

Epitaxial growth of $Y_2O_3:Eu$ thin films on $LaAlO_3$

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We report the epitaxial growth of europium-activated yttrium oxide ($Y_2O_3:Eu$) (001) thin films on $LaAlO_3$ (001) using laser ablation deposition at a substrate temperature of 775 °C and 10 Hz pulse repetition rate. The orientation relationship between the films and the substrates is $[110]Y_2O_3\parallel[100]LaAlO_3$ and $[-110]Y_2O_3\parallel[010]LaAlO_3$ which results in a lattice mismatch of only 0.8%. Transmission electron microscopy (TEM) of the films reveals the single crystalline $Y_2O_3:Eu$ thin film to contain small pores. Scanning transmission electron microscopy (STEM) imaging of the films shows the substrate always terminates with the Al sublattice. Moreover, the STEM reveals that no precipitates of Eu had formed in the films. © 1999 American Institute of Physics. [S0003-6951(99)05441-8]

Numerous efforts have been made to prepare yttrium oxide (Y_2O_3) thin films for applications in ultralarge scale integration (ULSI) gate insulators, ULSI capacitors, and, by addition of a suitable dopant species, for electroluminescence devices.¹⁻⁴ Single crystalline thin films are of great importance for devices because of their reduced defect content which can result in improved properties. Thus, growth of single crystal films has attracted much attention, and in the past decade many different deposition techniques and substrates have been tried.⁵⁻¹³ Fukumoto, Choi, and co-workers^{5,6} reported the heteroepitaxial growth of Y_2O_3 (YO) films on silicon, but the atomic structure of the interface was not determined. In this letter, we report the epitaxial growth of YO thin films doped with ~4 wt % Eu on a $LaAlO_3$ substrate. Z-contrast scanning transmission electron microscopy (STEM)¹⁴ is employed to directly image the atomic structure of the film/substrate interface.

It is well known that the Y_2O_3 has a C-type rare-earth sesquioxide structure, closely related to the fluorite structure with a cell parameter $a=1.060$ nm and space group $T_h^7(Ia3)$.¹⁵⁻¹⁸ In the fluorite lattice, each cation is surrounded by eight anions located at the corner of a cube. The C-type structure is derived by removing one quarter of oxygen atoms and slightly rearranging the remaining ones.^{8,19} For 75% of the cations the vacancies lie at the ends of a face diagonal, while for the other 25% they lie at the ends of a body diagonal. Therefore, each yttrium atom is surrounded by only six oxygen neighbors forming two different types of distorted octahedral structure in the unit cell, called S_6 and

C_2 .²⁰ Eight yttrium atoms have the S_6 symmetry and the other 24 atoms have the C_2 symmetry. From the crystallographic structure one can deduce that the distance of two neighboring Y atoms along the $\langle 100 \rangle$ direction of YO is 0.5302 nm, and along the $\langle 110 \rangle$ direction it is 0.375 nm. $LaAlO_3$ (LAO) is a rhombohedral structure with lattice parameters $a=0.378$ nm, $\theta \leq 90.5^\circ$, very close to a cubic structure. The lattice mismatch with the $\langle 110 \rangle$ direction of the YO is therefore less than 0.8%, and so we would anticipate epitaxial growth of single crystalline YO thin films on the LAO (001) substrate to be feasible.

Eu activated YO thin films were deposited by laser ablation²¹⁻²³ on (001) LAO substrates at a temperature of 775 °C and a deposition rate of 10 Hz. Pulses from a Lambda Physik 305i laser (wavelength 248 nm, pulse length 25 ns) are passed through a quartz window to irradiate the phosphor target material, YO:Eu, creating an expanding plume. The typical distance between the target and the substrate was ~5 cm, and energy densities were approximately 2.0–3.5 J/cm². The films were grown on LAO to a total thickness of 0.3 μm, in an oxygen ambient pressure that ranged from 50 to 600 mTorr. Rocking curve measurements indicate a full width at half maximum (FWHM) of 0.1°. Cross sectional slices were obtained by cutting the LAO along the [100] or [010] directions (using pseudocubic indexing) and then gluing face to face in the usual way. Both plan view and cross section specimens were prepared for transmission electron microscope (TEM) and/or STEM observations by mechanical grinding, polishing, and dimpling, followed by Ar-ion milling using an E. A. Fichione ion polishing system, a 13° incident angle, and a beam voltage of 3.5 kV initially, reducing to 1.0 kV for final milling. TEM bright field images and electron diffraction patterns were recorded in a Philips EM-400 electron microscope operated at 100 kV. Z-contrast imaging was conducted in a VG HB603 STEM at 300 kV.^{14,24}

Figure 1 is a low magnification TEM micrograph and

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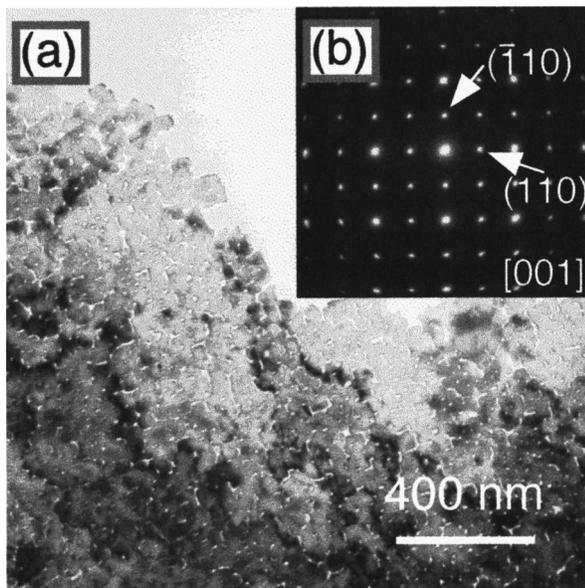


FIG. 1. Plan view TEM image (a) and corresponding electron diffraction pattern (b) of a laser ablation deposited YO:Eu thin film, showing the formation of a good single crystalline film containing numerous voids. The electron projection is along the [001] zone axes of the YO:Eu crystalline thin film.

corresponding selected area electron diffraction pattern (EDP) of a plan view sample of the YO:Eu thin film. The diffraction pattern indicates an almost perfect single crystal film, but the image shows numerous small voids, suggesting an island growth mechanism with incomplete coalescence of the islands.

A cross section image of the sample is presented in Fig. 2(a), showing the smooth surface, sharp interface, and a uniform thickness of 300 nm maintained over the entire region. Figure 2 also shows selected area EDPs of the film (b) and the LAO substrate (c), showing the orientation relationship to be $[110]YO \parallel [100]LAO$ and $[-110]YO \parallel [010]LAO$. The columnar structure of the film is also apparent from the cross section image, with small rotations between neighboring grains giving the strong diffraction contrast. Each individual column, however, appears to be a good single crystal, which implies that the presence of the voids may avoid the need for a high density of dislocations between the grains to accommodate the rotations, and/or a high level of stress within the

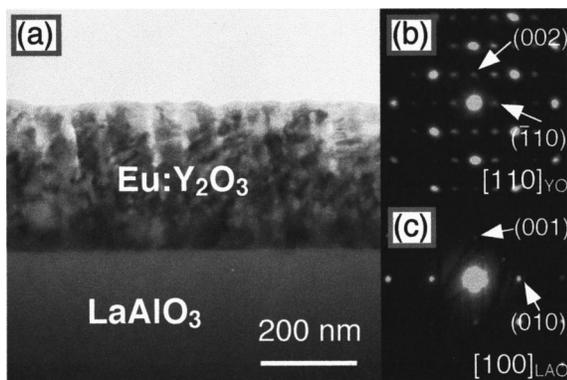


FIG. 2. Cross section TEM image (a) and corresponding electron diffraction patterns of the as-grown YO:Eu film (b) and the LAO substrate (c) showing the orientation relationship to be $[110]YO \parallel [100]LAO$ and $[-110]YO \parallel [010]LAO$.

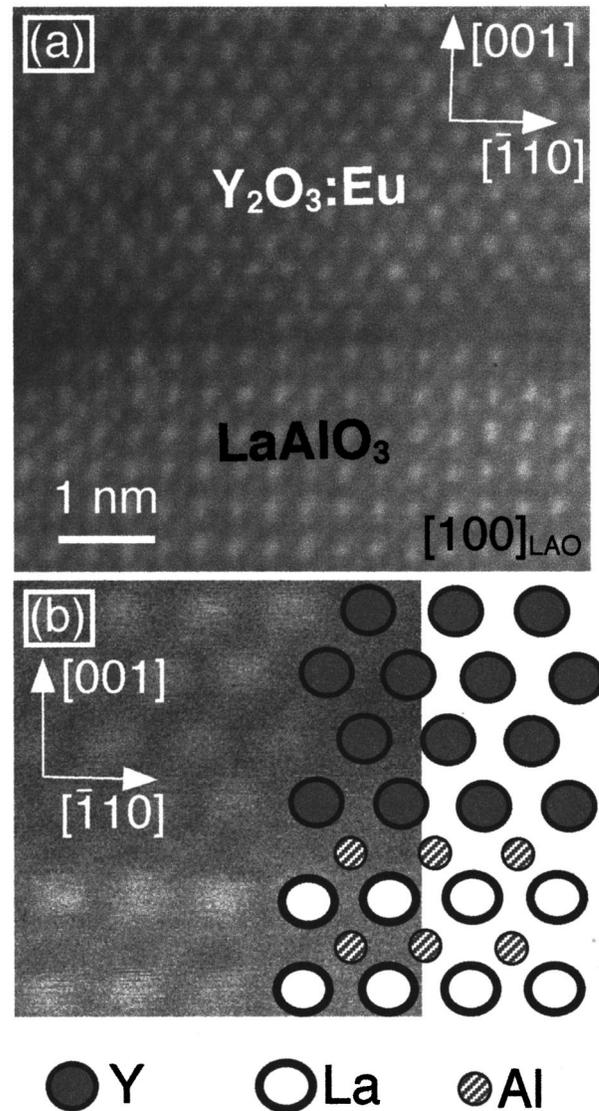


FIG. 3. (a) Z-contrast STEM dark field image showing the atomically abrupt interface, (b) higher magnification image showing clearly the Al terminated substrate, as shown in the schematic.

grains. The dominant direction of the voids is not crystallographic, suggesting that it is related to the deposition direction not being normal to the substrate.²⁵ The sample was not rotated during film deposition.

In order to determine the detailed interface atomic structure, high-resolution Z-contrast STEM imaging of the samples was carried out. The Z-contrast image is a direct image with intensity highly localized about the atomic column positions and approximately proportional to the mean square atomic number (Z). Thus the La and Al columns in LAO, and the Y columns in YO, are directly distinguishable in a Z-contrast image taken along the [010] zone axis of the LAO substrate. Figure 3(a) is an atomic resolution Z-contrast STEM image of the film/substrate interface. The bright spots in the film are Y columns, the bright spots in the substrate La columns, and the less bright spots Al columns. The O columns are not visible. Also shown in Fig. 3(b) is a higher magnification Z-contrast image that shows clearly the atomic structure of the interface. The substrate is seen to terminate with the Al plane, which matches directly onto the Y layer of the film as shown in the schematic.

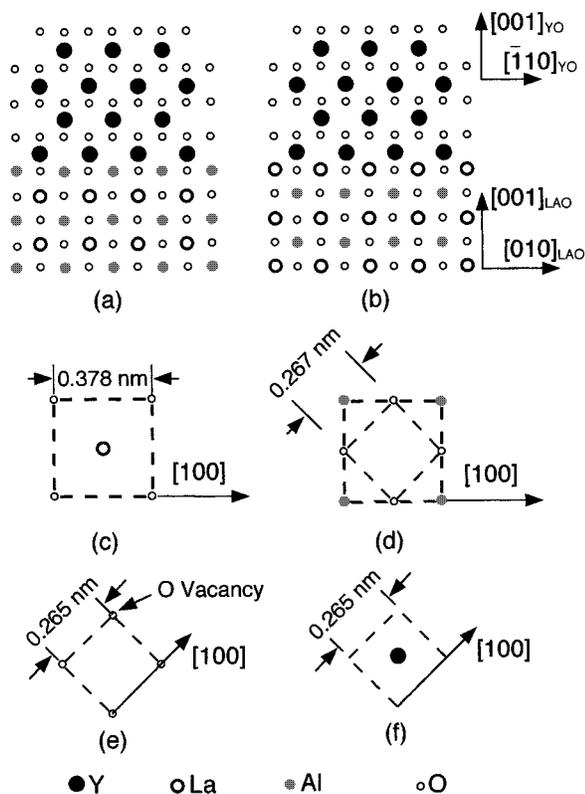


FIG. 4. Schematic interface structures for YO on the Al terminated surface (a), and on the La terminated surface of LAO (b). Atomic arrangements on the substrate (001) surface are shown for La termination (c), and Al termination (d). The atomic arrangements on the alternating oxygen and Y {004} planes in YO are shown in (e) and (f).

Figure 4 is a schematic of two possible interface structures corresponding to the two possible terminations of the (001) substrate, either the $(\text{AlO}_2)^-$ or $(\text{LaO})^+$ planes. Figures 4(c) and 4(d) show these two planes, while Figs. 4(e) and 4(f) show the two (001) planes of YO, comprising pure Y and O. The full unit cell of the YO structure is four times the dimensions shown due to ordering of the O vacancies. For $(\text{AlO}_2)^-$ termination of the substrate, the four oxygen positions match almost exactly the oxygen positions in the YO. The Y atoms can sit over the center of the four O positions in Fig. 4(d), directly over the La site in the plane below, as seen in the image of Fig. 3(b). The interfacial Y is then coordinated by seven oxygen atoms instead of six, which may be compensated by some additional oxygen vacancies. In contrast, if the substrate is terminated by LaO, each Y sitting directly over one oxygen in the LaO plane, then each Y is substantially undercoordinated. This explains the observed termination and the fact that no single layer height steps were observed.

Another important aspect of the work concerns the possibility of Eu precipitation in the YO films. Z-contrast STEM is very sensitive to Eu with $Z=63$. In our observations, however, no sign of any precipitation was found, or of any preferential segregation to the surfaces of the columnar grains. This implies that the Eu was distributed uniformly within the films.

In conclusion, we have successfully grown epitaxial single crystalline YO films doped with Eu on LAO substrates

by laser ablation. Z-contrast STEM reveals the substrates are always Al terminated, and no evidence of nonuniform Eu distribution was found.

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- ¹L. Manchanda and M. Gurvitch, *IEEE Electron Device Lett.* **9**, 180 (1988).
- ²T. S. Kalkur, Y. R. Kwor, and C. A. Paz de Araujo, *Thin Solid Films* **170**, 185 (1989).
- ³S. J. Duclos, C. D. Greskovich, and C. R. O'Clair, *Mater. Res. Soc. Symp. Proc.* **348**, 503 (1994).
- ⁴G. Blasse and B. C. Grabmaier, *Lumini. Mater.* (Springer, Berlin, 1994).
- ⁵H. Fukumoto, T. Imura, and Y. Osaka, *Appl. Phys. Lett.* **55**, 360 (1989).
- ⁶S. C. Choi, M. H. Cho, S. W. Whangbo, C. N. Whang, S. B. Kang, S. I. Lee, and M. Y. Lee, *Appl. Phys. Lett.* **71**, 903 (1997).
- ⁷R. P. Rao, *Solid State Commun.* **99**, 439 (1996).
- ⁸K.-I. Onisawa, M. Fuyama, K. Tamura, K. Taguchi, T. Nakayama, and Y. A. Ono, *J. Appl. Phys.* **68**, 719 (1990).
- ⁹A. F. Jankowski, L. R. Schrawyer, and J. P. Hayes, *J. Vac. Sci. Technol. A* **11**, 1548 (1993).
- ¹⁰W. M. Cranton, D. M. Spink, R. Stevens, and C. B. Thomas, *Thin Solid Films* **226**, 156 (1993).
- ¹¹S. L. Jones, D. Kumar, R. K. Singh, and P. H. Holloway, *Appl. Phys. Lett.* **71**, 404 (1997).
- ¹²K. G. Cho, D. Kumar, D. J. Lee, S. L. Jones, P. H. Holloway, and R. K. Singh, *Appl. Phys. Lett.* **71**, 3335 (1997).
- ¹³K. G. Cho, D. Kumar, S. L. Jones, D. J. Lee, P. H. Holloway, and R. K. Singh, *J. Electrochem. Soc.* **145**, 3456 (1998).
- ¹⁴S. J. Pennycook, "STEM: Z-contrast," in *Handbook of Microscopy*, edited by S. Amelinckx, D. van Dyck, J. van Landuyt, and G. van Tendeloo (VCH, Weinheim, Germany 1997), p. 595.
- ¹⁵J. L. Daams, P. Villars, and J. H. N. Vanvucht, *Atlas of Crystal Structure Types for Intermetallic Phases* (ASM International, Materials Park, OH, 1994), p. 6706.
- ¹⁶M. G. Paten and E. N. Maslen, *Acta Crystallogr.* **19**, 307 (1965).
- ¹⁷B. H. O'Conner and T. M. Valentine, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **25**, 2140 (1969).
- ¹⁸M. Faucher and J. Pannetier, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **36**, 3209 (1980).
- ¹⁹W. v. Schaik and G. Blasse, *Chem. Mater.* **4**, 410 (1992).
- ²⁰F. Jollet, C. Noguera, N. Thomat, M. Gautier, and J. P. Duraud, *Phys. Rev. B* **42**, 7587 (1990).
- ²¹J. Fitz-Gerald, S. J. Pennycook, H. Gao, V. Krishnamoorthy, J. Marcinka, W. Glenn, and R. Singh, *Mater. Res. Soc. Symp. Proc.* **502** (1998).
- ²²J. Fitz-Gerald, T. Trottier, R. K. Singh, and P. H. Holloway, *Appl. Phys. Lett.* **72**, 1838 (1998).
- ²³D. Kumar, J. Fitz-Gerald, and R. K. Singh, *Appl. Phys. Lett.* **72**, 1451 (1998).
- ²⁴N. D. Browning, M. F. Chisholm, and S. J. Pennycook, *Nature (London)* **366**, 143 (1993).
- ²⁵E. S. Machlin, *Materials Science in Microelectronics* (Giro, Croton-on-Hudson, 1995).