<table>
<tr><td> </td><td>Experiment title:
Surface structure changes during Anodic Oxidation and Passivation of Si(100) in KOH Solution</td><td>Experiment number:
26-02-299</td></tr>
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From: 1 March 2006
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<tr><td>Shifts: 21</td><td>Local contact(s):
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<tr><td colspan="3">Names and affiliations of applicants (* indicates experimentalists):
D.Nguyen*, H.Philipsen*, A.J. Koekkoek, I.A.Shah*, P. Tinnemans* and E. Vlieg*</td></tr>
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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 further determining the interface structure and surface termination of Si(111) under etching conditions with electrochemical control as well as Si(100) under comparable conditions.

The experiment was troubled with a difficult start. We lost two days of beam time, one day due to a poorly planned crystal change on the S-line monochromator and one day due to poor handling of the H-line monochromator by one of the local staff. Luckily, other local staff got the monochromator back in operation in a very short time, minimizing the delay of this incident. On top of this, the diffractometer alignment took more time than normal. In total this meant that 50% of the beamtime was lost before we could start the actual experiment.

We used an experimental cell designed to do *in situ* X-ray investigation of the silicon (111). 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 20.0 keV, the X-ray absorption is around 40% (the same value as calculated) so enough intensity is available to do the experiment. Sample preparation was done in a fume-cupboard of the ESRF Chemical Lab. In order to obtain the optimal surface for SXRD (minimum roughness), a recipe comparable with the RCA clean has been used. The native oxide layer was removed prior to etching, using a simple 5% HF dip of 40 seconds. The completely prepared cell with sample was mounted and aligned as such on the (2+3) diffractometer in vertical scattering geometry. The KOH concentration was kept at 0.001M to avoid fast roughening of the surface, since the surface will roughen kinetically during etching. We have used a potentiostat to obtain good control of the electrochemical potential during etching.

Despite the loss of several days, we decided not to start with Si(100) (the actual aim of the experiment), but to fill in some gaps in our earlier data set on Si(111). In this we were successful. In particular we measured reliable specular, or (00), rods for two values of the electrochemical potential: -1.3 V, corresponding to the Open Circuit Potential and leading to a H-terminated surface, and +1.0 V, a value at which the surface becomes oxygen terminated. To complete the data set, (10) and (20) rods were measured as well. These data should allow us to derive the nature of the liquid layering at the interface. Preliminary analysis of the passivated surface (at +1.0V) indicates relaxation of silicon lattice to compensate for the

newly formed Oxygen layer on top of the silicon lattice. Further analysis should allow us to derive the nature of this surface layer.

During the slow change of the electrochemical potential from -1.3 to 1.0 V we observed the (1,0.0.4) reflection and saw very clear changes, demonstrating the sensitivity of our method, see Figure 1. We will combine these X-ray diffraction results with spectroscopy data that we plan to obtain in the near future.

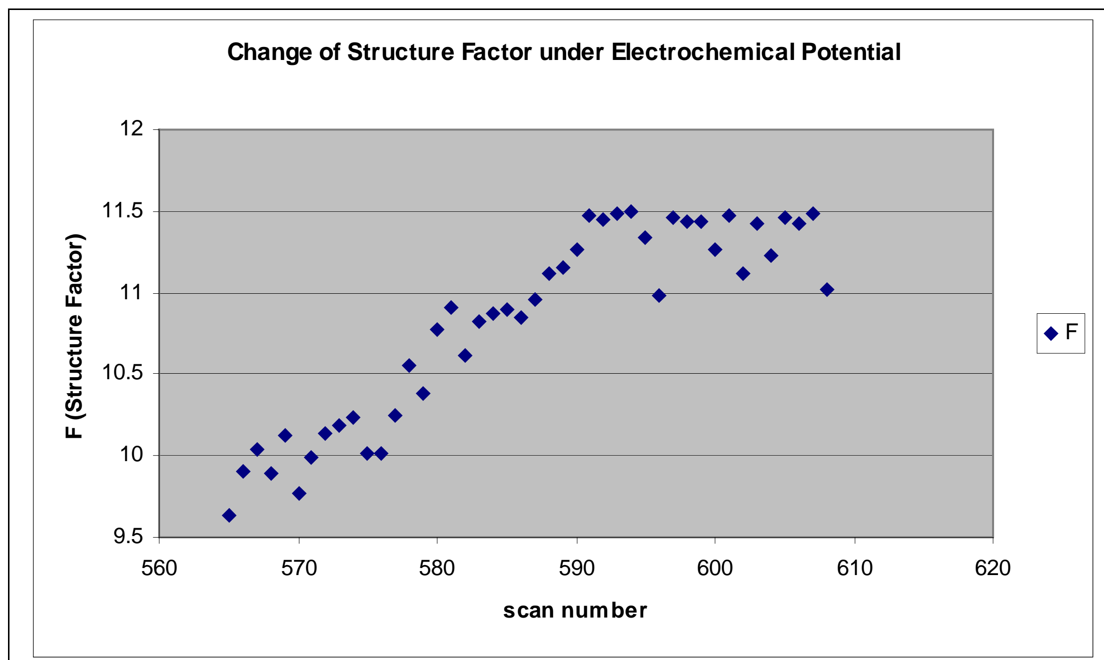

Figure 1 The change of the structure factor of the (1,0,0.4) reflection by sweeping the electrochemical potential with 0.5mV/sec. At Scan 567 the applied voltage is –1.3V, at scan 609 it is +1.0V. A linear change in structure factor is observed until –0.1V is reached. After that the structure factor does not change anymore. The surface has shifted from H-terminated to O-terminated.

The data we obtained in our first experiment using this system (26-02-261) suggested OH-termination at the open circuit potential. We have now learned that these data, without potential control, are not reliable because the X-ray beam induces a small current that shifts the potential value and leads to oxidation. In this experiment we found unambiguously a H-terminated Si(111) surface at Open Circuit Potential when the potential was fixed at the Open Circuit Value.

Due to the little remaining time, we could only measure part of a rod on Si(100). This shows that this surface is smooth enough to do the in situ X-ray diffraction measurements. We plan to obtain such data in the future.