Wetting Phase Transition at the Surface of Liquid Ga-Bi alloys: An X-ray Reflectivity Study

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X-ray reflectivity measurements of the binary liquid Ga-Bi alloy reveal a dramatically different surface structure above and below the monotectic temperature $T_{\text{mono}} = 222^\circ\text{C}$. A Gibbs-adsorbed Bi monolayer resides at the surface at both regimes. However, a 30 Å thick, Bi-rich wetting film intrudes between the Bi monolayer and the Ga-rich bulk for $T > T_{\text{mono}}$. The internal structure of the wetting film is determined with Å resolution, showing a theoretically unexpected concentration gradient and a highly diffuse interface with the bulk phase.

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I. INTRODUCTION

A thick wetting film may be stable at the free surface of a binary immiscible liquid mixture and the temperature dependent formation of this surface film is strongly influenced by the bulk critical demixing of the underlying bulk phase. In contrast to surface segregation, where a monolayer of the low surface tension component forms at the interface of the binary mixture, wetting is a genuine phase transition occurring at the interface resulting in the formation of a mesoscopically or macroscopically thick film. To date, nearly all studies of wetting phenomena have been carried out with dielectric liquids dominated by long-range van der Waals interactions and the experimental techniques used achieve mesoscopic resolution only. For binary alloys dominated by screened Coulomb interactions, evidence for a wetting transition has so far been obtained only for Ga-Bi and Ga-Pb. In the case of Ga-Bi, the formation of a Bi-rich wetting film has been detected by ellipsometry in the temperature range from 220°C to 228°C. However, since the film thickness is much smaller than the wavelength of visible light, ellipsometry cannot provide Å-resolution structural information. By contrast, x-ray surface scattering techniques allow determination of the structure of the wetting film with atomic resolution and address issues such as the internal structure of the film and its evolution from molecular to mesoscopic thickness, none of which was hitherto addressed by any of the previous measurements.

The wetting phase transition is depicted schematically in Fig. 1. Below the bulk critical point of demixing, $T_{\text{crit}}$, the bulk phase separates into two immiscible phases, the high density Bi-rich phase and the low density Ga-rich phase. Below the characteristic wetting temperature $T_{\text{w}} < T_{\text{crit}}$, the high density phase is confined to the bottom of the container as expected (see Fig. 1a). As discussed in more detail below, for Ga-Bi, the high density phase is solid in this case and $T_{\text{w}}$ coincides with the monotectic temperature $T_{\text{mono}}$. In contrast, above $T_{\text{w}}$ the high density phase completely wets the free surface by intruding between the low density phase and the gas phase in defiance of gravity (see Fig. 1b).

II. SAMPLE PREPARATION

The Ga-Bi alloy was prepared in an inert-gas box using at least 99.9999% pure metals. A solid Bi ingot was placed in a Mo pan and supercooled liquid Ga was added to cover the Bi ingot. At room temperature, the solubility of Bi in Ga is less than 0.2 at%. Increasing the temperature results in continuously dissolving more...
Bi in the Ga-rich phase with solid Bi remaining at the bottom of the pan up to the monotectic temperature, \( T_{mono} = 222^\circ C \). The initial Bi content was chosen to be high enough that the two phase equilibrium along the miscibility gap could be followed up to few degrees below \( T_{crit} \) without crossing into the homogeneous phase region (see Fig. II.1). The temperature on the sample surface was measured with a Mo coated thermocouple. The alloy was contained in an ultra high vacuum chamber and the residual oxide on the sample was removed by sputtering with Ar\(^{+}\) ions.

Surface sensitive x-ray reflectivity (XR) experiments were carried out using the liquid surface spectrometer at beamline X22B at the National Synchrotron Light Source with an x-ray wavelength \( \lambda = 1.24 \AA \) and a detector resolution of \( \Delta q_z = 0.03 \AA^{-1} \). The background intensity, due mainly to scattering from the bulk liquid, was subtracted from the specular signal by displacing the detector out of the reflection plane.

III. EXPERIMENTAL TECHNIQUES

The intensity reflected from the surface, \( R(q_z) \), is measured as a function of the normal component \( q_z = (4\pi/\lambda) \sin \alpha \) of the momentum transfer. The XR geometry is depicted schematically in the inset of Fig. II. R\((q_z)\) therefore yields information about the surface-normal structure as given by

\[
R(q_z) = R_F(q_z)|\Phi(q_z)|^2 \exp[-\sigma_{cw}^2 q_z^2],
\]

where \( R_F(q_z) \) is the Fresnel reflectivity of a flat, infinitely sharp surface and \( \Phi(q_z) \) is the Fourier transform of the local surface-normal density profile \( \tilde{\rho}(z) \).

\[
\Phi(q_z) = \frac{1}{\rho_\infty} \int dz \frac{d\tilde{\rho}(z)}{dz} \exp(iq_z z)
\]

with the bulk electron density, \( \rho_\infty \). The exponential factor in Eq. II.1 accounts for roughening of the intrinsic density profile \( \tilde{\rho}(z) \) by capillary waves (CW):

\[
\sigma_{cw}^2 = \frac{k_B T}{2\pi\gamma} \ln \left( \frac{q_{max}}{q_{res}} \right).
\]

The CW spectrum is cut off at small \( q_z \) by the detector resolution \( q_{res} \) and at large \( q_z \) by the atomic size \( a \) with \( q_{max} \approx \pi/a \). However, \( \tilde{\rho}(z) \), can not be obtained directly from Eq. II.1 and we resort to the widely accepted procedure of adopting a physically motivated model for \( \tilde{\rho}(z) \) and fitting its Fourier transform to the experimentally determined \( R(q_z) \) as will be shown further below.

The reflectivity of pure liquid Ga exhibits a pronounced interference peak indicating surface-induced layering of ions near the surface (see Fig. III.2). Previous experiments on Ga-Bi at low temperatures show that the layering peak is suppressed in the liquid alloy and \( R(q_z) \) is dominated by a broad maximum consistent with a single Bi monolayer segregated at the surface as expected since \( \gamma \) is considerably lower for Bi than for Ga.

FIG. 2: (a) Fresnel normalized reflectivity \( R/R_F \) from Ga-Bi alloys for \( T < T_{mono} \): (●): 100 at% Ga; (△): 99.7 at% Ga (35°C); (×): 98.7% Ga (95°C); (○): 98.4% Ga (110°C); (○): 96.5% Ga (155°C); (○): 93.3% Ga (478°C) and (●): 93.2% Ga (207°C). Shaded line: fit to layered density profile of pure Ga (see Ref. 9); solid lines: fit to layered density profile of Ga plus Bi monolayer (see Ref. 10); broken lines: fit to Bi monolayer (this work). (b) Intrinsic density profiles normalized to \( \rho_\infty \) for Ga-Bi for 110°C \( ≤ \) \( T \) \( ≤ \) 207°C using the one-box model described in the text. The profiles essentially fall on top of each other and two representative fits are shown: 110°C (solid line) and 207°C (broken line). (c): Schematic representation of the (two-)box model. (d): CW roughness \( \sigma_{cw} \) for Ga-Bi alloys as a function of temperature using \( \gamma \) from our fit (●) and from macroscopic surface tension measurements (○, see Ref. 14).

IV. RESULTS

Here, we report x-ray measurements from liquid Ga-Bi for \( T \) up to 258°C encompassing the formation of the wetting film at \( T > T_{mono} \), the lowest temperature at which the liquid Bi-rich phase is stable. The actual wetting transition likely lies below \( T_{mono} \) but does
not manifest itself since the wetting film is solid for $T < T_{\text{mono}}$. Experimental evidence for this assumption has been found for the similar systems Ga-Pi\[12\] and K-KCl\[13\]. The discussion of the data is divided into two parts: (i) $T < T_w \approx T_{\text{mono}}$ (110°C–207°C) and (ii) $T > T_w$ (228°C–258°C). We present the results for $T < T_{\text{mono}}$ (scenario (a) in Fig. IV) first since this corresponds to the simpler surface structure with monolayer segregation but no wetting film.

**Below $T_{\text{mono}}$:** Fig. III(a) shows $R(q_z)$ from liquid Ga-Bi at selected points along the coexistence line between 110°C and 207°C. Since subsurface layering is impossible to resolve at these temperatures, we simply model the near-surface density, which is dominated by the Bi monolayer segregation, by one box of density $\rho_1$ and width $d_1$. The density profiles are shown in Fig. III(b) and the box model is shown schematically in Fig. III(c) (solid line). The best fit to $R(q_z)$ that corresponds to this density profile is represented by the broken lines in Fig. III(a).

The mathematical description of the general box model with a maximum number of two boxes is:

$$\tilde{\rho}(z) = \frac{\rho_0}{2} \left( 1 + \text{erf} \left( \frac{z}{\sigma_0} \right) \right) - \sum_{i=1}^{2} \frac{\rho_i}{2} \left( 1 + \text{erf} \left( \frac{z - d_i}{\sigma_i} \right) \right)$$

where $\sigma_0$ and $\sigma_i$ are the intrinsic roughnesses of each of the three interfaces. The total roughness, $\sigma$, of the interface between the vapor and the outermost surface layer is given by $\sigma^2 = \sigma_0^2 + \sigma_{cw}^2$ with $\sigma_0 = 0.78 \pm 0.15 \text{Å}$ for $T < T_{\text{mono}}$. As predicted by capillary wave theory, the product $\sigma_{cw}^2 \gamma$ (with $\gamma$ from our fits) depends linearly on $T$ (see Eq. 3 and (i) in Fig. III(d)) over the entire temperature range. This variation is essentially the same if $\gamma$ is not taken from our fits but from macroscopic surface tension measurements (\(\square\)). Apart from the increasing surface roughness, the structure of the surface does not change over the entire temperature range from 110°C to 207°C, as witnessed by the intrinsic density profiles that fall right on top of each other once the theoretically predicted temperature dependence of the CW roughness has been corrected for (Fig. III(b)). Between 212°C and 224°C, we observed rapid and random changes in the scattered intensity over the entire $q_z$ range. This unstable behavior of the surface is most likely due to the coexistence of patches of different film thickness induced by the temperature gradient of about 6K normal to the sample pan.

**Above $T_{\text{mono}}$:** The surface stabilized above $T_{\text{mono}}$ at about 228°C and a sharper peak in $R(q_z)$ appeared centered around 0.13 Å⁻¹ (see Fig. IV), indicating a thick film of high density forming near the surface. The persistence of the broad maximum centered around $q_z \approx 0.75 $Å⁻¹ indicates that Bi monolayer segregation is still present along with the newly formed thick wetting film. Several models were used to fit $R(q_z)$ but they all result in essentially the same density profiles. Here, we use the simple two-box model (see broken line in Fig. III(c) and Eq. 4). As can be seen in Fig. IV this simple model gives an excellent description of the experimentally obtained reflectivity. The pertinent density profiles describing the surface-normal structure of Ga-Bi alloys for $T > T_{\text{ mono}}$ are shown in the inset of Fig. IV and have the following features that can be compared to present predictions of wetting theory: (i) density, (ii) thickness and (iii) roughness of the wetting film.

(i) The concentration profile is highly inhomogeneous with a high density region at the outermost surface layer. The integrated density of this adlayer is consistent with a monolayer of the same density as the monolayer found for $T < T_{\text{mono}}$. However, the Bi monolayer segregated on top of the wetting film is rougher and broader than the Bi monolayer segregated on top of the Ga-rich bulk phase for $T < T_{\text{ mono}}$. This change in surface structure corresponds to a change in the intrinsic roughness of the interface liquid/vacuum, $\sigma_0$, from 0.78 ± 0.15 Å below $T_{\text{ mono}}$ to 1.7 ± 0.3 Å above $T_{\text{ mono}}$. However, the CW roughness still follows the predicted T-dependence of Eq. 3 (see Fig. III(d)).

This change of $\sigma_0$ upon crossing $T_{\text{ mono}}$ is possibly related to the fact that for $T > T_{\text{ mono}}$, the pure Bi monolayer segregates against a Bi-rich wetting film made out of atoms of different size and with repulsive heteroatomic interactions. By contrast, for $T < T_{\text{ mono}}$ this segregation takes place against almost pure Ga. The fact that the Bi monolayer segregation persists from partial wetting to complete wetting means that the wetting film does...
not intrude between the Ga-rich bulk phase and vacuum, as assumed by wetting theory, but between the Bi monolayer already segregated at the surface and the Ga-rich bulk phase. This should have a pronounced influence on the energy balance at the surface which ultimately governs the wetting phase transition. Even though the possibility of an unspecified concentration gradient is included in Cahn's general theory, to our knowledge, an inhomogeneous density profile is neither treated explicitly in theoretical calculations (see the homogeneous profiles displayed in refs. 11,12) nor found experimentally. At 228° C the density of the thick wetting film is \( \rho_2 = (1.25 \pm 0.03) \rho_\infty \) where \( \rho_\infty \) is the density of the Ga-rich bulk phase. This agrees very well with the ratio of the densities of the coexisting Bi-rich and Ga-rich phases in the bulk, calculated from the phase diagram to be 1.23. The density of the wetting film reaches \( \rho_\infty \) with increasing \( T \) (\( \rho_\infty = 1.18 \pm 0.03 \) at 238° C and 1.08±0.02 at 258° C) as the densities of the two bulk phases converge upon approaching \( T_{\text{crit}} \) (their density ratio is 1.20 at 238° C and 1.08 at 258° C). This strongly supports the conclusion that the thick wetting film is the Bi-rich bulk phase as predicted by wetting theory.

(ii) The thickness of the wetting film, \( d_2 \), at 228° C is determined from the density profile to be \( \sim 30 \text{ Å} \), consistent with a model-dependent estimate from ellipsometry results.\(^{1,2}\) In addition, the thickness of the wetting film is corroborated by independent grazing incidence diffraction experiments resolving the in-plane structure which will be reported elsewhere.\(^{13,14}\) The wetting film in this Coulomb liquid with short-range interactions is considerably thinner than wetting films that have been observed in dielectric liquids with long-range interactions.\(^{3,19}\) An important question concerning the thickness of a wetting film is whether the wetting film has been investigated in equilibrium. The fact that identical reflectivities were measured at 238° C taken 24 hours apart (Fig. IV), is strong evidence that the film thickness is in equilibrium in our study.\(^{16}\)

(iii) The roughness between the Bi-rich wetting film and the Ga-rich bulk film is much higher that the roughness of the free interface LM/vacuum. This is be expected since the interfacial tension between two similar liquids is generally much lower than the liquid/gas surface tension.\(^{20}\) On the other hand, it is not clear how sharp a concentration gradient should be expected between the Ga-rich and the Bi-rich phase and the interface may be essentially diffuse, independent of CW roughness. With increasing temperature, the wetting film becomes less well defined and it is not obvious whether this is due to the fact that the film is becoming slightly thinner, or if only the interface between two converging phases gets more diffuse. At any rate, we are far enough away from \( T_{\text{crit}} \) that the predicted thickening of the wetting film due to the increasing correlation length of the concentration fluctuations should not play a role. Once the thick wetting film has formed, it is not possible to cool the sample below \( T_{\text{mono}} \) since the Bi-rich wetting film remains at the surface and freezes.

V. SUMMARY

In summary, we investigated the structural changes occurring on atomic length scales at the surface of liquid Ga-Bi during the wetting transition. In the case of partial wetting (\( T < T_{\text{mono}} \)), a Bi monolayer segregates at the surface to lower the surface energy. Above the monotectic temperature complete wetting is found and a 30 Å thick wetting film intrudes between this monolayer and the Ga-rich bulk phase. This is the first time that the microscopic structure of a wetting film has been studied and that the concentration profile of the wetting film has been shown to vary on a level of several atomic diameters.

VI. ACKNOWLEDGMENTS

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1. J. W. Cahn, J. Chem. Phys. 66, 3667 (1977).
2. S. Dietrich, Physica A 168, 160 (1990).
3. S. Dietrich in: C. Domb and J. L. Lebowitz, Phase Transitions and Critical Phenomena, Vol. 12, Academic Press, 1988.
4. D. Nattland, P. D. Poh, S. C. Müller and W. Freyland, J. Non-Cryst. Solids 205-207, 772 (1996).
5. D. Chatain and P. Wynblatt, Surf. Sci. 345, 85 (1996).
6. J. S. Rowlinson and B. Widom, Molecular Theory of Capillarity, Clarendon Press, 1982.
7. H. Tostmann, E. DiMasi, P. S. Pershan, B. M. Ocko, O. G. Shpyrko, and M. Deutsch, Phys. Rev. B 59, 783 (1999).
8. T. B. Massalski et al., Binary Alloy Phase Diagrams, ASM International, 1990.
9. M. J. Regan et al., Phys. Rev. Lett. 75, 2498 (1995).
10. H. Tostmann et al., Ber. Bunsenges. Phys. Chem. 102, 1136 (1998).
11. N. Lei, Z. Huang and S. A. Rice, J. Chem. Phys. 104, 4802, 1996.
12. P. Wynblatt and D. Chatain, Ber. Bunsenges. Phys. Chem. 102, 1142 (1998).
13. H. Tostmann, D. Nattland and W. Freyland, J. Chem. Phys. 104, 8777 (1996).
14. K. B. Khokonov et al., Elektrokhimiya 10, 911 (1974); H. U. Tschirner et al., Wissenschaftliche Zeitschrift der Technischen Hochschule Karl Marx Stadt 26, 640 (1984).
The dip in density between the outermost Bi adlayer and the thick wetting layer can be modeled with an atomic model similar to the one used for Bi segregated on top of Ga with subsurface layering (see Ref. 10). Including subsurface layering provides a slightly improved fit but does not substantially alter the parameters of the wetting layer. For example, see p. 218 in Ref. 3 or p. 75 in Ref. 4.

D. Beysens and M. Robert, J. Chem. Phys. 87, 3056 (1987).

E. DiMasi et al., J. Phys: Condensed Matter, submitted (2000).

R. F. Kayser, M. R. Moldover and J. W. Schmidt, J. Chem. Soc. Faraday Trans. II 82, 1701 (1986).

J. Israelachvili, *Intermolecular & Surface Forces*, Academic Press, 1992.