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Monolayer Oscillation Observed by an Oblique-Incidence Reflectance Difference Technique for the Epitaxial Growth of Oxides *

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We report the optical oscillations with monolayer periodicity observed by an oblique-incidence reflectance difference (OIRD) technique on the epitaxial growth of Nb-doped $SrTiO_3$ on $SrTiO_3$ substrate. The periodicity was verified by the simultaneously measured reflection high-energy electron diffraction intensity oscillations. The OIRD oscillation damps during deposition, but can recover after the growth is interrupted for some time. We interpret the optical oscillations as a result of the periodic changes of the surface morphologies due to the two-dimensional layer-by-layer growth of thin films.

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Real time monitoring of the layer-by-layer growth of thin films with monolayer (ML) accuracy is of great importance to either high-quality thin-film fabrication or the study of growth mechanism. Reflection high-energy electron diffraction (RHEED) specular intensity oscillation is one such method, which has been routinely used to control thin-film thickness at atomic scale in molecular beam epitaxy[1,2] and laser molecular beam epitaxy (laser-MBE).[3] It is well established that RHEED intensity oscillations result from the periodic changes of surface morphologies (step density) associated with layer-by-layer growth.[4] The disadvantage of RHEED is that its application can be restricted to high vacuum environment. Optical probe techniques have no such problem. These have the advantage of being non-invasive and nondestructive, and can be used in any transparent ambient. Reflectance difference spectroscopy (RDS),[5,6] p-polarized reflectance spectroscopy (PRS)[7] and spectral ellipsometry (SE)[8] have been proven to be surface sensitive. Continuous monolayer oscillations have also been observed with RDS[6] and SE.[8] However, these oscillations are only obtained from semiconductor epitaxy as their measurements rely on surface optical anisotropy or surface reaction layer. There is no report of optical monolayer oscillations on complex oxide epitaxy, though oxides have become one of the most attractive fields which involve high-T_c superconductor, ferroelectric, dielectric and colossal magnetoresistance materials.

In this letter, we report on the continuous monolayer optical oscillations obtained by an oblique-incidence reflectance difference (OIRD) technique during the epitaxial growth of Nb-doped $SrTiO_3$ (Nb:STO) on $SrTiO_3$ (STO) substrate. OIRD is a new type of optical probe technique which has been demonstrated to be sensitive to a relative reflectivity change $\Delta R/R = 1\times10^{-5}$ and to a coverage change $\Delta\theta = 0.02\,\mathrm{ML}$.[9] Our previous work has demonstrated that the OIRD measurement does not rely on surface anisotropy.[10] In our theoretical work, optical oscillation has been predicted by modelling the thin film as a microscopic two-dimensional (2D) grating and solving Maxwell's equations.[11] Here, we report on the observed continuous monolayer OIRD oscillations. The monolayer periodicity is verified by simultaneously monitoring RHEED intensity oscillations. Damping of this optical oscillation and its recovery after interrupting the growth are also observed. Our study suggests that this optical probe technique may also be capable of monitoring the layer-by-layer growth of complex oxides as RHEED does. Moreover, this optical method may be of special importance in low vacuum or atmospheric environments where RHEED is ineffective.

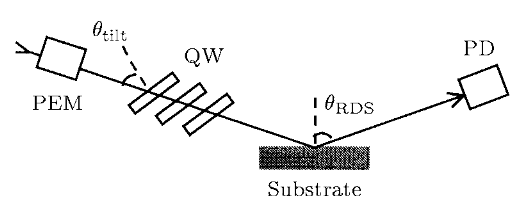

Fig. 1. Schematic diagram of the optical set-up for OIRD measurements: PEM, photoelastic modulator; QW, fused quartz parallel plate; PD, biased silicon photodiode.

The measurements were performed in a laser-MBE system.[12] A standard RHEED apparatus is equipped with its incidence plane coinciding with the [010] axis of the substrate. The incidence angle of the electron beam is about 3° with respect to the surface

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plane, which is the so-called "out-of-phase" condition for RHEED measurement. A charge-coupled-device camera is used to record the RHEED specular spot intensity. The sketch of the optical set-up of OIRD is schematically illustrated in Fig. 1. The laser beam with a wavelength of 632.8 nm from a 4 mW linearly polarized He–Ne laser is initially p-polarized. It is modulated by a photoelastic modulator (PEM) before it is incident on the substrate surface with a glancing angle of 6°. The p-polarization bisects the two principal axes of the modulator, which produces a phase shift between the two components along the principal axes at a frequency of $\Omega = 50$ kHz. The maximum phase is set at π or 180° The reflected beam is detected by a silicon photodiode (PD) and the photocurrent goes into a Stanford Research 510 lock-in amplifier. Three parallel plates are adapted to adjust the relative intensity of the s- and p-polarized component to make a near-zero background. The monitored OIRD intensity is given by[9,10]

$$I(2\Omega) = \frac{1}{2} J_2(\Phi) I_{\rm inc}[|r_{\rm p}(\theta_{\rm RDS}) t_{\rm p}(\theta_{\rm tilt})|^2 - |r_{\rm s}(\theta_{\rm RDS}) t_{\rm s}(\theta_{\rm tilt})|^2], \tag{1}$$

where $r_{\rm p}(\theta_{\rm RDS})$ and $r_{\rm s}(\theta_{\rm RDS})$ are the reflectance coefficients for p- and s-polarized light at the incidence angle $\theta_{\rm RDS}$, while $t_{\rm p}(\theta_{\rm tilt})$ and $t_{\rm s}(\theta_{\rm tilt})$ are the total transmission coefficients for p- and s-polarized light through the fused quartz plates at a tilt angle $\theta_{\rm tilt}$, respectively. $J_2(\Phi)$ is the Bessel function of the second kind. With proper adjustment of the three parallel plates, a near-zero background intensity can be obtained when $|r_{\rm p0}(\theta_{\rm RDS}) t_{\rm p}(\theta_{\rm tilt})|^2 = |r_{\rm s0}(\theta_{\rm RDS}) t_{\rm s}(\theta_{\rm tilt})|^2$. Thus the relative OIRD intensity can be given as

$$\frac{I}{I_{\rm p0}} = \frac{\Delta R}{R_0} = \frac{R_{\rm p}}{R_{\rm p0}} - \frac{R_{\rm s}}{R_{\rm s0}}, \tag{2}$$

where $R_{\rm p} \equiv |r_{\rm p}|^2$, $R_{\rm p0} \equiv |r_{\rm p0}|^2$, $R_{\rm s} \equiv |r_{\rm s}|^2$ and $R_{\rm s0} \equiv |r_{\rm s0}|^2$.

We monitored the heteroepitaxy of Nb:STO (the doping concentration is 10 mol%) on the STO (100) substrate simultaneously by OIRD and RHEED. The substrate temperature obtained from an optical pyrometer is around 660°C. Pure oxygen is introduced into the chamber through a nozzle set 5 cm ahead the substrate. The oxygen pressure monitored by a vacuum gauge (30 cm away from the oxygen nozzle) is 1.2×10^{-4} Pa. For laser deposition, laser pulses with a wavelength of 308 nm, duration of 30 ns, single-pulse energy of 260 mJ, repetition of 2 Hz are focused onto the ceramic target to yield an irradiation energy density of 1 J/cm^2. Under these conditions, it takes 36 pulses to deposit one monolayer layer Nb:STO.

Our main results are shown in Fig. 2. Four ML Nb:STO were first deposited by continuous depositing (Fig. 2a), then another three ML were deposited in the same way (Fig. 2b) after the growth was interrupted for 5 min. Good RHEED intensity oscillations (the upper) with only slight damping indicate that the present growth proceeds in a good layer-by-layer mode. OIRD signal (the lower) also shows oscillations.

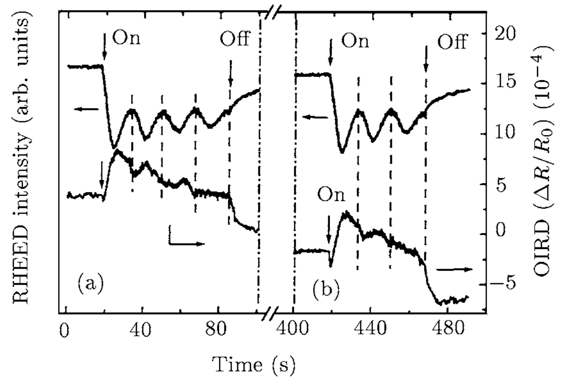

Fig. 2. Monolayer oscillations of RHEED specular beam intensity (upper) and OIRD (lower) for four ML continuous deposition (a) and three ML deposition after 5min interruption (b). Arrows labelled "On" and "Off" indicate the start and the end of each deposition. The dashed lines indicate the positive extreme of each RHEED oscillation.

We first compare the period and relative phase of the OIRD and RHEED responses. In Fig. 2, each dashed line at the positive extreme of RHEED intensity, which indicates the completion of each ML,[1,2] corresponds to a negative extreme of the OIRD signal. The periods of OIRD and RHEED oscillations are the same as 18 s. RHEED oscillation phase shift, which may occurs for the first maximum intensity due to the measurement condition,[2] does not take place here. As shown in Fig. 2, there is a phase delay between each negative extreme of OIRD and the positive one of RHEED even for the first one. The phase delay of each extreme is not strictly equal, which may be partly due to fast damping of the oscillations.

The amplitude $\Delta R/R_0$ of the first OIRD oscillation in Fig. 2(a) is about 3×10^{-4}, which damps out after the third one. The interruption significantly recovers the OIRD oscillations as shown in Fig. 2(b). The damping of OIRD oscillations is faster than that of RHEED intensity oscillations. The OIRD background intensity decreases as a result of interference oscillations due to the multiple reflection of the probing light from ambient/film and film/substrate interfaces.[7,13]

Another feature in the OIRD signal is the recovery. It is quite similar to the RHEED intensity recovery, which has been well known as surface smoothing.[1,2] The recovered OIRD intensity is lower than the initial one due to the decrease of the background intensity.

Now we discuss the possible origin of the OIRD oscillations. The similarity of the main features between the OIRD and the RHEED signals, i.e. the monolayer periodic oscillations, oscillation damping and intensity recovery after the growth is interrupted, suggests that the OIRD oscillations have the same origin as that of RHEED intensity oscillations. It is the periodic surface morphology change caused by the 2D layer-by-layer growth. Experimentally, Zhu and co-workers[14] have demonstrated that OIRD is morphology sensitive by monitoring the Ni surface during Ne–iron sputtering and subsequent heat annealing. It is known that the sputtering can cause surface roughening and subsequent annealing can lead to surface smoothing. They observed the increase of OIRD intensity during sputtering and the recovery during annealing.

Our previous numerical calculations[11] have predicted such OIRD oscillations by modelling the thin film as a microscopic 2D grating. The solution of Maxwell's equations of such a 2D grating leads to an effective multi-layer medium model. Thus, the surface structure of the growing thin film can be described as a three-layer stack, vacuum/surface layer/bulk film, with the dielectric constants as ε_0, $\overline{\varepsilon}$ and ε_1, respectively. Then the corresponding OIRD signal can be calculated with Fresnel's formulae. In our model, $\overline{\varepsilon} = \varepsilon_0(1-\theta) + \varepsilon_1\theta$, where θ is the surface coverage of the topmost layer. When the coverage θ varies from 0 to 1 in the so-called layer-by-layer growth mode, the effective dielectric constant $\overline{\varepsilon}$ will vary from ε_0 to ε_1. When the surface structure is the same for $\theta = 0$ or 1 and the second monolayer grows on the surface, the above process can be repeated. Thus the calculated OIRD signals will show monolayer periodic oscillations. Our experimental results directly testify to the numerical simulations.

The different damping speed and the phase delay between the OIRD and RHEED signals can be explained as different probing areas. The information obtained by RHEED is known to come from an area at a scale of the coherent length of the RHEED electron beam.[15] The typical coherent length of the RHEED electron beam is about 10 nm. However, the OIRD measurement does not rely on the coherent length of the probe light. Thus, the OIRD signal is expected to be an average result from the probe spot. At the scale of the probe spot (about 0.3 mm wide and 3 mm long in our measurement), the formation and overgrowth of defects will cause 3D-island growth and cause the damping of OIRD signals. The formation of defects within an area of 10 nm size is rather rarer than that within an area of several mm.

In summary, we report on the OIRD oscillations with monolayer periodicity of Nb:STO epitaxial growth. The periodicity is verified by simultaneous measurement of the RHEED intensity oscillations. The amplitude damps and the intensity can recover when the growth is interrupted. The oscillation after the interruption also recovers. We interpret the optical oscillations as a result of the periodical variation of the surface morphologies due to layer-by-layer growth. Our study suggests that the OIRD may also be as capable of monitoring thin-film layer-by-layer growth as RHEED. It is of special importance for low or non-vacuum environments where RHEED is ineffective.

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