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Citation: Appl. Phys. Lett. **103**, 082901 (2013); doi: 10.1063/1.4818718
View online: http://dx.doi.org/10.1063/1.4818718
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v103/i8
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APPLIED PHYSICS LETTERS **103**, 082901 (2013)

# Effect of growth induced (non)stoichiometry on the thermal conductivity, permittivity, and dielectric loss of $LaAlO_3$ films

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(Received 18 June 2013; accepted 28 July 2013; published online 19 August 2013)

The effect of growth-induced non-stoichiometry on the thermal and dielectric properties of pulsed-laser deposited $LaAlO_3$ thin films is explored. The composition of the $LaAlO_3$ films was characterized via X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry and it is revealed that small deviations in laser fluence result in deviations of cation stoichiometry as large as a few atomic percent. The thermal conductivity is also found to be especially sensitive to non-stoichiometry, with 3%-5% La-excess and La-deficiency resulting in 60%-80% reduction in thermal conductivity. The dielectric constant decreases and the loss tangent increases with increasing non-stoichiometry with differences between La-excess and La-deficiency. © *2013 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4818718]

Over the past decade, the perovskite $LaAlO_3$ has been considered as a possible candidate for "high-$\kappa$" gate dielectrics in complementary metal oxide semiconductor gate stacks (CMOS)[1–5] as a result of a larger band offset with Si, low atomic diffusion rates in $LaAlO_3$, and a lower likelihood of $SiO_2$ formation during processing as compared to other candidate dielectrics.[6–10] One of the primary limitations to the integration of $LaAlO_3$ in CMOS devices, however, is the high concentration of defects that are generally found in $LaAlO_3$. These defects can cause charge trapping, changes in transient threshold voltage, and degradation of Si carrier mobility.[11] If $LaAlO_3$ is to be used in such devices, it is essential to understand the nature of these defects, what gives rise to them, and how they affect the properties of the $LaAlO_3$ films so that they can be avoided or removed.

At the same time, much research has focused on the heterointerface between the band insulators $LaAlO_3$ and $SrTiO_3$ where a conducting state was discovered.[12] This conducting state has been studied in numerous experiments, and there have been a number of interesting findings related to these interfaces including the observation of magnetic ground states,[13] superconductivity,[14] and built-in polarizations.[15] Researchers have also probed the effect of growth conditions on the resulting interfacial conductance including suggesting a strong relationship between the transport properties and oxygen vacancies.[13] More recently it has been demonstrated that there is a strong link between $LaAlO_3$ cation stoichiometry, oxygen vacancy formation, and the subsequent behavior of the $LaAlO_3/SrTiO_3$ interface that is likely driven by non-stoichiometry induced defects.[16–18] Taken together, these studies demonstrate that understanding the origin and nature of point defects in the $LaAlO_3$ system is important for both its application as a high-$\kappa$ gate dielectric material and its role in the $LaAlO_3/SrTiO_3$ heterointerface. The current work examines $LaAlO_3$ films grown via pulsed-laser deposition (PLD) at a range of laser fluences. We utilize X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry to probe the chemical composition, time-domain thermoreflectance to probe the thermal conductivity, and capacitance-voltage studies to probe the dielectric properties of the films in order to understand the effect of non-stoichiometry-induced defects on film properties.

Thin films of $LaAlO_3$ between 100 and 300 nm in thickness were grown via PLD using a KrF excimer laser (LPX 205, Coherent) in 1 mTorr of oxygen at 750 °C (this temperature refers to the temperature of the Ag-paint used to provide thermal contact between the substrate and the heater plate as measured via pyrometry). Films were grown from a single crystal $LaAlO_3$ target (1 mm thick, $LaAlO_3$ (001)) at a laser repetition rate of 1 Hz while the laser fluence was varied between 1.2 and 2.0 $J/cm^2$ (details of the fluence determination are provided in Ref. 16). The films were grown on $SrTiO_3$ (001) and 0.5% Nb-doped $SrTiO_3$ (001) single crystal substrates (Crystec, GmbH). Consistent with previous studies the target was sanded, cleaned, and sufficiently pre-ablated to assure the target surface had reached steady state prior to growth.[19,20] Following the growth, films were cooled at 5 °C/min to room temperature at the growth pressure.

Films were characterized by an array of techniques to probe their chemical, electrical, and thermal properties. Chemical analysis of samples was completed using a combination of X-ray photoelectron spectroscopy (XPS, Kratos Axis XPS, monochromatic Al X-ray source with charge neutralization during collection via electron beam bombardment) and Rutherford backscattering spectrometry (RBS, incident ion energy of 2 MeV, incident angle $\alpha = 22.5°$, exit angle $\beta = 52.5°$, and a scattering angle $\theta = 150°$). Thermal conductivity was probed from films between 250 and 300 nm thick using time-domain thermoreflectance (TDTR).[21,22] Finally, electrical characterization included the study of dielectric constant and loss tangents of 110 nm Pt/300 nm $LaAlO_3$/0.5%Nb-$SrTiO_3$ capacitor structures using an Agilent 4284A LCR meter for frequencies between $10^3$ and $10^6$ Hz.

We begin by discussing the results of chemical analysis of the cation stoichiometry of these films. One non-destructive technique for characterizing film composition is to measure core-level photoelectron yields in XPS. For this study, we focus on the La 3$d$ and Al 2$p$ core electron peaks,

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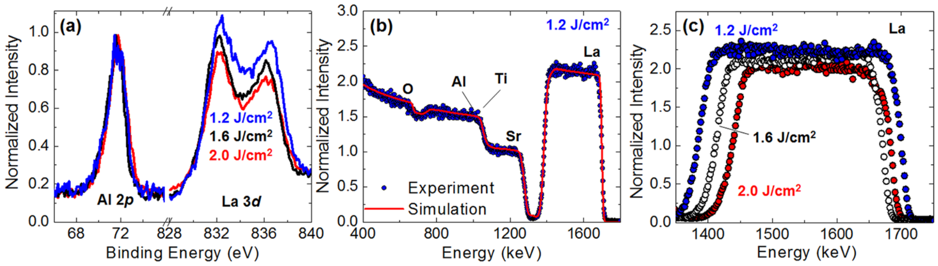

FIG. 1. Film composition for $LaAlO_3$ films as a function of laser fluence. (a) XPS spectra for various $LaAlO_3$ films where each spectrum has had the Tougaard background subtracted, and (for display purposes) the Al 2*p* peak has been normalized to unity. (b) RBS spectra of the $LaAlO_3$ film grown at 1.2 J/cm$^2$. (c) A zoom in view of the difference in the La-edge between each growth condition from the RBS studies. For all RBS spectra the Sr-edge height has been normalized to unity for comparison.

as those peaks represent the dominant contributions to the XPS signal for $LaAlO_3$ and provide direct insight into the cations of interest [Fig. 1(a)]. We calibrated the XPS signals using the same $LaAlO_3$ single crystals used as targets.[23] Briefly, the calibration was achieved by collecting spectra across the appropriate energy range for the core electron peaks of interest and then applying a Tougaard background simulation method to determine the intensity of the peaks. Based on these intensities the CasaXPS software calculates the chemical composition of the single crystal which is adjusted by fixing the sensitivity factor of the La 3*d* peak to published values and tuning the relative sensitivity factor of the Al 2*p* peak until the calibration sample achieves the composition value of 50% La as noted from the crystal suppliers. These sensitivity factors are then applied to all the films which undergo a similar analysis process.

To augment the XPS and to probe the stoichiometry throughout the thickness of the film (since XPS is limited to measuring composition within a few nanometers of the surface) we used RBS [Fig. 1(b)] to further probe the stoichiometry [Fig. 1(b)]. Cross-correlated XPS/RBS studies were performed on over ten samples with the values obtained from both methods generally being the same within 1%. The accuracy of the XPS and RBS studies was determined to be ±1% and ±0.8% of the La-content (as defined as $[La]/([La]+[Al]) \times 100$), respectively.[16]

Consistent with prior studies, large deviations in stoichiometry are seen to occur from relatively small variations in the laser fluence. From both the XPS and RBS studies, we observe that intermediate laser fluence (i.e., 1.6 J/cm$^2$) yields films with nearly stoichiometric cation compositions. Increasing the laser fluence yields La-deficient films [red data, Fig. 1] and decreasing the laser fluence yields films with La-excess [blue data, Fig. 1]. From our analysis we can summarize as follows. The XPS (RBS) studies reveal that growth at fluences of 1.2, 1.6, and 2.0 J/cm$^2$ result in La-content values of 55% (54%), 51% (50%), and 46% (48%), respectively. Thus growth at low fluence results in 4%-5% La-excess, growth at intermediate fluences results in nearly stoichiometric films, and growth at high fluence results in 2%–4% La-deficiency. It should be noted, however, that the fluence required to obtain stoichiometric films is likely to be highly system-specific with differences in the deposition process (e.g., differences in pulse duration, pulse-to-pulse energy stability, beam profile, beam divergence, target density, growth temperature, etc.) likely giving rise to deviations in the laser fluence required to produce stoichiometric films. The trend of going from La-excess to stoichiometric to La-deficient with increasing laser fluence should, however, remain similar.

Thermal conductivity has been shown to be a sensitive metric for determining film quality, with ideal stoichiometry being a necessary benchmark for achieving values close to that of the bulk. We measured thermal conductivity via TDTR using a 80 nm film of Al as the optical transducer [Fig. 2]. Consistent with prior work,[23] the thermal conductivity of the films shows a strong dependence on laser fluence and, therefore, film composition. Nearly stoichiometric films grown at a laser fluence of ∼1.6 J/cm$^2$ show the highest as-grown thermal conductivity. Increasing the laser fluence to 2.0 J/cm$^2$ (resulting in a 2%–4% La-deficiency) results in a reduction of the thermal conductivity by ∼60% compared to stoichiometric films. Likewise, reduction of the laser fluence to 1.2 J/cm$^2$ (resulting in a 4%–5% La-excess) reduces the thermal conductivity in the film by nearly 80% as compared to the stoichiometric films. The observed stoichiometry-dependence of the thermal conductivity is a direct manifestation of how defects in materials impact phonons. These observations are well matched to prior work in modelling defects in non-stoichiometric $LaAlO_3$ (Ref. 24) which predict

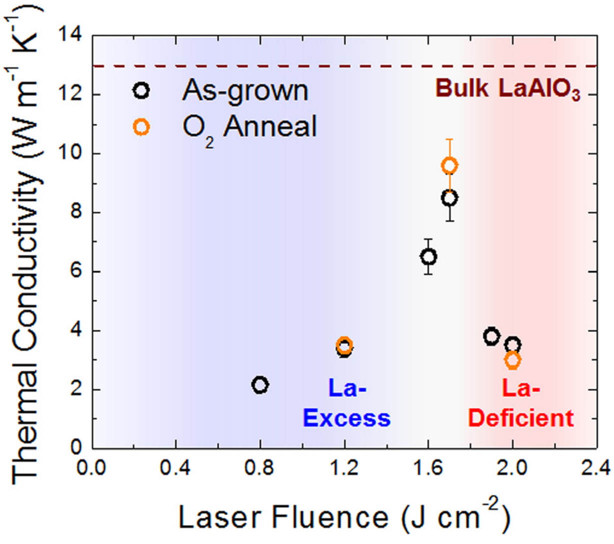

FIG. 2. Thermal conductivity of $LaAlO_3$ films as a function of laser fluence for as-grown (black, open circles) and post-annealed (orange, open circle) samples. After annealing, negligible changes in thermal conductivity are observed in La-excess and La-deficient samples (some data points overlap).

cation vacancy point defects acting as the primary accommodation for such non-stoichiometry (as opposed to secondary phase formation common in other oxide systems). We hypothesize that these point defects serve to increase disorder in the system, thereby increasing phonon scattering rates and driving a reduction of the thermal conductivity that is essentially symmetric about the nearly stoichiometric films.

It should be noted that even nearly stoichiometric $LaAlO_3$ films did not possess thermal conductivity values that match measurements of bulk substrates ($13 \pm 1\ W\,m^{-1}\,K^{-1}$). There are a number of possible explanations for this observation. First, due to the difficultly in controlling stoichiometry to better than 1%, it is possible that the nearly stoichiometric films are, in fact, slightly off stoichiometric, and due to the sensitivity of thermal conductivity to stoichiometry, this could account for slightly diminished thermal conductivity values. In this same vein, some RBS spectra show a slight increase in La-content in the near surface area for films thicker than 200 nm. It appears that continuous growth from the same target leads to a slight drift in the composition, possibly due to preferred ablation during the growth process for long deposition times. TDTR requires relatively thick films (i.e., >200 nm) in order for the film thermal conductivity derived from experimental data to be insensitive to interfacial thermal resistances and substrate thermal properties. Therefore, diminished thermal conductivities could be the result of the small stoichiometry deviations that occur over long deposition times. Finally, due to the high adatom kinetic energy associated with the PLD growth process, it is possible to have lattice-distorting knock-on damage and/or oxygen non-stoichiometry that can further reduce the thermal conductivity. To probe, this, we subjected 3 samples (nearly stoichiometric, La-excess, and La-deficient) to 1-h anneals at 1000 °C in 1 atm of oxygen (orange, open circles, Fig. 2). The effects of the annealing process are dependent on film stoichiometry. Nearly stoichiometric samples are seen to increase their thermal conductivity by ∼10%, indicating that the anneal potentially heals some amount of knock-on damage or oxygen non-stoichiometry. In the case of the non-stoichiometric $LaAlO_3$ films, however, the anneal does not appreciably change the observed thermal conductivity. This suggests that the diminished thermal conductivity is likely driven by non-stoichiometry which cannot be alleviated by a simple anneal.

Room temperature permittivity ($\varepsilon_r$) and dielectric loss (tan $\delta$) were calculated from capacitance-voltage measurements made across the frequency range $10^3$–$10^6$ Hz. The $\varepsilon_r$ of nearly stoichiometric ($1.6\ J/cm^2$) and La-excess ($1.2\ J/cm^2$) films were found to be essentially constant at ∼26 across the 4 decades of frequency studied here [Fig. 3(a)]. Moving to La-deficient films ($2.0\ J/cm^2$) resulted in a slight decrease in the overall magnitude of $\varepsilon_r$ [Fig. 3(a)]. Similar trends were observed in the dielectric loss [Fig. 3(b)]. Both the nearly stoichiometric and La-excess films exhibited lower dielectric loss (<0.01) at all frequencies studied, although the nearly stoichiometric films had a slightly higher loss in the higher frequency regime. The La-deficient films, on the other hand, exhibited enhanced losses at all frequency ranges with low frequency measurements yielding the highest losses. The changes in dielectric permittivity and loss provide more insight into the nature of the defects in these various films. While thermal measurements indicated an increase in defects for both cases, these measurements indicate that the defects possess different electronic behavior for the La-excess and La-deficient films.

Due to the importance of $LaAlO_3$ as both a candidate high-$\kappa$ dielectric and in the $LaAlO_3/SrTiO_3$ heterointerface, numerous modeling studies have probed the expected defect structures in this material.[11,17,24–26] Although the details are still a matter of contention, the various approaches are beginning to condense on the following trends. First, in samples exhibiting La-excess most models suggest the formation of a neutral vacancy complex (i.e., in Kroger-Vink notation $2V_{Al}''' + 3V_O''$). In samples exhibiting La-deficiency (or Al-excess), on the other hand, the defect possessing the lowest energy which is also compatible with the overall chemistry of the material is a neutral vacancy on the La-site (i.e., $V_{La}^{x}$). Consistent with these predictions, recent high-resolution scanning transmission electron microscopy studies[17] that focused on the *B*-site structure of $LaAlO_3$ show that La-excess samples possess a local accumulation of *B*-site vacancies while La-deficient samples do not. Thus, the observed properties can be interpreted in this context. First, the presence of defects (be they individual or clusters of point defects) results in a diminished thermal conductivity due to the disruption of the lattice and the dominant lattice contribution to thermal conduction. Second, the presence of neutral vacancy pairs and clusters in La-excess films results in no extra charge donated to the lattice and thus there is minimal effect on both the dielectric permittivity and loss. Third, it is thought that La-deficient films possess neutral vacancies on the La-site which requires that three-electrons be donated to the lattice for each such vacancy. It should be noted that these

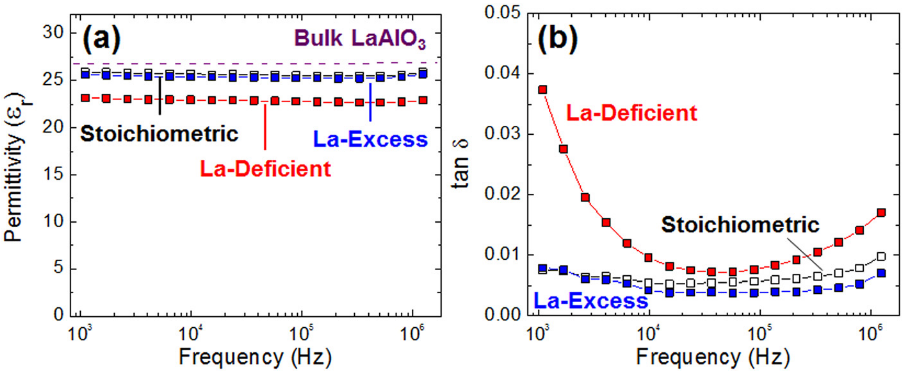

FIG. 3. (a) Dielectric permittivity and (b) loss tangent for $LaAlO_3$ films grown to possess La-excess, stoichiometric, and La-deficient compositions.

additional electrons are likely not free to move about the lattice. All films reveal room-temperature resistance $>50\,\mathrm{M\Omega}$ (at 300 K), consistent with what is expected for LaAlO$_3$ where even heavily alloyed films (possessing $>10\%$ of ionic dopants) do not exhibit measureable conductivity until $>400\,^{\circ}\mathrm{C}$.[27] Instead these carriers are likely bound to (or nearby) the defects (thereby maintaining the relative high resistance of the films) but can locally work to screen the polarizability of the material and lead to losses and reduced permittivity. This would be consistent with the fact that the loss tangent is only slightly increased for the La-deficient samples as compared to the stoichiometric and La-excess films at room temperature.

We have shown that variations in LaAlO$_3$ stoichiometry are readily achieved by small changes in PLD laser fluence. These changes in stoichiometry can impact the thermal conductivity and dielectric response in significant ways. Both La-excess and La-deficiency were seen to decrease the thermal response by $\sim$20% for every 1% we are off in La-content films. The change in the dielectric permittivity and loss was somewhat asymmetric, however, with La-excess having no appreciable change of the permittivity or loss and La-deficiency decreasing the permittivity by $\sim$10% and increasing the low-frequency loss by a factor of $\sim$4. Based on prior work in LaAlO$_3$ defect modelling, this is likely due to an increase in carriers in La-deficient films that does not occur in La-excess films. Considerable work over the past decade investigated LaAlO$_3$ for applications such as high-$\kappa$ gate dielectrics and nanoelectronics based on exotic hetero-interfacial phenomena. In pursuit of these goals, however, we demonstrate that it is important to be mindful of how growth techniques and conditions can impact the defect structure of the subsequent film and how these defects can control the desired responses. By combining non-destructive chemical characterization with thermal and dielectric measurements, it is possible to obtain films with the desired response via careful tuning of the growth conditions.

The authors would like to acknowledge the help and scientific insights of David G. Cahill (TDTR), Rick Haasch (XPS), and Doug Jeffers (RBS). The work was supported by the National Science Foundation and the Nanoelectronics Research Initiative under Grant No. DMR-1124696 and the Department of Energy under Grant No. DEFG02-07ER46459. The experiments were carried out in part in the Materials Research Laboratory Central Facilities.

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