Epitaxial growth of high quality WO_3 thin films

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ABSTRACT

We have grown epitaxial WO_3 films on various single-crystal substrates using radio-frequency (RF) magnetron sputtering. While pronounced surface roughness is observed in films grown on $LaSrAlO_4$ substrates, films grown on $YAlO_3$ substrates show atomically flat surfaces, as demonstrated by atomic force microscopy (AFM) and X-ray diffraction (XRD) measurements. The crystalline structure has been confirmed to be monoclinic by symmetric and skew-symmetric XRD. The dependence of the growth modes and the surface morphology on the lattice mismatch is discussed.

Tungsten trioxide (WO_3) is a well-known electrochromic material which changes color under an applied electric field.[1-5] It is also very sensitive to NO_x exposure, and hence it is used to fabricate gas sensors.[6-10] Both of these applications require WO_3 to be grown in a thin film form. Various methods have been used to prepare WO_3 thin films, including thermal evaporation,[2,7,11,12] chemical vapor deposition (CVD), [9,13] sputtering, [6,8,14-17] and pulsed laser deposition (PLD).[18,19] Films prepared on glass or Si substrates usually have amorphous or polycrystalline structure and rough surfaces.[9,15] Growth of epitaxial films of WO_3 on single-crystal substrates such as $SrTiO_3$, MgO, and sapphire has been reported as well.[13,16,18,20] However, because of large lattice mismatch the surface morphology of these films has been inadequate for superlattice growth or for surface-sensitive experiments such as electrolyte gating,[21-26] which generally require atomically flat surfaces and interfaces with a root-mean-square (rms) roughness less than 1 nm. Our main goal here has been to develop a method, relatively simple if possible, of fabricating atomically smooth WO_3 films suitable for such experiments.

In the present study, we synthesized epitaxial WO_3 thin films on single-crystal $LaSrAlO_4$ (LSAO) and $YAlO_3$ (YAO) substrates using RF magnetron sputtering technique. X-ray diffraction (XRD) measurements show that in either case the

films are epitaxially oriented with respect to the substrates. Both LSAO and YAO substrates as-purchased come with atomically flat surfaces, as we verified by atomic force microscopy (AFM) scans before growth. However, only films grown on YAO substrates with the surfaces polished perpendicular to the crystallographic [110] direction (for brevity, (110) YAO in what follows) have atomically flat surfaces, as demonstrated by AFM and XRD measurements. Our data indicate that the lattice mismatch between the film and the substrate plays a key role in controlling the growth mode and the surface morphology.

The WO_3 can be viewed as a cubic ReO_3 structure with eight WO_6 octahedra centered at the eight corners. The center of the cube is empty, and hence the structure is easily distorted and tilted upon heating or cooling, with concomitant symmetry lowering. Five different crystal structures of WO_3 have been observed below 1,000 K.[27-29] At room temperature, the most stable structure is γ-monoclinic with the following lattice parameters: a_1 = 7.306 Å, b_1 = 7.540 Å, c_1 = 7.692 Å, and β = 90.88°; note that this unit cell contains eight WO_3 formula units.

LSAO substrate has a tetragonal structure with an in-plane lattice constant a = 3.754 Å. At room temperature, the lattice mismatch between the substrate and the WO_3 film, defined as $\varepsilon = (a_s - a_f)/a_s$, is –0.4% in one direction and 2.7% in the other. (Note that in order to compare LSAO and WO_3 on equal footing, one has to double the lattice constant of LSAO in each direction.) Another substrate that we explored, YAO, has an orthorhombic structure with the lattice constants a_0 = 5.176 Å, b_0 = 5.307 Å, and c_0 = 7.355 Å. Along the [110] direction, the lattice mismatch between YAO and the γ-monoclinic WO_3 is +0.7% (7.355 Å vs. 7.306 Å) along the a-axis and –1.7% (7.413 Å vs. 7.540 Å) along the b-axis.

In the present study, WO_3 films were deposited in an RF magnetron sputtering system at a growth temperature varied from 550 ℃ to 850 ℃. The pressure during growth was kept at 60 mTorr with an O_2/Ar ratio 4:1. The growth rate was kept at approximately 1 nm/minute. The film thickness was determined using X-ray reflectivity measurements. Fig. 1 shows XRD patterns for seven WO_3 films deposited on (001) LSAO substrates at various growth temperatures. All these films were grown at the same RF power (60 W) and for the same time (1 hour), and are of similar thickness, determined to be around 60 nm. For the γ-monoclinic WO_3, a peak around 23.1° is expected, corresponding to the out-of-plane lattice constant c=7.692 Å. For films grown at a temperature ≤ 650 ℃, the XRD pattern indeed shows a single peak at about 23.1°, suggesting that the films are epitaxial and the structure is monoclinic. However, as the growth temperature increases to 700 ℃ and above, extra peaks show up in the XRD patterns, while the main peak near 23.1° diminishes and finally disappears at 850 ℃.

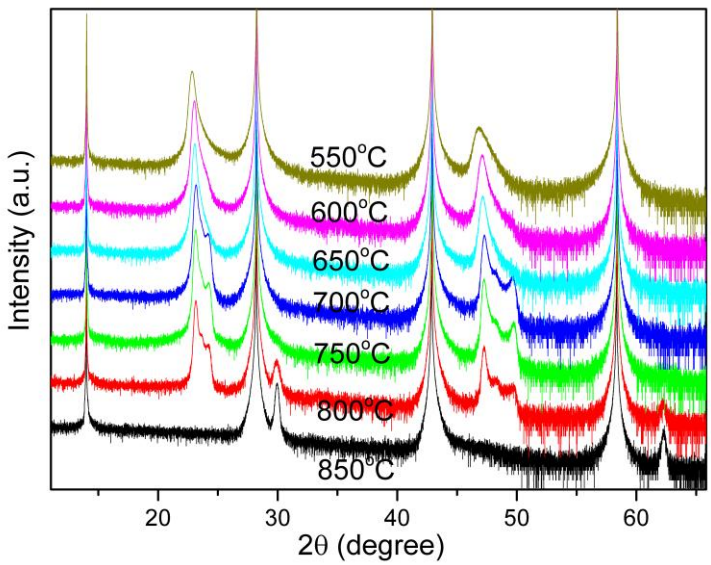

FIG. 1 (Color online) Wide-angle XRD patterns (triple axis, ω-2θ coupled scan) of WO_3 films grown at different temperatures on (001) LSAO substrates.

Although the WO_3 films grown on LSAO at temperatures ≤ 650 ℃ are epitaxially aligned with respect to the substrate, their surfaces are not atomically flat, as can be seen from a typical AFM image shown in Fig. 2. The rms surface roughness is about 1.2 nm, and the entire film surface is covered by grains with a diameter of about 100 nm, indicating a three-dimensional (island) growth mode.[30] We have grown dozens of films on LSAO substrates at various temperatures with thicknesses ranging from 10 nm to 100 nm, the RMS roughness falls in the range of 1 to 10 nm. These films are epitaxial but fall short of our goal of fabricating WO_3 samples with atomically flat surfaces.

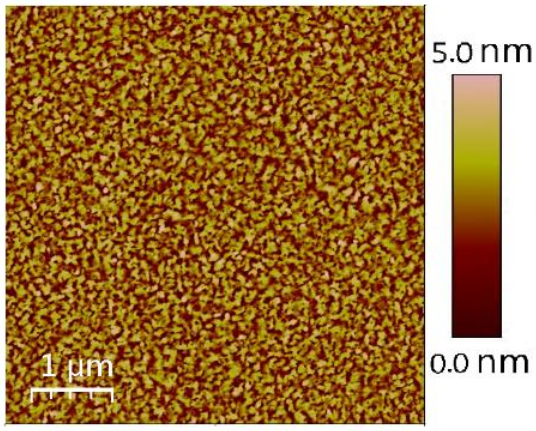

FIG. 2 (Color online) A surface height AFM image of a 60 nm thick WO_3 film grown at 600 ℃ on (001) LSAO surface

In an attempt to improve the surface morphology, we have deposited WO_3 films on (110) YAO substrates. Sputtering was done at temperatures between 750 ℃ and 850 ℃, with other conditions similar to what we have used before in the growth of WO_3 films on LSAO. In Fig. 3, we show a typical AFM image of a WO_3 film grown on a (110) YAO substrate. One can clearly discern steps and terraces. The average RMS roughness is only 1.6 Å, indicating that the film surface is indeed atomically flat. In the bottom panel in Fig. 3, we show the height-profile scan obtained from a horizontal cut across the AFM image. The step heights are found to be either 3.5 Å or 7 Å, corresponding to one-half or one unit cell of WO_3, indicating a two-dimensional (layer-by-layer or step-flow) growth mode.[30]

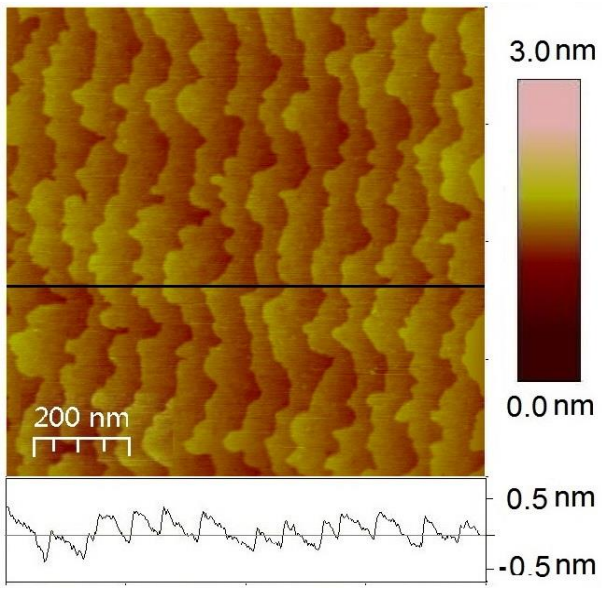

FIG. 3 (Color online) (Top) Surface height AFM image of a 14 nm WO_3 film. The black line indicates where the AFM profile shown in the bottom was taken. (Bottom) Cross-sectional profile of a horizontal cut across the top image.

Fig. 4 shows wide angle X-ray diffraction patterns of WO_3 films with thickness ranging from 4 nm to 84 nm, grown on (110) YAO substrates. A very high crystal quality is apparent from very pronounced finite-thickness (Laüe) fringes, which testify that the film surfaces and the substrate-film interfaces are perfect and parallel on the atomic scale and the film is single-crystalline throughout its whole thickness. Only the peaks corresponding to the (00n) family of crystallographic planes of WO_3 can be seen over the entire scan range ($5° < 2\theta < 85°$). The out-of-plane lattice constant calculated from the WO_3 Bragg peak (84nm film) is 7.73(2) Å, which matches the known monoclinic structure. The in-plane lattice constants have been determined to be 7.31 Å and 7.51 Å from skew-symmetric XRD measurements of (202) and (222) reflections, as shown in Fig. 5, which are also consistent with the monoclinic structure.

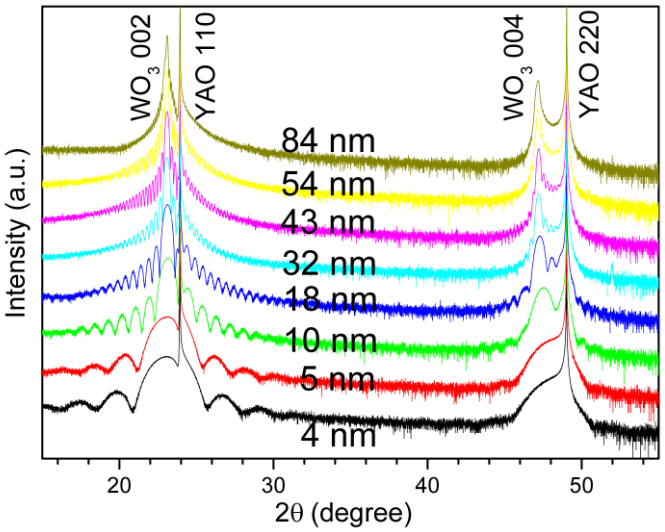

FIG. 4 (Color online) Wide-angle x-ray diffraction of WO_3 films grown on (110) YAO substrates, with the film thickness ranging from 4 nm to 84 nm.

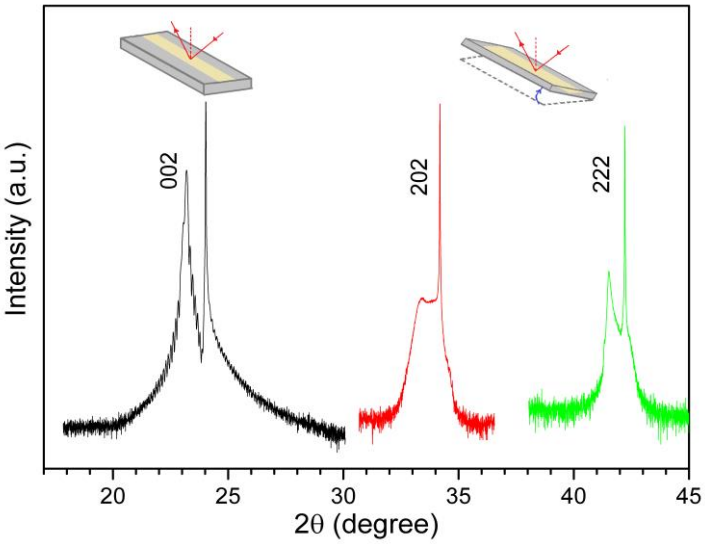

FIG. 5 (Color online) Symmetric and skew-symmetric X-ray diffraction of an 84 nm WO_3 film grown on (110) YAO substrate. In the skew-symmetric scan, the sample is tilted over a fixed angle around the axis that is parallel to the sample surface and the plane of the incident and diffracted beam.

Comparison of films grown on LSAO and YAO substrates suggests that it is possible to grow epitaxial films on substantially mismatched ($\varepsilon > 2\%$) substrates, if the growth conditions (especially the growth temperature) are appropriately adjusted. However, the growth mode and thus the surface morphology may be very different. For III-V semiconductors, it is known that the lattice mismatch plays a crucial role in determining the film growth mode and surface morphology.[31-33] In general,

the growth mode depends on the competition of the free energy of a film/epilayer (σ_f) and the surface energy of a substrate (σ_s). For a lattice-mismatched system, σ_f consists of the total surface energy of the epilayer and the strain energy that results from the lattice mismatch. The island morphology always provides a larger surface energy than that of a flat film. However, the strain energy stored in islands is always less than that stored in a flat film. Thus, in the case of a sufficiently large lattice mismatch, even though the surface energy of the epilayer favors a flat film morphology, the total free energy of the film may still favor an island morphology if the reduction in strain energy is large enough to offset the increase in surface energy.[34] Furthermore, it has been shown that films grown under a tensile strain tend to crack much more readily than those under the compressive strain.[31] In the present study, the in-plane area of the unit cell of γ-monoclinic WO_3 is 2.3% smaller than that of the (001) LSAO (quadrupled) while being 1.0% larger than that of a (110) YAO. Thus, one would indeed expect the stretched WO_3 films on LSAO to crack more readily, and have a rougher surface, than the compressed WO_3 films on YAO substrates.

In summary, we have grown atomically flat epitaxial WO_3 thin films on (110) YAO substrates using RF magnetron sputtering. We have also shown that films grown on the other substrates such as (001) LSAO may have an epitaxial orientation, if the growth temperature is in the range of 550 ℃ to 650 ℃. However, WO_3 films on LSAO always show island morphology with a much larger rms surface roughness. We ascribe this to the facts that WO_3 has a larger lattice mismatch with LSAO than with YAO, and that the tensile strain in WO_3 films on LSAO makes them crack more readily than the compressed WO_3 films on YAO.

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