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Epitaxial stabilization of single crystal anatase films via reactive sputter deposition

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Abstract

Single crystal-like TiO_2 films possessing the anatase crystal structure have been realized on (001) $LaAlO_3$ using reactive sputter deposition. The anatase polymorph could be epitaxially stabilized over a wide range of deposition temperatures and oxygen pressures. Both in-plane and out-of-plane X-ray diffraction measurements reflect a high degree of crystallinity for the deposited films. Thickness oscillations in the X-ray diffraction intensity and atomic force microscopy measurements indicate that the films are remarkably smooth, with surface morphology that is limited by that of the substrate. This result illustrates the effectiveness for epitaxy in stabilizing metastable phases, in particular for anatase, through matching of lattice spacing and nucleation chemistry.
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1. Introduction

For many years, there has been significant interest in the properties and application of semiconducting oxide thin films. These materials find utility in a number of applications, including transparent conductors [1], chemical sensors [2,3], and optical components. Semiconducting oxides of technological interest include In_2O_3, SnO_2, ZnO, CdO and TiO_2. For titanium dioxide, three different polymorphs can be realized, each with distinguishing electronic, optical, and structural properties that can be exploited. The crystalline phases of TiO_2 are rutile (tetragonal, $a=4.585$ Å, $c=2.953$ Å), anatase (tetragonal, $a=3.784$ Å, $c=9.515$ Å), and brookite (orthorhombic, $a=9.184$ Å, $b=5.447$ Å, $c=5.145$ Å). Rutile represents the stable phase at high temperatures, and is the easiest to realize as phase-pure crystals or thin films. However, for many applications, anatase displays interesting properties and performance. The refractive index for anatase is 2.55 as compared to 2.73 for rutile. It possesses a bandgap of 3.2 eV and a static dielectric constant of 31 [4–6]. As with rutile, anatase can be made an n-type semiconductor with a carrier density, n, on the order of $10^{19}/cm^3$ via cation substitution or by Ti interstitials [7–9]. Hall mobility has been measured as high as 20 cm^2/V s with the effective mass of anatase, $m^*=m_e$ [5]. These properties for anatase yield attractive material performance in photocatalysis and dye-sensitized photovoltaics [10]. In addition, it has been recently reported that ferromagnetism is observed at room temperature in transition metal doped semiconducting anatase thin films [11]. This result is particularly important in the development of electronics based on the manipulation of electron spin. Spin injection through ferromagnetic semiconducting contacts appears to be an effective means of introducing spin-polarized electrons for novel spin-based electronic device concepts.

For applications dependent on the semiconducting properties of anatase, carrier transport will depend critically on crystallinity. Grain boundaries and/or secondary phase boundaries are unacceptable for optimizing mobility and conductivity. As a low-temperature polymorph, polycrystalline anatase thin films are typically

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realized via deposition at low temperature where crystallinity is not optimal [12–15]. In most cases, polycrystalline TiO_2 films possess either a mixture of rutile and anatase, or solely rutile [16–19]. For fundamental studies of material properties, the synthesis of single crystal, phase-pure anatase is highly desirable. Recent efforts have shown that phase-pure anatase thin films can be realized via epitaxial stabilization on single crystal substrates [20–24]. In general, epitaxial stabilization offers a means by which metastable phases can be realized for conditions that would normally be thermodynamically unsuitable. Recent work on epitaxially stabilized anatase has focused on pulsed-laser deposition or molecular beam epitaxy. While yielding promising results, neither technique is attractive for application. For this reason, the synthesis of high-quality anatase using deposition techniques that are amenable to large-scale synthesis is highly desirable.

2. Experimental details

In this paper, we report on the epitaxial stabilization of anatase on (001) $LaAlO_3$ using reactive sputter deposition. Film properties are examined as a function of deposition conditions. X-ray diffraction results indicate that the TiO_2 films are essentially single crystal-like anatase based on the in-plane and out-of-plane rocking curves. Film morphology measurements indicate that the films are extremely smooth as well. As reactive sputter deposition is applicable to large-area deposition and high throughput, these results will have significant impact with regards to potential electronic applications of anatase thin-film materials.

The film-growth experiments were carried out using a reactive RF magnetron sputter deposition system equipped with a load-lock for substrate exchange. A quartz lamp heater provided substrate heating up to 750 °C. Two-inch diameter Ti disks were used as the sputtering targets. The target to substrate distance was approximately 12 cm. The base pressure of the deposition system was on the order of 5×10^{-8} torr. Single crystal (001) $LaAlO_3$ was chosen as the substrate material as it provides an excellent in-plane lattice match ($a=3.788$ Å) with c-axis oriented anatase. The (001) $LaAlO_3$ substrates were cleaned in trichloroethylene, acetone, and ethanol prior to mounting on the sample platen with Ag paint. Oxygen was used as the oxidizing species for the experiments reported in this paper. A typical deposition time was 2 h. Sputter deposition was performed at an Ar pressure of 15 mtorr and an RF power of 250 W.

3. Results and discussion

The epitaxial stabilization of anatase on $LaAlO_3$ could be achieved over a large range of growth conditions. In general, epitaxial anatase films were realized for growth temperatures between 500 and 700 °C and oxygen partial pressure $10^{-4}\leq P_{O_2}\leq10^{-2}$ torr. Fig. 1 shows X-ray diffraction data taken along the surface normal for films deposited in various oxygen partial pressures at 700 °C. Epitaxial anatase is observed over the entire range of pressures, with evidence for a small amount of secondary rutile phase for the films grown at $P_{O_2}\leq10^{-4}$ torr. Conductivity could be controlled via oxygen partial pressure during film growth. The film deposited at $P_{O_2}\leq10^{-4}$ torr exhibited a slight coloration indicating mobile carriers due to oxygen deficiency. Conductivity measurement confirms that these films are semiconducting. A detailed study of carrier transport in these films will be reported elsewhere.

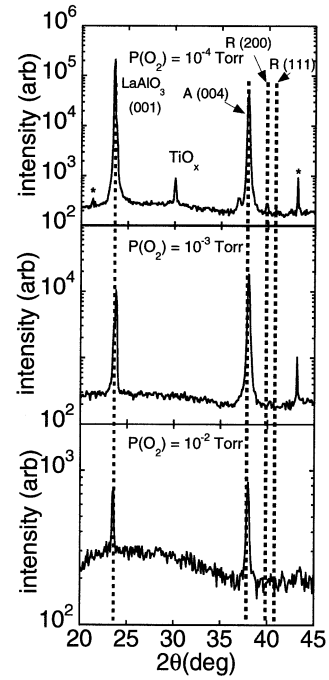

Fig. 1. X-ray diffraction scans for epitaxial anatase films grown in various oxygen pressures at 700 °C. Locations of diffraction peaks for anatase (A) and rutile (R) phases are indicated. Peaks marked by * are anomalous reflections from the substrate. The peak at ~30° can be assigned to a titanium sub-oxide, TiO_x [25].

Anatase films with excellent crystal quality as determined via $CuK\alpha_1$ X-ray diffraction were obtained at 650–700 °C with $P_{O_2}=10^{-3}$ torr. X-ray diffraction θ–2θ scans for a film deposited at $P_{O_2}=10^{-3}$ torr are shown in Fig. 2. The plot shows no evidence for rutile as a secondary phase. X-ray intensity Laue oscillations observed in the high-resolution scan shown in Fig. 2b through the anatase (004) peak are due to the finite number of TiO_2(001) planes in the thin film. These coherency oscillations are indicative of a film thickness that is extremely uniform and a surface that is extremely flat. From the spacing of the oscillation peaks, the film thickness was calculated to be 705 Å, which is in

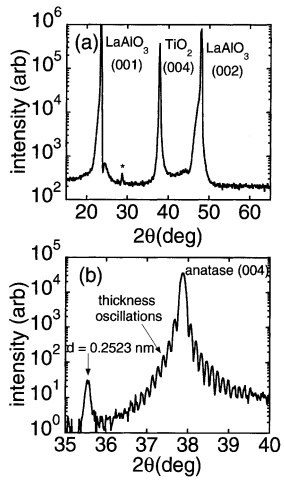

Fig. 2. X-ray diffraction ϕ-2ϕ scans of anatase film grown at 700 °C in $P_{O_2}=10^{-3}$ torr, showing (a) low-resolution and (b) high-resolution (Ge111 analyzer crystal) scans, with the latter showing Laue intensity oscillations indicative of a smooth film.

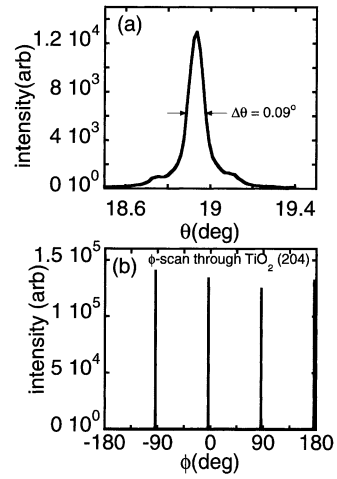

Fig. 3. X-ray diffraction (a) rocking curve through the (004) and (b) ϕ-scan through the (204) peak peaks.

agreement with surface profilometer measurements. The low-angle shoulder near the $LaAlO_3$ may indicate some interfacial reaction between the substrate and film and can also be influenced by film-substrate interference effects. The origin of the impurity peak at $d=2.523$ Å is also unknown, but may be strained rutile(101). Note that the intensity scale is logarithmic, indicating that only a small percentage of this impurity phase is present. The rocking curve through the TiO_2 (004) peak is shown in Fig. 3a. The full-width-half-maximum (FWHM) is only 0.09°, reflecting the high degree of crystallinity for the film. The in-plane crystallinity of the film was measured via a ϕ-scan through the TiO_2 (204) peak as shown in Fig. 3b. The four-fold symmetry of the diffraction peaks indicates a cube-on-cube in-plane alignment of the (001) anatase film with the (001) $LaAlO_3$ substrate. The in-plane FWHM $\Delta\phi=0.10°$, again reflecting a high degree of crystallinity in the film. The single crystal-like nature of the film is remarkable considering that anatase is a metastable phase. From the high-resolution X-ray diffraction data, the lattice parameters for the tetragonal film are $a=b=3.790$ and $c=9.495$ Å. This indicates that the film is slightly compressed in-plane and expanded along the c-axis relative to bulk anatase lattice constants. In-plane compressive strain is consistent with the film's in-plane spacing being clamped to that of the substrate lattice spacing, which has a rhombohedral-distorted $GdFeO_3$ structure with $a=3.788$ Å and $\alpha=90°\ 4'$. Note that the films deposited at 700 °C and $P_{O_2}=10^{-3}$ torr are insulating.

For potential electronic and optical applications, surface morphology is extremely important as it determines optical scattering loss and heterojunction properties. Atomic force microscopy (AFM) was used to measure the film roughness. Fig. 4 shows an AFM image for the film grown at $P_{O_2}=10^{-3}$ torr and $T=700$ °C. The RMS roughness of the film is only 2.1 nm, which is on the order of that observed for the $LaAlO_3$ substrate. This result is consistent with the X-ray intensity oscillations shown in Fig. 2 indicating that the film surface is extremely flat.

4. Conclusion

In conclusion, single-phase (001) anatase thin films have been realized via epitaxial stabilization on (001)

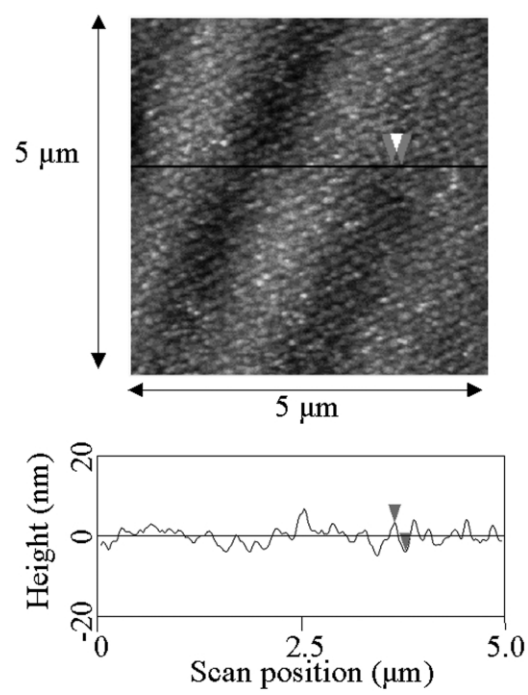

Fig. 4. Atomic force microscopy image of anatase film. RMS roughness is 2.1 nm.

$LaAlO_3$ substrates using reactive sputter deposition. The crystallization of the films is excellent, with rocking curves as narrow as 0.09°. Film roughness was essentially that of the substrate. This result should prove enabling for future activities in understanding and exploiting the electronic and optical properties of anatase without the interfering effects of grain boundaries or rutile secondary phase.

Acknowledgments

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References

[1] H.L. Hartnagel, A.L. Dawar, A.K. Jain, C. Jagadish, Semiconducting Transparent Thin Films, Institute of Physics, Bristol, 1995.
[2] H. Meixner, U. Lampe, Sensors Actuators B 33 (1996) 198.
[3] A. Rothschild, F. Edelman, Y. Komem, F. Cosandey, Sensors Actuators B B67 (2000) 282.
[4] H. Tang, H. Berger, P.E. Schmid, F. Levy, Solid State Commun. 92 (1994) 267.
[5] H. Tang, K. Prasad, R. Sanjines, P.E. Schmid, F. Levy, J. Appl. Phys. 75 (1994) 2042.
[6] H. Tang, H. Berger, P.E. Schmid, F. Lévy, G. Burri, Solid State Comm. 87 (1993) 847.
[7] E. Yagi, R.R. Hasiguti, M. Aono, Phys. Rev. B 54 (1996) 7945.
[8] J.W. DeFord, O.W. Johnson, J. Appl. Phys. 54 (1983) 889.
[9] L. Forro, O. Chauvet, D. Emin, L. Zuppiroli, H. Berger, F. Lévy, J. Appl. Phys. 75 (1994) 633.
[10] S. Sato, Shokubai (catalyst) 31 (1989) 469.
[11] Y. Matsumoto, et al., Science 291 (2001) 854.
[12] M.D. Wiggins, M.C. Nelson, C.R. Aita, J. Vac. Sci. Technol. A 14 (1996) 772.
[13] P. Löbl, M. Huppertz, D. Mergel, Thin Solid Films 251 (1994) 72.
[14] L.-J. Meng, M. Andritschky, M.P. dos Santos, Appl. Surf. Sci. 65/66 (1993) 235.
[15] J.V. Grahn, M. Linder, E. Fredriksson, J. Vac. Sci. Technol. A 16 (1998) 2495.
[16] J.D. DeLoach, C.R. Aita, J. Vac. Sci. Technol. A 16 (1963) 1998.
[17] J.-H. Kim, S. Lee, H.-S. Im, Appl. Surf. Sci. 151 (1999) 6.
[18] L. Escobar-Alarcón, E. Haro-Poniatowski, M.A. Camacho-Lopez, M. Fernandez-Guasti, J. Jimenez-Jarquin, A. Sanchez-Pineda, Appl. Surf. Sci. 137 (1999) 38.
[19] J. Aarik, A. Aidla, V. Sammelselg, H. Siimon, T. Uustare, J. Crystal Growth 169 (1997) 496.
[20] M. Murakami, Y. Matsumoto, K. Nakajima, T. Makino, Y. Segawa, T. Chikyow, P. Ahmet, M. Kawasaki, H. Koinuma, Appl. Phys. Lett. 78 (2001) 2664.
[21] Sugiharto, S. Yamamoto, T. Sumita, A. Miyashita, J. Phys.: Condens. Matter 13 (2001) 2875.
[22] H. Tang, K. Prasad, R. Sanjinès, P.E. Schmid, F. Lévy, J. Appl. Phys. 75 (1994) 2042.
[23] S. Chen, M.G. Mason, H.J. Gysling, G.R. Paz-Pujalt, T.N. Blanton, T. Castro, K.M. Chen, C.P. Fictorie, W.L. Gladfelter, A. Franciosi, P.I. Cohen, J.F. Evans, J. Vac. Sci. Technol. A (Vacuum, Surfaces, and Films) 11 (1993) 2419.
[24] W. Sugiyama, et al., Jpn. J. Appl. Phys. Pt. 1 (36) (1997) 7358.
[25] JCPDS-International Center for Diffraction Data card 23-1078.