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In situ optical characterization of $LaAlO_3$ epitaxy on $SrTiO_3(001)$

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Abstract – We followed the growth of $LaAlO_3$ (LAO) on TiO_2-terminated $SrTiO_3(001)$ *in situ* using a combination of a special monochromatic ellipsometry at photon energy of 1.96 eV and reflection high-energy electron diffraction (RHEED). We find that the phase of the ellipsometric ratio, defined as $\rho \equiv r_p/r_s \equiv \tan\Psi \exp(i\Delta)$, changes linearly with the LAO film thickness. From the 4th unit cell (uc) up to the 11th unit cell, the slope of change in Δ is different from that for the initial three unit cells and yet there is no abrupt change in Δ when the LAO thickness increases from 3 uc to 4 uc. We explore structural and electronic processes in the $LaAlO_3$-$SrTiO_3$ system that may be responsible for such an *in situ* observed optical response.

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Electronic properties of polar $LaAlO_3$ films on non-polar $SrTiO_3(001)$ attract much research attention in recent years [1–7]. When a normally insulating $LaAlO_3$ (LAO) film forms on TiO_2-terminated $SrTiO_3$ (STO), the film abruptly becomes conductive in directions parallel to the LAO-STO interface when the film thickness reaches 4 unit cells (uc). Such LAO-STO systems also exhibit novel superconducting and magnetic properties at low temperatures. The onset of interfacial conductivity is qualitatively attributed to a transfer of electric charges from the LAO film to the vicinity of the LAO-STO interface, presumably the nature's way to contain "the polarization catastrophe" in which the electrostatic potential difference between the LAO film surface and the LAO-STO interface diverges as the LAO film thickness increases. The origins and properties of these excess charges remain to be fully understood. Very recently Rusydi and coworkers reported an *ex situ* optical conductivity study of LAO films on STO over a wide range of photon energy and confirmed the transfer of 0.5 e^- to the LAO-STO interfacial region when the film thickness reaches and exceeds 4 unit cells [8–13]. In arriving at their conclusions, these authors made the following simplifying assumptions: 1) up to 3 unit cells, the LAO film has a homogeneous optical dielectric constant; 2) when the film thickness exceeds 3 unit cells, the LAO film including the first three unit cells again has a homogenous but different optical dielectric constant from that of an LAO film with thickness up to 3 unit cells. Under these assumptions, they further concluded that an interfacial layer with a thickness of ~ 5 nm emerges on the side of STO when the LAO thickness exceeds 3 unit cells. These assumptions need to be confirmed experimentally as other simplifying assumptions can lead to significantly different conclusions on how optical conductivities vary across the LAO-STO interface and through the LAO film as functions of deposited LAO film thickness as well as photon energy. *In situ* measurements of optical dielectric constants even at one or a few selected photon energies *during growth* suffice for such confirmation or otherwise.

In this letter, we report an *in situ* ellipsometry study of the growth of LAO films on TiO_2-terminated $SrTiO_3(001)$ in real-time so that we effectively measure the optical dielectric constant of each LAO monolayer (one unit cell thick, *i.e.*, uc) as it forms on the growth surface, albeit at a single photon energy of 1.96 eV. Our results confirm most assumptions made by Rusydi and coworkers and further raise new questions on what happen as the LAO film thickness reaches the critical value of 4 uc. Our findings illustrate the importance of *in situ* characterization in thin film growth for complementing *ex situ* sample analysis in

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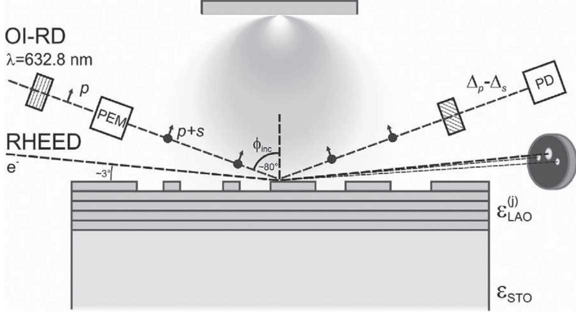

Fig. 1: Sketch of a pulse-laser deposition (PLD) station equipped with a high-pressure reflection high-energy electron diffraction (RHEED) system and an oblique-incidence reflectivity difference (OI-RD) system. Specular RHEED intensity is used to determine the thickness of the deposited $LaAlO_3$ (LAO) on TiO_2-terminated $SrTiO_3(001)$ (STO) substrate. The oblique-incidence reflectivity difference (OI-RD) is used to measure the optical dielectric response of the LAO-STO system.

order to fully understand the complex physics involved in LAO-STO systems and related oxide hetero-structures.

The experiment is conducted in a pulsed-laser-deposition (PLD) chamber equipped with a reflection high-energy electron diffraction system (RHEED) and a custom monochromatic (2 eV) ellipsometry system as illustrated in fig. 1. Restricted by other preparation and analysis instruments that are designed and equipped to the growth chamber, the incidence angle for the ellipsometry detection is limited to around 80°. Similar ellipsometry systems have been shown previously as being well suited for *in situ* monitoring thin film growth under a wide range of ambient conditions and for providing insightful information on growth modes and compositions of the films [14–17]. Single crystal wafers of $SrTiO_3(001)$ (CrysTec, Germany) of 5 mm × 5 mm in size are used as substrates. A single crystal wafer of $LaAlO_3$ (CrysTec, Germany) is used as the ablation target. During deposition, the STO substrate with TiO_2 termination is in 8×10^{-4} mbar oxygen and is heated with a *cw* laser from behind to a nominal growth temperature of 800 °C. We monitor the quality and thickness of the deposited $LaAlO_3$ film with the intensity of specular RHEED. We simultaneously record the optical dielectric response of the LAO-STO system at photon energy of 1.96 eV ($\lambda = 632.8$ nm from a He-Ne laser) with the ellipsometry system.

For the ellipsometry measurement, we directly detect $\delta\Delta$ of the standard ellipsometric ratio $\rho \equiv r_\mathrm{p}/r_\mathrm{s} \equiv \tan\Psi\cdot\exp(i\Delta)$ in response to a ultrathin LAO film on STO. Generally one should be able to measure both $\delta\Delta$ and $\Delta\Psi$ [15]. In our present study the latter is not available. Since the LAO film thickness (< 5 nm) and the width of the interfacial region ($d_\mathrm{Interface}\sim 5$ nm) is much less than the wavelength of the photon, $\delta\Delta$ contains additive contributions from the STO substrate ε_STO, the interfacial region ($\varepsilon_\mathrm{Interface}$), and each deposited LAO monolayer or uc ($\varepsilon^{(j)}_\mathrm{LAO}$, d_0, $j = 1,\ 2,\ 3,\ldots$) as follows [14–17]:

$$\delta\Delta = \frac{4\pi\cos\phi_\mathrm{inc}\tan^2\phi_\mathrm{inc}\varepsilon_\mathrm{STO}}{(\varepsilon_\mathrm{STO}-1)\left(\varepsilon_\mathrm{STO}-\tan^2\phi_\mathrm{inc}\right)\lambda} \times\left[\frac{(\varepsilon_\mathrm{STO}-\varepsilon_\mathrm{Interface})(\varepsilon_\mathrm{Interface}-1)\,d_\mathrm{Interface}}{\varepsilon_\mathrm{Interface}} + \sum_{j=1}\frac{\left(\varepsilon_\mathrm{STO}-\varepsilon^{(j)}_\mathrm{LAO}\right)\left(\varepsilon^{(j)}_\mathrm{LAO}-1\right)d_0}{\varepsilon^{(j)}_\mathrm{LAO}}\right], \tag{1}$$

$d_0 = 0.382$ nm is the thickness of one LAO uc. $\phi_\mathrm{inc} = 80°$ is the incidence angle of the illuminating light beam (He-Ne laser) employed in our ellipsometry system. It is clear from eq. (1) that the rate of change or the slope of $\delta\Delta$ as a function of the LAO thickness is proportional to $(\varepsilon_\mathrm{STO}-\varepsilon_\mathrm{LAO})(\varepsilon_\mathrm{LAO}-1)\,d_0/\varepsilon_\mathrm{LAO}$ for each newly added LAO uc and to $(\varepsilon_\mathrm{STO}-\varepsilon_\mathrm{Interface})(\varepsilon_\mathrm{Interface}-1)\,d_\mathrm{Interface}/\varepsilon_\mathrm{Interface}$ if an interfacial region emerges.

For transport properties, we measured the interfacial resistance and the Hall Effect of a sample with 11 LAO uc grown on STO substrate after the growth at room temperature. The electrical contacts to the buried LAO/STO interface were made by ultrasonic Al-wire bonding. The room-temperature sheet resistance of the 5 mm × 5 mm LAO/STO sample is $R_\mathrm{s} = 8.9\,\mathrm{k}\Omega$, determined in a van der Pauw configuration. The sheet carrier density is $n_\mathrm{s}\approx 1\times10^{14}\,\mathrm{cm}^{-2}$, determined through the Hall Effect with a BIO-RAD HL55 system. Both the sheet resistance and the interfacial charge carrier density are comparable to previously reported values of samples grown under similar conditions [18–20]. We performed additional interfacial resistance measurements on samples with different LAO thicknesses and confirmed that 4 LAO uc was indeed the critical thickness for onset of interfacial conduction.

In fig. 2 we show the RHEED intensity and the ellipsometry signal $\delta\Delta$ simultaneously acquired during deposition of 11 LAO uc on TiO_2-terminated $SrTiO_3(001)$. Panel (a) displays the specular RHEED *vs.* deposited LAO thickness. The RHEED signal is used to monitor the crystalline quality of the LAO film and to mark the thickness of the film. The RHEED intensity goes through a transition from 1 uc to 3 uc before settling down to a sustained oscillation from the 4th uc up to the 11th uc. The decreases in average RHEED intensity and in oscillation amplitude are the results of a reduced electron reflectivity of a smooth LAO surface compared to that of a smooth STO surface. The width of the transition region (3 uc) being close to the critical thickness (4 uc) is accidental and is determined by the penetration depth of the RHEED electrons.

Panel (b) displays the simultaneously recorded ellipsometry signal $\delta\Delta$. Up to 3 uc, $\delta\Delta$ varies linearly with the LAO thickness with the same slope. Based on eq. (1) and the absence of an interfacial region concluded from the optical conductivity study of Rusydi and coworkers, this

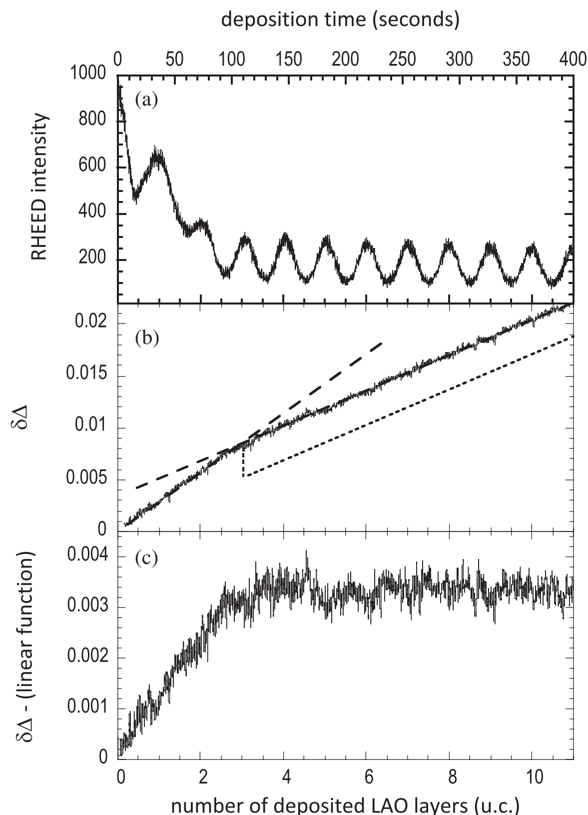

Fig. 2: (a) Intensity of specular RHEED *vs.* thickness of the deposited LAO film on TiO_2-terminated $SrTiO_3(001)$ during pulsed-laser deposition at 800 °C and in an oxygen ambient of 8×10^{-4} mbar. (b) Simultaneously acquired ellipsometry signal $\delta\Delta$ from the same surface. The optical signal varies linearly with the thickness and goes through an abrupt change in slope when the thickness increases to above 3 unit cells (uc) as indicated by the long dashed lines; (c) the difference between $\delta\Delta$ and a linear function with the same slope as the second part of the optical signal for a better illustration of both the linear dependence on the LAO thickness and the slope change in $\delta\Delta$.

shows that the optical dielectric constant $\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$ (at 1.96 eV) is same for all three LAO uc. As the thickness increases from 3 uc to 4 uc, $\delta\Delta$ continues to increase but by a lesser amount. From 4 uc to 11 uc, $\delta\Delta$ further increases linearly with a slope noticeably smaller than the slope for the first 3 uc. To clearly see the slope change, we show in panel (c) the difference between the optical signal and a linear function of the LAO thickness having the same slope as that of $\delta\Delta$ from 4 uc to 11 uc. It is clear that $\delta\Delta$ varies linearly with the thickness and its slope (but not amplitude) abruptly changes between 3 uc and 4 uc. Since an interfacial region forms when the 4th uc is deposited and remains unchanged as the LAO thickness increases further to 11 uc based on the work of Rusydi and coworkers, we can conclude from eq. (1) that the LAO film from 5th to 11th uc has a homogenous optical dielectric constant $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$, thus *partly* confirming one of the assumptions made by Rusydi and coworkers. Since $\varepsilon_{\mathrm{LAO}}$ (~ 4.38) is smaller than $\varepsilon_{\mathrm{STO}}$ (~ 5.77) and is closer to $\varepsilon_{\mathrm{STO}}$ than to unity, the slope of $\delta\Delta$ is mostly determined by $\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{LAO}}$ (see eq. (1)). The slope change as displayed in panels (b) and (c) indicates that $\varepsilon_{\mathrm{LAO,above\,4\,uc}} > \varepsilon_{\mathrm{LAO,initial\,3\,uc}}$. This may seem at odds with fig. 5(a) of Rusydi *et al.* at photon energy of 1.96 eV that showed $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$ being smaller than $\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$ by ~ 1. This discrepancy however is within the experimental uncertainties of the extracted optical dielectric constants for LAO films near 2 eV in their study of these authors: the total error in Δ from the fitting and the measurement in their spectral ellipsometry study is 0.5° or 0.0085 radians. Since the net change in Δ due to 2–3 uc of LAO on STO is only 0.0085 radians, the errors in both $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$ and $\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$ are comparable to $\pm|\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{LAO}}| \sim \pm 1.4$ in the study of Rusydi *et al.*

What about the 4th uc and the initial three LAO uc now with additional LAO formed on top of them? Furthermore, given what is known to have occurred when the LAO film increases from 3 uc to 4 uc, it seems odd that only the slope but not the amplitude of $\delta\Delta$ goes through an abrupt change. For one thing, if an interfacial region of thickness $d_{\mathrm{Interface}} \sim 5$ nm suddenly forms on the STO side of the LAO/STO interface, we would expect a step-like change in $\delta\Delta$ proportional to $(\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{Interface}})\, d_{\mathrm{Interface}}$ according to eq. (1). The fact that this did not happen may be reconciled if we accept the proposition of Rusydi *et al.* that the lattice and/or electronic structures of the first three uc go through abrupt changes so that the optical dielectric constant of these 3 uc changes from $\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$ to $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$ (see fig. 4 and fig. 5 of Rusydi *et al.*) and the optical dielectric constant of the 4th uc is also $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$. This alone would cause $\delta\Delta$ to change by an amount proportional to $(\varepsilon_{\mathrm{LAO,above\,4\,uc}} - \varepsilon_{\mathrm{LAO,initial\,3\,uc}})\,(3d_0)$ that is negative (the dotted line in panel (b) of fig. 2). The separate change in $\delta\Delta$ due to the emergence of the interfacial region is proportional to $(\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{Interface}})\, d_{\mathrm{Interface}}$ and may compensate for $(\varepsilon_{\mathrm{LAO,above\,4\,uc}} - \varepsilon_{\mathrm{LAO,initial\,3\,uc}})\,(3d_0)$. Such a complete compensation can only be accidental and requires at least $\varepsilon_{\mathrm{Interface}} < \varepsilon_{\mathrm{STO}}$. The requirement $\varepsilon_{\mathrm{Interface}} < \varepsilon_{\mathrm{STO}}$ again seems at odds with the extracted $\varepsilon_{\mathrm{Interface}}$ as shown in fig. 5(c) of Rusydi *et al.* We note that the discrepancy is nonetheless within the experimental uncertainty for the extracted $\varepsilon_{\mathrm{Interface}}$ in their study as the error in $\varepsilon_{\mathrm{Interface}}$ is comparable to $\pm|\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{Interface}}|$ and thus $\varepsilon_{\mathrm{Interface}}$ can very well be less than $\varepsilon_{\mathrm{STO}}$.

The accidental nature of a complete cancellation of effects from the interfacial region and the structural change in the first three uc leads to the question whether other scenarios may be at work that also explain the optical response as shown in fig. 2(b) in this study and reported by Rusydi *et al.* For this exploration, we recall that the total LAO film thickness (< 4.5 nm) and the presumed interfacial region (~ 5 nm) add to less than 10 nm and are small compared to the wavelength (633 nm) of the photon at 2 eV. As a result, effects of the LAO film and the interfacial region on the ellipsometry ratio and the reflectivity

are small and *additive* as illustrated in eq. (1). This means that the *ex situ* analysis of optical conductivity data alone cannot determine the location of the "interfacial region". Furthermore because the thickness and the optical dielectric constant of the interfacial region appear together as $(\varepsilon_{\mathrm{STO}} - \varepsilon_{\mathrm{Interface}})\,(\varepsilon_{\mathrm{Interface}} - 1)\, d_{\mathrm{Interface}}/\varepsilon_{\mathrm{Interface}}$ and are to be determined from the fit, one may not determine both simultaneously in the thin film limit [16,17].

We now discuss whether the roughness of the growth surface, for an insulating LAO film (< 4 uc) and a conducting LAO film (≥ 4 uc), may have contributed at least partly to the thickness dependence of the optical response as shown in fig. 2. Zhu and coworkers demonstrated previously that such *in situ* ellipsometry can be used to detect variations in step edge density during epitaxial film growth and during ion-sputtered erosion of a crystalline surface [14–17]. In a layer-by-layer growth as illustrated in fig. 2(a), the step edge density (number of unit cells residing at step edges per unit area) varies periodically. However its overall amplitude is small compared to the terrace density (number of unit cells residing in the terraces per unit area) and thus the change in optical signal due to the step density variation is less than 1/40–1/10 of the signal due to the deposition of one LAO unit cell on STO [14–17]. A number of theoretical studies of LAO on STO predicted that 1) oxygen vacancies at concentrations as high as 1/4 per unit cell can accumulate at the surface of a conducting LAO film (with thickness ≥ 4 uc) [21,22] and 2) detectable lattice distortions exist in an insulating LAO film (with thickness < 4 uc) [23–25]. Both mechanisms may cause *different*, addition surface roughness in form of step edges. According to a mean-field description of the optical response from step edges by Zhu [16], in order for such extra surface roughness to alter equally the optical dielectric constants for the 4th through 11th LAO monolayers, the extra step edge density must increase linearly with the thickness of the LAO film. This contradicts fig. 2(a) where we find the amplitude of RHEED oscillation remains un-damped from the 4th through 11th LAO monolayer, —indicating that even if theoretically predicted oxygen vacancies at the surface of a conducting LAO film may cause additional surface roughness, the latter does not increase and thus cannot modify optical constants from the 4th to 11th LAO monolayers uniformly. As to the surface roughness that may arise from the lattice distortions predicted to exist in an insulating LAO film, its effect and the electronic effect of the distortions can contribute to the optical constant of the 1st through 3rd LAO monolayers, but not to that of the conducting LAO film when the thickness exceeds 4 uc. In this case the sudden lift of lattice distortions at the LAO thickness of 4 uc will need to be compensated in full accidentally or we would observe a step-like change as illustrated by the short dotted line in fig. 2(b).

In conclusion, we demonstrated that *in situ* characterization of ultrathin films *during growth* using a high-sensitivity ellipsometry (in this case, oblique-incidence reflectivity difference) even at single photon energy complements *ex situ* spectral ellipsometry characterization and other *ex situ* measurements. In the case of LAO films on TiO_2-terminated STO, it helps unraveling what happen near the interface of this system when it abruptly becomes conductive at the critical thickness of 4 uc. In our present study the *in situ* ellipsometry measurement confirms the main assumptions made by Rusydi *et al.* that from 1 uc to 3 uc the optical dielectric constant is a constant ($\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$) and from 5 uc to 11 uc it is also but a larger constant ($\varepsilon_{\mathrm{LAO,above\,4\,uc}}$). In addition if the optical dielectric constant of an LAO film with the thickness over 4 uc is indeed a homogenous constant of $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$ including the initial first three uc, we must conclude that $\varepsilon_{\mathrm{Interface}}$ is smaller than $\varepsilon_{\mathrm{STO}}$ (at least at 2 eV) so that the formation of the interfacial region produces an effect on $\delta\Delta$ opposite to the effect due to the change in optical dielectric constant for the first 3 uc from an initial value $\varepsilon_{\mathrm{LAO,initial\,3\,uc}}$ to a larger value of $\varepsilon_{\mathrm{LAO,above\,4\,uc}}$.

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