Fabrication, microstructure, and mechanical properties of tin nanostructures

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ABSTRACT

Vertically aligned, cylindrical tin nanopillars have been fabricated via an electron beam lithography and electropolishing method. Characterization by a non-destructive synchrotron X-ray microdiffraction (μSXRD) technique revealed that the tin nanostructures are body-centered tetragonal and are likely single-crystalline, or consist of a few large grains. The mechanical properties of tin nanopillars with average diameters of 920 nm, 560 nm, and 350 nm were studied by uniaxial compression in a nanoindenter outfitted with a flat punch diamond tip. The results of compression tests reveal strain rate sensitivity for nanoscale tin deformation, which matches closely to the previously reported bulk tin values. However, unlike bulk, tin nanopillars exhibit size-dependent flow stresses where smaller diameter specimens exhibit greater attained strengths. The observed size-dependence matches closely to that previously reported for single-crystalline face centered cubic metals at the nanoscale. μSXRD data was used to compare the dislocation density between as-fabricated and deformed tin nanopillars. Results of this comparison suggest that there is no measurable accumulation of dislocations within deformed tin nanopillars.

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1. Introduction

With the advancement of small-scale fabrication techniques in recent years, applications of nanometer sized tin structures have gained considerable interest. In the microelectronics industry, tin is a promising replacement of lead in elemental metal and alloy solders for chip packaging. This is in part due to their low melting temperature, ductility, excellent wetting properties, high electrical conductivity, and electrical reliability [1–3]. Since tin and tin-alloy structures used in microelectronic solder technology are part of the load bearing components, their mechanical properties approaching the nanometer scale are critically important for product reliability and lifetime. Another interesting application of tin is in the area of lithium ion battery anodes, where nanostructured tin-based anodes are being studied in order to improve charge storage and anode lifetime [4]. In order to attain the desired functionality and lifetime of these small-scale components, a thorough understanding of nanoscale tin deformation mechanisms are required.

This work has two main goals. Initially, we develop fabrication processes and integration methods for cylindrical tin nanopillars. Secondly, the time dependent mechanical behaviors of these tin nanopillars are characterized by uniaxial compressive loading. The results presented here will help to understand how tin nanostructures behave during mechanical deformation. In addition, the new knowledge gained from this work will also expand the current understanding in small-scale mechanical properties to the deformation mechanisms governing low melting temperature nanostructures. The melting temperature of tin is ∼232 °C, corresponding to a homologous temperature of approximately 0.6 in ambient conditions. At room temperature, tin exists as its β-allotrope, also known as white tin. It has a body centered tetragonal (BCT) crystal structure with c/a = 0.5456 [5]. Of the three stable tin allotropes, only white tin is of interest in chip packaging and electronic applications due to its metallic nature. According to Yang and Li, there are twelve possible slip systems in the BCT tin crystal, with at least six readily observed in the bulk scale deformation of tin [5]. Three of the most commonly observed BCT tin slip systems near room temperatures are: (a) (110)[111], (b) (110)[001], (c) (100)[010] [6]. The dimension of the Burgers vectors are \( b[111] = 0.4411 \text{ nm}, b[001] = 0.3157 \text{ nm}, b[100] = 0.5819 \text{ nm}, \) and \( b[101] = 0.6629 \text{ nm} [5]\). The shear modulus of tin is 17.93 GPa at room temperature [5]. Like many other metals, bulk β-tin exhibits
strain rate sensitivity where the flow stress varies with the deformation rate. Strain rate and other time dependent mechanical behaviors, i.e. creep deformation, of bulk–scale tin have been studied in detail by Sherby [7], Frenkel et al. [8], Weertman and Breen [9], Breen and Weertman [10], Yang and Li [5], Chu and Li [6], Mohamed et al. [11], Raman and Berriche [12], and Mayo and Nix [13]. They observed that the relationship between the creep deformation rate ($\dot{\varepsilon}$) and the stress ($\sigma$) can be described by a simple relationship:

$$\dot{\varepsilon} = K\sigma^n$$  \hspace{1cm} (1)

where $K$ is a constant depends on material parameters, such as, the elastic modulus and the diffusivity of the metal. The stress exponent ($n$) for tin reported in the literature has a wide range of values, from ~3.6 to ~11. These variations depend on several factors, including testing temperature, microstructure, crystalline orientation, grain size, stress level applied, and measurement technique. Breen and Weertman [10] measured the steady state creep properties of polycrystalline tin at 21.1 °C and their results indicate a stress exponent value of ~4.6. Creep deformation behaviors of bulk tin single-crystals near the ambient conditions were characterized by Chu and Li [6] with impression creep techniques. They reported the stress exponent values with the ingot orientations of [0 0 1], [1 0 0], and [1 1 0] are 4.4 (40 °C), 4.5 (50 °C), and 5.0 (60 °C), respectively. The temperature values shown correspond to the isothermal testing conditions. With the reports discussed above, the mechanical properties of bulk tin structures are well characterized and documented. However, to the best of our knowledge no investigations on the small–scale deformation behaviors of tin nanostructures have been performed. Nanoscale mechanical properties of a wide variety of metals (e.g. Au, Ni, Cu, and Mo) have been the focus of numerous research activities [14–40]. Nearly all of these studies reveal that metals, when reduced to the nanoscale, exhibit remarkably different mechanical behaviors compared to that in bulk [41]. However, this effect had not been properly studied in tin nanostructures.

It is important to distinguish the current study with the previous work by Raman and Berriche [12] or Mayo and Nix [13] who used nanoindentation to characterize the creep deformation behavior of tin. One of the most important distinctions is the nanoindentation tip geometry. These authors used sharp pyramid tips which locally concentrate stress at the apex of the contact and along the edges of the pyramid. Therefore, mechanical strains introduced are not uniformly distributed within the contact area. In the current study, a flat diamond punch is used and the nanoscale stress–strain response is homogeneously distributed throughout the nanopillar specimen. Another important difference is the sample geometry. Pervious authors used bulk samples with the configuration of elastic half-spaces. The stress field generated on these samples during the indentation is extremely complex and consequently, it is very difficult to eliminate all artifacts. In the current work, the cylindrical tin nanopillars produced are geometrically similar to the specimen configurations used in conventional uniaxial compression tests. The stress–strain response generated in our tests with a flat diamond punch is expected to be uniform throughout the nanoscale column.

Herein, we report an integration method to fabricate arrays of isolated, vertically aligned tin nanopillars by using the electron beam lithography and electroplating technique [42]. Arrays of tin nanopillars ranging from ~70 to 920 nm in diameter with aspect ratios (height/diameter) of ~2–4 and separation distance of 10 μm were successfully manufactured. The microstructure of electroplated tin nanopillars was investigated by a non-destructive synchrotron X-ray micro-diffraction (μSXRD) technique. This method uses a micron-focused polychromatic (white) X-ray beam to obtain Laue diffraction patterns of the tin nanostructures which in turn can be used to determine the grain orientations, local residual stresses and strains, and dislocation densities of the tin nanopillars.

The mechanical properties of tin nanopillars with average diameters of 350 nm, 560 nm, and 920 nm were characterized by using a uniaxial microcompression technique. The results show that size-dependent flow stresses are observed for both deformation modes and show a power-law relationship similar to that previously reported for other single-crystalline metallic nanopillars [41]. The flow stress data also revealed that the strain rate sensitivity in tin nanostructures is very similar to the bulk tin creep deformation results reported by Chu and Li [6]. Mechanically compressed tin nanopillars were inspected carefully by scanning electron microscopy (SEM). The post-deformation SEM analysis revealed evidence of bulging, extrusion, and fine wrinkling in additional to crystallographic shear off-sets. Analysis of tin nanopillars following compressive loading by μSXRD yielded a qualitative comparison of dislocation density change. The results show no discernable change in the dislocation density within the tin nanopillar microstructure following deformation to over 20% engineering strain.

2. Experimental methods

2.1. Electron beam lithography process

Fig. 1 shows the integration scheme used to produce tin nanopillars. The fabrication method involves lithographic patterning of polymethylmethacrylate (PMMA) resist with electron beam lithography, followed by tin electroplating into the prescribed resist template. Preparation of the substrate began with Si (001) wafers, which were coated with a 20 nm-thick titanium adhesion layer and a 100 nm-thick gold layer deposited by electron beam evaporation. The metalized substrates were spin coated with various concentrations of 950 kD PMMA dissolved in anisole (MicroChem Corp.), then baked at 180 °C for approximately 15 min. An array holes with various diameters was patterned in the PMMA resist by exposure using a Leica EBPG 5000+ electron beam lithography system operating with an acceleration voltage of 100 kV. The patterned

![Schematic drawings of electron beam lithography and electroplating fabrication process for tin nanopillars developed in this work.](image-url)
PMMA layer was developed in 1:3 solution of methylisobutylketone and isopropyl alcohol (IPA) for \( \sim 60 \) s followed by 5 s rinse with IPA. The resulting feature size after PMMA development was holes 70–920 nm in diameter. Before electroplating, the silicon wafer was diced into square 1 cm\(^2\) chips with the patterned PMMA resist template in the chip center.

2.2. Tin nanopillar electroplating

Tin electroplating was performed under alternating current conditions using a parallel two-electrode configuration. The tin plating solution was made in-house and consisted of 22 g/L tin(II) sulfate (95.5%, Alfa Aesar) and 75 g/L sulfuric acid. About 200 mL of the prepared solution was used for electroplating. The solution was prepared fresh for each sample and mechanically stirred for approximately 30 min prior to deposition to ensure its homogeneity. The gold/titanium seed layer underneath the resist template acted as the cathode, and a high purity tin rod (6 mm diameter, 99.9985%, Puratronic\textsuperscript{®} from Alfa Aesar) was used as a soluble anode. The plating bath was maintained at room temperature and mechanically stirred throughout the deposition process. A Teflon backing and custom gold coated brass clips were used to mount the PMMA coated substrates in the solution and electrically interface with the gold/titanium cathode layer. The total cathode area, which included the patterned PMMA coated substrate, a blank 1 cm\(^2\) chip, and the gold clips, was maintained at \( \sim 3.5 \) cm\(^2\), and the distance between the anode and the cathode was kept at approximately 25 mm.

Tin electroplating was initiated with a short current pulse at 50 mA/cm\(^2\) for 5 s. This step was necessary to promote metal nucleation in all pores and to increase the final nanopillar yield and homogeneity. Subsequently, electroplating was conducted using an alternating current technique with 0.5 s of cathodic current at 7.5 mA/cm\(^2\) followed by 0.1 s of anodic current at 5 mA/cm\(^2\). The alternating current technique was used to promote homogeneous deposition. Total plating times ranged from 15 to 60 min depending on the pillar diameter and desired aspect ratio, with shorter times for the smaller diameters. After the electrochemical deposition, the PMMA resist was stripped in acetone for at least 30 min and nanopillars were inspected by SEM. Prepared tin nanopillars are expected to have a native oxide thickness approximately 5–8 nm, which was observed by transmission electron microscopy of tin nanowires electroplated in polycarbonate membranes [43].

2.3. Microstructural characterization using synchrotron X-ray microdiffraction

The microstructure of as-fabricated and uniaxially compressed 920 nm diameter tin nanopillars was characterized by the \( \mu \)SXRD technique at the Beamline 12.3.2 at the Advanced Light Source.
Synchrotron facility of the Lawrence Berkeley National Laboratory. Conventional structural characterization methods, such as electron backscattered diffraction and transmission electron microscopy, were not employed since exposure of low-melting temperature metals to high energy electron beams may result in the activation of thermally assisted processes like dislocation climb, defect annihilation, and grain growth. Details of this μSXRD technique have been described elsewhere [44–46]. The unique capability of μSXRD as a local nanoplasticity probe stems from the continuous range of wavelengths in a white X-ray beam. This allows Bragg’s law to be satisfied even when the lattice is locally rotated or bent, resulting in the observation of asymmetric broadening/streaking in the Laue diffraction peaks. Since geometrically necessary dislocations (GNDs) are directly related to the local lattice curvature, this technique can be used to determine the density of GNDs [45,46]. This has proven to be useful in the study of length scale effects involving uniaxially compressed submicron pillars of single-crystalline gold [47], nanoindented bulk copper single crystals [48], low melting temperature electroplated indium nanopillars [33], and nanoscale Cu/Nb single-crystalline multilayer materials [49]. The symmetric broadening of the Laue diffraction peaks, in the mean time, is useful to provide an indication of the relative of statistically stored dislocations (SSDs) [50].

Samples were mounted on a precision XY Huber stage and the μSXRD Laue diffraction patterns were collected using a MAR133 X-ray charge-coupled device (CCD) detector and analyzed using the XMAS software package [44]. Once the array of pillars was located by using the synchrotron X-ray microfluorescence scanning, fine diffraction scanning was performed on the nanopillars of interest. The results from the Laue diffraction peak provide microstructural information of the tin nanopillars, such as, crystal orientations, stresses/strains, dislocation densities and configurations. A comparison of the dislocation densities and configurations of tin nanopillars before and after the compression test would elucidate the plasticity involved during the deformation.

2.4. Uniaxial compression testing

Uniaxial compression tests were conducted on tin nanopillars with average diameters of 920 nm, 560 nm, and 350 nm. An in situ nanoindenter (Nanomechanics, Inc., Knoxville, Tennessee) with a custom diamond flat punch tip with a square cross-section dimension of 8 μm × 8 μm was used for testing the nanopillar specimens. All mechanical tests were conducted in ambient conditions. Tin nanopillars were compressed with nominal engineering strain rates of approximately 0.01 s⁻¹, 0.001 s⁻¹, and 0.0001 s⁻¹. The strain rate was defined by the ratio between the constant prescribed displacement rate and the initial height of the nanopillar being tested. Nanopillars were inspected with SEM prior to compression and only those specimens with an aspect ratio (height/diameter) of approximately 3:1 were used for the mechanical testing.

3. Results and discussions

3.1. Nanopillar geometry and initial microstructure

Fig. 2 shows a SEM micrograph revealing an array of 920 nm diameter tin nanopillars. This figure demonstrates that a high production yield of tin nanostructures is achieved with the fabrication processes presented above. To demonstrate the versatility of the nanoscale fabrication processes developed in this work, tin nanopillars with diameters between 70 and 920 nm were prepared and inspected using SEM. Care was taken to measure the diameters of these structures at the middle point of each nanopillar.

Fig. 3(a)–(e) shows representative micrographs of the solid and vertically oriented tin nanopillars with smooth side walls.

As-fabricated tin nanopillars with a diameter of 920 nm were characterized using the non-destructive μSXRD Laue diffraction technique. Smaller nanopillars were not tested due to the lack of reliable diffracted X-ray signals. Close up views of the (406) and (624) diffraction peaks taken from a Laue diffraction pattern obtained from a single as-fabricated tin nanopillar are shown in Fig. 4(a) and (b) respectively. For this tin nanopillar, a single unique Laue diffraction pattern (not shown) belonging to a body-centered tetragonal (BCT) crystal was identified for the entire nanopillar volume. This indicates that the tin structures produced for this work are likely single-crystalline. However, another possibility is that the specimen consists of a very large grain which occupies the majority of the nanopillar volume and any remaining grains are too small to diffract enough incident X-ray signals for detection. In either case, it is clear that the mechanical response of such a small specimen would be dominated by the dislocation activities in the single large tin crystal. From the Laue diffraction pattern, the tin nanopillar was indexed as body-centered tetragonal (BCT) with Laue reflection of the (110) plane and that of silicon (100) plane are very close to each other (within ~0.2°). This indicates that the vertical axis of the pillar is normal to the (110) plane. It is important to note that only a very small fraction of fabricated nanopillars were investigated by the μSXRD technique, thus the analysis presented in Fig. 4 does not necessary apply to the ensemble of nanopillars. However, the results shown in Fig. 4 are a good indication that it is likely the elec-
The two representative peaks in Fig. 4(a) and (b) are diffuse in nature, which is consistent with the small nanopillar dimensions. The geometry of the peaks is mostly circular which strongly indicates a well annealed tin crystal with no excess initial dislocations of the same signs, i.e. no GNDs. To quantify the Laue spot intensity profile, the tin nanopillar (4 0 6) peak was further analyzed along the intensity traces at a particular $\chi$ direction and along the $2\theta$ axis, as illustrated in Fig. 5(a). The intensity profiles were fitted with Lorentzian curves as shown in Fig. 5(b). The full-width half-maximum (FWHM) measurement shows a peak broadening of 0.439° for the (4 0 6) Laue diffraction spot. This peak broadening consists of three contributions: crystal size effect, instrumentation, and the possibility of random dislocation storage during fabrication of the nanopillars, i.e. non-zero initial dislocation density.

### 3.2. Stress–strain behavior of tin nanopillars

Fig. 6(a)–(c) shows the representative engineering stress–strain curves obtained from uniaxial compression experiments of tin nanopillars with average diameters of 920 nm, 560 nm, and 350 nm. All deformed with strain rate of $\sim 0.001 \text{s}^{-1}$.
Fig. 7. (a) Pre- and (b) post-compression SEM images of ~920 nm diameter tin nanopillar.

Fig. 8. (a) Pre- and (b) post-compression SEM images of ~560 nm diameter tin nanopillar.

Fig. 9. (a) Pre- and (b) post-compression SEM images of ~350 nm diameter tin nanopillar.
the structure is deformed slowly. In contrast, the yield strength

tion rate. The data reveals that the material strength is low when

clearly show that the tin flow stresses are sensitive to the deforma-

sions of three different diameters: 350 nm, 560 nm, and 920 nm. For

The data in this plot includes results from nanopillar compres-

sion in a greater number of crystallographic slip planes to occur

lar sidewalls. The material extrusion type of deformation in tin

strain is compensated by material extrusions from the nanopil-

graphs. This type of crystallographic shear behavior has been

reported in almost all deformed single-crystalline metallic nanopil-

atures were observed for all three nanopillar sizes. Even

though fine crystallographic slip lines are not apparent on the

post compression images, examples of gross deformation by shear

along crystallographic planes can be found in these SEM micro-

graphs. This type of crystallographic shear behavior has been

reported in almost all deformed single-crystalline metallic nanopil-

lers [14–25,27–31,38–41]. Another deformation characteristic that

can be found in Figs. 7–9 is sidewall surface wrinkles and bulges

perpendicular to the loading direction. All compressed tin nanopil-

ars showed this type of plastic deformation where the compressive

strain is compensated by material extrusions from the nanopil-

lar sidewalls. The material extrusion type of deformation in tin

nanopillars is not unexpected. At high homologous temperatures, a

large number of slip systems will be activated which allows defor-

mation in a greater number of crystallographic slip planes to occur

simultaneously. The consequence is that fewer discrete slip planes

are observed in the post-compression nanopillar, and instead strain

resembles extrusion like deformation.

3.3. Post compression SEM analysis

To further understand how small-scale tin structures behave

plastically, all nanopillar specimens were carefully inspected before

and after compression using high resolution SEM. Typical elec-

tron micrographs of tin nanopillars with average diameters of

920 nm, 560 nm, and 350 nm before and after uniaxial compression

at strain rate of ~0.001 s\(^{-1}\) are shown in Figs. 7–9, respec-

- tively. These figures show two distinct plastic flow features –

crystallographic shear off-sets and material extrusion. Both defor-

mation features were observed for all three nanopillar sizes. Even

- though fine crystallographic slip lines are not apparent on the

post compression images, examples of gross deformation by shear

along crystallographic planes can be found in these SEM micro-

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simultaneously. The consequence is that fewer discrete slip planes

are observed in the post-compression nanopillar, and instead strain

resembles extrusion like deformation.

3.4. Influence of strain rate and nanopillar size

Engineering flow stresses of tin nanopillars measured at 5.0%

nominal strain are plotted as a function of strain rate in Fig. 10(a).

The data in this plot includes results from nanopillar compres-

sions of three different diameters: 350 nm, 560 nm, and 920 nm. For

the two largest nanopillar sizes of 560 nm and 920 nm, the results

clearly show that the tin flow stresses are sensitive to the deforma-

tion rate. The data reveals that the material strength is low when

the structure is deformed slowly. In contrast, the yield strength

increases when the specimen is compressed at a fast strain rate. In

order to show a clear trend of strain rate sensitivity, the average

flow stress values of 560 nm and 920 nm diameter nanopillars are

plotted in Fig. 10(b), where the error bars correspond to one stan-

dard deviation. Fig. 10(b) shows a noticeable increase in 920 nm

diameter tin nanopillar strength from ~46 to 112 MPa when the

strain rate increases from 0.0001 s\(^{-1}\) to 0.01 s\(^{-1}\). Similarly, for the

560 nm diameter tin nanopillars, the data shows an increase from

~61 to 96 MPa for the same increase in strain rate.

The general relationship between the uniaxial strain rate and

creep stress has been well documented and is displayed in Eq. (1).

To compare the tin nanopillar strain rate sensitivity with the bulk

samples from the previous studies, the data from Fig. 10(b) are

fitted with Eq. (1). The stress exponent extracted from this curve

fit is approximately 5.54 ± 1.53, where the spread corresponds to

one standard deviation. This value agrees with the single-crystal

impression creep results reported from Chu and Li [6], with expo-

nent values measured near room temperatures in the range of

4.4–5.0. The results indicate that the strain rate sensitivity of single-

crystal tin nanostructures is similar to bulk.

Fig. 11 shows the tin nanopillar engineering flow stress results

measured at 5.0% nominal strain plotted as a function of feature

size. These structures were compressed at a constant strain rate of

\(\sigma \sim D^{-0.572}\) 

\(\text{strain rate } \sim 0.001 \text{ s}^{-1}\)
A ~920 nm diameter tin nanopillar after uniaxial compression to ~22% engineering strain. Pre and post compression SEM images of the tin nanopillar are shown in (a) and (b) respectively, with the corresponding engineering stress–strain curve displayed in (c).

~0.001 s\(^{-1}\). The figure also includes the average values from each nanopillar size where the error bars correspond to one standard deviation. The attained stresses at ~5.0% engineering strain are approximately 72.8 ± 36.3 MPa, 96.4 ± 33.9 MPa, 131.5 ± 39.1 MPa for 920 nm, 560 nm, and 350 nm diameter tin nanopillars respectively. As shown in Fig. 11, tin nanopillars exhibit a size effect where reducing the sample dimension produces stronger specimens. Since the nanopillars tested in this work were electroplated, rather than fabricated using standard focused ion beam (FIB) milling techniques, arguments of ion beam damage to the nanopillar cannot account for the increase in strength for small tin nanopillars.

Similar size-dependent strengthening has been reported previously for metallic nanopillars fabricated in nickel [14–17], gold [19–21,30], copper [22–24], and molybdenum [28–30,37,38,40]. In a recent review by Uchic et al. [41] on the small-scale mechanical properties of metals, it was illustrated that single-crystalline metallic nanopillar specimens which exhibit yield strength size effects follow an empirical power-law relationship between the strength of the sample (σ) and the nanopillar diameter (D):

\[ \sigma \propto D^\gamma \]  

(2)

The parameter γ is the power-law exponent. In their work, Uchic et al. showed that most size-dependent strengthening data for nanoscale FCC single-crystalline metals, such as Ni, Au, Cu, and Al, could be collapsed onto a single line by plotting the normalized resolved shear effective stress versus pillar diameter [41]. The result of this normalization yielded a power-law exponent of ~0.6. Recently, the small-scale mechanical properties of body centered cubic (BCC) metals have also been explored in uniaxial compression and tension [28–31,34,37,38,40,51]. It is interesting to note that the deformation characteristics and size effects observed for single-crystalline BCC nanopillars deviate from FCC specimens for reasons attributed to crystal structure [28,51]. For example, Kim et al. [40] showed that BCC tungsten, molybdenum, tantalum, and niobium have size effect power law exponents of ~0.44, ~0.44, ~0.43, and ~0.93 respectively, and Han et al. showed BCC vana-
Medium has a size effect power-law exponents of −0.79 [34]. These values are quite different from the FCC results summarized by Uchic et al. [41].

To compare the size dependence of BCT tin structure with the FCC and BCC specimens, flow stress data from Fig. 11 were fitted with Eq. (2) and an exponent value of $-0.572 \pm 0.114$ was obtained, a value very close to the FCC size effect power-law exponent of −0.6, but not the BCC values. This suggests that even though tin has a different crystal structure (BCT versus FCC) the small-scale mechanical properties of BCT tin may operate by a similar size-dependent mechanism to FCC metals. One of the possible explanations of the similarity may be due to the low melting temperature of tin at $\sim 232$ °C. During deformation in ambient conditions, a greater number of slip systems are thermally activated in metals with low melting temperatures. According to a recent review on tin deformation mechanisms by Yang and Li [5], there can be as many as 12 possible activated slip systems in a tin crystal, which is similar to FCC crystals. In addition, it has been well documented that the BCT tin critical resolve shear stresses (CRSS) are very sensitive to temperatures. For example, Nagasaka [52] report that the CRSS of the tin (1 0 0)[0 1 0] slip system decreases nearly exponentially in the temperature range of 200–320 K, with the CRSS values reduced from approximately 0.7 MPa to 0.2 MPa. The CRSS values for other tin slip systems, such as the (1 1 0)1/2[1 1 1] system, also exhibits near exponential temperature sensitivity. It requires roughly 4.6 MPa to shear this plane and direction at 200 K, but only 1 MPa near 320 K. The significant reduction of the CRSS values at room temperature and a large number of thermally activated glide planes available for dislocation motion may also explain why the nanoscale deformation behavior of BCT tin is similar to other FCC metals at nanoscale.

In addition to the low melting temperature of tin, a detailed inspection of a BCT tin unit cell reveals that it has a close resemblance of a FCC diamond structure [5]. In addition to the one atom at the center and eight atoms at the corners of the tin unit cell, there are four other atoms on four different faces. Therefore, a BCT tin unit cell contains four atoms with each atom having four nearest neighbors and can be interpreted as a distorted diamond cubic structure [5]. The similarity between the strength size effect in BCT tin and FCC metals at the nanoscale is not unreasonable.

### 3.5. μSXRD study of deformed tin nanopillars

To understand the tin nanopillar deformation mechanisms in greater details, μSXRD techniques were used to characterize their microstructures and dislocation density after deformation. Fig. 12(a) and (b) shows SEM micrographs of a tin nanopillar before and after compression to approximately 22.0% engineering strain respectively. The strain rate used to compress this specimen was $\sim 0.001$ s$^{-1}$. Crystallographic shear off-sets and lateral surface wri...
kinking/extrusion are both observed in the post-compression SEM image. This is consistent with the deformation mechanisms observations in Figs. 7–9. The stress–strain data collected from uniaxial compression of this tin nanopillar is plotted in Fig. 12(c). The stress–strain behavior includes similar strain bursts to those illustrated previously in Fig. 6. It is important to note that this particular pillar was only characterized by μSXRD after the compression test. No information was collected in the as-fabricated state.

The μSXRD analysis of the deformed tin nanopillar again identified only one unique body-centered tetragonal (BCT) Laue diffraction pattern for the entire nanopillar volume, indicating the compressed nanopillar is single-crystalline. The Laue diffraction pattern indicates the compressed tin nanopillar is BCT with the plane normal to the vertical axis of the pillar close to the tin (2 0 4) plane. Two individual Laue diffraction spots of (2 0 4) and (1 0 5) were extracted from this pattern and plotted in Fig. 12(a) and (b), respectively. The shapes of these two Laue spots are fairly regular with circular geometry suggesting random distribution of dislocations due to the nanopillar deformation. Qualitatively, the Laue diffraction peaks of this deformed specimen are similar to the as-fabricated tin nanopillar shown in Fig. 4(a) and (b).

Qualitative analysis of the (2 0 4) Laue diffraction peak in Fig. 13(a) were also conducted along the intensity traces at a particular χ and along the 2θ axis. This profile was fitted with Lorentzian curves as shown in Fig. 13(c). The FWHM value of this peak broadening is approximately 0.458° for the compressed tin nanopillar. When compared with the peak broadening between as-fabricated and post compression spots shown in Figs. 5(b) and 13(c), the results show that there is an angular width difference of ~0.019°. This variation is within the experimental error and resolution of the μSXRD technique. The angular resolution in the μSXRD experiments is limited by the charge-coupled device (CCD) camera pixel size which translates to resolution limit of ~0.03° in the Laue spot width measurement. No significant change in the peak broadening is expected here from the small crystal size, as well as the instrumentation before or after the deformation. It is then also reasonable to propose that there is no significant change in the peak broadening due to random dislocation density associated with the nanopillar deformation. The Laue diffraction results discussed here suggest that the defect density in this tin nanopillar after compression is very similar to the as-fabricated tin nanopillar described in Fig. 4. This may indicate that the nucleation and multiplication rates of dislocations during the uniaxial compression process are offset by the dislocation annihilation rate at the nanopillar surface. Thus, there is no significant increase or accumulation of dislocations in these small tin structures. Such a finding is similar to that reported earlier by Budiman et al. [47] in an ex situ study of single-crystalline gold nanopillars fabricated from by FIB milling, despite different crystal structures.

4. Conclusions

In conclusion, we have developed fabrication and integration techniques to produce large grain BCT tin nanopillars with diameters as small as 70 nm. Tin nanopillar flow stress data measured at different deformation rates indicate that these nanostructures possess similar strain rate sensitivity to their bulk counterpart, where the strength of tin increases with deformation rate. Additionally, the strength of tin nanopillars was observed to increase with reduced diameter. This flow stress size dependence appears to have the same characteristics as other single-crystalline FCC metals tested in uniaxial compression at the nanoscale. Microstructural characterization by μSXRD indicates that there is no drastic increase of dislocation within the compressed tin nanopillars. This suggests that the rate of dislocation generation by the deformation process is offset by annihilation at the nanopillar surface.

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