is possibly promoted by the fact that the silicon samples are placed horizontally at the bottom of the Teflon beakers. Understanding and control of a time dependency of the Si-(111) etching process and the influence of IPA is highly important in the manufacturing process of MEMS devices as the anisotropy ratio, i.e. the ratio between the etch rates of {100} and {111} faces is expected to change in time as well.
Figure 3.10: $R_{ab}$ ($\kappa$) values obtained by the Lichtfigur method for etching in 2 M KOH solutions with and without 1 M IPA added (left), and $R_{ab}$ as a function of IPA concentration (right).

Figure 3.10 (right) shows the effect of adding different IPA concentrations to the 2 M KOH etching solution at 60°C. The etching time is kept at 20 hours, after which period a stationary situation is obtained.

Figure 3.11: (A) DICM image of a silicon (111) surface etched in a 2 M KOH water-free IPA solution: no etch pits are observed. (B) Same as (A), but now with 1% w/w added water: small, circular, etch pits are visible. Etching as a result of the water molecules is confirmed by a slight attack of manually introduced scratches.

Small concentrations of added IPA significantly alter the shapes of the etch pits from rounded to triangular and even concave. At an IPA concentration of 1 to 2 wt%, $R_{ab}$ rapidly decreases from 0.9 to 0.6 and goes further down to a minimum value of 0.4 at 6 wt% IPA (equal to 1 M). Then, $R_{ab}$ gradually rises again going towards a value of one for an IPA concentration of 90 wt%. In the limiting case of the IPA solution containing 1 wt% of water, very shallow, flat-bottomed circular pits are formed as shown in figure 3.11 B. This indicates
3.6 Conclusions

that the value of $R_{ab}$ goes to one for the limiting case of water-free IPA solutions. These results indicate that a thin layer of IPA on top of the hydrophobic hydrogen-terminated Si-(111) surface is easily formed, even if the concentration of the additive is small. As concluded elsewhere [14], this leads to a decrease in $P_{st}$, which results in triangular pits. For increasing IPA concentrations beyond 6 wt%, the step radius $\kappa$, and thus $P_k/P_{st}$ goes down to one. As for the highest IPA concentrations the etch rate and step velocity are very slow, this indicates that here not only $P_{st}$, but also the kink removal rate, $P_k$, decreases.

In order to determine the etch rate in the limiting case of water-free IPA solutions, etching was also performed in a specially prepared water-free solution. In this case the surface was not etched at all and no pits were formed (figure 3.11 A). This was verified by making a small scratch on the surface, which did not show any detectable change. A similar zero etch rate in the absence of water has also been reported for silicon etched in water-free ethylenediamine with pyrocatechol as additive [15]. The water-free experiment once more demonstrates the essential role of $H_2O$ in the etching process as proposed in literature [6]. The $OH^-$ ions only act as a catalyst in the reaction

$$Si - H + H_2O \overset{OH^-}{\Rightarrow} Si - OH + \frac{1}{2}H_2 \uparrow.$$  

(3.3)

This result also shows that the IPA is not reacting, so it cannot take over the role of $H_2O$ by forming $Si - O - C_3H_8$ reaction products. It only acts as a surfactant, locally altering the differences in etch rates of kink and step atoms at the surface.

3.6 Conclusions

The Lichtfigur technique is an easy and powerful optical method to gather information on the average morphology of etch pit patterns on crystal surfaces. This method, which maps the distribution of pit slopes, is complementary to DICM and PSI, which provide information on individual pits. Application of the Lichtfigur technique to KOH etched silicon-(111) surfaces showed that for standard aqueous KOH solutions the pit morphology is approximately circular and does not change with etching time. On the other hand, in KOH solutions with IPA as an additive the pit shape depends on etching time, starting from circular and going to triangular in a period of about 20 hours. Further it was shown that the pit shape is strongly influenced by IPA concentration. A few percent of IPA is sufficient to turn circular pits into trigons, which again become circular for IPA concentrations exceeding 90%. The observations are
interpreted in terms of changes in step curvature, which is determined by the relative etch rates of silicon atoms at step and kink positions. Finally, it was experimentally proven that in alkaline water-free IPA solutions no etching of silicon occurs. This demonstrates that, in contrast to water, IPA itself is not an etchant.
References


Chapter 4

Influence of additives on alkaline etching of silicon(111)

1 Apart from temperature and alkaline concentration the surface morphology of silicon surfaces after wet chemical etching is also profoundly influenced by the presence of additives in the etchant solution. In this study the influence of several organic (aprotic, protic and ionic) additives on the density and shape of etch pits on etched Si-(111) surfaces is investigated using optical microscopy and the Lichtfigur technique. For all the additives used, the number density of the pits increases by 1 to 3 orders of magnitude. The triangularity of the pit shape, expressed by a dimensionless number, $R_{ab}$, increases substantially as well. These alterations are attributed to local desolvation of reaction products by the organic additives in a thin 'surfactant' layer in the vicinity of the silicon surface. Chemisorption of additive molecules does not play a role in this process.

1 Published in Journal of Crystal Growth & Design, 9 (2009), 4315.
4.1 Introduction

The development of silicon technology for the use in modern day IC industry has lead to many applications and can be considered as a major revolution in manufacturing. Besides its electronic properties, silicon also has useful mechanical qualities, which can be exploited in Micro Electro Mechanical Systems (MEMS). Ideally, these properties can be integrated in small scale systems, such as micro sensors and Lab-on-a-Chip applications. The increasing demand for MEMS has boosted the research in the fundamentals of the wet-chemical anisotropic etching process, required to produce such devices [1, 2, 3, 4]. Like IC-technology, MEMS technology is following the same challenge of downsizing scales for small dimension applications.

An important aspect in improving process reliability is the control of the etch rate ratio of the \{100\} faces and the \{111\} faces of silicon, the latter etching significantly slower in alkaline solutions. This difference in etch rates of the two crystal orientations in silicon is exploited in manufacturing complex structures by using lithographic techniques and aqueous etchant solutions of potassium hydroxide (KOH) or Tetra Methyl Ammonium Hydroxide (TMAH). The etching of crystalline silicon at open circuit conditions (OCP) in KOH solutions is a complicated process, however the following overall reaction is generally accepted in the literature [5, 6, 7]:

\[
\text{Si} + 2 \text{H}_2\text{O} + 2 \text{OH}^- \rightarrow \text{SiO}_2\text{(OH)}_2^- + 2 \text{H}_2 \uparrow
\]  

Although the detailed mechanism is not fully understood, it is generally accepted that first \text{OH}^- attacks the Si-H surface bond under formation of \text{H}_2, followed by a subsequent step in which \text{H}_2\text{O} reacts with the subsurface bonds in which the surface atom dissolves. Understanding the reaction mechanism and the role of additives therein is of great importance in understanding the surface development during etching. For Si-(100), many investigations on the wet chemical etching process and the surface morphology obtained have been conducted [8, 9, 10]. Si-(111), however, received comparably less attention, despite the fact that its etching behavior is highly important in controlling the etch rate ratio of the two major planes, and thus the final shape of the etched structures after alkaline etching. As shown in our previous study [11], numerous shallow triangular or rounded pits are formed upon etching Si-{111} faces in aqueous KOH solutions. Defect delineation, using different dislocation etchants showed that these pits are not related to defects in the crystal. We proposed that the presence of reaction products locally increases the etch rate, resulting in the formation of point-bottomed etch pits.
4.1 Introduction

The etch rate in aqueous KOH solutions is found to be dependent on the solution and additives therein [1, 12]. The surface morphology of Si-(111) also changes under different etching conditions: additives and time have a significant influence on the pit morphology observed on the surface after etching [11]. In order to influence the silicon etching process, the use of numerous additives, like pyrocatechol and ethylene diamine [7], hydrogen peroxide [13] and etchants, like TMAH [14, 15], NH₄OH [16, 17], KOH, and hydrazine [18] have been reported in literature. One of the most commonly used additives for KOH etching is isopropanol [19]. It is often used to prevent undercutting or to produce smoother etched surfaces.

The present study focuses on the wet chemical etching of Si-(111) in standard KOH solutions and mixtures with different additives. The surfaces obtained are investigated using the Lichtfigur method and Differential Interference Contrast Microscopy (DICM), to obtain information on the average pit shape and density. First 'clean' solutions are used at different KOH concentrations and temperatures as a reference. The surface morphologies of these crystals are compared with the patterns obtained after etching in KOH solutions containing different organic additives. The choice of the additives is mainly based on miscibility with water, molecule shape and size and being ionic, protic or aprotic (see Figures 4.1 and 4.2). The results are interpreted in terms of desolvation of reaction products enhancing pit formation and physisorption or chemisorption of the additives at the crystal surface during etching.

![Non-ionic additives used in the wet chemical etching of silicon (111) in alkaline solutions.](image)

**Figure 4.1:** Non-ionic additives used in the wet chemical etching of silicon (111) in alkaline solutions.
Figure 4.2: Ionic additives used in the wet chemical etching of silicon (111) in alkaline solutions.

4.2 Experimental

4.2.1 Etching procedure

The samples investigated were cut from p-type silicon-(111) Cz wafers (Okmetic, Boron doped, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, resistivity 5-10 Ω·cm, miscut < 0.5°). The silicon used was as-grown and not subjected to any further heat treatment. Sample sizes varied between 2 and 4 cm². Prior to etching, the samples were washed with high Ohmic (ρ ~ 15 MΩ·cm) ultrapure water to remove dust, followed by cleaning in HNO₃ 69 % for 15 minutes to remove organic contaminants, followed by rinsing in ultrapure water. A dip in diluted HF (5 % in ultrapure water from 48 % HF Merck, p.a.) was used to remove the native oxide layer on the silicon, followed by a rinse in ultrapure water. Subsequently, the samples were placed in a Teflon beaker containing an aqueous KOH or KOH / IPA solution with or without additives, sealed with parafilm to avoid evaporation and etched for 20 hours in duplo by placing the beakers in a thermostatic bath with an accuracy of 0.1° C. Etching was stopped abruptly prior to microscopic and Lichtfigur examination, to obtain well-defined surface patterns. For this purpose, after separation from the etching solution, the samples were rinsed with ultrapure water and subsequently immersed in concentrated sulfuric acid (98 %) for at least 15 minutes. After this, the specimens were rinsed in ultrapure water and dried in a flow of dry nitrogen.

The etching experiments in clean KOH solutions and in solutions containing IPA additives were carried out for four different concentrations (0.1 M, 0.5 M, 2 M and 5 M KOH) and eight temperatures ranging from 30 to 90°C with 10°C intervals. The IPA concentration was kept at 1 M, which is undersaturated for all KOH concentrations used. Two different alkaline concentrations (0.5 and 5 M KOH) were used at 50°C for the additives other than IPA. These organic
4.2 Experimental

compounds (all pro-analysi), aprotic, protic as well as ionic ones, were added to the etching solution in a 1 M concentration. The ionic compounds were added as potassium salts. As reaction products are known to influence the etch pits observed on the etched Si-(111) surface, also etchant solutions were prepared in which reaction products are dissolved. This etchant was prepared by dissolving \( \approx 50\text{g/l} \) of grinded silicon to a 0.5 and 5 M KOH solution at 50°C. The solutions obtained were used in the same manner as previously described.

4.2.2 Surface Characterization

The etch pit patterns obtained were examined using Differential Interference Contrast Microscopy (DICM) in reflection mode. Using this optical method, the shallow etch pit patterns with side wall inclinations of less than one degree can be easily resolved. Using this technique, the number density of the etch pits as well as the detailed morphology of individual pits were determined. Quantitative information on the shape of a number of individual pits was obtained by optical profilometry, using a Wyko NT 1100 Phase Shifting Interferometer. To gather information on the average pit shape, the Lichtfigur method was used. The Lichtfigur technique is a simple and old technique to investigate the symmetry and slope distribution of surface patterns after crystal growth or etching [20, 21]. The set-up is schematized in figure 4.3. A parallel beam of laser light (HeNe, 10 mW, \( \lambda = 632.8\text{ nm} \), Spectra Physics Inc.), 2.5 mm in diameter, is reflected from the etched Si-(111) surface. The reflected beams are projected on a translucent screen via a beam splitter and the image obtained in this way is recorded using a digital camera. The method yields average information about the population of etch pits as the diameter of the laser beam is about 2 orders of magnitude larger than the average pit size.

For an ideal collection of trigonal pits with planar side walls of identical slope, the Lichtfigur consists of only three dots, reflecting the trigonal symmetry of the Si-(111) face. In reality, the shape of the pits ranges from rounded to triangular to concave and the slopes of different pits vary to some extent. So the actual Lichtfigur pattern is in fact an extended distribution of many ‘tiny’ reflections. To express the average pit shape in one number, we here use a shape factor \( R_{ab} \), which is explained in Chapter 3.
4.3 Results

4.3.1 KOH and KOH-IPA etching

Before carrying out the etching experiments, the influence of oxygen on the surface morphology and pit density was verified by etching under argon atmosphere. The KOH solutions were first thoroughly flushed with argon and then the silicon specimens were etched under an argon atmosphere for 20 hours at 40°C. As compared to etching under ambient conditions, no significant difference in pit density and pit shape was found for the 2 and 0.5 M KOH solutions used. Therefore, further experiments were conducted under normal, atmospheric conditions.

Typical etch patterns obtained at $T=50^\circ$C and 5 and 0.5 M KOH concentration, are displayed in figures 4.4a and 4.4b. An increase in pit density and triangularity can be recognized for the lower concentration. As reported in our previous study [11], the etch pits formed after KOH etching are not related to dislocations, stacking faults and point defects. This was confirmed once more in this study by application of Sirtl [22, ?] and Gabouze [23] defect revealing etchants to several KOH etched specimens.

Figure 4.5a shows the pit density as a function of etchant temperature and KOH concentration without additive. It can be clearly seen that the number of pits per unit surface area is minimal between 60 to 70 °C, regardless of KOH
4.3 Results

Figure 4.4: Morphology of Si-(111) etched for 20 hours at 50.0°C in aqueous KOH solutions: (a) 5 M KOH, no additives; (b) 0.5 M KOH without additives; (c) 5 M KOH with 1 M IPA; (d) 0.5 M KOH with 1 M IPA; (e) 5 M KOH with 1 M dioxane; (f) 0.5 M KOH with 1 M dioxane; (g) 5 M KOH with 1 M acetate; (h) 0.5 M KOH with 1 M acetate.
concentration. Further, the density increases several orders of magnitude upon lowering the temperature from 60 to 20 °C at higher KOH concentration or by decreasing the KOH concentration at elevated temperatures. The triangularity, expressed by a decrease of $R_{ab}$, increases largely for lower concentrations, but shows a minimum around 50°C, as presented in figure 4.6a.

![Figure 4.5](image)

**Figure 4.5:** Etch pit density at different temperatures and KOH concentrations without (left) and with 1 M IPA added to solutions (right). The numbers are powers of ten and indicate the number of pits per mm².

The effect of adding IPA to the solutions on pit density and triangularity is summarized in figures 4.5b and 4.6b. The major effect of IPA is a decrease in $R_{ab}$, that is, an increase in triangularity of pit shape, at higher temperatures. Concave shapes ($R_{ab} < 0.5$) are observed for $T > 60°C$ and $[\text{KOH}] < 4$ M. The pit density variation resembles that observed in standard KOH solution, but the average pit density is roughly 1 order of magnitude higher.

To compare differences in absolute etch rates, with and without IPA, Si-(111) specimens with thin Si₃N₄ masks were used. After etching, the height difference between masked areas and bare, etched silicon areas were measured by optical profilometry. Results, as well as measured pit slopes for 0.5 and 5 M solutions are given in Table 4.1. A more elaborate study of absolute etch rates including experimental details will be given in a forthcoming paper [24]. The data shows that at the lower alkaline concentration IPA reduces the etch rate by a factor 2.8, whereas for 5 M KOH solutions no significant difference is found.
4.3 Results

Figure 4.6: Etch pit triangularity, expressed by $R_{ab}$, at different temperatures and KOH concentrations without (left) and with 1 M IPA added to solutions (right).

Table 4.1: Absolute etch rates of Si-(111) at 60°C in 0.5 M and 5 M solutions, with and without 1 M of additive IPA. The pit triangularity $R_{ab}$ and step curvature $\kappa$ are also listed.

<table>
<thead>
<tr>
<th>KOH (M)</th>
<th>IPA (M)</th>
<th>Vert. etch rate $v_1$ (nm/min)</th>
<th>Pit slope $\alpha$ (mrad)</th>
<th>Hor. etch rate $v_{step}$ (nm/min)</th>
<th>$R_{ab}$</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>—</td>
<td>9.0 ± 0.6</td>
<td>6.3 ± 0.3</td>
<td>1400</td>
<td>0.98</td>
<td>1.06</td>
</tr>
<tr>
<td>5.0</td>
<td>1</td>
<td>8.4 ± 0.5</td>
<td>9.8 ± 0.5</td>
<td>850</td>
<td>0.87</td>
<td>1.55</td>
</tr>
<tr>
<td>0.5</td>
<td>—</td>
<td>13.2 ± 0.5</td>
<td>5.5 ± 0.3</td>
<td>2400</td>
<td>0.87</td>
<td>1.55</td>
</tr>
<tr>
<td>0.5</td>
<td>1</td>
<td>4.7 ± 0.5</td>
<td>4.7 ± 0.2</td>
<td>1000</td>
<td>0.72</td>
<td>3.16</td>
</tr>
</tbody>
</table>

4.3.2 Organic additives

Although IPA is one of the most commonly used additives in silicon etching, its effect is not unique and other additives can cause similar effects during etching. Different organic compounds, both aprotic, protic and ionic (see figures 4.1 and 4.2), were added in 1 M concentration to 0.5 and 5 M KOH etching solutions at 50°C. The results, that is, pit density and triangularity, for the various additives are presented in figures 4.7 and 4.8, respectively. Figure 4.4c-h display several DICM micrographs of the pit patterns obtained in this way. Most importantly, it can be concluded from the graphs that for all the additives applied, both the pit density and the pit triangularity show a substantial increase as compared to the pure KOH solutions. This holds for both the 0.5
and 5 M KOH solutions, the effect being somewhat stronger for the 0.5 M KOH solutions. No relation between molecular size and pit density or \( R_{ab} \) was found for the non-ionic additives. The three ionic additives suggest an increase in pit density and triangularity for increasing molecule size. Finally, the average pit density and triangularity do not differ much for the ionic and non-ionic additives. Comparing figure 4.7 and 4.8 suggests an increase of pit triangularity for higher pit densities. Plotting \( R_{ab} \) as a function of log (pit density) for all the experiments, confirms such a relation \([R_{ab} = 1.1 -0.114 \log(\text{pit density})]\), but the correlation coefficient of \( R = 0.72 \) is not high.

4.3.3 Silicon reaction products

To mimic the effect of reaction products in an alkaline etching solution, silicon was dissolved in a 0.5 and 5 M KOH solution and etching experiments were performed at 50°C. Results are shown in figures 4.7 and 4.8. It can be seen that the 'silicate' additives lead to an increase in pit density, which is similar to that for the organic additives. The pit triangularity does not show a large change, which is similar to that for the pure KOH solutions, but different from the organic additives.
4.4 Discussion

4.4.1 Pit density

In a previous paper [11], we concluded that the etch pits formed after KOH etching of silicon \{111\} result from an autocatalytic process in which an accumulation of silicate reaction products at the pit bottom locally enhances the downward etch rate. Defects in the crystal lattice are not involved in pit formation. In this study we found that the addition of organic, water-soluble compounds to the etching solution results in a large increase in pit density. This increase amounts a factor $10 - 10^3$ for the 5 M KOH solutions and $10^2 - 10^3$ for the 0.5 M KOH solutions. The increase in pit density is not introduced by differences in molecule size, proton donor capability, ionogenity or the possibility to form chemical Si-additive bonds. If so, then not all the organic compounds added would increase the pit density. Therefore, we conclude that this multiplication effect is not due to physical or chemical interaction of the additives with the substrate surface. The increase in pit density is most likely explained by an increase of the number of accumulated silicate reaction products, like silicate colloid particles [25, 26], which promote etch pit formation. This increase can be realized by adding organic additives, which lower the solubility of the silicon reaction products. Desolvation of the reaction products was confirmed by adding IPA to aqueous KOH solutions in which a considerable amount of silicon was dissolved. In contrast to the solution without IPA additive, this leads to a substantial precipitation of solid silicate products after some time. As will be elucidated in the following section, this effect is enhanced by the presence of a ‘surfactant layer’ with increased concentration of additive, which further reduces the solubility of the reaction products near the surface. The above-mentioned role of reaction products of silicon etching in promoting pit formation is confirmed by the increase of pit density if KOH solutions containing dissolved silicon are used. Although adding organic additives increases silicate product accumulations and thus etch pit density, their catalytic action in downward etching is not increased. For the 5 M solutions the vertical etch rate is not changed, for the 0.5 M KOH solutions the etch rate is decreased, which might be explained by an interaction of the additive with the crystal surface, thereby hindering the access of the reactants $\text{H}_2\text{O}$ and $\text{OH}^-$ and removal of reaction products. A decrease in overall etch rate is not necessarily in conflict with an increased number of etch pits, as pits are always formed if the accumulated reaction products introduce a local increase in etch rate at the pit bottoms. These local differences determine pit formation and not the overall, absolute etch rate.
4.4.2 Pit triangularity

The addition of organic compounds increased the triangularity of the etch pits for all the experiments carried out in this study. For pure KOH solutions at 50°C the pit shape is almost rounded, but upon adding the organic compounds they turn more faceted, bounded by steps propagating toward <112>, that is, monohydride (SM) steps [27, 28]. This indicates a change in the etching process.

![Figure 4.9](image)

**Figure 4.9**: Step and kink positions at a monohydride step on Si-(111). The rate of removal of a double backbonded atom at a kink site is $P_k$; that of a triple bonded atom at a step site is $P_{st}$. If $P_k \gg P_{st}$, the step is stripped off by successive removal of kink atoms along <101> and the step tends to be straight; if $P_k \approx P_{st}$, then the step is more or less randomly attacked and loses its tendency to straighten.

**Kinks and step curvature.**

The monohydride steps on the (111) face of silicon are bounded by triple bonded Si-atoms; the kinks on these steps involve double bonded Si-atoms. The propagation velocity of the steps and the shape of the etch pits is determined by the rates of step atom removal $P_{st}$, and kink atom removal, $P_k$ (Figure 4.9). If the ratio $P_k/P_{st}$ is high, which implies stripping of the steps by quick removal of kinks, steps tend to be straight and the observed shape of the pits is faceted. This was found in the cases of alkaline etching with additives. On the other hand, if $P_k/P_{st}$ is small, which implies a comparable removal rate of kink and step atoms, the resulting pit shape is rounded, as is observed in the case of...
pure KOH solution. In the appendix the propagation velocity of the monohydride steps, \( v_{st}(0) \), is related to the product of the step-atom and kink-atom removal rates and increases for increasing \( P_k / P_{st} \). Furthermore, the relative radius of step curvature, \( \kappa \), decreases for decreasing values of \( P_k / P_{st} \). Here \( \kappa \) is defined as the quotient of the radius of curvature of a monohydride step advancing in the \(<1\bar{1}2>\) direction and its distance from the pit center. A relation between \( \kappa \) and \( R_{ab} \) can be estimated by considering the curved pit sides as circle segments intersecting each other at the three corner points of the pits. A geometrical analysis then gives

\[
\kappa \approx (2R_{ab}^2 - R_{ab})^{-1}
\]

that is, the relative step radius and thus the ratio \( P_k / P_{st} \) decreases for increasing \( R_{ab} \). As follows from figure 4.7, adding the organic compounds leads to a decrease in \( R_{ab} \) as compared to ‘clean’ KOH solutions. This implies a decrease of \( \kappa \) and thus an increase of \( P_k / P_{st} \) in all cases, but no conclusion can be drawn whether this is due to an increase of \( P_k \) or to a decrease in \( P_{st} \). For 1 M IPA as an additive the step velocity is reduced and \( \kappa \) is increased for both the 5 and 0.5 M KOH solutions (see table 4.1). From this it follows that

\[
\frac{v_{st}}{v_{st}^{\text{clean}}} < 1 \quad \Rightarrow \quad \frac{P_{st}^{\text{IPA}}}{P_{st}^{\text{clean}}} \cdot \frac{P_k^{\text{IPA}}}{P_k^{\text{clean}}} < 1
\]

and

\[
\frac{\kappa^{\text{IPA}}}{\kappa^{\text{clean}}} > 1 \quad \Rightarrow \quad \frac{P_k^{\text{IPA}} / P_{st}^{\text{IPA}}}{P_k^{\text{clean}} / P_{st}^{\text{clean}}} > 1
\]

so that \( P_{st}^{\text{IPA}} < P_{st}^{\text{clean}} \). This means that adding IPA to the KOH solution reduces the nucleation rate of kinks, which occurs by removal of triple bonded Si-atoms from the \(<1\bar{1}2>\) steps. Unfortunately, no conclusion can be drawn with regard to the relative rates of kink removal.

The role of additives.

The question that now arises is how do the additives affect step velocity and pit shape? A possible explanation involves chemical bonding of the additives to the crystal surface, for instance, by the formation of Si-O bonds in the case of IPA [19]. This would block surface positions and retard chemical etching. This mechanism might hold for alcohols, but other, including aprotic, organic compounds show similar morphologic effects on pit shape, but are not capable of forming covalent bonds with
the silicon substrate. After etching using clean and IPA-containing KOH solutions, in all cases the silicon surfaces were water repellent, that is, hydrophobic. This points to a hydrogen terminated surface, though an IPA-terminated surface cannot be ruled out. In the latter case a Si-O bond is formed and the hydrophobic part of the molecule points away from the surface. Therefore, an additional experiment was carried out, using 1 M ethylene-glycol as an additive. This will have similar bonding as IPA. After etching in both 0.5 and 5 M KOH solutions the surface was again water repelling. This indicates that this molecule is not chemically bonded to the surface, as in that case one of the two OH-groups would be pointing away from the surface making it hydrophilic. Forming a bridged structure of Si – O – CH₂ – CH₂ – O – Si, which might be water repelling is very unlikely as the distance between adjacent silicon atoms on the (111) surface with free bonds is 3.80 Å, whereas the separation of the two oxygen molecules in glycol is 2.42 Å. This observation confirms our conclusion that chemical bonding to the substrate surface does not explain the effect of organic additives in KOH etching of Si-(111).

The above observation of hydrophobicity also indicates that during etching the Si surface is mainly hydrogen terminated. This agrees with the generally accepted reaction mechanism in reference [2] and in Figure 4.10, reaction I. Only the few atoms at the step and kink position are temporarily -OH terminated, which only occurs at the moment they are etched away. This is much less than 1% of the total number of surface atoms. After removal of these atoms, the neighboring Si atoms are hydrogen terminated again.

An alternative, more likely explanation is preferential physisorption of additive molecules on the Si-(111) surface. As the Si-(111) surface is hydrogen terminated during etching and thus is hydrophobic, it is expected that the organic additive molecules, which have a weaker polarity than the water molecules, are preferentially adsorbed on the surface. This lowers the (Si-H)-solution interfacial energy, because the surface free energy of water (72 mJ/m²) is considerably higher than that of the additives used (23 - 57 mJ/m²). As a consequence, the concentration of additive in the first few molecular layers on top of the surface is considerably higher than in the bulk phase. In this 'surfactant' layer the concentration of H₂O and OH⁻ is substantially less than in the bulk solution. In addition, the solubility of the reaction products in this layer is largely decreased due to an anti-solvent effect. All this largely changes the conditions for etching
and slows down etch rates, increases pit triangularity and pit densities, in a similar way as observed for the solutions with low OH\(^{-}\) concentration.

### 4.4.3 Silicate Chemistry

From this study and previous work \[11\], it is concluded that the formation of pits on Si-(111) after KOH etching is induced by an autocatalytic process, in which an accumulation of reaction products at the bottom locally enhances downward etching. Most likely these reaction products involve silicate clusters \[25, 26\], which easily form by polymerization in the alkaline etchant solutions \[29\], a process enhanced by the presence of metal impurities in the solution \[30\] or at lower alkaline concentrations.

![Figure 4.10: Chemical dissolution of silicon in KOH solutions. Reaction scheme I: Mechanism in absence of silicate reaction products; Reaction scheme II: Possible reaction paths in the presence of silicate reaction products.](image)

Reaction scheme I in figure 4.10 shows the generally accepted reaction mechanism of the chemical dissolution of silicon in KOH solution. In this process the surface Si-H bond and the Si-Si back-bonds are subsequently broken by OH\(^{-}\) and H\(_2\)O molecules and replaced by Si-OH bonds, leading to silicate reaction products entering the solution. In the presence of silicate reaction products, which possess OH-groups, the role of the H\(_2\)O and OH\(^{-}\) can be (partially) taken over by the silicates, as summarized in reaction scheme II. Considering this mechanism a multitude of etching possibilities come into existence, one or several of which can lead to the formation of polymerized silicate clusters which enhance the downward
etching at the pit bottoms. In this model an increased amount of silicate particles does not necessarily increase the downward etch rate, but only increases the number of etch pits, as more aggregates act in parallel as observed experimentally.

### 4.5 Conclusions

Wet-chemical etching of Si-(111) in aqueous KOH solutions depends on both KOH concentration and temperature, resulting in a significant influence on surface morphology. In all cases, shallow, point-bottomed etch pits are formed. The density and triangularity of the pits, as measured by the Lichtfigur technique and optical microscopy, show a minimum around 50-60°C and tend to increase for lower KOH concentrations. Adding Isopropanol or other organic compounds to the caustic etchant solutions affects the surface morphology as well: in all cases the pit density and pit triangularity increase as compared to ‘clean’ solutions applied at the same conditions. The additives used never lead to smooth surfaces free from pits.

The increase in pit density at lower temperatures and KOH concentrations as well as by adding the organic compounds is explained by a decrease in solubility of silicate reaction products. This leads to an increased amount of accumulated reaction products at the crystal surface, which locally catalyzes vertical etching and thus promotes etch pit formation.

The observed increase of triangularity of the etch pits is a consequence of an increased ratio of removal rates of silicon atoms at kink and step positions. As all the additives used, regardless of being ionic, protic or aprotic, show a similar behavior, it is concluded that their influence on this ratio is not due to chemisorption. We presume that due to preferential physisorption of the organic additives on the hydrophobic monohydride Si-(111) surface a thin ‘surfactant’ layer with a reduced content of water forms during etching. As a result of reduced solvation, the OH⁻ concentration is lower in this surface layer as compared to the bulk solution and the silicate reaction products are hindered to dissolve in the etching solution. This leads to the observed increase in pit triangularity and pit density.
4.5 Conclusions

Appendix

The propagation of steps during etching proceeds by the removal of atoms at step positions followed by a subsequent removal of atoms at the kink positions as depicted in Figure 11. For a monohydride step on \{111\} Si the probability (rate) of removal of a triple bonded atom from a step position is \( P_{st} \), and that of a double bounded atom at a kink position is \( P_k \). The propagation velocity as well as the curvature of a step is determined by \( P_{st} \) and \( P_k \). It is shown in ref [31] that the velocity of a monohydride step propagating at an angle \( \theta \) from the exact <112> direction is given by (eq 19 in ref [31])

\[
v_{st}(\theta) = d \sqrt{\left(\frac{2}{3}\right)^3 \left(P_k \sin \frac{3\theta}{2}\right)^2 + P_{st} \cdot P_k},
\]

where \( d \) is the distance between two nearest neighbor silicon atoms. For a monohydride step advancing in the exact <112> direction (\( \theta = 0 \)), the velocity equals

\[
v_{st}(0) = d \sqrt{P_{st} \cdot P_k}
\]

The radius of the curvature of a step in this direction is given by the stiffness [32]

\[
r(t) = v_{st}(0) \cdot t + \frac{d^2 v_{st}(\theta) \cdot t}{d\theta^2} |_{\theta \to 0}
\]

where \( t \) is the time elapsed since the step nucleated at the pit bottom. The relative radius of step curvature is given by

\[
\kappa(r) = \kappa = \frac{r(t)}{v_{st}(0) \cdot t} = 1 + \frac{1}{v_{st}(0)} \cdot \frac{d^2 v_{st}(\theta)}{d\theta^2} |_{\theta \to 0}
\]

or by using equation 4.5

\[
\kappa = 1 + \frac{2 P_k}{3 P_{st}}
\]

In view of the approximation made in deriving equation 4.5 [31], the above expressions for \( v_{st}(0) \) and \( \kappa \) do not hold if \( P_k/P_{st} \) is close to one. However, despite this limitation also here \( v_{st}(0) \) and \( \kappa \) still increase with increasing \( P_k/P_{st} \) and \( P_k/P_{st} \) values, respectively.
References


REFERENCES

Chapter 5

X-Ray analysis of the silicon (111) surface during alkaline etching

\(^1\) We present a surface X-Ray diffraction determination of the silicon (111)-liquid interface structure. Using diluted aqueous potassium hydroxide (KOH) and ammonium fluoride \(\text{NH}_4\text{F}\) etchant we have observed that the crystal surface is hydrogen terminated and is not reconstructed at open circuit potential. Our results show distinct differences in crystal structure and significant differences in crystal morphology for different electrochemically applied potentials. We have determined that partial liquid ordering of water on the crystal surface is observed at open circuit potential and we have in-situ observed the growth of the oxide layer by birth and spread.

\(^1\)Accepted for Publication in Surface Science (2011).
5.1 Introduction

Aqueous Potassium Hydroxide (KOH) and Ammonium Fluoride (NH₄F) solutions are commonly used as etching solutions in wet chemical anisotropic etching of silicon, a widely used bulk technique in the manufacturing of Micro Electro Mechanical Systems (MEMS) [1, 2]. In terms of chemical and electrochemical reaction mechanisms, the etching process appears to be well understood, [3, 4, 5, 6]. The simplicity of the overall reaction, however, masks the complicated etching mechanism and the solid-liquid interactions at the surface involved. Understanding the fundamental way in which the silicon {111} surface etches is of high importance in understanding and influencing the aspect ratio of etching different crystallographic planes of silicon, the basis of MEMS manufacturing.

Several studies have discussed the surface termination during alkaline wet chemical etching [7, 8, 9, 10] and all conclude a H-terminated silicon surface, representing bulk termination. A variety of studies has been conducted to investigate the dynamic changes during etching [9, 11, 12] and the role of surface preparation. As a result, several reaction mechanisms are proposed, which comprise comparable reaction steps. More recently, experiments were performed to further investigate the surfaces under electrochemical etching conditions [5, 6]. These researches were conducted to study the dynamic changes during etching, e.g. by using voltammetry, spectroscopy or optical methods. Although these methods have been used extensively, the resulting information on the interface structure is only derived indirectly. Therefore, the most suitable in-situ techniques are scanning probe microscopy and surface X-ray diffraction. Observing the surface with Atomic Force Microscopy (AFM) and Scanning Tunneling Microscopy (STM) provides interesting and detailed information on small areas [7, 13]. On the contrary, the surface X-Ray diffraction technique provides direct information on large sample areas.

The aim of this study is to gather information on both surface structure as well as its interaction with the etchant liquid on top of the silicon surface under etching conditions. This is helpful in obtaining a microscopic picture of surface events during etching. Surface X-Ray Diffraction (SXRD) is a very suitable technique for studying the solid-liquid interface of the silicon in the alkaline etchant. Therefore we present an in-situ SXRD investigation of the silicon-etchant interface under electrochemically controlled conditions. This research focuses on the solid-liquid interface of
5.2 Experimental Procedure

In order to perform in-situ Surface X-Ray Diffraction on this system, the surface has to be clean and smooth at an atomic level and etching needs to proceed slowly to avoid kinetic roughening during measurements. In addition, the electrochemical potential of the sample needs to be controlled in order to avoid rapid roughening by etching through the electrochemical pathway. Subtle changes in sample preparation can have detrimental effects on the obtained surface quality and therefore an extensive investigation was undertaken to obtain the best recipe for atomically smooth surfaces and the best type of cell to be used.

5.2.1 Sample Cell

The purpose of the sample cell is to observe the surface structure by X-rays during etching. A reflection geometry with a thin liquid film is not suitable and therefore a transmission geometry was chosen. At the same time radiation absorbance should be minimized when using the cell. All the materials used in the sample cell need to be inert to the chemicals used during the experiments. From these main requirements a cell was designed and constructed as shown in figure 5.1.

In designing the in-situ cell, the sample surface was chosen to be above all other cell parts, as in this way the incoming X-rays arriving at very low angles are not blocked. The cap was made of poly(methyl methacrylate) (PMMA) with a thickness of 1 mm, as this has the lowest absorbance of X-rays in the energy range used and of the suitable materials available. PMMA allows the tubing to be designed with minimum thickness, while keeping optimal mechanical strength. The other parts of the cell were made from standard laboratory glassware as these are easily available and quickly cleaned or replaced. Another consideration taken into account was the ease of filling and replacing the cell with different solutions before and during experiments.

The sample holder on which the silicon sample was mounted was made...
Figure 5.1: Schematic drawing of the silicon sample in the cell and a photograph of the set-up mounted on the diffractometer of ID03 at the ESRF.

out of Kel-F. The choice for this material was based on its high mechanical strength in combination with its ease of shaping and chemical inertness. To create a back contact with the working electrode, the silicon sample was
5.2 Experimental Procedure

scratched from the backside and cleaned with Piranha Acid for 10 minutes to remove any organic contaminants and consecutively rinsed 10 times with ultrapure water and blown dry in a stream of argon. Ga-In eutectic was applied to part of the silicon backside and the sample was glued to the copper back contact on the remaining part using a two component epoxy resin. Experiments showed that a direct contact between glue and etching solution leads to additional roughness and therefore in the optimum design a viton O-ring is mounted on the silicon sample to seal the sample. This assembly is then placed in a Kel-F sample holder and tightened with a nut from the back side to assure a leak-proof connection. The connection was tested for conductivity in a saturated KCl solution, after which the sample was rinsed 10 times with ultrapure water. All connections in the cell were sealed with silicone and viton O-rings (see figures 5.1 and 5.2).

Eventually, to obtain a well-defined initial surface for surface diffraction, the silicon sample was immersed in an NH₄F solution. This extremely anisotropic etchant is known to give ultra-flat silicon(111) surfaces, given the condition that the solution is oxygen-free and the sample is ‘cathodically protected’ by a sacrificial anodic area [7, 12, 14, 15, 16, 17, 18]. To create such a sacrificial area, the silicon samples were connected to a Cu mount in such a way that the sample sides remain in free contact with the solution as can be seen in figure 5.2 and thus provide the cathodic protection, in accordance with ATR and FTIR measurements [5]. Experimentally, X-Ray photons can excite electrons into the conduction band and introduce a photocurrent through the electrochemical pathway [4, 5]. This leads to significant etching and creates surface roughness that hinders the measurement of proper diffraction rods. Specifically on n-type material this effect is observed and preliminary experiments confirmed these observations. To avoid this, full electrochemical control is necessary and p-type material has to be used. A cathodic potential (-1.3V) is applied and low etchant concentrations are chosen. To avoid influence of photocurrents induced by normal light, all experiments were performed in the dark by fully covering the cell with thin aluminium foil, to minimize blockage of the X-rays. The Cu working electrode is joined with a Pt counter electrode and Saturated Calomel Electrode (SCE) reference electrode in an electrochemical setup in which a potentiostat is used for electrochemical control. The Pt and SCE electrodes are placed in the designated positions of the in-situ cell. The electrodes are connected with the potentiostat, first the reference, then the counter and finally the work-
Figure 5.2: Schematic drawing of the sample cell used for the X-ray diffraction experiments: (a) overview; (b) detail showing the Kel-F sample holder with the silicon crystal mounted on top. The sides of the silicon crystal are unprotected and serve as a sacrificial area promoting oxide removal and formation of stepped terraces. The total height of the cell is approximately 15 cm.

ing electrode. The potentiostat (PalmSens) is set on a cathodic potential applied to the silicon sample before filling the cell with etchant solution, to avoid surface roughening due to the initial etching of the surface. The experiments were performed at room temperature and during etching the current was measured using the potentiostat.

Hexagonal shaped p-type silicon (111) samples, with 6.8 mm diameter and cut from p-type silicon (111) wafers (Okmetic, Boron doped, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, resistivity 5-10 Ω·cm, miscut < 0.5°) were used. The hexagonal shape of the silicon fits best with the shape of the used o-rings and thus a leak tight sealing of the sample back contact is achieved. The silicon used was as-grown and underwent several cleaning steps to reduce the impact of any organic or metal impurities. This was followed by extensive rinsing in ultrapure water and drying under argon atmosphere.

In comparison to other cell setups [19, 20], the simplicity of use, easy replacement of parts and the possibility to follow the surface structure before and after filling the solution in the cell, proved this cell to be versatile. The sample could be aligned before surface preparation and etching commenced, but at the cost of a lower signal-to-noise ratio due to the
extra liquid surrounding the sample.

5.2.2 Pretreatment

As silicon oxidizes when exposed to air or oxidizing solutions, it is always covered by a thin oxide surface layer. The underlying (111) surface is rough. Therefore, preparing atomically smooth surfaces is very difficult. To start with, everything has to be ultra clean and all contamination has to be removed. Therefore all handling equipment was rinsed 10 times with ultrapure water, followed by a cleaning step with Piranha Acid (98% H$_2$SO$_4$ : 35% H$_2$O$_2$ 3 : 1), and again rinsed 10 times with ultra pure water.

To minimize the presence of oxygen and thus limit the possibility of uncontrolled surface oxidation, extra effort was taken to remove oxygen from the solutions. In a cleaned Kel-F vial Ammonium Fluoride (NH$_4$F) etchant solutions were bubbled with Argon for at least 10 minutes, then some ammonium sulfite crystals were added to the fluoride solution and the Teflon vial is closed and left for 5 minutes, to deoxygenate the etchant solution [14, 15, 16] and settle the ammonium sulfate crystals. The aqueous KOH solution is degassed with Argon for 30 minutes to purge oxygen from the etchant solution.

The Kel-F sample holder with Si-(111) sample is mounted onto the base of the in-situ cell. The in-situ cell is then closed by placing the covering tube on the cell base. Subsequently the cell is flushed with argon for 10 minutes and mounted onto the diffractometer stage. Then the cell is filled with the prepared etchant solution.

5.2.3 Surface X-Ray Diffraction

The surface X-ray diffraction technique (SXRD) is very useful for the structure determination of the interface between a crystal surface and solution [21]. In SXRD, diffracted X-ray intensities along so-called crystal truncation rods are measured [22]. These rods are tails of diffuse intensity connecting the bulk Bragg peaks in the direction perpendicular to the surface. Their exact shape is determined by the atomic structure of the solid-liquid interface.

In the setup used (see figure 5.1), the silicon crystals can be completely surrounded by bulk etchant solution, but ambient air conditions are also possible. The experiments were performed at the DUBBLE,
ID03 and ID32 beam lines of the European Synchrotron Radiation Facility (ESRF) (see figure 5.3) in Grenoble, using an X-Ray energy of 20 keV, as lower X-ray energies do not sufficiently penetrate the liquid layer surrounding the samples, while higher energies give less intensity and inconveniently small scattering angles.

Figure 5.3: The European Synchrotron Radiation Facility in Grenoble.

The sample cell is coupled to a (2+3) diffractometer [23] operating in a vertical geometry in case of the DUBBLE beamline and to a horizontal Z-Axis diffractometer [24] in case of ID32 and ID03. In order to describe the silicon (111) surface lattice and to index the X-Ray reflections, we use a (111) surface unit cell. The lattice vectors of this cell are expressed in terms of the conventional cubic lattice vectors.

\[
\mathbf{a}_1 = \frac{1}{2}[\overline{1}0\overline{1}]_{\text{cubic}}, \quad \mathbf{a}_2 = \frac{1}{2}[\overline{1}10]_{\text{cubic}}, \quad \mathbf{a}_3 = [111]_{\text{cubic}},
\]

with

\[
|\mathbf{a}_1| = |\mathbf{a}_2| = \frac{1}{2}\sqrt{2a}, \quad |\mathbf{a}_3| = \sqrt{3}a.
\]
where $a = 0.5431$ nm is the lattice constant of silicon. The correspond-
ing reciprocal lattice vectors are defined by $a_i \cdot b_j = 2\pi \delta_{ij}$. The momentum
transfer vector is given by $Q = h b_1 + k b_2 + l b_3$, with $(hkl)$ the diffraction
indices. With our choice of the the surface unit cell the index $l$ corre-
sponds to the direction perpendicular to the surface. Rocking scans were
used to measure the integrated intensities of the $(hkl)$ reflections. They are
converted into structure factor amplitudes by applying the appropriate ge-
ometrical and resolution corrections [25]. This correction procedure puts
all rods on the same relative scale, except for the specular data. The neg-
ative values for diffraction index $l$ are obtained by inverting the structure
factors according to Friedel’s rule. The parameters describing the different
models are fitted to experimental structure factors using a $\chi^2$ minimiza-
tion. Surface roughness is characterized by the root-mean-square (rms)
roughness as derived from a Poisson model, as this was found to give the
best results [26]. Model calculations and fitting are done using the ROD
program [27].

5.3 Results & Discussion

5.3.1 Optimization of the Preparation Method

The preparation of a silicon sample surface for surface X-ray diffraction
can routinely be done in an ultrahigh vacuum environment, but is diffi-
cult under wet-chemical etching conditions. As will be described below we
tested several process steps and sequences of processing steps. Each sam-
ple starts with the roughness of the native oxide. Ideally, etching should
remove this roughness by having a fast rate at surface steps and a very low
one at terraces. At the same time, prolonged etching will always increase
the roughness by hole nucleation at the terraces, also known as kinetic
roughening. So a balance between oxide removal and surface roughness
has to be achieved. We learned that KOH concentrations above $10^{-2}$ M
gave rapid kinetic roughening, and thus we used in most cases $10^{-3}$ M
KOH solutions.

Several etching solutions were used to remove the oxide layer: 5% HF,
buffered HF (7%)/NH$_4$F (40%) and NH$_4$F in concentrations between 2
and 40%. In all cases the oxide layer was removed effectively. We deter-
mined the resulting surface roughness by measuring the (10) rod in-situ.
A Poisson roughness model gave the best fits to these data. The root-
mean-square (rms) roughness is used as the roughness parameter. The effect of roughness on the crystal truncation rod intensity can be seen in figure 5.4 where the (10) rod is depicted for different roughnesses. When the surface is perfectly smooth (rms = 0), the truncation rod intensity decreases slowest from the Bragg peak and the full crystal truncation rod can be measured. We were unable to achieve such zero roughness, but as figure 5.4 shows, improving from 3.1 to 2.2 Å makes a large difference. For 2.2 Å the entire rod can be measured, for 3.1 Å only the parts close to the Bragg peaks.

![Figure 5.4](image)

**Figure 5.4:** Measured data (solid squares) are from the (10) rod of silicon(111) under NH₄F etching conditions. This corresponds to a roughness of 2.2 Å, as determined from the fit (dashed curve). To illustrate the effect of roughness on the rod profile, two additional calculations are shown: zero roughness and a rms roughness of 3.1 Å.

In order to determine the starting roughness the (10) rod was measured for silicon samples with native oxide. An average roughness of 3.1 Å was found. Figure 5.5 shows one data set together with two fits: one for an oxygen and one for a hydrogen terminated surface. As expected, the oxygen termination gives a better result, but the roughness makes a precise structure determination impossible.

Different approaches were tried to achieve minimum surface roughness. The first routes comprised of full sample surface preparation under *ex-situ*
5.3 Results & Discussion

Figure 5.5: The (10) rod of a silicon sample with native oxide on top. Two fits are shown: one with an oxygen and one with a hydrogen atom connected to the topmost silicon atom.

conditions. The sample cleaning was performed in a fumehood under local argon atmosphere and after cleaning and removal of the oxide layer using a 5% HF solution, the sample was built in the cell under Argon atmosphere and transported to the experimental hutch, where it was mounted on the diffractometer stage. After mounting the sample cell, it was crystallographically aligned and the surface roughness was measured. Next, the cell was filled with a $10^{-3}$ M KOH solution, which was beforehand bubbled with argon to expel oxygen. Etching commenced and collection of the crystal truncation rod data was started. The use of 5% HF yielded unsatisfactory results. The roughness achieved by this cleaning strategy was 3.1 Å at best, however on average a roughness of 3.5 Å was obtained, as can be seen in Table 5.1. As the oxygen in the solution is not completely expelled, and HF is an isotropic etchant, the cleaned surface is likely to either re-oxidize or remains atomically rough.

In order to replace the HF with a more anisotropic oxide removing solution, the combination of HF/NH$_4$F solution was tested, as the pres-
ence of extra ammonium fluoride in solution could decrease the surface roughness. However, this was not the case. The oxide layer is completely removed, but the obtained surface is atomically very rough (rms 6 Å). The origin of this roughness lies again in the isotropic etch nature of the HF, randomly attacking the oxide surface.

Next we tried using NH$_4$F instead of HF. The sample was prepared under a fumehood with a 40% NH$_4$F solution and transported to the diffractometer for mounting, followed by filling of the cell with KOH solution. This gave better results, but a lack of reproducibility was observed in the obtained surface roughness that ranged from 2.8 to 3.4 Å (see Table 5.1).

To test the influence of oxygen during silicon oxide removal, a degassed 5 M KOH solution was used to remove the oxide in-situ. The oxide removal was followed using X-ray diffraction. The structure factor is a measure for the crystal structure and roughness. In this case, the (1 0 0.5) peak was used as its collection time was fast enough to monitor structural changes. As figure 5.6 shows, initially the intensity is constant because the interface is still underneath a thinning oxide layer. When the interface is reached, the roughness increases as seen by a drop in intensity. The surface becomes smoother after oxide removal. However, on a somewhat longer timescale the surface roughness increases due to kinetic roughening caused by the high KOH concentration in the solution. This kinetic roughening was also observed in several experiments with less concentrated KOH solutions. A roughness of 3.3 Å is determined in this case.

After learning the difficulty of achieving a smooth surface and the sensitivity of the etching process, we took a critical look at the various steps and made several improvements:

1. The presence of epoxy glue in contact with the etching solution pollutes the solution, as observed by chromatography. We, therefore, used an o-ring to avoid contact between epoxy and solution. The o-ring mount has the added advantage that the side faces of the sample are in full contact with the solution and act as a sacrificial anodic area for the top surface.

2. HF leads to larger roughness after oxide removal than NH$_4$F and thus only NH$_4$F is used for oxide etching.

3. Oxygen should be completely avoided, and thus we abandoned the
5.3 Results & Discussion

Figure 5.6: In situ observation of the structure factor of the (1 0 0.5) surface sensitive reflection during surface preparation in 5 M KOH solution. The structure changes from a relatively rough oxide terminated surface into a smoother hydrogen terminated surface through an intermediate rougher state.

The improved preparation procedure starts with a full cleaning of the silicon sample, attaching the sample to the sample holder and creating a back contact. Then the sample holder is mounted in the cell, using a viton o-ring to achieve a leak tight connection of the silicon back contact. The sample holder is then placed in the cell. The cell is connected to the potentiostat. The etching is controlled by applying a potential that is negative (-1.3 V) towards the open circuit potential to minimize roughening resulting from electrochemically induced etching. This method is described as cathodically protecting the surface [28]. The sides of the silicon sample provide the same functionality, as their crystal orientations are more prone to etching compared to the (111) orientation, creating galvanic protection. After this the cell is closed and mounted on the diffractometer, followed by alignment of the crystal. The aligned sample is then measured for the

ex-situ approach. The NH₄F etchant is thoroughly degassed using argon bubbling and ammonium sulfite [14] is used to effectively bind the remaining oxygen in a full in-situ preparation under argon.


**Table 5.1:** Overview of surface roughness after different preparation conditions. During sample preparation the applied electrochemical potential was kept at -1.3V.

<table>
<thead>
<tr>
<th>Connection</th>
<th>Time (min)</th>
<th>Pretreatment (M)</th>
<th>measuring condition</th>
<th>Roughness Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>epoxy</td>
<td>15 (s)</td>
<td>none</td>
<td>native oxide</td>
<td>3.1</td>
</tr>
<tr>
<td>epoxy</td>
<td>45 (s)</td>
<td>5% HF</td>
<td>10⁻³ M KOH</td>
<td>3.5</td>
</tr>
<tr>
<td>epoxy</td>
<td>15</td>
<td>40% NH₄F/HF</td>
<td>10⁻³ M KOH</td>
<td>6.1</td>
</tr>
<tr>
<td>epoxy</td>
<td>40</td>
<td>40% NH₄F/HF</td>
<td>10⁻³ M KOH</td>
<td>6.6</td>
</tr>
<tr>
<td>epoxy</td>
<td>3.5</td>
<td>40% NH₄F</td>
<td>10⁻³ M KOH</td>
<td>3.4</td>
</tr>
<tr>
<td>epoxy</td>
<td>5</td>
<td>40% NH₄F</td>
<td>10⁻³ M KOH</td>
<td>3.0</td>
</tr>
<tr>
<td>epoxy</td>
<td>15</td>
<td>40% NH₄F</td>
<td>10⁻³ M KOH</td>
<td>2.8</td>
</tr>
<tr>
<td>epoxy</td>
<td>30</td>
<td>40% NH₄F</td>
<td>10⁻³ M KOH</td>
<td>2.9</td>
</tr>
<tr>
<td>epoxy</td>
<td>60</td>
<td>40% NH₄F</td>
<td>10⁻³ M KOH</td>
<td>3.0</td>
</tr>
<tr>
<td>o-ring</td>
<td>25</td>
<td>none</td>
<td>5 M KOH</td>
<td>3.3</td>
</tr>
<tr>
<td>o-ring</td>
<td>28</td>
<td>none</td>
<td>4% NH₄F</td>
<td>2.6</td>
</tr>
<tr>
<td>o-ring</td>
<td>63</td>
<td>none</td>
<td>4% NH₄F</td>
<td>2.3</td>
</tr>
<tr>
<td>o-ring</td>
<td>17</td>
<td>none</td>
<td>8% NH₄F</td>
<td>2.2</td>
</tr>
<tr>
<td>o-ring</td>
<td>15</td>
<td>none</td>
<td>40% NH₄F</td>
<td>2.5</td>
</tr>
<tr>
<td>o-ring</td>
<td>40</td>
<td>none</td>
<td>8% NH₄F/H₂O</td>
<td>2.1</td>
</tr>
<tr>
<td>o-ring</td>
<td>40</td>
<td>8% NH₄F/H₂O</td>
<td>10⁻³ M KOH</td>
<td>n.a.</td>
</tr>
<tr>
<td>o-ring</td>
<td>40</td>
<td>none</td>
<td>8% NH₄F/H₂O</td>
<td>2.5</td>
</tr>
<tr>
<td>o-ring</td>
<td>40</td>
<td>8% NH₄F/H₂O</td>
<td>10⁻³ M KOH</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Initial oxide roughness and then the cell can be filled with NH₄F etching solution to start the oxide removal.

In order to see if there is an optimum etching time in NH₄F, we observed the oxide removal and subsequent etching *in-situ* after filling the cell with etchant solution. Also here the (0 -1 0.5) reflection was used. As figure 5.7 shows, initially the intensity is constant because the interface is still underneath a thinning oxide layer. When the interface is reached, the roughness increases as seen by a drop in intensity. Subsequently, the interface becomes smoother, a process that takes about 15 minutes for a
2.16 M (i.e. wt8%) NH₄F solution. This procedure finally yields the desired result, because the surface roughness is now sufficiently reduced (rms = 2.1 Å) to measure full crystal truncation rods. The resulting surface was then used as the starting point for measuring full crystal truncation rods in the NH₄F solution. The available measurement time of the etching process increases with decreasing NH₄F concentration and the optimum NH₄F concentration was chosen 8%, as oxide removal and surface preparation were less controllable at lower concentration and kinetic roughening increased at higher concentrations, hindering the effective data collection.

To compare the etching properties of the NH₄F solution and KOH solution, a sample was prepared in-situ in 2.16 M NH₄F solution, flushed with H₂O that was subsequently replaced with KOH solution. For all three conditions the roughness was determined. The prepared surface has a roughness of 2.5 Å. Replacing the NH₄F etchant with water, increases the roughness, but the introduction of KOH reduces it again. On this sample a data set in KOH was collected.
5.3.2 Surface termination

The interface structure of Si-(111) was measured in-situ in 2.16 M NH₄F as well as in 10⁻³ M KOH solution under an applied potential of -1.3 V. For both environmental conditions more than 50 non-equivalent reflections were measured on two different samples. The agreement factors are 12% in both cases, when averaged over equivalent reflections for the specimens used in each type of experiment [29]. The data set consists of the (00) and (10) rods for the KOH solution and the (00), (10) and (20) rods for the NH₄F solution. The specular, or (00), rod provides information about the electron density perpendicular to the surface, whereas the two other rods are sensitive to in-plane ordering as well. We focus first on the crystal surface termination and therefore ignore the specular rod, which is the most sensitive to the liquid structure at the interface.

The results for etching in NH₄F solution are shown in figure 5.8. Having only a limited data set, we start with a simple model to fit the data in which a bulk-terminated crystal has either O or H on top. The (10) and (20) rods were fitted simultaneously, using a scale factor and the roughness as fitting parameters. The Si Debye-Waller parameter is fixed at 0.5 Å². The $\chi^2$ of the model is 1.41 for a hydrogen on top and 4.27 for oxygen, which is a strong confirmation of the expected H-termination (see Table 5.2). As a next step, we added a relaxation of the topmost Si layer. Such a relaxation will result in smaller relaxations in deeper layers, but the X-ray data set is too limited to allow such a full refinement. Instead we used the X-ray data to refine the topmost relaxation and employed a Keating potential [30] to estimate the other relaxations. A Keating potential is suitable for describing the covalent bond structure of Si. We used as bond length parameter $\alpha = 0.201$ and bond angle parameter $\beta = 0.0183$. The fitting software allows a simultaneous optimization of the fit for the X-ray data and the lattice energy. We find a significant improvement in the fit, in which the $\chi^2$ value now becomes 1.01 for a small inward relaxation by $-0.07 \pm 0.03$ Å (Using the Keating potential this corresponds to a relaxation of $-0.06$ and $-0.02$ Å in layer 2 and 3 respectively). A similar relaxation for the O-terminated surface also improves the fit, but the results remain much worse than for the H-termination. Despite the limited data set, we can thus clearly distinguish the two terminations, and even deduce a small relaxation.

For the data analysis in KOH we followed the same steps and again
conclude that the surface is H-terminated (see Table 5.2 and figure 5.9). Including a relaxation does not give a significant improvement in the fit, partly because of the higher surface roughness in the KOH solution and the smaller data set. The relaxation now appears to be outwards, instead of inwards as in the case of NH₄F, but the error in the relaxation is too large to conclude there is a genuine relaxation. Because of the limited data in the KOH solution, the distinction between H or O-terminated models is less clear than in the case of NH₄F, but the asymmetry of the (10) rod around l=1 still supports our conclusion.

Figure 5.8: (10) and (20) Rod of silicon (111) in 2.16 M NH₄F solution. The dashed curve represents the oxygen terminated surface, the solid curve represents the hydride terminated surface. The H-fit follows the data much better than the O-fit.

Figure 5.9: (10) Rod of silicon (111) in 10⁻³ M KOH solution. The dashed curve represents the oxygen terminated surface, the straight curve represents the hydride terminated surface. The H-fit follows the data better than the O-fit.
Our SXRD observations show that the surface is hydrogen terminated under wet chemical etching conditions. This is consistent with other research [7, 12, 9, 33], in which the hydrogen termination is observed using different techniques. Atomically flat surfaces have previously been investigated using atomic force microscopy (AFM) [11] in NaOH solutions. However, these measurements provide information on the local surface structure, our studies provide information on the overall surface structure and confirm the AFM measurements. The formation and dissolution of silicate reaction products in KOH and NH4F solutions is different. The better dissolution of silicon fluoride reaction products [34], compared to silicon hydroxide reaction products [36, 37] may effect the etching and surface roughness. The NH4F solution etches on step sites and the fluoride silicates remain in solution. In the KOH solution etching is less site specific [38] and the reaction products can locally enhance etching, leading to a more random surface attack and increased pit formation [?]. This may provide an explanation for the comparably higher surface roughness observed in KOH solutions.

5.3.3 Liquid ordering at the interface

After fitting the crystalline surface structure, a closer look was taken at the interface structure including the liquid layer by considering the (00) rod as well. This was only done for the surface in NH4F, because the
KOH treated surface was too rough. In order to fit the data, we need a model that now includes the liquid side of the interface. Having found, from the other rods, the optimally relaxed crystal structure with hydrogen termination and a surface roughness of 2.1 Å, we use this to describe the crystal and place a liquid layer on top. A generic model is used in which the amount of charge density in the liquid at various heights can be optimized. The etching liquid mainly contains water and NH₄F, but since X-rays are insensitive to H and hardly distinguish between N, O and F atoms, the liquid layer is described as oxygen layers on top of the relaxed crystal. By using an out-of-plane Debye-Waller factor and an occupancy for each layer, the effective charge density can be modeled. Two such layers were found to be sufficient. The best fit is depicted in figure 5.10 and the corresponding parameters are listed in table 5.2.

![Figure 5.10:](image)

**Figure 5.10:** (00) Rod of silicon {111} in 2.16 M NH₄F solution. The dashed curve represents the hydride terminated surface in absence of a liquid. This demonstrates that a liquid layer is needed to fit the data. The fit of a H-terminated surface with a liquid on top follows the data best.

The corresponding calculated electron density distribution across the interface for the NH₄F solution is shown in Figure 5.11. The peak labeled Si is the topmost layer of the silicon crystal. Its occupancy is fixed to one. The next peak is the hydrogen covalently bonded at the silicon surface. On the liquid side we find two well-defined layers, representing the water at the surface. We found no lateral ordering in the two water layers, so the lateral Debye-Waller parameter for these layers is fixed at a $B_{||} = 1000$ Å², making these invisible in all rods except the specular. The occupancy
Table 5.3: Best fit parameters for the NH$_4$F solution. The z-positions are given with respect to the unrelaxed Si top layer.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Parameter</th>
<th>NH$_4$F solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-2</td>
<td>$z$ [Å]</td>
<td>8.4 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>$B_{\perp}$ [Å$^2$]</td>
<td>154 ± 21</td>
</tr>
<tr>
<td></td>
<td>Occupancy</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>O-1</td>
<td>$z$ [Å]</td>
<td>4.4 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>$B_{\perp}$ [Å$^2$]</td>
<td>35 ± 5</td>
</tr>
<tr>
<td></td>
<td>Occupancy</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Si</td>
<td>$z$ [Å]</td>
<td>-0.07</td>
</tr>
<tr>
<td></td>
<td>$\chi^2$</td>
<td>0.2</td>
</tr>
</tbody>
</table>

of the water layers lies between 1 and 1.2. Adding more layers does not change this observation and the following layers correspond to a fully disordered bulk liquid. An occupancy above 1 is possible, because each layer can contain more than one water molecule per surface unit cell and the layers may contain heavier solvated ions.

Figure 5.11: Electron density distribution across the interface for the NH$_4$F solution.

As the liquid layer in contact with the silicon surface does not show lateral ordering, hydrogen bonding with the hydrogen terminated surface
5.3 Results & Discussion

is not likely or very weak and an ice-like surface structure is not expected as observed for Ag [39] and NaCl [40]. This indicates a weak interaction between liquid layer and crystal surface. The loose bonding of the water layer is in agreement with the hydrophobic interaction of the surface with this layer and suggests a predominantly Van der Waals interaction.

Figure 5.12: Top view of the Si(111) surface with the most likely positions of the water molecules on top of the silicon surface. The encircled Si atoms lie higher compared to the other Si atoms as a consequence of the tetragonal covalent bonding of the atoms in the crystal. The hydrogen atoms on top of the encircled Si atoms are not shown.

Figure 5.12 shows three possible positions of a water molecule on top of a hydrogen terminated (111) Si surface. The Si-Si surface atom distance is 3.84 Å, the Si-H bond distance 1.48 Å, and the Van der Waals radii are 1.40, 1.20 and 2.0 Å for oxygen, hydrogen and silicon, respectively. If we assume a Van der Waals radius of approximately 1.6 Å for water, we can calculate the three most likely z-positions of the water molecule on top of the hydrogenated Si-(111) surface (See figure 5.12). Position 1 corresponds to a water molecule located in between the silicon atoms, the calculated distance is 3.2 Å. For position 2, the z-distance is 3.52 Å and the water molecule is positioned on top of a lower silicon atom. In the last case when the water is positioned at location 3, the calculated distance is 4.3 Å.

The observed z-distance is 4.4 Å. This suggests that the water molecules are located at position 3, i.e. on top of a Si-H surface unit. This is rather unexpected and a full explanation for this distance can not be given, as the contacting electrolyte can also contain species such as solvated ions.
and other species. But the large distance of the first water layer from the crystal surface as compared to the water layers on ionic, hydrophylic surfaces of NaCl [40, 41] and KH2PO4 [42] \((z = 1.3 - 2 \text{ Å})\) confirms the weak interaction of the water with the hydrogen terminated (111) silicon surface.

The random orientation of the loosely bonded first water layer in combination with the calculated distances provide a possible explanation for the slow and rate-limiting attack of the silicon backbond by the water during etching, since the water molecule has to order itself quite specifically to ensure a good bonding position to this backbond. As this requires a particular preferential orientation of the water molecule, it is accompanied with an unfavourable increase of potential energy.

5.3.4 Surface structure during and after oxidation

As the silicon oxidizes at potentials past the peak potential, i.e. the voltage giving maximum current [5], the structure of the interface and the resulting oxide layer under changing potential can be followed by ramping the applied potential from \(-1.3\) V to \(+1\) V to ensure complete anodic passivation of the surface. All the previous experiments were conducted under a cathodically applied potential of \(-1.3\) V, to minimize surface roughening during surface preparation and etching. The influence of applying a potential is now further investigated for a \(10^{-4}\)M KOH solution. The sample is prepared and aligned as described in the previous sections.

As shown in figure 5.13, during oxidation the structure factor of the \((0, -1, 0.5)\) reflection of the hydrogen terminated surface decreases and finds its minimum just before the peak potential of the measured current is reached, indicating an increased roughness. As the peak potential is passed, the structure factor increases rapidly, as oxide is formed on top of the crystal. The sequence of increasing and decreasing roughness shows that the oxide layer forms through birth and spread. Initially, separate oxide islands are formed giving a rough surface, but through coalescence of these islands the surface becomes smoother again.

After oxidation of the surface, the interface structure was measured by SXRD using the \((10)\) rod (see fig. 5.14). The same fitting procedure as previously described was used. The data shows the surface to be oxygen terminated, as expected, even though the difference with hydrogen termination is quite small. After fitting and energy minimization, no sig-
5.3 Results & Discussion

Figure 5.13: Top: the linear voltage sweep and corresponding current through the system. Bottom: the resulting change in the (0 -1 0.5) reflection, going from a hydrogen terminated surface, through a rough phase and ending in an oxidized surface.

Significant relaxation (-0.01 ± 0.02 Å) of the top Si layer was found (see table 5.4). The additional oxide layers are invisible to the (10) rod, i.e. they are disordered with respect to the substrate. Unfortunately, the interface roughness is too large to derive additional structural details.
Figure 5.14: The (10) rod of silicon after *in-situ* oxidation of the surface. The dashed curve represents a fit for an oxygen terminated surface, the solid curve for a hydride terminated surface. The best fit corresponds to an oxygen terminated surface.

Table 5.4: Overview of fits on the Si-(111) surface after oxidation

<table>
<thead>
<tr>
<th>Atom</th>
<th>Etchant</th>
<th>Relaxation (M)</th>
<th>x²</th>
<th>Roughness Å</th>
<th>Displacement Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>KOH</td>
<td>no</td>
<td>1.73</td>
<td>4.0 ± 0.4</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>KOH</td>
<td>yes</td>
<td>1.31</td>
<td>3.9 ± 0.4</td>
<td>-0.3 ± 0.2</td>
</tr>
<tr>
<td>O</td>
<td>KOH</td>
<td>no</td>
<td>1.01</td>
<td>3.9 ± 0.4</td>
<td>0</td>
</tr>
<tr>
<td>O</td>
<td>KOH</td>
<td>yes</td>
<td>0.93</td>
<td>4.0 ± 0.4</td>
<td>0.00 ± -0.01 ± 0.02</td>
</tr>
</tbody>
</table>

5.4 Conclusions

Preparing an atomically smooth silicon (111) surface for the *in-situ* surface X-Ray diffraction analysis of the interface structure turns out to be quite troublesome. It is very sensitive to a variety of impurities, in particular oxygen. By choosing a full *in-situ* approach of preparation, a suitable surface for measuring complete crystal truncation rods could be obtained. In this process the removal of the oxide layer and the subsequent smoothing of the silicon surface could be followed by a measurement of the (0 -1 0.5) structure factor in time.

The surface X-Ray diffraction method has confirmed the H-termination
5.4 Conclusions

of Si-(111) under etching conditions in both NH₄F and KOH solutions. We observed a small but significant relaxation of the top layer of the silicon crystal structure for the NH₄F solution. Time resolved etching revealed the surface evolution in aqueous KOH and NH₄F solutions to be comparable. The etched surfaces in NH₄F solutions are smoother compared to the surfaces etched in KOH solutions and in both cases no surface reconstruction was observed. The etch chemistry of fluorine based alkaline etchants thus shows a higher anisotropy and better dissolution of reactions products, benefitting the surface smoothness.

The first water layer on top of the silicon surface in NH₄F solution shows lateral disorder, which indicates that the water molecules are loosely bonded by Van der Waals interactions, with the hydrophobic Si-H surface. This provides a possible explanation for the observed slow reaction kinetics. The surface roughness in KOH solutions was too high to properly determine the liquid ordering on top of the crystal.

We have monitored in situ the transition of H-terminated Si-(111) to O-terminated Si-(111) in KOH solution as a function of applied potential. The oxide grows on the surface through a birth and spread mechanism. The resulting oxide on top of the silicon has a high roughness, which is comparable to the H-terminated surface. Therefore, no further structure details could be obtained.
SURFACE DIFFRACTION
References


REFERENCES


Chapter 6

Absolute etch rates in alkaline etching of silicon (111)

The absolute etch rate of silicon(111) during wet-chemical etching in aqueous KOH solution has been investigated with optical interferometry, using masked samples. The etch rate is constant at $0.62 \pm 0.07 \mu$m/hr and independent of alkaline concentration for 1 to 5 M KOH solutions at 60 °C. Only at lower alkaline concentrations, the etch rate decreases. Adding Isopropanol slightly lowers the absolute etch rate. The activation energy of the etching reaction is $0.61 \pm 0.03$ eV in standard KOH solutions and $0.62 \pm 0.03$ eV with 1 M Isopropanol added to the solution. This indicates that the reaction is determined by reaction kinetics and not by transport limitations. In all cases the surfaces are covered by shallow etch pits, not related to defects in the crystal. This implies that the actual factor that determines the etch rate is the 2D nucleation of new vacancy islands at the bottom of these pits. This process is likely catalyzed by a local accumulation of reaction products, which preferentially occurs near the mask edges.

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1 Sensors and Actuators A Physical, 164 (2010), 154160.
6.1 Introduction

Anisotropic wet-chemical etching of silicon is an extensively used process and an essential step in micro-electromechanical systems (MEMS) manufacturing [1, 2, 3, 4, 5]. The process is based on the significant difference in etch rate between the {100} and {110} faces vs the {111} faces of the silicon crystal [6, 7, 8, 9]. As the Si-{111} plane is the slowest etching plane in KOH solution [10, 11, 12, 13, 14], wet-chemical anisotropic etching is normally applied to masked (110) and (100) wafers, resulting in complex three-dimensional structures bounded by {111} planes. The difference in etch rate between the slowest {111} faces and the other two crystallographic orientations of silicon during etching is also known as the anisotropy ratio, which is a major factor in determining MEMS quality.

In contrast to the fast etching (100) and (110) planes, knowledge of the absolute etch rates of ‘exactly’ oriented {111} faces is still lacking. In addition to the processing of (100) and (110) Si wafers, knowledge of Si-{111} etching is also important for the processing of (111) oriented wafers as a route to obtain smooth surfaces and different kinds of free-standing microstructures [10, 15, 16, 17].

A second aspect of the wet-chemical etching of Si-(111) using alkaline etchants is its mechanism, which totally differs from that of the other silicon crystal orientations. Whereas the KOH etching of the other, either exact or vicinal, Si-faces (hkl) involves step flow, step bunching, pyramid formation or kinetic roughening [18], the etching of the exact {111} plane proceeds by a repeated 2D nucleation of vacancy islands. This process, which is likely induced by a local accumulation of reaction products, leads to the development of numerous shallow, point bottomed etch pits [19, 20]. Such a process of step generation can be induced by the stress fields around dislocations or stacking faults ending on the (111) face [21, 22], but in our study the pits are not related to defects and the 2D nucleation of steps is likely induced by a local accumulation of silicate reaction products [19, 20]. However, quantitative data on the kinetics of this etching process is not yet available.

Methods based on the etching of wagon wheel patterns [11, 23, 24, 25] or of semiconductor (hemi)spheres [26, 27] have the advantage of yielding dissolution rates for a whole range of orientations in a single experiment. Unfortunately, these otherwise powerful approaches do not provide information on the etch rate of the exact {111} face, as this is readily
etched away and replaced by vicinal faces close to \{111\}. This follows from the kinematic wave theory of crystal dissolution, according to which the slowest etching face on a curved surface will disappear during etching [27]. Examination of cleaved silicon samples with etch structures bounded by \{111\} faces, using optical microscopy or scanning electron microscopy (SEM), can provide information on absolute etch rates of \{111\} surfaces. However, this approach is quite tedious and the etch rate might be affected by the presence of the mask contacting the \{111\} faces. Another experimentally very challenging way of determining the etch rates is by using *in-situ* STM observation of the Si-(111) surfaces during etching [28]. Although this method provides detailed information on the etching process at a nanometer scale, the measured etch rates are not representative for the larger scales used in MEMS technology. Moreover, this method can only be used for relatively low alkaline concentrations. From the above it is clear that, although measuring absolute etch rates of Si-\{111\} accurately is highly relevant in MEMS technology, it has been proven not to be a trivial exercise.

A large number of studies have been carried out on the etch rate and surface morphology of the \{100\}, \{110\} and other \{hkl\} faces of silicon etched in alkaline solutions, with and without additives, e.g. see references [29, 30, 31]. However, the \{111\} faces received less attention, as the commonly used methods for the measurement of etch rates are not suited for the slowly etching \{111\} faces.

In this study we determine accurate \{111\} etch rates by etching partially masked Si-\{111\} wafers followed by measurement of the resulting height differences between the masked and free surface areas using phase shifting interferometry (PSI). By this straightforward approach the problems encountered by the methods mentioned above are avoided. The absolute etch rates are measured with and without isopropanol (IPA) additive and as a function of time, the diameter of the non-masked areas, KOH concentration and temperature. The activation energy of the wet-chemical etch reaction is determined from the temperature series. Complementary to the etch rate measurements, the morphology of the etched surfaces is inspected using PSI and differential interference contrast microscopy (DICM). These morphologic observations provide important information on the influence of mask edges on the surface profile and the measured etch rates.
6.2 Experimental procedures

6.2.1 Sample Preparation

All samples were prepared from Czochralski grown, 4-inch (111)-oriented p-type silicon wafers supplied by Okmetic (boron doped, resistivity 5-10 Ω-cm, diameter 100 ± 0.5 mm, thickness 525 ± 25 μm, misorientation < 0.5°). The sample wafers were masked by LPCVD deposition of a 300 nm thick (low stress) silicon-rich nitride (SiRN) layer. Conditions: 9200 mTorr, 850°C, 70 sccm SiH2Cl2, 18 sccm NH3. To obtain oriented arrays of circular openings, one lithography step was used after wafer alignment along the wafer flat. This alignment facilitates determination of the crystallographic orientation of the surface patterns after etching. The circular areas in the nitride layer were opened by a plasma etch (Dry Reactive Ion Etching (DRIE)) followed by a short fluoride etch (48% HF) and removal of the photo resist. The mask obtained in this way consists of a pattern of circular openings with diameters 0.5, 1, 2 and 5 mm. The masked samples were diced into samples of 20.0 × 20.0 mm².

Prior to the etching experiments, the samples were cleaned in Piranha Acid (98% H2SO4 : 35% H2O2 3 : 1) for 10 minutes to remove organic deposits and then immersed in ultrapure water (ρ ~ 15 MΩ·cm) for 15 minutes. The final nitride removal in the mask openings was done using 48% HF, followed by a thorough rinse in ultrapure water. After cleaning, etching was carried out by placing the diced samples in a Teflon beaker, containing 200 ml of aqueous KOH solution, which was sealed with parafilm to avoid evaporation. Standard aqueous KOH (Merck, p.a.) solutions were used of 2.0 and 5.0 M concentration, by dissolving the KOH pellets in ultrapure water. In one part of the experiments, the standard solution was used, in the remaining experiments IPA (Merck, selectipur VSLI) was added to the solution at a concentration of 6.5 wt% relative to water (equal to about 1 M IPA). To investigate the time behaviour of etching, the samples were etched for time intervals of 2 up to 20 hours at 60°C in duplo by placing the beakers in a thermostatic bath with an accuracy of 0.1°C. Prior to microscopic examination, the etching process was quenched by immersing the sample in diluted sulfuric acid (10%) for at least 10 minutes. After this, the specimens were rinsed in ultrapure water and blown dry in a flow of argon.
6.2 Experimental Procedures

6.2.2 Sample Analysis

The etch rates were derived from the measured height differences between the masked and etched surface areas of the specimen crystals. The measurements were carried out using white light PSI (Wyko NT1100), a method capable of gauging height differences ranging from a few tens of micrometers down to nanometers. In interpreting the measurements a correction is made for the 300 nm thick masking layer. Figure 6.1 shows a top view and a depth profile of a circular mask opening after etching, as obtained by PSI.

![Figure 6.1](image)

**Figure 6.1:** Determination of the vertical etch depth by using white light phase shifting interferometry. A circular opening of 1 mm is measured to accurately determine the depth profile of the etched silicon. (a) Overall image showing the depth distribution represented as a variation in gray level. (b) Depth profile along the horizontal line in (a). The crystal was etched for 8 hours in a 5 M KOH solution with 1 M IPA added, at T = 60°C.

By choosing longer etching times, the influence of the slight misorientation of the non-masked surface areas with respect to the exact (111) plane can be ignored, as prolonged etching will overcome this effect because the etch pits formed with slopes of about 0.5° are steeper than this misorientation. The etch depths (rates) given in figures 6.2 to 6.5 were measured at the center of the circular mask openings. Each point in these graphs represents the average value of the etch depth of minimal three different mask openings of identical size. The surface morphology of the samples was examined using DICM, by which method the shallow slopes of the step and pit patterns can readily be imaged. This is different from using...
scanning electron microscopy (SEM), which is the standard method for imaging MEMS structures. By application of this technique, which allows for higher magnifications, the shallow pit inclinations on the etched surfaces could hardly or not be imaged. Therefore, we were not able to obtain morphologic information on the narrow \{111\} side walls bounding the etched mask openings.

### 6.3 Results

#### 6.3.1 Etch rates

Prior to performing the actual etch rate measurements, we verified the influence of ambient oxygen on the silicon etch rate. This was done by comparing etch rate measurements in standard 5 M KOH solutions for 20 hours at 60°C, with oxygen or argon bubbling or no bubbling of the liquid. As no significant differences in etch rates were observed, further experiments were carried out under normal atmospheric conditions, without bubbling of an inert gas.

The etch behavior was followed in time for 2 and 5 M aqueous KOH solutions without and with 1 M IPA additive. As can be seen in figure 6.2, the etch depth increases linearly in time in all four cases. This indicates that the etch rate is constant, regardless of KOH concentration and the presence of IPA additive. The etch rate is slightly less if IPA is added to the solution.

From figure 6.2 the etch rates are determined by linear fitting of the etch depth as a function of time. The absolute etch rate of Si-(111) in 5 M KOH solution at 60°C is 0.55 µm/hr (equals 9.2 nm/min); lowering the alkaline concentration to 2 M does not alter this etch rate. The addition of 1 M IPA to the solution does not significantly alter the etch rate at 5 M KOH concentration as it drops to 0.52 µm/hr. At the lower alkaline concentration, the etch rate with IPA drops to 0.42 µm/hr, which is a slight, but significant, decrease. A slight difference is observed for the different mask opening diameters that are used for etching. An increased diameter of the circular openings leads to a decrease in etch rate as can be seen in figure 6.3. As the vertical etch depth is proportional with time for all diameters, it can be concluded that the differences in etch rates do not change in time and when the diameter would go to infinity the rim effects are not observed.
To determine the activation energy, $E_a$, of the wet-chemical etching process, etch rates were measured at temperatures in the range from 40 to 80°C with 10°C intervals. At all temperatures alkaline solutions with
Figure 6.3: Vertical etch depth as a function of the reciprocal mask opening diameter (5 M KOH, without or with 1 M IPA added, T = 60°C). The values at 1/D = 0 provide an estimation of the etch rate for infinite mask openings.

Figure 6.4: Arrhenius plot of etch rate (nm/min) versus reciprocal temperature for Si-(111) in 5M KOH solutions without (left) and with 1 M IPA added (right). Etching time: 20 hours; mask opening 5 mm.

5 M KOH without and with 1 M of additive IPA were used. The activation energy of the wet-chemical etching process can be determined on the
6.3 Results

basis of etch rates, \( R(T) = R_0 \exp(-E_a/kT) \), observed at these different temperatures. Here \( R_0 \) is a constant, \( k \) is Bolzmann’s constant and \( T \) is temperature.

Figure 6.4 gives Arrhenius plots, \( \ln(R(T)) = R_0 - E_a/kT \), for the standard 5 M KOH solution without and with 1 M IPA. From the slope of the linear curve the activation energy, of the clean solution and that with IPA added is determined 0.61 ± 0.03 eV and 0.62 ± 0.03 eV, respectively, for the 5 mm mask openings. This shows that adding IPA does not change the activation barrier of the reaction significantly. Subtle differences in \( E_a \) were observed for the different mask openings, going from 0.5 eV to 0.64 eV for diameters from 0.5 to 5 mm etched in the ‘clean’ solutions. The values around 0.6 eV indicate that the etch reaction is kinetically limited instead of diffusion controlled, as in that case \( E_a \) would be roughly 0.2 eV [32]. The measured values for \( E_a \) are in the same range as determined for Si-(100) (0.61 eV) and Si-(110) (0.56 eV) [12] and the variation within those measurements can be ascribed to differences in sample geometry.

![Figure 6.5](image)

**Figure 6.5:** Etch rate of Si-(111) as a function of KOH concentration for pure solutions and solutions containing IPA and silicate reaction products, corresponding with 50 grams Si per liter solution. The crystals were etched for a period of 20 hours at 60°C. Mask diameter: 5 mm.
Figure 6.5 depicts the influence of KOH concentration on the Si-(111) etch rate. The vertical etch rate is relatively low at low alkaline concentration and increases to a maximum value at 1 M concentration and then remains constant at 0.62 ± 0.07 μm/hr in the regime between 1 and 5 M KOH concentration. For all concentrations, it is observed that IPA reduces the absolute etch rate to some extent, which remains constant at 0.50 ± 0.02 μm/hr for 1 to 5 M KOH. This indicates that in both cases the etch reaction is insensitive to alkaline concentration above 1 M KOH. We see no drop in etch rate at higher concentrations as reported in literature for other (hkl) faces [33].

Combining this result and the observed activation energies, it follows that the absolute etch rate of a {111} surface in 1 to 5 M KOH solutions is given by 
\[ R = \left(1.08 \pm 0.12\right) \times 10^9 \exp\left\{-\frac{7085 \pm 350}{T}\right\} \text{μm/hr for pure KOH solutions and } R = \left(1.17 \pm 0.05\right) \times 10^9 \exp\left\{-\frac{7180 \pm 350}{T}\right\} \text{μm/hr for KOH solutions with 1 mole IPA added.}\]

6.3.2 Morphology

Application of PSI to image the height profile of the etched surface in the circular mask openings always showed a curved, convex surface with maximum height at the center (see figure 6.1). The slope of the profile is typically about 0.5°, which is similar to the slope of the etch pits formed after KOH etching [19]. This suggests that the sources generating the etch steps are pits distributed along the periphery of the mask openings. Confirmation was obtained by DICM, revealing a multitude of etch pits, the bottoms of which coincide with the mask edges. This preferential distribution was observed both for etching in pure KOH solutions, generating circular pits (figure 6.6a) and for solutions with IPA added, giving triangular pits (figures 6.6b and 6.6c). Steps originating from these pits propagate towards the center of the mask openings, forming the convex surface profiles. Pits are also nucleated in the mask center, but their activity is less compared to those at the rim. Figure 6.6b and 6.6c illustrate the competition of step generation from the pits near the mask edges and those at the central part of the mask opening. In figure 6.6b, which corresponds to a mask opening of 1 mm diameter, the central pits are not yet ‘overetched’, but for the smaller opening of 0.5 mm in figure 6.6c the central pits are completely overruled.

A closer look at the surface patterns also reveals silicon areas being
6.4 Discussion

etching underneath the mask (figure 6.6a and 6.6c). As the step patterns are not perturbed in this region and the pits remain symmetric in and outside the mask region, this once more indicates that etching is not determined by volume diffusion. Otherwise, the step velocity would be slower underneath of the mask, resulting in distorted pit shapes.

We here note that no steps are generated from the intersection lines between the bottom \{111\} face and the adjacent, inclined \{111\} faces in the underetched regions below the mask. All the steps emerge from pits. No morphologic information could be obtained for these narrow \{111\} side wall faces. In references [34] and [35] it was found, by using DICM, that \{111\} wall faces on masked Si-(100) wafers can etch via the pit mechanism or by steps nucleated at the mask - (111) face intersection line.

A possible explanation for the high density of etch pits aligned along the mask edges is the presence of dislocations formed by stresses, introduced by the SiN mask patterns. An alternative explanation is a local accumulation of silicate reaction products near the mask edge, capable of generating steps via an autocatalytic process during etching [19, 20]. To verify the presence of dislocations or stacking faults near the mask edges, the mask was completely removed by etching in concentrated phosphoric acid (85%), followed by a Sirtl etch [36]. This defect delineating procedure did not reveal any kind of linear or planar defect. No differences were observed between masked and non-masked areas and areas near the mask edge. Thus the pits do not result from dislocations or other faults that are introduced by the low-stress nitride masks.

6.4 Discussion

The actual factor determining the etch rate of Si-(111) in our experiments is the 2D nucleation rate of vacancy islands (or 2D holes) at the pit bottoms. The activation energy of this process is 0.61 eV, which is higher than the activation energies of 0.50 eV [33, 37] and 0.53 eV [13] reported in literature for Si-(111). However, these values were obtained by KOH etching of hemispherical specimens and wagon wheel patterns, respectively. Because for these geometries the Si-(111) surfaces are slightly curved or vicinal, the etching is determined by the propagation of existing steps. Therefore, the lower activation energies represent the etch process at the steps, rather than the nucleation of new vacancy islands on an exact
Figure 6.6: DICM pictures of etch patterns in the circular mask openings: (a) Standard 5 M KOH solution, showing rounded pits with bunched step patterns near the mask rim; (b) 5 M KOH solution with 1 M additive IPA for a mask opening of 1 mm, showing numerous pits near the mask rim in the process of overruling the triangular pits at the center. (c) Standard 5 M KOH solution with 1 M additive IPA for a smaller mask opening of 0.5 mm. Here no pits are visible at the central part; all steps are generated by the tiny triangular pits near the mask rim (see inset) and propagate towards the center of the mask opening.
6.4 Discussion

(111) plane [38, 39]. The higher activation energy observed in our study complies with the fact that a terrace atom is more firmly bonded to the crystal surface than a step site atom.

The observed activation energy of 0.61 eV indicates that the vertical etching process is largely dominated by surface kinetics rather than material transport. However, further interpretation of $E_a$ is difficult as presumably a range of successive reaction steps is involved during silicon atom removal at the pit bottom. This is further complicated by the fact that the vertical etching is catalyzed by a local accumulation of reaction products [19].

The activation barrier for etching in solutions with IPA added does not differ significantly from clean KOH solutions. This indicates that IPA is not chemically involved in the vertical etching process. The slight decrease in etch rate might be due to the surfactant action of IPA, forming a physisorption layer on the surface [19, 20]. This 'masking' effect reduces the etch rate. In contrast to the nucleation of 'new layers', IPA has a dramatic effect on the etching process at the step sites. As shown in figure 6.6, the pit patterns are rounded for pure KOH solutions and triangular for IPA containing solutions. This observation is explained in our previous work by an increase of the ratio of kink site and step site atom removal rate upon adding IPA [19, 20].

We think that the observed decrease in the etch rate upon adding silicate reaction products to the KOH solution, as shown in figure 6.5, is due to the main compounds, which are monomeric, like Si(OH)$_4$. Pit formation is induced by silicate aggregates at the pit bottoms, locally enhancing the etch rate as compared to the rest of the surface [19, 20]. Therefore, there is no conflict between the decreased etching rate and pit formation, as different silicon reaction products are involved.

PSI measurements show that the surface profile of the etched silicon in the circular mask openings is convex shaped (figure 6.1) with a high density of etch pits near the mask periphery, coinciding with the overhanging mask edge (see figures 6.6 and 6.7). All the observed step patterns originate from this circular array of pits near the mask edge or from pits elsewhere on the surface. The mask itself as well as the inclined {111} side faces in the underetched region below the mask do not act as a step source.

A convex surface profile, similar to that observed in our study, as well as an enhanced etch rate for smaller mask openings have been predicted by
Figure 6.7: Schematic view of the surface profile obtained at the beginning (A) and after prolonged (B) etching in a circular mask opening, leading to a convex surface profile.

Kuiken [40], using a mathematical model for wet-chemical etching through a shallow hole in a mask. In his model he assumed etching to be completely diffusion controlled as well as isotropic, as experimentally observed by Svetovoy [41], using isotropic etchant HF/HNO$_3$/H$_2$O etchant solution. This is essentially different from the present case, where KOH etching is dictated by surface kinetics and is highly anisotropic. So, an alternative explanation has to be searched for.

In previous work [19] we concluded that the formation of etch pits results from preferential etching at the pit bottoms, catalyzed by a local accumulation of silicate reaction products. This implies that the high density of etch pits coinciding with or just in front of the mask edge results from a preferential development of such silicate aggregates at the mask edges during the earlier stages of etching (see fig 6.7a). Upon continued etching, these particles persist and etch pits coinciding with the mask edges develop and then expand, leading to the observed convex surface profile. This is schematized in figure 6.7b. We think that the preferential clustering of silicate reaction products near the mask edge is induced by the presence of a re-entrant corner at the intersection line of the SiN mask and the silicon surface. This can be a favorable place for aggregate
formation as a result of a local reduction in surface energy. The slight increase in etch rate for openings with smaller diameter is not readily explained by the above consideration. But, following Kuiken’s model, this observation suggests that volume diffusion still plays a minor role in the etch process.

6.5 Conclusions

In this study we measured absolute etch rates of Si-(111) in aqueous KOH solutions with and without IPA additive. As masked samples with circular openings were used, data is obtained which is representative for the actual 2D nucleation process of new vacancy islands at the bottom of etch pits generating new steps, rather than for the propagation of existing steps on vicinal surfaces close to (111), as reported in literature. This removal of new layers proceeds by an autocatalytic process promoted by an accumulation of silicate reaction products at the bottom of the etch pits. The rate of this etching is determined by KOH concentration (up to 1 molar), temperature, mask opening diameter and IPA additive. An activation energy of 0.61 eV was obtained from etch velocity measurements at different temperatures, which indicates that the formation of new 2D nuclei is determined by surface kinetics instead of mass transport. As the activation energy for solutions with IPA added does not differ significantly from that measured for clean solutions, it follows that this additive is not chemically involved in the vertical etching process at the pit bottoms. Examination of the surface morphology showed that all the step patterns are generated from shallow etch pits, which are not related to dislocations. These pits are preferentially distributed along the mask edges, which points to a preferential formation of silicate aggregates at the re-entrant corner of the mask edges during the earlier stages of etching. Our study shows that the etch rate of the exact Si-(111) surface, which is a major factor determining the anisotropy ratio in MEMS device production is determined by the nucleation process of vacancy holes at the bottoms of shallow etch pits. Control, or even better, avoiding the formation of these pits is the road to improving the anisotropy ratio and thus the quality and reliability of wet-chemical etching.
References


REFERENCES


Chapter 7

Electrochemistry and morphology of silicon \{111\} etching in alkaline solution

7.1 Introduction

Anisotropic, wet-chemical etching of silicon is an important step and a widely used process in device manufacturing [1, 2]. The process is based on a significant difference in etch rate between \{100\} and \{110\} faces with respect to the slowly etching \{111\} face of silicon [3, 4, 5, 6]. Therefore, wet-chemical anisotropic etching is normally applied to masked \{100\} and \{110\} wafers, leading to complex three dimensional structures defined by \{111\} planes. The eventual functionality of microelectromechanical systems (MEMS) strongly depends on the shapes and surface roughness that result from the etch rate differences of the various crystallographic orientations [7]. The etching of Si-(100) in aqueous KOH solution is extensively studied and known to depend on temperature, applied potential and alkaline concentration [3, 8, 9]. The etching of Si-(111) has received less attention. Recently we have investigated etching of Si-(111) more extensively by studying surface morphology and etch pit morphology as a function of concentration, temperature, time and additives [10, 11] and concluded that the Si-(111) etching proceeds through an autocatalytic process, in which increased amounts of reaction products nucleate pits at the silicon surface, locally catalyzing vertical etching and thus promoting etch pit formation. In a recent study, the etching of \{100\} and \{111\} silicon in alkaline solution was also investigated by electrochemical methods...
[8]. In that work it was shown that upon recording voltammograms under etching conditions, starting from the open circuit potential the current increases as the applied potential becomes more positive (figure 1.3(a)). Eventually, the anodic current reaches a maximum value after which it decreases strongly. For potentials more positive than the peak potential, the surface becomes passivated with an oxide layer, which largely retards etching, i.e. chemical dissolution. Electron injection was proven to be the origin of the anodic current for both n- and p-type silicon [9, 12] (figure 1.3b). As the measured anodic current results directly from surface chemical reactions, electrochemical measurements are a sensitive probe for chemical reactivity of the surface during etching. Here we combine the morphology and electrochemistry approaches to look at two different aspects of silicon etching. First, the surface morphology and etch rate are investigated as a function of electrochemical conditions. We shall take a closer look at the etched surface and the influence of the applied potential on the vertical etch rate and pit morphology using differential interference contrast microscopy and the Lichtfigur method. Second, the evolution of the surface reactivity during etching at open circuit potential is monitored electrochemically by taking scanning voltammograms at various intervals during chemical dissolution of the silicon. These two subjects will be addressed separately in sections 7.3 and 7.4.

7.2 Experimental

7.2.1 Sample preparation and ex-situ characterization

All samples were cut from Czochralski grown 4 inch (111)-oriented silicon wafers, n-type (phosphorus doped, 1 - 10 Ω-cm) and p-type (boron doped, 5-10 Ω-cm), supplied by Okmetic. The samples were sawn into sizes of 20.0 x 20.0 mm². Before use, the samples were cleaned in concentrated nitric acid (Merck, # 1.00456, 69%, p.a. quality, 30 min immersion) to remove organic deposits and then immersed for 15 min in ultrapure water. Native oxide was removed by a 40 seconds dip in a 5% HF solution (Aldrich, p.a. quality), followed by a rinse in ultrapure water. The masked samples for absolute etch rate measurements were prepared by deposition of a 300 nm thick (low stress) silicon-rich nitride (SiRN) masking layer on the wafers by LPCVD (200 mTorr, 850°C, 70 sccm SiH₂Cl₂, 18 sccm NH₃). One lithography step was used after
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wafer alignment along the wafer flat, to ensure the starting conditions. The mask consisted of a pattern of circular openings with a diameter of 0.5, 1, 2, and 5 mm. These circular openings in the nitride layer were opened by a plasma etch (DRIE) followed by a short fluoride etch (48%). The masked samples underwent the same cleaning treatment after preparation as the unmasked samples. To investigate ex-situ the influence of applied potential on surface morphology and thus pit shapes, the etched silicon surfaces were examined using phase shifting interferometry (PSI) [14], differential interference contrast microscopy (DICM) and the Lichtfigur technique [16]. Etch rates of the (111) surfaces were derived from the height differences between the mask-free, etched silicon surface areas and the mask edges of the SiN mask, by using PSI.

7.2.2 Electrochemical measurements

All samples were mounted on a copper block in a Kel-F holder, using a GaIn eutectic as an Ohmic contact on the backside of the silicon. The cell was sealed by means of a Buna-N O-ring. The silicon was the working electrode in an electrochemical cell with a platinum counter (Pt) electrode and a saturated calomel electrode (SCE) as reference and all potentials were defined with respect to the SCE, see also ref [8]. A PalmSens potentiostat was used and computer-controlled by PalmSens software. Temperature control was achieved using a thermostatic water bath (Heko, accuracy 0.1°C). After connecting the electrodes, the samples were placed in a Teflon beaker, containing ~ 200 ml of 5 M aqueous KOH solution (Merck, # 1.05033, used as received), which was covered with Parafilm to avoid evaporation. The solutions were preheated to 60°C. All samples were etched for 20 hours at 60°C at ambient conditions. The measurements were performed in the dark and under applied potential; reference measurements were performed at OCP (-1.3 V). The etching reaction was quenched in a 10% sulfuric acid solution (prepared from Merck, # 1.00731, p.a. quality, at least 15 min immersion); after this the specimens were thoroughly rinsed with ultrapure water and blown dry in a stream of argon.

7.2.3 In-situ Lichtfigur method

The in-situ monitoring of the surface evolution in time was conducted using the Lichtfigur method, which was extensively introduced and applied...
in other work [11, 16]. Figure 7.1 shows a schematic of the set-up. The adaptation to in-situ measurement was achieved by using the in-situ electrochemical cell [13] with a pumping system (Watson-Marlow, SciQ-323), flowing aqueous KOH solution through the cell at a temperature of 60°C. The in-situ cell was connected to a large buffer vessel, which was kept at constant temperature with an accuracy of 0.1°C using a Julabo water bath. In the Lichtfigur setup, the silicon surface was aligned along its wafer flat orientation and exposed to a laser beam (HeNe, 10 mW, \( \lambda = 632.8 \text{ nm} \), Spectra Physics Inc., spot size on the sample surface was 2.5 mm in diameter). The light reflected from the specimen surface was
projected on a translucent screen via a beam splitter and the Lichtfigur image thus obtained was recorded using a CCD camera. The experimental setup was kept in the dark and the sample was exposed to the laser beam only for taking a snapshot.

7.3 Etch rate and morphology versus electrochemical potential

7.3.1 Absolute etch rates

In a different investigation [14], the etch rate of Si-(111) was measured using samples with circular mask openings; the etch depth was found to increase with decreasing hole diameter and the etching proceeds through the formation of etch pits. Choose sufficiently long etch times, the etching has become stationary in time. The measured depth profile thus represents the nucleation rate of the new layers at the pit bottoms. In this study we investigated the influence of the applied potential on this autocatalytic process using these masked samples. To avoid any initial effects, the samples were etched at 60°C for 20 hours in 5 M KOH solution. The largest hole diameter (5 mm) was used for comparison between the applied potentials.

![Graph](image.png)

**Figure 7.2**: Vertical etch rate of p-type Si-(111). The open circuit potential $U_{oc}$ is -1.3 V.
Figure 7.2 depicts the influence of the applied potential on the vertical etch rate. At cathodic potentials, no measurable influence of the applied potential on the etch rate was observed. On going towards a more positive potential, the etch rate increases and shows a maximum etch rate of $0.8 \pm 0.08 \mu$m/hr, at an applied potential of -1.0 V, which is more than twice that at $U_{oc}$. This is similar to the etch rate of silicon (100), except that the etch rate of silicon (100) is two orders of magnitude higher [17]. At this point the influence of the electrochemically enhanced oxidation of the silicon is more pronounced, being comparable to the chemical pathway. At more positive values the etch rate decreases strongly. This is most likely associated with surface passivation, by anodic oxide, which is known to be present for sufficiently positive potentials [15]. This oxide layer slows down further downward etching at the pit bottoms and is expected to alter the surface morphology to a large extent. The observed etch rates closely follow the current density as a function of applied potential as is reported in literature [9].

7.3.2 Surface morphology

The surface morphology of p-type Si-(111) after etching was observed using DICM and the Lichtfigur method. The pit shapes change drastically on changing the applied potential, as shown in figure 7.3. At open circuit potential and below (-1.5V), the pits are largely bounded by $<112>$, i.e. monohydride steps. Shifting the applied potential to more positive values, the pit shape reverses and after passing the peak potential at -1.0 V the pits are bounded by $<112>$, i.e. dihydride steps. For potentials of -0.8 V and higher, etch pits are no longer visible and only a flat, featureless surface is obtained. The corresponding Lichtfigur map only shows a single dot. Here the surface is passivated by an anodic oxide layer.

The pit angles were measured using PSI. The results are displayed in figure 7.5 for p- and n-type silicon. The angle $\alpha$ is defined as the inclination angle of one side plane of a triangular etch pit and $\beta$ is the slope of the intersecting line of the two opposing planes of the etch pit as can be seen in figure 7.4 and reference [16].

The pit slopes $\alpha$ and $\beta$ provide quantitative information on the lateral propagation of the steps, as the horizontal etch rate is proportional to the vertical etch rate through the pit slope. We observe a significant spread in the values, which is due to secondary effects that influence the
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Figure 7.3: Pit shapes of etched p-type Si-(111) as a function of applied potential, determined with DICM and the Lichtfigur method. The samples were etched at 60°C in 5 M KOH solution for 20 hours. The different parts show the pit shapes from left to right at -1.5 V vs SCE (a), open-circuit potential (-1.3 V) (b), -1.1 V vs SCE, -0.9 V vs SCE (d) and -0.7 V vs SCE (e).

Figure 7.4: Schematic drawing of top and side view of an etch pit characterized by the angles $\alpha$ and $\beta$.

outcome. However, within the observed spread, for both p- and n-type silicon, the pit slopes remain constant for applied potentials below -1.0 V. This indicates that the step propagation as a function of applied potential is roughly proportional to the vertical etch rate. When the applied potential exceeds -1.0 V (i.e. passivation is approached), the pit orientation reverses as follows from the reversal of the pit angles $\alpha$ and $\beta$. This reversal was also found by DICM and the Lichtfigur technique. In the case of p-type silicon, the pits appear slightly more circular compared to n-type. Furthermore, for p-type an increase of the absolute values of $\alpha$ and $\beta$, while for n-type a decrease in pit angles is observed in this potential.
Figure 7.5: Pit angles of etched p-type (top) and n-type (bottom) Si-(111), determined with PSI. Angles $\alpha$ and $\beta$ are given as a function of applied potential. For both dopant types step anisotropy reversal is observed for potentials more positive than -1.1 V. The samples were etched at 60°C in 5 M KOH solution for 20 hours.

To investigate the rate of change in time the in-situ Lichtfigur technique was applied. First, the silicon was etched close to OCP (-1.3 V) for 1 hour. The Lichtfigur patterns obtained after that period were approximately circular, indicating rounded etch pits ($\alpha \simeq \beta$). Then, the potential was switched to -0.9 V, which is in the passivation range. The pattern
changed after 25 minutes as a result of a changing morphology of the etch pits and confirms the results obtained by the ex-situ methods. This result also shows that morphology changes can be controlled by electrochemical methods within a time interval of several tens of minutes.

7.3.3 Impact of electrochemical potential on etching

From the above, it is clear that the electrochemical potential has a major impact on the alkaline etching of Si-(111). At OCP etching is completely determined by chemical processes, in which the first step, comprising the replacement of Si-H termination by Si-OH, is rate-limiting [8]. Upon increasing the potential to -1.0 V the etch rate increases by a factor of 2.3. This indicates that the electrochemical pathway of this rate limiting hydrogen substitution makes a similar contribution to the etching process as the chemical route. Further increasing the chemical potential in the anodic regime leads to passivation of the surface and a large reduction in etch rate. However, a current is still measured, which indicates that anodic oxidation still proceeds, but at a lower rate. We think that the etching process is limited by chemical dissolution of the oxide surface layer formed in this potential regime, which is replenished by anodic oxidation.

Apart from etch rates, also the surface morphology of the crystals is affected by the electrochemical potential. The major change upon going to the passivation regime is a reversal of etch pit orientation from largely ‘monohydride’ i.e. <112>, step orientation to ‘dihydride’, i.e. <112>, orientation. This reversal in orientation is likely explained by the anodic oxidation of silicon atoms at the step positions. At OCP, the monohydride step atoms, which are triply bonded to the crystal surface are most stable [19]. However, upon anodic oxidation, the hydrogen at the dihydride steps is partly replaced by bridging oxygen atoms as shown in figure 7.6. Oxygen atoms bridging between two silicon atoms have been reported for oxidized Si-(100) surfaces, which are similar to <112> steps [18]. This energetically favorable configuration stabilizes the ‘dihydride’ steps [19].

Upon further increasing the potential into the passivation range, i.e. -0.8 V and beyond, leads to a featureless flat surface without pits. Instead of only the steps positions, now the complete (111) surface is covered by an oxide layer. No evidence was found for the presence of steps by using DICM. The absence of pits and steps suggest that there are no preferred
Figure 7.6: The propagation of etching proceeds along the most stable steps orientations on the (111) surfaces. The lines represent the shapes of the resulting etch pits and their most stable shape. The most stable step orientations under the cathodic etching conditions correspond to the monohydride-terminated steps on (111) (left), under anodic etching conditions they correspond to dihydride-terminated steps, also known as kinks (middle). The right picture represents a combined situation of etching along kinks and steps as observed at open circuit potential, the resulting shape is a convolution of the left and middle picture.
7.4 Surface reactivity at OCP as a function of time

In previous work by Philipsen et al., it was shown that electrochemical measurements can be used for studying the reactivity of silicon surfaces during wet chemical etching [8, 17]. During chemical dissolution of silicon, reaction intermediates are produced, from which electrons can be injected into the conduction band, resulting in an anodic current measured in the external circuit (see figure 1.3). As the production rate of reaction intermediates is directly coupled to chemical reactivity of the etching surface, the shape of a voltammogram provides information on the number and type of reactive surface sites [8].

To monitor the surface reactivity in time, voltammograms were measured every 20 minutes during etching of a p-type silicon {111} surface at OCP. The silicon was allowed to dissolve under open-circuit conditions in between the electrochemical measurements. To record such a voltammogram, the applied potential was scanned with a fixed rate towards more positive values and the current was recorded. For these measurements, a scan rate of 5 mV/s was chosen as this results in a clear separation of the various contributions to the current in a potentiodynamic recording [8]. After each scan, the surface is covered with anodically grown oxide, which starts to dissolve after potential control is released. Therefore, after each measurement silicon dissolution is interrupted for a short time, as compared to the time interval between successive measurements. The results are shown in figures 7.7 and 7.8.

Clearly visible in figure 7.7 is the change of the shape of the voltammograms in time, which indicates that the number and type of reactive sites change in time. On scanning the potential, the current starts to increase, it reaches a maximum value and decreases again as the surface becomes passivated with anodically grown oxide. Both the magnitude of the current peak and its position, i.e. the peak potential, give an indication of the surface reactivity at that moment. The evolution of the position of the peak potential, the maximum current and the passivation current
Figure 7.7: A series of voltammograms measured at regular time intervals. After each measurement the anodic oxide was left to dissolve and the silicon etching recommenced at open-circuit potential. The p-type Si-(111) samples were etched at 60°C in 5 M KOH solution for 20 hours.

measured at 0 V are depicted in figure 7.8.

Figure 7.8: Evolution of peak and passivation current during etching in 5 M KOH solution at 60°C at open circuit conditions (top). Evolution of the peak potential under the same conditions (bottom).

When the etching is started, the peak potential shifts to the cathodic side, i.e. from -0.59 V to -0.76 V (see figure 7.8), during the first 100 min-
utes of etching. In this period, also the peak current and the passivation current change: both show an increase, following the shift in peak potential. This effect is not due to temperature changes at the beginning of the experiment. We verified that the sample reached a constant temperature after only a few minutes and that the use of different vessel materials or other changes in the experimental setup did not alter this observation. We think that the change is associated with an initial change in surface morphology. During the first two hours of etching this surface changes from a flat (111) surface into a surface covered by etch pits. This leads to changes in the number and type of reactive sites, altering the voltammograms. At prolonged etch times, that is after the first period of 100 minutes, the potential of the main peak shifts from -0.76 V to -0.66 V. Moreover, this peak broadens and splits into several subpeaks after about 500 minutes of etching. Also the peak current changes. Interesting in this respect is that the change in peak current is very similar to the inverted change of the peak potential. The passivation current does not show a change in this period, but keeps a constant value. This indicates that at an applied potential of 0 V passivation is not complete and anodic oxidation persists to some extent and is in equilibrium with chemical dissolution. In addition to the main peak, after about one hour of etching a second peak starts to develop at the cathodic side (≈ -1.05 V) of the major peak. The position of this secondary peak is close to that of a maximum peak potential for a (100) silicon surface etched on the same conditions [8]. In contrast to the (111) face this surface is dominated by dihydride bonds. However, we never observed (100) microfacets on KOH etched Si-(111) surfaces. Therefore it is likely that this peak is associated with the presence of dihydride atoms at the steps of the circular etch pits formed on the crystals. In a previous study we found that after an initial period of a few hours there was no change in surface morphology and pit shape upon prolonged etching [16]. This implies that the broadening and splitting of the main potential current after 500 minutes is not paralleled by an alternation of the surface features viewed by DICM. We therefore think that these changes in the potential and current are due to an accumulation of silicate reaction products near or at the surface. Such an accumulation cannot be traced by DICM and by the Lichtfigur method.
7.5 Conclusions

In this work we showed that the electrochemical potential has major influence on the absolute etch rate and surface morphology of Si-(111) during alkaline wet-chemical etching. Using electrochemical methods, the formation of etch pits at open circuit potential has been followed by the changes in peak potential and its position. Starting from open circuit potential the etch rate increases for increasing potentials up to a maximum value at the peak potential and then decreases rapidly. At this maximum rate potential, the electrochemical contribution to the rate limiting step of the etching process is similar to the chemical contribution and the absolute etch rate is twice the value at open circuit potential. Going towards the passivation potential range, first the step atoms oxidize, which leads to a reversal of pit orientation. This is explained by the presence of bridging oxygen atoms at the 'dihydride' steps, which are required to construct the oxide layer on top of the silicon. In the passive range the surface is covered by a thin oxide layer and the etch rate is very low. Under this condition a featureless surface without pits is obtained. Apart from control, electrochemistry can also be used as an in-situ tool to gather knowledge on the type and number of reactive surface sites. The shape of voltammograms recorded during etching of Si-(111) at OCP provides information on the development of etch pits during the first few hours of etching. This leads to a shift of the peak potential to more anodic values and to the emergence of a secondary peak, which is characteristic of 'dihydride' steps. At a later stage the primary peak broadens and splits, which might be explained by an accumulation of silicate reaction products on the crystal surface. Voltammograms can thus be used for following surface morphology evolution. Our study demonstrates that electrochemistry is a powerful tool to simultaneously control and monitor the processes during wet chemical etching of Si-(111). As this crystal face is of major importance in micro machining silicon, it provides further opportunities in achieving better control and reliability in MEMS technology.
References


Summary

Anisotropic etching of silicon in alkaline solutions is a widely used technology in manufacturing of Micro Electro Mechanical Systems (MEMS), which is based on the different etch rates of the various crystal planes of silicon. It allows the manufacturing of complex, well-defined three-dimensional geometries, which can be used in various applications, such as sensors, actuators or micro-fluidic systems. The reproducibility of this wet-chemical anisotropic etching, however, is still not fully understood, as many factors influence the etch rates of the different crystal planes. The etching behaviour of slowest etching plane (Si-(111)) plays a key role and is further investigated. This thesis describes the efforts to investigate the influences on the surface morphology of {111} silicon during etching in alkaline solutions. We put effort to investigate the chemical interaction between additives, reaction products and observed surface morphology on both atomistic and macroscopic morphological level. Understanding the interaction at the silicon surface provides the opportunity to obtain better control of the surface development and thus the evolved surface morphology after etching, hinting towards a better control and reproducibility of the anisotropic wet chemical etching of silicon.

In chapter 2 the role of several parameters including reaction products on the etching of silicon are investigated. The local formation of etch pits by presence of reaction products changes the surface. When the silicon {111}, the slowest etching face, is etched using different aqueous solutions of KOH, in all cases shallow, point bottomed etch pits are formed. It was found that etchant concentration, temperature, transport limitation and the addition of isopropyl alcohol (IPA) change the number density and morphology of the pits to a large extent. Sirtl delineation etching proved that the pits are not related to dislocations or stacking faults in the crystals. We proposed that etch pit formation is autocatalytic in nature and is triggered by accumulation of reaction products at
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the bottom of the pits, locally enhancing the downward etch rate. This autocatalytic process also explains the formation of the concave shaped pits, obtained after etching in KOH solution with IPA additive.

In chapter 3 we introduce a method for the analysis of surface morphology applied to etched silicon {111} surfaces. The so-called Lichtfigur analysis is used to determine the average pit morphology of etched silicon surfaces. It is an effective method in surface analysis complementary to optical microscopy. The surface morphology of silicon {111} after wet chemical etching in aqueous KOH solution has been investigated by this technique. The morphology of etched silicon{111} does not change significantly in pure KOH solutions as a function of time. In solutions containing additive isopropanol, however, the etch pits evolve from circular to triangular, with a final shape that depends on the isopropanol concentration. It has been experimentally proven that the IPA additive does not participate in the etching reaction and no etching occurs in the absence of water, which implies that OH\(^-\) only serves as a catalyst.

In chapter 4 we use the Lichtfigur analysis to investigate the influence of additives and reaction products on the etching behaviour of silicon {111}. Apart from temperature and alkaline concentration, the surface morphology of the silicon surfaces after wet chemical etching is also profoundly influenced by the presence of additives in the etchant solution. The influence of several organic (aprotic, protic and ionic) additives on the density and shape of etch pits on etched Si-(111) surfaces is investigated using optical microscopy and the Lichtfigur technique. For all the additives used, the number density of the pits increases by 1 to 3 orders of magnitude. The triangularity of the pit shape, expressed by a dimensionless number, \(R_{ab}\), increases substantially as well. These alterations are attributed to local desolvation of reaction products by the organic additives in a thin 'surfactant' layer in the vicinity of the silicon surface. Chemisorption of additive molecules does not play a role in this process.

In chapter 5 we discuss the atomic structure of silicon under etching conditions. We present a surface X-Ray diffraction determination of the silicon{111}-liquid interface structure. Using diluted aqueous potassium hydroxide (KOH) and ammonium fluoride NH\(_4\)F etchant, we have observed that the crystal surface is hydrogen terminated and is slightly relaxed to compensate for the presence of the etching solution. Our results show distinct ordering of the first liquid layer on basis of Van der Waals interactions in NH\(_4\)F solutions during etching and differences in crystal
structure and significant differences in crystal morphology for different electrochemically applied potentials.

In chapter 6 we take a closer look at the absolute etch rate of silicon (111) and the influence of additives. The absolute etch rate of silicon (111) during wet chemical etching in aqueous KOH solution has been investigated with optical interferometry, using masked samples. The etch rate is constant at 0.55μm/hr and independent of alkaline concentration for 1 to 5 M KOH solutions at 60°C. Only at lower alkaline concentrations, the etch rate decreases. Adding isopropyl alcohol does not significantly alter the absolute etch rate. The activation energy of the etching reaction is 0.61 ± 0.03 eV in standard KOH solutions and 0.62 ± 0.03 eV with 1 M Isopropanol added to the solution. This indicates that the reaction is determined by reaction kinetics and not by transport limitations. In all cases the surfaces are covered by shallow etch pits, not related to defects in the crystal. This implies that the actual factor that determines the etch rate is the 2D nucleation of new vacancy islands at the bottom of these pits. This process is likely catalyzed by a local accumulation of reaction products.

In chapter 7 morphology observations are combined with electrochemistry measurements. As the etch rate doubles under more positively applied potential, the pit morphology changes as well and a change of pit shape is observed. The influence of electrochemical potential on the etch rate and morphology of p- and n-type Si-(111) surfaces is studied by using interference microscopy and the Lichtfigur method. Applying a potential more positive than the open circuit potential increases the etch rate, while the pit orientation reverses from monohydride to dihydride termination. A further increase of the potential leads to passivation of the surface and a featureless surface morphology. Finally, by measuring voltammograms at regular time intervals the evolution of the surface morphology during etching was recorded.
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Het anisotroop etsen van silicium in nat-chemische alkalische oplossingen is een veel gebruikt proces in de productie van MEMS structuren. Het verschil in etssnelheid van de verschillende kristalvlakken maakt het mogelijk om complexe driedimensionale structuren te vormen, die gebruikt kunnen worden in verschillende applicaties, zoals sensoren, actuatore of micro-fluid systemen. De reproduceerbaarheid van dit nat-chemische etsen is echter nog steeds niet volledig begrepen, want veel parameters beinvloeden de etssnelheid van de verschillende kristalvlakken. Het etsgedrag van het langzaamst etsende vlak, silicium (111), speelt hierbij een heel belangrijke rol en is verder onderzocht. Dit proefschrift beschrijft de inspanningen om de invloeden op de oppervlaktemorfologie van silicium (111) tijdens het etsen in alkalische oplossingen te onderzoeken. We hebben gepoogd om de chemische interactie tussen additieven, reactieproducten en oppervlakte-morfologie te onderzoeken op zowel microscopisch als ook macroskopisch nivo. Het begrijpen van de interacties aan het silicium oppervlak levert de mogelijkheid om betere controle op de oppervlakte ontwikkeling te krijgen en dus op het uiteindelijk geëtste oppervlak, waarmee een betere reproduceerbaarheid van het etsproces wordt bereikt.

In hoofdstuk 2 wordt de invloed van verschillende parameters, inclusief reactieproducten, op het etsen van silicium bestudeerd. De vorming van locale etsputten geïnduceerd door reactieproducten veranderen het oppervlak. Het silicium {111}, het langzaamst etsende vlak, vertoont de vorming van puntvormige etsputten met een heel flauwe helling, bij het gebruik van verschillende alkalische oplossingen. De alkalische concentratie, temperatuur, transportbeperkingen en toevoeging van isopropyl alcohol (IPA) veranderen de putdichtheid en morfologie van de putten in zeer grote mate. Sirtl delineatie etsen toonde aan dat de gevormde putten niet gerelateerd zijn aan dislocaties of roosterfouten in de kristallen. Wij hebben voorgesteld dat het vormen van etsputten autocatalytisch van
Samenvatting

aard is en gestimuleerd wordt door de opeenhoping van reactieproducten in de putbodems, daarbij lokaal de neerwaartse etssnelheid versnellend. Dit autocatalytische proces verklaart ook de vorming van concaveputten, gevormd na het etsen in KOH oplossing met IPA toevoeging.

In hoofdstuk 3 introduceren wij een analysemethode om oppervlakte morphologieën te bepalen en passen die toe om silicium{111} na natchemisch etsen in KOH te onderzoeken. Deze zogenaamde Lichtfiguur Analyse wordt gebruikt om de gemiddelde putmorfoologie te bepalen van de geëtste siliciumoppervlakken. Het is een effectieve methode om complementair aan microscopische observatie een oppervlakteanalyse uit te voeren. De morfologie van geëtst silicium{111} verandert niet significant in pure KOH oplossingen bij verschillende etstijden. In alkalische oplossingen met IPA echter, veranderen de etsputten van circulair naar driehoekig met een uiteindelijke vorm die afhangt van de IPA concentratie. Experimenteel is aangetoond dat de IPA niet deelneemt in de etsreactie en dat het etsen geen doorgang vindt bij de afwezigheid van water, wat tevens de katalytische werking van het OH−ion bevestigt.

In hoofdstuk 4 wordt de Lichtfiguur analyse gebruikt om de invloed van additieven en reactieproducten op het etsgedrag van silicium (111) te bestuderen. Naast dat temperatuur en alkalische concentratie de morfologie van silicium oppervlakken beïnvloeden, wordt deze ook sterk bepaald door additieven in de etsoplossing. De impact van verschillende organische additieven (protisch, aprotisch, ionisch) in de etsoplossing op de dichtheid en vorm van de putten op de geëtste silicium (111) oppervlakken is onderzocht met optische microscopie en de Lichtfiguur methode. Voor alle gebruikte additieven nam de putdichtheid toe met 1 tot 3 ordes van grootte. De putdriehoekigheid, uitgedrukt in het dimensieloze getal R_{ab}, veranderde ook substantieel. Deze veranderingen worden toegekend aan de lokale desolvatie van reactieproducten door verhoogde concentratie van organische additieven in een dunne laag in de nabijheid van het siliciumoppervlak. Chemisorptie van de additieven moleculen speelt geen rol in dit proces.

Hoofdstuk 5 behandelt de atomaire structuur van silicium onder etsende condities. We gebruiken de oppervlakte rontgendiffractie methode om de grenslaag tussen vloeistof en kristal te bepalen. Gebruik makend van verdunde KOH en NH₄F oplossingen, hebben we bepaald dat het oppervlakte waterstof getermineerd is en dat de bovenste kristallagen subtiel gerelaxeerd zijn om de interactie met de vloeistof te compenseren. Onze
resultaten tonen een duidelijke vloeistof ordening van de eerste vloeistof laag op basis van Van der Waals interacties in NH₄F oplossingen tijdens etsen en duidelijke verschillen in oppervlaktestructuur en morfologie voor verschillende electrochemische potentiaal.

De bepaling van de absolute etssnelheid van silicium (111) en de invloed van additieven worden verder onderzocht in hoofdstuk 6. Hierbij wordt de absolute etssnelheid van silicium (111) in waterige kaliumhydroxide oplossingen onderzocht met optische interferometrie, gebruik makend van silicium dat is voorzien van een etsmasker. De etssnelheid is constant en bepaald op 0.55μm/hr en is bij 60 °C onafhankelijk van de alkalische concentratie in de oplossingen van 1 tot 5 M KOH. Alleen bij lagere alkalische concentraties gaat de etssnelheid omlaag. De toevoeging van IPA verandert de etssnelheid niet significant. De activeringsenergie van de etsreactie is 0.62 ± 0.04 eV in standaard KOH oplossingen en 0.61 ± 0.04 eV met 1 M IPA toegevoegd aan de oplossing. Dit geeft aan dat de reactie bepaald wordt door reactiekinetiek en niet door transportbeperking. In alle gevallen waren de oppervlakken bedekt met nagenoeg vlakke etsputten, die niet gerelateerd waren aan kristaldefecten. Dit betekent dat de eigenlijke etssnelheid bepaald wordt door de 2D nucleatie van nieuwe oppervlaktevacatures in de bodem van deze putjes. Dit proces wordt met grote waarschijnlijkheid gekatalyseerd door lokale accumulatie van reactieproducten.

In hoofdstuk 7 worden morfologieobservaties gecombineerd met electrochemische metingen. De etssnelheid verdubbelt bij een meer positief aangelegde potentiaal, waarbij zowel de putmorfologie als ook de putvorm veranderen. De invloed van electrochemische potentiaal op de etssnelheid van zowel p- als n-type silicium(111) is bestudeerd door gebruik te maken van interferentie microscopie en de Lichtfigur methode. Het aanleggen van een positievere potentiaal ten opzichte van de Open Circuit Potentiaal resulteert in een 180 °orientatie verandering van de putten van monohydride naar dihydride terminatie. Verdere verhoging van de potentiaal leidt tot oppervlakte passivatie met als gevolg een vormloze oppervlakte morfologie. De evolutie van de oppervlaktestructuur wordt tijdens etsen op gezette tijdsintervallen gevolgd middels het scannen van voltammogrammen.
Samenvatting
Acknowledgements

Most likely this will be the first part of my thesis that many people will read, when receiving it. I admit, it is the part most people look forward to, as many times, I did too. Although this research is completed, the future keeps hold of many more to discover, unravel and understand.

To start with I really wish to thank both Elias and Willem for their patience to help me to complete my thesis, I deeply and sincerely respect the support you both gave me in the end, especially during the famous last bits which kept lasting longer and longer for whatever unexpected or unwanted reasons.

Elias, I wish to thank you and I really appreciate the trust you have given to me to let me start my PhD. Your patience, calmness and dry sense of humour has been an example to get things done. Your dedication to crystal growth and specifically surface diffraction is really remarkable. I enjoyed the introduction to this field and the frequent visits to the ESRF in Grenoble. Surely the surface X-Ray diffraction subject we chose to investigate turned out far from trivial compared to our initial expectations. All these trips to the ESRF were full of experimental surprises and unexpected problems. As many wild ideas and thoughts were crossing my mind, how to resolve the diffraction problem, your calm and structured way of working has really helped me bring to this thesis to a successful end. I truly appreciate your support and confidence you kept in me despite all the setbacks and delays. But in the end the result counts.

Willem, I admire your passionate, gifted and humorous way of performing science. Attending your lectures was always inspiring. As many know, your health is unfortunately not the best, however, your scientific output is remarkable and you lead by example easily. You have always helped to come up with good intuitive answers, whenever I was wondering how to join things together. Your knowledge on crystal growth is remarkable; it should be combined in a standard work like the Ullmann’s encyclopedia.
Therefore, I am anxiously waiting for the moment you have finished the book you are writing. Your fascination for astronomy, birds (both alive and cooked) and wines are well-known. A visit at your house, was always possible when I needed some more fresh ideas and help in solving problems. Thank you so much for your patience and support. "De Beer is geschoten!"

Hugo, although you were not directly connected to my research, you were always in for good discussions and mirroring different views. Whenever you would come by to discuss any subject with Zjak, it was hard not join in the discussion. Your storage in front of our old room, was remarkable.

Duy "Best Asian Noodles" Nguyen for the good cooperation in the STW project team, which I joined as the last one. Without your endless discussions, support and science fun at the ESRF and funny sessions bringing up more questions, rather than finding answers the outcome would not have been the same. I recollect the night shifts at the ESRF, tasting 10 different sorts of noodles to pass the night. Harold, I also wish to thank you for all the good discussions and the help in preparing the samples for many experiments. Thanks for showing me around at l’Ecole Polytechnique and especially for finding ways to obtain atomically smooth surfaces and discuss matters while enjoying a good steak. Somehow food appears to have been a nice topic for the three of us, especially the part of enjoying it. This was of course a great excuse to regularly meet each other for further discussions. With respect to cooking, I cannot say that everybody was capable of surpassing the "Chicken Tonight" dish.

Miko Elwenspoek, John Kelly and Henri Jansen. The three of you were a great support to me as you all showed enormous interest in our research. Henri, I have to admit that you can ask tons of questions. And Miko, although it took a while, I did succeed in mentioning "reliability" in this thesis. Actually it has captured my interest strongly. Most of the failures I met, were of random nature. From the STW user’s committee, I wish to thank especially Dr Arno Steckenborn from Siemens who has shown great interest in all of our work and Dr Leo Korstanje from STW for organizing all meetings smoothly.

Good work is never done without a good and experienced technical staff. Jan van Kessel, for arranging all the materials, equipment, orders and off course the nice fresh and many times way too strong coffee in the morning. It must have been a scarce moment in which I could find you not
smiling. Moreover with your voice it was hardly impossible not to know your location. I dearly appreciate all the efforts you took in arranging what seems to be the impossible. If Jan was not there, I could rely on Wiesiek, who has helped me out with the AFM. Wil "de man met de gouden handjes" Corbeek, for all his technical support and willingness to fix all last minute repairs. Hans Lighart from the Debye Institute, Utrecht University for arranging things Jan could not arrange, due to the infamous new logistical system in Nijmegen (The famous Teflon rod). I want to thank all the men from the Mechanical Workshop and Glass Workshop for all their help. It is a pity that research revolves more and more around flashy legal and financial advisors guiding people through legalities for funding, rather than good and experienced technical staff to support real experiments.

I wish to thank all staff members at beamlines ID32, ID03 and BM26 at the ESRF, for their support in the experiments. Special thanks to Dr. Harald Müller of the Chemistry lab, who was always helpful in providing chemicals and laboratory facilities and Paul Tinnemans, our Dutch connection, for showing us around in Grenoble and his lovely little flowery beamline "Chez Paul". Actually, I have to think deeply to find out who has not given help in all these experiments at the ESRF. Every set of experimental runs required a new team due to whatever reason. In the end almost the whole solid state chemistry department has participated in the diffraction experiment.

One person was always there to provide support and care to the whole department, our secretary Elizabeth. As where Jan can be recognized by his voice, your presence was noted through the fast pace of your walking.

As a PhD student you are lucky to guide students in their projects. My students were Benjamin, Arjan, Maaike, Aryan and Joep. All of you have contributed in parts of this research and each of you has specific qualities that can be expressed in extensive poetry, funny lines or jokes. Benjamin, initially you intended to do a two week introduction, it eventually became a full project. Your characteristic approach and unique grunting during failing experiments was really a joy to experience. Besides this unique way of finding interesting approaches, you did help me in using the Lichtfigur technique in this thesis, I hope you have completed your own PhD now. We will not forget your Cafe au Lait in Grenoble. Maaike, from you I have learned that writing and correcting a literature study can be a very challenging task. For you, tea and chocolates were your favorite food and
Acknowledgments

you will immediately recognize this thesis cover. Arjan, you are a typical cook, once you start a recipe you will not stop testing tons of variety on the same subject. Your practical approach turned out to be very useful in getting things done. It took me quite some time to work out all your data. I remember your interest in beers, especially Belgian ones. I hope you have enjoyed your journeys to Taiwan for your own research. Aryan, the enormous amount of bad luck you faced while doing experiments, was remarkable. Especially the frozen thermostat bath was not seen before. Now you have become the new Dutch connection in Grenoble. Finally Joep, you have a great positive drive in life: your enthusiasm in solving problems is contagious. However, I still do not know if you have finalized your assignment paper. Since there have been so many other students, I wish to thank you all for the good atmosphere.

A special thanks I wish to give to Zjak van Eupen, as we had to share the smallest room in the old (now demolished) department for three consecutive years. Later on in the new building I shared the room with Edwin, Maurits and Paul Poodt and Paul Tinnemans. I enjoyed the many good discussions on a variety of subjects in science and live.

The Solid State Chemistry department itself was a great atmosphere to work, the coffee corner discussions, the risk parties, festivities and outings. They were all great and enjoyable. Later on, the Applied Material Science group joined in and the cooperation worked out nicely, as I have used much of their equipment available for experiments. Thanks Gerard, Peter, John, Paul and Harrie for your help there. Since there have been so many other people at both departments, I wish to thank in complete random order: Daniel, Jan Los, Edwin, Paul V., Cristina, Fieke, Sander, Arno, Rienk, Wim, Herma, Menno, Neda, Natalia, Gerbe, Tim, Nick, Gunther, Jan Weyher, Ton, John, Paul Hageman, Hina, Carmen and Joop.

I wish to thank both my parents for their help and support to us when we faced difficult times, you have always been willing to help and support. Even though you did not really understand much of what my research was about, I could see you tried to understand it. My family, I wish to thank for their support and interest, even when things kept getting delayed. Elie and Frans, I wish to express my thanks to you for taking care of Qasim with so much love and care. Without any hesitation the two of you were always there to help us out. My friends, colleagues and former colleagues, I wish to thank for encouraging me to complete this thesis.

Salma, our life together has not followed predictable paths, to say the
least. We have enjoyed great times and shared enormous grief. Either way, I simply love you and just feel happy with you and hope that we can enjoy life to the maximum. Sometimes, I guess we just need to accept things the way they are and make the best out of it.

My dearest daughter Aysha, although you are not with us here today, my memory of you will never leave my heart. Your arrival in this world changed my life completely. You are my little bright angel and bring me "Tears in Heaven". My love for you is out of this world and there is always a part of me looking for you.

Qasim, the joy and happiness you provide to me, gives me enormous lust for life. I am so thankful for your presence; my love for you I cannot describe. Your strength, determination and liveliness has brightened my life. You live up to your name and distribute enormous happiness in my life and of many others. You make me realize every day, what really counts in life.

A PhD thesis, holds the name Philosophy Doctorate. After years of hard work, dedication and eventually nice results, it offers a good opportunity to reflect on the achievements and cast a philosophical view on the achieved results and to present a view on the worldly matters from a different perspective. As PhD refers to "the love of wisdom" or the pursuit of in-depth knowledge, this approach can be turned around and used as a reflection of ones own in-depth knowledge with respect to the broader picture of life. Eventually one arrives at the point of reversing the approach in a pursuit of widening ones field.

I have been considering writing a history lesson from the perspective of the elements, and their importance in life and how elements changed the role of mankind in this world. The current events in the world made me change this thought. Four major issues currently dominate political and media agendas: religion, democracy, information control and natural resources.

It is free to state that history is the science told by the survivor, written by the winner and then perceived in the eyes of the beholder. Within this context it is valid to state that history and the resulting political sciences are far more challenging due to their spurious nature compared to chemistry and physics. Fortunately the latter two are less influenced by opinion, politics, religion and subjectivity as e.g. biology, where in a number of
cases objective fact finding has lead to surprising judgements on basis of religious misconceptions and doctrines. As a result, the need for scientific explanation and misinterpretation of experimental results has lead to surprising interpretations of these facts and even doubtful new views, such as intelligent design. An interesting development is the continuing balance between need for spirituality and scientific fact finding. This has resulted in a discussion of believe and fact finding, even more absurd resulting in prosecution of fellow human beings with the passage of time. Unfortunately mankind has not learned much ever since and comparable discussions nowadays arise in which religion is mocked as backward and on the issue of evolution as the only way to go. Sadly enough in a different way, religion is still used as a method of suppression and license to kill. The cause of it is obviously the theorem that "our" religion is the best, the necessary requirement for inviting interested people.

To address the dilemma of science and religion, I use a mathematical analogue, namely orthogonality. It is within orthogonality, where we could find common ground for peaceful co-existence of science and religion. One can describe science and religion as two independent vectors of a multi-dimensional universe, next to time and space and any other descriptive phenomenons. All these vectors form a minimum basis set to create a linear span of how the universe is perceived by humans and their values. It is within the personal perception of any human being to combine these base vectors by any means possible. The linear combination of the basis set will therefore always result in an iterative approximation to span the universe. It is exactly this iterative approximation that yields food for fierce debating, since each personal universe is introduced with an error. The crux of the matter is that nobody knows the error up front and addressing this error comes at a cost of statistical uncertainty.

Referring to statistical uncertainty, the field of social and medical sciences find themselves facing complex matters, described in statistical analogues. This will create room for widespread misinterpretation, due to again the introduced uncertainty. This was recognized already for a long period and quoted to sum it all: Lies, damn lies and statistics.

Civilizations and empires come and go through history. As such knowl-
edge also comes and goes and history tells us, not everything remains preserved for future generations. Different parts of the world are in different phases of development. As other parts of the world excelled in different fields of science, the western world was doomed in gloomy dark ages, only to people perceive life in a narrow-minded religious dictatorship. Freely interpreted, the pope would keep them ignorant and fearful and the king would keep them poor. Tidings changed however and around the world we see people liberate themselves from dictatorship in the period of Enlightenment. Nowadays, comparable trends in other parts of the world happen, surprisingly with a different analogue. It is frequently the religion that is used as a vehicle for liberation in combination with freedom of information, since the only place where freedom of speech was somehow upheld, was ironically the place of worship. Fortunately this is not a complete picture, since the social media and their role in information control, have shown that government control on information is more and more under pressure. Media image has become more powerful compared to the actual truth. Therefore more rules and regulations are imposed on people under the false pretence of counteracting terrorism. In this sense social media have positively opened up the world. The downside of social media on the other hand, is the openness it gives to information. Both trends provide a serious concern for more breach of privacy. As the government primary task is to provide safety and protection for its citizens, the justification can be made to collect information and on the other hand individuals choose themselves to open up and share their life in cyberspace. Taking this into account, both approaches come with a risk of breaching privacy and security. Whether this is justified depends, since Justice and Law are two completely different concepts, the prior refers to truth and reconciliation, the latter refers to the outcome of a political process; A process that can provide justification for terrorism, as the ones freedom fighter can be the enemy's terrorist.

The first industrial revolution was characterized by the massive utilization of steam engines, opening opportunities for large scale industrialization. The use of steam engines was encouraged by the availability of cheap fuel, carbon, first wood and coal, later on through large scale deployment of oil and natural gas reserves. Eventually this lead to the development of the chemical and oil industry as we know it today, with massive diversity achieved by using standard unit operations. Nowadays carbon based fuel burning is used to generate steam for electricity production. Although
the technology has significantly improved, the thermodynamic principle is known only for the last 200 years. Materials have improved and in fact electricity production strongly resembles the use of tweaked steam engines. Better materials have allowed significantly higher steam pressures and temperatures to be used, improving efficiency of power plants. The mind set however, has not changed to new concepts and different approaches to life cycle analysis and overall impact of processes on sustainability. Still enormous amounts of energy are dissipated as heat into the environment, wasted due to thermodynamic inefficiency. Although trends are visible, still many possibilities for improvement are neglected. Technology wise a variety of alternatives are available to improve energy efficiency and different ways of producing energy and energy conversion.

From a reliability point of view, it is justifiable to rely on dependable, but limited technologies. The other argument is that investment in maturing a variety of technologies to improve independence comes at a high cost. The last point is the focus on decentralization of energy production in combination with diversity and higher recycling of household waste and sewer water close to home. In the end the customer benefits in the long run from diversity in supply, autarky from suppliers and less transport losses. The technology is available, however the political willingness to invest and dare to change is not there. Therefore the energy problem is not a technological problem, it is a political problem. Obviously this just remains a short subjective reflection on matters, since there are so many more fields to incorporate, but to sum it all:

It is in Science we find answers and in Arts we find expression, Engineering is the ultimate expression of Arts and Sciences.
List of Publications


2. I. A. Shah, B. M. A. van der Wolf, W. J. P. van Enckevort, and E. Vlieg, ”Wet chemical etching of silicon {111}: Autocatalysis in pit formation.” *J. Electrochemical Society*, 155 (2008), J55,

3. I. A. Shah, B. M. A. van der Wolf, W. J. P. van Enckevort, and E. Vlieg, ”Wet chemical etching of silicon {111}: etch pit analysis by the Lichtfigur method”, *Journal of Crystal Growth*, 311 (2009), 1371,


5. I. A. Shah, W. J. P. van Enckevort, and E. Vlieg, ”Absolute etch rates in alkaline etching of silicon (111)” *Sensors and Actuators A - Physical*, 164 (2010), 154160,

Curriculum Vitae

Ismail Shah was born on 9th of January 1973 in Vroomshoop, where he attended elementary school. He passed secondary education at the Chris­
telijk Lyceum Almelo in 1990. Afterwards he started his study in Chemical
Engineering at Twente University of Technology. During his studies he
performed his intern at Shell Research in Amsterdam on homogeneous
catalyst retrieval from viscous products. His MSc. project was done at
the Department of Chemical Engineering at the University of Cape Town
(South Africa) where he simulated the diffusion of n-Hexane in Zeolite
ZSM-5. This work was supervised by Dr. K. J. Möller in collaboration
with Prof. dr. W. J. Briels and completed end of 1997.

He joined the Netherlands Statistics CBS and focussed on sampling
and income statistics. He moved to Philips Semiconductors in Nijmegen,
starting in Shift Management, followed by assignments in Engineering. Af­
terwards he worked as a Process Technologist at Suikerunie Puttershoek,
foocussing on sugar crystallization.

He then started his PhD research at the IMM laboratory of Solid State
Chemistry led by Prof. dr. E. Vlieg at the Radboud University of Ni­
jmegen under supervision of Dr. W. J. P. van Enckevort. He investigated
the influences on the anisotropic etching of silicon in alkaline solutions, es­
specially surface morphology using different experimental techniques. Dur­
ing his studies he supervised the work of several students and assisted in
lecturing Thermodynamics and Microscopic Techniques. He presented his
research at several meetings.

He started working at NXP Semiconductors as a Material Character­
ization Engineer, investigating a variety of materials related problems.
From material analysis he moved to process development in the field solar
cell production at OTB Solar and at Solland Solar. Recently he started
as Reliability Engineer at DAF Trucks, using statistical tools to analyze
failures and to facilitate reliable engine development.