Structure of liquid Sn on Ge(111)

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We present an x-ray-diffraction structural analysis of liquid Sn layers of monolayer thickness absorbed on Ge(111) surfaces. Above the melting temperature, we find that the Sn atoms display both liquidlike and solidlike behavior. The liquid shows both perpendicular and lateral ordering. The Sn/Ge(111) system allows us to investigate the influence of temperature on the liquid structure. Our most important observation is that the structure of the liquid Sn layer changes gradually with temperature from more solidlike to more liquidlike.

I. INTRODUCTION

The structure of a liquid in contact with a solid plays an important role in properties such as flow, lubrication, and wear. This structure is also important in crystal growth, where it influences, for example, the incorporation of impurities and the final growth shape of the crystal.[1,2] Theoretical studies predict that ordering of the liquid extends over a few atomic distances and exhibits layering perpendicular to the surface as well as ordering parallel to the surface.[3,4] Little is known about the parallel ordering of the liquid. Howe[5] used high-resolution transmission electron microscopy to investigate the solid-liquid interface between crystalline Pd_3Si and amorphous $Pd_{80}Si_{20}$ and found ordering in the liquid in the first atomic layers. Layering of the liquid perpendicular to the surface has been observed in a few experimental studies, e.g., in electrode/electrolyte interfaces[6] and in liquid gallium in contact with a hard wall.[7]

In the context of surface melting, the nature of a liquid film in contact with a solid has also been investigated.[8,9] It was found that the thickness of the liquid layer (termed ''quasiliquid'') increases upon approaching the bulk melting point. Attempts to measure the ordering in the quasiliquid surface layer, however, have not been successful.[10,11] Additionally, considerable experimental as well as theoretical work has been conducted on intercalation compounds[12–14] in which liquidlike alkali layers are embedded in a graphite host.

The ordering of the liquid near the interface is likely to depend on several parameters, such as the temperature and size match between liquid and solid. No prior experimental information is available on this. Therefore the aim of this study is to determine the structure of a liquid in contact with a solid as a function of temperature for liquid Sn monolayers absorbed on Ge surfaces. The Sn/Ge(111) system can be considered as a model system for crystal growth, in particular for the case of liquid phase epitaxy (LPE) from thicker layers.

The Sn/Ge(111) system is comparable to Pb/Ge(111), a system that has received considerable attention.[15,16] It was found that above an order-disorder transition temperature, the Pb layer shows both liquidlike and solidlike behavior. To develop a better understanding of this dual character we present here the structure of the thin liquid with varying

temperature. Because of its lower vapor pressure compared to Pb, Sn is more suitable than Pb for a study above the melting temperature.

Ichikawa[17,18] determined the phase diagram of the Sn/Ge(111) system and found an order-disorder transition at coverages between 1 and 1.6 monolayers (ML's) at a temperature T_m of 170 °C, similar to the Pb/Ge(111) system.[16] Below T_m, and depending on the coverage, the Sn/Ge surface exhibits a $3 \times 3\sqrt{2}$ or a $\sqrt{91} \times \sqrt{3}$ reconstruction. Above this transition the reconstruction disappears, and Ichikawa found evidence for a liquidlike structure of the Sn layer. The ordering in the liquid was not investigated.

Using x-ray diffraction, we find presently that (i) the Sn layer is well ordered below the melting point and that (ii) the properties of the layer *gradually* change from more solidlike to more liquidlike above the melting point.

II. EXPERIMENTAL DETAILS

To denote the surface structure, we use a surface unit cell for Ge(111) whose lattice vectors are expressed in terms of the conventional cubic lattice by $\mathbf{a}_1 = \frac{1}{2}[10\bar{1}]$, $\mathbf{a}_2 = \frac{1}{2}[\bar{1}10]$, and $\mathbf{a}_3 = \frac{1}{2}[111]$. The cubic coordinates are in units of the germanium lattice constant (5.66 Å at 300 K). The corresponding reciprocal lattice vectors $\{\mathbf{b}_i\}$ are defined by $\mathbf{a}_i \cdot \mathbf{b}_j = 2\pi\delta_{ij}$. The momentum transfer $\mathbf{Q}$, which is the difference between the incoming and outgoing wave vectors, is denoted by the diffraction indices (hkl) in reciprocal space: $\mathbf{Q} = h\mathbf{b}_1 + k\mathbf{b}_2 + l\mathbf{b}_3$.

The surface x-ray-diffraction experiments were performed at beamline ID3 at the ESRF (Grenoble) using a wavelength of 1.2 Å. The setup consists of an ultrahigh vacuum chamber, which was coupled to a z-axis diffractometer.[19,20] The crystal was mounted in the UHV chamber with the surface normal in the horizontal plane. All data were obtained with a small, constant incident angle ($\sim$1.0°) and varying exit angles.

The Ge(111) crystal (miscut $\sim$0.2°) was cleaned by repeated cycles of sputtering and annealing until a clear $c(2 \times 8)$ reconstruction was obtained. A Knudsen effusion cell was used for the deposition of the Sn atoms. For every data set a fresh Sn layer was deposited with a coverage of approximately 1.5 ML's (Table I). At coverages below 1 ML, the Sn layer did not show the liquidlike behavior described

TABLE I. Best-fit parameters at different temperatures.

Fit parameter	150 °C ($<T_m$)	200 °C ($>T_m$)	300 °C ($>T_m$)	Ref. 25[b]	Ref. 16[b]
In-plane Debye-Waller factor (Å^2)	4.5±1.0	12±2(T_1,T_4), 5±2(H_3)	12±2(T_1,T_4), 6±3(H_3)		
Height T_1 atom (Å)	2.58±0.10	2.55±0.04	2.64±0.03		
Height H_3 atom (Å)	3.73±0.05	3.58±0.07	2.82±0.12		
Height T_4 atom (Å)	4.17±0.10	4.11±0.07	3.47±0.12		
Height liquid Sn	2.42[a]	2.33±0.15	2.46±0.16		
# ML liquid Sn atoms	0.01±0.05	0.07±0.04	0.42±0.09		
# ML at T_1 sites	0.93±0.10	0.84±0.04	0.82±0.06	0.77	0.89
# ML at T_4 sites	0.19±0.05	0.24±0.04	0.26±0.03	0.19	0
# ML at H_3 sites	0.28±0.05	0.22±0.02	0.07±0.02	0.37	0.29
Coverage (ML)	1.41±0.15	1.37±0.08	1.56±0.12	1.33	1.25
χ^2	4.8	3.5	3.1		

[a]Fixed value.

[b]For Pb/Ge(111).

below. Full data sets, which include crystal truncation rods (CTR's h, k integer),[21] in-plane data ($l=0.2$), specular data ($h=k=0$), and radial scans[15] were taken at temperatures of 150±20 °C, 200±20 °C, and 300±20 °C, where T_m =170°. All measured intensities were converted to structure factors by applying a standard procedure.[22] Model calculations and fitting were done using the ROD program.[23]

III. RESULTS

Surface x-ray diffraction can probe both the structure and the ordering at the interface. A completely liquid Sn layer gives rise to cylindrical [two-dimensional (2D)-liquid] or spherical (3D-liquid) shells of diffuse scattering, from which the pair-correlation function can be deduced.[15] Such a liquid layer does not contribute to reflections with an in-plane momentum component. In contrast, a solid, commensurate Sn layer does not give rise to shells of diffuse scattering, but appears in the substrate crystal truncation rods. This difference is due to the long-range translational order in a solid Sn layer and the short-range order in a completely liquid Sn film. A Sn layer with both solid and liquid properties will be visible in both types of data.

In order to observe the diffuse scattering caused by the liquid layer, radial scans were performed in the $[h\,k]$ $=[1\,2]$ direction, where no Ge scattering is expected except thermal diffuse scattering [Fig. 1(a)]. No liquid ring is present at 150 °C (below T_m). Thus, as expected, the Sn layer is solid at this temperature. In contrast, at 200 and 300 °C a diffuse ring is observed. Additional radial scans in different directions revealed a similar peak at the same radius. This clearly indicates the presence of a liquid. Following Gray *et al.*,[24] the position of the liquid ring corresponds to a Sn-Sn distance of 3.8 and 3.4 Å for 200 and 300 °C, respectively. Figure 1(b) shows the position of the liquid ring in radial scans at different perpendicular momentum transfers for both a two-dimensional and three-dimensional liquid at 300 °C. The three-dimensional liquid is present as small droplets which form when extra Sn is deposited on the two-dimensional layer. This demonstrates that the diffuse scattering forms a cylinder in reciprocal space for a two-

dimensional layer and a sphere for a three-dimensional layer. A similar observation was made by Gray *et al.* for lead on germanium.[15]

To establish the lateral structure of the Sr layer, both the (10) and (20) rods were measured at our standard three temperatures, see Fig. 2. The solid curve is a theoretical calcu-
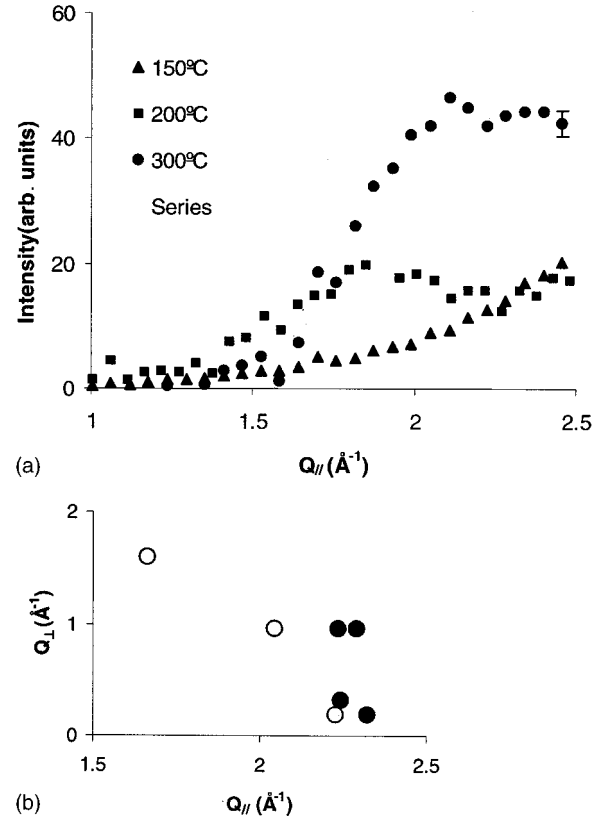

FIG. 1. (a) Radial scans in the $[h\,k]=[1\,2]$ direction at three temperatures, one below the phase transition (triangles) and two above the phase transition (squares and circles). The liquid ring is clearly seen around $Q_\parallel=2$. The increase at higher $Q_\parallel$ is due to thermal diffuse scattering from the Ge substrate. (b) Position of the liquid ring measured at different $Q_\perp$ for a 3D Sn liquid (open circles) and a 2D Sn liquid (solid circles) for $T=300$ °C.
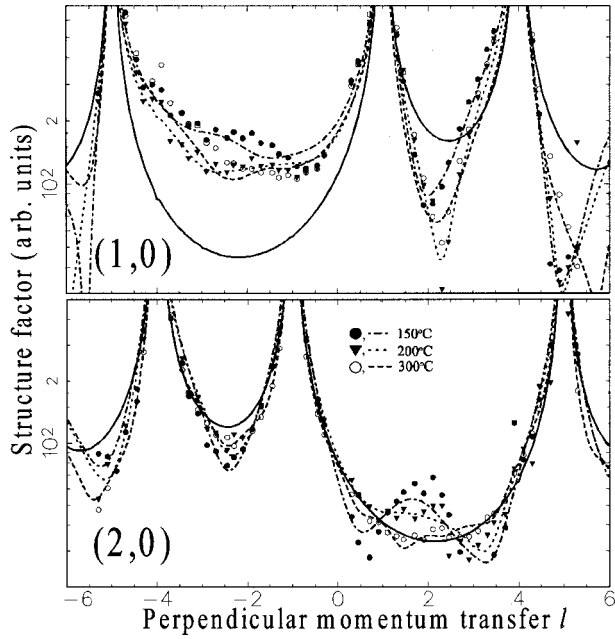
FIG. 2. Structure factor amplitudes of the (10) and (20) crystal truncation rods. Measured structure factors are indicated by symbols. The solid curve represents a calculation for bulk terminated Ge(111). The dot-dashed, dotted, and dashed curves represent the best fits for 150, 200, and 300 °C, respectively.
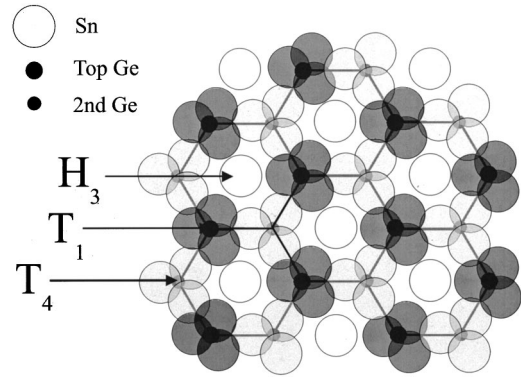

FIG. 3. Schematic top view of the average structure at 300 °C. The grayscale of the Sn atoms approximately indicates the occupancy. Due to the symmetry of the Ge (111) structure the Sn atoms can be displaced in three symmetric directions. In Table I the occupancy of the three atoms at one lattice site are added up to give a total value.

lation for a bulk terminated Ge(111) surface. The (10) rod does not follow this calculation at any temperature, which implies that the Sn atoms have a significant contribution to this rod at all temperatures. The (20) rod shows a different behavior; at low temperatures the measured structure factors do not resemble the calculated bulk curve, whereas at higher temperatures the structure factors gradually change until they almost coincide with this curve. Thus the contribution of the Sn atoms to the (20) rod is highest at low temperatures and almost disappears at high temperatures.

Summarizing the results, one can say that the radial scans show that the Sn layer has liquid properties while the CTR's demonstrate its solid features. Above T_m the Sn layer therefore has *both solid and liquid* properties. As in the liquid film during surface melting, the Sn layer can be called a quasi-liquid.

IV. ANALYSIS

In order to describe the behavior of the Sn quantitatively, we need a model that accounts for both the solid and the liquid character we observe. There are two possibilities for this. One is to use the method that Reiter and Moss[12,13] developed for intercalation compounds and thus model the Sn as a perturbed, but uniform, liquid. The alternative is to describe Sn as a solid that is gradually losing its solid properties. Since our analysis shows that the Sn layer is not uniform but contains different sites at all temperatures investigated, the latter solidlike model is more suitable. This is similar to the model that de Vries *et al.*[16] used for the Pb/Ge(111) system.

For the analysis we have used the (1×1) Ge(111) surface

cell defined above, which has three lattice sites with three-fold symmetry (Fig. 3). In our model, the Sn atoms can be in a solidlike or liquidlike state. The solidlike Sn atoms are placed on top of one of the three symmetric lattice sites and are allowed to have a lateral displacement. In that case, all three symmetric directions are modeled to occur simultaneously in different surface domains. A model without in-plane relaxations gave a bad fit for both temperatures above T_m. Sn atoms in the liquidlike state are mobile, without a fixed position on the surface. We model the liquid atoms by a single layer with a very high in-plane Debye-Waller parameter (so they do not contribute to the CTR's). Note that the system is expected to be dynamic. The high Debye-Waller parameters and the liquidlike behavior indicate that the Sn atoms are mobile and will rapidly change from one state into the other. Relaxation in the Ge substrate was found to be negligible.

The two-state model describes our data well for all temperatures. Figure 2 shows the best-fit model calculation for the (1 0) and (2 0) rods together with the measured structure factors, while Table I lists the best-fit parameters. Note that the fit is based on the entire data set, including specular and in-plane data. The in-plane displacements are 0.5 Å (0.4 Å) and 0.8 Å (0.4 Å) at 300 °C (250 °C) for the T_1 and T_4 site, respectively.

As mentioned before, below T_m the surface is reconstructed,[17,18] and cannot be described fully by our 1 $\times 1$ model. The above approach effectively projects the reconstructed structure onto the 1×1 unit cell. This simple approach allows us to compare the structure below T_m with the results of the liquid structure.

An important characteristic of the system is the distribution of the Sn atoms among the two states. Below T_m, the Sn layer is solid and all atoms are near lattice sites. In the fit we find indeed a liquid coverage of less than 0.01 ML. Above T_m the number of liquidlike Sn atoms increases as a function of temperature (from 0.07 ML at 200 °C to 0.42 ML at 300 °C) while the number of solidlike Sn atoms decreases. The distribution over the two states is shown in Fig. 4. Re-
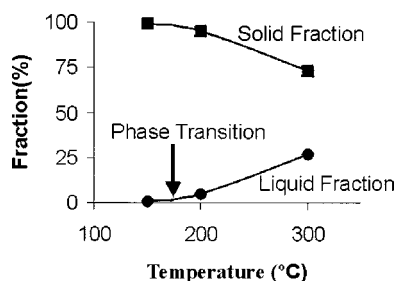
FIG. 4. Fraction of Sn atoms in the solid state (squares) and liquid state (circles) at different temperatures.

markably, the distribution is found to keep on changing far above the phase-transition temperature. The increasing liquidlike fraction shown in Fig. 4 is in accordance with the radial scans [Fig. 1(a)], which show a corresponding increase in the intensity of the liquid ring. The fits and the radial scans thus clearly show that the Sn structure changes from more solidlike to more liquidlike with temperature.

The Debye-Waller factor of the solidlike Sn increases with the temperature, as expected. Remarkably, the increase is stronger for the T_1 and T_4 positions than for the H_3 position (Table I). This could be an indication of different melting behavior of the Sn atoms at the different positions. Compared with the Pb/Ge(111) system,[16] the increase in Debye-Waller factors is smaller in the Sn/Ge(111) system. This is probably due to the smaller size of Sn compared with Pb, leading to a better size match with the Ge surface.

The temperature also influences the crystallographic structure. The height of the Sn atoms and the distribution of the Sn atoms over the three lattice sites change with temperature. Figure 3 shows the average position of the Sn atoms at 300 °C, the grayscale indicates the occupancy of the different sites. Below T_m, the height of the Sn atoms corresponds roughly to the height in an α-Sn crystal. This configuration

does not change at the phase transition, but is lost if the temperature is further increased.

The distribution of the Sn atoms over the three lattice sites changes gradually with temperature, as can be seen in Table I. For comparison, both the experimental values and the values found with molecular dynamics for the Pb/Ge(111) system are included.[16,25] The occupancy of the T_1 position is in all cases the largest and changes least with temperature. The experimental values of the Pb/Ge(111) system are only determined at one temperature so no comparison can be made of the temperature behavior.

The molecular dynamics studies of the Pb/Ge(111) system[25] sketch a similar picture as ours for Sn/Ge(111). These studies showed that above the phase transition the Pb layer becomes mobile but that the atoms still spend an important fraction of their time close to lattice sites.

V. SUMMARY

In summary, our analysis shows that the liquid Sn exists as a dynamic, 2D layer with Sn atoms residing preferentially on sites imposed by the Ge(111) lattice. The structure of the liquid Sn layer changes gradually with temperature from more solidlike to more liquidlike. The most important change is the decrease of the percentage of Sn atoms near lattice sites at higher temperatures. The question arises whether this behavior changes if the liquid layer changes from two dimensional to three dimensional. Unfortunately, the Sn/Ge(111) system is not suitable to investigate this, because the Sn layer does not completely wet the Ge surface at higher coverage.

ACKNOWLEDGMENT

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