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Interface-induced microstrain in $La_{0.67}Ca_{0.33}MnO_3/YBa_2Cu_3O_7$ superlattices

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ABSTRACT

Epitaxial $La_{0.67}Ca_{0.33}MnO_3/YBa_2Cu_3O_7$ superlattices with varying modulation lengths are produced by pulsed laser deposition and their detailed structural characterization is performed by X-ray diffraction. It is shown here that $YBa_2Cu_3O_7$ layers in all superlattice specimens have considerably high microstrain values, which are probably interface induced. The large distortions in the vicinity of the interfaces may alter the electronic structure and, hence, may have important consequences on the electrical and magnetic properties of the superlattice systems.

1. Introduction

An extensive research has been devoted to layered cuprates and doped rare-earth manganites in the recent years due to their interesting electronic properties such as high-T_c superconductivity and colossal magnetoresistance, a drastic reduction in the electrical resistivity during application of a magnetic field [1–6]. Both materials can be regarded as a member of the family of strongly correlated electron systems for which the underlying physics is based on a complexity of electronic interactions at comparable energy scales, superimposed to electron–lattice interactions close to phase transitions [7,8]. This competition can give rise to local inhomogenities in the electronic phases, the so-called nanoscale phase separation, which is regarded as the cause of the colossal magnetoresistance effect. Furthermore, the delicate balance among these phases can be disturbed and entirely diverse physical states can be stabilized via only very small external perturbations [9–11].

Recent advances in the thin-film deposition techniques open the way to produce epitaxial superlattices of these materials having atomically sharp interfaces with negligible interdiffusion [12–15]. These superlattices are ideal systems to investigate novel concepts like: (i) the interplay between superconductivity and magnetism. It has been reported that proximity of ferromagnetic metallic oxides to a superconductor suppresses both the Curie temperature and the transition temperature to the superconducting state, denoted by T_c [16]. Additionally, a magnetic coupling between the ferromagnetic layers is observed below the T_c of the superconducting layer [17]. (ii) The interfaces between the layers can have unusual properties, absent in both constituents of the superlattice alone. An antiferromagnetic coupling of the Mn and Cu spins across the interface has been observed due to an orbital reconstruction of Cu and Mn orbitals, adjacent to the interface [14]. Furthermore, it was shown that a very high carrier mobility can be obtained at the interfaces of the $LaAlO_3/SrTiO_3$ superlattice although both materials are actually insulating [12]. These new properties can dominate over the bulk properties of the constituents due to the high fraction of atoms affected from the interfaces.

Although the common belief is that the structural properties are of cardinal importance in terms of the resulting electronic properties for both cuprates [13,18] and manganites [19,20], systematic studies are rare (especially for their superlattices) and dominated by high-resolution transmission electron microscopy (HRTEM) investigations, which give information on a minor portion, not necessarily representing the whole specimen, and high-resolution X-ray diffraction (XRD) experiments in combination with computer simulations [13,16] (see Ref. [21] for general

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aspects of this technique and, also, Refs. [22–24] for its application to superlattices of some other materials).

In this study, a dedicated structural characterization of $La_{0.67}Ca_{0.33}MnO_3$ (LCMO)/$YBa_2Cu_3O_7$ (YBCO) superlattices is given. In addition to more basic information such as phase purity, epitaxial relationship, modulation length, interface quality and mosaicity, application of XRD line-broadening analysis to the reflections of YBCO, which are not overlapping with LCMO, allows one to extract information about the microstrain (i.e. related to the local variations in interplaner spacing) in the YBCO layers alone. It is shown here that YBCO layers in the superlattices have considerably high microstrain values. Moreover, an inverse correlation is identified between the microstrain and modulation length, suggesting that the observed microstrain is presumably interface-induced. Hence, the physical states of the constituents of superlattices can be rather different from the bulk of the same material, especially in the vicinity of the interface regions. These new physical states may be the structural driving force behind the modification of the electronic and magnetic properties at the interfaces, as the recently proposed orbital reconstruction scenario.

2. Experimental details

Three superlattices (denoted by S1, S2 and S3) were deposited on (0 0 1) $SrTiO_3$ (STO) substrates by conventional pulsed laser deposition (PLD) with different nominal modulation lengths, $\Lambda = t_{YBCO} + t_{LCMO}$, where t_{YBCO} and t_{LCMO} are the thicknesses of individual YBCO and LCMO layers, respectively. The YBCO was the first layer on the STO substrate whereas the LCMO was the top layer of the stack. The different values of Λ were achieved by pulse counting technique after calibration depositions for each layer. The parameters Λ and n, where n is the number of repetitions in the superlattice, pertaining to each superlattice specimen are summarized in Table 1. For the sake of comparison with the superlattice specimens, a trilayer (denoted by S4), consisting of a 100-nm-thick LCMO layer on the (0 0 1) STO substrate, a 100-nm-thick YBCO layer as the middle layer and a 50-nm-thick LCMO layer as the cap layer, was also produced.

Pole figure measurements for 117 reflections of YBCO were performed in a Philips X'Pert MRD diffractometer, equipped with an Eulerian cradle, parallel beam optics and a position-sensitive detector, using Cu Kα radiation.

The overview 2θ–ω and high-resolution ω–2θ scans (2θ is the angle between the incident and the diffracted X-ray beams; ω is the angle between the incident beam and the specimen surface) were carried out by a high-resolution four-circle Bruker D8 Discover diffractometer, having a Göbel mirror, 4-bounce Ge (0 2 2) channel-cut monochromator, Eulerian cradle and a scintillation counter, using Cu $K\alpha_1$ radiation.

The data for line-broadening analysis were collected by a Bruker D8 Discover diffractometer with an Eulerian cradle. The Cu Kα radiation emerging from a microfocus rotating-anode X-ray source (Bruker TXS) was converted into a monochromated and quasi-parallel beam by a collimating X-ray mirror (Xenocs) [25]. The diffracted beam passed a parallel-plate collimator (acceptance angle 0.23°) before being detected by a scintillation counter.

The crystallite size, D, and the microstrain (describing the local variations in lattice spacings), ε, in the direction perpendicular to film surface were determined by XRD line-broadening analysis employing two methods: (i) single-line-broadening method and (ii) Williamson–Hall method [26–28]. In both methods, the measured diffraction profile is assumed to be a convolution of an only structurally broadened profile (structural broadening can be due to small crystallite size and/or microstrain (i.e. local variations in the lattice spacings) originated from lattice imperfections) with the instrumentally broadened profile. In the single-line method, the structurally broadened and the instrumentally broadened profiles are approximated by Voigt functions (i.e. the convolution of a Lorentz function and a Gauss function). The integral breadths of the Lorentz and Gauss components of the structurally broadened profiles are obtained from the integral breadths and the Voigt parameters (*VP*; i.e., the ratio of the full-width at half-maximum intensity (FWHM) to the integral breadth) of the measured profiles employing the Voigt method [26,27]. It is assumed that the Lorentz component of the structurally broadened profile is due to the small crystallite size whereas the Gauss component of the structurally broadened profile is caused by microstrains. On the other hand, size, microstrain and instrumental broadenings are assumed to be Lorentzian and, thus, linearly additive in Williamson–Hall analysis. The differentiation of size and microstrain broadenings is based on the dependence of each broadening type on θ [28]. In order to determine the instrumentally broadened profile of the diffractometer as a function of diffraction angle 2θ, 13 *hkl* reflections of a LaB_6 (NIST SRM660a) standard powder sample were measured.

Table 1
The nominal modulation length, Λ, the thickness of YBCO layer, t_{YBCO}, the thickness of LCMO layer, t_{LCMO}, the number of repetition, n, and the measured modulation length, Λ_m, of the superlattice specimens.

Specimen	Λ (nm)	t_{YBCO} (nm)	t_{LCMO} (nm)	n	Λ_m (nm)
S1	20	10	10	12	17.4±0.1
S2	30	20	10	10	26.2±0.2
S3	40	30	10	7	35.3±0.2

3. Results and discussion

Only the 00*l* reflections of both materials and the associated superstructure peaks are observed in 2θ–ω scans within the range between 5° and 120°, suggesting that the *c*-axes of YBCO and LCMO are oriented perpendicular to the film surface. Modulation length is calculated for each superlattice specimen from the distance between the superstructure peaks in high-resolution ω–2θ scans (see Fig. 1); Λ is 17.4, 26.2 and 35.3 nm for S1, S2 and S3, respectively, agreeing well with the nominal values (cf. Table 1) within the experimental accuracy. At least three superstructure peaks (SL) are clearly visible on the right side of the main peak for all specimens. The absence of SL -4 and SL 4 peaks in Fig. 1(a) may stem from an inhomogeneous and asymmetric strain profile through the thickness as reported in Ref. [29]. In Figs. 1(b) and (c), the superstructure peaks on the left side of the main peak are lacking, presumably due to large Λ values, possible fluctuations in Λ and strong overlap with the substrate peak. The ω–2θ scan of the trilayer specimen S4 is also presented in Fig. 1(d) to provide a comparison with the superlattice specimens. Representative for all specimens, the 117 pole figure of YBCO for specimen S1 is represented in Fig. 2(a). Four-fold symmetry is observed and inclination angle of the YBCO-related peaks ($\psi \sim 30°$) is consistent with the angle between (1 1 7) and (0 0 1) planes. The four peaks at $\psi \sim 45°$ stem from the 220 reflection of STO, close to the 117 reflection of YBCO in the 2θ scale. The rotation angle, φ, between YBCO- and STO-related peaks is approximately 45°, inline with the expected epitaxial relationship (i.e. *a*-edge of the cubic substrate corresponds to the *a*- and *b*-edges of the YBCO layer). Fig. 2(b) illustrates the rocking curves of four specimens around the 005 reflection of YBCO. The full-width at half-maximum intensity is around 0.4° (i.e. close to instrumental broadening) for the