In Situ Growth of Epitaxial $YAlO_3$ Thin Films by Metal-Organic Chemical Vapor Deposition

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The successful integration of high-temperature superconducting (HTS) materials into active and passive microelectronics technologies depends crucially upon advances in the fundamental science of thin film formation and performance.[1] To this end, considerable progress has recently been made in the growth of HTS films by both physical vapor deposition (PVD) and metal-organic chemical vapor deposition (MOCVD) techniques.[1] Equally important for multilayer device fabrication is the quest for lattice-matched, chemically compatible, low dielectric constant/low dielectric loss materials for use as substrates, buffers, dielectrics, insulators, and overlayers.[2-4] As in HTS film formation, MOCVD offers the attraction for insulating ceramic film growth of the ability to coat complex shapes, simplified apparatus, adaptability to large scale/area depositions, and depositions at low temperatures.[5-7] $YAlO_3$ is an example of a promising insulating material for HTS device applications, having a good lattice and thermal expansion match with YBCO, BSCCO, and TBCCO as well as excellent dielectric properties ($\epsilon \approx 16$ at 77 K, 10 GHz; $\tan \delta = 1 \times 10^{-5}$ at 77 K, 10 GHz).[8] Furthermore, $YAlO_3$ exhibits no phase transitions between 25 and 1300 °C, which in other materials results in twinning and degradation of film properties.[8] We report here the first in situ (not requiring a postanneal) deposition of phase-pure epitaxial thin films of $YAlO_3$ by MOCVD.

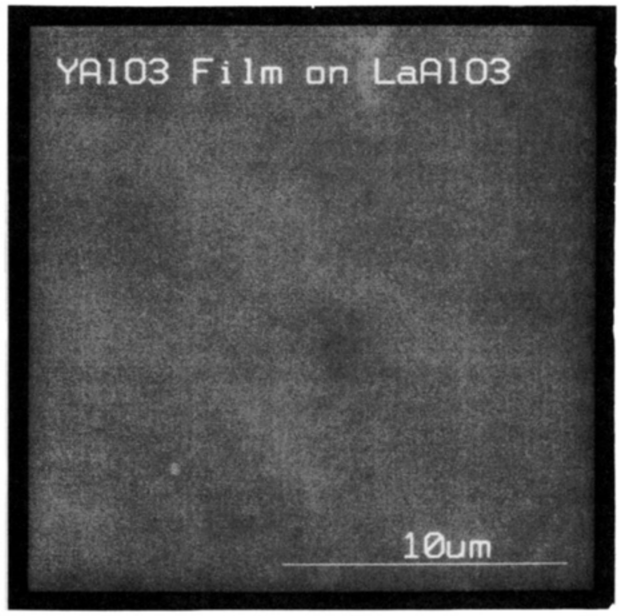

Figure 1. Scanning electron micrograph of an as-deposited MOCVD-derived $YAlO_3$ film on a (110) $LaAlO_3$ substrate.

Efficient MOCVD processes depend crucially upon the development of high-purity metal-organic precursors with a high and stable vapor pressure as well as predictable gas-phase reactivity. Strategies for precursor design include encapsulation of the metal ions in sterically encumbered, nonpolar ligation environments.[9,10] In the present case, the complexes $Y(dpm)_3$ (dpm = dipivaloymethanate), $Al(acac)_3$ (acac = acetylacetonate) represent an embodiment of this strategy and are successfully employed as volatile metal-organic precursors for $YAlO_3$.

MOCVD of $YAlO_3$ films was carried out in a horizontal stainless steel reactor having individual inlet tubes for introducing the volatile, metal-organic precursors as well as the reactant gas N_2O. Deposition was carried out at a system pressure of 1.5 Torr (background pressure = 0.10 Torr), and the single crystal (110) $LaAlO_3$ substrate (indexed here in the rhombohedral system) was heated resistively to 800 °C. N_2O (99.0%) was introduced at 150 sccm immediately upstream of the susceptor. The precursors $Y(dpm)_3$ and $Al(acac)_3$ were synthesized[11] from

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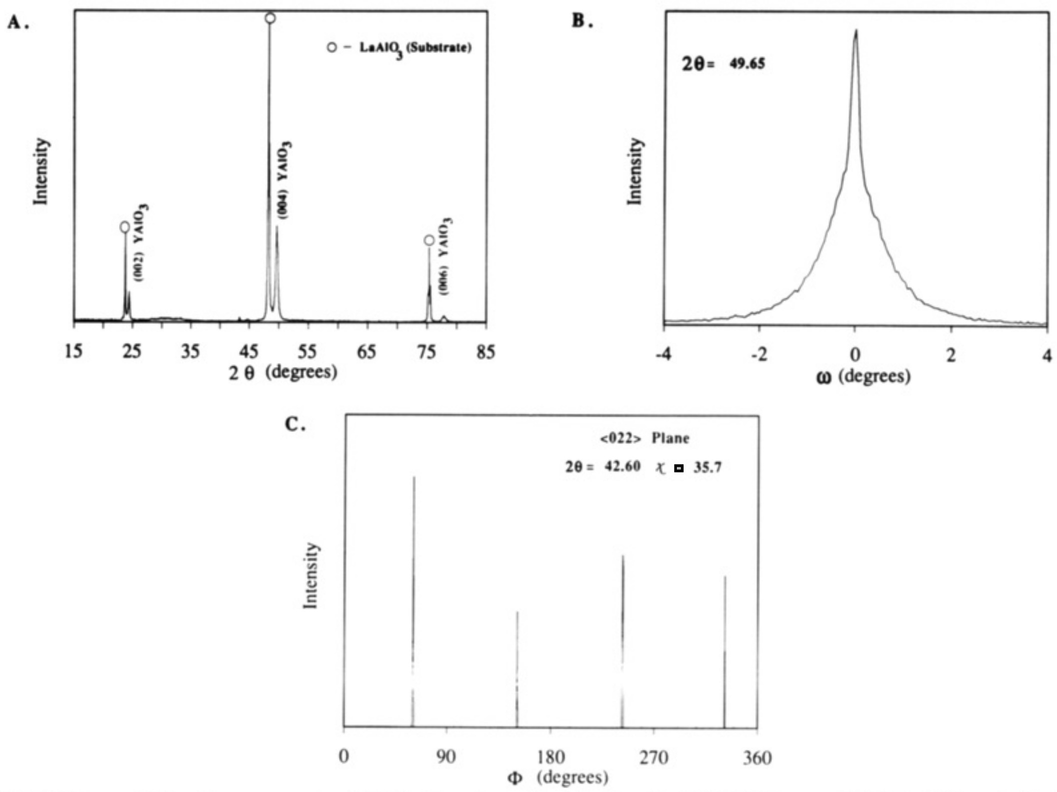

Figure 2. (A) θ–2θ X-ray diffraction scan of a $YAlO_3$ film deposited by in situ MOCVD on a (110) $LaAlO_3$ substrate. (B) X-ray diffraction ω scan rocking curve of the (004) reflection of an MOCVD-derived $YAlO_3$ film on a (110) $LaAlO_3$ substrate. The fwhm of the reflection is 0.44°. (C) X-ray diffraction ϕ scan of an MOCVD-derived $YAlO_3$ film on a (110) $LaAlO_3$ substrate.

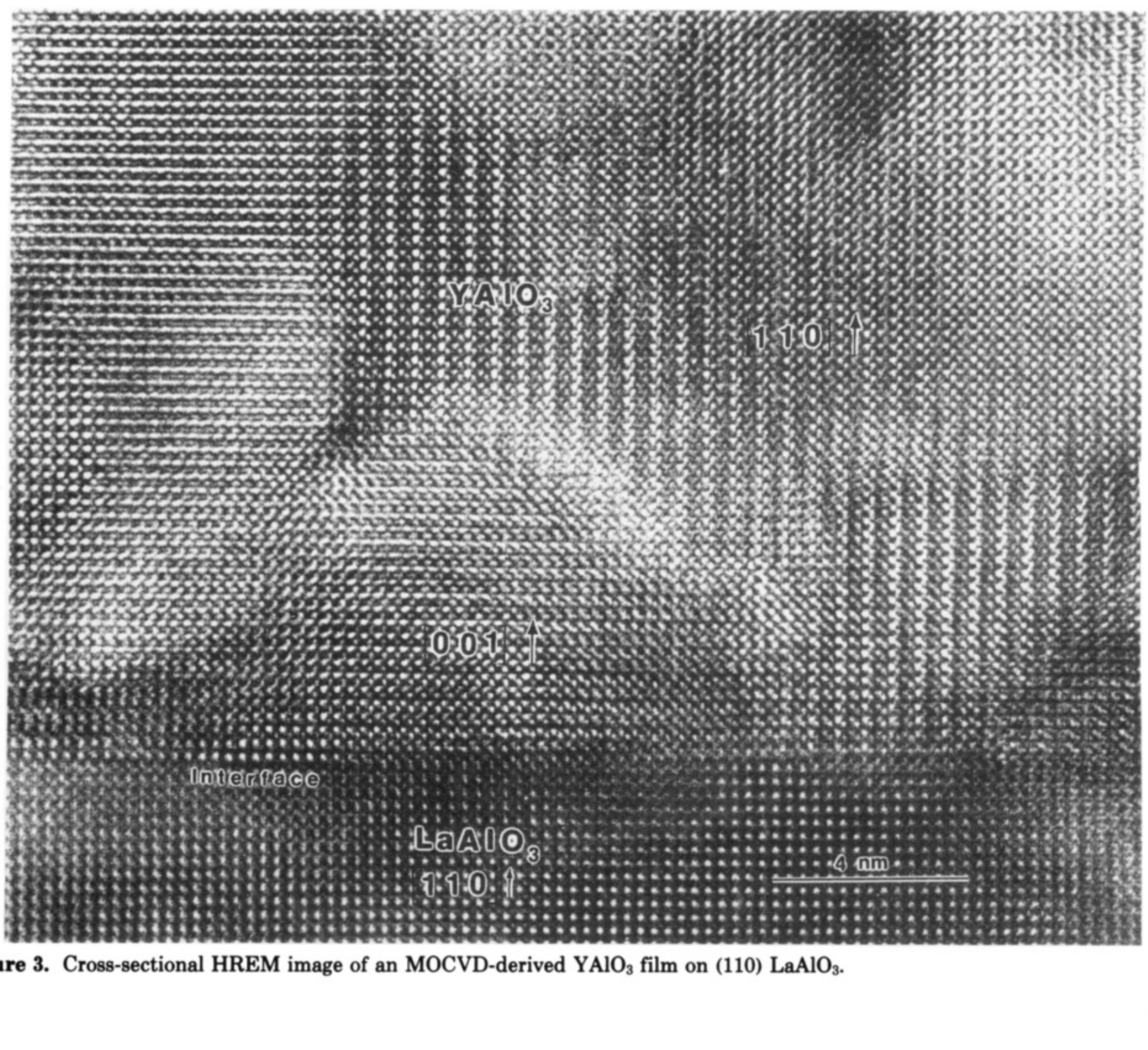

Figure 3. Cross-sectional HREM image of an MOCVD-derived $YAlO_3$ film on (110) $LaAlO_3$.

high-purity metal starting materials and were multiply sublimed. The precursors (~5.0 g each) were contained in individual thermostated (100 °C) 250-mL Pyrex round bottom flask reservoirs and were transported to the reaction chamber by Ar flowing at 100 and 40 sccm, respectively. Typical film growth rates were ~1.0 μm/h.

As evidenced by SEM images (Figure 1), the present in situ grown $YAlO_3$ films have a smooth, mirrorlike surface, in contrast to typical results for metal oxide films grown by two-step MOCVD/postanneal processes.[12] X-ray diffraction (Ni-filtered Cu Kα radiation) θ–2θ scans of the MOCVD-derived $YAlO_3$ films (Figure 2A) reveal phase purity and a high degree of texturing. The coincidence of the (002) and (110) diffraction planes renders initial differentiation of film (001) and (110) growth orientations ambiguous (vide infra). Diffractometric rocking curves (ω scans) performed with a double crystal diffractometer (Cu Kα radiation) indicate a high degree of alignment/perfection of the film growth planes with respect to the substrate surface. Thus, the full width at half maximum (fwhm) of the $YAlO_3$ (004)/(220) reflection was determined by least-squares fitting of the data to be 0.44° (Figure 2B) versus 0.11° for the corresponding (220) reflection of the single-crystal substrate. A ϕ scan was 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 89° or 91°. A typical ϕ scan of the ⟨202⟩ family of diffraction planes (Figure 2C) exhibits the requisite 2-fold (nearly 4-fold) symmetry, hence demonstrating a high level of in-plane epitaxy.

Cross-sectional high-resolution electron microscopy (HREM) was used to further define the microstructure of the epitaxial $YAlO_3$ growth. As can be seen in Figure 3, the films show sizeable regions of single-crystal, defect-free, and epitaxial growth with atomically abrupt film–substrate interfaces. The HREM images and selected area diffraction patterns (Figure 4) also reveal that the present MOCVD-derived $YAlO_3$ films actually consist of two types of structurally related domains which are not readily distinguishable by standard X-ray diffraction techniques: one with the *c* axis perpendicular to the substrate surface and the other with the [110] direction perpendicular to the substrate surface, corresponding to growth with (001) and (110) orientations, respectively.

In summary, these results demonstrate that phase-pure, highly oriented, epitaxial thin films of the perovskite dielectric $YAlO_3$ can be efficiently grown in situ on (110) $LaAlO_3$ substrates by MOCVD at 800 °C using Y and Al β-diketonate precursors. Application of this approach to the fabrication of more elaborate multilayer architectures as well as extensions to other dielectric and photonic metal oxide materials is currently under investigation.

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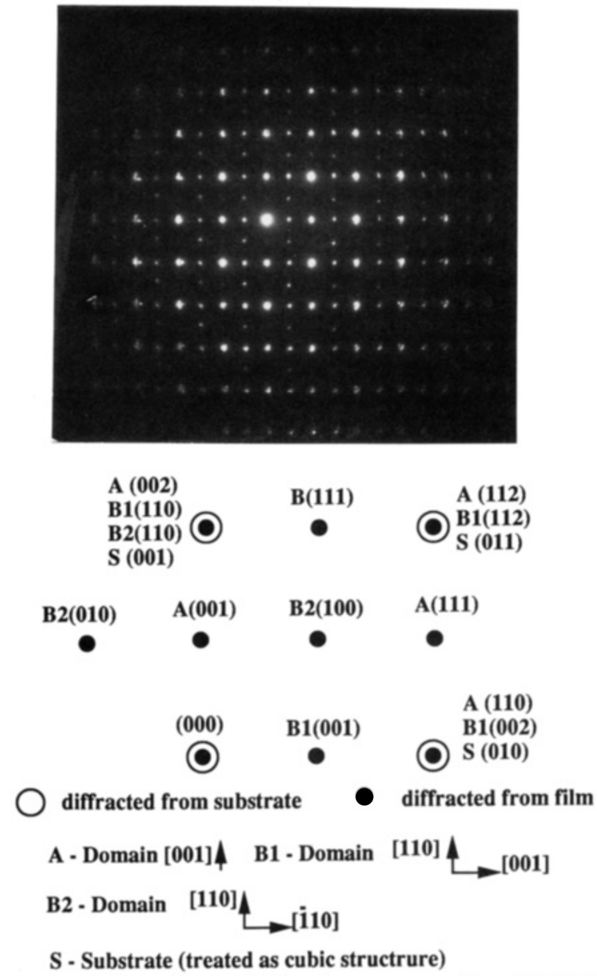

Figure 4. Selected-area diffraction pattern of an MOCVD-derived $YAlO_3$ film on (110) $LaAlO_3$ by TEM. The electron beam is perpendicular to the film surface.

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