

## The Early Stages of Si Roughening in Fluoridic Media: a Surface Analytical Study Using Synchrotron Radiation Photoelectron Spectroscopy and Scanning Probe Microscopy

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The transition from atomically smooth electrochemically hydrogenated silicon surfaces towards spurious and more distinct roughening is investigated in dilute ammonium fluoride solutions at slightly acidic pH. The photoelectrochemical experiments are done under potential and light flux control in the region of divalent dissolution of Si. We extend an elaborate dissolution model [1] with respect to intermediates and its energetics and follow the roughening process by surface analytical methods. For identification of reaction intermediates, the binding energy shifts,  $\Delta E_b$ , measured for the Si 2p core level with high surface and spectral resolution using SRPES are correlated with predictions for the silicon partial charge  $\rho$  of intermediates calculated by density functional theory. In the so-called initial state model [2], a linear relationship between  $\rho$  and  $\Delta E_b$  is found for some surface species, which have been postulated in the model of Allongue, Kosta-Kieling and Gerischer (AKG) (see fig.1). The presence of species with two backbonds and H, OH or H, F termination towards the solution is indicated, thus supporting the AKG model at least in part. The r.d.s. of the overall dissolution reaction is given by the slowest and/or strongest bound species which are consequently most likely to be found on the surface. Hence, ligand exchange and the first solvolytic splitting of the backbonds appears rate determining. Fig. 2 shows a photoelectron spectrum of the Si 2p core level and the deconvolution of the spectrum into four features: the bulk signal, a surface core level shift due to the Si - H termination of the (111) surface and two signals from higher oxidised Si surface species, related to OH and F termination. In addition, evidence for a precipitate of the reaction,  $\text{SiOHF}_3$ , is found (see Fig.1).

In atomic force microscopy (AFM) experiments, the successive roughening was followed on float zone n-Si(111) (which exhibits about two orders of magnitude less O content and less growth defects). The results show that roughening starts at the reentrant sites of the zig-zag structure obtained after H-termination (dissolution charge passed 0.25 bilayers) and increases with anodic potential as well as with time. Fig. 3 shows a surface image for dissolution of three bilayers at 0.15V anodic from the rest potential, held for 60s. One clearly sees remnants of the terrace structure but also increased pit formation with pit depths ranging from one to six bilayers. It appears that a branching in the dissolution reaction occurs from sole removal of atoms of terraces (AKG model) without pit formation towards increased pitting at reentrant sites and corners of terrace steps which then extend further. For a larger variety of solution parameters, we have evaluated the introduced rms roughness  $R_a$  with respect to the

charge passed, Q, and obtain a linear relationship between  $\log R_a$  and Q with different slopes for the molarity of the  $\text{NH}_4\text{F}$  solution. We interpret this by reaction branching between terrace removal and pit formation, not included in the AKG model.

### References:

- [1] P. Allongue, V. Costa-Kieling, H. Gerischer, *Electrochim. Acta* 40 (1995) 1353  
[2] D. Briggs, J.C. Riviere, chapter 3 in: *Practical Surface Analysis*, eds. D. Briggs and M.P. Seah, Wiley & Sons, 1982

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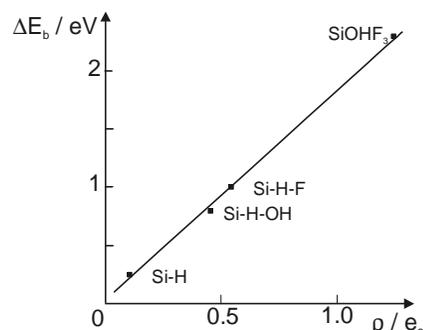


Fig. 1. Observed Si binding energy shifts vs. calculated partial charges

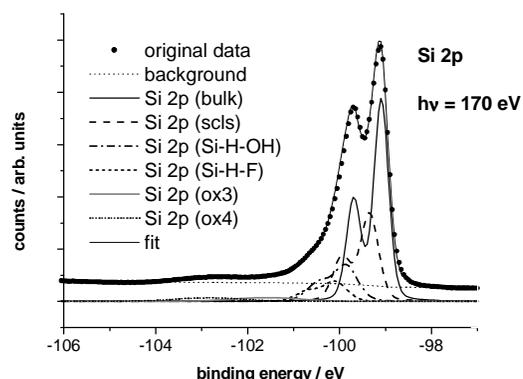


Fig. 2. Photoelectron spectroscopy data for the Si 2p core region after sample emersion slightly positive of ocp.

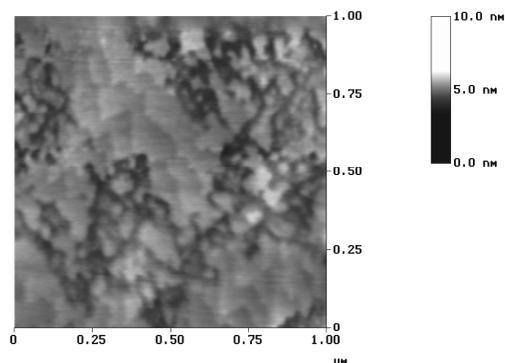


Fig. 3. AFM micrograph of Si(111) after sample emersion slightly positive of ocp (see text).