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A-Site Order Control in Mixed Conductor $NdBaCo_2O_{5+\delta}$ Films through Manipulation of Growth Kinetics

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The electronic, magnetic, and ion transport properties of the perovskite-based cobalt oxides $RBaCo_2O_{5+\delta}$ (R: rare earth ions) are sensitive to oxygen stoichiometry.[1−5] Growth of thin films of these materials is complicated because they are accessible in either A-site cation ordered or disordered forms at the same composition. Their oxygen vacancy content is strongly coupled to the extent of structural ordering between the large Ba^{2+} and smaller R^{3+} cation on the A-site.[6−9] Layered A-site ionic order doubles the repeat distance along the *c*-axis from a_P ($a_P \sim 0.39$ nm for a perovskite unit cell) to $2a_P$ and induces ordering of oxygen vacancies of the $RBaCo_2O_5$ composition (Figure 1a). This structure strongly enhances the ionic conductivity of excess oxygen introduced to afford the $RBaCo_2O_{5+\delta}$ mixed conductors.[10,11] These materials have high mixed ionic and electrical conductivity and show great potential in applications such as cathodes for solid oxide fuel cells and gas separation membranes.[10−14] To enable these oxides to be integrated into devices it is necessary to precisely control the interfaces of thin films while directing the A-site cation order that produces their high ionic mobilities.[15,16] Pulsed laser deposition (PLD) has the versatility to vary important deposition parameters and control growth kinetics.[17] By monitoring the growth using in situ reflection high energy electron diffraction (RHEED), atomic scale control of the growth is possible.[18] This paper shows that manipulation of the growth kinetics allows control of the deposition on a unit cell scale to afford layer-by-layer growth with atomically smooth interfaces of materials that display either A-site cation order or disorder.

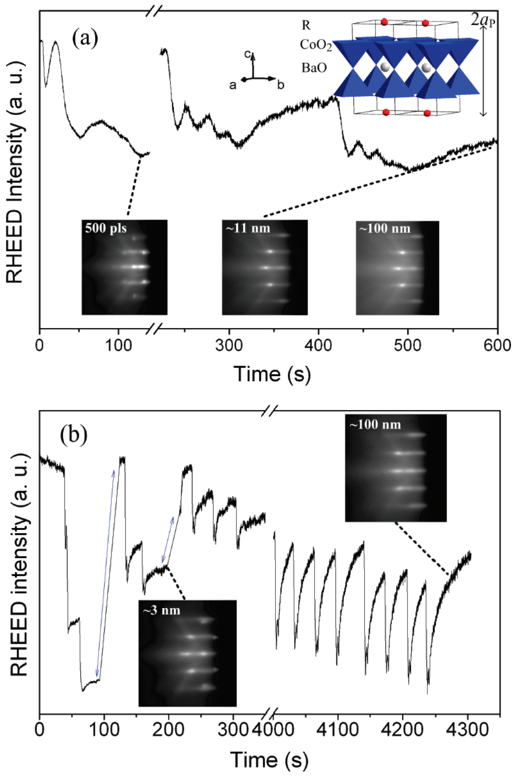

Figure 1. Intensity variation of the specular reflection in conventional mode (a) and in interval mode (b). The RHEED patterns are recorded along [110] azimuthal direction. The arrows correspond to manual change of the RHEED intensity scale. For (a) the observations show a transition in the growth mode, while for (b) 2D nucleation and growth occurs throughout the deposition. In (a) as a result of 2D nucleation and growth beginning to occur on an increasing number of unit cell levels, the oscillations were damped, and RHEED intensity data was not shown for the later stages of growth. The crystal structure of $RBaCo_2O_5$ (*Pmmm*, $a_P/a_P/2a_P$) is shown in the upper part of (a) with the dark and light spheres representing the ordered A cations.

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A series of $NdBaCo_2O_{5+\delta}$ (NBCO) films was examined. To estimate film/substrate misfit an average cell length of $a_P/a_P/2a_P$ is assumed for the ordered bulk and $a_P/a_P/a_P$ for the disordered bulk material.[6,7] Films were deposited on single-crystal (001)-$SrTiO_3$ substrates to favor a low in-plane strain (less than 1%). PLD was performed in a Neocera system (248 nm KrF lambda Physik laser), and the deposition was monitored with a STAIB high pressure RHEED system.[19] The incident angle of the 30 kV electron beam was 1−3°. Films were deposited in 1 mTorr of oxygen from a stoichiometric $NdBaCo_2O_{5+\delta}$ target, which was fabricated using a conventional solid-state reaction with high purity Nd_2O_3, $BaCO_3$, and Co_3O_4 precursors. Two methods were used for the growth: a “conventional” mode and an “interval” mode. For the conventional mode, the laser was continuously fired at the target with a repetition rate of 4 Hz. For the interval deposition mode,[20,21] the laser was fired in bursts of pulses at 20 Hz, followed by intervals without deposition. Two sets of growth conditions were used. A substrate temperature of 850 °C and laser energy of 250 mJ were used to obtain a high vapor phase supersaturation and a deposition rate of 56 pulses per a_P unit cell. For a deposition rate of 79 pulses per a_P unit cell, a substrate temperature and laser energy of 800 °C and 200 mJ were used.

Figure 1 shows the evolution of the intensity of the specular (00) RHEED reflection and the associated diffraction patterns, recorded at different stages of growth with the incident beam along an [110] azimuthal direction. During the conventional deposition (850 °C; 250 mJ), as shown Figure 1a, irregular variations in the specular intensity (regular oscillations visible after an initial drop with no clear oscillations during the growth of the first four to eight $2a_P$ unit cells) and in the diffraction patterns (spotty then streaky with Kikuchi lines) are observed. It is evident that a transition in the growth mode occurs during the earlier stages (four to eight $2a_P$ unit cells) to two-dimensional (2D) nucleation and growth. Energy and entropy considerations show that it is unfavorable to see a transition from a 3D growth process to a 2D growth process. However, spiral growth is a 2D growth process and thus might be feasible.[22,23] To test this hypothesis, the deposition was halted after 500 pulses (∼3.5 nm) and 2000 pulses (∼14 nm). From a thickness calibration, it is apparent that each RHEED oscillation corresponds to the growth of one a_P perovskite unit cell, that is, one-half of an ordered NBCO unit cell. The surface morphologies of the film were then measured by atomic force microscopy (AFM, AGILENT 5600LS), as shown in Figure 2. A variable roughening of the film surface occurs with increasing thickness. This is shown by a root-mean-square (rms) roughness of 0.933 ± 0.015 nm for 500 pulses; 4.004 ± 0.937 nm for 2000 pulses (Figure 2a); and 0.887 ± 0.250 nm for a 100 nm thick film (Figure 2b). 2000 pulses correspond to both the highest roughness measured by AFM and the point at which RHEED oscillations are first observed along with the streaky RHEED pattern. Features, recognized as nuclei or possibly growth spirals, were observed and are similar to those reported for $YBa_2Cu_3O_{7-\delta}$ films,[22−24] particularly after 500 pulses and less so after 2000 pulses. As the film thickness increases, these spirals coalesced leading to a 2D nucleation and growth. This transition can be attributed to variations in supersaturation in the initial stages at the growth surface.[24] The resulting structure of a cross section of 34 nm thick film has been studied by transmission electron microscopy (TEM) using a JEOL JEM3010HR microscope. Figure 3a confirms that the film is free of any columnar structure. The image contrast indicates that the film/substrate interface is perturbed over a thickness of approximately 3−5 nm which corresponds to the region of the growth mode transition. A Fourier transform (Figure 3b) of the image exhibits a doubling of the out-of-plane lattice parameter compared with $SrTiO_3$ and a single perovskite parameter for the in-plane direction. This suggests (1) epitaxy and the absence of misfit with the substrate and (2) the absence of in-plane superstructure, meaning that the film crystallized in the average bulk ordered structure with an oxygen stoichiometry probably different from $\delta = 0.5-0.69$.[7]

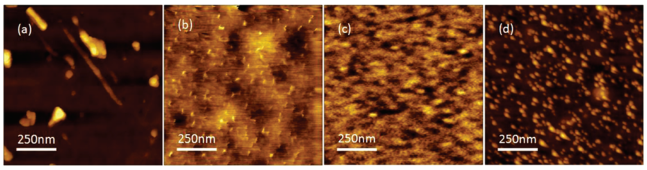

Figure 2. AFM topography images corresponding to various thicknesses of $NdBaCo_2O_{5+\delta}$ films grown by conventional deposition (a) 2000 pulses (rms = 4.004 ± 0.937 nm), (b) 100 nm (rms = 0.887 ± 0.250 nm) and by interval deposition (c) 2058 pulses (rms = 0.401 ± 0.040 nm), (d) 100 nm (rms = 2.560 ± 0.260 nm).

To promote 2D nucleation and growth rather than spiral formation in the initial stages of growth, the interval deposition approach was used.[20,21] A high supersaturation is achievable, caused by a high pulse frequency, which favors a large number of small 2D islands. Figure 1b shows the RHEED intensity during growth in conditions (850 °C; 250 mJ). Deposition over short intervals at 20 Hz of two oscillations corresponding to one ordered NBCO unit cell ($2a_P$) as sufficient A site ions are deposited to occupy both layers in the ordered structure was followed by a period without deposition. After each burst of deposition, a recovery of RHEED intensity was observed as a result of relaxation of the surface structure. Each recovery period can be fitted to a single time constant indicating that a single 2D nucleation

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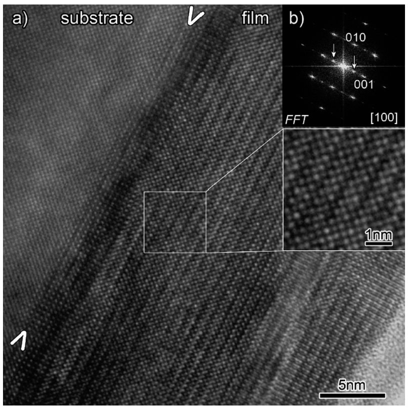

Figure 3. (a) High resolution TEM image for a cross-section of a 34 nm ordered $NdBaCo_2O_{5+\delta}$ film grown by conventional mode. The film/substrate interface is highlighted by two arrows. (b) Fourier transform where arrows show the doubling of the lattice parameter along [001] direction.

and growth process occurs. This time constant varies within the growth of the first five unit cells after which it reaches a constant value of 7.3 ± 1.6 s. The initial variation can be attributed to additional growth processes taking place in early stages such as misfit accommodation. This 2D growth mechanism is confirmed by AFM measurements where a low surface roughness is observed throughout the growth. The rms is 0.500 ± 0.022 nm after 588 pulses; 0.401 ± 0.040 nm after 2058 pulses (Figure 2c); and 2.560 ± 0.260 nm after 100 nm (Figure 2d). By manipulating the growth kinetics, 2D nucleation and growth is promoted by the high supersaturation in the interval growth method resulting in layer-by-layer growth from the deposition of the initial layer.

Figure 4a,b displays the X-ray diffraction (XRD PANalytical X'Pert with Co Kα_1 radiation, $\lambda = 0.1789$ nm) patterns of the NBCO films grown by the interval and conventional deposition processes. A series of five (00l) reflections for NBCO films confirms the highly oriented growth. The out-of-plane c-parameters were found to be $c = 0.789 \pm 0.001$ nm for the interval mode and $c = 0.788 \pm 0.001$ nm for the conventional mode. These values confirm the cationic Nd/Ba order observed by TEM. Furthermore, when interval deposition is carried out under the same conditions (850 °C; 250 mJ) but with only one single a_p unit cell corresponding to one oscillation deposited in each burst, A-cation order is still observed with the out-of-plane lattice constant corresponding also to the cationic order with $c = 0.791 \pm 0.001$ nm. This means that the A-site cation ordering in the NBCO films is due to a slower ionic diffusion process that occurs after growth of the substructure and not an instantaneous cationic ordering, as the initial single layer cannot be ordered along c over a $2a_p$ distance because equal numbers of Nd and Ba A-site cations are deposited in each single unit cell thick burst. To confirm this hypothesis, an NBCO film was deposited using the conventional mode in the (800 °C; 200 mJ) conditions where layer-by-layer growth occurs. Under these growth conditions, no diffraction features in the XRD pattern are observed from the cation-ordered perovskite structure (Figure 4c), and this is confirmed by TEM (Figure S1, Supporting Information). This shows that the Nd and Ba cations are randomly distributed on the A-site. This sample was subsequently annealed at the higher temperature of 850 °C, and no cation ordering was apparent which indicates that ordering is not just temperature dependent. Both the lower temperature and laser energy (800 °C; 200 mJ) effect the kinetics in such a way that order in the structure cannot be achieved due to a lower mobility in both the growing and the immediate subsurface layer. Conversely, the combination of an increased temperature and laser energy (850 °C; 250 mJ) imparts enough kinetic energy on the already formed subsurface layer to allow the ordering process to take place. These observations highlight that the A-site ordering is linked to the laser energy and temperature, implying that the higher diffusivity in the two top layers under the (850 °C; 250 mJ) growth conditions is not solely due to the increased temperature.

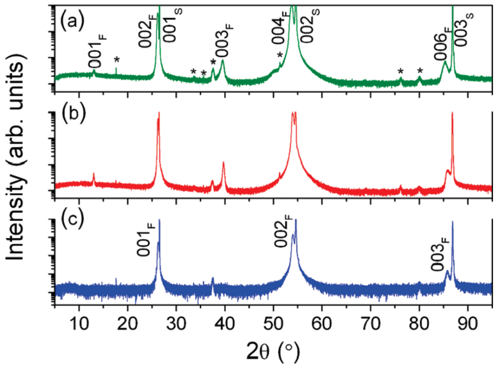

Figure 4. $\theta/2\theta$ XRD scans of (a) (850 °C; 250 mJ) interval deposition ordered film, (b) (850 °C; 250 mJ) conventional deposition ordered film and (c) (800 °C; 200 mJ) conventional deposition disordered film. F, S, and stars indicate respectively film, substrate and substrate imperfections.

By adjusting the growth kinetics via control of temperature and laser energy, cation-ordered units ($c \sim 2a_P$) or cation-disordered units ($c \sim a_P$) can be selectively incorporated into the $NdBaCo_2O_{5+\delta}$ structure. Consequently growth can be controlled on a unit cell level selectively between order variants of the same composition while retaining layer-by-layer growth. Interval deposition offers this control from the onset of growth and thus opens routes for systematically depositing heterostructures of these complex oxides with cation order and thus property control, whereas conventional deposition initially affords "spiral" growth without smooth interfaces.

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Supporting Information Available: Figure S1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.