



Atomic layering and misfit-induced densification at the Si(111)/In solid–liquid interface



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ARTICLE INFO

Article history:

Received 1 August 2013

Accepted 24 October 2013

Available online 9 November 2013

Keywords:

Solid–liquid interfaces

Semi-conductor metal interfaces

Surface x-ray diffraction

ABSTRACT

We report on the solid–liquid interface structure between Si(111) substrates and indium at temperatures just above its melting point. At similar metal–semiconductor interfaces, liquid density enhancements have been observed by Reichert et al. [1]. Our surface x-ray diffraction study reveals that there is pronounced layering of the liquid near the interface. The data allow for identifying both layering length scales: the interlayer distance of 2.2 Å and the decay length of approximately 15 Å. Furthermore do we find the very first layer of indium adjacent to the Si(111) to be partially laterally ordered at the substrate's hollow sites. We introduce a hard sphere packing model that can explain the experimentally observed layering distance and anisotropic order. This packing also reveals that due to the misfit between the size of the indium atoms and the periodicity of the substrate, the indium atoms can pack together closer than in the bulk liquid. These results show that the lateral interaction between the substrate and the liquid directly influences the layering distance and that the resulting packing can account for part of the previously observed enhanced densities.

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1. Introduction

Solid–liquid interfaces are relevant for processes in a range of areas, including biology, physics, chemistry and engineering. The interaction between a solid and a liquid, and its emerging interface structure, is of importance for obtaining an understanding of e.g. transport properties around cells or friction and lubrication in mechanical systems. In particular, the interactions between the solid and the liquid on the nanometer scale govern nanotechnological fabrication processes which take place at these interfaces. Also growth of high quality semi-conducting devices by for example the Vapour–Liquid–Solid (VLS) method or Liquid Phase Epitaxy (LPE) takes place at solid–liquid interfaces between semi-conductors and metals. In order to obtain a microscopic understanding of crystal growth at such interfaces, it is mandatory to gain a detailed picture of the interface at the atomic scale. The details of compositional changes induced by segregation and the characteristic width over which the atomic order changes from solid to liquid are important to understand the energetics and kinetics governing crystal growth. In addition, such studies will be important for identifying the combination of parameters which allow for nanoscale control over the growth.

A number of studies have been performed on (sub)monolayer liquid films [2–7] on a substrate, but in order to see the evolution to a bulk liquid thicker films have been investigated [8]. Such studies revealed

several structural properties of the interfacial liquid, such as atomic layering [9], local five-fold symmetry [10] and preferential in-plane ordering of the first layer(s) [11]. Only few studies on a limited number of systems have been conducted and a complete description of the solid–liquid interface structure is still missing. The main reason is that the atomic interactions, needed for theoretical calculations, are difficult to compute and that experimentally the deeply buried interfaces are difficult to address with traditional probes. Reichert et al. [1] have investigated several semi-conductor/metal solid/liquid interfaces and made the puzzling observation of a huge densification up to 40% of the liquid near the interface. The densification extends up to 2 nm into the liquid, much larger than any screening length in the investigated metals. Nevertheless, Reichert et al. argue that the phenomenon is of electronic nature by the metal continuously feeding the semi-conductor's conduction band with electrons. The change in valence, and subsequently of the atomic radii, is thought to result in a denser packing. The same densification phenomenon, albeit less pronounced, has been observed at the Hg–Al₂O₃ interface [12]. A recent molecular dynamics study of this interface concludes that even without the assumption of electron transfer (and a corresponding shrinkage of the atoms) a densification is expected [13]. These studies raise the question to what extent the densification phenomenon applies generally to solid–liquid interfaces. Here we target this problem by studying the atomic stacking, which should comply with all the experimentally observed phenomena, such as layering, local five-fold symmetry and densification. The most important result is that the lateral interaction between the substrate and liquid can result in local densification. This phenomenon can

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account for part of the previously found huge enhancements, which still can be only explained by unusually short quasi-liquid interatomic distances.

Here we report on the interface structure between liquid indium and a Si(111) substrate. The main observations are that atomic layering occurs with a very small spacing and extends up to approximately 7 layers into the liquid. Furthermore, the very first layer of the indium atoms shows in-plane order, whereby the atoms preferentially occupy hollow sites of the underlying Si(111) substrate. We also investigate how such an ordered indium layer serves as a template for further quasi-liquid metal layers. By making use of the model set out by Spaepen [14], we show how the misfit between the indium atoms' size and the substrate's in-plane lattice constant can lead to a densification compared to bulk liquid indium of the first quasi-liquid layer(s).

The remainder of this article is organized as follows. First we describe x-ray scattering from solid–liquid interfaces. This section also introduces the structural fit models used in our data analysis. Next we present the experimental data and the resulting fits. In a separate section the hard-sphere packing model is introduced, after which this model is compared with the experimental results and discussed in relation to other solid–liquid interfaces.

2. X-ray scattering from solid–liquid interfaces

Crystals show long-range atomic order whereas liquids only display short-range order. Hence, the corresponding scattering patterns, which can be calculated through Fourier transform of the real-space electron densities, are very different. At the interface between solids and liquids some of the solid's Fourier components will be transmitted to the liquid in a thin region close to the interface. By measuring the crystal truncation rods (CTRs) of the solid in contact with the liquid, it is possible to determine the degree by which the liquid orders with respect to the solid [11]. The challenge to experimentally solve the complete 3D atomic structure of a solid–liquid interface lies in the fact that the signals obtained by such diffraction techniques are relatively weak, because of the disorder, and are further obscured by the relatively high background signal from the bulk liquid scattering [15].

Atomic layering will result in a Bragglike feature on the specular CTR at a point in reciprocal space $Q = 2\pi/d$, with d the layer spacing and $Q = 4\pi\sin(\theta)/\lambda$ the momentum transfer (where θ is half the scattering angle and λ is the wavelength). Such a layering signal was found at the AuIn–InP(111) interface, giving evidence of a layering distance of 2.3 Å [16]. Densification and/or layering phenomena which appear on a length scale several times the layering distance are expected to show up at lower momentum transfer in the scattering pattern. To the best of our knowledge, so far there has been only one study attempting to reveal both length scales [12]. Those data did not show a clear Bragglike feature and the details for this system seem to be rather subtle, which might also come from the use of a miscut substrate.

In the next sections the structural model and the scattering calculation used in the data analysis are presented.

2.1. In/Si(111) scattering calculation

Fig. 1 shows schematically the atomic-scale model that is used in the data analysis.

The scattering amplitudes are calculated by summing over the individual atoms' scattering contributions:

$$F(Q) = \frac{F^{Si}(Q)}{1 - e^{-iQc}} + \sum_{j=1} \theta_j f^{In}(Q) e^{-\frac{1}{2}U_j^{\parallel} Q^2} e^{-\frac{1}{2}U_j^{\perp} Q^2} e^{iQ \cdot r_j}, \quad (1)$$

with F^{Si} the bulk silicon structure factor, Q the momentum transfer, θ_j the occupancy of the j -th atom, f^{In} the indium atomic scattering factor, U^{\parallel} and U the squared mean displacement amplitudes of the atoms

parallel and perpendicular to the interface and r_j the atomic positions. The first term at the right-hand-side renders the well-known CTR [17] of the Si(111) substrate. The values U for the displacements are related to the Debye–Waller parameters by $B = 8\pi^2 U$, where in the present case the physical origin of the disorder is not only temperature vibration around an average position but also the fact that the scattering object is quasi-liquid: the average atomic positions are substantially smeared out [11]. The interface introduces an anisotropy between the in-plane and out-of-plane directions. It is therefore expected that the atoms will order differently in the two directions, which can be modelled by the use of different values for U^{\parallel} and U . In particular, the CTRs with $h, k \neq 0$ also probe atoms with in-plane order. To solve the complete 3D structure of the interface both the specular and CTRs with in-plane momentum transfer are needed.

Fig. 1 shows the top view structure of the first indium layer on the Si(111) substrate surface. As discussed later on, we obtain the best fits when a single layer of indium atoms preferentially occupies Si(111) hollow sites. The next layers of indium, starting from 2, do not show any in-plane ordering and are described in the models using very large values for U^{\parallel} . In this way their scattering contributes only to the (0,0) CTR and not to any having in-plane momentum transfer. The summation over indium layer 2 and further of Eq. (1) is then calculated with a specific profile describing the degree of perpendicular ordering in the near interface region: close to the interface the ordering will be higher (and the values for U lower) than further away.¹ We have also tested the so-called distorted crystal model [18], which has been successfully used to describe liquid layering in other systems. For the data obtained here this did not lead to high quality fits, mostly because that model failed to give an adequate description over the total Q -range.

The best fit results are obtained when the scattering contributions of the indium atoms quickly diminish with distance j from the interface, either by a vanishing profile for θ_j or by a diverging profile for U_j^{\perp} . Although the parameter θ implies the presence of atoms, it is actually the scattering strength that is probed; not all the atoms illuminated by the x-ray beam will contribute to the CTR signals. Different profiles have been tested during the data analysis and two of these, hereafter referred to as models 1 and 2, will be shown here. The purpose of presenting two models is to explore the boundary values and sensitivity of the used method towards the different structural features that are contained by the data. It also shows that different ways of parameterizing a density profile can lead to very similar solutions, by which means the significance of certain details is tested.

2.2. Model 1

In the first model, the layerwise occupancies θ_j and amplitudes U_j^{\perp} from Eq. (1) are chosen to have the following form:

$$\theta_j = \theta_0 \frac{1}{2} \operatorname{erfc} \left[\left(j - j_0^{\theta} \right) / \sigma_{\theta} \right] \quad (2)$$

and

$$U_j^{\perp} = 2U^{\perp} / \operatorname{erfc} \left[\left(j - j_0^U \right) / \sigma_U \right], \quad (3)$$

¹ Eq. (1) includes to some extent the liquid scattering by the use of very large values for U , which would mean that the atom is completely disordered. This is, however, not a correct description of liquid scattering, of which the well-known profiles exhibit several peaks as a function of momentum transfer. It has to be emphasized that here this (bulk) liquid scattering pattern is treated as background, and as such subtracted from the raw data in order to reveal the contribution of the ordered interface region to the scattering. As a result, those atoms that are given very large values of U in the model do not contribute significantly to the CTRs as shown in Fig. 3. This is particularly true for the atoms making up the bulk liquid electron density further away from the interface. This situation is similar to the way in which x-ray reflectivity data are analyzed. Often, the derivative of the electron density $d\rho/dz$ is Fourier transformed in such models, which results in a zero contribution from constant density profiles.

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