An efficient and reliable growth method for epitaxial complex oxide films by molecular beam epitaxy

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Transition metal oxide heterostructures and interfaces host a variety of exciting quantum phases and can be grown with atomic-scale precision by utilizing the intensity oscillations of in situ reflection high-energy electron diffraction (RHEED). However, establishing a stable oscillation pattern in the growth calibration of complex oxides films is very challenging and time consuming. Here, we develop a substantially more efficient and reliable growth calibration method for complex oxide films using molecular beam epitaxy.

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By adjusting Sr (or Ti) source temperature (flux rate), in Sr-rich condition and decreases in Sr-poor condition. Eliminating this beating pattern is necessary for precise film growth but it is very time consuming due to the long beating period as the stoichiometry approaches its ideal value. Stable RHEED oscillation pattern can only be achieved when Sr and Ti shutter times are both accurate. A misleading false "stable" RHEED pattern can be formed when the beating becomes very weak as the film surface becomes rough. All together, these complicated RHEED oscillation patterns and the sensitive incident angle dependence make the shuttered method unfavourable in calibrating the growth parameters for complex oxide heterostructures and interfaces.

In contrast to the shuttered method, the RHEED oscillation pattern in a co-deposition process is simple and clear, which is most likely due to the less abrupt flux discontinuities. In Fig. 2a, we show a typical calibration process by co-deposition method where both Sr and Ti atoms are deposited on the substrate simultaneously. Only a monotonic drift of the overall intensity of the oscillations with no "double peaks", beating or other complicated patterns are observed. No clear dependence of the incident angle is observed neither. Similar to the shuttered method, the overall oscillation intensity increases in Sr-rich condition and decreases in Sr-poor condition.

The monotonic intensity drift can be eliminated. Within a few tens of oscillation periods, a stable RHEED oscillation pattern was established and the period corresponds to the correct shutter times for the growth of a full monolayer of SrO and TiO$_2$. Therefore, this co-deposition calibration process is significantly more reliable and efficient than the shuttered method by reducing the calibration time by at least an order of magnitude.

Moreover, the rate of the overall intensity drift is found to be proportional to the accumulation rate of excess Sr or Ti atoms. As shown in Fig. 2b, the RHEED intensity reaches its maxima when a full SrO layer is formed on the surface due to the accumulation of excess Sr atoms. This is consistent with the fact that the SrO terminated surface gives the maximum RHEED intensity in the shuttered growth process. Accumulating more excess Sr atoms on the film surface results in a decrease of the overall diffraction intensity and the oscillation amplitude since the film surface crystalline quality becomes worse. In fact, this shares the same origin with the formation of "double peak" pattern in the shuttered growth process. Similarly, a minimum intensity is observed when a full TiO$_2$ terminated surface is formed by the accumulation of excess Ti atoms.

Assuming a linear dependence of the overall intensity
drift on the accumulation rate of excess Sr atoms, the amount of off-stoichiometry in Sr$_{1+\delta}$TiO$_3$ films can be quantified by Eq. (1),

$$\delta \approx \frac{d}{A}$$  \hspace{1cm} (1)

where, $d$ is the intensity drift during the growth of a unit cell (u.c.) and $A$ is the intensity difference between the RHEED diffraction of SrO-terminated and TiO$_2$-terminated SrTiO$_3$. For more reliable estimation, the $d$ values should be read after the oscillation amplitude and source temperature (flux) are both stabilised.

The validity of this first order estimation of the amount of off-stoichiometry $\delta$ using Eq. (1) was checked by comparing $\delta_{\text{RHEED}}$ calculated using Eq(1) and $\delta_{\text{QCM}}$ measured by a quartz crystal microbalance (QCM). From the data shown in Fig. 2, $\delta_{\text{RHEED}}$ (2.4%) agrees reasonably well with $\delta_{\text{QCM}}$ (2.3%). From our experience, Eq. (1) typically overestimates the amount of off-stoichiometry and $\delta_{\text{RHEED}}$ can be up to 1.5$\delta_{\text{QCM}}$ in some extreme cases, but this is still meaningful in practice. In contrast to the assumption of simple linear dependence of the diffraction intensity on the SrO coverage used in Eq. (1), more accurate estimation of $\delta$ should consider the exact sinusoidal-like dependence of the diffraction intensity on the SrO coverage.

Using co-deposition method, we can precisely control the film stoichiometry. As shown in Fig. 2c, a set of 40 nm thick epitaxial Sr$_{1+\delta}$TiO$_3$ films were grown on (001) SrTiO$_3$ substrate using a co-deposition method. For the stoichiometric SrTiO$_3$ film, XRD $\theta$-2$\theta$ scans around the SrTiO$_3$ (002) diffraction peak show no sign of peak splitting or Kiessig fringes, indicating the nearly perfect stoichiometry and crystalline structure of the homoepitaxial SrTiO$_3$ film[6]. In our experiments, the overall intensity drift of RHEED oscillations is found to be sensitive to Sr:Ti flux ratio. A minor change (0.1 °C) of the Sr source temperature (about 0.3% flux variation) can result in a clear drift of the overall oscillation intensity (not shown), indicating the Sr:Ti ratio can be controlled with a deviation less than 0.3%.

One of the major advantages of the MBE technique is the extreme flexibility provided by the shuttered method, which is essential in growing heterostructures, superlattices and interfaces of exciting correlated quantum phases. To show that the shutter times calibrated by the co-deposition technique can be directly used to grow complex structures using shuttered method, a series of RP strontium titanate (Sr$_{n+1}$Ti$_n$O$_{3n+1}$) films were grown on (001) SrTiO$_3$ substrates. In RP layered perovskites (A$_{n+1}$B$_n$O$_{3n+1}$), the ABO$_3$ blocks are interrupted by a rock-salt AO-AO double layers [18]. The crystalline quality of RP structure is very sensitive to the dose of each sublayer [19]. RP series host a variety of exciting properties including high temperature superconductors[20], colossal-magnetoresistance oxides[21], spin-triplet superconductors[22,23], and unconventional ferromagnets[24].

As shown in Fig. 3, XRD data of $n = 1, 2, 6$, RP films grown on (001) SrTiO$_3$ substrates exhibit clear and sharp diffraction peaks and clear Kiessig fringes, indicating the high quality of all RP films. The homoepitaxial SrTiO$_3$ (the $n = \infty$ member) film show no sign of peak splitting or Kiessig fringes, indicating the close stoichiometric match of SrTiO$_3$ films. These results demonstrate that the co-deposition method and shuttered method can be combined to grow complex heterostructures and interfaces in an efficient and reliable manner.

In summary, we show that the RHEED oscillation pattern in the co-deposition growth of SrTiO$_3$ is simple and clear by only exhibiting sensitive and monotonic dependence on the Sr:Ti flux ratio. By adjusting the Sr source temperature carefully, a stable RHEED oscillation pattern can be established and its period can be used as the precise shutter times for the shuttered growth of SrTiO$_3$ and SrTiO$_3$ based superlattices and interfaces. The combination of co-deposition calibration and shuttered final film growth is an efficient and reliable growth method for complex oxide superlattices, interfaces, and will be applicable to...
helpful for the further improvement of other high-k oxide epitaxy layers as well.

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