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Ferroelastic twin structures in epitaxial WO₃ thin films

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Tungsten trioxide is a binary oxide that has potential applications in electrochromic windows, gas sensors, photo-catalysts, and superconductivity. Here, we analyze the crystal structure of atomically flat epitaxial layers on YAlO₃ single crystal substrates and perform nanoscale investigations of the ferroelastic twins revealing a hierarchical structure at multiple length scales. We have found that the finest stripe ferroelastic twin walls along pseudocubic (100) axes are associated with cooperative mosaic rotations of the monoclinic films and the larger stripe domains along pseudocubic (110) axes are created to reduce the misfit strain through a commensurate matching of an effective in-plane lattice parameter between film and substrate. The typical widths of the two fine and larger stripe domains increase with film thickness following a power law with scaling exponents of ~0.6 and ~0.4, respectively. We have also found that the twin structure can be readily influenced by illumination with an electron beam or a tip-based mechanical compression. © 2015 AIP Publishing LLC.

In recent years, much attention has been paid to twin/domain walls as a low dimensional mesoscopic entity exhibiting exotic physical properties distinct from bulk properties.¹–¹³ One of the noticeable materials to illustrate the significance of twin walls is tungsten trioxide (WO₃). Many interesting phenomena at ferroelastic twin walls have been discovered such as electronic conduction in contrast to the insulating bulk,¹⁴ superconductivity at low temperatures,¹⁵ and ionic migration.¹⁶,¹⁷ Moreover, alkali-metal doped or oxygen reduced WO₃ occupies 5d orbitals of tungsten ions as an n-type conductor¹⁸–²² that might further expand the versatile features of twin wall. However, until now, the usability has been mainly studied based on bulk crystals or nano-structures,²³–²⁷ and few studies have been made on epitaxial films.²⁸–³¹ Furthermore, creation of the twin wall structure in an epitaxial WO₃ film has not been achieved yet. This is a clear limitation to further advance our understanding of twin wall functionalities and explore new possibilities in this material. Advantages of epitaxial films associated with controllable thickness, effects of heteroepitaxial interface including misfit strain, tunability of the orientation, and periodicity of domain walls can be broadly beneficial to the manipulation of the inherent functionalities of WO₃.

In this paper, we report on the crystal structure of epitaxial WO₃ layers on a nearly matched (110)ₖ (hereafter the subscript “₀” represents the orthorhombic index) surface of YAlO₃ substrate. We have found that atomically flat epitaxial films show an exotic ferroelastic twin domain arrangement with a hierarchical structure at multiple length scales made of monoclinic building blocks. These ferroelastic domains sensitively respond to electron beam irradiation and mechanical pressure.

In our experiments (for the details of experimental methods, see Ref. 32), WO₃ thin films were grown on (110)ₖ-oriented YAlO₃ substrates (orthorhombic, a = 5.18 Å, b = 5.31 Å, c = 7.35 Å, √2apc × √2apc × √2apc) by pulsed laser deposition. WO₃ has a crystal structure similar to the ABO₃ perovskite except for an empty A-site, which undergoes various structural transitions with temperature variation (monoclinic → triclinic → monoclinic → orthorhombic → tetragonal with increasing temperature).³³,³⁴ Near room temperature, there are two competing phases called γ-WO₃ and δ-WO₃. The γ-WO₃ has a monoclinic crystal structure (space group P2₁/n, a = 7.306 Å, b = 7.540 Å, c = 7.692 Å, β = 90.88°) with a volume of ∼2apc × ∼2apc × ∼2apc, where apc is a pseudocubic lattice parameter (hereafter the subscript “pc” represents the pseudocubic cell),³⁵ exhibiting its peculiar twin structure.³⁵ The δ-WO₃ is triclinic with lattice parameters (P₁, a = 7.309 Å, b = 7.522 Å, c = 7.678 Å, α = 88.81°, β = 90.92°, γ = 90.93°).³⁶

A representative surface topographic image of a 610-nm-thick WO₃ film exhibits a well aligned ferroelastic twin structure with a herringbone pattern (Fig. 1(a)). The twin domains have a width of ~30 nm, which is more clearly recognized in the AFM deflection contrast representing the slope of height (Fig. 1(b)). Since the fast scan axis of the AFM tip was parallel to the [001]ₖ axis, the contrast for only the [110]ₖ-axis-parallel fine stripe domains (fine-domains) is clearly identified in the deflection image. A schematic of the herringbone twin structure in Fig. 1(c) shows the fine stripe

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domains parallel to [001]₀ or [110]₀ axes at a length scale of a few 10 nm. Larger stripe macro-domains, which are rotated by ±45° relative to the fine domain walls, are present at a larger length scale (a few 100 nm), and they can be classified into two variants in terms of the aligning axes. Furthermore, orthogonal bundles of the macro-domains, each of which contains a single variant of stripe macro-domains, are found at a few micron length scales. The bumpy twin walls were observed at the boundaries between two adjacent bundles creating the irregular shaped super-macro-domain structure (Fig. 1(d)).

To investigate the microscopic origin for the hierarchical twin structure, we characterized the crystal structure through x-ray θ-2θ scans and reciprocal space maps (RSMs) for a 200-nm-thick film. In Fig. 2(a), the θ-2θ scan exhibits the (001)₀pc and (002)₀pc diffraction peaks of the WO₃ film. The out-of-plane lattice parameter of the WO₃ film was determined to be 3.84(8) Å, which is almost the same as the bulk c-axis pseudocubic lattice parameter of the monoclinic phase (3.84(6) Å). Besides, the full-width-at-half-maximum (FWHM) of the small range ω-rocking curve measured at the (001)₀pc WO₃ peak (inset of Fig. 2(a)) was 0.061°. In addition to this sharp central peak, a larger range scan revealed the existence of two satellite peaks at off-axis ω-angles of ±0.82° (see Fig. S2(b) in Ref. 32). This can be clearer in a RSM for the (002)₀pc reflection in the HL-plane (Fig. 2(b)). Accordingly, we know that the ab-plane of the film is not exactly parallel to the substrate but tilted by χ ~0.82° and there are four variants in terms of the tilt directions. It is also worthwhile mentioning that this mosaic tilt angle of ~0.82° detected in this thick-thickness regime (>100 nm) is gradually reduced with film thickness and eventually the tilt becomes negligible when films are thinner than ~50 nm.

To further clarify the crystal structure including in-plane lattice parameters, RSMs for two asymmetric peaks (103)₀pc and (113)₀pc were measured for the 200-nm-thick film (Figs. 2(c) and 2(d)). To interpret the RSMs, we first consider a model of pseudocubic unit cell imposed by a monoclinic distortion similar to the monoclinic unit cell of bulk WO₃ (M₀ in Fig. 2(e)). Given a monoclinic angle β and four-fold twins, RSMs for {H0L}₀pc or {K0L}₀pc reflections of M₀ result in three split peaks (red crosses in Fig. 2(c)). Two of them ((H0L)₀pc and (-H0L)₀pc) are shifted toward −L or +L directions by an equal k-space distance away from the expected pseudo-tetragonal position deduced from (00L)₀pc peaks; the
in-plane H position of them gives the reciprocal of the a-axis lattice parameter and the extent of splitting is related to the monoclinic angle $\beta$. In addition, the third peak detected at the expected L without any shift corresponds to \{0KL\}$_{pc}$ reflections. The in-plane k-space position of the peak gives information of b-axis lattice parameter. To ensure the model of unit cell, we would also check the peak positions of \{HHL\}$_{pc}$ reflections. If the model is correct, the peaks of \{HHL\}$_{pc}$ should be split into two variant peaks and the amount of split along L-axis should harmonize with the aforementioned L-split between (H0L)$_{pc}$ and (–H0L)$_{pc}$ peaks.

With this in mind, we next extract the lattice parameters of the WO$_3$ thin film from the measured RSMs. Different from the usual peak split tendency, both the RSMs in this case seemed to produce the peak split along the horizontal H-axis rather than the L-axis. It arose from the fact that the normal of ab-plane of film was tilted by $\pm0.82^\circ$ with respect to the normal of substrate creating four-fold mosaic domains. Thus, the experimental results, which at first seemed to be different from the expectation, can now be understood by introducing mosaic tilts into the interpretation. The (103)$_{pc}$ and (103)$_{pc}$ peaks were rotated around the K-axis by $-0.82^\circ$ and $+0.82^\circ$, respectively. Being traced along powder arcs to recover the case without the mosaic tilt, the original k-space positions could be found and marked by red crosses on the maps (Fig. 2).

With the monoclinic structural model, we could determine the pseudocubic lattice parameters of the WO$_3$ thin film to be $a = 3.65(6)$ Å, $b = 3.75(9)$ Å, $c = 3.84(8)$ Å, and $\beta = 89.1(7)^\circ$. We note that the deviation of monoclinic angle ($\beta$) from 90° has a very similar value to the tilt angle ($\gamma \sim 0.82^\circ$). In fact, the appearance of split peaks coincidentally along the horizontal axis stems from the following situation. As described in the schematic (Fig. 2(e)), the monoclinic unit cell of the WO$_3$ film is rotated around the local b-axis so that the c-direction is perpendicular to substrate. This happens because sharing the same c-axis of neighboring fine domains is favorable for minimizing the elastic deformation at the twin walls. It was also found that the (103)$_{pc}$ and (103)$_{pc}$ peaks subject to the mosaic rotation were of diffuse shape along the horizontal reciprocal axis in accordance with the vertical twin walls separated by the short width of fine domains (a few 10 nm). On these grounds, we can conclude that the origin of the fine twin domains is due to the cooperative mosaic tilt of monoclinic unit cells, thereby producing $+a$ and $-a$ fine domains. On the other hand, the a-axis lattice parameter was slightly smaller than that of the substrate, while the b-axis lattice parameter was larger. A recurring appearance of a-axis and b-axis domains, i.e., the macro-domain structure, is necessary to effectively minimize interfacial misfit strain energy with the substrate offering a nearly matched interface on average.

To investigate the cross sectional area of a WO$_3$ film, a transmission electron microscopy (TEM) study was performed for a 70-nm-thick WO$_3$ film (Fig. 3). In the weak-beam-dark-field (WBDF) TEM image of the as-prepared sample with a zone axis along [001]$_o$, (Fig. 3(a)), strained-pillar structures were recognized through the contrast depending on local strain. The widths of pillars were measured to be less than 10 nm. Although these dense twin walls can be attributed to the relatively thin thickness of the film as compared to the film used for the AFM image, one should be cautious to conclude that the measured width in TEM represents the fine-domain width of the film accurately. The TEM specimen was fabricated in a way that the foil thickness along the zone axis was very thin for electron transmission, which would lead to a different mechanical boundary condition from that of the as-grown film. In reality, the twin structure observed at the initial stage in the film was easily relaxed by illumination with a weak electron beam with a flux of 14 pA/cm$^2$ (Fig. 3(b)). The illumination gradually removed twin walls and associated individual fine domains to form remaining larger domains. The susceptibility of the twin structure to external perturbation leads us to conjecture that the twin walls are primarily involved in large strains and strain gradients being less relevant to interfacial reconstruction or/and defect accumulation in this thin film. The instability of twin walls in TEM specimen did not allow careful high-resolution TEM studies on the twin walls, but it was possible to examine the relaxed phase of WO$_3$ regarding the epitaxial coherency and interfacial structure between film and substrate. Figure 3(c) shows a Z-contrast high-angle-Anular-dark-field scanning TEM (HAADF-STEM) image for an interfacial region. It was observed that a WO$_2$ sub-layer was formed right on the YO layer of the substrate and W atoms occupied only the B-sites of the perovskite keeping the A-site empty. Figure 3(d) shows a selected-area-electron-diffraction (SAED) pattern for the interfacial region. The red spots can be indexed to the diffraction peaks of WO$_3$ and the green spots to the ones of YAlO$_3$. The detection of exact square reciprocal cell of WO$_3$ indicates the monoclinic $ca$-plane in this relaxed film was parallel to the zone axis. Misalignment between the reciprocal cells of YAlO$_3$ and WO$_3$ by $\sim1.5^\circ$ along the horizontal reciprocal axis indicates...
that the pseudocubic c-axis of substrate makes an angle of \( \sim 1.5^\circ \) with that of the film, which is expected in the orthorhombic substrate.

Next, the thickness dependence of the fine- and macro-domain widths was examined using multiple samples with different thicknesses. As examples, in-plane piezoresponse force microscopy (PFM) images of four representative samples with thicknesses of 42 nm, 81 nm, 202 nm and \( \sim 400 \text{nm} \) are shown in Figs. 4(a)–4(d). Remarkably, macro-domains were visible in the PFM images enabling us to evaluate their macro-domain widths by Fourier-transforming the PFM images (insets of Figs. 4(a)–4(d)).

Because the monoclinic phase of WO\(_3\) with a space group of \( P2_1/n \) is centrosymmetric, the significant enhancement of piezoresponse on either side of macro-domain walls is unexpected. It is most likely due to the fact that the twin wall areas are subject to large deformation against the nearby macro-domain lowering local symmetry. Moreover, films under the mosaic tilt are expected to create a large strain gradient to reconcile with flat substrates underneath, leading to the involvement of flexoelectric polarizations. It has been found that an oxygen deficient sheet layer can be a non-centrosymmetric tetragonal phase. A more rigorous mechanism of the unusual piezoresponse and microscopic atomic arrangements at the twin walls and interfaces still remain unexplored.

The double logarithmic plot of domain widths versus film thickness was carefully obtained (Fig. 4(e)). The linear slope in the log-log plot determines the scaling exponent to be \( 0.60 (\pm 0.01) \) for the macro-domain. Similarly, the value of the fine-domain is determined to be \( 0.42 (\pm 0.05) \). These scaling exponents significantly deviate from the 0.5 expected in the typical Landau-Lifschitz-Kittel law. Similar deviation has been reported in the ferroelectric domains of multiferroic BiFeO\(_3\); irregular domain walls characterized by a roughness exponent and a fractal Hausdorff dimension exhibit the domain size scaling with an exponent \( \sim 0.6 \). It will be an interesting topic to investigate the fractal-like behavior in this hierarchical twin structure in future studies.

Finally, we address the rearrangement of the macro-domains by the AFM tip-based mechanical force. For an as-grown 53-nm-thick WO\(_3\) film, in-plane PFM image was captured to visualize (at nominally low loading force of approximately 50–100 nN) the initial ferroelastic domain microstructure as shown by Figure 5(a). Thereafter, within the initially visualized region (shown by dashed-line frame in Figs. 5(a) and 5(b)), a contact mode scan with a grounded AFM-tip exerting a comparatively high-loading force of approximately 2.5 \( \mu \text{N} \) was performed. All fast scan axes are along [1\( \bar{1} \)0]\(_{\text{w}}\), including the compressive scan. In Fig. 5(a), super-macro-domain boundaries are indicated by white solid lines in the selected area (the dashed box). After scanning the dashed-line region with a compressive force of 2.5 \( \mu \text{N} \), the in-plane PFM image (Fig. 5(b)) was captured under the same conditions as before, and allows a direct comparison between the pre- and post-loading images. As shown in the (b) in-plane PFM images, macro-domains were rearranged by the mechanical force. All the white scale bars indicate 500 nm.

**FIG. 4.** Thickness-dependent domain widths. (a)–(d) In-plane PFM images at the selected WO\(_3\) thicknesses. The interval between neighboring bright (or dark) contrasts corresponds to the macro-domain width. It has a tendency to be wider with increasing film thickness. Bright (dark) contrast represents in-plane piezoresponse pointing to the positive (negative) vertical direction. Tip orientations during measurements are depicted at the right corner. All the scale bars indicate 500 nm. (Inset) The Fourier transform of the in-plane PFM image. All the Fourier transform images have the same size and the unit of tick labels in (d) is \( \text{mm}^{-1} \). (e) The double logarithmic plot of the macro-domain \( (m) \) and fine-domain \( (f) \) widths versus the film thickness. Because of the AFM resolution limit, fine-domain widths of four samples were obtained through AFM images (solid blue circles), and the others from the horizontal satellite peaks observed in the H-scans of x-ray diffraction (open blue circles).

**FIG. 5.** Domain reorientation induced by the AFM tip-based nano-mechanical force. (a) In-plane PFM image in the as-grown state of a 53-nm-thick WO\(_3\) film. The orientation of AFM tip during the experiment is expressed by the tip cartoon. Fast scan axis of the tip was along [1\( \bar{1} \)0]\(_{\text{w}}\), and the slow scan direction was [001]\(_{\text{w}}\). Dashed-line box represents the area where the scan with a loading force of 2.5 \( \mu \text{N} \) was performed. White solid lines are super-macro-domain boundaries. As shown in the (b) in-plane PFM images, macro-domains were rearranged by the mechanical force. All the white scale bars indicate 500 nm.
comparison with initially observed domain-microstructure. Within the area where a high mechanical pressure was applied, the super-macro-domains and their boundaries were displaced, which means mechanical-force induced rearrangements of macro-domains (Fig. 5(b)). Because the irregular-shaped bundles do not fit with each other exactly, some local domains and their boundaries near the edges of the super-macro-domains could be highly strained. The more unstable boundaries are likely to be rearranged toward the stable state.

In summary, the comprehensive structural study of epitaxial WO₃ thin films on YAlO₃ substrates provided useful insights into their inter-relevance among the monoclinic cell, four-fold mosaic tilt, misfit strain, and the emergence of a ferroelastic hierarchical twin structure (including fine-, macro-, super-macro-domains).

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32See supplementary material at http://dx.doi.org/10.1063/1.4938396 for the materials synthesis and experimental methods including the process of finding macro-domain and fine-domain widths.
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