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| | **Experiment title:**<br>**Surface Structure changes during Anodic Oxidation and Passivation of Si(111) in KOH solution** | **Experiment number**:<br>Si-1288 |
| **Beamline**: ID32 | **Date(s) of experiment**:<br>From: 26 September 2005<br>To: 5 October 2005 | **Date of report**:<br>28-2-2006 |
| **Shifts: 21** | **Local contact(s)**:<br>Frank Renner | |
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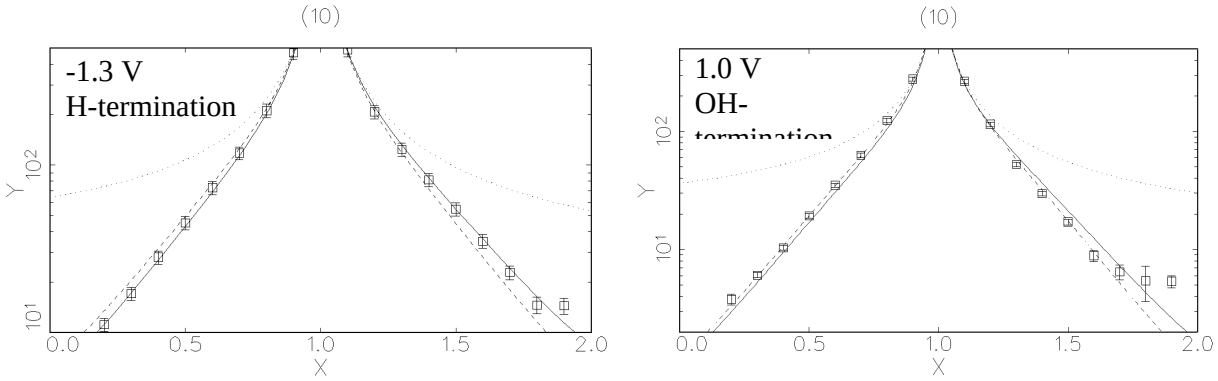
## Report: (max. 2 pages)

A well-known anisotropic etching solution for creating Micro Electro-Mechanical Structures (MEMS) in silicon is potassium hydroxide (KOH). Because of its importance, this process has been studied by several methods and models have been developed for the various chemical steps involved. The silicon surface is expected to be predominantly hydrogen-terminated in KOH solutions. For the etching reaction to start and continue, the surface has to be partly OH terminated. The aim of the experiment was to check the validity of these models by determining the interface structure and surface termination of Si(111) under etching conditions with electrochemical control.

We used an improved version of the experimental cell we used in an earlier experiment 26-02-261, allowing the use of somewhat larger samples and, more importantly, control of the electrochemical potential. The cell uses a transmission geometry in order to have optimum etch conditions and was found to work very well. Using an X-ray energy of 18.0 keV, the X-ray absorption is around 40% (the same value as calculated) so enough intensity is available to do the experiment. We used a horizontal scattering geometry, because this gives an optimum footprint on ID32. Sample preparation was done in a fume-cupboard of the ESRF Chemical Lab. In order to obtain the optimal surface for SXRD (minimum roughness), several cleaning recipes have been tested and compared by measuring partial data sets on samples. Best results were obtained for a simple 5% HF dip of 40 seconds to remove the native oxide prior to etching. All the preparation steps together resemble the so-called RCA clean. Even under the optimum conditions, the initial surface roughness is about 3 Å, which means that the intensity of the rods rapidly decreases away from the bulk Bragg peaks (see also the figure). This roughness equals the roughness of the oxide-silicon interface of the starting sample, so none of the cleaning recipes we tested improved this roughness. The KOH concentration was kept at 0.01M to avoid fast additional kinetic roughening of the surface. A few drops of saturated KCl solution were added to improve the conductivity of the solution for electrochemical measurements. We have used a potentiostat to obtain good control of the electrochemical potential during etching.

In experiment 26-02-261 the data indicated that at Open Circuit Potential (i.e., no potential control), the surface was OH terminated, which was in contradiction with expectations and other experimental techniques. We now learned that the intense X-ray beam leads to an electrical current and a shift in the potential towards higher values. Using our improved cell, we could fix the electrochemical potential to –1.3 V to guarantee the Open Circuit Potential needed for etching. At this potential, we have measured the (00), (10), (20) (11) and (21) rods and all their equivalents. The data show unambiguously a better fit for an H-terminated surface ($\chi^2 = 0.7$), compared to –OH ($\chi^2 = 1.6$), see the figure. Thus the Si(111) surface remains bulk terminated under these etching conditions. Both (00) and (10) data provide information about a partial liquid layering on top of the surface, however, scanning the (00) rod was tedious and did not provide




*The (10) rod of Si(111) during KOH etching. Squares represent the data. The solid curve is calculated for an H terminated surface. The dashed curve represents an OH-terminated surface. The data indicate that the surface is H-terminated at -1.3 V and OH-terminated at 1.0 V. For comparison, the dotted line shows the intensity calculated for a perfectly smooth surface.*

sufficiently reliable data, to make conclusive remarks at this moment.

Switching the applied potential to +1.0V resulted in a differently terminated surface, where the surface is clearly not hydrogen terminated. The data fit best to an oxygen-terminated surface as can be seen in the figure, but the analysis is still in progress. The measured data set in this case is limited due to lack of time: only the (00), (10), (20) and (11) rods have been measured, but not their equivalents. The (00) rod and (10) rod indicate the presence of liquid ordering at the interface. However, the data set does not suffice to draw conclusive remarks.

We further obtained partial data sets at a range of voltages between -1.3 V and +1.0 V. This shows that the surface make a gradual transition between the two possibilities.

The data shows (1) that reliable data can be obtained and (2) that, with proper control of the electrochemical potential, the overall behavior agrees with proposed etching mechanisms. No surface relaxation is found, but with the present surface roughness, our sensitivity is limited. We find evidence for liquid ordering/layering at the interface, but a more precise specular rod data is needed to quantify this.