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In-situ Synchrotron X-ray Studies of the Microstructure and Stability of In_2O_3 Epitaxial Films

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We report on the synthesis, stability, and local structure of In_2O_3 thin films grown via rf-magnetron sputtering and characterized with in-situ x-ray scattering and with focused x-ray nanodiffraction. We find that In_2O_3 deposited onto (001)-oriented single crystal yttria-stabilized zirconia substrates adopts a Stranski–Krastanov growth mode at a temperature of 850°C, resulting in epitaxial, truncated square pyramids with (111) side walls. We find that at this temperature the pyramids evaporate unless they are stabilized by a low flux of In_2O_3 from the magnetron source. We also find that the internal lattice structure of one such pyramid is made up of differently-strained volumes, revealing local structural heterogeneity that may impact the properties of In_2O_3 nanostructures and films.

Epitaxial thin films offer tremendous opportunity to design a wide spectrum of properties in materials that can be tailored via targeted synthesis strategies. For example, differences in controllable growth parameters intrinsic to a specific synthesis technique can dictate the structure of the material being formed and, correspondingly, the electrical, optical, and microstructural properties. Thus, providing a window into the structural changes that occur during synthesis with in-situ structural characterization, as we do here, will help enable the design of thin film materials with precisely controlled properties.

In this work, we focus on the synthesis of films of In_2O_3 , an n-type semiconductor that has found widespread application as a transparent electronic conductor when doped with materials like Sn¹. Given its technological relevance, different methods for the synthesis of In_2O_3 thin films have been studied in detail^{2–5}, often employing yttria stabilized zirconia (YSZ) as a growth substrate because of the low lattice misfit between the two materials^{6–8}.

In various studies, it has been found that In_2O_3 forms smooth continuous films when deposited on (111)-oriented YSZ, whereas on the YSZ (001) surface at sufficiently high temperatures, In_2O_3 tends to form epitaxial “nano-pyramids” with (111) side walls and (001) flat tops^{9,10}. The origin of this unique microstructure is attributed to a difference in surface energy between the crystallographic faces of In_2O_3 ¹¹. The (111) face of In_2O_3 has the lowest surface energy as compared with the (110) or (001) faces. Formation of square flat-topped pyramids allows In_2O_3 to form (111)-oriented

facets while maintaining an epitaxial relationship with the (001) surface of the substrate. However, different microstructures of In_2O_3 films on YSZ have been observed when the free energy of In_2O_3 surfaces has been altered by varying indium or oxygen content in the growth environment¹².

Additionally, the mechanism of formation of nano-pyramids depends on the synthesis method. Studies of In_2O_3 growth on (001) YSZ by plasma-assisted molecular beam epitaxy (PA-MBE) monitored with in-situ reflection high energy electron diffraction (RHEED)⁵ indicated that under these growth conditions nano-pyramids form by Volmer-Weber growth (pyramids nucleate and grow without the formation of a full wetting layer covering the YSZ surface). Here we report on in-situ x-ray studies of In_2O_3 grown on YSZ via rf-magnetron sputtering that reveal a different growth mode that has not yet been observed in this system. We find that In_2O_3 formation on (001) YSZ follows Stranski–Krastanov (S.K.) growth, in which a thin wetting layer of In_2O_3 precedes the formation of flat-topped nano-pyramids. We find that the deposited In_2O_3 is unstable at elevated temperatures, and we describe the conditions under which it can be stabilized. After growth, we use focused x-ray beam nanodiffraction to probe structural heterogeneity within a single nano-pyramid stabilized to room temperature, demonstrating the observed growth dynamics can lead to complex local structure. These observations shed light on the nucleation and growth of In_2O_3 during sputtering, the evolution of film morphology, its stability, and the development of inhomogeneous strain states.

For this study, films were grown by rf-sputtering using an x-ray-compatible 90° off-axis magnetron growth chamber built for use at Sector 12-ID-D of the Advanced Photon Source (APS).^{13,14} Films were grown at temper-

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FIG. 1. Intensity oscillations measured at the specular CTR from a YSZ (111) surface at a $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ positions during the deposition of an In_2O_3 at 850°C via magnetron sputtering.

atures of 850°C in a gas mixture of 70% Ar / 30% O_2 at a pressure of 30 mTorr, corresponding to an oxygen partial pressure of 9 mTorr (1.2 Pa). During the growth process, 16 keV x-rays were utilized to perform grazing-incidence and high-angle x-ray scattering measurements as a function of time. During these measurements, intensity variations on and about the substrate crystal truncation rod (CTR) were monitored with an x-ray area detector. Time-dependent changes in the CTR and adjacent diffuse scattering were used to characterize film growth modes. Intensity changes in the grazing incidence small angle x-ray scattering (GISAXS) patterns were used to monitor the average morphology of the film during synthesis. In-plane, grazing incidence, reciprocal space scans and non-specular CTR scans were used to establish the strain state and crystal orientation of the films. Focused x-ray beam raster scans were performed at the HXN beamline at the NSLS-II synchrotron using a ~ 50 -nm-diameter (FWHM) beam (10.4 keV energy) to map strain heterogeneity within an individual nano-pyramid stabilized to room temperature.^{15,16} Sputtering of In_2O_3 on both (111)- and (001)-oriented single crystal YSZ substrates was studied, resulting in smooth films and in truncated nano-pyramids. We describe both cases here, but focus primarily on the growth, stabilization, and microstructure of nano-pyramids.

Fig. 1 shows intensity oscillations measured at the specular CTR of a (111)-orientated YSZ substrate during the deposition of In_2O_3 at 850°C . The intensity oscillations shown in red were measured at the $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ specular CTR position (YSZ reciprocal lattice units) and are plotted alongside the integrated diffuse intensity (blue curve) recorded adjacent to the CTR. Heteroepitaxial growth oscillations with a period of ~ 70 s persist in the specular CTR intensity throughout the deposition. At the YSZ $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$ position on the specular CTR, one heteroepitaxial growth oscillation corresponds to an increase in film thickness of $\frac{3}{2}$ unit cells of In_2O_3 in the (111) direction or $(\frac{3}{2\sqrt{3}} \times a_o^{\text{In}_2\text{O}_3})$ where the bulk value of $a_o^{\text{In}_2\text{O}_3} = 10.114 \text{ \AA}$.⁶ During the first 80 seconds of

FIG. 2. Intensity oscillations measured at the specular CTR from a YSZ (001) surface at a $(0, 0, \frac{1}{3})$ positions during the deposition of In_2O_3 at 850°C .

growth, the heteroepitaxial CTR growth oscillations are modulated by shorter period homoepitaxial growth oscillations, each corresponding to a thickness increase of $\sim \frac{1}{2}$ unit cell of In_2O_3 in the (111) direction. In this initial stage of growth, oscillations are also present in the diffuse scattering intensity, indicating that the film grew in a layer-by-layer mode up to a thickness of ~ 1.13 units cells¹⁷. The disappearance of the short-period oscillations in both the CTR and diffuse intensity after 80s indicate a transition to step-flow growth. The heteroepitaxial growth oscillations persist after the transition to step-flow-growth due to interference between x-rays reflecting off the top and bottom interfaces of the film as it grows.¹⁸ Though we observed a change in growth mode, the In_2O_3 deposited on (111) YSZ retained a smooth film morphology, consistent with previous findings, and in contrast to what is expected on (001) YSZ substrates.

Fig. 2 shows integrated CTR and adjacent diffuse scattering (red and blue curves respectively) measured at the specular $(0, 0, \frac{1}{3})$ position from a YSZ (001)-oriented substrate during deposition of In_2O_3 . As compared to growth on (111) surfaces, these intensity traces do not provide a conclusive fingerprint of the underlying growth process. To capture the details of the evolving film morphology, we utilize GISAXS patterns measured during growth. GISAXS encodes information about the average morphology of the film in the illuminated volume. In this experiment, the grazing incidence beam was aligned with the YSZ [110] direction such that the specular CTR and CTR streaks originating from the (111) pyramid facets were simultaneously captured on the detector. This experiment took advantage of the fact that the (111) pyramid walls of all islands were identically oriented, intersecting the substrate along a [110] YSZ direction. This island geometry was verified by post-growth atomic force microscopy (AFM) of a stabilized In_2O_3 film. A representative image is shown in Fig. 3(a). In GISAXS patterns from the nano-pyramids, the angled (111) side facets are expected to produce CTR streaks at 54.7° .^{19,20} Additionally, the specular CTR will be visible in the pattern. The time evolution of the intensity

FIG. 3. (a) Representative AFM image of In_2O_3 pyramids on a YSZ (001) surface showing that the nano-pyramids adopt the same orientation relative to the substrate. Also shown is the relative orientation of the x-ray beam during GISAXS measurements. (b) an in-situ GISAXS pattern measured prior to the growth on In_2O_3 . (c) a typical in-situ GISAXS pattern measured during the growth of In_2O_3 pyramids on a YSZ (001) surface at 850°C . The inset shows a GISAXS simulation of truncated square pyramids that agrees well with experiment (q -axes same as experimental pattern).

of both the pyramidal facet and specular CTRs reveals details about the formation of the film nanostructure.

A typical GISAXS pattern measured after 200 seconds of growth is shown in Fig 3(c), after the nano-pyramids are fully formed. Diagonal CTRs in the pattern originating from the pyramid side walls are seen (one of which is bound by ROI 2), as well as the specular CTR (bound by ROI 1). The experimentally measured pattern compares well to a GISAXS simulation (Fig 3c inset) of a population of truncated square pyramids with heights ranging from 30-50 nm calculated with the BornAgain software package²¹. This good correspondence verifies that the in-situ GISAXS measurements can be used to identify pyramid formation and growth. For comparison, a GISAXS pattern measured prior to growth is shown in Fig. 3(b), showing no (111) streaks.

Fig. 4 shows integrated intensity from regions of the GISAXS pattern sensitive to the low-angle CTR and (111) pyramid facets as a function of growth time (respectfully, ROI 1 and ROI 2 in Fig 3(b)). The initial stage of growth (labeled regime I in the plot) features ~ 1.5 heteroepitaxial growth oscillations of the specular CTR, is marked by the absence of (111) side-wall streaks, and lasts 25 seconds. A transition in the characteristics of the growth occurs after this point (labeled regime II) in which the low angle CTR intensity rises monotonically rather than oscillating, and pyramidal facet streaks appear and grow in intensity. The observed behavior indicates that the In_2O_3 pyramids form via the S.K. growth mechanism, in which a thin layer of In_2O_3 first wets the YSZ surface (regime I) followed by a transition to nano-pyramid nucleation and growth driven by difference in

FIG. 4. Intensity extracted from different regions of a GISAXS scattering pattern during In_2O_3 growth. The red line shows intensity from the low angle specular CTR and the blue shows intensity from the angled side streaks (scaled by $5\times$). The black dashed line marks the opening of the shutter to the In_2O_3 source.

FIG. 5. Intensity extracted from the low angled specular region (red) and the angled side streak region (blue) of a GISAXS pattern during the growth and the subsequent evaporation of In_2O_3 at 850°C . The black dashed line marks the opening and closing of the shutter to the In_2O_3 source.

free energy between the crystallographic faces of In_2O_3 ²² (regime II). This growth mode has not previously been reported in In_2O_3 thin films, and is likely specifically related to the reactive sputtering growth environment.

Once formed, however, we find that In_2O_3 films decompose at the $\sim 850^\circ\text{C}$ growth temperature, unless stabilized or quenched to room temperature. Fig. 5 shows regimes I and II (as in Fig. 4, but for another film grown under similar conditions) after which the In_2O_3 sputtering source was shuttered, halting growth²³. Once the shutter was closed, subsequent changes in the GISAXS ROI intensities suggest that the In_2O_3 islands first ripen then evaporate, indicated by regimes III and IV respectively. Regime III shows an abrupt drop of intensity of the specular CTR followed by an intensity rise. Concurrently, the (111) CTRs also gain intensity. This behavior is consistent with (001)-oriented In_2O_3 surfaces being less stable than (111)-oriented surfaces at high temperature. Under such circumstances, one can ex-

pect the (001)-oriented wetting layer to both evaporate into the environment and diffuse to incorporate into the nano-pyramids. This causes the initial intensity drop of the specular CTR, followed by an increase in specular and (111) CTR intensities as the nano-pyramids briefly ripen. After the wetting layer disappears, both the specular and (111) CTR intensities drop (regime IV) during film evaporation, indicating that under these conditions neither the (001)- or (111)-oriented In_2O_3 surfaces are fully stable.

However, we find that providing a low-power flux of In_2O_3 from the sputtering target counteracts evaporation at the growth temperature and stabilizes the film. Referring again to Fig. 4, we show that after growth regimes I and II, in which the power supplied to the sputtering source was 30W, the intensities measured from ROIs 1 and 2 of the GISAXS pattern stabilize and no longer evolve so long as a sputtering power of 7-9W was maintained (regime V). This film stabilization strategy allowed us to measure In_2O_3 Bragg peaks at the growth temperature and confirm that the In_2O_3 film had a bixbyite structure that was epitaxially oriented relative the YSZ substrate and had a lattice parameter corresponding to bulk In_2O_3 (*i.e.* a relaxed lattice). Stabilizing the pyramids in this manner during cooling also enabled the film structure to persist in ambient conditions, allowing for ex-situ study of lattice characteristics within an individual nano-pyramid using focused x-rays.

Fig 6 shows the pronounced heterogeneity of strain within a single epitaxial In_2O_3 nano-pyramid as revealed by scanning nanodiffraction measurements. Fig 6(a) shows the experimental geometry employed in which a ~ 50 -nm-diameter focused beam illuminates a single In_2O_3 nano-pyramid. Diffraction near the In_2O_3 (004) Bragg peak was mapped as a function of position by rastering the sample in 50 nm steps while simultaneously mapping indium fluorescence. The sample was scanned in the x, z plane as indicated. The Bragg angle for the (004) reflection was 13.6° , and at this fixed angle a raster scan will create an “edge-on” image of the pyramid resulting in a triangular shape. The fluorescence map in Fig 6(c) shows the indium distribution of the nano-pyramid studied here. The white contour delineates its border. A summation of all (004) diffraction patterns measured at scan positions within this contour is shown in Fig 6(b). Four individual diffraction patterns measured at different locations within the pyramid and representative of those used to make Fig 6(b) are shown in Fig 7. This pattern shows two peaks originating from the pyramid, the primary peak along the specular (00L) CTR, corresponding to the unstrained bulk In_2O_3 lattice parameter $a_o^{\text{In}_2\text{O}_3}$, as well as a weaker peak located off the CTR. The off-CTR peak corresponds to strained In_2O_3 with an out-of-plane lattice parameter that is contracted by 1.8% relative to the bulk, and with an orientation that is tilted by 0.7° along a $\langle 110 \rangle$ In_2O_3 direction (normal to the scattering plane). This likely corresponds to a volume of the nano-pyramid that is not yet fully relaxed and

FIG. 6. a) A schematic of the scanning x-ray beam nanodiffraction measurement wherein the sample was oriented to satisfy the In_2O_3 (004) Bragg condition in the horizontal scattering plane. b) A summation of 70 diffraction patterns measured at different locations on a single In_2O_3 nano-pyramid with a 10.4 keV 50-nm-diameter x-ray beam. The detector field of view shown spans $1.9^\circ \times 1.5^\circ$ along q_x, q_z respectively. A map of In fluorescence measured at every scan point is shown in c). The two diffraction ROIs shown in (b) were used to make the integrated intensity maps in (d,e) which correspond to In_2O_3 (004) film peaks on and off the specular CTR respectively. (Individual diffraction patterns from several scan positions are shown in Fig 7.)

is accommodating in-plane epitaxial strain. We support this claim by pointing out that in Reference¹⁰, partially-relaxed In_2O_3 islands of comparable size grown on YSZ were shown to also adopt a similar lattice tilt of 0.9° along the $\langle 110 \rangle$ direction, and an out-of-plane contraction of lattice parameter of up to 1.2% was observed, corroborating predictions based on elastic energy calculations.

These two diffracting features originate from different volumes of the nano-pyramid, as shown in Fig 6(d),(e). These plots were generated by mapping the integrated counts within the regions bounded with white and black boxes in Fig 6(b) as a function of scan position at the Bragg peak. We see that the relaxed peak intensity (Fig 6(d)) varies substantially within the island in a manner distinct from the In fluorescence, which represents the material volume illuminated at each point. The higher integrated counts of the relaxed peak found near the base in the center of the pyramid reveals a region of lower defect content. We also observe a localized volume of the nano-pyramid that produces the off-CTR peak, with the lattice tilt and out-of-plane strain state described above, that maintains a degree of lattice matching with the substrate. Finally, weak In_2O_3 scattering on the CTR also appears uniformly on the sample surrounding the In_2O_3 pyramid, providing additional evidence of the S.K.

FIG. 7. Four positions from the scan of the In_2O_3 are shown (green dots in (a)) overlaid onto the In L-edge fluorescence map. The In_2O_3 (004) nano-diffraction patterns from each of these positions are shown in (b).

wetting layer that persisted through stabilization and quenching. This behavior suggests that the dynamics of In_2O_3 island formation, stabilization, and quenching involve non-trivial and inhomogeneous strain states¹⁰.

Through x-ray measurements, we have observed that In_2O_3 sputter-deposited on (001)-oriented YSZ at 850°C adopts an S.K. growth mode, which transitions from a thin wetting layer to the growth of epitaxial faceted flat-topped nano-pyramids with inhomogeneous internal strain. At the growth temperature, we find that the In_2O_3 film is unstable and will evaporate in different stages within minutes unless stabilized by continuously supplying In_2O_3 . Previous studies of In_2O_3 growth on (001) YSZ via PA-MBE observed a different growth mode behavior that was shown to be sensitive to environmental variables such as growth temperature, growth rate, and the ratio of indium to oxygen in the environment. Growth via magnetron sputtering provides a different set of environmental variables (e.g. ion energy, means of oxidation) that give rise to new synthesis pathways through which nucleation, growth, morphology, and local strain state can potentially be tuned in this and other technologically relevant oxide films. We conclude by pointing out that further insight as to the local structural details of S.K. growth can be gained by follow-up in-situ nano-focused x-ray beam studies. For example, a measurement such as in-situ micro-XAS (x-ray absorption spectroscopy)²⁴ performed at the In L-edge would provide pixel-resolved absorption edge spectra that could reveal whether fluctuations in local stoichiometry influence the growth mode transition. In-situ capabilities amenable to such an experiment are currently being developed at NSLS-II and APS.

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- ¹J. Gao, K. Kempa, M. Giersig, E. M. Akinoglu, B. Han, and R. Li, *Advances in Physics* **65**, 553 (2016).
- ²A. Bourlange, D. J. Payne, R. M. J. Jacobs, R. G. Egdel, J. S. Foord, A. Schertel, P. J. Dobson, and J. L. Hutchison, *Chemistry of Materials* **20**, 4551 (2008).
- ³O. Bierwagen and J. S. Speck, *Journal of Applied Physics* **107**, 113519 (2010).
- ⁴M. V. Hohmann, P. Ágoston, A. Wachau, T. J. M. Bayer, J. Brötz, K. Albe, and A. Klein, *Journal of Physics: Condensed Matter* **23**, 334203 (2011).
- ⁵O. Bierwagen, J. Rombach, and J. S. Speck, *Journal of Physics: Condensed Matter* **28**, 224006 (2016).
- ⁶S. B. Qadri and H. Kim, *Journal of Applied Physics* **92**, 227 (2002).
- ⁷H. Hayashi, T. Saitou, N. Maruyama, H. Inaba, K. KAWAMURA, and M. MORI, *Solid State Ionics* **176**, 613 (2005).
- ⁸ In_2O_3 has a bixbyite structure and a room temperature bulk lattice parameter of 10.114 Å. When grown on YSZ (bulk lattice parameter of 5.142 Å for 9.5 mol. % Y_2O_3 composition, In_2O_3 epitaxial thin films experience 1.2% tensile strain due to the 2-to-1 correspondence of film and substrate lattice parameters ().
- ⁹K. H. L. Zhang, V. K. Lazarov, H. H. C. Lai, and R. G. Egdel, *Journal of Crystal Growth* **318**, 345 (2011).
- ¹⁰K. H. L. Zhang, A. Bourlange, R. G. Egdel, S. P. Collins, R. J. Bean, I. K. Robinson, and R. A. Cowley, *ACS Nano* **6**, 6717 (2012).
- ¹¹K. H. L. Zhang, A. Walsh, C. R. A. Catlow, V. K. Lazarov, and R. G. Egdel, *Nano Letters* **10**, 3740 (2010).
- ¹²O. Bierwagen and J. S. Speck, *Journal of Applied Physics* **107**, 113519 (2010).
- ¹³C. M. Folkman, M. J. Highland, E. Perret, S. K. Kim, T. T. Fister, H. Zhou, P. M. Baldo, S. Seifert, J. A. Eastman, P. H. Fuoss, and D. D. Fong, *Review of Scientific Instruments* **84**, 025111 (2013).
- ¹⁴M. J. Highland, E. Perret, C. M. Folkman, D. D. Fong, C. Thompson, P. H. Fuoss, and J. A. Eastman, *Crystal Growth & Design* **16**, 6812 (2016).
- ¹⁵H. Yan, E. Nazaretski, K. Lauer, X. Huang, U. Wagner, C. Rau, M. Yusuf, I. Robinson, S. Kalbfleisch, L. Li, N. Bouet, J. Zhou, R. Conley, and Y. S. Chu, *Scientific Reports* **6**, a000596 (2016).
- ¹⁶E. Nazaretski, H. Yan, K. Lauer, N. Bouet, X. Huang, W. Xu, J. Zhou, D. Shu, and Y. S. Hwu, Y. and Chu, *Journal of Synchrotron Radiation*.
- ¹⁷J. Als-Nielsen and D. McMorrow, *Elements of Modern X-ray Physics* (Wiley, 2011).
- ¹⁸G. B. Stephenson, D. D. Fong, M. V. Ramana Murty, S. K. Streiffer, J. A. Eastman, O. Auciello, P. H. Fuoss, A. Munkholm, M. E. M. Aanerud, and C. Thompson, *Physica B: Condensed Matter* **336**, 81 (2003).
- ¹⁹G. Renaud, R. Lazzari, C. Revenant, A. Barbier, M. Noblet, O. Ulrich, F. Leroy, J. Jupille, Y. Borensztein, C. R. Henry, J.-P. Deville, F. Scheurer, J. Mane-Mane, and O. Fruchart, *Science* **300**, 1416 (2003).
- ²⁰G. Renaud, R. Lazzari, and F. Leroy, *Surface Science Reports* **64**, 255 (2009).
- ²¹J. Burle, C. Durniak, J. M. Fisher, M. Ganeva, G. Pospelov, W. Van Herck, and J. Wuttke, , version 1.81.
- ²²S. A. Chambers, *Surface Science Reports* **39**, 105 (2000).
- ²³We note that differences in the regime I growth behavior between the samples in Fig. 4 and 5 are due to differences in the roughness of the YSZ substrate surface ().
- ²⁴S. Pascarelli, O. Mathon, M. Munoz, T. Mairs, and J. Susini, *Journal of Synchrotron Radiation* **13**, 351 (2006).