Imaging the Hydrogen Absorption Dynamics of Individual Grains in Polycrystalline Palladium Thin Films in 3D

Allison Yau,† Ross J. Harder,‡ Matthew W. Kanan,†§ and Andrew Ulvestad*§

†Department of Chemistry, Stanford University, Stanford, California 94305, United States
‡Advanced Photon Source, Argonne National Laboratory, Argonne, Illinois 60439, United States
§Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

ABSTRACT: Defects such as dislocations and grain boundaries often control the properties of polycrystalline materials. In nanocrystalline materials, investigating this structure–function relationship while preserving the sample remains challenging because of the short length scales and buried interfaces involved. Here we use Bragg coherent diffractive imaging to investigate the role of structural inhomogeneity on the hydriding phase transformation dynamics of individual Pd grains in polycrystalline films in three-dimensional detail. In contrast to previous reports on single- and polycrystalline nanoparticles, we observe no evidence of a hydrogen-rich surface layer and consequently no size dependence in the hydriding phase transformation pressure over a 125–325 nm size range. We do observe interesting grain boundary dynamics, including reversible rotations of grain lattices while the material remains in the hydrogen-poor phase. The mobility of the grain boundaries, combined with the lack of a hydrogen-rich surface layer, suggests that the grain boundaries are acting as fast diffusion sites for the hydrogen atoms. Such hydrogen-enhanced plasticity in the hydrogen-poor phase provides insight into the switch from the size-dependent behavior of single-crystal nanoparticles to the lower transformation pressures of polycrystalline materials and may play a role in hydrogen embrittlement.

KEYWORDS: coherent X-ray imaging, phase transformation, defects, grain boundaries, thin films

Solute-induced phase transformations are of fundamental interest and technological importance in a variety of applications, including catalysis,1 battery charging,2,3 hydrogen storage and sensing,4,5 etc. The effect of solute-induced strain on the phase transformation dynamics has a rich history6,7 and continues to be investigated.8,9 In particular, the first-order phase transformation in the palladium–hydrogen system has garnered considerable interest.10–13 Palladium can readily absorb and desorb hydrogen at room temperature and moderate pressures.6 The system is characterized by a hydrogen-poor phase at low hydrogen concentrations and a hydrogen-rich phase at high hydrogen concentrations; both phases maintain a face-centered cubic (FCC) structure. In nanoparticles, the hydrogen-induced strain in the hydrogen-poor phase is due to both an interstitial solid solution and a hydrogen-rich surface layer, which saturates at hydrogen partial pressures well below the transformation pressure. The hydrogen-rich surface layer leads to a dramatic dependence of the transformation pressure on nanoparticle size. While the size effect has been well characterized for isolated, single-crystalline nanoparticles with sizes from 1 to 400 nm,15,16 experimental investigation into thin film grains is lacking. Defects in grains such as grain boundaries and dislocations have been traditionally viewed as important to the hydride phase transformation process, as they may act as traps for solute atoms, enhance diffusion of solute atoms into the crystal lattice, and facilitate.

Received: July 6, 2017
Accepted: October 16, 2017
Published: October 16, 2017
plastic deformation. Here we investigate palladium grains in a thin film in order to elucidate the effects of defects such as dislocations and grain boundaries on hydrogen absorption dynamics using Bragg coherent diffractive imaging (BCDI).

BCDI is a lensless X-ray imaging technique that uses computational algorithms in place of physical lenses to achieve high-resolution imaging. It can be used to visualize the Bragg electron density and atomic displacement fields of crystalline materials in three-dimensional (3D) detail and with nanometer resolution. Recently, BCDI has been used to investigate nanocrystals in a range of in situ and operando experiments, and, in particular, its sensitivity to defects such as dislocations and coherent twin boundaries is very useful in resolving the structure–function relationship at the nanoscale. BCDI was recently developed for imaging grains in polycrystalline thin films, allowing us to use this capability to investigate hydrogen absorption dynamics in individual grains.

RESULTS AND DISCUSSION

Palladium thin films of approximately 200 nm thickness were deposited onto quartz substrates using e-beam evaporation. The films were annealed in a N₂ atmosphere at 200 °C for 30 min to increase grain size and crystallinity. The resulting grain structure was mostly columnar through the film, but many smaller grains were also formed, resulting in a 3D microstructure in certain areas of the film. A representative electron backscatter diffraction (EBSD) image showing the film’s overall crystal orientation and the grain boundary distribution is shown in Figure 1a. Figure S1 shows the corresponding pattern quality map with the grain boundaries highlighted. The surface morphology of the Pd films is shown in additional electron microscopy images in Figures S2–S4.

The experiments were conducted in a gas flow cell using a series of stepped hydrogen partial pressures (pH₂) while the hydrogen absorption dynamics within selected grains were monitored with BCDI. The experimental setup is shown schematically in Figure 1b. In BCDI, the grain shape and internal strain field are resolved in 3D detail by recording the two-dimensional (2D) coherent diffraction patterns of a single Bragg peak while slightly rotating the grain with respect to the incident X-ray beam (Figure 1c). The diffraction patterns of specific grains are isolated from the rest of the film by utilizing a 400 × 600 nm² focused X-ray beam and a nonsymmetric (nonspecular) scattering condition. These 2D patterns are combined into a 3D pattern whose phases are determined through iterative phase retrieval. Once these phases are known, the real space image is generated through an inverse
Fourier transform. Based on the phase retrieval transfer function, these real space images of the Pd grains have spatial resolutions of approximately 10 nm (Figure S5) with a pixel size of 8 nm. The real space images are complex with the amplitude proportional to the Bragg electron density and the phase proportional to the displacement of atoms from their equilibrium positions. For further details, please see the Methods and Experimental Section.

Diffraction patterns were recorded in the vicinity of the Pd(111) Bragg peak using 9 keV X-rays. Figure 1c shows three consecutive scans, each taking 1–2 min, of an individual grain’s diffraction pattern at 22.4 Torr $p_{H_2}$. Each pattern shown in the figure is the sum of the $\sim$60 2D patterns taken during a scan. The Debye–Scherrer rings for both the hydrogen-rich and hydrogen-poor phases are illustrated by the white dotted arcs. The hydrogen-poor phase has a $2\theta$ scattering angle corresponding to a lattice constant of 3.89 Å, while the hydrogen-rich phase is characterized by a $2\theta$ scattering angle corresponding to a lattice constant of 4.03 Å. The first image shows the diffraction pattern of the grain in the hydrogen-poor phase right before the phase transformation, while the last image shows the pattern in the hydrogen-rich phase immediately after the transformation. Both phases were briefly captured on the detector simultaneously during the middle scan, implying both phases were temporarily present in the grain. Interestingly, the image for the last scan in Figure 1c

**Figure 2.** Local displacement and local strain fields at selected cross-sections of a single Pd grain in the hydrogen-poor phase after H$_2$ exposure. (a) Change in the $u_{111}$ displacement field for selected cross-sections after exposure to hydrogen. (b) Change in the $\partial_{111} u_{111}$ local strain field for the same cross-sections after exposure to hydrogen. Note that the strain is defined relative to the average lattice constant at the particular pressure. Thus, the homogeneous strain due to average lattice expansion is not shown. (c) 3D rendering of the initial shape of the grain at 0 Torr $p_{H_2}$. The black lines show the locations of the $z_1$–$z_7$ cross-sections discussed in (a) and (b) and are approximately 8 nm apart. The blue arrow shows the [111] direction, which is normal to a {111} facet, and the gray plane represents the substrate upon which the thin film is deposited. See Figure S8 for other cross-sections of the same grain and Figure S9 for the diffraction patterns used in the reconstructions. (d) 64 grains from three different films were studied to see the dependence of grain size versus the final $p_{H_2}$ before transitioning to the hydrogen-rich phase. The uncertainties in the $p_{H_2}$ measured are around $\pm$1 Torr. The specific film sample that each grain statistic is from is designated by the colors shown in the legend to account for any minor differences in adhesion to the substrate.
shows multiple reflections from neighboring grains along the hydrogen-rich phase (111) Bragg peak that appeared within seconds of the initial grain transitioning. If the lattice maintains its orientation during the transformation, the Bragg peak will appear on the hydrogen-rich phase ring at a position given by the intersection of the hydrogen-rich phase ring and a line normal to the hydrogen-poor phase ring, the location of which is shown by the white “×” drawn in the middle panel. The appearance of reflections along the hydrogen-rich ring that do not coincide with this normal line construction is indicative of grains undergoing a rotation during the phase transition.

We directly observed such a rotation of a grain’s crystal lattice during its phase transition for several different grains via movement of the Bragg peak along the Debye–Scherrer ring immediately before its transition to the hydrogen-rich phase. This phenomenon is illustrated by the white arrow in Figure 1c. For the individual 2D diffraction data, see Figure S6. This lattice rotation is likely due to the dislocations nucleated19,38 to accommodate the strain resulting from the 3.5% lattice mismatch between the two phases, which is consistent with previous studies on thin films.14,16,30,40 Unfortunately, the high number of dislocations nucleated during the phase transition makes the diffraction pattern (Figure S7a) of the hydrogen-rich phase too complex to obtain a reproducible real space reconstruction. The pattern is also complicated after returning to the hydrogen-poor phase (Figure S7b), which indicates that the dislocation formation is irreversible.

Having shown that we can isolate diffraction from single grains and track them through the hydriding phase transformation, we now discuss the observed transformation dynamics occurring within specific grains. We specifically focus on the interaction of hydrogen with defects such as dislocations and grain boundaries.

Dislocations are commonly cited in the literature as acting as fast diffusion pathways for hydrogen and as trapping sites for the absorbed hydrogen atoms.14,18,38 Hydrogen interacts strongly with edge dislocations, having a binding energy of approximately 60 kJ/mol with the dislocation core.18 Edge and screw dislocations are identified with the BCDI technique via displacement field vortices where the displacement increases in a spiral from $-d_{111}/2$ to $d_{111}/2$ when measuring the (111) Bragg peak; this corresponds to a spiral phase increase of $-\pi$ to $\pi$.16,30,40 Figure 2 shows an example of a grain with a pre-existing dislocation before exposure to hydrogen. The dislocation can be identified in the measured $u_{111}$ displacement fields of the cross-sections $z_1$–$z_5$, with $z_5$ showing the end of the dislocation as the next two cross-sections, $z_6$ and $z_7$, show no displacement field vortices (Figure 2a). Each cross-section is spaced approximately 8 nm apart, and their locations within the grain are shown by the black lines in the 3D rendering of the initial grain shape (Figure 2c). The sample from which we imaged the grain was stepped through 0, 11.6, 18.1, 22.7, and 25.6 Torr $p_{H_2}$. We only show the measured $u_{111}$ for the 0 and 22.7 Torr $p_{H_2}$ steps for clarity. Based on the $u_{111}$ displacement fields, the dislocation core does not seem to have moved with...
the addition of hydrogen. We also observe no change in the $\vartheta_{111}^{u_{111}}$ strain field after hydrogen exposure (Figure 2b), implying the dislocation is not acting as a trap for hydrogen atoms. If hydrogen atoms were being trapped by the dislocation, we would have seen an increase in tensile strain in the areas around the dislocation.

Grain boundaries, like dislocations, are also commonly cited in the literature as acting as fast diffusion sites and as locations that hydrogen likes to preferentially occupy (e.g., embrittlement studies). Both characteristics seem to be dependent on the nature of the grain boundary. Based on the distribution of boundaries in the film (see Figure S1b) and on the curvature of the grain area from which the cross-sections in Figure 2 are taken, the boundary regions shown are likely high-angle in nature. We do not see any increase in tensile strain (Figure 2b) around these regions and thus conclude that the high-angle boundaries do not act as hydrogen traps in the case of Pd. We also saw no evidence of a surface-rich hydrogen layer, which would have presented itself as an increase in tensile strain throughout the grain when compared to its initial strain state. The lack of a hydrogen-rich surface layer could be evidence that the grain boundaries are acting as fast diffusion sites, as we also see some interesting dynamics occurring around the boundaries of other grains (Figures 3−5). The strain fields of other cross-sections of the same grain that are further away from the dislocation, and thus less complicated to interpret, are shown in Figure S8. These cross-sections exhibit the same absence of change in their strain field with the addition of hydrogen. The strain fields for two other grains are shown in Figure S10.

The absence of a hydrogen-rich surface layer also explains the observed lack of size dependence on the $p\text{H}_2$ at which a grain transitions to the hydrogen-rich phase (Figure 2d). The plot shown contains the measurements of 64 grains across three different Pd films. The "size" of each grain was designated as the cube root of the total grain volume calculated from the 3D reconstruction: the effective cubic length. The small variance in the transformation pressure $p\text{H}_2$ between Pd film samples could be due to small errors in the measurement or from slight differences in the adhesion of individual films to their substrate. We also saw no size dependence when we calculated the average percent strain in the grain before it transitioned to the hydrogen-rich phase (Figure S11). Thus, in the absence of plasticity events, there are no changes in the atomic displacement field prior to the phase transformation and thus no formation of a hydrogen-rich surface layer.

As shown in Figure 1a, the Pd films consist of predominantly \(\sum 3\) (111) twin boundaries and random non-CSL (coincident site lattice) boundaries, most of which are high-angle (>15° misorientation) (see Figure S1b). Of the \(\sum 3\) (111) twin boundaries, BCDI is particularly sensitive to those coherent in nature (coherent twin boundaries or CTBs). Figure 3 shows an example of a reconstructed grain containing several CTBs. This grain is from the same thin film sample as the grain in Figure 2. Missing regions in the reconstruction along with minimal phase/displacement variation (Figure 3d) at the boundaries of the missing regions are characteristics of coherent twin boundaries. The mirror in the stacking sequence of \{111\} planes (Figure 3c) causes the CBA sequence of the FCC crystal to diffract to a different reciprocal space...
location than the parent ABC sequence, resulting in the missing areas of the grain reconstruction. When the stacking reverts back to the original order, the lattice planes diﬀract back to the same location as the original sequence. The phase oﬀset between two parent regions is related to how the stacking sequence terminates when it reverts back to the original sequence. As shown schematically in Figure 3c, the width \( l \) of the missing region must be some integer \( n \) multiple of the distance \( d_{111} \) between the \{111\} atomic planes. Assuming flat interfaces for ideal CTBs and the ABC stacking sequence, the missing twin regions can have widths of \( l = 3n d_{111} \), \( l = (3n + 2) d_{111} \), and \( l = (3n + 3) d_{111} \), which respectively correspond to phase offsets of 0 or \( 2\pi \), \( 2\pi/3 \), and \( 4\pi/3 \). Note however that actual coherent twin boundaries are inherently defective with areas consisting of partial dislocations and incoherent segments. These defects along with any strain in the grain will lead to deviations from the theoretical values in the measured phase oﬀsets.

When we look at the strain field in the cross-section shown (Figure 3d), we again see no signiﬁcant changes in the strain distribution with increasing \( \text{pH}_2 \) at the surface or at the boundary regions. However, upon examination of the \( u_{111} \) displacement ﬁeld, we do see twin boundary dynamics. We observe a change in the phase oﬀsets of the twinned regions (Figure 3d) that coincides with jumps in the lattice constant with increasing \( \text{pH}_2 \) (Figure 3b). Speciﬁcally, we see a phase oﬀset change from \( \sim \frac{2\pi}{3} \) rad to \( \sim 0 \) rad between piece 1 and 2 and also between piece 2 and 3 after increasing the \( \text{pH}_2 \) from 11.6 Torr to 18.1 Torr. These changes in phase oﬀsets essentially correspond to changes in the widths of the missing twinned regions through movement of the CTBs by a few atomic planes. Such movement of the CTB along its normal direction can only be caused by the gliding of dislocations along the twin boundary plane, causing the twin width to thin or thicken by one \{111\} atomic plane while maintaining the area of the boundary plane. These dislocations can be nucleated by shear stress at either the intersection of grain boundaries with the CTBs or from partial dislocations within the twin boundaries themselves. In piece 2 of the grain at 11.6 Torr, we observed a slight increase in the displacement variation at the boundary, which could indicate the nucleation of defects within the twin boundary. These defects then disappeared along with the observed movement of the CTBs at 18.1 Torr. We also see at 18.1 Torr the beginnings of another twin, labeled as piece 5, rotating into the Pd(111) Bragg condition.

Figure 5. Rotation of small grains in and out of the Pd(111) Bragg condition. (a) 2D cross-sections of 3D diﬀraction patterns showing the change in pattern as small twins rotate in and out of the Bragg condition. The last pattern shown is very similar to the ﬁrst pattern and is reﬂected in the displacement ﬁeld cross-section shown in (b). The pattern images are a sum of all the 2D patterns taken during a scan. Note that only a few of the patterns with the most obvious changes at 19.5 and 20.4 Torr \( \text{pH}_2 \) from the data set are shown for clarity. (b) Evolution of the displacement ﬁeld \( u_{111} \) for a side view cross-section taken through the grain center. The \( \text{pH}_2 \) at which each displacement ﬁeld is measured is shown with the approximate total time spent at that pressure listed in parentheses underneath. The time listed below each displacement ﬁeld is the change in time starting from when the ﬁlm is ﬁrst exposed to hydrogen at 11.7 Torr \( \text{pH}_2 \). The 3D rendering of the initial shape of the grain at 0 Torr \( \text{pH}_2 \) is also shown. The blue arrow indicates the \{111\} scattering vector. The gray line represents the location of the substrate relative to the grain. Dislocation cores are indicated with dotted black circles.
The observed nanoscale plasticity around the CTBs is interesting, as studies have suggested that hydrogen-enhanced plasticity caused by dislocations interacting with grain boundaries is responsible for hydrogen embrittlement. One study specifically observed that the crack initiation behavior at CTBs caused by hydrogen is similar to that caused by fatigue. In the grain discussed in Figure 4 and Figure 5, we observed even more plasticity events where twins rotated in and out of the Bragg condition. In the following discussion, we stress that the displacement field changes are due to plasticity events, i.e., deformations of the crystal lattice, and not due to hydrogen-rich surface layer formation.

The grain discussed in Figure 4 and Figure 5 is from a sample where smaller ρH₂ steps (0, 11.7, 18.2, 19.5, 20.4, 21.4, 22.2, and 23.8 Torr) were used in order to better observe the grain boundary dynamics. Figure 4 shows the correlation matrix, where each entry is the average Pearson r correlation coefficient between the 3D displacement fields at different time points (see the Methods and Experimental Section), 1 being identically correlated and 0 being not correlated. From the matrix, we can see that the grain undergoes many displacement field changes, especially at 19.5 Torr ρH₂. Interestingly, we also see in the matrix a yellow rectangular region in the off-diagonal corners that indicates that at 21.4–22.2 Torr the grain returned to the same 3D displacement field state it had at 11.7–18.2 Torr. Upon examination of the individual displacement fields themselves (see Figure 5b), we see that the many changes experienced by the grain are due to it breaking up into many smaller grains separated by twin boundaries that are now rotating in and out of the Pd(111) Bragg condition.

Figure 5 shows the many changes undergone by the grain over time while exposed to hydrogen. In Figure 5a we show selected coherent diffraction patterns that illustrate the obvious changes seen in the data itself as small grains rotate in and out of the Bragg condition. We have isolated the hydrogen-poor phase diffraction pattern, and thus changes to this pattern must be caused by hydrogen-poor phase crystalline regions with the same orientation as the originally selected grain. Figure 5b shows the reconstructions of that data. A 3D rendering of the initial “parent” grain shape is also presented. Upon exposure to hydrogen gas at the first 11.7 Torr ρH₂ step, we immediately saw some of the grain volume disappear. This disappearance of Bragg electron density could be caused by crystal rotation, nucleation of the hydrogen-rich phase, crystal amorphization, or crystal restructuring to different unit cell symmetries. In this case, it is due to grain rotation, as we observe parts of the disappeared Bragg electron density reappear upon increasing the ρH₂ to 19.5 Torr. Note that the area of the initial “parent” grain that rotated away had regions of high surface curvature, as judged by the sharp rounded corners shown in the lower right region of the isosurface and cross-section, and most likely consisted of highly disordered high-angle grain boundaries. The large excess of free volume from such a disordered structure could lead to an acceleration of hydrogen diffusion. It is also interesting to note that the 11.7 Torr ρH₂ that these large changes started occurring at is well below the measured 23.8 Torr transformation pressure. Phase transformations are typically thought to only occur close to the upper spinodal pressure.

Further observation of the displacement field shows that the grain boundaries are highly mobile, as small twins are seen rotating in and out of the Pd(111) Bragg condition starting at 19.5 Torr. This “twinning” and “detwinning” process is most likely mediated by dislocation nucleation and glide around the boundary regions. For example, the “detwinning” between t = 395 min and t = 397 min likely occurred via the simultaneous nucleation of multiple dislocations at a boundary that then glide through the missing twinned region and thereby reorient it back into the parent crystal. Evidence of single dislocations nucleating at the grain boundary and then gliding through the grain can be seen in several of the displacement field cross-sections, such as at t = 379 to 383 min and t = 393 to 397 min. At t = 433 min and after increasing the ρH₂ to 20.4 Torr, the grain returns to an earlier morphological state and maintains that shape upon increasing the ρH₂ to 21.4 Torr. We do not observe any other changes at or after 21.4 Torr prior to the phase transformation, indicating that the local lattice structure around the grain has reached a local free energy minimum. Whether this same state would be reached if a single pressure step to 21.4 Torr was used remains an open question. The large plasticity experienced by this grain before the phase transition even occurs could explain the fatigue-like cracking behavior observed at CTBs in other hydrogen-embrittlement studies.

However, we note that typical embrittlement studies notice a dramatic effect after one adsorption and desorption cycle, whereas our study investigates the initial stage of the first adsorption cycle. We used BCDI to observe in situ the effects of dislocations and grain boundaries on the 3D strain and displacement field dynamics of individual Pd grains during the hydriding phase transformation. Our results show that dislocations and high-angle grain boundaries do not act as traps for hydrogen, as there is no increase in tensile strain in the surrounding areas. Grain boundaries, however, seem substantially more mobile at low concentrations of hydrogen, which combined with the lack of a hydrogen-rich surface layer suggests that they may act as fast diffusion pathways. We show that pieces of the crystalline lattice are very mobile upon exposure to hydrogen, with coherent twin boundary dynamics occurring at pressures much lower than that needed to drive the phase transformation. Such hydrogen-enhanced plasticity, which itself has implications for the mechanism of hydrogen embrittlement, along with the lack of a hydrogen-rich surface layer sheds light on the switch from the size-dependent behavior of single-crystal nanoparticles to the lower transformation pressures of bulk polycrystalline materials.

CONCLUSIONS

METHODS AND EXPERIMENTAL SECTION

Pd Film Synthesis. Pd films of ~200 nm were deposited using e-beam evaporation onto quartz substrates at a deposition rate of 2 Å/s. The samples were annealed in a N₂ atmosphere at 200 °C for 30 min in a tube furnace.

Variable Pressure Bragg Coherent Diffractive Experiment Details. Experiments were performed at Sector 34-ID-C of the Advanced Photon Source at Argonne National Laboratory. A double crystal monochromator was used to select E = 8.919 keV X-rays with 1 eV bandwidth and a longitudinal coherence length of 0.7 μm. A set of Kirkpatrick-Baez mirrors was used to focus the beam to 0.6 × 0.4 μm² (horizontal by vertical). The rocking curve around the Pd(111) Bragg peak was collected by recording 2D coherent diffraction patterns with an X-ray-sensitive area detector (Medipix2/Timepix, 256 × 256 pixels, each pixel 55 μm × 55 μm, 512 × 512 pixels for observing the hydrogen-poor to hydrogen-rich phase transition). We used an incidence angle of 15° and did not use the symmetric (specular) reflection geometry, which leads to isolated diffraction peaks by...
limiting the number of grains under X-ray illumination. The Bragg angle for this experiment was approximately 2θ = 33°. The area detector was placed a distance of 0.4 m away from the sample. A total of 64 patterns were collected over an angular range of Δθ = ±0.2° for each 3D rocking scan. Scans were done either in 1 to 2 or 3 to 6 min. Grains were selected by scanning the sample in the X-ray beam. We used an oversampling ratio of 4–6 for our measurements. This parameter is important for phase retrieval.19 To transform the film, a 4% mole fraction H2 gas in He was flowed into a gas flow cell using a mass flow controller. The hydrogen partial pressure was controlled through a combination of changing the total pressure inside the cell and diluting the H2 gas stream with N2 gas using another mass flow controller. The total pressure inside the cell was measured using a capacitance manometer.

Phase Retrieval. The phase retrieval code is adapted from published work.18,50 The hybrid input–output19,20 and error reduction algorithms were used for all reconstructions. A total of 1050 iterations, consisting of alternating 40 iterations of the hybrid input–output algorithm with 10 iterations of the error reduction algorithm, were run for all diffraction patterns. This process was repeated five times for each reconstruction with five different random starts. The best reconstruction from the series of five random starts (quantified by the smallest sharpness metric) was then used in conjunction with another random phase start as a seed for another 10 reconstructions with another set of random starts. The sharpness metric is the sum of the absolute value of the reconstruction raised to the fourth power. Five generations were used in this guided algorithm.35 The final real space image of the crystal is complex, with the amplitude corresponding to the electron density from atomic planes in a particular Bragg orientation (Bragg electron density) and the phase corresponding to the electron density from atomic planes in a particular Bragg orientation (Bragg electron density). The Bragg electron density can be thought of as the amplitude of the (111) electron density Fourier component. Provided the diffraction is separated in reciprocal space, BCDI effectively “sees” an isolated particle, although the grain resides in the thin film and is surrounded by neighbors.

Strain Field Component Calculation. The strain field component is computed from the displacement field component via

\[
\partial_{11'i11} = \frac{\partial u_{111}}{\partial x_{111}} = \nabla u_{111} \hat{Q}_{111} = \left( \frac{\partial u_{111}}{\partial x}, \frac{\partial u_{111}}{\partial y}, \frac{\partial u_{111}}{\partial z} \right) \hat{Q}_{111}
\]

where \( \hat{Q}_{111} \) is the unit vector in the [111] direction. Note that defining strain requires defining a reference (unstrained) state. We adopt the convention that the average lattice constant, determined from the Bragg peak location, defines the unstrained state. As such, in the case of this experiment, increasing the hydrogen partial pressure will result in an overall lattice expansion and thus a different average lattice constant that is defined as the unstrained state.

Note that the full strain tensor is a 3 x 3 matrix that is made up of six independent components. In this work, we can only access one of those components, as we only measure the [111] reflection and thus only know the strain along the [111] direction. To obtain the full strain tensor, we would need to measure three more or non-coplanar reflections.35,54

There is uncertainty in the strains we measure due to the phase shift that results from propagation inside the crystals.54 Given the 9 keV X-ray energy that we use in this work, the strain error due to propagation in our experiment is 10⁻⁴ (0.01%).

Pearson r Correlation Coefficient. The ability to obtain quantitative, time-dependent displacement field maps leads to analysis tools for understanding dynamics. The 3D displacement field \( u_{111} \) of each measurement was reconstructed. All of those displacement fields are then correlated with each other using the Pearson \( r \) correlation coefficient, each entry in the matrix being the computed \( r \) coefficient between two different displacement fields.15 We use \( u_{111}(m) \) and \( u_{111}(n) \) to represent the two different displacement fields being compared. The equation for computing the Pearson \( r \) correlation coefficient is

\[
r(x_i, y_j) = \frac{\sum_{i=1}^{m}(x_i - \bar{x})(y_j - \bar{y})}{\sqrt{\sum_{i=1}^{m}(x_i - \bar{x})^2 \sum_{j=1}^{n}(x_j - \bar{y})^2}}
\]

where \( x_i \) is the displacement field value for a particular pixel in the 3D displacement field \( u_{111}(m) \) and \( y_j \) is the mean value of the whole 3D displacement field \( u_{111}(n) \). The sum is evaluated over the entire 3D displacement field. By definition, every displacement field is identically correlated with itself, and hence the diagonal (where \( m = n \)) is unity. The correlation is also symmetric in \( m \) and \( n \).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b04735.

Supplementary electron microscopy images and diffraction data; displacement and strain field analysis of additional grains from those in the text (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: auulvestad@anl.gov.

ORCID

Matthew W. Kanan: 0000-0002-5932-6289

Andrew Ulvestad: 0000-0003-4611-2561

Author Contributions

A.Y. and A.U. designed and performed the BCDI experiment. A.Y. synthesized the samples. All authors contributed to interpreting the results and writing the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. Work was supported by the U.S. DOE, Basic Energy Sciences, Materials Sciences and Engineering Division (BCDI technique and analysis, phase retrieval), and by the National Science Foundation CHE-1565945 (sample synthesis, electron microscopy). The authors thank Evan Maxey for helping to design the cell and Wonsuk Cha for helping to keep the beamline in running order.

REFERENCES


