

Melting behavior of as-deposited and recrystallized indium nanocrystals

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Abstract

Melting behavior of as-deposited and recrystallized indium nanocrystals is studied using reflection high-energy electron diffraction in its transmission mode. Indium films with mean thickness ranging from 1.5 to 10 monolayers (ML) deposited on highly oriented graphite at different substrate temperatures are studied. Atomic force microscopy is used to study the crystal size and morphology of the as-deposited and recrystallized nanocrystals. As-deposited films are found to form shallow nanocrystals with a flat top surface of different shapes, while the recrystallized nanocrystals are formed in the more rounded polyhedral shape. The change in the diffraction pattern intensity with temperature is used to probe the melting of the nanocrystals. The melting point is found to be lower than that of the bulk for both types of films and extends over a temperature range due to nanocrystal size distribution. The as-deposited films show an end melting point nearly equal to that of the recrystallized films except for the 1.5-ML film which shows an end melting point ~ 10 K lower than the recrystallized film. The deposition temperature is found to have a significant effect on the end melting point of as-deposited nanocrystals, while having a negligible effect on the end melting point of recrystallized nanocrystals.

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1. Introduction

The study of melting of metallic nanocrystals is of interest to fundamental understanding of the effect of reduced size and crystal shape on the melting phase transition [1–3]. The melting of nanocrystals that are free-standing, deposited on an inert substrate, embedded in a host matrix, or coated with a higher melting material have been theoretically and experimentally studied [1–14]. These nanocrystals showed structural as well as thermodynamical properties that are different from that of their own bulk materials. Some nanocrystals that are free standing or deposited on an inert substrate showed size-dependent melting point depression, in quantitative agreement with phenomenological thermodynamic models [2,5–7]. However, in other cases considerable superheating of some nanocrystals above the

equilibrium bulk melting point was observed [1,3,8,9]. Embedded or coated nanocrystals have also shown a size-dependent melting point depression, in some cases, as well as several degrees superheating in others [10–14].

The nanocrystal shape and external surface morphology determine its melting and solidification behavior. In addition, the nature of the nanocrystal interface with the host material or with the substrate affects its melting and solidification behavior [12,15]. Recrystallized nanocrystals can have shapes and external surface morphologies that differ from the as-deposited nanocrystals, and hence, the melting and solidification behaviors can differ between the two types [16,17]. Dark field electron microscopy was used to investigate the melting of bismuth crystallites in as-deposited and recrystallized bismuth films on a carbon substrate [8]. As-deposited films were found to have crystallites that are different in shape and in melting behavior from those recrystallized after melting. While a subset of the as-deposited crystallites, with elongated platelet shape, superheated by 7 K above the equilibrium bulk melting point, the

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recrystallized polyhedral hexagonal shaped nanocrystals in the as-deposited film showed melting point depression. Using the same technique to study the melting of lead nanocrystals, superheating by 2 K was found for extensively {111} faceted platelet-shaped nanocrystals formed in the as-deposited films. Lead nanocrystals with other shapes melted below the bulk melting point [9]. Indeed, nonequilibrium faceted nanocrystals have greater specific surface energy than equilibrium faceted ones and hence melt first [18]. Nanocrystals bounded by external facets with minimum energy surfaces are able to superheat above the bulk equilibrium melting point. By recrystallizing a 100-nm average thickness lead film previously deposited on a graphite substrate at room temperature, Métois and Heyraud were able to prepare some nanocrystals bounded by minimum energy facets with sharp edges that were able to superheat by ~ 3 K [19]. Using reflection high-energy electron diffraction, as-deposited lead films, grown on graphite at room temperature, showed superheating of up to 12 ± 2 K [20]. The observed superheating was attributed to the presence of two-dimensional (2D) {111}-oriented layers in the as-deposited film, while recrystallized films had the form of three-dimensional (3D) crystallites. When measuring the melting point and latent heat of fusion of 0.05–0.5 nm in radius tin particles using a nanocalorimetric technique, both were found to increase with the particle size. Also, the values obtained from the second heating cycle, recrystallized sample, were slightly higher than those obtained from the first heating cycle [21].

A change in the melting point upon recrystallization of embedded nanocrystals was also previously observed. An X-ray diffraction study of lead crystallites embedded in aluminum showed substantial superheating whose value depended on the heating cycle and on the inclusion size [22]. Due to annealing in previous heating cycles and possible coalescence, superheating found in the second cycle was lesser than that found in the first cycle.

The relatively low melting point of indium and its very low partial vapor pressure near its melting point, facilitate the melting studies of indium nanocrystals [5,23–26]. We recently reported on melting and solidification of indium nanocrystals recrystallized from the melt using in situ reflection high-energy electron diffraction (RHEED) [23]. The melting behavior was found to be dependent on the size distribution of the nanocrystals. Previous work did not compare the melting behavior of as-deposited with recrystallized indium nanocrystals. In the present work, we extend our previous study to include this comparison. The nanocrystal size and morphology is studied using ex situ atomic force microscopy (AFM). The effect of the nanocrystal shape and size on their melting behavior is studied.

2. Experiment method

Indium films of mean thickness ranging from 1.5 to 10 monolayers (ML) were deposited on highly oriented

(0002) graphite substrate in an ultrahigh vacuum chamber. The interaction between the deposited indium and the graphite substrate is known to be of the Van der Waals type, with no chemical reaction or inter-diffusion of indium in the graphite [23,27]. The film mean thickness is obtained by means of a quartz crystal thickness monitor, placed as close as possible to the substrate. The spacing between each deposited ML is taken to be the indium–indium bond length. Description of the setup and experimental methodology was discussed previously [23]. After deposition, the recrystallized films were heated to a temperature above the bulk melting point and slowly cooled down to a temperature below its supercooling temperature. The equilibrium polyherdal shaped indium nanocrystals were then formed for the recrystallized films, while the as-deposited nanocrystals grew in shapes that are dependent on the preparation conditions such as deposition rate and substrate temperature. The deposition rate was maintained almost constant, 0.04 – 0.07 nm s⁻¹, while a set of samples with different thicknesses were prepared at three different temperatures; 298, 348, and 398 K. RHEED patterns, obtained at room temperature, were used to characterize the grown indium nanocrystals. An ex situ AFM is used to study the surface morphologies and size distributions of as-deposited and recrystallized indium nanocrystals. The lateral and height resolutions of the AFM used are 1 nm and <0.1 nm, respectively, as specified by the manufacturer. Our lateral resolution, however, is limited by the end-tip diameter, which was less than 10 nm. The normalized intensity change of the RHEED (00) spot as a function of temperature is used to monitor the melting and solidification of the as-deposited and recrystallized indium nanocrystals. A K-type thermocouple, calibrated with an accuracy of ± 1 K and placed on the top of the substrate in contact with the indium film was used to measure the temperature. The measurements were conducted by raising the sample temperature from room temperature to 450 K in ~ 10 min, and then the heating stage power was turned off letting the sample cool down to near room temperature in ~ 30 min. The RHEED patterns were recorder during heating and cooling. Each RHEED pattern was acquired in ~ 0.17 s, thus, temperature changes during the acquisition were negligible.

3. Results and discussion

Independent of the deposition temperature and film thickness, indium gives a diffraction pattern that is characteristic of a transmission–reflection RHEED pattern with either the $<010>$ or $<100>$ indium tetragonal directions parallel to the $<001>$ graphite direction. Within the experimental uncertainty, no relative shift in position could be noticed in the RHEED spots between the as-deposited and recrystallized samples, indicating no change in the average unit cell. The pattern remains observable at all

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