Superheating and melting kinetics of confined thin films

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Abstract

Pb thin films confined in Al were synthesized by means of repeated cold-rolling from stacked Al/Pb/Al sandwiches and magnetron sputtering deposition, respectively. The layer thickness of the confined Pb thin films was in a range of 6–27 nm. Differential scanning calorimetry (DSC) was used to systematically study the melting behavior of the confined Pb thin films. Above the equilibrium bulk melting point, a melting peak of superheated Pb was noticed in DSC traces. The degree of superheating increases with a decreasing film thickness and an increasing heating rate. The melting kinetics of the superheated Pb thin films is analyzed in terms of the lateral growth mechanism. The observed superheating of Pb thin films is attributed to the suppressed melt growth by the epitaxial Pb/Al interfacial configuration.

Keywords: Thin films; Superheating; Melting; Kinetics

1. Introduction

Nowadays solid thin films have found more and more technological applications in modern industries, their thermal stability has become one of the critical concerns for future development and applications of this new materials family. Normally, thin films exhibit different thermodynamic properties and lower thermal stability against phase transformation, relative to their bulk solid counterparts. For example, the melting point (m.p.) of thin films is lower than the equilibrium m.p. of bulk solid ($T_{m}^{e}$), and it decreases with a reduction of the film thickness, especially in the nanometer regime [1–5]. The depressed m.p. in thin films, as also observed in ultrafine particles [6–9] and confined materials [10], has become one of the major obstacles for further decreasing the film thickness in practical applications. Therefore, exploration of possible approaches to elevate the instability temperature of thin films is of great significance.

Elevating melting point of metal particles has been successfully realized in a number of systems [11–22] when the particles are coated by (or embedded in) some high-$T_{m}^{e}$ metals with epitaxial particle/matrix interfaces. It has been repeatedly emphasized that melting of a solid was initiated by melt nucleation at solid surface or interface that normally occurs below its $T_{m}^{e}$ [24,25]. Suppressed heterogeneous nucleation of melt at the epitaxial interfaces is supposed to be a key factor that controls the superheating of these particles. Therefore, in order to achieve substantial superheating, the metallic particles must be single crystals and bonded by epitaxial interfaces all around to eliminate possible melt nucleation sites at grain boundaries or free surfaces.

However, the approach to superheating metallic particles is not viable for the superheating of two dimensional (2-D) solid thin films. Even though the melt nucleation at both surfaces of a thin film might be suppressed by constructing with a specific material, grain boundaries in the polycrystalline thin films and the exposed film edges can not be avoided and they will provide sites for melt nucleation. It has always been observed that the melting of thin...
films occurs at a depressed m.p., relative to $T_m^e$, whereas the superheating phenomenon in the confined solid thin films has scarcely been reported.

Previously, it was found from in situ XRD experiments that 20 nm thick Pb thin films confined by Al layers with epitaxial Pb/Al interfaces can be superheated substantially (by 3–10 °C) [27]. Besides the solid structure revealed by the XRD technique, the endothermic process is also expected to be detected when the superheated Pb thin films melt. In this work, we used differential scanning calorimetry (DSC), which possesses a high sensitivity that enables an accurate measurement of heat flow for a very small amount of solid melting, to determine the melting kinetics of superheated Pb thin films. Relevant effects of film thickness and heating rate on the degree of superheating were also studied. The samples of Pb thin films confined in Al prepared by means of two different techniques, cold rolling and sputtering deposition, were systematically studied by using DSC. With these experimental results, melting kinetics of the superheated thin films is analyzed in terms of 2-D nucleation and lateral growth mechanism.

2. Experimental technique

2.1. Sample preparation

2.1.1. Sample A: Pb/Al thin films made by means of cold rolling from stacked Al/Pb/Al sandwiches

Al and Pb foils with a purity of 99.99% were alternately stacked to make an Al/Pb/Al sandwich. The sandwich was then repeatedly rolled and folded at ambient temperature until the nominal thickness of the Pb layers was reduced into the nanometer scale. At intervals, the as-rolled ribbon was annealed at 320 °C to eliminate work hardening. To release the strain and stabilize the Pb/Al interface, the as-rolled Pb/Al samples were finally annealed at 320 °C for 30 min.

The additive Pb/Al interfaces were processed in a way of simultaneous elongation of the Al/Pb/Al sandwich. This rolling process can produce fresh Pb/Al interfaces and avoid interfacial oxidation. The thickness of one Al/Pb/Al sandwich layer, as a whole, was 1/256 that of the as-rolled ribbon after eight times of folding and rolling. The nominal layer thickness of one Pb thin film layer in the sandwich can then be calculated by the thickness ratio of the initial foils. For instance, the thickness of an as-rolled ribbon is 12 μm, which was rolled from the Al/Pb/Al foil sandwich with layer thickness of 20/10/20 μm, respectively. Then a Pb layer with nominal thickness of 9 nm was obtained. By controlling the thickness of the as-rolled ribbon, samples A with different thicknesses of Pb layer were produced.

2.1.2. Sample B: modulated Pb/Al multilayers made by means of sputtering deposition

Pb/Al multilayer films were DC sputtering deposited at room temperature on a native oxide Si(100) surface. The chamber was evacuated to 1 × 10⁻⁶ torr prior to deposition and the atmosphere was purified Ar gas during sputtering. The purity of both Al and Pb targets was 99.99%. The deposition rates of 0.5 nm/s for Al and 3 nm/s for Pb were determined by the relationship between the employed deposition power and the film thickness with a relative error within 5%. Because the sputtering was under the same condition, the deposition time control resulted in a definite layer thickness. Modulated multilayer [Al(20 nm)/Pb(y nm)], were deposited, where y denotes the film thickness of Pb layer in nanometer. The period value n adopted for each sample was determined by $y \times n \approx 1000$.

2.2. Microstructure and film thickness characterization

X-ray diffraction (XRD) analysis on a Rigaku D/Max 2400 X-ray diffractometer operated at 150 mA, 50 kV with Cu Kα radiation was employed to characterize the structure of both types of samples. Transmission electron microscopy (TEM) on the JEM-2010 with an accelerating voltage of 200 kV was used to observe the morphology of Pb films in sample A with a planar-view and a cross-sectional view. The thickness examination of the Pb layer was performed by scanning electron microscopy (SEM) once the focused ion beam (FIB) cross-sectional cutting finished. Such processes were carried out on a FEI Nova 2000 Nanolab system equipped with electron and ion beams. The energy dispersive X-ray spectrometer (EDS) accessory from EDAX on the system was used for composition analysis.

2.3. Thermal analysis of melting of Pb thin films

The melting behavior of the Pb thin films was investigated in a Perkin-Elmer Pyris 1 differential scanning calorimeter in a purified flowing Ar atmosphere. The temperature of the DSC was calibrated within an accuracy of 0.1 °C by using standard pure Zn and In samples. The accuracy of heat flow measurement is about 0.01 mW. The melting point of the solid Pb that we used was measured to be 327.5 °C. Both types of samples were cut into pieces 4 mm × 5 mm in size and sealed in aluminum pans. The employed heating rates were 10 and 20 °C/min.

3. Results

3.1. Microstructure

Fig. 1 shows the typical XRD profiles of the as-rolled Pb/Al sample A and as-sputtered sample B. The diffraction peaks of Pb and Al are clearly visible for both samples. The lattice constants of Pb and Al determined from quantitative XRD analysis are consistent with the tabulated data, indicating no solid solution is formed between two elements during cold rolling or sputtering. Note that there is a (111) growth texture in sample B by comparing the relative peak intensities of (111) to (200) or (220) for Pb diffraction.
As indicated in our previous papers [27, 28], from the TEM planar-view observations, Pb films are fragmentary rather than continuous layers throughout the rolled strip, as shown in Fig. 2(a). The size of Pb fragments range from about a few tens of nanometers to a few microns. For a small portion (less than 10%) of Pb thin films confined in the Al, cubic–cubic orientation relationships between Pb and Al were identified [27, 28], for example Pb[011]/\ Al[011] and Pb[111]/\ Al[111], which was determined from selected area electron diffraction (SAED) pattern of the planar-view image, as shown in Fig. 2(b). A TEM cross-section observation for the sample A with 22 nm Pb layers, as indicated in Fig. 2(c), confirmed that the Al/Pb/Al sandwich was evenly deformed and the observed thickness of Pb thin films is comparable to the calculated nominal thickness within an error of 10%.

Fig. 3 illustrates the laminar structure of the Pb/Al multilayer in sample B with 27 nm Pb layers. The light colored droplet like structures within Pb layers increased in dimension as a result of the electron beam irradiation during SEM observation. The film thickness of Pb layers is consistent

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with the calculated value in terms of the deposition rate and duration.

3.2. Melting of the confined Pb thin films in Al

Fig. 4 shows typical DSC traces of the confined Pb thin film melting of sample A. The DSC trace labeled (1) represents the first heating run from room temperature to 400 °C. Two obvious endothermic peaks are clearly seen: a major peak (P1) around 327 °C, very close to the bulk equilibrium m.p. \( T_e^m = 327.5 \) °C of Pb, and a small one (P2) at 380 °C, about 53 K above \( T_e^m \).

In order to uncover the origin of peak P2, repeated cooling and heating runs were conducted. In the subsequent three heating runs (labeled 2, 3, 4) after repeatedly cooling down to 327 °C (below \( T_e^m \)) and holding for 1 min, the endothermic peak appears at almost the same temperature and with the same enthalpy change (the integral of the endothermic peak). It is clear that the second endothermic peak P2 above \( T_e^m \) is reproducible (or reversible). Obviously, the endothermic peak P1 in the first heating run corresponds to the melting of most Pb films in the sample, of which the melting temperature is close to the bulk \( T_e^m \) of Pb, while peak P2 results from melting of a very small portion of Pb films that exhibits a substantial superheating.

In Fig. 4, one can find also that peak P2 in the second heating (labeled 2) appears at 375.0 °C, relative to 380.5 °C in the first heating run. This may be attributed to a small thickness increase due to the congregation of the Pb liquid between the Al walls, because the increment of the peak height or the peak area implies an increased volume of the superheated Pb solid. The thickness of the superheated Pb films was stabilized afterward and the melting point kept constant in the subsequent heating runs as shown in traces 3 and 4. The effect of thickness on superheating will be discussed in the following subsection.

In sample B series, DSC traces of Pb thin films melting also have two endothermic peaks, as shown in Fig. 5, similar to those in sample A. The major endothermic peaks P1 in both DSC traces, with a peak temperature (\( T_{p1} \)) at 327.6 °C, correspond to the melting of most Pb thin films with random interfacial structure. Above the equilibrium melting point of Pb, there is another endothermic peak...
P2 with a smaller enthalpy change. It is evident that the confined solid Pb thin films in superheated state exist in both types of samples.

In addition, the enthalpy changes for melting of the confined Pb thin film can be figured out by integrating the DSC endothermic peaks. For samples A, in Fig. 5(a), the enthalpy changes of P2 are about 5% that of the corresponding P1 on the same trace. For samples B, in Fig. 5(b), the ratios are about 10%. It follows that the portion of the superheating Pb thin films in samples A is smaller than that in samples B. This was expected, because as shown in the XRD analysis, the deposition and growth processes favor the formation of a (111) texture. Such a texture with the lowest surface or interfacial energy may increase the possibility of the deposited Pb layer to pose epitaxially with the deposited Al layers. As a result, the portion of qualified Pb thin films for superheating is increased.

3.3. Effects of film thickness and heating rate

The effects of film thickness and heating rate on the melting kinetics of the superheated Pb films were examined by means of a series of samples with different nominal Pb film thicknesses (9–27 nm for sample A and 6–18 nm for sample B). Fig. 5 shows the DSC traces of the two sample series. It was observed that with an increase of film thickness the first melting peak shows no change in its position, while the second one shifts to lower temperatures. The shape of the second peak seems not to be varied with different thicknesses and at different heating rates.

Fig. 6 displays the dependence of $T_{P2}$ on Pb film thickness at two different heating rates for both sample series. A clear increasing trend is seen for the degree of superheating ($T_{P2} - T_{m}$) with a reduction of film thickness. A maximum superheating was observed to be about 60 K for sample A with 9 nm Pb layers, and 80 K for sample B with 6 nm Pb layers. As the heating rate increases from 10 to 20 K/min, $T_{P2}$ is enhanced by about 5 ± 3 K for both samples.

4. Discussions

4.1. Interfacial condition for the superheating of a confined thin film

A liquid bonding to a solid wall may leave two or three atomic layers of ordered structure neighboring to the wall due to the surface freezing effect [25,26]. But for the case of Pb thin films confined in Al, the absorbed latent heat in the melting of such superheated atomic layers was estimated to be below the detectable heat flow in the calorimeter that we used. On the other hand, the epitaxially oriented interfaces between the embedded nanoparticles and the matrix as a key were often emphasized to contribute to the observed superheating of the particles [12,14,19], because the ordered interface may suppress the melt nucleation. However, in the case of confined thin films, the liquid emerges due to either the melt nucleation at film grain boundaries and film edges or the interface melting at randomly oriented interfaces between the film and the matrix. Therefore, the epitaxy interfaces must work in a different way for the superheating of the confined thin films from that of the embedded nanoparticles.

We suppose that the curvature of existing solid/liquid interface varies with the film/matrix configurations. Taking the Pb/Al system for instance, when the Pb/Al interface is epitaxially oriented, in terms of the balance condition of interfacial tensions as shown in Fig. 7(a), an interfacial energy relation of $\gamma_{Pb(l)/Al} < \gamma_{Pb(s)/Al}$ and a contact angle $\theta < \pi/2$ are obtained. Similar configuration was indeed
observed in In particles embedded in an Al matrix under high resolution TEM [23]. In contrast, when the interface is randomly oriented, the configuration of solid/liquid interface is as depicted in Fig. 7(b), where \( \gamma_{Pb(l)/Al} > \gamma_{Pb(s)/Al} \) and \( \theta > \pi/2 \).

The driving forces for the advancement of the melt front are different in these two cases. For epitaxially oriented interface, a positive \( \Delta \gamma \), in the case of randomly oriented interface, assists the melting to take place. In fact, preferential interface melting or melt nucleation can occur at the randomly oriented Pb/Al interfaces before reaching the balance configuration. The first endothermic peak in the DSC traces confirms the premelting process in the melting of the confined Pb thin films, of which the start temperature \( T_s \) (which defined as the temperature of the DSC trace where \( \gamma_{Pb(l)/Al} \)) is lower than \( T^c_m \). Some Pb melting induced by few oxide interfaces may also be included in the first melting peak, that is caused also by the interface melting. A similar explanation for the case of random interface can account for it.

In short, the pinning at the three phase line is responsible for the superheating, that is opposed to the superheating of thin interfacial atomic layers adjacent to solid matrix or the superheating as a result of the suppression of melt heterogeneous nucleation at epitaxial interface. But it is still an essential condition to obtain such a Pb thin film constrained epitaxially with Al that the superheating of Pb thin film can be achieved.

Melting temperature changes resulting from additional interfacial energy can be estimated in the frame work of thermodynamics. By including an interfacial energy term, the Gibbs free energy change of a melting transition for the confined thin film can then be given by

\[
\Delta G = \Delta G_v + \Delta \gamma
\]

where \( \Delta G_v \) and \( \Delta \gamma \) represent the free energy change for unit volume and interface per unit area, respectively. By assuming an unit volume with a definite thickness \( \lambda \) undergone solid–liquid transition, the change of melting point \( \Delta T \) can be obtained when \( \Delta G = 0 \),

\[
\Delta T = \frac{2T^c_m \gamma_{Al} \cos^2 \theta}{\lambda \Delta H_m (\pi/2 - \theta)}
\]

where \( \Delta H_m \) denotes the melting enthalpy. It turns out the algebra sign of \( \Delta T \) depends on the contact angle, \( \Delta T > 0 \) with \( \theta < \pi/2 \) implying a substantial superheating, otherwise \( \Delta T < 0 \) with \( \theta > \pi/2 \), implying a depressed melting temperature. This is consistent with preceding discussions.

4.2. Melting mechanism of the superheated thin film in a confined geometry

While the superheating temperature increases with a decreasing film thickness as predicted by the thermodynamic equation, the heating rate effect on the peak temperature may originate from kinetic difficulties. The superheating of embedded Pb nanoparticles was attributed to a heterogeneous nucleation difficulty at the ordered interface between the Pb particles and the Al matrix [14]. However, this interpretation is no longer pronounced in the case of the superheated Pb thin film, because the confined thin films have solid/liquid interfaces ready for melt growth. So the advancement of melt front must be under consideration instead of melt nucleation.

The growth kinetics of bulk Pb melt follows the well known Wilson–Frenkel (WF) normal growth law with a rate linear to a small superheating \( \Delta T \). It implies a continuous endothermic process while the temperature rises from \( T^c_m \) to \( T^v_m + \Delta T \). One endothermic peak of melting of the pure Pb sheet was always observed with an onset temperature of \( T^c_m \) in the DSC trace [29]. However, we found an isolated endothermic melting peak other than the normal one at a temperature much higher than \( T^c_m \). That refers to different growth kinetics from the normal growth.

Based on a proposed criteria [31,34], the lateral growth mechanism instead of the normal growth will be found when any area in the solid/liquid interface can reach a metastable equilibrium configuration in the presence of a driving force. It can also be applied to the specific case for the melting of confined thin films. As the film thickness decreased to nanometer scale, a metastable state of the
superheated solid film can meet due to the interfacial resistance induced by epitaxy configuration. In consequence, the melt front cannot be advanced unless new steps can nucleate from thermal fluctuations. Such a lateral growth kinetics predicts a sudden increment of growth rate at a certain superheating temperature, that accounts for the steep left side of the endothermic peak in the inset of Fig. 4.

To describe quantitatively the melting of the superheated thin film in the confined geometry, estimation is then performed in term of the classical kinetics of the lateral growth [30,34]. A new step nucleation is considered in the solid/liquid interface area, namely two-dimensional (2-D) nucleation. To form a nucleus, assuming a pillbox in a cylinder shape with a radius \( r \) and one interplanar distance height \( a \), then the Gibbs free energy change is

\[
\Delta G = 2\pi a \gamma_{sl} - \pi r^2 a (\Delta G_m) / V_s - K \Delta E_s
\]

(3)

where \( \gamma_{sl} \) denotes the solid/liquid interface energy, \( \Delta G_m \) is molar free energy change from solid to liquid, \( V_s \) is molar volume, \( \Delta E_s \) is strain energy density change per unit volume induced by the volume change in melting [32] and the mismatch between film and matrix [33]. The strain energy density change of 2-D nucleation at the solid/liquid interface is only a portion of that of the homogeneous nucleation, so a coefficient \( K \) has to be introduced with a value less than 1. From \( \partial \Delta G / \partial r = 0 \) and \( G_m = \Delta H_m \Delta T / T_m^2 \), a relationship between the critical radius \( r^* \) and superheating temperature \( \Delta T \) is given by

\[
r^*_{2D} = \frac{\gamma_{sl} T_m^2 V_s}{\Delta H_m \Delta T - T_m^2 V_s K \Delta E_s}
\]

(4)

As the superheating temperature increasing, the critical radius of 2-D nucleus is decreasing. Only if \( 2r^* \) was smaller than the film thickness, 2-D nucleation might occur. Thus a thinner film will result in a higher thermal stability against melting when the film is well confined.

\( \Delta G^* \) is the critical energy to form a 2-D nucleus, which can be obtained by substituting Eq. (4) into (3).

\[
\Delta G^*_m = \frac{\pi a \gamma_{sl}^2 T_m^2 V_s}{\Delta H_m \Delta T - T_m^2 V_s K \Delta E_s}
\]

(5)

The calculated critical energy of the 2-D nucleation is two orders of magnitude lower than that of the homogeneous nucleation and at least one order of magnitude lower than that of the heterogeneous nucleation with a reasonable contact angle of 30°. That is to say, the 2-D nucleation has the lowest energy barrier for the transition. Consequently, instead of the liquid homogeneous nucleation inside the Pb solid thin films or heterogeneous nucleation at the Pb/Al interface, the Pb melts prefer to 2-D nucleate at reserved solid/liquid interfaces and then grow into the solid film.

By taking \( \gamma_{sl} = 0.05 \text{J/m}^2 \), \( \Delta H_m = 4.8 \text{kJ/mol} \), \( V_s = 1.93 \times 10^{-5} \text{m}^3/\text{mol} \) and \( \Delta E_s = 1.2 \times 10^7 \text{J/m}^3 \) into Eq. (4), the degree of superheating varied with the film thickness \( 2(r^*_{2D}) \) is plotted in Fig. 8, which also includes the degree of superheating versus Pb film thickness from the experiments and the theoretical prediction plots of the 2-D nucleation and thermodynamics.

The experimental data scatter between the curves \( K = 1 \) and \( K = 0 \), indicating the maximum and minimum effect of the strain energy change on the superheating, respectively.

Note that the apparent degree of superheating is related to the heating rate as well, thus the heating rate effect on the degree of superheating has to be evaluated. Because the possible nucleation area is so small in confined thin films, it is assumed that each 2-D nucleation event might result in the formation of a new layer of a growth interface, namely the mononuclear growth proposed by Howe [30]. The velocity of advancement of the confined Pb melt front \( v_{2D} \) can simply be written as

\[
v_{2D} = K_m \left( \frac{\Delta T}{T} \right) \exp \left( \frac{-\pi a \gamma_{sl}^2 T_m^2 V_s}{kT(\Delta H_m \Delta T - T_m^2 V_s K \Delta E_s)} \right)
\]

(6)

Fig. 9. An estimated advancement of the Pb melt front with superheating temperature and time predicted by the mononuclear growth rate. The crosses with the heating rates indicate the apparent melting temperature.
where $K_m \approx 1.2 \times 10^{13}$ nm/s is the coefficient determined by the physical parameters of Pb, such as latent heat, self-diffusion coefficient at the solid/liquid interface and the active energy for 2-D nucleation etc. The advancement of the Pb melt front with elapsed time can be calculated from Eq. (6), as demonstrated with the curves labeled 1 nm and 100 nm in Fig. 9. For a transition controlled by such a 2-D nucleation and later growth process, the apparent melting temperatures will shift to a higher temperature with an incremental heating rate. For instance, the apparent melting point elevates by about 2 K when the heating rate increases from 10 K/min to 20 K/min, which is comparable with the DSC measurement results (5 ± 3 K). The plot of Fig. 9 indicates a much higher apparent melting point when applying an ultra fast heating ($10^{12}$ K/s) to an identical system.

5. Conclusions

(1) Samples of nanometer thick Pb films confined by Al layers were synthesized by means of repeated cold rolling and magnetron sputtering deposition, respectively. An evident endothermic melting peak in the DSC traces well above the equilibrium melting point was observed, which corresponds to melting of superheated Pb thin films.

(2) With a decrease in the Pb film thickness, the degree of superheating increases. When the Pb film thickness is as smaller as ~6 nm, the degree of superheating reaches about 80 K.

(3) The melting temperature of the superheated Pb thin films increases at higher heating rates.

(4) The melting kinetics of the superheated thin films are analyzed in terms of 2-D nucleation and lateral growth mechanism. The advancement of Pb solid/liquid interface can be suppressed when the surfaces of Pb thin films bond epitaxially with Al layers.

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