Cubic Dielectrics for Superconducting Electronics. *In Situ* Growth of Epitaxial Sr_2AlTaO_6 Thin Films Using Metalorganic Chemical Vapor Deposition

Bin Han, Deborah A. Neumayer, Bruce H. Goodreau, and Tobin J. Marks*

Department of Chemistry Materials Research Center, and the Science and Technology Center for Superconductivity Northwestern University Evanston, Illinois 60208-3113

Hong Zhang and Vinayak P. Dravid

Department of Materials Science and Engineering, and the Science and Technology Center for Superconductivity Northwestern University Evanston, Illinois 60208-3113

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In the drive to develop HTS (high-temperature superconducting)-based electronics,[1] the quest for new, chemically inert, HTS lattice/thermal expansion-matched, low dielectric constant/dielectric loss insulators represents a major theme.[2] Such materials are needed as buffers, dielectrics, substrates, "seed layers"[2a] and overlayers.[1,2] As for HTS film growth,[3] metalorganic chemical vapor deposition (MOCVD) offers the potential in the case of dielectric films of low growth temperatures, simplified apparatus, and amenability to the large-scale coating of substrates having complex shapes.[4] Among the dielectric materials of great current interest, the cubic ternary Sr_2AlTaO_6 (SAT) is particularly attractive since it exhibits an excellent lattice and thermal expansion match with YBCO, BSCCO, and TBCCO, a low dielectric constant and low tan δ,[5] as well as the absence of phase transitions between 25 °C and typical HTS film growth temperatures.[2g] The presence of the latter is known to seriously degrade the electrical/microwave characteristics of proximate HTS films.[2d] Unlike a number of the binary perovskite dielectrics, the crystal structure of SAT is cubic,[6] so that films having potentially deliterious multiple growth orientations[2b,4,7] are unlikely. We report here the first *in situ* growth of phase-pure, epitaxial SAT films by MOCVD as well as observations relevant to optimization of the MOCVD film growth process.

In situ MOCVD growth of SAT films was carried out in a horizontal metal reactor having individual inlet tubes for introducing the volatile, metalorganic precursors as well as the oxidant gas N_2O. The operating system pressure was 1.5 Torr (background pressure = 0.10 Torr). Cleaned single-crystal (110) $LaAlO_3$ (indexed here in the rhombohedral system) specimens were employed as the substrates. Within the reactor, the substrates were located in a resistively heated quartz tube. The temperature of the substrates was measured by a K-type nickel–chromium vs nickel–aluminum thermocouple attached to the back of the substrates. The deposition temperatures were maintained in the range 750–850 °C. N_2O was introduced at a flow rate of 200 sccm immediately upstream of the susceptor. The precursors $Al(acac)_3$ (acac = acetylacetonate) and $Sr(hfa)_2(tetraglyme)$ (hfa = hexafluoroacetylacetonate)[8] were synthesized from high-purity metal precursors and were multiply vacuum sublimed prior to use. $Ta_2(OCH_2CH_3)_5$ was obtained from Gelest Inc. and used as received. The precursors were contained in Pyrex reservoirs maintained at 90, 130, and 60 °C, respectively, and were transported to the reaction chamber by Ar flowing at 60–100 sccm.

X-ray diffraction studies of the MOCVD-derived SAT films reveal a very large sensitivity of composition and microstructure to the deposition conditions. Thus, films grown at 750 °C are multiphase and largely unoriented as indicated by θ–2θ scans (Ni-filtered Cu Kα radiation). Identified phases include SAT, SrF_2,[9] and $SrAl_4O_7$.[10] The source of fluoride is doubtless the hfa ligand. In contrast, film growth at a 800 °C substrate temperature, with all other conditions identical, yields phase-pure SAT thin films (Figure 1A). Diffractometric rocking curves of these films (ω scans) performed with a double-crystal diffractometer (Cu Kα radiation) indicate a low degree of alignment/perfection of the film growth planes with respect to the substrate surface. Thus, the films exhibit a full

(1) For reviews of this subject, see: (a) Singh, R., Nisenoff, M., Pavuna, D., Eds. Progress in High-Temperature Superconducting Transistors and Other Devices. II. *SPIE Proc.* **1992**, *1597*. (b) Heinen, V. O., Bhasin, K. B., Eds. Superconductivity Applications for Infrared and Microwave Devices. II. *SPIE Proc.* **1992**, *1394*. (c) Singh, R., Narayan, J., Shaw, D. T., Eds. Progress in High-Temperature Superconducting Transistors and Other Devices. *SPIE Proc.* **1992**, *1477*. (d) Bhasin, K. B., Heinen, V. O., Eds. Superconductivity Applications for Infrared and Microwave Devices. *SPIE Proc.* **1990**, *1292*. (e) Chi, C.-C.; van Dover, R. B., Eds. High-T_c Superconductivity: Thin Films and Applications. *SPIE Proc.* **1990**, *1287*.

(2) (a) Mukaida, M.; Miyazawa, S.; Kobayashi, J. In *Advances in Superconductivity. V*; Bando, Y., Yamauchi, H., Eds.; Springer-Verlag: Tokyo, 1993; pp 893–896. (b) Kobayashi, J.; Tazoh, Y.; Mukaida, M.; Sasaura, M.; Miyazawa, S. In ref 2a, pp 865–868. (c) Ito, W.; Okayama, S.; Homma, N.; Morishita, T. *Appl. Phys. Lett.* **1993**, *62*, 312–314. (d) Young, K. H.; Strother, D. D. *Physica C* **1993**, *208*, 1–6 and references therein. (e) Phillips, J. M.; Siegal, M. P.; van Dover, R. B.; Tiepel, T. H.; Marshall, J. H.; Brandle, C. D.; Berkstresser, G.; Strauss, A. J.; Fahey, R. E.; Sengupta, S.; Cassanho, A.; Jenssen, H. P. *J. Mater. Res.* **1992**, *7*, 2650–2657 and references therein. (f) Haefke, H.; Lang, H. P.; Sum, R.; Güntherodt, H.-J.; Berthold, L.; Hesse, D. *Appl. Phys. Lett.* **1992**, *61*, 2359–2361. (g) Findikoglu, A. T.; Doughty, C.; Bhattacharya, S.; Li, Q.; Xi, X. X.; Venkatesan, T.; Fahey, R. E.; Strauss, A. J.; Phillips, J. M. *Appl. Phys. Lett.* **1992**, *61*, 1718–1720. (h) Talvacchio, J.; Wagner, G. R. In ref 1d, pp 2–12.

(3) (a) Malandrino, G.; Richeson, D. S.; Marks, T. J.; DeGroot, D. C.; Schindler, J. L.; Kannewurf, C. R. *Appl. Phys. Lett.* **1991**, *58*, 182–184 and references therein. (b) Zhao, J.; Li, Y. Z.; Chern, C. S.; Lu, P.; Norris, P.; Gallois, B.; Kear, B.; Casandey, F.; Wu, X. D.; Muenchausen, R. E.; Garrison, S. M. *Appl. Phys. Lett.* **1991**, *59*, 1254–1256 and references therein. (c) Zhang, K.; Erbil, A. *Mater. Sci. Forum*, in press, and references therein. (d) Hirai, F.; Yamane, H. *J. Cryst. Growth* **1991**, *107*, 638–691 and references therein.

(4) (a) Han, B.; Neumayer, D. A.; Schulz, D. L.; Marks, T. J.; Zhang, H.; Dravid, V. P. *Appl. Phys. Lett.* **1992**, *61*, 3047–3049. (b) Han, B.; Neumayer, D. A.; Schulz, D. L.; Hinds, B. J.; Marks, T. J.; Zhang, H.; Dravid, V. P. *Chem. Mater.* **1993**, *5*, 14–16. (c) Han, B.; Neumayer, D. A.; Schulz, D. L.; Hinds, B. J.; Marks, T. J. *J. Vac. Sci. Technol. A* **1993**, *11*, 1431–1434.

(5) Gou, R.; Bhalla, A. S.; Sheen, J.; Ainger, F.; Erdei, S.; Subbarao, E. C.; Cross, L. E. *J. Mater. Res.*, in press. $\epsilon = 11.8$ (10 kHz), tan $\delta = 4.2 \times 10^{-5}$ (10 kHz) at 77 °C.

(6) Brandle, C. D.; Fratello, V. J. *J. Mater. Res.* **1990**, *5*, 2160–2164.

(7) Brorsson, G.; Nilsson, P. A.; Olsson, E.; Wang, S. Z.; Claeson, T.; Löfgren, M. *Appl. Phys. Lett.* **1992**, *61*, 486–488.

(8) (a) Zhang, J. M.; Wessels, B. W.; Richeson, D. S.; Marks, T. J.; DeGroot, D.; Kannewurf, C. R. *J. Appl. Phys.* **1991**, *69*, 2743–2745. (b) Timmer, K.; Spee, K. d. M.; Mackor, A.; Meinema, H. A.; Spek, A. L.; van der Sluis, P. *Inorg. Chim. Acta* **1991**, *190*, 109–117.

(9) Swanson, H.; Fuyat, A. *Natl. Bur. Stand.* (*U.S.*) Circ. 539, **1955**, *5*, 67.

(10) Appendino, P. *Rev. Int. Hautes Temper. Refract.* **1972**, *9*, 297.

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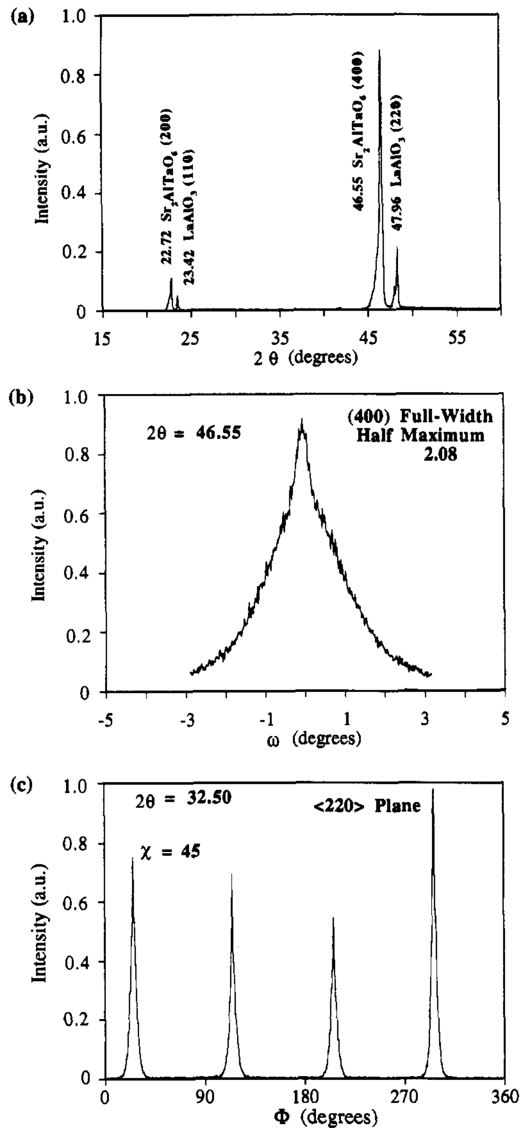

Figure 1. (a) θ–2θ X-ray diffraction scan of a Sr_2AlTaO_6 film growth by *in situ* MOCVD at 800 °C on a (110) $LaAlO_3$ substrate. (b) X-ray diffraction ω-scan rocking curve of the (400) reflection of an MOCVD-derived Sr_2AlTaO_6 film grown on a (110) $LaAlO_3$ substrate at 800 °C. The fwhm of the reflection is 2.04°. (c) X-ray diffraction ϕ-scan of an MOCVD-derived Sr_2AlTaO_6 film grown on a (110) $LaAlO_3$ substrate at 800 °C.

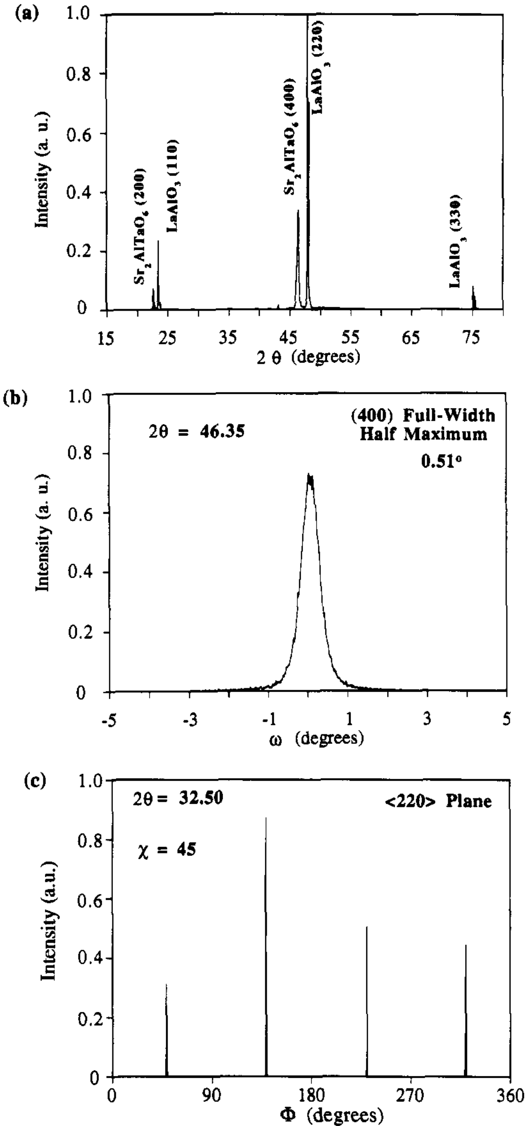

Figure 2. (a) θ–2θ X-ray diffraction scan of a Sr_2AlTaO_6 film grown by *in situ* MOCVD at 850 °C on a (110) $LaAlO_3$ substrate. (b) X-ray diffraction ω-scan rocking curve of the (400) reflections of an MOCVD-derived Sr_2AlTaO_6 film grown on a (110) $LaAlO_3$ substrate at 850 °C. The fwhm of the reflection is 0.51°. (c) X-ray diffraction ϕ-scan of an MOCVD-derived Sr_2AlTaO_6 film grown on a (110) $LaAlO_3$ substrate at 850 °C.

width at half-maximum (fwhm) for the Sr_2AlTaO_6 (400) reflection of 2.08° (Figure 1B; fit by least-squares analysis) versus 0.20° for the corresponding (220) reflection of the $LaAlO_3$ single-crystal substrate. In-plane ϕ-scans were also performed to assess the quality of the in-plane epitaxy using a diffractometer (Cu Kα radiation) equipped with a four-circle goniometer. In theory, four equivalent planes of reflection should be observed, repeating every 90°. Typical ϕ scans of the ⟨220⟩ family of Sr_2AlTaO_6 diffraction planes (Figure 1C) grown at 800 °C exhibit the requisite 4-fold symmetry but with rather broad peaks. Increasing the substrate temperature to 850 °C during deposition results in significant enhancement in growth plane alignment and crystallinity (Figure 2A). Rocking curves now exhibit a full width at half-maximum (fwhm) for the Sr_2AlTaO_6 (400) reflection of 0.51° (Figure 2B; fit by least-squares analysis). Typical ϕ scans of the ⟨220⟩ family of Sr_2AlTaO_6 diffraction planes (Figure 2C) exhibit sharp reflections having the requisite 4-fold symmetry; hence, a high level of in-plane epitaxy. SEM images of the 850 °C SAT films reveal smooth, featureless surfaces, while AFM images indicate smooth surfaces with roughness features on the order of ±75 Å.[11]

Cross-sectional high-resolution electron microscopy (HREM) indicates that the MOCVD-derived SAT films grow with sizable regions of defect-free, single-crystal epitaxial microstructure having an atomically abrupt interface with the $LaAlO_3$ substrate (Figure 3A). These images and selected area diffraction patterns (Figure 3B) reveal that the SAT films grow exclusively with a (100) growth orientation. Preliminary pulsed laser deposition studies to be discussed elsewhere, indicate that the present MOCVD-derived SAT films are suitable substrates for high-quality (T_c = 90.0 K) YBCO film growth.[11]

These results show that phase-pure films of the HTS lattice-matched ternary cubic perovskite dielectric Sr_2AlTaO_6 can be efficiently grown in a single orientation *in*

(11) Han, B.; Goodreau, B. H.; Roshko, A.; Rudman, D. A.; Marks, T. J., research in progress.

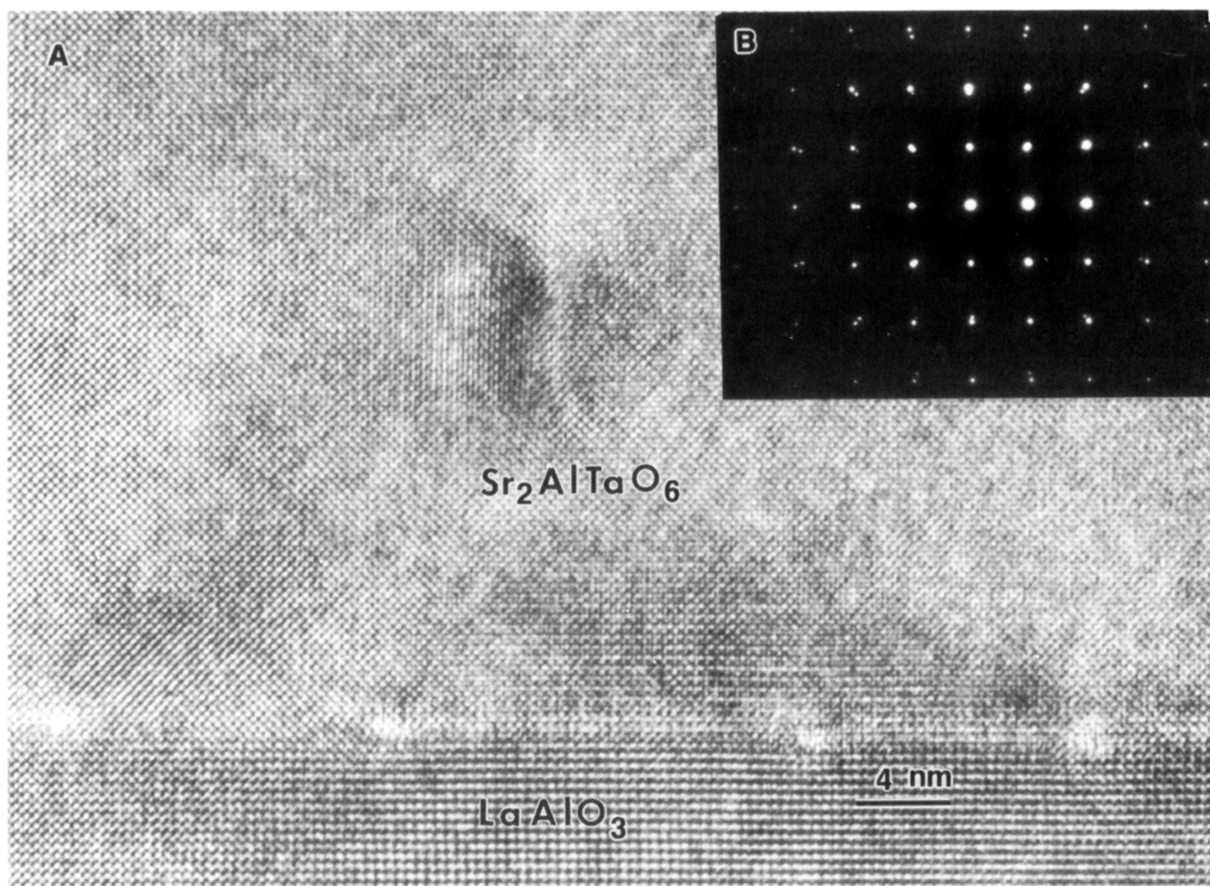

Figure 3. (a) Cross-sectional HREM image of an MOCVD-derived Sr_2AlTaO_6 film grown on (110) $LaAlO_3$ at 850 °C. (b) Selected-area TEM diffraction pattern of an MOCVD-derived Sr_2AlTaO_6 film grown on (110) $LaAlO_3$. The electron beam is parallel to the film surface.

situ on $LaAlO_3$ substrates by MOCVD. The deposition is highly sensitive to substrate temperature, presumably reflecting both the volatilities of the corresponding metal fluorides and kinetic aspects of the precursor thermolysis and film nucleation/growth/crystallization processes. Further studies of the growth process and applications to multilayer architectures are in progress.

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