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Deposition and x-ray characterization of epitaxial thin films of $LaAlO_3$

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ABSTRACT

Highly epitaxial thin films of lanthanum aluminate ($LaAlO_3$) have been obtained on strontium titanate ($SrTiO_3$) substrates by means of atomic layer deposition using $La(thd)_3$ (Hthd = 2,2,6,6-tetramethylhepta-3,5-dione), $Al(CH_3)_3$ and ozone as precursors. The system shows a near linear relationship between pulsed and deposited composition. Thin films with stoichiometric composition have been subject to thermal annealing at 650 °C under oxygen atmosphere, thereby achieving epitaxial films on Ti-O-terminated substrates of $SrTiO_3$. The thin film||substrate epitaxial relationship is determined to be $LaAlO_3(100)|LaAlO_3[100]||$-$SrTiO_3(100)|SrTiO_3[100]$ by use of synchrotron radiation. Selected films were also deposited on $LaAlO_3(100)$ to achieve homoepitaxy. This resulted in the observation of split peaks for high q-reflections, pointing towards slight differences in stoichiometry. For ultrathin films, Bragg satellites were observed around the specular reflections, coming from either surface- or interface reconstruction.

1. Introduction

The insulating lanthanum aluminate ($LaAlO_3$, LAO) with perovskite type structure (R-3c) has, due to its high-κ dielectric and thermal properties, been thoroughly studied for use in microelectronics and as a buffer layer in the growth of other perovskite type oxides [1–3]. In recent years, more exotic properties have been discovered, such as superconductivity on the interface between LAO and strontium titanate ($SrTiO_3$, STO) [4]. Recent data provide evidence of the coexistence of superconductivity and ferromagnetism at this interface [5], a rarely encountered phenomenon. These exotic effects seem to stem from a polarity discontinuity at the LAO/STO-interface due to the heterosystem maintaining the $AO–BO_2$ stacking sequence, giving rise to a polar LaO^+/TiO_2^0 interface. This in turn induces charge transfer effects and a 2D-electron gas [6,7] that exhibit superconductivity below 300 mK [8].

Careful investigations of interfacial structures and accompanying exotic effects require perfect interfacial morphology. This is commonly achieved by growth of a thin film of one compound on a substrate of the other terminated by a single structural species. Perovskite substrate surfaces do not naturally become single species terminated by simple cutting, however, a chemical route for TiO_2-termination of STO has been described by Kawasaki et al. [9]. The desired heterostructural interface can thus be obtained by depositing LAO on such a pre-treated substrate of STO. This has previously been attempted using pulsed laser deposition [10], molecular beam epitaxy [11,12] and sputtering [13] among other techniques.

This study aims at providing an easily achievable route to the LaO^+/TiO_2^0-interface by depositing a highly oriented thin film of LAO on a pre-treated, TiO_2 terminated STO substrate. Corresponding LAO films are further deposited on non-pretreated STO substrates for comparison. The films are deposited using atomic layer deposition (ALD), which is a chemical vapor deposition related technique, and using commonly available precursors. ALD utilizes a layer-by-layer self-limiting growth mechanism providing control of interfacial chemistry, conformality and film thickness at the (sub-)monolayer level. Deposition of ternary oxides by ALD is commonly achieved by sequentially introducing volatile gaseous metal-organic precursors separated by an oxide precursor usually consisting of water or ozone [14].

Deposition of polycrystalline LAO by ALD is previously reported by Nieminen et al. [15] using $La(thd)_3$ (Hthd = 2,2,6,6-tetramethyl-3,5-heptanedione) and $Al(acac)_3$ (acac = acetylacetonate) as precursors. Attempts using TMA (TMA = $Al(CH_3)_3$, trimethylaluminium) and $La(i\text{-}PrCp)_3$ (i-PrCp = isopropyl cyclopentadienyl) as precursors have been made to provide highly oriented thin films of stochiometric LAO on STO [16], although lacking saturative conditions for the $La(i\text{-}PrCpd)_3$ precursor. In this work we provide evidence of ALD growth of LAO using the precursor combination TMA/O_3 and $La(thd)_3/O_3$, giving rise to a clearly surface controlled stoichiometry and very high structural orientation on STO-substrates. The obtained film structures have been subjected to a detailed analysis using synchrotron radiation at the Swiss–Norwegian Beam Lines at ESRF, Grenoble.

2. Experimental

Thin films were deposited in a commercial F-120 Sat ALD-reactor (ASM Microchemistry) using $La(thd)_3$ (Multivalent), TMA (technical grade) and O_3 as precursors. Ozone gas was produced by an OT-020 (Ozone Technology) generator fed with pure O_2 (99.999%, AGA) and used at an approximate flow rate of 500 cm^3 min^{-1}. $La(thd)_3$

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was sublimated at 185 °C, whereas TMA was kept at room temperature in an external bubbler. A carrier-gas flow of 300 cm^3 min^{-1} was supplied from a Nitrox UHPN 3001 generator producing 99.9995% inert gas.

The films were deposited on 2.5 × 2.5 cm^2 substrates of Si(100) and soda lime glass and on 1.0 × 1.0 cm^2 substrates of $SrTiO_3$(100) $LaAlO_3$(100) and MgO(100). In addition, some $SrTiO_3$(100) substrates were etched for 10 min in a buffered NH_4F–HF solution (Sigma-Aldrich) to achieve Ti–O-termination as described by Kawasaki et al. [9]. All substrates were further cleaned by pulsing O_3 prior to the depositions.

A number of La:Al pulsing ratios were investigated while keeping the total amount of metal pulses as close as practically possible to 1000. The resulting films had thicknesses between 40 and 80 nm. Selected depositions totaling 100 metal pulses were performed for comparison and to facilitate interfacial studies. The deposition temperature was fixed to 250 °C, which is well within possible ALD-windows of the binary processes applied [17,18].

The basic pulse sequence was n^*(3 s La(thd)$_3$), 5 s purge, 3 s O_3,, 5 s purge, m^*(1 s TMA), 5 s purge, 3 s O_3 and 5 s purge where n and m were varied to control the stoichiometry. The individual pulse and purge times were chosen with basis of prior optimization of these processes on the selected ALD reactor, and are well within saturation limits for ALD-growth. An order of pulse sequences facilitating both maximum and minimum mixing of the different metal sub cycles were applied to study the effects of surface chemistry on the thin film growth.

Resulting thin films were annealed in oxygen atmosphere (99.9%, AGA) at 650 °C for 30 min after a 20 °C min^{-1} ramp rate to induce crystallization. The samples were rapidly cooled to room temperature after heating by placing them on a metal plate. The cooling process was estimated to take 5–10 s.

The thin films deposited using 2000 and 100 total precursor cycles (corresponding to a thickness of approximately 130 and 7 nm) were used for structural characterization both as deposited and after annealing. A Bruker D8 Discover x-ray diffractometer equipped with a Göbel mirror providing parallel Cu-Kα radiation in conventional θ–2θ geometry was used for all home-lab XRD (x-ray diffraction) studies. A similar diffractometer equipped with a Ge220 monochromator crystal and a Göbel mirror was used for the x-ray reflectivity (XRR) measurements. Films of specific structural interest were thoroughly studied at BM01A of the Swiss–Norwegian Beam Lines at ESRF, using a KUMA six-axis diffractometer and a CCD area detector from Oxford Instruments [19]. This setup was used for reciprocal space mapping and peak analysis leading to information on structural integrity.

The La/Al stoichiometry was determined using x-ray fluorescence (XRF) measurements (Phillips PW 1400 XRF) equipped with the standard-less UniQuant software, (Omega Data Systems, ver. 2, 1994). Spectroscopic ellipsometry (J.A. Woollam α-SE) was used for determination of film thickness by fitting the acquired data to a Cauchy function. Topographical studies were performed using atomic force microscopy (AFM, Park Systems XE-70), equipped with a PPP-CONSTCR tip (Nanosystems) in contact mode for optimum lateral resolution.

3. Results and discussion

3.1. Atomic layer deposition of the La–Al–O system

The combined TMA/O_3 and La(thd)$_3$/O_3 precursor systems were studied by initially combining the metal pulses in a manner to enhance mixing. The targeted 1:1 composition between lanthanum and aluminium was achieved for a pulsed ratio of 1:1 between the metal precursors. As can be observed in Fig. 1, the achieved, deposited composition shows a nearly linear relationship with the pulsed composition, in particular for pulsed compositions La/(La + Al) > 0.5.

The growth rate of the deposited films varies in a non-linear manner between those of the binary end members (Fig. 1). A rapid change in growth rate around the 1:1 achieved composition points at a change in surface chemistry for this ratio.

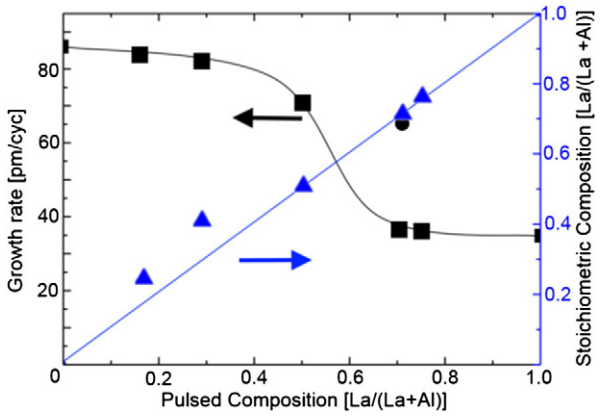

Fig. 1. Growth rate (black, left) and deposited composition (blue, right) as a function of the pulsed composition (La/(La + Al)). The black circle corresponds to a 5:2 pulsing ratio with minimal mixing in the supercycle.

The near linear relationship between pulsed and deposited composition, and in particular the rapid decay in growth rate around the 1:1 composition, is only true for maximum mixing of the metal sub cycles. As an example of the growth rate dependency on mixing conditions, in a deposition sequence composed of 5 sequential La(thd)$_3$ + O_3 pulses, and 2 sequential TMA + O_3 pulses, a growth rate of 64.3 pm/metal pulse was observed for the resulting film. This is in strong contrast to the 37.1 pm/metal pulse observed for maximum mixing of the metal precursor pulses. In both cases the stoichiometries of the films were similar.

Studies were undertaken for understanding the growth dynamics responsible for these observed deviations. The system proved to be highly complex, as the growth after a particular pulse seemed not only to be correlated to the preceding pulse, but also to the second and third preceding pulses. An analytical solution cannot be given, but the study provides evidence that both La(thd)$_3$ and TMA experience better growth conditions on an Al–O-surface than on a La–O-surface. This is also evident from Fig. 1, where the growth rate on each side of the stoichiometric composition is almost equal to the growth rate of the binary oxides.

3.2. XRD characterization of as-deposited and annealed films

The main focus was put on characterizing films containing $LaAlO_3$ phase, obtained by a 1:1 pulsed ratio of La(thd)$_3$ and TMA subcycles. This process was used to deposit films on substrates of Si(100), $SrTiO_3$(100), HF-etched $SrTiO_3$(100), MgO(100) and $LaAlO_3$(100). All comparative characterizations on the different substrates were performed on films deposited during the same run. Note that the $LaAlO_3$ unit cell is considered pseudocubic throughout this paper, and is not reduced to its proper rhombohedral cell. This is done to emphasize its structural relationship with $SrTiO_3$. All films were proven to be x-ray amorphous as deposited. For the films deposited on $LaAlO_3$(100), this was proven by means of x-ray reflectometry that identified a separate surface layer giving rise to Fresnel oscillations from the as-deposited films. Crystallization was imposed by subjecting the samples to thermal annealing at 650 °C for 30 min, see experimental section.

LAO films deposited on Si(100)- and MgO(100) remained amorphous after annealing, while ordering was observed by Homelab x-ray diffraction for 130 nm films deposited on $SrTiO_3$(100) substrates (Fig. 2). This may be explained by a smaller lattice mismatch of ~2% for the LAO/STO-systems, compared to a >10% mismatch for the LAO/MgO-system.