Sub-unit cell layer-by-layer growth of Fe$_3$O$_4$, MgO, and Sr$_2$RuO$_4$ thin films

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The use of oxide materials in oxide electronics requires their controlled epitaxial growth. Recently, it was shown that Reflection High Energy Electron Diffraction (RHEED) allows to monitor the growth of oxide thin films even at high oxygen pressure. Here, we report the sub-unit cell molecular or block layer growth of the oxide materials Sr$_2$RuO$_4$, MgO, and magnetite using Pulsed Laser Deposition (PLD) from stoichiometric targets. Whereas for perovskites such as SrTiO$_3$ or doped LaMnO$_3$ a single RHEED intensity oscillation is found to correspond to the growth of a single unit cell, in materials where the unit cell is composed of several molecular layers or blocks with identical stoichiometry, a sub-unit cell molecular or block layer growth is established resulting in several RHEED intensity oscillations during the growth of a single unit-cell.

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The physical properties of thin films are strongly influenced by their microstructure and morphology which, in turn, are determined by the deposition conditions and the growth mode. RHEED has proven to be a useful surface sensitive tool for monitoring in situ the growth of semiconductor thin films [1]. RHEED has also been successfully used for studying the growth of the complex copper oxide superconductors under high vacuum conditions [2, 3, 4]. Recently, high pressure RHEED systems have been developed allowing for the analysis of oxide thin films grown by Pulsed Laser Deposition (PLD) at high oxygen partial pressure of up to several 10 Pa [5, 6]. A common way of using RHEED in the analysis of thin film growth is the observation of the electron diffraction pattern during epitaxial growth. In this case intensity oscillations of the diffraction spots are associated with a layer-by-layer or Frank-van der Merwe growth mode [2]. The deposited material nucleates on the substrate surface forming two dimensional islands which are coalescing with increasing coverage. This process results in a periodic roughening and flattening of the film surface translating into RHEED intensity oscillations.

In this Letter, we report on the study of RHEED intensity oscillations during the PLD growth of the oxides Sr$_2$RuO$_4$, MgO, and magnetite (Fe$_3$O$_4$) from stoichiometric targets. We have used an ultra high vacuum Laser Molecular Beam Epitaxy (L-MBE) system with in-situ high pressure RHEED and a 248 nm KrF excimer laser [7]. It is well known that due to the ionic bond character in oxides the diffraction spots recorded during the PLD growth of a single crystal target. Note that in the first case every molecular layer is a molecular layer which is composed of one or several atomic layers or blocks with identical stoichiometry, a sub-unit cell molecular or block layer growth is established resulting in several RHEED intensity oscillations during the growth of a single unit-cell.

We first discuss the growth of the unconventional superconductor Sr$_2$RuO$_4$. This material is isostrophic to La$_2$CuO$_4$, which already has been studied by RHEED [4]. For structural reasons, a similar growth is expected for both materials. Fig. 1 shows the RHEED intensity oscillations of the (0, 0) diffraction spot recorded during the PLD growth of a c-axis oriented Sr$_2$RuO$_4$ film on a NdGaO$_3$ substrate. The layer-by-layer growth mode is achieved for a substrate temperature \( T_s = 950 \text{°C} \), an oxygen pressure of \( p_{O_2} = 20 \text{mTorr} \), a laser repetition rate of \( f_l = 5 \text{ Hz} \), and a laser energy density on the target of \( P_l = 1.2 \text{J/cm}^2 \). RHEED was performed with 15 keV electrons at an incident angle of 2.2°. To obtain the number of RHEED oscillations per unit cell, the film thickness has been determined precisely by X-ray reflectometry and then divided by the number of observed RHEED oscillations. The derived block thickness corresponds to half a unit cell (\( c/2 = 6.39 \text{Å} \)). Considering the crystal structure shown in the inset of Fig. 1.
Figure 1: RHEED intensity oscillations observed during the growth of Sr$_2$RuO$_4$. During the growth of a single unit cell two intensity oscillations are observed. The inset shows the crystal structure with two identical stoichiometric building blocks translated by (a + b)/2 within the ab-plane.

The result is intuitive: The unit cell consists of two identical layers which are displaced within the ab-plane by (a + b)/2, where a and b are the in-plane lattice vectors. Note that after the third oscillation the intensity of the maxima remains almost constant. The growth can be stopped and continued with almost unchanged modulation depth. After a certain film thickness the oscillations start to flatten out with an overall decrease of reflected intensity due to surface roughening because of a transition to island growth. The layer-by-layer growth mode can be re-established by thermal annealing. An interesting feature is that the RHEED intensity starts to increase immediately after starting the PLD process. However, this effect is only present for starting the growth on the substrate, but is absent for starting on the surface of an already grown Sr$_2$RuO$_4$ film. Therefore, we believe that this effect is not related to the diffraction conditions, but more likely to a change of the surface structure and morphology of the substrate due to the partial coverage with the thin film material. A similar effect has been observed for isostructural La$_2$CuO$_4$ as well as for GaAs. We finally note, that our high quality Sr$_2$RuO$_4$ films have lower resistivity values ($\rho \lesssim 20 \mu \Omega \text{cm at 300 mK}$) than those reported so far in literature. However, these values are still about ten times larger than those required for superconductivity ($\rho \lesssim 1.5 \mu \Omega \text{cm}$).

As the second example we discuss the growth of a MgO cap layer on a magnetite thin film, which will be discussed below. Both films were grown under the same growth conditions ($T_s = 330^\circ \text{C}$, $p_N = 2 \times 10^{-3} \text{ mbar}$, $f_L = 2 \text{ Hz}$, and $P_L \approx 5 J/\text{cm}^2$) leading for both materials to a layer-by-layer growth mode. First the magnetite thin film was grown on a MgO substrate with atomically flat surface (3 Å rms roughness) followed by the MgO cap layer. Fig. 2 shows X-ray reflectometry data of a Fe$_3$O$_4$ (36 nm)/MgO (9 nm) bilayer. Fitting the data gives the thickness of the MgO and Fe$_3$O$_4$ layers with an error of less than ±5%. As already described above, from the MgO layer thickness and the observed number of RHEED oscillations we obtain the result that two RHEED oscillations correspond to the growth of a single MgO unit cell shown in Fig. 2. Again, the intuitive explanation for this observation is the fact that the unit cell of MgO consists of two identical stoichiometric layers displaced along the ab-plane by (a + b)/2. After the deposition of the MgO cap layer, the surface morphology was examined in-situ by Atomic Force Microscopy. The rms surface roughness averaged over an area of 1 µm$^2$ was below 2 Å, i.e. even below that of the MgO substrate. This result is consistent with a dominant layer-by-layer growth mode observed for the whole bilayer.

As the last example we discuss the growth of Fe$_3$O$_4$ thin films on MgO substrates. Fig. 3 shows the RHEED intensity vs. time which has several interesting features. First, the modulation depth decreases continuously with increasing film thickness, if the ablation is not interrupted. Since the intensity of the maxima decreases while the intensity of the minima increases, we ascribe this to a gradual transition to the step-flow-growth mode which leaves the reflected intensity unchanged. The layer-by-layer growth mode can be re-established by annealing the sample for about 100 s in the deposition atmosphere. Second, there is a huge increase of the RHEED intensity directly after starting the PLD process. In contrast to the case of Sr$_2$RuO$_4$, this effect is observed reproducibly after each growth stop and not only if the deposition is started on the bare substrate. Note that the RHEED intensity vs. time curves in Fig. 3 are obtained from the (0, 2) diffraction spot. For this spot the electrons reflected from different growth planes interfere constructively (in-Bragg condition). In this case for purely coherent scattering no RHEED oscillations are expected. The fact that we do observe RHEED oscillations is caused by multiple and diffuse, incoherent scattering.

Figure 2: X-ray reflectometry data (solid line) and simulation data (broken line). The inset shows the MgO unit cell ($a = b = c = 0.4211$ nm) consisting of 2 Mg$^{2+}$ and 2 O$^{2-}$ ions.
ing which results in an increasing (decreasing) intensity with increasing (decreasing) step density [11]. Therefore, starting from a smooth surface the RHEED intensity first increases due to the increasing step density. That is, a π-phase shift of the intensity oscillation relative to those recorded for off-Bragg condition is obtained. A similar behavior has also been found for semiconductor growth [8, 12, 13]. This interpretation is consistent with a third observation: after stopping the growth of Fe$_3$O$_4$, the intensity decreases. Since it is natural to assume that annealing leads to a smoother surface, i.e. smaller step density, it is evident that the measured intensity of the (0,2) spot is decreasing with time. The relevance of multiple scattering processes is also manifested by the presence of Kikuchi lines. The RHEED pattern in the inset of Fig. 8 indicates that the resonant enhancement is due to both, coupling to surface bound states, and three-dimensional diffraction [13].

From the measured film thickness and the number of RHEED oscillations, for Fe$_3$O$_4$ we obtain four oscillations per unit cell. Considering the unit cell of Fe$_3$O$_4$ with the inverse spinel Fe$_3$Sn structure $(a = b = c = 0.8396\text{nm})$, one can identify the corresponding molecular layers each consisting of the composition Fe(A)$_2$$^3^+$(Fe(B)$_2$$^3^+$+Fe(B)$_2$$^2^+$O$_8$$^-$). The letters A and B refer to the tetrahedral A-site and the octahedral B-site, where the B-site is equally occupied by Fe$^{3+}$ and Fe$^{2+}$ ions. These building blocks cannot be mapped onto each other by lattice translations. We note that our high quality, 30-50 nm thick magnetite films have a saturation magnetization at room temperature close to the theoretically expected value of 4.0 μ$_B$/f.u., that is, the saturation magnetization is comparable to the best results reported in literature so far [14]. We further note, that recently four RHEED intensity oscillations per unit cell have been observed for the layered manganites. Interestingly, there the basic building block corresponds to only half the layer thickness expected according the chemical composition $\frac{1}{2}$(La,Sr)$_3$Mn$_2$O$_7$ [15].

In summary, we have grown Sr$_2$RuO$_4$, MgO, and Fe$_3$O$_4$ epitaxial thin films by PLD from stoichiometric targets. Our results show that high pressure RHEED allows to monitor the epitaxial growth of the complex oxide materials on a sub-unit cell level. We have observed a molecular or block layer growth mode where the basic building blocks are determined by the chemical composition provided by the stoichiometric target material. For materials with units cells consisting of several block layers of identical stoichiometry, several RHEED oscillations per unit cell are observed.

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Figure 3: RHEED intensity oscillations of two series of laser pulses during the growth of a Fe$_3$O$_4$ thin film on a MgO substrate. The right-hand inset shows the RHEED pattern. For the RHEED oscillations the intensity is integrated within the rectangle around the (0,2) spot. The left-hand inset shows the unit cell of magnetite consisting of four Fe$_3$O$_4$ formula units.

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