

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 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_4F 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_4F 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 $0.55\mu\text{m/hr}$ 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 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.