Observations of the Melting Transition in Thin Lead Films

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The first direct observation of the melting transition of a uniformly flat (20-Å-thick) Pb film, sandwiched between two amorphous Ge films, is reported. The transition was observed by transmission electron microscopy with dark-field imaging. The melting transition occurred over a broad temperature range, and was continuous and reversible. It is concluded that the transition proceeds by a disordering mechanism rather than the formation of a liquid-solid interface. The transition was not homogeneous but proceeded at a rate of disordering that was greater from the Pb-Pb grain boundaries than from the Pb-Ge interfacial region.

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Recently, it was reported[1] that the Pb melting transition was suppressed and broadened in modulated Pb/Ge foils as the thickness of the Pb approached a 2D solid. This was observed by x-ray diffraction and differential scanning calorimetry. The onset of melting was observed at temperatures well below the bulk melting temperature, T_m, of Pb. In addition, the melting transition was broadened over a 40° temperature range, with complete melting occurring at temperatures below T_m. For 20-Å-thick layers, the melting point depression was on the order of 45 °C. The breadth of the transition was 40 °C. The mechanism leading to the depression and broadening of the melting transition, which had all the characteristics of a higher-order phase transition, was not understood.

The thinness of the Pb layers makes this phenomenon amenable to study by hot-stage transmission electron microscopy (TEM). The melting transition is readily observable in the dark-field image as the intensity of a diffracting Pb grain is proportional to the square of the structure-factor amplitude. Observation of the transition in bright field was not feasible since diffraction is weak and variation in the image contrast through the transition was not observable. Additionally, in bright field as well as dark field only a fraction of the grains are observable (i.e., satisfy the Bragg condition).

Trilayers of Ge/Pb/Ge were prepared by evaporation as discussed in a previous paper.[1] The films were deposited on cleaved KCl single crystals at 77 K. After deposition the films were floated onto 200-mesh Cu grids and clamped between two fine-mesh Cu grids to ensure good temperature uniformity and to prevent buckling of the film. The films were studied on a hot stage in a transmission electron microscope (TEM Philips EM300). The hot stage consisted of a small circular resistively heated coil mounted in the specimen holder. The temperature was measured by a platinum–10% rhodium thermocouple embedded in the specimen mount. The measurement of the absolute temperature could not be determined by reading the thermocouple voltage with a high degree of confidence. The temperatures at which onset and completion of the melting transition occurred were variable from sample to sample. However, the breadth of the transition was consistently about 40 °C as noted by a diminishing intensity of the dark field and grains of Pb starting to shrink in size. Cooling the sample in the middle of the transition region resulted in an increasing intensity of the dark-field image with grains of Pb appearing to enlarge. This was observed for the faintest images that could be seen on the microscope screen. This variation in the start of the transition was an experimental artifact in which one of the contributing factors was the heat transfer between the specimen mount and thin film. However, the thermocouple readings could be used as a reliable indicator of relative temperature changes. Beam heating effects were observed to be minimal at the levels used for observation. This was confirmed by our observing no further melting upon slightly focusing the electron beam in the middle of the melting transition.

The melting behavior of the film was examined in dark field. In this mode, the beam is tilted so that only those grains which are diffracting to a selected area of the diffraction pattern will appear bright. Since the grain size of the Pb grains ranged from 25 to 250 Å, the dark-field image of a single grain could not be selected. The dark-field conditions were set to permit the simultaneous observation of many grains of Pb with crystallographic orientations of the (111) and (200) planes in the diffracting condition. The sample was equilibrated at each temperature for about half an hour. The beam was directed onto the film as seldom as possible to avoid contamination. During heating and cooling, the beam was turned off. By means of a reference mark on the film, an area could be quickly found and photographed.

Ambiguity of interpretation of the dark-field images can be a result of tilting of the specimen or repositioning of the objective aperture of the electron microscope after heating or cooling cycles. These factors would cause dark-field images of particular grains to disappear and

images of other grains to come into view as the diffracting conditions changed. Consequently, the dark-field exposure plates were checked to ensure that the vast majority of the grains stayed in view between thermal cycles.

The existence of Pb islands or nonuniform film thickness, which could affect the interpretation of the observations, was totally eliminated as a factor by examination of the films with micro-Rutherford scattering. This technique uses an annular detector to measure the intensity of the elastically scattered electrons at a set angle in a scanning electron microscope. The intensity of the elastically scattered electrons from any position in the scan is proportional to $\sum_i n_i Z_i^\alpha$, where n_i is the number of atoms of type i with atomic number Z_i in a cylinder of diameter defined by the lateral resolution of the microscope, and where $\alpha = 1$ or 2 corresponds to fully screened or bare atoms. Because Pb has a much higher atomic number than Ge, the fraction of the total scattered intensity due to the thin layer of Pb is significant. The scanning electron microscope has a lateral resolution of 20 Å and the total field of view is about 1 μm. For a structure composed of 20 Å of Pb sandwiched between two 100-Å layers of Ge, the fraction of the scattered intensity from the Pb would be between 16% and 33% depending on the value of α. A variation of one atomic layer of Pb would result in an intensity variation of between 2% and 5%. The observed variation of the intensity of the elastically scattered electrons is about 0.4% which indicated thickness variation of less than one atomic layer of Pb within the lateral resolution diameter of 20 Å over the total field of view.

Figures 1(a)–1(c) show dark-field photographs of a 20-Å-thick Pb film sandwiched between two 100-Å layers of amorphous Ge. The figures are a sequence of the same region of the film at room temperature, at about 50% ($\pm$20%) transformed and cooled back to room temperature. Although the figures show only a small region of the film, the observations which were made were characteristic over the complete film area and several different samples.

There were three main characteristics which were consistently observed. First, each grain melted over the same broad temperature transition range (approximately 40 °C) and the breadth of the melting transition was independent of grain size. Grains which differ in size by more than an order of magnitude melted over the same temperature range (see the grains labeled A). Second, the transition, as observed by the variation of intensity of the dark-field image, proceeded both from the grain boundary and the Ge interface. The rate of the transition is larger from the grain boundary than the Ge interface. Since the film is only 20 Å thick, the larger grains would have completely disappeared for equivalent horizontal and vertical transition rates. Apparently, the controlling factor on the rate of the transition is not the surface-to-volume ratio of a grain. Third, the grains approximately retained their shapes, including both positive and negative curvatures as the transition proceeded. This was a reversible effect with temperature (see the grains labeled B).

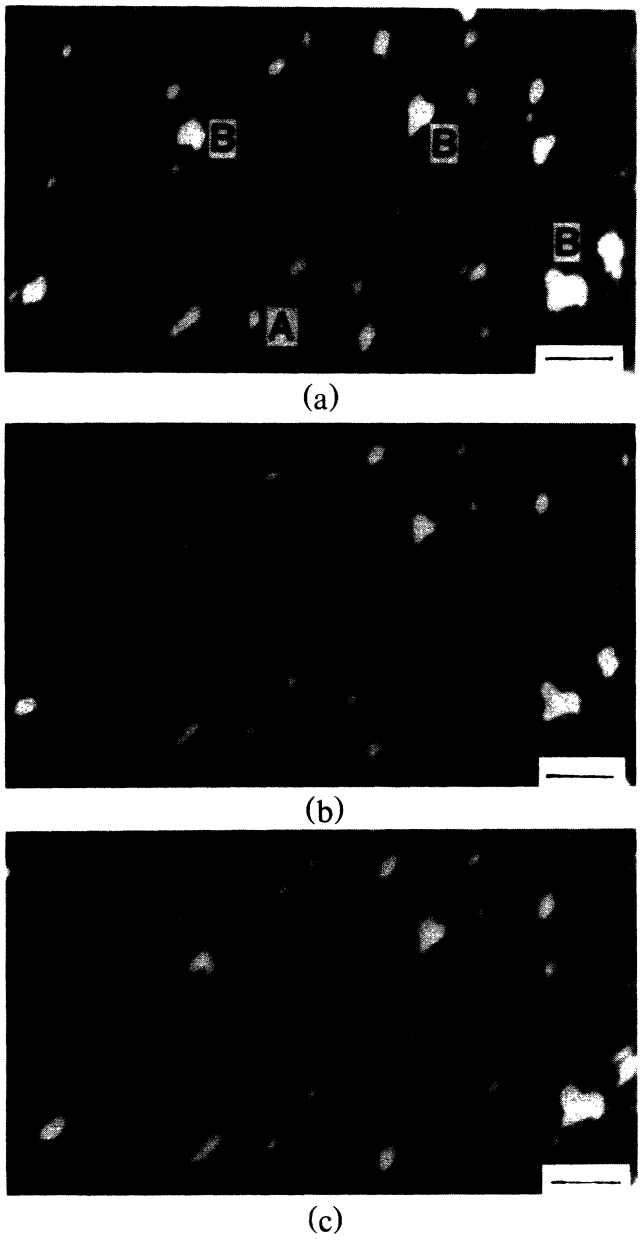

FIG. 1. Dark-field TEM showing a heating and cooling cycle of a 100-Å Ge/20-Å Pb/100-Å Ge sandwich. (a) and (c) Room temperature. (b) Halfway through the melting transition. The line marker corresponds to 300 Å.

Although many of the grains shown in Fig. 1(b) seem to have disappeared, faint images of them are still visible on close examination.

From the above observations it is apparent that the

melting transition is not a solid-to-liquid phase transition. If it were, small grains would have completely melted at temperatures below those for large grains and the grains would have melted to circular or polygonal shapes. Also, it is apparent that the observed disappearance of the image of the grain is not associated with normal Debye-Waller effects (see Ref. 1, Fig. 5). The existence of both positive and negative curvatures of the interfaces with reversibility cannot be reconciled with the interfacial energy considerations for a liquid-solid transition with an abrupt interface. A plausible explanation, consistent with the differential scanning calorimetry measurements of Ref. 1, is that the melting transition occurs over a broad range of temperature by a disordering mechanism. By the time the temperature reaches the Pb melting temperature, the latent heat of fusion has been consumed by the disordering process. Normally, an order-disorder transition would on the average occur uniformly throughout the volume of the material. In this case, the transition occurs at a greater rate from the region of the Pb-Pb grain boundary. Evidently that particular interface is elastically softer, permitting larger in-plane vibrations of the Pb atoms, or is a source of defects needed for generating the transition.

Continuous melting is not usually expected in three dimensions within the approximation of Landau theory. This is due to the existence of the third-order term in the expansion of the free energy in terms of the order parameter, which in turn leads to a latent heat. However, it has been shown[2,3] that a semi-infinite system, which has a first-order bulk transition, can exhibit a higher-order phase transition at the interface. This can be described as the growth of a layer of disordered phase, whose thickness grows logarithmically as the melting temperature is approached.

Kikuchi and Cahn[4] have calculated the melting of a two-dimensional lattice-gas model with a grain boundary by a cluster-variation method. They found that well below the melting point of the crystal a continuous structural transition to a low-density layer with liquidlike properties is formed near the center of the boundary and grows as the melting temperature is approached.

There have been recent experimental observations[5] in agreement with the description of the melting transition described in this paper. Rutherford backscattering experiments were made on a Pb single crystal. It was observed that a small amount of surface disordering occurred in the temperature range of 550–560 K. From 560–600 K the surface layers disordered totally (possibly to a liquid, the authors assert) with the thickness of the disordered layer increasing approximately logarithmically as Tm is approached. Their experimental technique cannot distinguish between a totally disordered solid or a liquid phase. However, the onset of disordering 40 °C below Tm is consistent with our previous[1] and current observations.

A broadened melting transition was observed in a thin (20-Å) continuous Pb film in dark-field transmission electron microscopy. The breadth of the transition was found to be the order of 40 °C. The transition was found to be continuous and reversible, and it had the characteristics of being a second-order transition. The majority of the diffracting grains in the dark-field image shrank in size upon heating and regrew to their approximate original shapes and sizes upon cooling. Both positive and negative curvatures of the grain shapes persisted after partial melting and regrowth. Taking into account the observations reported in Ref. 1, in particular the calorimetry and x-ray diffraction results, we conclude that the melting transition is probably an order-disorder transformation. Based on the assumption that the grain-boundary region is softer for in-plane atomic vibrations in comparison with the Ge interface, the disordering tends to start and grow at a greater rate from the grain boundary.

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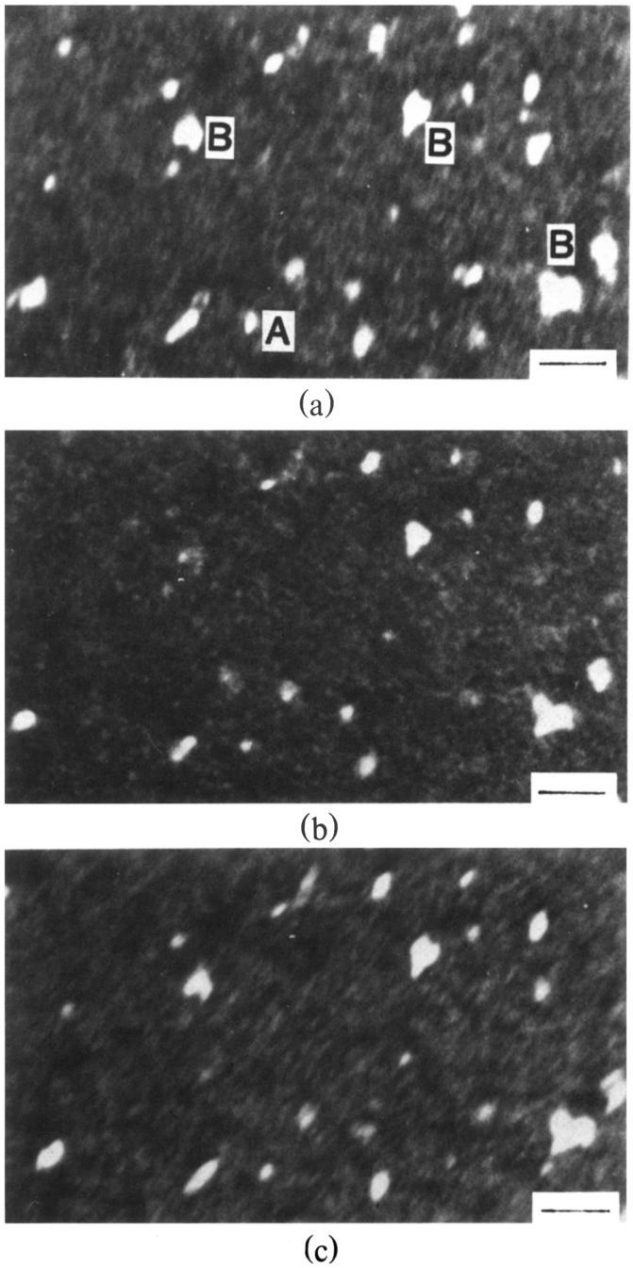

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