Interfacial Properties of Liquid Alloys :An Experimental study on Ga-Bi and Ga-Ge

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Abstract

Interfacial phase like wetting and prewetting transitions are of considerable interest in physics and chemistry of condensed matter since the represent phase transition is reduced dimensionality. Besides this, interfacial properties are of profound practical and technological interest. Most systems studied experimentally in this respect are characterized by Van der Waals intermolecular interactions. However, in the last few years is shown that Coulomb liquids like liquid alloys or metal molten salt solutions exhibit interfacial phase transition similar to those known in Van der Waals systems.

In order to get more insight into these phenomena the fluid-vapor interface of two different alloy systems have been studied using ellipsometry. Ga-Bi is binary ally, with large positive deviations from Raoult's law, exhibiting a distinct miscibility gap. Approaching liquid-liquid coexistence a bi-rich film completely wets the fluid-vapor interface. As can be estimated from ellipsometric results the film thickness jumps, at the monotectic temperature to a value of about 50 Å . In contrast, Ga-Ge shows continuous miscibility and deviates much less from ideal mixing. As the Ge concentration in liquid Ga increases along the solid-liquid coexistence curve the optical properties at the surface also vary continuously, which can be modeled within a simple effective medium approach .

Résumé

Les transitions de phase aux interfaces, comme le mouillage et prémouillage sont d'une importance considérable en physique et en chimie. A côté de ces propriétés interfaciales, la majorité des systèmes étudiés expérimentalement dans cet ordre sont caractérisés par des interactions intermoléculaires du type Van der Waals. Cependant dans les dernières années, il a été montré que les liquides présentent des interactions Coulombiennes sont similaires aux alliages liquides ou aux solutions des métaux des sels fondus et montrent une transition de phase aux interfaces similaires à celles connues dans les systèmes présentant des interaction du type Van der Waals . Dans le but de comprendre ces phénomènes aux interfaces fluide-vapeur, deux alliages différents ont été étudié en utilisant la technique ellipsométrique.

Ga-Bi est un alliage binaire avec des déviations largement positives des lois de mélange de Raoult et montrant une lacune de miscibilité importante. En approchant la coexistence de l'interface liquide-liquide, un film de Bi mouille l'interface fluide-vapeur. A partir des résultats ellipsométriques il a été possible d'évaluer l'épaisseur du film, celle ci avoisine 50 Å . cependant le système Ga-Ge montre une miscibilité continue et dévie moins du mélange idéal. Comme la concentration de Ge dans Ga liquide augmente le long de la courbe de coexistence solide liquide, les propriétés optiques à la surface varient aussi d'une manière continue pouvant être modélisées à partir d'une approche d'un milieu effectif simple.

1. Introduction

Wetting phenomena and interfacial phase transitions are growing interest in condensed matter physics. Since the time of Cahn's paper critical point wetting [1] a variety of theoretical as well as experimental work has been published in this field [2,4]. However, in most cases only fluid systems whose intermolecular interactions are not governed by ionic or screened Coulomb forces have been considered. Although solid metal surfaces play some role as substrate materials the wetting behavior of Coulombic liquids such as molten salts or liquid metals is neither experimentally well established nor theoretically understood. This is rather surprising as alloys and their interfacial properties and wetting behavior are of some technical importance. First experiments within the homogeneous series of the alkali metal-alkali halide systems have been reported. They show a growing trend of the fluid metals to be wetted by a salt-rich layer on going from heavier (Cs-CsCl and Rb-RbCl)) to be lighter (Na-NaCl) systems [5,6,7]. This trend is accompanied by a strong increase of the width of the miscibility gap in theses systems [8] which reflects the sensitivity of thermodynamic behavior to the gradual change of intermolecular interactions in these series.

We have performed new ellipsometric experiments on Ga-Bi and compare these to an older experiment on Ga-Ge, both carried at the liquid-vapor interface. Special attention was given to the preparation of liquid sample surface to reduce the influence of oxygen impurities on the wetting properties.

The alloys have been selected for the following reasons:

i. They exhibit different phase behavior in both the bulk phase as illustrated in fig.1 [9,10].

ii. Both systems have galium as one pure component in common.

iii. The optical properties of pure components differ strongly [11,12] and,

iv. The liquid phase that is expected to completely wet the second liquid phase and the vapor phase should have a higher density to make the wetting process observable at the liquid-vapor interface. We have employed single wavelength ellipsometry to study the liquid surface continuously with time and with increasing temperature along the coexistence line.
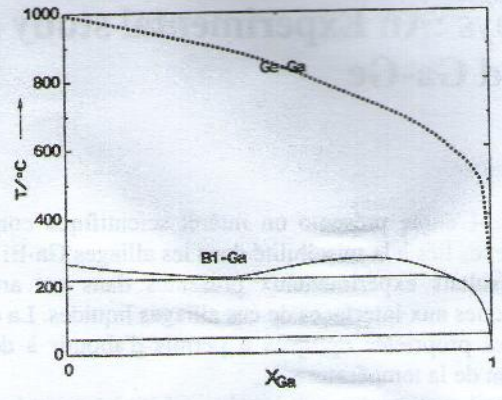

fig.1 Phase diagrams of Bi-Ga (solid lines) and Ge-Ga alloy (dashed line)

2. Experimental

The ellipsometer that is used in this study is similar to that described by Stobies et Al [13]. Apolarised light beam hits the surface of interest at an angle on incidence Φ_o. The intensity of the reflected light is modulated by rotating polarizer, accumulated to obtain a suitable signal to noise ratio and finally Fourier transformation to determine the ellipsometric angle ψ and Δ [14] with

$$\tan g\,\psi \cdot \exp(i\Delta) = \frac{R_p}{R_s},$$

$R_{p(s)}$ being the parallel (normal) component of the reflected amplitude [14]. The complex dielectric function is then caculated within a simple two phase model.

As light sources, an Xe are lamp tunable lasers have been employed which can be aligned to the ellipsometer using fiber optics. The principal arrangement of vacuum chamber furnace and sampler holder is demonstrated in fig.2.

The alloys is heated in a molybdenum crucible with a resistance furnace in a UHV chamber. During the experiments, a pressure of 10^{-6}Pa, was achieved which was found sufficient to measure no change of the optical constants within experimental errors over several days.

Special attention was focused on the determination of the temperature in the bulk phase and at the liquid surface. Unfortunately, syrometric methods for
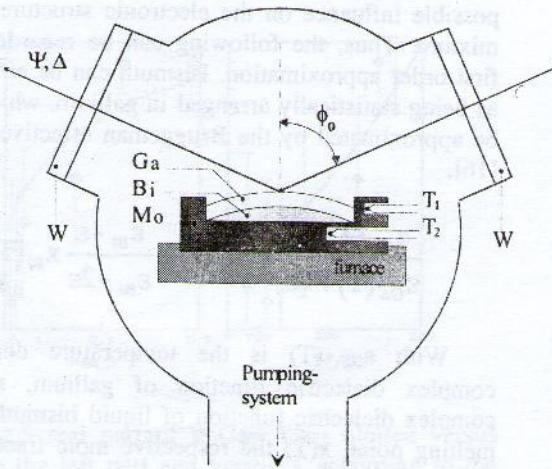
fig.2 Shematic drawing of the UHV Chamber, the furnace, the sample and the reflection Geometry of the ellipsometry experiment.
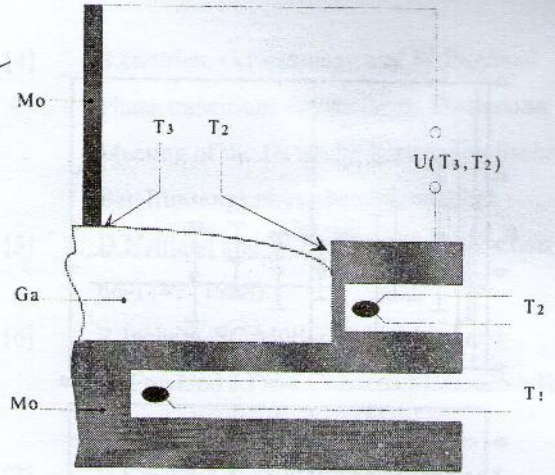
fig.3 Schematic for temperature calibration at point T_3 thermoelectric force $U(T_3, T_2)$ is measured.

the absolute temperature determination are not suitable due to the poor black body characteristics of the liquid metal surface.

conditions no significant difference between T_1 and T_2 was found but a gradient to the center of the liquid surface (T_3) had to be considered. In order to quantify this a molybdenum rod was placed in the center of the liquid surface and the EMF of the following circuit was measured:

Mo (at 20°C) – Mo / Ga (at T_2) – Ga/Mo (at T_3) – Mo (at 20°C).

The thermoelectric force U(T3,T2) is given by thermopowers of liquid gallium S_{Ga} (T) [15] and of solid molybdenum S_{Mo} [16], respectively:

$$U(T_3, T_2) = \int_{T_2}^{T_3} S_{M_o}(T)\,dt + \int_{T_2}^{T_3} S_{G_a}(T)\,dt$$

All sample handling, the filling procedure and the mounting of crucible in the UHV chamber were performed in an Ar glovebox (H_2O < 1ppm, O_2 < 2ppm). In the crucible liquid gallium was poured over liquid bismuth or solid germanium. According to the phase diagrams Bi (or Ge) is dissolved in the liquid phase at which the ellipsometric experiment As shown in fig.3, two thermocouples measure the temperature in the center (T_1) and at the top edge (T_2) of the crucible. Under the experimental takes place. The purity of the substance (99,999%) was sufficient and not the limiting factor for the quality of the reflecting surface.

3. Results and Discussion

In this paper we use two approaches denoted as two phase and three plane models. The first simply assumes the interface as the contact plane of two homogeneous semi-infinite bulk phases, which in our case are the liquid and the vapor. To take segregation and wetting films into account the three phase model was employed: ψ and Δ now depend on the complex film dielectric functions of bulk liquid, of the covering film and the film thickness.

In fig.4 we present ε of Ga_{85} Bi_{15} at 600nm, which was measured in the UHV apparatus. The data below a temperature of approximately 100°C correspond to a Bi content in the liquid phase of $x_{Bi} \approx$ 0.015 scatter considerably. This is also visible in independent observation experimental runs. It is an experimental observation that below this temperature the surface curvature of the sample is still strong at a drop diameter of 40mm and the acquisition of reproductible data is difficult. This may be due to the still existing high surface tension of the mixture [15].

At higher temperature with increasing solubility of Bi in Ga the surface of the sample becomes fletter and the reproductibility of the data improves substantially. Since the optical properties of the pure components differ strongly in the real part of ε and much weaker in the imaginary part, ε_2 is included for completeness in this figure.
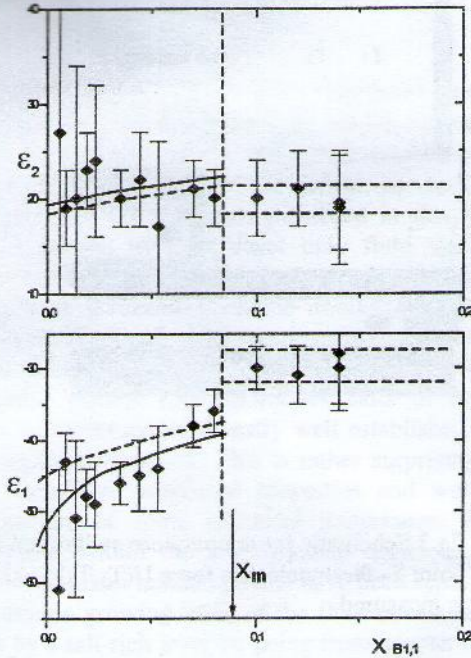
fig.4 full symbols: ellipsometric results of ε_1 and ε_2 at 600nm of Ga_{85}-Bi_{15} for details see text.

Above 100°C ε_1 increases monotonically within the error bars. At a temperature of about 220°C it jumps to higher value and remains nearly constant up to the maximum temperature of this experiment, 285°C.

In the following we derive a simple approach to model the experimental results on $Ga_{85}.Bi_{15}$ as shown in fig.4.

For the description of the optical properties of the liquid phase in Ga-Bi at solid (Bi)-liquid (Ga-Bi) coexistence one has to take two effects into account: first, the temperature dependence of the dielectric function phase and the change of the effective electrons. This is approximated through the temperature dependence of the complex dielectric function of pure gallium known from the literature [11]. At 600nm and in the temperature range between 50 and 450°C ε_1 and ε_2 could have be phenomenologically described by cubic polynomes. The second point concerns the influence on the optical properties due to the increasing bismuth mole fraction with increasing temperature along the coexistence curve.

For this problem neither experimental nor theoretical data are available. So we decided to approximate this by calculating an effective medium consisting of a mixture of pure gallium an bismuth. Since these compounds do not form intermetallic or semiconducting compounds with a drastic change of the band structure, this approach seems to be applicable. We are aware that this does not exclude a

possible influence on the electronic structure of the mixture. Thus, the following can be regarded as a first order approximation. Bismuth can be envisaged as being statistically arranged in gallium, which may be approximated by the Bruggeman effective theory [16].

$$\frac{\varepsilon_{Ga}(T)-\varepsilon}{\varepsilon_{Ga}(T)+2\varepsilon} \times G_a(T) + \frac{\varepsilon_{Bi}-\varepsilon}{\varepsilon_{Bi}-2\varepsilon} \times_{Bi}(T) = 0$$

With ε_{Ga} (T) is the temperature dependent complex dielectric function of gallium, ε_{Bi}, the complex dielectric function of liquid bismuth at the melting point, x(T) the respective mole fractions of the liquid phase along the coexistence curve and ε the effective medium complex dielectric function depending on both T and x.

Within the model half of the increase of ε_1 along the coexistence line up to the monotectic point is due to the temperature change, the oder half is due to the compositional change.

In fig.4 the experimental data on ε_1 are compared to the above model, represented as solid line. Leaving out two points at low bismuth mole fraction the change of ε_1 with x_{Bi} is well described and the quantitative agreement is satisfactory within our experimental error bars. In the concentration regime $0.015 \leq x_{Bi} \leq 0.053$ the ellipsometric data of ε_1 are systematically lower, at $0.070 \leq x_{Bi} \leq 0.083$ they are higher yhan the model going beyond the monotectic point, denoted x_m in fig.4, ε_1 jumps discontinuously and remains nearly constant as function of the mole fraction. Here the gallium rich bulk phase is assumed to be wetted by a non microscopically thick bismuth-rich film. To get an estimated of the film thickness d, we calculated a three phase model with:

$$\varepsilon_{bulk} = -38.3 - i21.0 \text{ and}$$

$\varepsilon_{film} = -21.0 - 1.22.3$ as effective medium dielectric functions at a wave length of 600nm for $x_{Bi}=0.085$ and $x_{Bi}=0.06$, the compositions of the coexisting liquid phases at the motectic point. Our ellipsometric data are consistent with a film thickness of 40 to 50 $\overset{o}{A}$. The calculated film thickness depends in a moderate way on the dielectric functions used as input values.

Assuming pure bismuth as the film phase above an effective medium gallium-rich bulk phase would lead to $20A \leq d \leq 40 \overset{o}{A}$. On the other hand pure liquid gallium as bulk phase and an effective medium as film yields $50A \leq d \leq 75 \overset{o}{A}$.

Thus, $50 \overset{o}{A}$ seems to be a good estimation for the thickness of the wetting film in this experiment.

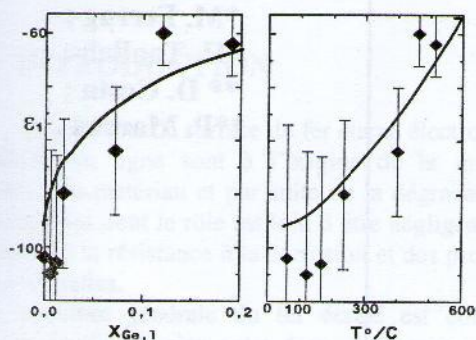In the left part fig.5 we present ε_1 at 1107 nm of the system Ga-Ge as function of the germanium mole

Fig.5 real part of ε Ga_{77} Ga_{23} plotted versus $X_{Ge,1}$ in the left part and versus T according to the diagram in the right part. Full symbols: ellipsometric measurement at 1107nm.

Fraction in the liquid phase, in the right part the same data set is plotted versus temperature according to the phase diagram. Here we applied the same effective medium model using the temperature dependent dielectric function of gallium and the dielectric function of germanium at the melting point. The agreement is satisfactory within the error limits of the experimental data. Together with the spectroscopic information this demonstrates that the optical properties of this system vary continuously along the coexistence curve and neither a wetting transition nor a macroscopic surface segregation occurs up to a temperature of 500°C at solid-liquid coexistence.

In summary, we have presented ellipsometric experiments on the surface properties of the alloys Ga-Bi and Ga-Ge. The former exhibit a wetting transition at the monotecti point, i.e. the solid-liquid-liquid-vapor tetra point.

The system Ga-Ge does not show a similar phenomenon. Its optical properties can be described from melting point of gallium up to 500°C corresponding to $x_{Ga}=0.18$ by effective medium models described above.

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