

Melting of Pb as it approaches a two-dimensional solid

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The melting behavior of modulated Pb-Ge foils has been investigated by differential scanning calorimetry and x-ray diffraction. As the Pb layer thickness decreases, the melting temperature is depressed and broadened. For a 20-Å-thick Pb film, the start of the transition is 45°C below the bulk melting temperature and the transition breadth is on the order of 40°C. The transition has the characteristics of being second order. The normal thermodynamic variables and macroscopic interfacial energy considerations have been eliminated as mechanisms for broadening the transition by a series of first-order transitions.

I. INTRODUCTION

Recently Halperin and Nelson,¹ using the formalism of Kosterlitz and Thouless,² have proposed that melting for a two-dimensional (2D) crystal is a second-order dislocation-mediated transition. For the lack of experimental observations, investigators have resorted to molecular dynamic or Monte Carlo calculations using Lennard-Jones potentials or electron solids to test the validity of this theory. This had led to further confusion as there have been claims of support^{3,4} and claims of non-support⁵⁻⁸ of the model.

In general, melting is an interface initiated transition and as such resembles 2D melting on a periodic substrate potential. There are both experimental observations^{9,10} and theoretical model calculations¹¹⁻¹³ to substantiate interface initiation of melting. Once a stable solid-liquid interface is formed it can freely propagate, with only a very slight superheating, into the solid limited only by kinetic parameters. The difficulty in making meaningful experimental measurements of this interface controlled transition is that interface-volume ratios are usually small. The interface-volume ratio can be greatly increased, while still maintaining an appreciable volume of material, by fabricating compositionally modulated films, i.e., by alternately depositing two different materials. For the purpose of studying melting, it is desirable to deposit two materials with widely separated melting temperatures, which are essentially insoluble in each other. The Pb-Ge system offers a likely choice to satisfy these criteria. The melting temperatures are separated by 609°C and their mutual solubilities are negligibly small at the Pb melt-

ing temperature.¹⁴⁻¹⁶ By continually reducing the Pb thickness, the characteristics of the melting transition can be measured as the surface-to-volume ratio increases and the material approaches a 2D solid interacting with a substrate.

II. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUES

Modulated structures of Pb-Ge were prepared by alternately depositing each of the components from heated evaporation sources in a vacuum of 2×10^{-8} Torr. The thickness of each layer and rate of deposition were controlled by two quartz crystal monitors. The substrates were either sapphire disks (7.9-mm diameter, 0.5-mm thick) or mica. The sapphire disks were used for differential scanning calorimetry experiments and mica was used for the x-ray experiments. Any effects due to different substrates were eliminated by initially depositing 1000 Å of Ge. After deposition of the modulated structure, it was capped by another layer of 500 or 1000 Å of Ge. All deposition was performed with the substrate maintained at a temperature of 77 K. Examination by transmission electron microscopy (TEM) revealed the as-deposited Pb films were in layers with no detectable tendency for island formation. Encapsulation by the Ge layers constrains the Pb to stay in thin uniform layers. If the substrate was held at room temperature during deposition, the Pb layers clustered into islands before the subsequent Ge layer could constrain it.

Differential scanning calorimetry (DSC) measurements were performed by a DuPont 910/1090 thermal analyzer. Differential measurements were

made between two sapphire disks, one with the deposited modulated film. The heating and cooling were done in an argon atmosphere at a rate of 5°C/min. The residual unbalance in the specific heat between the sapphires, which results in a finite constant slope of the output of the DSC scan as the temperature is increased, was eliminated by computational analysis. Therefore, the traces from the DSC were indicative of either a peak in the specific heat or the enthalpy of fusion of the sample. This type of measurement cannot distinguish between the two types of thermal effects. The DSC curves were normalized on the basis of equivalent weights of Pb.

X-ray measurements were made in a Rigaku high-temperature attachment on a General Electric x-ray diffractometer. The temperature could be linearly ramped or held at a fixed value.

III. RESULTS AND DISCUSSION

Figure 1 shows the high-temperature heating and cooling DSC scans for 1 μm of Pb encapsulated between two 1000-Å layers of Ge. The melting and solidification transitions are sharp, indicating no appreciable temperature gradients. The total instrumental and material hysteresis upon melting and resolidifying is about 1–2°C. The second melting of the sample (not shown) is essentially identical to the first heating. This curve is also essentially identical to a DSC scan of a small piece of Pb placed in the calorimeter on a sapphire disk. That is 1 μm of Pb between Ge has bulk-behavior

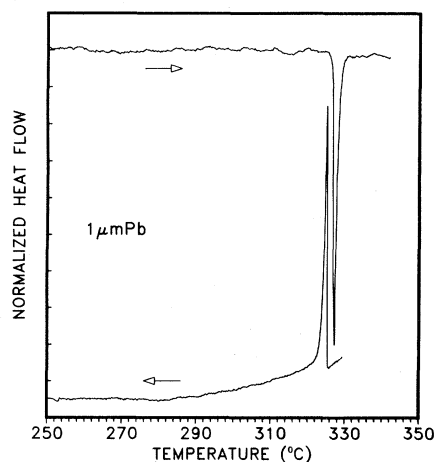


FIG. 1. DSC heating and cooling scans for 1 μm of Pb between two 1000-Å layers of Ge.

melting and shows, as expected, no solubility effects from Ge. Not shown on the curve (and all subsequent curves) is an exothermic reaction which occurs between 135 and 180°C. The source of the exothermic reaction is the transformation of Ge from the amorphous state to the microcrystalline state. This was verified by x-ray diffraction and TEM. The size of the microcrystallites is very small, the order of 20–30 Å. Consequently, the Pb layers melt in contact with a Ge interface which is crystalline and probably can be classified as rough.

Figure 2 shows DSC scans of a 444-layer Ge-Pb modulated foil in which the Pb is melted twice. The thicknesses of the Ge layers and Pb layers are 60 and 20 Å, respectively. There are five observations that are apparent from the scans: (1) The gross features of the transformation from solid-to-liquid Pb are the same whether the film is vapor deposited or resolidified from the melt. This is significant since, as will be shown later, the crystallographic texture of the Pb is drastically different. All the various thicknesses of Pb layers examined in this study showed essentially the same reproducible behavior on the second melting of the Pb. (2) There is a small amount of Pb, about 10%, as determined from the area of the DSC scan, which melts at the bulk transition temperature. The source of this bulk melting is from the edge of the film where the Pb layers can connect. This hypothesis was tested by taking a multilayer foil and creating more edge area by breaking it into pieces and observing that the area in the bulk transition region of the DSC scan greatly increased while the area associated with the main portion of the transi-

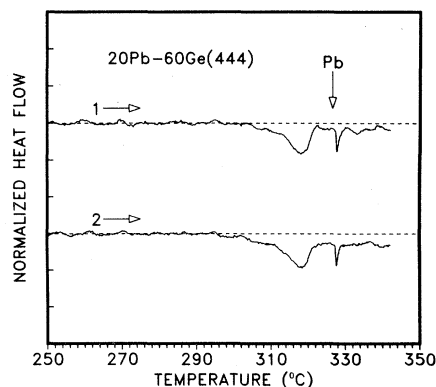


FIG. 2. DSC scans for a modulated Pb-Ge foil with 444 layers. The Pb layer thickness is 20 Å. Curve labeled 2 corresponds to the second melting of the same sample.

tion decreased. (3) The melting transition of the portion of the sample which has this bulk behavior is very sharp followed by the exponential decay as the sample comes to equilibrium with its surroundings. Consequently, to the scale of the observations of this study, there are no temperature gradients in the sample. (4) The melting transition of thin Pb layers is suppressed below the bulk melting temperature. This would be expected and could be rationalized using a number of theoretical models which include the surface or interfacial contributions to the total free energy of the solid. (5) Although the magnitude of the suppression is not readily explainable, the melting transition is extremely broad with a shape which is reminiscent of the specific-heat curve of a second-order phase transition. But, as already pointed out, the DSC measurement cannot discriminate between a specific-heat peak and a series of first-order phase transitions.

The DSC scan of the cooling cycle from the completely melted Pb state showed the same broad transition region, but a hysteresis which was much larger than the bulk Pb hysteresis.

Figure 3 shows the DSC scans for various

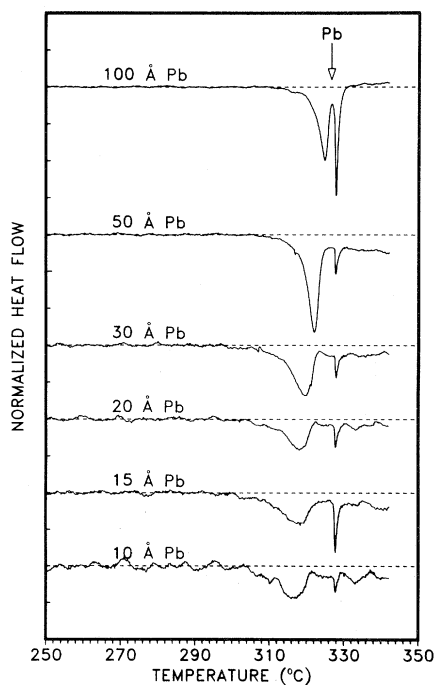


FIG. 3. DSC scans for modulated Pb-Ge foils for variable Pb layer thickness. The Ge layer thickness has a constant value of 60 Å. The vertical deflection for each of the curves are normalized to equivalent weights of Pb.

thicknesses of Pb. All the films had a constant Ge layer thickness of 60 Å and the curves are normalized to a unit weight of Pb. The total film thickness ranged from 3 to 4 μm for the samples. It is apparent from the figure that as the thickness of the Pb layers decreases, there is a monotonic decrease in the melting temperature and a broadening of the transition. There are three significant temperature suppressions which can be denoted and measured from the bulk Pb melting temperature on each of the DSC scans. The suppressions of the start of the transition (ΔT_s), the peak of the transition (ΔT_p), and the end of the transition (ΔT_e). Figure 4 shows the behavior of each of these three depression temperatures as a function of reciprocal Pb layer thickness. It would be expected based upon a macroscopic model using interfacial energy concepts for the depression in melting temperature, that the depression in melting would depend upon the surface-to-volume ratio, that is, be proportional to the reciprocal of film thickness. For the thinner Pb layers, it is apparent that no such behavior is observed.

The melting transition was also studied by high-temperature x-ray diffraction. For comparison against the bulk melting transition and to evaluate instrumental effects, a 1-μm Pb layer was deposited between two 1000-Å Ge films. The substrate was mica and the deposited film was 12-mm square. Figure 5 shows the peak intensity of the Pb (111) reflection as the sample is heated and cooled through the melting transition. The heating and cooling rates were 5°C/min. As the sample changed temperature, the diffractometer was periodically adjusted so as to keep the detector at

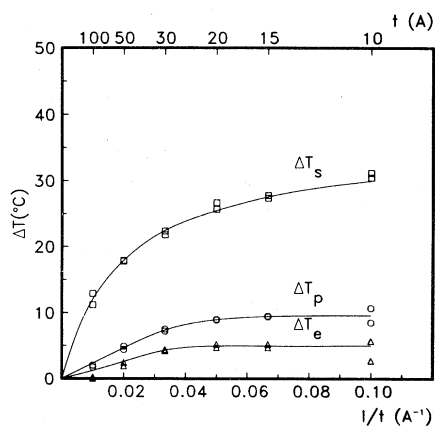


FIG. 4. Melting transition depressions of the start (ΔT_s), the peak (ΔT_p), and the end (ΔT_e) measured from the bulk Pb transition as a function of reciprocal layer thickness.

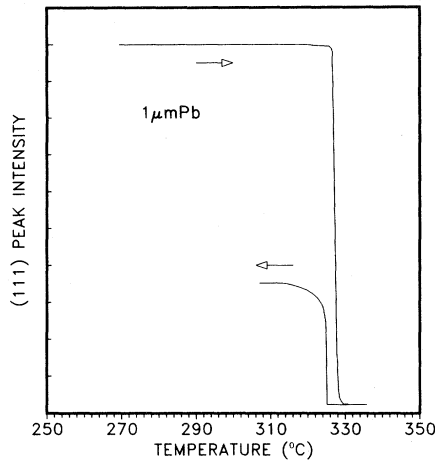


FIG. 5. Peak intensity of the (111) reflection for 1 μm of Pb between two 1000- \AA Ge films on heating and cooling through the bulk Pb melting transition.

the (111) peak position. There was a small shift to a lower Bragg angle due to the thermal expansion of Pb. As can be seen in Fig. 5, the melting transition is quite sharp and Debye-Waller effects are small. The hysteresis is small and the difference in temperature between the start of the melting and start of the solidifying transition is only about 1.5°C. Therefore, compared to the magnitude of the effects presented in this paper, the material and instrumental hysteresis effects are of no significance.

The modulated film studied by high-temperature x-ray diffraction consisted of 355 layers of Pb with a thickness of 20 \AA separated by 60- \AA layers of Ge. The as-deposited Pb layers had a very high degree of (111) texture. The intensity of the (111) to the (200) reflection was 50:1 (a random orientation would have an intensity ratio of 2:1). The x-ray beam irradiated only the center portion of the deposited foil. Consequently the edge effects of melting as manifested in the DSC experiments should not be evident. Figure 6 shows the continuous heating and cooling traces for the intensity of the (111) reflection as a function of temperature. The heating and cooling rates were 2°C/min. It was also observed that during the heating cycle, the Pb(111) peak sharpened in the same temperature range that the Ge transformed from the amorphous to microcrystalline state. The origin of this diffraction effect is presently being investigated.

There are three observations which can be made from the traces of Fig. 6: (1) The melting transition on heating and cooling again occurs over a broad transition region of temperature. (2) There

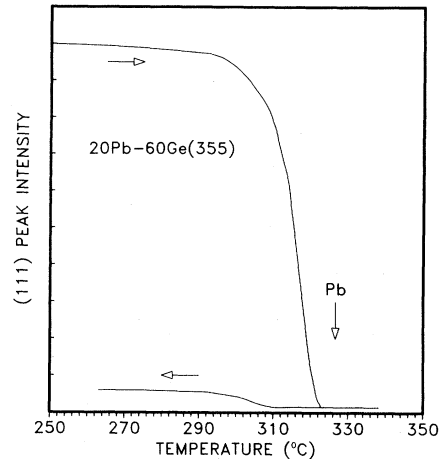


FIG. 6. Peak intensity of the (111) reflection for a modulated Pb-Ge foil on heating and cooling through the bulk Pb melting transition. The foil consists of 20- \AA Pb layer and 60- \AA Ge layer repeated 355 times.

is a large hysteresis, the order of 21°C, between the melting and solidification curves. As will be shown later, this is true only when the Pb is completely melted. (3) There is a large change in the intensity of the (111) reflection after melting. The Pb resolidifies with a random orientation. Examination of a melted and resolidified thin Pb layer between two layers of Ge by TEM shows that the confined Pb retains the layer morphology.

Rather than continuously varying the temperature, another sample was held at a fixed temperature in the transition region and isothermal scans of the (111) peak were made. Figure 7 shows the relative peak intensity of the (111) reflections as a

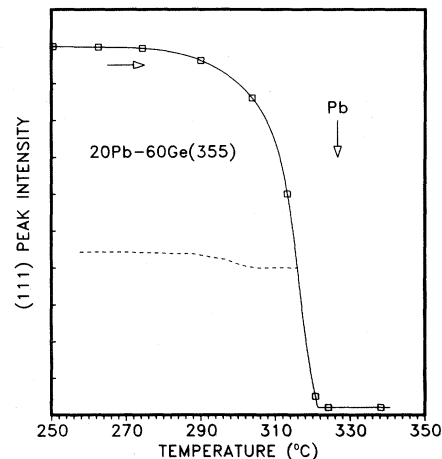


FIG. 7. Isothermal measurements of the (111) peak intensity as a function of temperature. The dashed curve indicates the expected behavior for partial melting and resolidification for an island morphology—see text.

function of temperature. The sample was held at temperatures 5–10 min before the scan was made. It was noted that the shape of the peak (full width at half maximum) did not significantly change through the melting transition and it was symmetrical about the maximum. Also as the intensity of the peak was decreasing, there was no evidence of an enhanced thermal diffuse peak appearing about the (111) reflection that might be associated with an excessive Debye-Waller factor. As can be seen from Fig. 7, the transition starts about 45°C below, and is complete about 5°C below, the bulk Pb melting point. The start of the transition as seen by the x-ray diffraction technique is lower than that as seen by the DSC technique, probably due to the lack of sensitivity of the latter technique for very small amounts of transformed material.

The depression in the melting temperature of thin Pb layers can be justified by several theoretical models, although the functional form, as previously noted, is a more complex question. At the present time it cannot be said definitely what the mechanism is for the broad melting transition as the sample approaches a 2D solid. However, several obvious causes can be eliminated. The three common external thermodynamic variables which can lead to a broad transition; varying composition, temperature gradients, and pressure gradients, are not responsible. Composition cannot be a factor since, as previously noted, the two components are practically insoluble in each other. The depression in the melting point of Pb, from the maximum quantity of Ge which can be dissolved in it, is 0.1°C.¹⁴ Temperature gradients cannot be a cause since they would have also been evident in the DSC and x-ray measurements of the melting transition of bulk Pb. Pressure or pressure gradients can also be eliminated as a cause by observing the position and shape of the (111) diffraction peak. The increase in the melting temperature of Pb with pressure is 6°C/kbar.¹⁷ For a 40°C melting transition breadth, the required pressure variation through the melting transition would be of the order of 7 kbar. The shift in diffraction angle (2θ) for this change in pressure (using the published value for the compressibility of Pb¹⁸ and the conditions of the x-ray diffraction experiment) would be of the order of 0.14° towards a higher angle. No such peak movement or peak distortion was observed. A peak movement of 0.03° would have easily been resolved and, as previously indicated, the peak was symmetrical and the peak shift, the order of 0.12° between 200°C and com-

plete melting, was toward a lower Bragg angle, consistent with thermal expansion of the Pb.

Another possible source of the broad transition might be attributed to the formation of isolated islands of Pb. Each island would melt a different temperature depending upon its size. This hypothesis can be experimentally tested. It has been previously shown that when the Pb was completely melted there was a large temperature hysteresis upon resolidifying and the crystalline phase loses the (111) texture upon resolidification and assumes a more random orientation. Consequently, if the sample consisted of isolated islands and is taken partially through the melting transition and then resolidified, a hysteresis and reduction of the intensity of the (111) reflection would be expected, i.e., as illustrated by the dashed curve in Fig. 7. To the contrary, thermal cycling up and down through the transition range showed reversibility, no hysteresis, and the intensity of the (111) reflection depended only upon temperature, as long as the Pb was not completely melted. This observation was made for the heating and cooling sequences, in terms of percentage transformed, of 2→5→2→10→2→60→10→2. The intensity of the (111) reflection was measured with the sample held at the fixed temperature corresponding to the percentage transformed. The fact that the intensity of the (111) reflection returned to the same premelted value would imply that Pb resolidified epitaxially onto the unmelted Pb. These x-ray results show that the Pb in the layers is continuous (at least over dimensions much greater than the thickness).

The variation of the Pb thickness within a layer can also be ruled out as a cause for the breadth of the transition under the assumption of a macroscopic first-order phase transition, where the interfacial energies make a significant contribution to the total free energy of the system, and the interfacial energies or the difference between the interfacial energies of liquid and solid Pb in contact with Ge are constant independent of the curvature or roughness of the interface. Since there is a depression in the melting temperature of Pb as the surface-to-volume ratio increases, the following condition must hold:

$$\sigma_s > \sigma_l + \sigma_{sl} ,$$

where σ_s and σ_l are the interfacial energies between Ge and solid and liquid Pb, respectively, and σ_{sl} is the interfacial energy of the liquid-solid Pb interface. Melting would be expected to be initiated at the interface in the region where the Pb film

has minimum thickness. This would be the location where the lowest fluctuations in the local free energy at the liquid would be expected to occur. The interface also serves as the source of defects or vibrational instabilities which have been proposed for melting. Once a stable liquid skin had formed at the interface, i.e., the nucleation barrier had been overcome, then it requires little or no additional driving force for the liquid-solid interface to move into the bulk of the Pb film from the interface. However, by simple analysis it is easy to verify that the driving force is even greater, with no impediments, to spread the liquid skin along the interfacial boundary. Consequently, once a portion of a stable liquid skin forms, the whole Pb layer must melt upon an infinitesimal increase in temperature under the previously listed assumptions.

The breadth of the transition cannot be rationalized on the basis of a statistical deviation of the layer of the individual Pb layers from the average layer thickness. For the 20-Å Pb film, experimental controls maintain the average thicknesses of the individual layers constant to a deviation of less than 2%. In this thickness range, the characteristics of the melting transition are insensitive to the average layer thickness as shown by the DSC measurements (Figs. 3 and 4). If the breadth of the transition was due to a distribution of layer thicknesses, then the distribution would have to be similar for the 20-, 15-, and 10-Å modulated foils, which is impossible if mass is to be conserved.

IV. CONCLUSIONS

The melting behavior of Pb in contact with Ge as the thickness of the Pb approaches a 2D solid has been investigated. The melting transition has been reduced significantly in temperature. This can be attributed to the interfacial contributions to the free energy of the system. Since there is a reduction in the melting temperature, the interfacial energy between the Ge and solid Pb must be greater than the sum of the two created interfaces, i.e., Ge and liquid Pb, and liquid and solid Pb. As the thickness of the Pb layers is reduced from 100 Å to 10 Å, the magnitude of the melting depression does not appear to follow the surface-to-volume ratio of the Pb, but tends to asymptoti-

cally approach a limiting value. Also, as the thickness of the Pb is reduced, the melting transitions broadens over a range of temperature. X-ray diffraction experiments on a 20-Å Pb layer thickness film indicates that the melting transition occurs over a 40°C temperature range. The transition has the attributes of a second-order phase transition, being continuous and reversible. It has been shown that the common external thermodynamic variables; composition, temperature gradients, and pressure gradients, are not contributing factors to broadening the transition. Additionally, the Pb layers are essentially continuous and the broad transition cannot be attributed to variable-size islands or layers of Pb independently melting. Under the assumptions of a classical macroscopic first-order phase transition with the difference in the interfacial energies between solid and liquid Pb against Ge independent of interface curvature, interface roughness, and Pb thickness, the transition must be sharp.

The explanation of the observation of a continuous reversible melting transition of Pb, in this modulated structure, as the thickness approaches a 2D solid is not definitive at this time. Possible explanations may be attributed to, the following mechanisms: (1) The transition is a second-order, dislocation-mediated transition as proposed by Halperin and Nelson. (2) The melting transition is an interface controlled phase transition where the proximity of the Ge is interacting with the liquid-solid interface of the Pb via an electronic oscillation making the transition appear as continuous. (3) Interfacial roughness and/or topography causes Pb to melt by a series of first-order phase transitions. Such a concept could only be accepted on the basis of a microscopic theory which would also have to explain the large breadth observed for the transition.

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