ESRF	**Experiment title:** Structure of solid-liquid interfaces	**Experiment number**: SI-678
Beamline: ID15A	**Date of experiment**: First year: 18.03.-27.03.01, 24.06.-02.07.01, 13.11.-20.11.01 Second year: 14.02.-22.02.02, 03.06.-11.06.02, 27.08.-10.09.02, 10.12.-19.12.02	**Date of report**: 05.08.2003
Shifts: 138	**Local contact(s)**: Dr. Veijo Honkimäki	*Received at ESRF:*

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Exact dates of beam times:

18.03.01	27.03.01	18 shifts	+9 shifts for setup
24.06.01	02.07.01	15 shifts	+9 shifts for setup
13.11.01	20.11.01	15 shifts	+6 shifts for setup
14.02.02	22.02.02	18 shifts	+6 shifts for setup
03.06.02	11.06.02	18 shifts	+6 shifts for setup
27.08.02	10.09.02	30 shifts	+12 shifts for setup
10.12.02	19.12.02	24 shifts	+3 shifts for setup

Final Report:

The structure and properties of functional interfaces have moved into the focus of current research. Especially with the rise of nano sciences interfaces will be even more important and new tools for investigating deeply buried interfaces have to be developed. In previous experiments we have demonstrated the first successful implementation of an instrument to investigate deeply buried interfaces using x-ray energies above 70keV.
This lead to the observation of a fivefold local symmetry in liquid lead at the solid-liquid interface Pb(liq.)-Si(100) /1/, which has long been conjectured in literature. This unique information has become possible by exploiting two experimental devices: We have captured and aligned the local liquid building blocks at a properly selected wall and observed the point symmetry of the associated liquid scattering using evanescent x-ray waves as produced by total reflection at the internal wall-liquid interface.

It was the goal of this long term project to investigate solid-liquid interfaces systematically with special emphasis on the influence of the point symmetry of the single crystal surface and the degree of incommensurability between the solid and the liquid. Realising the potential of the new instrument we have expanded our program. We started to investigate kinetic processes such as the inner oxidation of a deeply buried silicon interface by a lead-oxide layer intervening between (bulk) liquid lead and clean Si(111). We investigated the melting behavior of ice in contact with a SiO_2-wall. In addition we did further experiments on deeply buried organic interfaces composed of a liquid (e.g. water, ethanol) in contact with a chemically modified Si substrate (silanes/silicon). A major experimental step was the implementation of compound refractive lenses (CRLs) in the setup in collaboration with A. Snigirev. In collaboration with the beamline staff at ID15 we have also performed detailed test programs on additional options for beam line optics optimized for high energy microbeam diffraction at both endstations ID15A and ID15B within this project.

Experiments

For the experiments we used the setup that has been developed in two previous experimental campaigns (MI-339, SI-504, SI-583). We apply two different interface sensitive scattering techniques, namely grazing angle diffraction (GAD) using the effect of total internal reflection at high photon energies and reflectivity measurements (XR). This allows us to penetrate bulk solid substrates in order to determine the structure of liquids parallel and normal to the solid substrate. For the long term project ID15A supplied a new granite block, which improved the stability of the setup in comparison with the previously used concrete block (SI-583) where we could not reach the stability that is mandatory for our experiments. The samples were prepared in Stuttgart and transported in-situ (UHV, Ice-chamber) to the ESRF. At the start of each experiment we had to assemble and configure our specially designed diffractometer which accounts for the setup time. At this point we want to emphasize that we continually improved the resolution and stability of our setup within this long term project. As a result we could decrease the setup time from twelve shifts to three. Most recently we have installed 2 sets of compound refractive lenses (CRLs) providing a focused high energy beam at the sample position that provides increased stability and flux in comparison to the previously used collimator. Most importantly, the focal spot can now be shifted online from the sample position to the detector position in order to exploit the full potential of both scattering techniques (GAD and XR) employed in the experiments. The sketch in Fig.1 shows the actual state of the setup which comprises a new technique for x-ray transmission-reflection measurements for the study of deeply buried interfaces using high-energy microbeams.

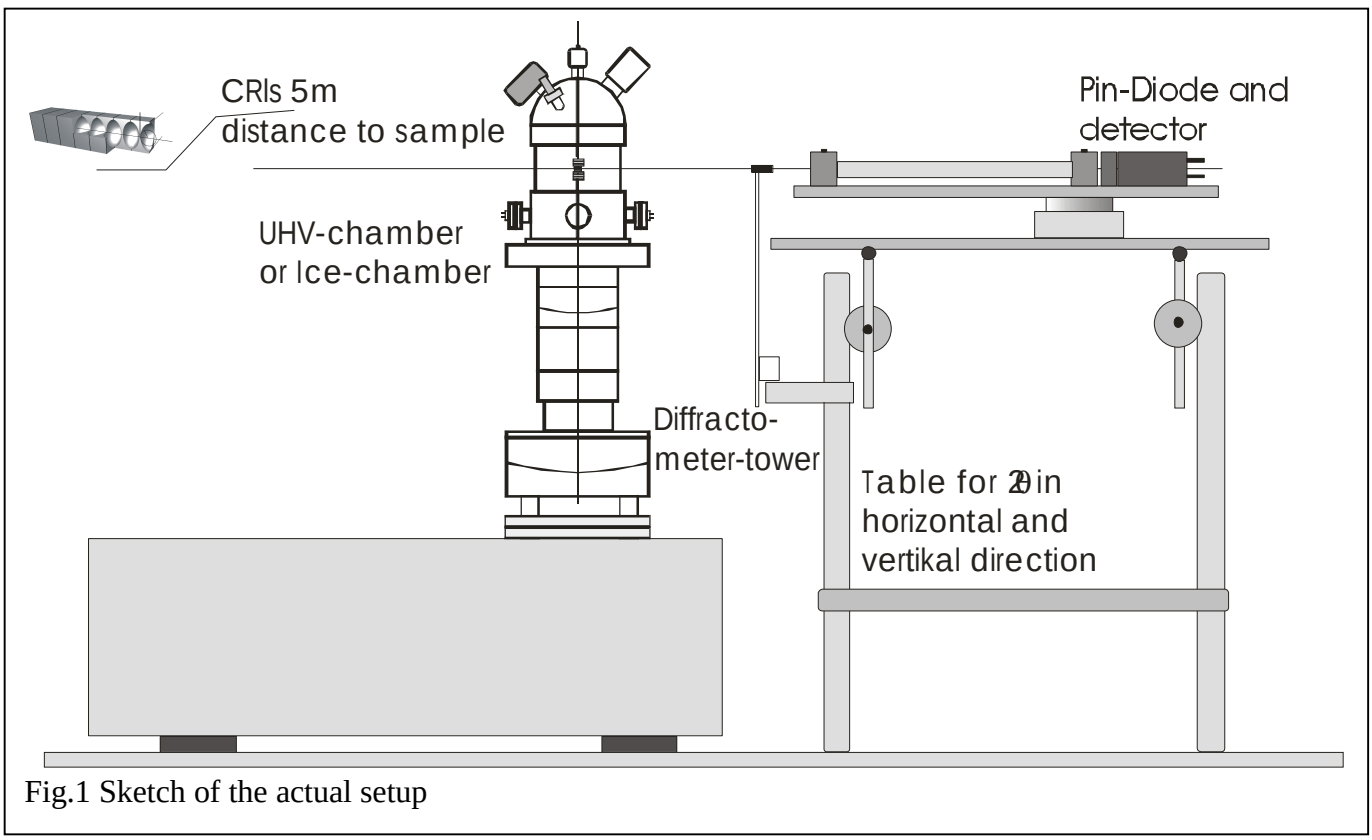

Fig.1 Sketch of the actual setup

The scheme has been published in /3/.

With this setup we have routinely achieved the required beam stability with respect to the sample (drift <0.5µm/shift and <10 µrad/shift) after an initial relaxation of the entire setup to an equilibrium temperature. For the experiments we used high energy x-rays (71.5keV, bandwidth of 160eV) optimized for liquid scattering experiments.

Results

In a first set of measurements we investigated the system In(liq.)-Si(100). The signal to background ratio of this system is decreased by an order of magnitude compared to the previously studied system Pb(liq.)-Si(100). We focused on two aspects: Resolving the *in plane* structure of the system and the *out of plane* structure in comparison with the Pb(liq.)-Si(100) system. For the lead-silicon system we found a second (unexpected) length-scale (approx. 20Å) with density oscillations perpendicular to the interface. The indium-silicon system exhibits a similar second length scale (see Fig.2). This additional oscillation period is superposed onto the atomic layering previously observed at Ga(liq.)-Diamond interfaces (Huisman et al., 1997). We attribute this new length scale to the changes in the in plane structure in a thin liquid contact layer at the interface. In a later experiment we could increase the sample quality and thus we could resolve reflectivities up to q_z=1Å^{-1}. This allows to resolve features in the electron density down to 5Å (see Fig.3). Currently we assume that the profile shows pronounced atomic layering, with density oscillations on larger lenght scales superposed and reaching into the bulk liquid on a length scale larger than the length scale extracted from the pair correlation function of the bulk liquid. This new length scale could clearly be identified in our measurements. However, the observation of atomic layering at the interface requires reflectivity measurements up to q_z=3Å^{-1}. This requires Si substrates with a roughness <2Å^{-1}. We have achieved this only recently (in collaboration with the optics group at the ESRF) by a gradual improvement of polishing and preparation procedures. In order to exclude substrate effects (we penetrate 20mm of crystalline Si) we have performed a set of reflectivity measurements at different azimuthal angles with respect to the substrate. The results prove the new length scale in the density profile to be independent of the azimuth. By a careful theoretical investigation of the excited Bragg reflections of the silicon substrate and a comparison with the transmitted intensity we could prove that the observed features are not originating from secondary effects in the Si substrate. A complete modeling is currently underway. Fig.3 demonstrates the resulting electron density profiles. The main feature is the large density increase in a thick layer adjacent to the interface, which decays oscillatory to the bulk density of the liquid.

The measurement of the *in plane* structure factor of the indium-silicon solid-liquid interface turned out to be

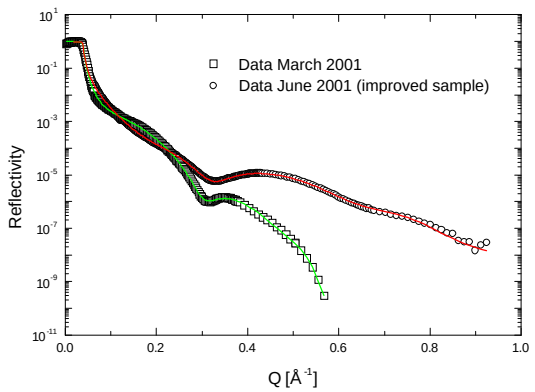

Fig.2 Reflectivity at the In(liq.)-Si(100) interface. Comparison of two curves from two different beamtimes. The latter one shows much more details and gives more resolution in the eletron density profile.

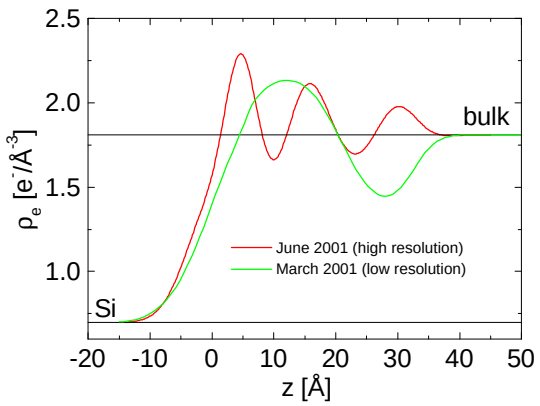

Fig.3 Electron density profile extracted from the reflectivity measurements in Fig.2. Note the increased resolution in the electron density profile due to the improved sample quality.

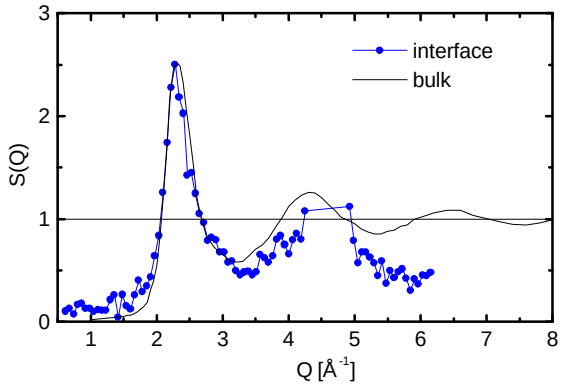

Fig.4 In plane structure factor at the solid-liquid interface In(liq.)-Si(100). The bulk curve is taken from literature /4/.

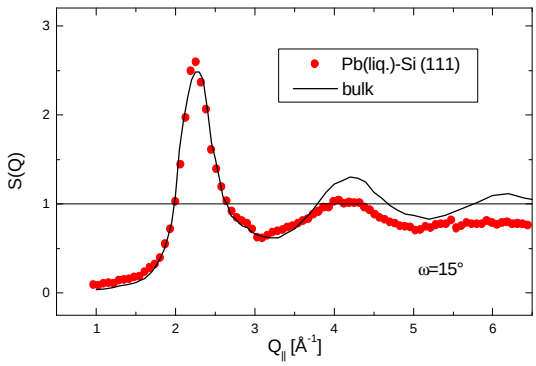

Fig.5 Comparison of in plane structure factor with bulk structure factor of liquid Pb at the Pb(liq.)-Si(111)-interface.

very time consuming. The critical angle of total internal reflection for this system is α_c =0.032° at an x-ray energy of 71.5keV. In order to avoid the footprint of the illuminating beam (vertical height 8µm) spreading into the bulk liquid the incident angle has to be adjusted between α_i =0.023° and α_c. We succeeded in determining the *in plane* structure factor background free up to the second maximum in the liquid structure factor (see Fig.4). The scattering depth is defined by the incidence angle to 70Å. In order to determine the *in plane* structure factor more precisely at reduced scattering depths we have recently increased the stability of the setup and the incident photon flux by an order of magnitude due to changes in the beamline optics /2/, /3/. This will allow us to determine the in plane structure of the interface In(liq.)-Si(100) with comparable accuracy to the Pb(liq.)-Si(100) interface. The most important upgrade for the future will be the installation of a permanent high precision diffractometer at ID15. To summarize this part we found evidence that the system In(liq.)-Si(100) shows similar behavior to the system Pb(liq.)-Si(100), where the interfacial liquid structure is determined by an abundance of (noncrystalline) fivefold coordinated (dynamic) building blocks assembled at the top sites of the Si substrate.

Owing to the smaller incidence angles and lower scattering cross section for the indium-silicon-system, which requires long data collection runs under very stable conditions, we continued to perform measurements at the system Pb(liq.)-Si(111). The Si(111) surfaces have been polished and prepared identically to the Si(100)-samples. The (111) surface of Si exhibits a complicated 7x7-reconstruction after the standard in situ flash cleaning process that we apply. This surface reconstruction is not very stable. Offering more than a monolayer of metallic material at the solid-liquid interface the reconstruction of the silicon surface has been removed.

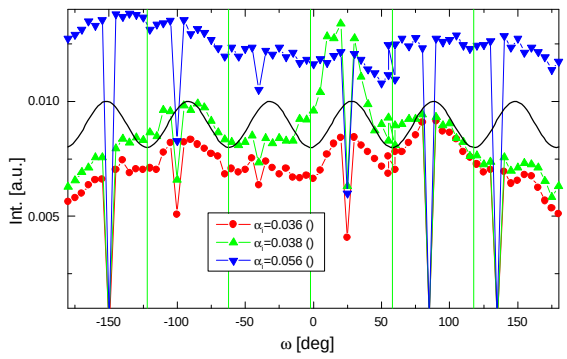

Fig.6 In plane modulation of liquid structure factor of lead at the Pb(liq.)-Si(111)-interface. Indications of a sixfold modulation can be seen. The six sharp dips are due to the steel rods around the chamber.

The non-reconstructed Si(111)-surface is closer packed than the Si(100)-surface. Therefore, the interface potential between Pb and Si is different for both surfaces, which promotes the formation of different structures at the interface. Indeed for thin layers of lead (about two atomic layers) a commensurate low temperature phase exists for Pb on Si(111).

For the interface Pb(liq.)-Si(111) we were able to measure a week modulation of the in plane liquid structure factor. In figure 6 several azimuthal scans on the first maximum of the liquid structure factor are shown at different incidence angles (scattering depth). Only the scans close to the critical angle (<0.04°) exhibit the modulations. They vanish for

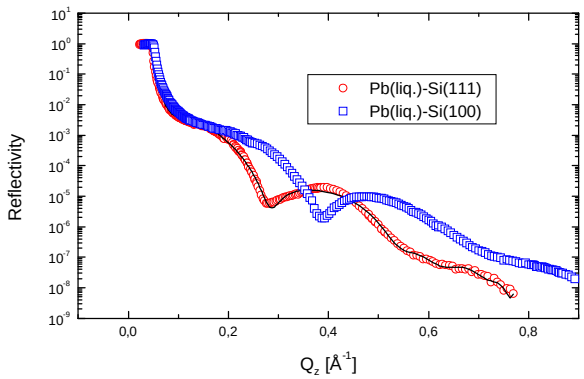

Fig.7 Comparison of the reflectivity at two different crystal surfaces Si(111) and Si(100). The length scales are slightly changed.

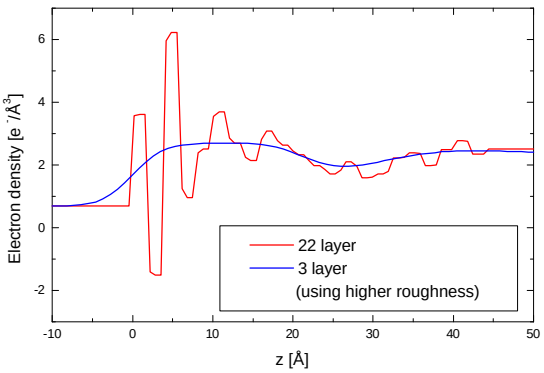

Fig.8 Density profiles at the Pb(liq.)-Si(111) interface. The oscillatory profile yields a lower chi-square value with many more free parameters.

angles above the critical angle where the signal results mainly from bulk scattering. The measurements evidence a sixfold modulation of the liquid structure factor in contrast to the Pb(liq.)-Si(100)-interface where we found a fivefold modulation of the first peak in the structure factor.

Reflectivity measurements at the interface Pb(liq.)-Si(111) yield similar results as for the previously investigated systems. As mentioned before the z-resolution of the electron density profile is limited to $\Delta z = 2\pi/q_{max} \sim 6$Å. Fits of the reflectivity curve show again a thick layer of increased density followed by a layer of decreased density compared with the bulk-electron-density (s. Fig.7 and 8). The measured reflectivity profile is consistent with pronounced atomic layering superposed on density oscillations extending deeply into the bulk liquid. The major difference in comparison to the Pb(liq.)-Si(100)-system is a slight change of the overall layer thickness /5/.

We devoted one experimental campaign to tackle the frequently asked question about intervening oxide layers at the solid-liquid interface. For this purpose we prepared a lead-oxide layer of a thickness of approximately 250Å between a (111) oriented silicon surface and bulk liquid lead. During the experiments the sample was heated to 335°C > T_M^{Pb}. At this temperature lead is liquid while PbO remains solid (the melting temperature for PbO is 888°C). Other Pb_xO_y components are less stable or energetically less favorable and therefore unlikely to exist in the layer. Hence, the oxide layer was solid at this temperature as could be verified during preparation at the free surface before contacting. In our previous experiments the oxide layer was completely removed by sputtering with argon ions prior to contacting the liquid with the clean solid surface. For the purpose of this experiment, however, the sputter process was stopped and the oxide covered liquid brought into contact with the clean silicon substrate. Immediately after contacting the sample was cooled to room

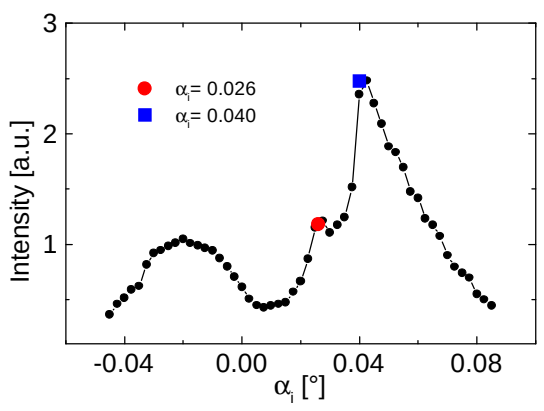

Fig.9 Incident angle scan at the first sharp diffraction peak of the structure factor of liquid lead.

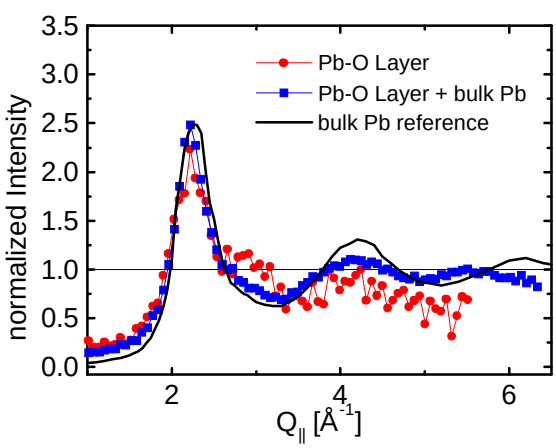

Fig.10 Measured in plane structure factor at various incident angles. (cp. Fig.9)

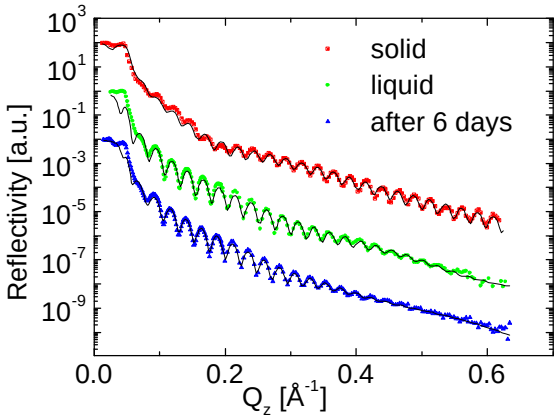

Fig.11 Reflectivity from an intermediate oxide layer

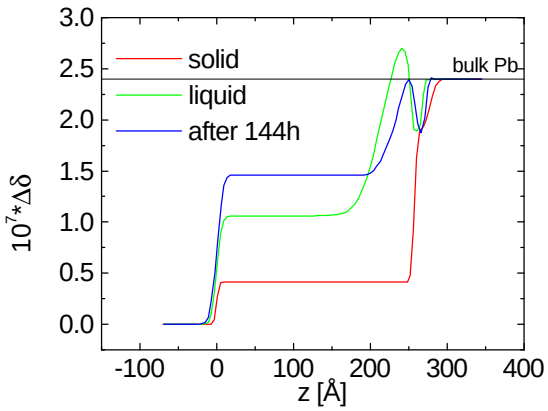

Fig.12 Electron density model for the reflectivity Shown in Fig.11

temperature. Employing high energy x-rays we investigated then the structure of the interface. By scanning the incidence angle α_i and integrating the signal on the exit angle α_f at an *in plane* momentum transfer q=2.18Å^{-1}, which is the position of the first peak in the structure factor of liquid lead, we could clearly identify the additional oxide layer at the interface (see Fig.9). Due to the decreased electron density compared to bulk liquid lead the layer is producing a second interfacial peak in the incidence angle spectrum with a critical angle of α_c=0.026^o (the broad peak at negative incidence angles is identified as a bulk signal transmitted through the edges of the sample). The measurement of the *in plane* structure factor with the interface aligned to both critical angles allows to determine the influence of an interfacial oxide layer onto the structure factor. At small scattering depths with respect to the Si (α_c=0.026^o) the structure factor is entirely determined by the presence of the amorphous PbO-layer. We can clearly identify the first peak in the structure factor, whereas other maxima at larger momentum transfer values are absent. (s. Fig.10) Tuning the incidence angle to the critical angle for pure lead in contact with Si (α_c=0.040^o) the structure factor starts to resemble the structure factor of bulk liquid lead. A comparison with the bulk liquid structure factor taken from literature /4/ reveals the modifications of the structure factor due to the presence of the oxide layer.

We have then performed reflectivity measurements up to a perpendicular momentum transfer q_z=0.6Å^{-1}. The measurements were repeated several times within a single block of beam time. The results are summarized in Fig.11, which shows the measured reflectivity together with fits according to the electron density model shown in Fig.12. At temperatures below the melting point of lead we find a well defined oxide layer with sharp interfaces to the Si substrate and the (solidified) bulk lead. The thickness of the oxide layer is 250Å. Upon melting the overall thickness of the layer between the silicon and the bulk liquid (lead) increases slightly. The roughness on both sides of the oxide layer increases, especially the roughness at the interface to the liquid lead. This leads to a damping of the Kiessig fringes at large momentum transfer q_z. The more pronounced effect is the increase of the electron density in the oxide layer as a function of time. Since the oxide layer was stable at the free surface of the bulk liquid for several weeks before contacting the surface to the Si substrate, we attribute the increase in the electron density at elevated temperatures to an internal (slow) oxidation process, whereby the oxygen is diffusing to the Si substrate forming an energetically favorable SiO_2 layer. As the electron density of the SiO_2 layer is almost identical to the electron density of the Si substrate the additional layer does not produce any prominent features in the reflectivity curves. The measurements demonstrate that our technique is well suited for the investigation of kinetic processes at deeply buried solid-solid interfaces /6/.

Ice experiments
Introduction

Ice is abundant on the earth's surface and plays a crucial role for many processes in nature and technology (e.g. glaciers, atmospheric chemistry, ice films on airplane wings). It is well established that the free surface of ice shows strong surface melting which has been studied in detail in our group /7/. Ice in our environment usually occurs in contact with another solid, therefore it is an important question whether ice in contact with another solid shows interfacial premelting as well. The melting behaviour of ice interfaces are expected to depend on the material in contact with ice but also its morphology. Up to now, interfacial melting of ice is an unsolved problem and adequate experimental methods to study such deeply buried interfaces in-situ were not available or lacking the necessary resolution (as for neutron reflectivity). High-energy x-ray reflectivity allows to deduce the density profile across a deeply buried interface with nearly atomic resolution and would therefore be an ideal tool to explore the interfacial melting of ice. In the framework of this long-term proposal we performed a successful first experiment which shows the feasability of measurements at the ice-SiO_2-Si interface.

Experimental

The setup was identical to the experiments at In-Si and Pb-Si interfaces. This time, however, we used a special sample chamber which accommodated a very stable control of the sample temperature via Peltier elements. For sample preparation, characterization, storage and mounting, we operate a cold room at the MPI in Stuttgart. The samples were prepared from high purity single crystal ice provided by J. Bilgram/ETH Zürich and carefully contacted with clean single crystal Si covered by a native oxide layer. The surface roughness is expected to enhance interfacial melting, therefore a rough substrate was chosen despite of its disadvantages for reflectivity measurements.

Results

Due to the surface morphology (correlated surface roughness), the incident angle (α_i) profiles that we measured have a characteristic line shape. At α_c and $2\alpha_f$-α_c (α_c = critical angle) so-called "Yoneda wings" appear due to the roughness of the surface. The specular peak displays a Lorentzian line shape and broadens significantly with increasing exit angle (α_f). Therefore, a complete α_i-profile has to be measured for every point on the reflectivity curve in order to determine the integrated intensity of the specular peak.
The resulting reflectivity curves at T = -30°C and T = -1°C differ significantly. Whereas the curve measured at -30°C shows the Fresnel reflectivity of a sharp interface modified only by the surface roughness and the presence of a native oxide layer, additional features appear in the reflectivity curve at -1°C. Careful analysis shows that a layer with different electron density emerges at the interface. This layer consists of the quasiliquid formed due to interfacial melting. In a more detailed future study, we will be able to investigate the interfacial melting behavior as a function of temperature. Analyzing the reflectivity curves will provide detailed information on the thickness as well as the density of the quasiliquid layer.

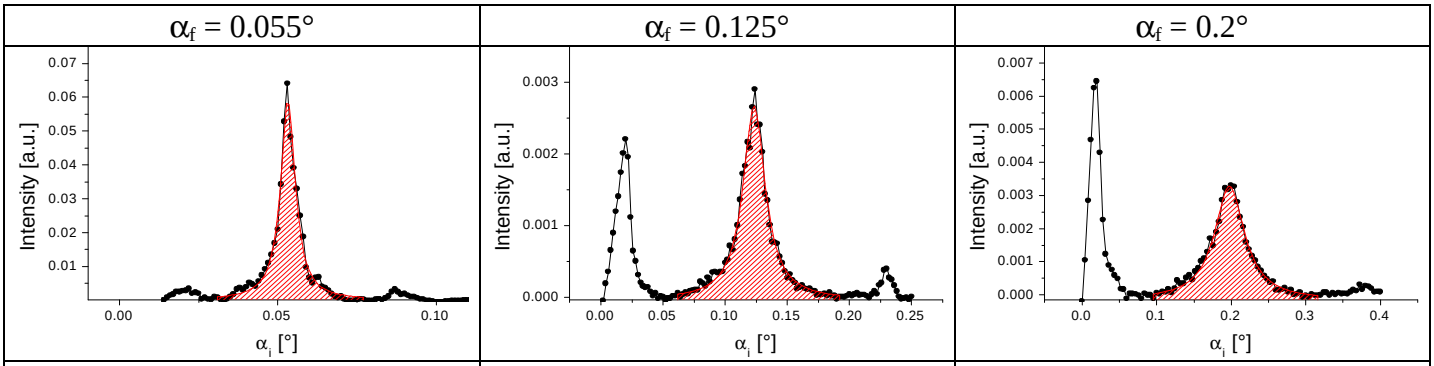

Fig. 13 Incident angle (α_i) profiles for different exit angles (α_f). The peaks at symmetric positions around the central peak position are the so-called "Yoneda wings". The specular peak in the center (Lorentzian line-shape) broadens due to correlated surface roughness. Its integrated intensity is the reflectivity for the corresponding α_f.

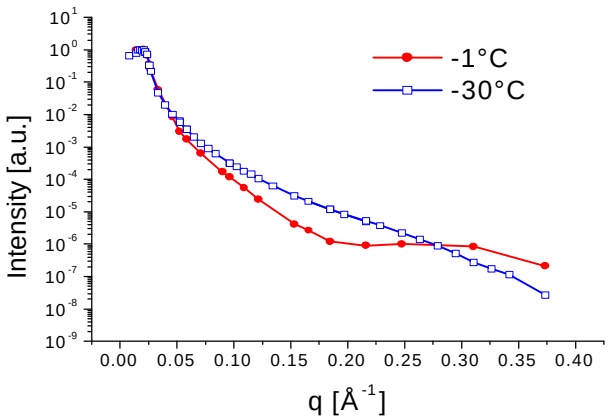

Fig. 14 Measured reflectivity for two different temperatures (filled symbols). The solid lines are guides for the eye. Upon approaching the melting point, emerging interference fringes show the formation of an additional layer with different electron density, i.e. the quasiliquid layer formed by interfacial melting.

Summary

The methods and instrumentation that we have developed successfully within this long-term project have demonstrated their potential for structural investigations at deeply buried interfaces. Within this long-term project we could develop the techniques to a point where they can be applied routinely by the ESRF user community. As a consequence we have submitted a proposal for a new end station at ID15A dedicated to high energy x-ray microbeam investigations at deeply buried interfaces to the German Federal Ministry for Science and Education (BMBF).

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