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Heteroepitaxy of $LaAlO_3$ (100) on $SrTiO_3$ (100): In Situ Growth of $LaAlO_3$ Thin Films by Metal–Organic Chemical Vapor Deposition from a Liquid Single Source

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The growing demand for the fabrication of multilayer structures based on superconductor–insulator–superconductor (SIS) arrays has spurred intense scientific investigation over the past few years on growth of both epitaxial HT_c films[1] and insulating layer substrates.[2] Multilayer arrays with several (up to 15 or more) epitaxial layers were effective in applications to superconducting quantum interference devices (SQUID)[3] and, therefore, considerable attention has been devoted to insulating materials required to grow substrates, buffers, interlayers, or overlayers. These films must possess surface structures that promote epitaxial growth in the subsequent HT_c layers and must have suitable dielectric properties for optimum device performance.

Many different techniques were applied to the deposition of insulating metal oxide films. For instance, a variety of buffer layers, such as MgO,[4] $SrTiO_3$,[5] $LaAlO_3$,[6] $NdAlO_3$,[6] $NdGaO_3$,[6] were produced by PVD (physical vapor deposition) techniques. The metal–organic chemical vapor deposition (MOCVD) technology proved an interesting alternative or complement to PVD techniques for a large variety of different materials, ranging from HT_c films to insulating CeO_2,[7] $NdGaO_3$,[8] $YAlO_3$,[9] $PrGaO_3$,[10] and Sr_2AlTaO_6[11] layers. MOCVD presents several advantages over PVD techniques, and in particular two important issues are of major relevance, namely, the possibility of a large area deposition and easy extension to large-scale production.

Lanthanum aluminate is among the most suitable insulator for SQUIDs fabrication and is the most appropriate substrate for microwave applications. Few studies have been reported on the growth of $LaAlO_3$ on Si substrates by PVD techniques[6] and on sapphire[12a] and $SrTiO_3$[12b] substrates by sol–gel processes. As far as we know, application of the MOCVD technique is limited to the related deposition of $YAlO_3$ on $LaAlO_3$ substrates.[9]

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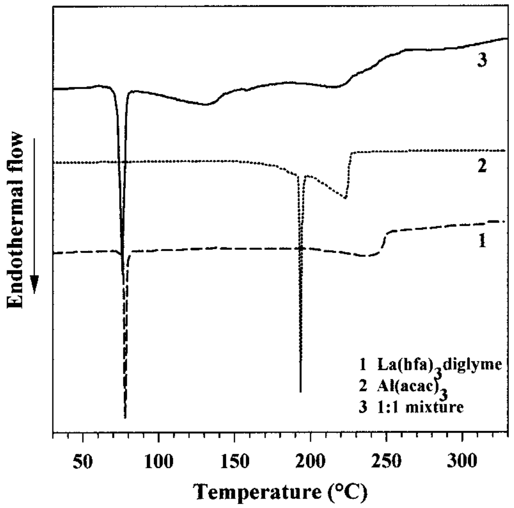

Figure 1. DSC curve of the La$(hfa)_3$·diglyme and Al$(acac)_3$ 1:1 mixture (—) compared to the curves of the pure La$(hfa)_3$·diglyme (— — —) and Al$(acac)_3$ (- - -) precursors.

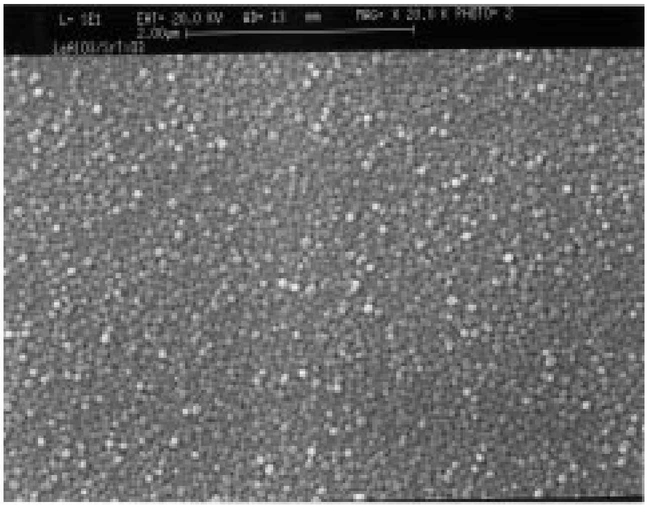

Figure 2. Scanning electron micrograph of an in situ deposited $LaAlO_3$ (100) film on $SrTiO_3$ (100).

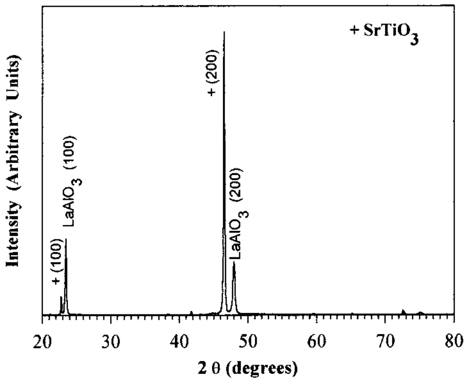

Figure 3. $\theta-2\theta$ XRD pattern of an in situ deposited $LaAlO_3$ (100) film on $SrTiO_3$ (100).

In this paper, we report on a very simple, low-cost route to high-quality $LaAlO_3$ (100) films on $SrTiO_3$ (100) substrates. The novelty of the present approach relies upon the use of the new La$(hfa)_3$·diglyme [Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, diglyme = bis-(2-methoxyethyl)ether] complex, which acts as a solvent for the aluminum precursor, thus affording a two-component liquid source.

The quality of any MOCVD process crucially depends on prerequisites of precursors.[13] Reproducible results are always associated with a careful control of the deposition parameters and, even more important, to highly pure precursors with clean decomposition pathways and constant mass-transport properties. We have recently reported on the accurate tailoring of the molecular architecture to yield new second-generation lanthanide precursors with excellent properties.[14-16] One of these precursors, La$(hfa)_3$·diglyme, has been applied to the MOCVD of $LaAlO_3$. Key characteristics of the new La$(hfa)_3$·diglyme precursor are high thermal stability even after melting and high vapor pressure,[14] which warrant constant transport rates (also under atmospheric pressure) from a liquid source. Even more interesting, it acts as a liquid solvent for the aluminum precursor. Indeed, the La$(hfa)_3$·diglyme adduct easily dissolves Al$(acac)_3$ (Hacac = acetylacetone) in a large concentration range. In Figure 1 the differential scanning calorimetry (DSC) curve of the 1:1 mixture is compared with data of the individual precursors, La$(hfa)_3$·diglyme and Al$(acac)_3$. In both cases of individual precursors, there is evidence of endothermic peaks due to melting (78.2 °C, La$(hfa)_3$·diglyme; 192.5 °C, Al$(acac)_3$) and to evaporation from melts (200−253 and 195−230 °C, respectively). In the case of the two-component single precursor, the lower temperature peak (74.0 °C) represents melting of the La$(hfa)_3$·diglyme component, while the second endothermic broad peak (85−160 °C) may be associated with Al$(acac)_3$ dissolution. Note, in this context, that the endothermic peak (192.5 °C) expected for the Al$(acac)_3$ melting is not observed in this case. Finally, the last, higher temperature (180−255 °C) endothermic process represents the evaporation of the two components. Optical microscope, polarized light data of the two-component mixture upon heating are in agreement with these conclusions, since the melting of the La$(hfa)_3$·diglyme is detectable at 73-75 °C, while still colored Al$(acac)_3$ crystals can be observed in the 75−90 °C interval. Afterward, they begin to dissolve and the dissolution is complete at 160 °C.

It is interesting to note that there is no evidence of ligand exchange both in the gas phase and in the melted multicomponent mixture. In fact, the FAB mass spectrum of the 1:1 mixture shows only the peaks due to the fragmentation of individual precursors,[16] namely, $[La(hfa)_2\cdot diglyme]^+$, $[La(hfa)\cdot diglyme + F]^+$, $[La\cdot diglyme + 2F]^+$, and $[Al(acac)_2]^+$. Moreover, preliminary ^{13}C MAS NMR experiments on the 1:1 melt (125 °C) show well-resolved resonances attributed to the individual precursors.

The consequent possible use of a two-component single source for $LaAlO_3$ film growth introduces an overall simplification in the MOCVD process as com-

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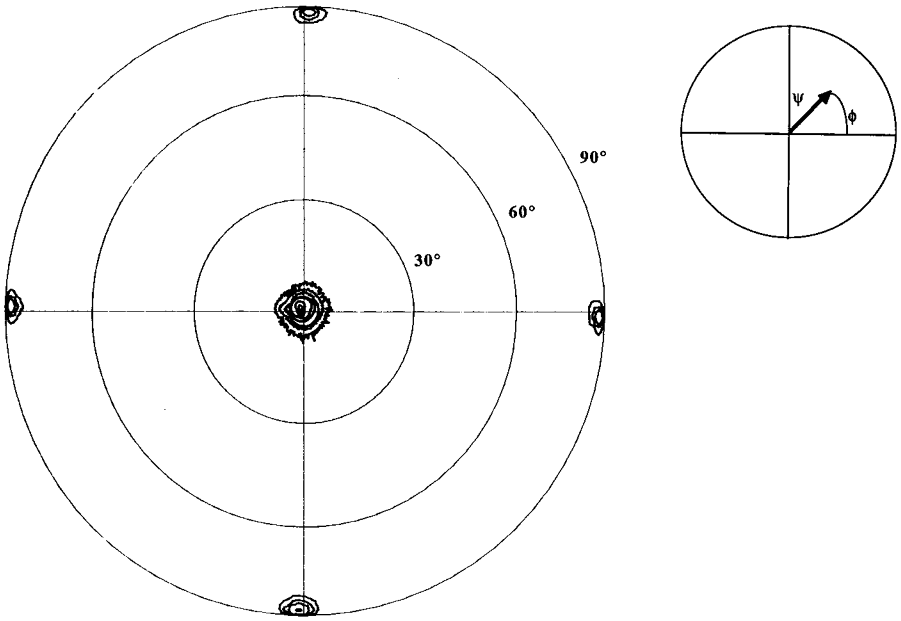

Figure 4. (002) $LaAlO_3$ pole figure ($2\theta = 48.06°$). The inset shows pole figure angle definition (ψ, ϕ).

pared with alternative possibilities adopting either external- or internal-source, multicomponent reactors. The present approach, in fact, does not require multiple temperature controllers of sublimation zones/bubblers to maintain the required 1:1 stoichiometry in the vapors. The present liquid La/Al single source can be therefore used in a simple, economical, horizontal, monocomponent reactor[17] and allows constant and efficient mass-transport of a 1:1 La/Al mixture even for very long experiments. Note that the run to run reproducibility is very good with a high yield (>80%) of $LaAlO_3$ films possessing excellent properties.

To date issues of multicomponent precursors have been successfully attempted using flash vaporization techniques from a mixture of solid, liquid, or dissolved precursors.[18]

The MOCVD reactor assembly presently used consists of a horizontal hot-wall quartz reactor fitted with individual inlet tubes for the carrier (Ar, 100 sccm) and reaction (humid O_2, 100 sccm) gases. The single source reservoir is an Al_2O_3 boat placed inside the reactor in the sublimation zone. It can be resistively heated in a wide temperature range to control the growth rate. In present experiments, the evaporation temperature was 130 °C while the substrate temperature was varied in the 850−1050 °C range. Depositions were carried out at 3.0 Torr (background pressure 0.2 Torr).

In situ grown $LaAlO_3$ films have mirrorlike surfaces. Scanning electron microscopy (SEM) images (Figure 2) show that films are highly smooth and consist of ~80 nm grains uniformly distributed. Energy dispersive X-ray analyses (EDX)[19] show, in addition, that the films always have the expected chemical composition independent of the substrate temperature in the entire range presently investigated. Note, in this context, that early experiments adopting separated precursors evaporated at the same temperature have shown that the film composition depends on the deposition temperature.[20] The film thickness, evaluated by combining SEM/EDX mapping, ranges from 300 to 600 nm, depending on the deposition time. The typical growth rate is 10 nm/min.

Figure 3 shows the $\theta-2\theta$ XRD pattern collected in Bragg−Brentano (BB) geometry. The two lines observed in addition to the expected (001) and (002) $SrTiO_3$ reflections can be identified as the (001) and (002) of the $LaAlO_3$ perovskite structure. Actually, $LaAlO_3$ has a 0.2% rhombohedral (r) distortion;[21] therefore, the (001) and (002) lines of the pseudocubic structure should be referred to as (012) and (024), respectively, in the correct r indexing (according to ICDD card #31-22[22]). Nevertheless, the simpler pseudocubic indexing will be used in the following.

The BB pattern clearly indicate a *c*-axis preferred orientation of $LaAlO_3$, even though no further information on the in-plane growth can be obtained from this measurement. To gain further insight into the in-plane crystallography, the (002) $LaAlO_3$ pole figure has been collected using a parallel beam geometry (PB) and a four-circle goniometer. An intense pole at $\psi = 0°$ and four distinct poles near $\psi = 90°$ and $\phi = 0, 90, 180,$ and $270°$, respectively, have been found (Figure 4), in

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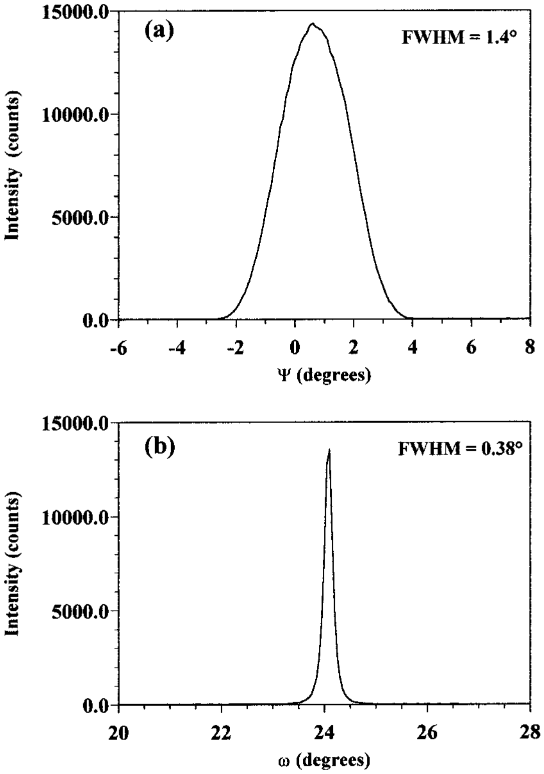

Figure 5. ψ-Scan across the (002) $LaAlO_3$ maximum at $\psi = 0°$ (a). Rocking curve of the (002) $LaAlO_3$ reflection (b).

accordance with the typical cube-on-cube growth:

$$[001]\ SrTiO_3\ \|\ [001]\ LaAlO_3, [100]\ SrTiO_3\ \|\ [100]\ LaAlO_3$$

Concerning the presence of secondary growth directions, note that the background in Figure 4 is below 20 counts (lowest contour), whereas the pole maximum is 17 000 counts; therefore, secondary growth directions can be ruled out within the limit of sensitivity of the used technique. As to $LaAlO_3$ mosaicity, a ψ-scan across the (002) $LaAlO_3$ maximum at $\psi = 0°$ (Figure 5a) indicates a good in-plane texture, with a fwhm of 1.4° and an intensity maximum at $\psi = 0.68°$. Note that the shift of 0.68° in the intensity maximum is related to the miscut of the $SrTiO_3$ single crystal. Additional pole figures, reported as Supporting Information, are indication of good in-plane orientation.

Further information has been obtained from the rocking curve, measured after correcting for the slight misorientation in substrate orientation. In fact, as indicated by the low intensity of the substrate peak in the BB pattern of Figure 3, the single-crystal substrate (and the $LaAlO_3$ thin film) is not perfectly aligned along the goniometric axis. This can be attributed to minor imperfections in the cut of the $SrTiO_3$ crystal along [*h*00], a frequently observed feature of single-crystal substrates used for thin film deposition. Therefore, the rocking curve of the (002) $LaAlO_3$ reflection has been recorded after correcting ψ and ϕ angles in order to optimize the intensity of the (00*l*) substrate and thin film peaks. In addition, any possible peak overlapping effect between (002) lines of substrate and the thin film has been precluded by adopting a very narrow incident beam vertical slit ($^1/_{32}$°). The rocking curve shown in Figure 5b (fwhm $\cong$ 0.38°) confirms the low mosaicity of the $LaAlO_3$ thin film.

The good quality of the films has been tested by depositing superconducting films of the TlBaCaCuO family[23] by MOCVD and thallium vapor diffusion. Preliminary results indicate that the present MOCVD-grown $LaAlO_3$ films induce epitaxial growth of *a*-axis orientated TlBaCaCuO films. This may be proposed as a possible route for the fabrication of Josephson-like *a*-*c* junctions. In fact, deposition of $LaAlO_3$ (100) on half of a $SrTiO_3$ (100) substrate allows the fabrication of *a*-*c* junctions based on TlBaCaCuO materials.

In summary, high quality $LaAlO_3$ (100) films were epitaxially grown on $SrTiO_3$ (100) substrates from a liquid single-source consisting of a solution of $Al(acac)_3$ in $La(hfa)_3$·diglyme. Preliminary data on the use of these films to grow HT_c TlBaCaCuO films provide an indication that they are very attractive layers to fabricate Josephson junctions of the *a*-axis/*c*-axis type.

The described approach, which uses a precursor as a solvent for the other components, is rather interesting and can be applied to the in situ fabrication of multicomponent films using a monocomponent reactor. Note that this approach is very promising for low-cost manufacturing and economical scale-up of high-quality $LaAlO_3$ films.

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Supporting Information Available: Additional pole figures (3 pages). Ordering information is given on any current masthead page.

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