11-Surfaces, Interfaces and Thin Films

11.01 - Surface/Interface Structures

MS-11.01.01 3D SURFACE STRUCTURE DETERMINATION BY X-RAY DIFFRACTION. By R.G. van Silfhout, EMEI, c/o DESY, Hamburg, Germany.

For many years X-ray diffraction has been a standard technique to determine the atomic structure of bulk crystals. Its application to the study of surfaces is more recent and became possible with the availability of synchrotron radiation sources. The object of recent experimental surface X-ray diffraction work performed so far was to figure out the in-plane (2D) structure of surfaces using a grazing incidence geometry.

A new development is to include measurements along crystal truncation rods (CTR's) in the analysis. This integration of crystallography with CTR analysis enables a full 3D structural determination.

We review the basic principles of CTR analysis, 3D structural determinations and show examples of recent accomplishments in the field, with the emphasis on III-V semiconductor surfaces, which have been studied intensively.

MS-11.01.02 STRUCTURE DETERMINATION OF THE 3x3 SUPERSTRUCTURE OF THE (111)-SURFACE OF InSb BY THREE-DIMENSIONAL X-RAY DATA. By J. Wever, H.L. Meyerheim, V. Jahns, W. Monz and H. Schulz, Institut für Kristallographie, Universität München, Theresienstr. 41, 8000 München, Germany.

Several attempts have been made to solve this structure by two-dimensional in-plane data, including our group. Up to now all attempts were unsuccessful. We combined now the in-plane data with the intensities along of the superstructure reflections perpendicular to the surface. We used these data for the first time to calculate a so-called periodic-nonperiodic Patterson function. The structure could be solved by interpretation of a section through this Patterson-density at w=0. This density showed main features which did not appear in the Patterson density calculated with the in-plane data only which represents a projection of the three dimensioned Patterson-density on the (uv) plane. This demonstrates clearly, that the whole three dimensional information is needed for solving more complicated surface structures. The structure refinements gave an excellent weighted R-value of 5% and a GOF of 1.3. The InSb(111) surface was prepared in UHV by Ar+ ion bombardment and annealing at 673 K for ca. 1/2 h and subsequent slow cooling to room temperature at about 2K/min. X-ray measurements were performed at the wiggler beam line at HASYLAB (Hamburg, Germany) and in the laboratory utilizing a rotating anode source. An incidence angle of 0.7° was chosen. The maximum X-ray exit angle was 69° which allowed to measure reflections up to |h| = 72. The angular resolution was limited by the Soller slits to 0.4° in-plane and 0.8° out of plane. The sample size was 12x12 mm². The data set consisted of 24 superstructure lattice rods measured in steps of 1=0.4°. A total of 218 symmetrically independent reflections were used. The in-plane data set consisted of 73 reflections. All vacancy and trigon models which had been proposed for the (111) surfaces of compound semiconductors can be ruled out. Additionally all models based on relaxations and models preserving the 3m symmetry of the unreconstructed surface could be ruled out as well. This is in agreement with recent STM measurements which showed the existence of two types of rings of atoms above the top layer, one type of elliptical shape occurs with three orientations and a second type of ovoidal shape occurs with two orientations [1]. The final structural model exhibits similarities to the model derived recently for the (19x19) reconstruction of the GaAs(111) surface from STM measurements [2]. These two types of atom rings are staggered above the top layer such that each ring saturates 6 dangling bonds. The rings are centered around an Sb atom.

The surface undergoes a reversible phase transition at about 600 K. No hysteresis could be detected indicating an order-disorder transition. However, the possible existence of an ordered high temperature phase cannot be ruled out because only the disappearance of the reflections in [010] direction could be measured.

References

MS-11.01.03 IN-PLANE STRUCTURE OF Si(111):As-x:1X1 SURFACE STUDIED BY GRAZING-ANGLE X-RAY RECOMBINATION-WAVE MEASUREMENTS. By Osamu Sakata and Kyos Hashizume, Res. Lab. of Engineering Materials, Tokyo Institute of Technology, Nagatsuta, Midori, Yokohama 227, Japan.

Arsenic deposition on c-Si(111) surface removes the $7\times7$ reconstruction to give a simple $1\times1$ LEED pattern. There is a great deal of data supporting As atoms substituting for the top half of the silicon (111) double plane to terminate the surface with a nonreactive line pair orbital. X-ray standing-wave (XSW) work (Patel, Golvchenko et al., Phys. Rev. B 1987, 36, 7179) shows As atoms lying at 0.17 A above the unrelaxed bulk terminated (111) top-layer Si atoms with a nearly perfect crystalline order in the vertical direction, but ion scattering data suggests some disorder in the Si(111)As-$1\times1$ surface structure (Copel, Tromp & Kneller, Phys. Rev. B 1988, 37, 10758). We will show here that the As atoms actually occupy the high-symmetry sites on Si(111) surface with little disorder in the in-plane direction. An As K emission signal was observed from Si(111):As-x:1x1 samples in a high vacuum chamber using XSW's in the grazing-angle geometry (Jacc & Bodeyfe, Phys. Rev. B 1990, 42, 5396). XSW's created from the Si(200) Bragg planes with 14.5 keV synchrotron X-rays had an intensity modulation parallel to the surface. Emission profiles were observed from monolayer As atoms at glancing incidence angles $\phi$ close to the critical angle for total external reflection, $\phi_c$. Unlike in the ordinary geometries, emission profiles at $\phi < \phi_c$ in our geometry with an h vector nearly parallel to the surface show characteristics dependence on the degree of order of fluorescing surface atoms in the in-plane direction. A very good agreement was found in the observed and calculated profiles assuming As atoms lying on the (2x2) planes with a high order.

MS-11.01.04 A DYNAMICAL EFFECT OF CRYSTAL TRUNCATION ROD AND ITS APPLICATION TO X-RAY STUDY OF Cu9Au (001) SURFACE. By H.-H. Hung, S.L. Chang, and K.S. Liang, Synchrotron Radiation Research Center, Department of Physics, National Tsing-Hua University, Taiwan and Exxon Corporate Research, NJ, USA.
Recently, we have studied the surface order-disorder transition of CuAu(001) using grazing incidence x-ray diffraction [1]. Detailed surface x-ray truncation rod scans reveal novel surface ordering phenomena. In this presentation, we will discuss the analysis of the rod intensity based on a modified dynamical theory. The wavefields are derived in a form which can be treated as decoupled refraction modes characterized by Fresnel's coefficients. The corresponding dispersion surface is analytically constructed from the Bragg law and Snell law in k-space so that the geometric picture of surface-normal scan is readily described. Using this formulation, the calculated (100)-(110) rod profile of CuAu in the order phase agrees with the experimental ones. Problems in the calculation for the disordered phase will be discussed.


**MS-11.01.05 Phase Transformations on Stepped Surfaces**

Chiral Melting of Si(111) * and Facetting of Misoriented Pt(001) 1

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Two x-ray scattering experiments carried out on stepped surfaces — Si(111) and misoriented Pt(001) — will be described. (a) Theoretical studies indicate that they understand continuous phase transformations in two-dimension. The exception is the disordering of a 5-fold commensurate state into an incommensurate state. The (3 x 1)-to-(2 x 1) transition of the Si(111) surface occurs at a temperature of 1030 K. Our results provide a detailed characterization of the transition, including the observation of antiphase setting, which complete theory of two-dimensional phase transitions must be able to explain. (b) What happens to a stepped surface at elevated temperature? One striking phenomenon that may occur is facetting, in that the distribution of steps is no longer uniform across the surface; instead, the surface is composed of highly stepped regions and flat terraces. Facetting is analogous to the interface structure of a liquid-vapor interface. We have also observed that stepped Pt(001) surfaces show reversible faceting transformations. Above 770 K, the step are uniformly distributed. Between 770 and 1030 K, the surface is composed of smooth, step-reconstructed regions, together with smooth, stepped, unreconstructed regions. The step separation varies as (kT - E_0)/kT to the power of 3/2, consistent with simple theoretical ideas. By 1030 K, the step separation reaches 6 A, whereafter there is a second transformation. At the second faceting transition, the step separation jumps to 80 A while at the same time the stepped surface restructures.

1With D. Maroudas, R. Bringer, and K. Bhushan (MIT)

**MS-11.01.06 APPLICATIONS OF X-RAY SCATTERING TECHNIQUES FOR THE STUDY OF ELECTROCHEMICAL INTERFACES.** By Hooyou You*, Materials Science Division, Zoltan Nagy, and D. J. Zurawski, Materials Science Division and Chemical Technology Division, Argonne National Laboratory, Argonne, Illinois 60439

A brief description of the theory and practice of synchrotron x-ray scattering technique will be presented with emphasis on the unique characteristics of this technique that make possible the in situ structural examination of solid interfaces buried under a layer of solution, and some recent applications of the technique will be reviewed for the investigation of electrochemical interfaces. The examples will include (1) structural studies of under-potential-deposited monolayers, (2) studies of surface reconstruction of gold single crystals, (3) study of electrochemical passive film formation at the copper/solution interface, and (4) a study of structural changes of Pt(111) single crystal surface associated with incipient oxidation and reduction. In the latter work, it was shown that lifting of Pt atoms occurred, and this result substantiated the long-standing hypothesis for the place-exchange mechanism of oxidation of metal/solution interfaces. It was found that if the amount of charge transferred during the oxidation did not exceed 1.5 e/atom, the initial flat surface could be completely recovered after reduction of the oxide. While, if more charge was transferred during oxidation (up to 3.5 e/atom at 1.7 V measured from hydrogen evolution), the top layer of the surface was irreversibly roughened.

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**MS-11.01.07 ADSORPTION OF HEXAETHYLENE GLYCOL MONODODECYL ETHER AT THE AIR-WATER INTERFACE STUDIED BY NEUTRON DIFFRACTION.** By J.K. Lu*, R.K. Thomas and J. Penfold, Physical Chemistry Lab, Oxford University, U.K.

Neutron reflection has been used to study the structure of the soluble monolayer of hexaethylene glycol monododecyl ether (C12E6) adsorbed at the air-water interface. The concentration was fixed at the c.m.c. (7.5 x 10^-5 M). To obtain a unique structure solution, the measurements of reflectivity profiles involved using a group of partially deuterated surfactants: H2C12E6O, deg.-H2C12E6O, H2C12D1E6O, C12H11903, and a combination of ten reflectivity profiles were measured.

The structure parameters were obtained by analysing the reflectivity profiles using the recently developed kinematic approximation. The area per molecule at the c.m.c. was found to be 55 ± 2 A^2, and the number of water molecules associated with each surfactant to be 11 ± 1. Assuming the distribution of the alkyl chain, the head group and the water disturbed region to be uniform in shape, the thicknesses were 19.5 ± 2 Å and 13 ± 1 Å respectively. The cross distances between the centres of the three distributions were determined directly and that between the alkyl chain and the head was found to be 9 ± 0.5 Å, that between the chain and the solvent to be 10 ± 0.5 Å, and that between the head and the solvent to be 2 ± 1 Å. The degree of extent of alkyl chain associated with water was thus calculated to be 0.52 and that of the chain with the EO groups was 0.54.

The distribution of the first three EO groups was found to be nearly overlapping with that of second three EO groups. The widths were found to be 18 ± 2 Å, compared with 19.5 ± 2 Å for the total six EO groups.