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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

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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 $[Al(20\ nm)/Pb(y\ nm)]_n$ 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.