Investigation of Early Stages of Porous Silicon Formation by Photoelectron Spectroscopy using Synchrotron Radiation and AFM

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The initial and early stages of self organised structure formation on silicon(111) in dilute fluoride containing solutions at moderate pH is investigated by photoelectron spectroscopy(PES) using synchrotron radiation and atomic force microscopy(AFM). A low-contamination well established combined electrochemistry/UHV surface analysis system is used in which the samples are excluded from any ambient atmosphere and electrochemically processed in a nitrogen-purged UHV-attached chamber. The PES results are obtained by interupting the photoelectrochemical roughening process in the potential range where porous Si is formed, i.e. below and at the first current maximum in the I-V curve. We analyse the PES data in order to further elaborate a model for the divalent dissolution of Si, particularly to determine possible rate determining steps as their reaction products are more likely to be found on the surface. As reference, we use the surface condition of the electrochemically H-terminated surface.

We analyse the O 1s, F 1s and Si 2p lines with variable photon energy thus changing the surface sensitivity. AFM results show increased roughening depending on anodisation with respect to the rest potential being largest at the first current maximum. Under our experimental conditions, the roughening is still small with a calculated rms roughness parameter of 2.6nm. Although oxidised Si is found in at least 3 discernible states (including a surface core level shift due to hydrogenation), no evidence for Si in silicon oxide is found, particular upon inspection of the O 1s line. Evidence that the first step in solvolytic back bond splitting is the r.d.s. is presented and compared to the electron injection step in the dissolution reaction.

It is found that the surface chemical state changes considerably in the small investigated potential range of about 0.3V. Even on very well H-terminated surfaces, remnants of OH, water and a very small amount of fluoride anions are present. Upon anodisation, an increased amount of O in water, fluoride, Si-F species, OH and a higher oxidised Si species, presumably a precipitate from the dissolution process with Si bound to OH and 3 F are found. In the detailed data analysis we also consider the possible influence of the roughening on the PES results. The data are discussed in comparison with density functional calculations (DFT)of the partial charge and configuration of the Si atoms in the dissolution model.