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2008 J. Phys.: Condens. Matter 20 355007

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Is surface crystallization in liquid eutectic AuSi surface-induced?

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Received 7 May 2008

Published 12 August 2008

Online at stacks.iop.org/JPhysCM/20/355007

Abstract

Recent x-ray measurements have revealed surface crystallization in the liquid eutectic Au_{0.82}Si_{0.18} alloy accompanied by a pronounced surface-induced layering with a thickness of seven to eight well-defined atomic layers. For the crystalline surface monolayer a stoichiometry of AuSi₂ has been determined, implying a strong Si surface enrichment. In this study we have analysed the composition at the interface with vacuum of the solid and liquid eutectic alloy by means of x-ray photoelectron spectroscopy (XPS). Evaluation of the XPS spectra using a homogeneous interface model and an inhomogeneous interface model clearly indicates a strong interfacial enrichment of Si in agreement with the x-ray measurements. In an interfacial layer of 2 nm thickness the average Si concentration is nearly three times larger than that in the bulk. However, the XPS spectra give evidence for a low concentration (~3 at.%) of oxide impurities at the interface—in all probability SiO₂—which raises the question of whether surface crystallization in this alloy is surface-induced or driven by SiO₂ nucleation centres.

1. Introduction

Considering a plane liquid/vapour interface the temperature of which is lowered toward the bulk triple point, a surface-induced freezing or crystallization transition may occur whereby a solid-like, ordered quasi-2D layer forms at the interface. This phenomenon has been observed and is well characterized for several complex molecular liquids such as alkanes or liquid crystals—for a recent review see [1]. It is less well studied and understood in the case of liquid metals and alloys.

In MD simulation calculations of the liquid and supercooled Au surface Celestini *et al* [2] found first indications of ‘a packed surface layer structurally akin to a defected 2D triangular solid’ which on further cooling extrapolates to a hexatic transition. Bulk crystallization should set in starting from the surface inwards. According to the theory of freezing in two dimension by Halperin and Nelson [3], such a fluid–hexatic transition is predicted. The first experimental observation of surface freezing in a metallic system was reported by Rice and co-workers [4]. They studied the surface of a liquid Ga–Pb alloy dilute in Pb by x-ray reflectivity and grazing incidence x-ray diffraction (GIXD). On lowering the temperature toward the eutectic

point they observed a first-order fluid–hexatic transition followed by the formation of a hexagonally ordered Pb monolayer. Further investigations of dilute and concentrated Ga-based alloys (GaX, X = Bi, Pb, Tl) by different spectroscopic methods—capillary wave spectroscopy [5], second harmonic generation [6], spectroscopic ellipsometry [7] and x-ray photoelectron spectroscopy [8]—clearly showed the occurrence of surface freezing transitions at temperatures above the liquidus line of these alloys [5–8]. In the bulk they are characterized by a wide Ga-rich liquid–X-rich liquid miscibility gap. Associated with this bulk phase behaviour the liquid/vapour interface exhibits complete wetting transitions along the Ga-rich side of the liquid–liquid coexistence curve [9]. Consequently, thin X-rich wetting films of 1–2 ML thickness reside at the interface at conditions off of coexistence. Taking this into account we have suggested a model whereby surface freezing in these alloys is considered as freezing of strongly undercooled quasi-2D wetting films [9].

Very recently surface-induced crystallization has been reported for the liquid eutectic AuSi alloy [10]. The bulk phase diagram of this system is very dissimilar to the Ga-based alloys above: it exhibits only a very deep eutectic at $T_E = 363 \pm 3^\circ\text{C}$ with a composition corresponding to Au_{0.82}Si_{0.18} [11]. Therefore, a complete wetting transition cannot be expected. X-ray measurements [10] reveal a crystalline monolayer with a Au₄Si₈ structure above 360 °C which transforms at 371 °C

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into a different surface structure existing up to at least 410 °C. Furthermore, a strongly enhanced surface-induced layering of seven to eight layers is found which are liquid-like in lateral direction but well defined in the normal direction.

In this communication we report a detailed analysis of the surface composition of liquid Au_{0.82}Si_{0.18} at variable temperature up to 500 °C employing x-ray photoelectron spectroscopy (XPS). Assuming a 2 nm thick layering and using an appropriate slab model we find, indeed, a strong Si enrichment at the interface in qualitative agreement with the results of [10]. However, all XPS spectra up to 470 °C exhibit a clear oxide peak which we assign to surface enriched SiO₂.

2. Experimental details

Measurements have been performed with an Omicron Nanotechnology Multiprobe P system equipped with an XPS/AES spectrometer and a scanning tunnelling microscope (STM). In this study we focus on XPS measurements. XPS spectra were recorded with a magnesium anode x-ray source (Mg K α , 1253.6 eV) and a hemispherical electron energy analyser operating at a pass energy of 50 eV in steps of 0.2 eV. For a quantitative analysis of the spectra the intensities I_i have been determined by integration of the peaks after a linear background correction. Reference spectra have been taken of a Au(111) film, a Si wafer and a SiO₂ glass plate at room temperature under the same instrumental conditions. The Au_{0.82}Si_{0.18} alloy samples have been made available to us by the authors of [10] and hence were identical to those of the x-ray experiments. They were contained in Mo crucibles of cylindrical shape with an inside diameter of 13 mm and a height of 7 mm. The upper half of this cylinder had a conical shape so that the liquid alloy surface became nearly flat once it wetted the Mo walls. Before measurements the alloy sample surfaces were cleaned by Ar-ion sputtering and skimming with a heated W wire inside the preparation chamber of the spectrometer at a base pressure of $\sim 10^{-10}$ mbar. They were then transferred to the analysis chamber at a base pressure below 10^{-10} mbar. The temperature of the samples was varied with a resistance heater underneath of the Mo container; the temperature was recorded with a Ni–NiCr thermocouple whose tip stuck inside a boring in the bottom of the Mo crucible. The thermocouple was calibrated against the eutectic temperature of 363 °C of the alloy and the relative accuracy is estimated to be ± 3 K. The reproducibility of the XPS intensities in different heating and cooling cycles was found to be better than 3% which gives an indication of the relative errors of these measurements; the absolute error of the energy scale of the spectra is estimated to be ≤ 0.2 eV. For further details on STM measurements see [12] or [8].

3. Results and discussion

Figure 1 shows a selection of typical XPS spectra of the interface of solid and liquid Au_{0.82}Si_{0.18} alloys. In the liquid state the intensities of the Au signals increase slightly in the temperature interval $380 \leq T$ (°C) ≤ 500 , whereas those of the Si signal show a weak reduction. The corresponding

peaks of the solid surface exhibit a clearly reduced intensity possibly indicating a rough surface—see also the STM image in figure 3 below. Remarkable is a weak but clear oxide peak at 532.5 eV in comparison with the O 1s excitation in am-SiO₂ at 532.6 eV [13]. It disappears only at temperatures above 470 °C. This oxide peak resists different heating and cooling cycles followed by repeated sputtering of the seemingly clean surface. Its intensity remains constant over several days at a constant temperature below 470 °C and a base pressure of $\leq 10^{-10}$ mbar which clearly indicates that it is not due to adsorption of O₂ impurities resulting from the UHV chamber. So we conclude that this impurity, presumably SiO₂, is dissolved in the bulk alloy and is strongly enriched at the liquid/vacuum interface. It is known that SiO_x dissolves in liquid Si with an equilibrium concentration of $\sim 10^2$ ppm [14]; how its activity changes with addition of Au to our knowledge is unknown.

In order to quantify the surface composition of the ternary system Au–Si–SiO₂ we consider two different interfacial configurations: a homogeneous and an inhomogeneous model. Since we are mainly interested in the relative changes of the surface compositions with temperature we first use the simplest approximation of the homogeneous model where the surface mole fraction of a component A, $x_A^{(\sigma)}$, inside the analysis depth is given by [15]:

$$x_A^{(\sigma)} = (I_A/I_{A,0}) / \left(\sum_i I_i/I_{i,0} \right), \quad (1)$$

where the I_i are the intensities of the XPS signals of species i in the sample and the $I_{i,0}$ are the respective values of the reference spectra of the pure component i recorded with the same instrumental settings. The result of such an evaluation for the Au_{0.82}Si_{0.18} alloy is shown in figure 2, whereby a ternary interphase of Si, Au and SiO₂ has been taken into account. Four regions may be distinguished. In the solid alloys (region I) the $x_i^{(\sigma)}$ are nearly constant, amounting to $x_{\text{Si}}^{(\sigma)} = 0.41$, $x_{\text{Au}}^{(\sigma)} = 0.56$ and $x_{\text{SiO}_2}^{(\sigma)} \sim 0.03$; so, with respect to the bulk phase, Si is obviously strongly enhanced at the interface. In region II ($363 \leq T$ (°C) ≤ 420) $x_{\text{Si}}^{(\sigma)}$ decreases by roughly 10% with increasing temperature. In this temperature interval grazing incidence x-ray diffraction measurements reveal surface crystallization at least up to 410 °C, with a first-order phase transition of the surface structure at 371 °C [10]. In region III and IV the $x_i^{(\sigma)}$ within experimental error stay constant, in region IV no more oxide is detected at the interface.

Taking into account the pronounced surface-induced layering observed in the x-ray reflectivity measurements [10], analysis of the XPS spectra by an inhomogeneous model is more appropriate. For this aim we have used a simple binary slab model for the interfacial region and calculated $x_{\text{Si}}^{(\sigma)}$ and $x_{\text{Au}}^{(\sigma)}$ according to the following equation, see also [15]:

$$I_i/I_{i,0} = x_i^{(\sigma)} (1 - \exp(-d/\lambda_i \cdot 0.95)) + x_i^{(b)} \exp(-d/\lambda_i \cdot 0.95). \quad (2)$$

In this expression $x_i^{(\sigma)}$ is the interfacial mole fraction of component i , $x_i^{(b)}$ the corresponding bulk value, d the slab

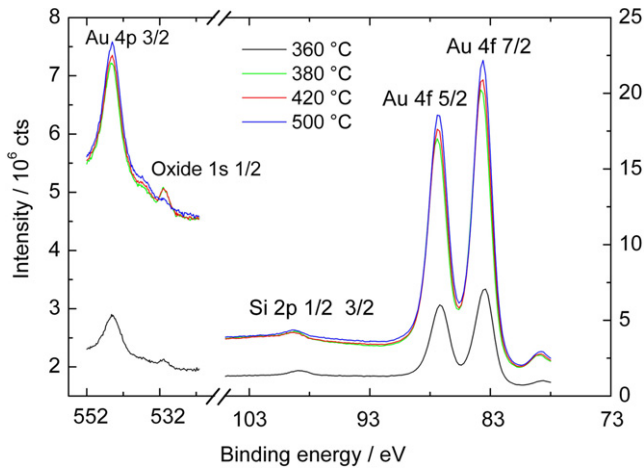


Figure 1. XPS spectra of eutectic Au_{0.82}Si_{0.18} at selected temperatures below and above the eutectic temperature of 363 °C; note the different intensity scale for the left and right part of spectra.

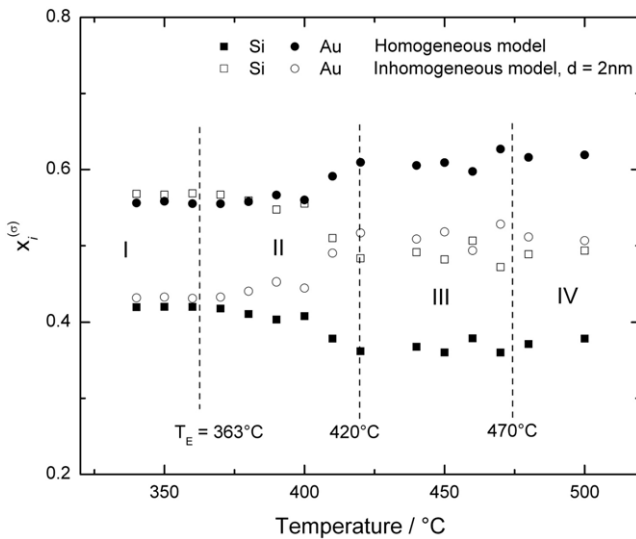


Figure 2. Surface mole fraction, $x_i^{(\sigma)}$, versus temperature of Au_{0.82}Si_{0.18} alloys determined from XPS spectra by a homogeneous and inhomogeneous interfacial model; for details see the text.

thickness, λ_i the inelastic mean free path of the photoelectrons corresponding to the attenuation length, and the instrumental constant $0.95 = \cos \Theta$ where Θ is the angle of emission from the surface normal. In the actual evaluation we have worked with the intensity ratios, i.e. $(I_{Si}/I_{Si,0})/(I_{Au}/I_{Au,0})$ and have taken the Au 4f and Si 2p signals with the corresponding mean free path values of 14.5 and 27.4 Å, respectively [16]. For the slab thickness we have chosen a value of 2 nm which approximately corresponds to the depth of the layering range of seven to eight well-defined atomic layers as determined from x-ray reflectivity measurements [10]. The result of this calculation is included in figure 2. As can be seen the slab model yields a further enhancement of Si in the interfacial region with a value of $x_{Si}^{(\sigma)} \sim 0.6$ at lower temperatures. The temperature variation of the surface compositions resulting from both the homogeneous and inhomogeneous model is

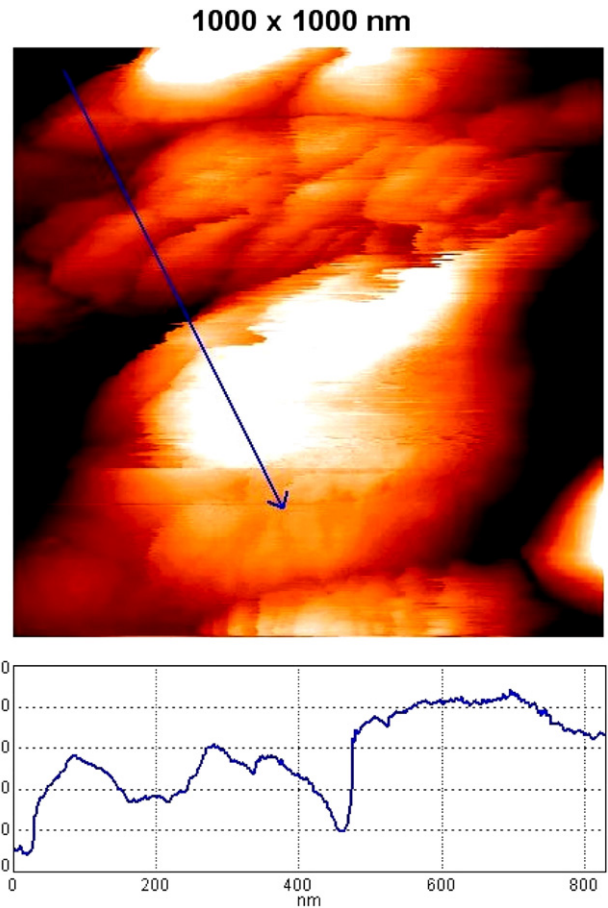


Figure 3. STM image of the surface roughness of a Au_{0.82}Si_{0.18} alloy quenched from 370 °C to room temperature ($V_b = 0.2$ V, $I_t = 0.2$ nA); the height profile is given below.

similar. Summarizing these results of the XPS spectra analysis we can state that a strong enrichment of Si by almost a factor of three relative to the bulk composition occurs in the interfacial region in solid and liquid Au_{0.82}Si_{0.18} near the eutectic temperature. This is in qualitative agreement with the x-ray reflectivity results, where at 370 °C a composition of the top layer of ~ 70 at.% Si has been reported [10].

In the case of surface freezing films in both dilute and concentrated Ga–Bi and Ga–Pb alloys the surface structure could be determined with atomic resolution by STM whereby the films have been quenched and measured at room temperature [8]. It was found that the topography of the films—characterized by large atomically flat terraces—is identical to that of pure Bi(0001) and Pb(111). We tried a similar STM experiment for the Au_{0.82}Si_{0.18} alloy quenched from 370 °C to room temperature. The corresponding STM image together with a height profile is presented in figure 3. We could not observe the expected Au₄Si₈ surface structure determined by GIXD measurements [10]; instead, we saw a very rough surface as shown in figure 3. Obviously, the crystalline monolayer of Au₄Si₈ is destroyed on cooling below the eutectic temperature.

In conclusion, XPS measurements of the eutectic Au_{0.82}Si_{0.18} alloy exhibit a large enrichment of Si at both the solid and liquid/vapour interface for temperatures near the

eutectic. In an interfacial layer of 2 nm thickness the average Si concentration is almost a factor of three higher than in the bulk. This strong interfacial enhancement of Si is consistent with recent observations from x-ray measurements. Furthermore, the XPS spectra give evidence of a low concentration of an oxide impurity enriched at the interface which we assign to am-SiO₂. So the question remains if surface crystallization in this alloy is really surface-induced or is due to SiO₂ nucleation centres?

Acknowledgments

Support of this work by DFG through project FR 299-18, by Karlsruhe Institute of Technology, KIT, and Fonds der Chemischen Industrie is acknowledged.

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