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Plasticity of indium nanostructures as revealed by synchrotron X-ray microdiffraction

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ABSTRACT

Indium columnar structures with diameters near 1 μm were deformed by uniaxial compression at strain rates of approximately 0.01 and 0.001 s^{-1}. Defect density evolution in the nanopillars was evaluated by applying synchrotron Laue X-ray microdiffraction (μSLXRD) on the same specimens before and after deformation. Results of the μSLXRD measurements indicate that the dislocation density increases as a result of mechanical deformation and is a strong function of strain rate. These results suggest that the rate of defect generation during the compression tests exceeds the rate of defect annihilation, implying that plasticity in these indium nanostructures commences via dislocation multiplication rather than nucleation processes. This is in contrast with the behaviors of other materials at the nanoscale, such as, gold, tin, molybdenum, and bismuth. A hypothesis based on the dislocation mean-free-path prior to the multiplication process is proposed to explain this variance.

1. Introduction

With the increased insertion of nanoscale electronic and photonic devices into technological applications, understanding the mechanical behavior of small scale structures becomes increasingly important to ensure life-time and reliability of these products. In the context of mechanical properties, one of the important scientific discoveries was the emergent size dependence of yield strength in metals once their dimensions are reduced to the micron and sub-micron scales [1–9]. For example, as the dimensions of the feature size in face-centered cubic metal like Au are reduced to less than 1 μm, their yield strengths may increase by ~80 times [10]. One of the possible explanations for this size dependence deeply in the sub-micron regime is the *dislocation starvation* effect. The premise of this theory is that as the dimension of single crystals are reduced to nanometer scale, mobile dislocations glide along their slip planes to the free surfaces relatively unimpeded, and therefore annihilate at the free surface without significant interactions with other defects. The result is a net reduction in the mobile dislocation density within the nanostructure during mechanical deformation. As the sample is further deformed, the few remaining mobile dislocations cannot accommodate the imposed plastic strain, and therefore new dislocations have to be nucleated, which requires high stresses. As the nanostructures get smaller, the number of available dislocation sources decreases, and their operation strength increases, which leads to the ever higher stresses in smaller samples [1,3,9]. This notion of dislocation starvation, coined by the authors as "mechanical annealing", has also been demonstrated via in situ compression of single crystalline nickel pillars [6]. Shan et al. [6] used an in situ transmission electron microscope (TEM) nanoindenter to illustrate this size effect and showed that the initial dislocations in a focused ion beam (FIB) -fabricated 160 nm diameter nickel pillar completely disappear upon mechanical deformation. Budiman et al. [11] used a non-destructive synchrotron Laue X-ray microdiffraction technique to perform ex situ characterization of the defect density within gold nanopillars before and after the compression tests. These μSLXRD results showed no detectable increase of the Laue spot diffraction peak broadening, which indicates there is no net increase of defect density in the small-scale structures after the mechanical

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deformation. Therefore, this study was further experimental support for the dislocation starvation theory. For specimens in micron sizes, Maaß et al. [12–14] used the Laue X-ray microdiffraction techniques to characterize the microstructure evolution of FIB fabricated metallic micropillar specimens during the uniaxial compression tests. Their results indicated for large gold and other metal structures the size effect is affected by strain hardening and strain gradients.

The size dependence in mechanical strength has now been extensively investigated for single-crystalline metals with high melting temperatures, such as molybdenum [4], titanium [15], gold [10], nickel [1], magnesium [16,17], niobium [18], tungsten [18], tantalum [18], and others. Conversely, these types of studies for low-melting temperature metals have been scarce: indium [19], bismuth [20] and tin [21]. At ambient conditions, the motion of dislocations in the high melting temperature crystals is often constrained to a specific slip system, whereby the dislocations glide along the crystal planes with the lowest critical resolved shear stress (CRSS) until they reach the free surface, shearing the crystal along that crystallographic plane. However, in low melting temperature materials like soft face-centered-tetragonal (FCT) indium with melting temperature of ~156 °C (corresponding to a homologous temperature at room temperature near 0.7), dislocation motion even at room temperature may become non-conservative via thermally activated processes like cross-slip and dislocation climb. Therefore, the mean-free path of a mobile dislocation in the low-melting temperature metals is expected to be significantly shorter than that in the high melting temperature metals, while the overall distance traveled may be significantly longer. This increases the probability of dislocations interacting with one another and with other defects in the course of their motion, possibly leading to dislocation density increase via multiplication in the indium nanostructures.

The primary objective of this work is to examine the deformation mechanism operating in mechanically deformed indium nanopillars by performing ex situ μSLXRD characterization of the defect density evolution in the nanostructures. The dislocation defects detected by this technique can be either statistically stored dislocations (SSD) or geometric necessary dislocations (GND). Specifically, the defect density in indium nanopillars with diameters near 1 μm is explored before and after uniaxial compression tests performed in a nanoindenter outfitted with a custom flat diamond tip. Since indium has a low melting temperature of ~156 °C, thermally activated processes for vacancy diffusion and dislocation cross-slip or climb are expected to have a non-trivial contribution in the mechanical deformation of these structures. Our μSLXRD results reveal that the Laue diffraction peaks broaden after the mechanical compression tests, suggesting defect accumulation during the deformation. A semi-quantitative analytical technique is developed to estimate the net dislocation density increase due to the deformation process. This analysis reveals an estimated ~2.5 times net increase of defects in the pillar.

2. Experimental methods

The indium nanopillars investigated in this work were fabricated using the electron beam lithography and metal electroplating technique developed by Burek and Greer [22]. The specific procedure used to generate indium nanopillars is described in detail [19]. The methodology is briefly summarized here. First, a 20 nm thick titanium adhesion layer and a 100 nm gold seed layer were deposited on a silicon (1 0 0) wafer, followed by spin-coating of polymethylmethacrylate (PMMA) resist. Standard electron beam lithography techniques were then used to pattern an array of holes in the PMMA resist layer. Indium nanopillars were deposited into the PMMA resist template by direct current electroplating. The PMMA was then dissolved in acetone, leaving an array of vertically aligned and isolated indium nanopillars for subsequent testing. The resulting indium nanopillars were approximately 920 nm in diameter. A fifteen-day minimum rest period was maintained for all indium nanopillar samples prior to microstructural or mechanical characterization. This rest period ensured that thermally activated processes, such as grain growth or annihilation of fabrication induced defects at free surfaces, reached equilibrium at room temperature prior to testing.

The microstructure of as-fabricated and uniaxially compressed 920 nm diameter indium nanopillars was characterized by the μSLXRD technique with Beamline 12.3.2 [23–25] at the Advanced Light Source synchrotron facility at Lawrence Berkeley National Laboratory. This non-destructive technique was utilized in various previous studies [26–29] due to its suitability in examining the defect structure of sub-micron and nanometer scale specimens. The μSLXRD technique is especially useful for low melting temperature metals since conventional structural characterization methods, such as TEM and electron backscattered diffraction will expose the structure to high energy electron beams. Such exposure may significantly alter the specimen microstructure and internal defect structure during analysis. In contrast, the energetic X-rays used in the μSLXRD technique are not damaging to the internal nanopillar structure since there is negligible change in the sample temperature during measurements.

Each indium nanopillar sample was mounted on a MICOS high precision XY-positioning stage (resolution of 0.05 μm) and raster scanned under the white X-ray beam with the purpose of locating the nanostructures. This imaging process provided both X-ray microfluorescence (μXRF) and the X-ray microdiffraction information of the scanned area. The μSLXRD patterns were collected using a MAR 133 X-ray charge coupled device (CCD) detector with pixel size near 100 μm and analyzed using a custom-made XMAS software package [23,24]. Once the individual nanopillar of interest was located and identified, a second μSLXRD scan of the local area was conducted to obtain detailed diffraction data from the selected structure. In a typical experiment, the X-ray scan area of an individual nanopillar is a $\sim 10 \times 10\ \mu m^2$ square with 0.5 μm step sizes. This scan area was designed to ensure that the diffraction pattern generated by the crystals within the indium nanopillar would be captured in at least one of the collected Laue X-ray diffraction images. This μSLXRD scan process involved the collection of 400 CCD frames, which required 3–4 h to collect. The exposure time for each frame was 5 s, in addition to about 10 s of electronic readout time.

To understand the dislocation dynamics within indium nanostructures, selected indium nanopillars were characterized by μSLXRD before and after uniaxial compression experiments for the same specimens. The compression tests were conducted at Stanford University using an Agilent NanoXP (Agilent/MTS, Knoxville, TN) nanoindenter outfitted with and a custom fabricated flat ended diamond tip and operating in continuous stiffness mode. Two indium pillars were selected and compressed at two different engineering strain rates, $0.01\ s^{-1}$ and $0.001\ s^{-1}$. This strain rate here is defined as the ratio between the constant nominal displacement rate and the initial height of the structure. To reduce the room temperature annealing effects during the period between the nanopillar deformation and the post compression μSLXRD characterization, the deformed indium specimens were stored in the dry ice sublimation environment (−78.5 °C) during transportation. The Laue X-ray diffraction peak widths measured before and after uniaxial compression were then compared to provide important insights about the microstructural changes associated with dislocation dynamics in the deformed indium nanostructures.