Characterisation of anisotropic etching in KOH using network etch rate function model: influence of an applied potential in terms of microscopic properties

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Abstract. Using the network etch rate function model, the anisotropic etch rate of p-type single crystal silicon was characterised in terms of microscopic properties including step velocity, step and terrace roughening. The anisotropic etch rate data needed have been obtained using a combination of 2 wagon wheel patterns on different substrate and 1 offset trench pattern. Using this procedure the influence of an applied potential has been investigated in terms of microscopic properties. Model parameter trends show a good correlation with chemical/electrochemical reaction mechanism and mono- and dihydride terminated steps reactivity difference. Results also indicate a minimum in (111) terrace roughening which results in a peak in anisotropic ratio at the non-OCP applied potential of -1250 mV vs OCP.

1. Introduction
Anisotropic wet chemical etching of silicon in concentrated alkaline solutions is a widely used bulk micromachining technique for MEMS technology. The difference in etch rates of various crystalline orientations in a single silicon crystal allows for a relative simple manufacturing process of complex structures. Most commonly used etching solutions include potassiumhydroxide (KOH) and tetramethyl ammonium hydroxide (TMAH).

Anisotropic etching using KOH solutions have been used successfully for several decades, but the fundamental basis of the etching mechanism is still unclear. On a molecular/chemical level, the etching process, in terms of the chemical/electrochemical reaction mechanisms, seems relatively clear [1,2]. How these mechanisms translate on a microscopic level, where phenomena such as step patterns and terrace roughening are important, is still unclear.

In this work we have characterised anisotropic etching in terms of microscopic properties using the network etch rate function model proposed by Veenendaal et al.[3]. To obtain the necessary experimental data in the form of anisotropic etch rates of silicon, a combination of 3 micro machined sample types were used, including 2 wagon wheel patterns on different substrates and an offset trench pattern sample. Using the network model and the measurement samples, the influence of an external electrical bias on anisotropic etching, has been described in terms microscopic properties.

2. Theory

2.1. Network etch rate function model
Many current etch models are Monte Carlo type models which rely on molecular and chemical information. Etch rates are determined by crystalline structure, chemical bond strength and reaction probabilities [4, 5]. Although these models can accurately describe the etching process on a molecular scale, they give little information on a microscopic scale. Experimentally determining these microscopic scale properties and influences is difficult as conventional etch experiments generally yield anisotropic etch rates which, on their own, do not give sufficient information concerning surface roughening and step patterns. Due to the scale of these properties, direct observation is also difficult.

The network etch rate function model however is a microscopic scale model and can be used to describe these anisotropic etch rates in terms of these properties. It uses a microscopic step etch mechanism approach which is based on the fact that the overall etch rate of Si in alkaline solutions is predominantly determined by the movement of steps over crystallographic stable Si surfaces. The model distinguishes two types of surface steps, which are steps present on stable (100) crystalline planes and steps present on (111) crystalline planes, both having different step etch velocities. The step density of an actual surface can be calculated by determining the inclination angle between the surface and the stable (100) or (111) crystalline planes depending on the step types. Any arbitrary surface can then be described as a combination of (100) and (111) step densities. A network assembly of all these step density will then yield the overall perpendicular etch rate of that particular surface. The model also contains step velocity anisotropy which is a function of the planar orientation of the steps. The step velocity is dependent on the angle of the steps and the so called periodic bond chains (PBC). These particular chains are derived from crystallographic information and can be seen as the most stable step orientations on a particular stable plane. For (111) surfaces, 3 PBC’s are present per (111) plane, while (100) planes only have 2 PBC’s per plane.

Using this model to fit anisotropic etch rate data and examining the parameter trends can yield much information concerning microscopic properties.

2.2. Electrochemistry in silicon etching

Xia et al. [6] have shown that the etch rate of Si (100) in a KOH solution is a function of an externally applied electrical potential. Previous work [7] has also shown that this applies to both the anisotropy and the absolute etch rates. These observations indicate that at electrochemical controlled conditions, etching follows a combined chemical/electrochemical mechanism. This mechanism shows that applying a positive electrical bias in respect to the open circuit potential (OCP) will increase electrochemical oxidation, resulting in anodic current and suppression of chemical etching. At larger positive potentials the surface will passivate, effectively inhibiting the chemical etching and additional electrochemical oxidation. Previous results have also indicated a difference in reactivity between monohydride terminated steps present on (111) surfaces inclined towards [112] and dihydride terminated steps present on (111) surfaces inclined towards the [112] surface normal. The results indicate that in qualitative terms the step velocity of dihydride terminated steps are more reactive towards both chemical etching and electrochemical oxidation. Using the network model in combination with electrochemically controlled etch rate experiments, these observations can be quantified.

3. Experimental procedure

To determine the anisotropic etch rates in a crystallographic orientation range sufficient for the use in conjunction with the network model a combination of 3 types of micro machined samples were used. Two of the sample types contained pre-etched maskless wagon wheel patterns, similar to the patterns first described by Wind et al [8]. These patterns have been manufactured into a silicon substrate using reactive ion etching (RIE) and contain wedges with well-defined vertical sidewalls which form the initial surfaces for etching experiments. Etch rates can be determined by measuring the retraction length of the individual wedges. The wagon wheel pattern design consists of 180 equally spaced wedges arranged in a circular array. The wedges are 1° wide, 1400 μm long and approximately 50 μm
high. These patterns have been manufactured on both (100) and (110) orientated substrates. Together both sample types yields etch rate data over 2 orientation ranges perpendicular to each other including the mayor crystalline orientations (100), (110) and (111).

The wagon wheel patterns were manufactured using Czochralski grown (100) or (110) p-type (boron doped, 5-10 Ω.cm) silicon wafers supplied by Okmetic. Standard photoresist lithography was used to transfer the wagon wheel pattern to the wafer which was subsequently dry etched using the Bosch process. A layer of aluminium was deposited on the back of (110) wagon wheel pattern samples forming the electrical back contact necessary for electrochemical controlled experiments. On the other samples, which include the (100) wagon wheel patterns, this procedure was replaced by a simpler GaIn back contact step prior to the etching experiments.

Wagon wheel patterns have a disadvantage in that, due to the geometry of the design, very low etch rates cannot be measured. These include the important etch rates near the true (111) orientations. The offset trench pattern design was used to obtain the anisotropic etch rates of these orientations. This design consists of an array of short dry etched rectangular trenches of which the long sidewalls are at various offset angles to the true (111) orientation. Perpendicular etch rates was determined by measuring the under etch underneath a nitride mask. The advantage of this method to other under etch-based methods (such as V-grooves) is that, as with wagon wheel patterns, the starting surfaces are well defined with specific offset angles. A disadvantage compared to the wagon wheel technique is that for reliable under etch measurements, etch times must be greatly increased to obtain sufficiently large under etch distances and the presence of a mask can introduce mask effects, which can create step sources and influence the perpendicular etch rate. The total design consist of 61 separate trenches with a maximum offset range of -3.0° to +3.0° towards the (111) orientation with a 0.1° step size. The trenches are 800 μm long and 100 μm wide and approximately 50 μm deep.

Offset trench patterns were manufactured using (110) orientated wafers identical to the ones used for (110) wagon wheel patterns. 300 nm silicon rich nitride (SiRN) was deposited on the wafers using LPCVD. The sample design was aligned to the primary wafer flat and transferred using standard resist lithography. The pattern was etched into the SiRN using RIE, subsequently the trenches were etched using the Bosch process.

Electrochemical controlled etch experiments were performed inside a Teflon vessel, without any mechanical agitation. The electrochemical setup consists of a Pt counter electrode (Radiometer M24Pt) and a saturated calomel electrode (SCE, Radiometer REF401) which functions as a reference electrode. The silicon sample which acts as the working electrode, was mounted inside a KEL-F holder. The electrical back contact was isolated from the solution using of viton o-rings. External potential differences were applied using a potentiostat (Princeton, 366A), current and voltage were monitored using a series of multimeters (HP, 34401A) connected to a computer for data acquisition.

Prior to the etching experiments, the top surface of the samples were cleaned in 65% HNO₃ (Merck, GR for analysis) followed by deionised water (Millipore, 18 MΩ.cm) in order to remove contaminants. If necessary an electrical back contact was formed by locally removing the native oxide or SiRN by scratching the back of the samples with a diamond tip pen. GaIn euctecticum (Aldrich) was applied to the back to obtain an ohmic contact. The etching solution consists of 5.0 mol/l KOH solution (prepared from Merck KOH pellets, Selectipur). The solution was continuously bubbled using Argon. All experiments were done in the dark at a temperature of 50°C. The native oxide present on the samples was removed directly within the setup using the etching solution itself and was monitored by measuring the OCP as a function of time. After the native oxide removal, a fixed potential was applied and the subsequent etch time were 60 min for wagon wheel patterns and 180 min for offset trench patterns.

The wagon wheel retraction as a result of anisotropic etching was determined by using a combination of microscopic observations and digital image compositing. Viewed at an angle with oblique lighting, microscopic images were taken of the individual wedges using fixed reference points. The individual wedge point retraction lengths and therefore the etch rates were obtained by digitally compositing the images. The under etch rates of the offset trench patterns, which are equal to the
perpendicular etch rates, were determined using a combination of microscopic observation and digital image analysis. Images of the specific under etch were subject to a digital image profiling procedure, which accurately determines the perpendicular under etch distances.

4. Results and discussion

4.1. Model fit

Figure 1. Network etch rate function model fit of the anisotropic etch rates at -1500 mV vs SCE.

Figure 1 shows a graph of the etch rate measurement results at one particular applied potential. Experimental data of all 3 sample types are plotted sequentially for clarity. The inset shows a detailed view of the results of the trench offset sample. The model fit is included in the graph together with the actual data points used for the model fit. Note that the experimental data at orientations near the (110) are not included in the fit. Closer examination of the available experimental data and the model indicates that the model cannot predict a trend similar to the measured trend near (110) orientations. This indicates that the etching of near (110) surfaces does not follow the step etch mechanism as is outlined in the model. Excluding these data points from the final data analysis therefore does not have significant consequences on the overall model fit. The graph also show an absolute etch rate discrepancy between the (110) etch rate measured on a (100) wagon wheel pattern and a (110) wagon wheel pattern. SEM observations of the wedges show that this discrepancy is a result of a difference in the orientation of the characteristic (110) tree trunk morphology. This difference leads to different shaped wedge points which in turn will lead to a difference in measured retraction length. Data points at (111) orientations measured using the (110) wagon wheel pattern are also excluded. The necessary values for this region are provided by the trench samples. The model fit itself is very accurate with a regression coefficient higher then 0.99 (for all data fits) indicated that anisotropic etching can be successfully be described by a step etch mechanism.
The anisotropic etch rate were measured at various applied potentials, ranging from \(-1500\) mV vs SCE, which is close to OCP, to \(-875\) mV vs SCE which is close to the passivation potential. The significant microscopic parameters obtained from the model fit are plotted in figures 2 and 3 as a function of the applied potential. It should be noted that due to the mathematics of the model, the absolute values of these parameters have little physical significance, the relative trends in these parameters yield the most interesting microscopic information.

4.2. Step velocity and step roughening

In figure 2, the left graph shows the step velocity parameter of both (100) and (111) steps. The results show a decrease in both step velocities at more positive potentials which is consistent with an increase in electrochemical oxidation. The right graph shows the step roughening parameters as a function of the applied potential. These parameters determine the anisotropy in step velocity depending on the angle between the steps and the PBC’s. The (111) step roughening parameter has a strong connection with the mono/dihydride step termination. A roughening of 0 would indicate a monohydride step velocity of 0 and a dihydride step velocity determined by the step velocity parameter. A roughening of 1 means that monohydride and dihydride step velocity are equal and determined by the (111) step velocity parameter. The parameter trend shows an increase, indicating that the difference in etch rates between mono- and dihydride terminated steps becomes smaller at more positive potential, that is consistent with the higher reactivity of dihydride terminated steps towards electrochemical oxidation. At very positive potential the step anisotropy disappears.

4.3. (111) Terrace roughening and anisotropic ratio

In figure 3, the (111) terrace roughening parameter (left) and anisotropic ratio as a function of the applied potential.
In figure 3, the left graph shows the terrace roughening parameters which can be seen as the isotropic etching component of a stable crystalline plane devoid of steps. The (111) etch rate in particular is largely determined by this terrace roughening parameter. The trend as a function the applied potential shows a minimum terrace roughening at the non-OCP potential of -1250 mV vs SCE which translate in a minimum (111) etch rate. The reason for this minimum is still unclear. Coupled with a almost constant (100) etch rate at these applied potential it can be calculated that the anisotropic ratio shows a peak at -1250 mV of around 350 while for other potentials including the OCP the anisotropic ratio ranges from the 50 and 100 (right graph).

5. Conclusions
The anisotropic etch rates of silicon in a KOH solution have been characterised using the network etch rate function model. Using measurement data obtained electrochemically controlled etch experiments using 2 types of wagon wheel pattern samples and an offset trench pattern, the influence of an externally applied potential have been described in terms of microscopic properties. These properties include the step etch velocity, step roughening and terrace roughening. The step velocity parameter trends obtained from the measurements at various applied potential are consistent with the combined chemical/electrochemical reaction mechanism where increased oxidation inhibits chemical etching. The (111) step roughening can be coupled to mono- and dihydride reactivity difference. The observed parameter trends indicate a higher reactivity of dihydride terminated steps towards chemical etching and electrochemical oxidation. It can also been seen from the trends that anisotropy in (111) steps disappears at very positive potentials. Examination of the terrace roughening trend shows a high dependency of the actual (111) etch rate to the (111) terrace roughening. The trends also show a minimum in both (111) terrace roughening and etch rate at the non-OCP potential of -1250 mV vs SCE which results in a peak in the anisotropic ratio.

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