Giant Metal Compression at Liquid-Solid (Pb-Si, In-Si) Schottky Junctions

H. Reichert,[1] M. Denk,[1] J. Okasinski,[1] V. Honkimäki,[2] and H. Dosch[1,3]
[1]*Max-Planck-Institut für Metallforschung, Heisenbergstraße 3, D-70569 Stuttgart, Germany*
[2]*European Synchrotron Radiation Facility, F-38043 Grenoble, France*
[3]*Institut für Theoretische und Angewandte Physik, Universität Stuttgart, D-70569 Stuttgart, Germany*
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Using a high-energy x-ray transmission-reflection scheme we have studied the density profile of solid-liquid Schottky contacts close to the interface. We found a massive disturbance of the electronic system on the liquid metal side at different interfaces with pronounced density anomalies on a new length scale. The liquid metal at the interface forms a strongly compressed layer followed by a density depleted layer. The experimental evidence points to a charge transfer phenomenon in the metallic system. Control experiments performed at a metal-insulator interface confirm this picture.

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One current research strategy in modern materials science is to bring different materials into direct contact in various nanogeometries in order to create new phenomena which are generated by the chemical, electric, and magnetic structure of and across the emerging interfaces. In order to tailor such interface-controlled phenomena, it is mandatory to understand, on a microscopic level, how the two different systems in contact influence each other across the interface. Such proximity effects are usually expected to occur within an interfacial regime, as determined by the relevant interactions and by internal transport processes, respectively, and should be particularly pronounced, when the materials and phases that are brought in contact are drastically different in their chemical and electronic behavior. Generic examples are solid-liquid and metal-semiconductor interfaces.

The effect of a solid wall onto the structure of the adjacent liquid has been investigated by theory in great detail [1–3] predicting a liquid density oscillation normal to the wall with a period and decay length which are governed by the bulk nearest neighbor distance d_{NN} and the bulk liquid correlation length ξ, respectively. The experimental observation of this packing phenomenon for simple liquids is challenging and has been obtained for only two systems so far. X-ray reflectivity [4] and high-resolution TEM studies [5] were able to demonstrate atomic layering at a Ga-diamond interface and a Pb-Al_2O_3 interface, respectively.

Metal-semiconductor junctions—known as Schottky contacts—form the basis of the earliest man-made hybrid interface structures and to the first man-made solid-state devices [6–8]. The electronic structure across the Schottky contact exhibits the characteristic band deformation at the semiconductor side of the interface (see Fig. 1). It is generally accepted that no specific change in the electronic structure should be induced on the liquid metal side of the interface, since the high-density Fermi liquid limits all electronic screening effects within the metal to a rather small interfacial layer given by the metallic screening length, $\lambda_F = 2\pi/k_F$, which is of the order of 1 Å.

In this Letter we consider a liquid metal (Pb and In) in direct contact with Si(100) and Si(111) single crystals and consider, in particular, the structure of the liquid metal at the interface. We will provide clear-cut and unambiguous experimental evidence, as obtained from extended *in situ* high-resolution x-ray reflectivity of buried liquid lead-Si(100) and liquid In-Si(100) interfaces, that rather unusual densification phenomena emerge on the liquid metal side which can only be understood if the electronic system of the liquid metal adjacent to the semiconducting wall is severely perturbed within a regime as extended as 3 nm. This rather unexpected response of a bulk liquid metal in contact with Si has not been accessible experimentally until the development of high-energy x-ray microbeams at modern third generation synchrotron radiation facilities which allow nondestructive high-resolution insight into the structure of deeply buried interfaces. In what follows we describe the details of our experiments and the obtained results. Since the results pose serious challenges to our current understanding of liquid metals, we will put strong emphasis on the experimental details and present some elementary considerations which could guide future theoretical efforts to understand quantitatively this phenomenon.

For the handling of the liquid metal and the solid semiconductor surface, we have used a specially designed UHV *in situ* preparation and diffraction chamber. The liquid metal is kept in a cylindrical Si trough, while the cylindrically shaped Si sample is mounted above the liquid and translated down onto the liquid surface. The Si substrates were cut from undoped and *n*-doped Si ingots. Prior to mounting in the UHV chamber, the Si substrates (*n* doped with $P, R = 13\ \Omega\,\mathrm{cm}$) were polished and cleaned with standard recipes. The design of the UHV chamber allows one to clean the liquid metal and the Si surfaces separately by Ar ion sputtering and flash heating, respectively, before they are brought into contact at a temperature of $T = T_m^{\mathrm{Pb}} + 10\ \mathrm{K} = 337.5\,^{\circ}\mathrm{C}$. Finally, the Si surface is in contact with a Pb layer of several millimeter thickness. By using independent heating stages and thermocouples on

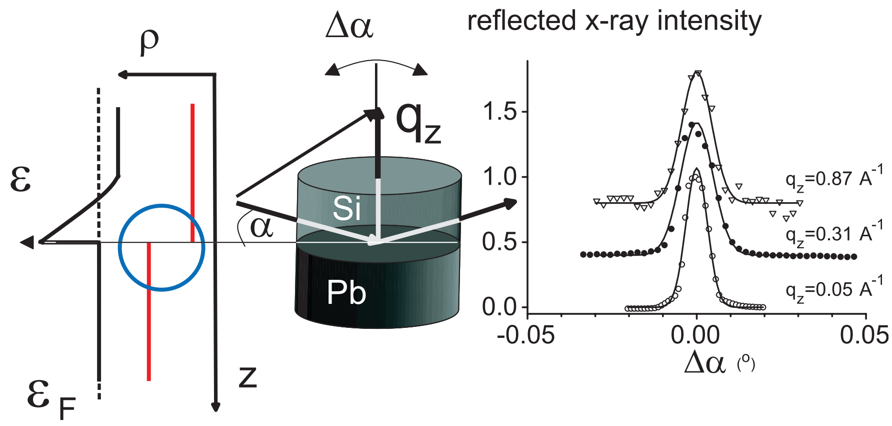

FIG. 1 (color). Band structure of a Schottky junction across the interface with ϵ_F as the Fermi energy of the metal. Band bending occurs on the semiconductor side (n doped) of the interface. The center part shows a sketch of the x-ray reflectivity experiments for the determination of the density profile across the interface (blue circle). Selected detector scans of the reflected x-ray beam at various perpendicular momentum transfer values q_z are shown on the right side for a Pb-Si(100) interface. The measured width is 160 μrad.

both sides of the emerging interface, temperature gradients across the interface are minimized.

X-ray reflectivity measurements from a variety of solid-liquid Schottky interfaces have been performed at the high-energy beam line ID15A at the European Synchrotron Radiation Facility. In all experiments the energy of the x-ray beam was typically 71 keV at a flux of 5×10^{10} ph/s (for details of the experimental setup, see [9,10]). The focused high-energy x-ray beam with a typical cross section of 25 μm $\times$ 4 μm and a collimation to 35 μrad penetrates the sample (20 mm long, attenuation length 17 mm) from the Si side of the interface at almost normal incidence, thus illuminating only the metal-semiconductor interface (see sketch in Fig. 1), where the incoming x-ray beam is then internally reflected. The reflected beam has been monitored by a scintillation counter after adjusting the vertical collimation such that the reflected beam is fully integrated by the detector.

Figure 1 shows some of the raw data as obtained from the liquid Pb-Si(100) interface: rocking scans parallel to the interfaces across the specular rod for various perpendicular momentum transfers q_z. As can be seen, the highly collimated x-ray microbeam and the high quality interface give rise to very clean reflected intensities and a rather small width given by the resolution function of the instrument and the curvature of the interface. The integrated specular intensities are then plotted versus q_z to give the x-ray reflectivity profile of this interface (open black circles in Fig. 2). The dashed line is a theoretical reflectivity curve (Fresnel curve) expected for a bulk-terminated Pb-Si interface. We note here that it reproduces very precisely the observed critical edge for total internal reflection ($q_c = 0.053$ Å^{-1} in Fig. 2) which is determined by the bulk electron density difference between Si ($\rho = 0.7$ Å^{-3}) and Pb ($\rho = 2.5$ Å^{-3}). This confirms that the prepared Pb-Si interface is well defined.

Interestingly and most surprisingly, the observed x-ray reflectivity profile deviates very strongly from the predicted curve for $q > q_c$, giving very clear experimental evidence that the density of the liquid Pb adjacent to the Si wall is severely perturbed. We applied different fitting strategies to the experimental reflectivity profile in order to test the sensitivity of the data to various microscopic details of the electron density profile. It turned out that a simple two-layer model provides the best generic model for the electron density profile. The final result for the two-

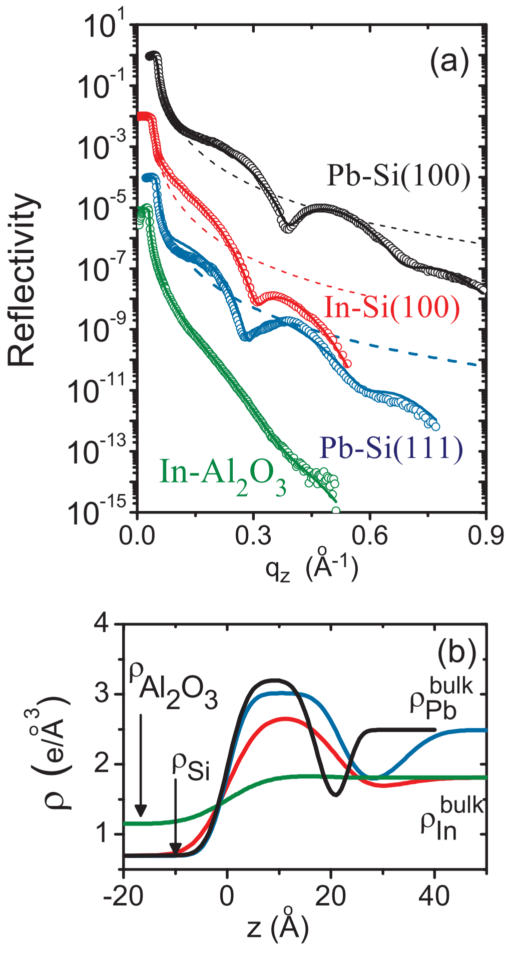

FIG. 2 (color). (a) Reflectivity from the Pb-Si(100) (black), In-Si(100) (red), Pb-Si(111) (blue), and In-Al_2O_3 (green) interface (the curves are offset for clarity). Solid lines denote best fits to the data using the generic two-layer model, while dashed lines indicate the corresponding Fresnel reflectivities of an ideally sharp interface. (b) Electron density profiles for each interface deduced from the final fit of the reflectivity profile.

layer model implemented within the Paratt formalism [11] is shown as the black solid line in Fig. 2. The electron density profile deduced from the fits is shown in Fig. 2(b); it exhibits an extended densified layer followed by a depletion layer. Other, more elaborate models allow one to reproduce the measured reflectivity perfectly with only insignificant changes to the generic two-layer electron density profile. Note that this density anomaly should not be confused with the atomic layering at free liquid metal surfaces [12]. These density oscillations at a free liquid metal surface appear on the atomic length scale with a typical period of d_{111}.

Our x-ray observations challenge current models of liquid metals and Schottky junctions in a threefold way: (a) They show that liquid Pb in contact with Si undergoes a giant densification of $\approx 30\%$ driving the density of the interfacial metal layer far beyond the value in the closed-packed solid. (b) This densification process takes place within an interfacial layer of about 1.7 nm thickness, which is 1 order of magnitude larger than the screening length λ_F in the metal system. (c) The layer of increased density is followed by a density depleted layer, which is not fully compensating the excess density in the layer directly adjacent to the interface.

We have no final explanation at hand to rationalize these observations. However, it is apparent that a densification of liquid Pb by $\Delta\rho/\rho \approx 0.3$ is only possible if the ionic radii of the liquid Pb ions adjacent to the Si wall shrink by $\Delta r = (\Delta\rho)^{1/3} \approx 10\%$ (see Fig. 3). Since this can only be accomplished by charge transfer phenomena, it becomes apparent that one has to reconsider the electronic phenomena and processes at the metal side of the junction. Interestingly, there are no robust theories available which are able (a) to predict the behavior of a liquid metal in contact with a semiconducting wall and (b) to predict the ionic radius of a metallic ion as a function of a local charge transfer. Thus, in order to get a first estimate, we use the known ionic radii of Pb salts [13], in which Pb occurs in different ionization states (see Fig. 3): We deduce from a linear interpolation that a charge transfer of $\Delta Q \approx 0.70e$ per Pb ion is needed to explain the observed shrinkage in the ionic radius. It should be noted that we are fully aware of the fact that this argument gives only a very crude guidance in estimating the effect of charge transfer onto the size of the Pb ion in liquid Pb.

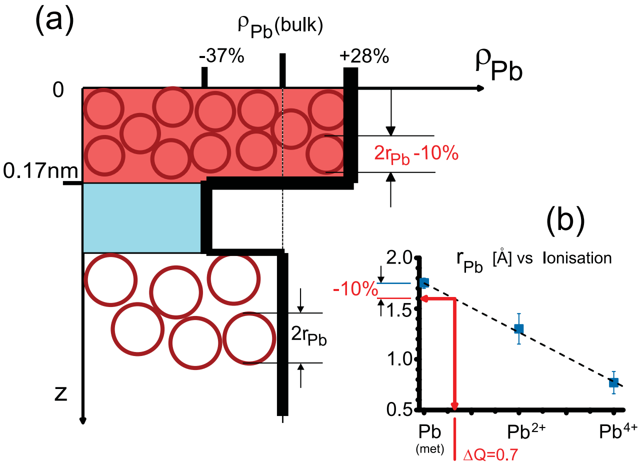

FIG. 3 (color). (a) Sketch of the density profile of the interface using the interpolated values of the ionic radii. (b) Ionic radius of Pb in different oxidation states. The straight line is a fit to the data taken from Ref. [13].

In order to corroborate the conjecture that this giant densification of a liquid metal in contact with a semiconducting wall is a generic phenomenon at metal-semiconductor interfaces and that a charge transfer is responsible for it, we carried out three control experiments, measuring x-ray reflectivity profiles from (a) liquid In in contact with Si(100), (b) liquid Pb in contact with Si(111), and (c) liquid In in contact with insulating Al_2O_3 (Fig. 2).

Most interestingly, in the first two cases, we observed the same pronounced reflectivity profile as the one described above. Observing the same generic electron density profile for a different metal (here In) demonstrates that the observed density anomalies are a common feature at such interfaces (see Fig. 2). The second measurement, using a differently oriented Si substrate, shows that this anomalous metal density profile is quite independent of the exact structure of the semiconductor interface (see Fig. 2). In the third case, liquid In at an insulating wall, the effect is virtually gone ($\Delta\rho/\rho < 0.02$), and we observe almost pure Fresnel reflectivity from a rough interface in the accessible momentum transfer range (see Fig. 2) indicating a metal electron density profile without anomalies. We conclude from this that the x-ray data and the shrinkage of the ionic radius of Pb/In at the Si(100) and the Si(111) interfaces are very robust experimental facts. Somewhat less robust is the deduced charge transfer of $\Delta Q \approx 0.70e$ from the Pb ions to the semiconductor within an interfacial layer of approximately 1.5 nm. In what follows we speculate about the origin of this interfacial phenomenon and the observed values.

Surface states at the metal-semiconductor interface may play a key role: The Si(100) and Si(111) surfaces exhibit dangling bonds which lead to the well-known surface reconstructions under UHV conditions [14]. The strain energy associated with the local distortion of the surface atoms is typically 2 eV [15]. When the metal is brought into contact with a Si(100) or a Si(111) surface, the reconstruction is lifted; i.e., the dangling bonds are saturated by metal electrons, which in turn leads to a negatively charged interface. This implies that the total charge at the interface should correspond to the integrated charge depletion on the metal side of the interface.

From this discussion one may conclude that the observed giant densification of the liquid metal adjacent to the semiconducting wall could in fact be rationalized. Much less apparent is the observed length scale involved in the problem, i.e., the thickness of the ultra dense liquid layer being 1.7 nm (for Pb). Static screening in such high-

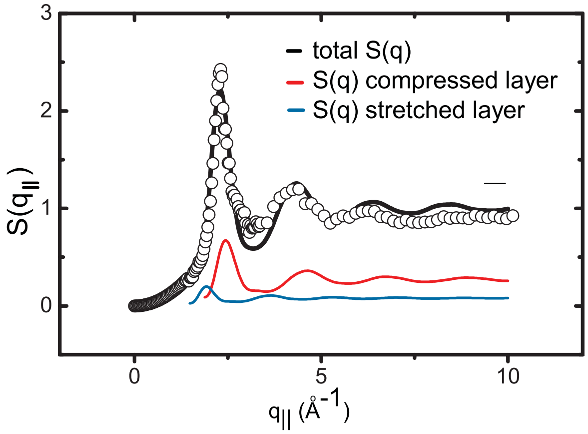

FIG. 4 (color). Measured and calculated (black line) in-plane structure factor $S(q_{||})$ constructed from compressed (red line) and stretched (blue line) pair distribution functions $g(r_{||})$ in the two layers.

density Fermi liquids occurs within $\lambda_F = 2\pi/k_F$, which is of the order of 0.1 nm, thus 1 order of magnitude less than observed; in turn, simple screening effects can safely be ruled out. However, perhaps it is significant that the electronic mean free path, $\lambda_D = v_F \tau_R$ (v_F denotes the Fermi velocity and τ_R the relaxation time), has a typical value of 1.5–2.0 nm for Pb and In in the liquid phase close to the melting temperature (see [16]) which is almost identical to the measured length scale. If this dynamic quantity does enter the scenario, this would imply that nonequilibrium electrons or holes are permanently spilled into the metal side of the interfacial regime which subsequently equilibrate with the Fermi liquid. While such thermally driven uphill currents from the semiconductor over the Schottky barrier into the metal (see Fig. 1) are well known ("thermionic emission"), it is completely unclear at this stage whether they play a role here and how this would interfere with the aforementioned surface charge effects. If the disclosed superdense metal layer is, however, associated with nonequilibrium electrons, the simple flat electronic band structure at the metal side as depicted in Fig. 1 is not correct.

Similarly speculative is the origin of the depletion layer which is also a very robust experimental observation. Apparently, the transition from the superdense layer to the asymptotic bulk density requires in metallic systems such a layering phenomenon.

We finally address our earlier studies of liquid Pb in contact with Si(100) [17] which disclosed a pronounced fivefold azimuthal symmetry in the structure factor parallel to the hard Si wall, while the shape of the liquid structure factor remains virtually unchanged compared to bulk liquid Pb. Figure 4 shows the x-ray data as recorded within the evanescent x-ray decay length of 5.5 nm. In order to verify whether the observation of a superdense interfacial layer containing Pb ions with a reduced ionic radius is in conflict with this liquid structure factor, we simulated the expected intensity distribution (black line in Fig. 4) by assuming compressed and stretched pair distribution functions $g(r_{||})$ [18] within the two layers adjacent to the solid Si wall (red and blue lines in Fig. 4). We find that the measured structure factor parallel to the wall appears to be rather insensitive to the oscillatory modifications of the density profile of the metal at the interface.

In summary, we have presented a rather puzzling new interfacial phenomenon which emerges at liquid Pb/Si and liquid In/Si interfaces. Rather straightforward x-ray reflectivity measurements exhibit very unusual intensity oscillations which can only be understood if one assumes a giant densification of the liquid metal adjacent to the semiconductor. The densification of more than 30% can only be understood if one introduces a charge transfer phenomenon between the metal and the semiconductor leading to a shrinkage of the ionic radius of the metal ions. The thickness of this layer is around 1.5–2 nm and thus beyond any screening length. These observations are a serious challenge to our current understanding of such interfaces and invite theorists working in the field to develop a microscopic model.

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