Electrochemical Modification of Semiconductor Surfaces Studied with X-rays

Jörg Zegenhagen
European Synchrotron Radiation Facility ESRF
B.P. 220, F-38043 Grenoble Cedex, France

Electrochemical processing of semiconductor surfaces is in the focus of interest because of the importance of various wet chemical treatments in the semiconductor industry. Among the different electrochemical processing steps, metallization is arguably the most important. A prominent issue is the improvement of metal interconnects and here notably recent advances by using electrochemical deposition of Cu and the electrochemical structuring of the Cu deposited surface. However, despite significant advances in industrial applications, the structural processes at semiconductor electrodes are still poorly understood on a microscopic level. This is mostly due to the lack of analysis tools, which are applicable in the presence of the electrolyte. For metal electrodes, in-situ studies using scanning tunneling microscopes have brought about a wealth of information. However, the technique is very difficult to apply in-situ for semiconductor electrodes and X-ray techniques remain the only methods, which are suited to provide the needed structural information on the atomic and nano-scale.

In this talk, I will describe how to employ synchrotron x-radiation to the in-situ study of semiconductor electrolyte intefaces by using proper in-situ cells [1,2] and report how we applied x-ray tools such as grazing incidence x-ray diffraction (GIXRD) and the standing waves (XSW) technique to the analysis of the surface structure of electrochemically modified GaAs and Si electrodes. The GIXRD and XSW technique complement each other nicely and yield information about the structure of surfaces on the microscopic, nano, and atomic scale.

The XSW technique [3] utilizes x-ray diffraction for creating an interference field, then recording the scattering from this interference field, which exists in the region of overlap of the incident and reflected x-ray waves and adopts the spacing of the diffracting planes. The planes of this wavefield can be moved by half its spacing upon traversing the range of total reflection by changing the angle of incidence on the sample or the energy of the incident x-rays. Consequently, the x-ray fluorescence yield of a particular atomic species will exhibit a specific response as a function of angle (or energy), which is indicative of the position of these particular atoms with respect to the lattice planes of the substrate. The XSW technique allows an element specific and precise structural analysis of minute quantities of an adsorbate (less than 1/100 ML), even if it does not exhibit long-range order [4]. I will report about how we used the XSW technique to analyse in-situ the structure of metal adsorbates on GaAs(001) and Si(111) in the low coverage regime[5,6,7].

The GIXRD technique is ideal for investigating the structure of clean surfaces on the atomic, nano and microscopic scale. We can analyze the internal structure, symmetry, size and dimensionality of the unit cells of adsorbate and epilayers as well as their long-range order. The technique is equivalent to common single crystal diffraction, but surface sensitivity is gained by working at a very shallow angle of incidence, limiting the penetration of x-rays into the crystal to a few atomic layers. The other notable feature, which is utilized, is the fact that only a three dimensional infinite object gives rise to sharp Bragg spots, whereas an object, terminated by a surface, exhibits characteristic diffuse scattering, connecting the Bragg peaks in the direction normal to the surface. This diffuse scattering is observed from two-dimensional adsorbate layers but also from the clean substrate, representing the so-called crystal truncation rods (CTRs). Even if the surface lacks a particular superstructure, the CTRS can be analyzed and their profile is characteristic of the structure the surface on the atomic and microscopic level [8].

I will present examples of how we employed the GIXRD technique to investigate the structure and ordering of GaAs(001) electrodes in sulphuric acid and hydrogen terminated Si(111) electrodes in H_2SO_4. While GaAs(001) surfaces in UHV always exhibit reconstructions with mostly twofold periodicity, characteristic of As or Ga dimer formation, we did not find any indication of this in the electrolyte. Thus, we could conclude that As or Ga dimer formation is inhibited by the presence of the electrolyte. By potential controlled hydrogen etching of an amorphous As layer on GaAs(001) in sulphuric acid, a well defined and smooth GaAs surface can be prepared [9]. The excellent structural quality and smoothness of electrochemically prepared Si(111):H can also be proven by CTR scattering.

Finally, I will report about investigations of the epitaxy of metals such as Pb, Cu, and Au, deposited on GaAs(001) and Si(111):H electrodes, using GIXRD in-situ and ex-situ and compare the findings with UHV deposited surfaces

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