

Investigation of initial stages of structure formation processes on silicon electrodes by photoelectron spectroscopy using synchrotron radiation and in-situ AFM

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Structure formation on Si has a wide range of applications. Among them are sensors, light coupling systems for photovoltaic solar cells(1) and, for instance, photonic crystals(2). Despite recent results to form ordered arrays for the latter two applications, the demand for further miniaturization necessitates the control of structure formation in the 0.1micrometer range. One of the relevant structure formation processes takes place in the divalent dissolution regime of Si in fluoride containing solutions. Ordered macropore arrays with high aspect ratios have been formed photoelectrochemically which act as photonic crystals(3). A reduction of the pore dimensions results in an increase of the photonic gap. New light coupling systems for photovoltaics also demand highly controlled induced structures. For both cases the investigation of the initial phases of the structure formation can provide essential information for better growth control.

For a detailed study, we investigate the divalent dissolution at Si electrodes in dilute ammoniumfluoride solutions at pH values where the dissolution is slow. The potential range lies between the rest potential and the first current maximum of the photocurrent – voltage curve. The results are compared with the prediction of Gerischer and coworkers(4) who developed a detailed microscopic model for the dissolution reaction.

Photoelectron spectroscopy(PES) has been performed using an established combined electrochemistry/surface analysis system(5) which has been installed at the U49/2 beamline at the synchrotron BESSY II. We use the photon energy to change the surface sensitivity of the spectra for the respective elements. Upon sample emersion at the first photocurrent maximum(j1), we observe a surface core level shift whose relative contribution to the overall signal gives a measure for the remaining H coverage from the preparation. A rather large Si(I) and a weaker Si(IV) signal is found. The O1s line does not show silicon dioxide. Oxygen is present in the form of OH and O in water. The F 1s line shows fluoride and a larger signal of Si – F species.

The dissolution model predicts that one of the two dissolution charges results from electron injection into the conduction band. Preliminary results show that this appears to be the rate limiting step and that other processes like ligand exchange and solvolytic splitting of Si backbonds are fast.

In the considered potential range, roughening of the surface occurs. In order to be able to interpret the photoelectron spectroscopy data correctly, the measurement of the surface topography is important. This has been done in a series of in-situ measurements using atomic force microscopy performed in an electrochemical cell at the same electrode potentials as for the spectroscopy. We find a substantial roughness at j1 which is implemented in the evaluation of the PES data(6). The valence band photoelectron spectra are analyzed with respect to the observation of a surface radical postulated in the model(5) and whether the Si(I) species induces a band bending due to charge exchange between this defect and the semiconductor. Further results obtained close to the rest potential and at intermediate potentials will be described and evaluated.