Determination of Pb Equilibrium Shapes and Surface Melting Behavior by Coherent X-ray Diffraction

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Introduction

The shape of a crystal held in equilibrium with its vapor is determined by minimizing its total surface free energy. Because the free energy has a strong directional dependence, the equilibrium crystal shape, when it is far from melting, is typically dominated by certain low index facets that have the lowest energy per unit area. In fcc materials these tend to be the {111} and {100} planes [1-3]. As the temperature is increased, entropic effects reduce the area of the facets and increase the area of the rounded regions between them, leading to spherical shapes near melting. If the exact equilibrium shapes of a given material were known over a range of temperatures, the surface free energies of all crystallographic directions would be known for that material [4].

Of equal interest is the method by which crystals melt. It has been proposed that within a few degrees of melting, a liquid film develops on certain surfaces, but not the surfaces that correspond to the lowest surface energies. This proposition has mostly been based on results from ion channeling experiments [5]. It is possible that these observations were a result of increased vibration of the atoms near the surface of the crystal — a sort of surface enhanced Debye-Waller factor.

Both of these phenomena are ideally suited for study by means of coherent x-ray diffraction (CXD) [6, 7]. The shapes of nano- and microcrystals can be accurately determined by using this method. Because it is a diffraction-based method, it is sensitive to the crystallinity of a sample. Therefore, a liquid layer would not contribute to the diffraction pattern, while a volume of crystalline material with strong vibrations would diffract as if it had a decreased density.

Methods and Materials

These experiments were carried out in the CXD experimental station at UNI-CAT beamline 34-ID at the APS. A Pb film was vapor deposited *in vacuo* on a Si wafer with its oxide intact to minimize the Pb-substrate interaction. A vacuum of 3×10^{-9} Torr was maintained throughout the experiment. After deposition, the film was raised to the melting point of Pb (323°C) by using direct heating through the substrate. Upon heating, the Pb film broke up into randomly oriented balls with a range of sizes from tens of nanometers to a micrometer, as shown in Fig. 1.

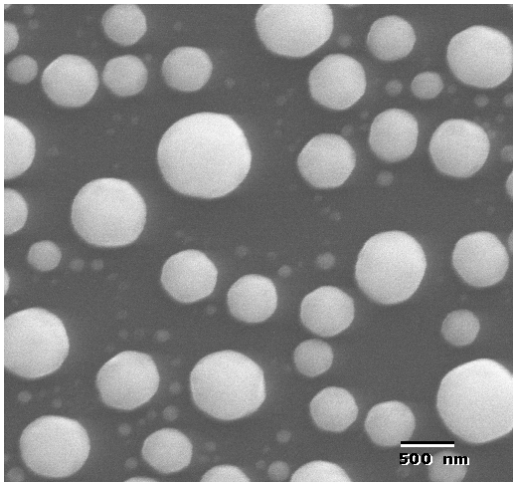

FIG. 1. Scanning electron microscope (SEM) image of Pb crystals on Si/SiO_2 substrate taken after about 24 hours of exposure to the atmosphere. The grains measured in this experiment were between 0.5 and 1.0 μm.

Roller blade slits were typically close to 10 μm^2 so that a small number of grains were illuminated. The {111} powder ring was thus sparsely populated, and a CXD pattern could be measured for a single grain. X-rays at 8.9 keV were used in order to coincide with the maximum efficiency of the Roper Scientific direct-reading charge-coupled device (CCD). A 2-D diffraction pattern could then be measured about a {111} peak. A 3-D diffraction pattern, as shown in Fig. 2, was composed by rocking the sample theta in 0.01° steps and taking a series of 2-D patterns. This process was repeated over a range of temperatures near the melting point of Pb.

Results and Discussion

The diffraction pattern shown in Fig. 2, taken within 1° of melting, includes a central maximum, rings corresponding to the Fourier transform of a sphere, and flares arising from the facets of the crystal. By using iterative phase retrieval algorithms, a real space function corresponding to the diffracting density could be recovered. The most recent example is shown in Fig 3. The reconstruction shows numerous facets in addition to rounded regions. The reconstruction of 3-D diffraction

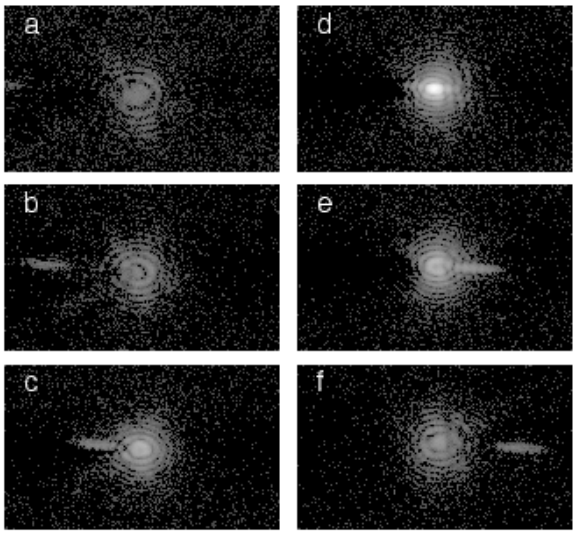

FIG. 2. Every fourth slice through a 3-D CXD pattern. These slices show less than half the range of q-space measured.

patterns taken at other temperatures is still necessary before melting models can be analyzed.

Acknowledgments

We would like to thank H. Hong and C. Benson of the UNI-CAT staff for their valuable assistance. UNI-CAT is supported by the U.S. Department of Energy (DOE) under Award No. DEFG02-91ER45439. It is supported by the Materials Research Laboratory at UIUC (DOE; State of Illinois Board of Higher Education, Higher Education Cooperation Act; and National Science Foundation); Oak Ridge National Laboratory (DOE under Contract No. DE-AC05-00OR22725 with UT-Battelle, LLC); National Institute of Standards and Technology (U.S. Department of Commerce); and UOP LLC. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No W-31-109-ENG-38. The SEM measurement was performed in the Center for Microanalysis of Materials at UIUC, which is partially supported by DOE under Grant No. DEFG02-91-ER45439.

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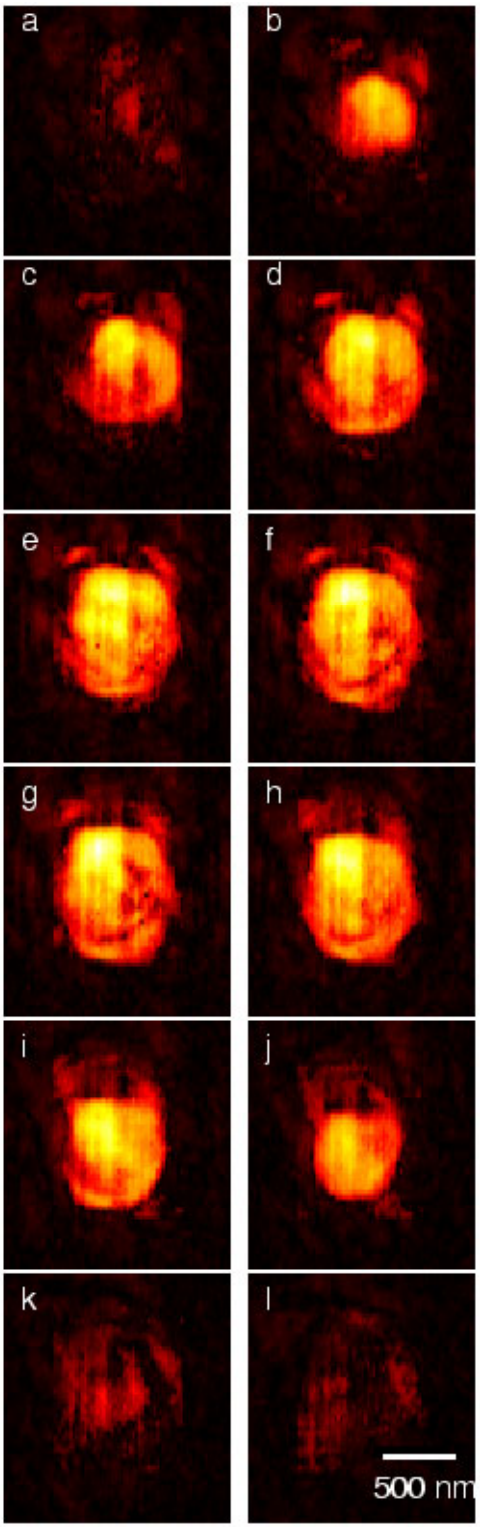

FIG. 3. Slices through a 3-D reconstruction of the crystal that produced the diffraction pattern in Fig. 2, as reconstructed by phasing the diffraction pattern.

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