Substrate Surface Engineering for Functional Ceramic Thin Film Growth

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Abstract. A concept is introduced, using oxide substrates for functional ceramic thin film deposition beyond their usual application as chemical inert, lattice-matched support for the films. The substrates are applied as a functional element in order to controllably modify the atom arrangement and the growth mode of cuprate superconductors and colossal magnetoresistance materials. These materials have been chosen as prototypes of the general class of perovskite functional ceramics. One example studied is the use of epitaxial strain to adjust the relative positions of cations and anions in the film and thus modify their physical properties. The other makes use of vicinal cut $SrTiO_3$ which enables the fabrication of regular nanoscale step and terrace structures. In $YBa_2Cu_3O_{7-x}$ thin films grown on vicinal cut $SrTiO_3$ single crystals a regular array of antiphase boundaries is generated causing an anisotropic enhancement of flux-line pinning. In the case of La-Ca-Mn-O thin films grown on vicinal cut substrates it could be demonstrated that magnetic in-plane anisotropy is achieved.

1. Introduction

The physical properties of perovskite-type functional ceramic thin films are known to sensitively depend on details of deviations from their ideal composition and/or crystal structure. Substrate-induced lattice strain, substrate surface morphology and growth-induced defects are some examples for extrinsic effects playing an important role in determining thin-film properties and consequently the application potential of functional ceramics [1–5]. The sensitivity of the physical properties on the structure arises from the origin of the functionality at the level of sub-unit cells. In the case of the doped rare earth manganites, e.g. the bonding distance and bonding angle of the Mn-O-Mn building block determines the charge transfer of an electron from Mn to Mn via the oxygen, thus control the bandwidth, metallicity and the appearance of ferromagnetism [6, 7]. In high temperature superconductor [HTS] cuprates such as $La_{1-x}Sr_xCuO_4$ the distance of the apex oxygen from the CuO_2 planes affects the Cu4s–O2p hybridization and thus doping and T_C [8, 9].

The multicomponent chemical composition of the ceramic materials combined with their complex crystal structure represents a much higher degree of sophistication for a thin-film technology compared to that of metals and semiconductors. Consequently, to understand the film growth process and modify it intentionally in order to open a path for defect control, is a tremendous challenge. In contrast to metals and semiconductors where the deposition temperature for epitaxial growth from the vapor phase is around 20% (metals) to 40% (semiconductors) of the melting temperature, T_M, for ceramics such as the HTS cuprates much higher values of around (0.7–0.8) T_M are required. This reflects the chemical dissimilarity of the constituent cations and their quite different diffusion coefficient at the substrate surface at growth conditions. The general problem of the vapor deposition of oxides with complex chemical composition and large unit cells to fabricate singlecrystal-type epitaxially grown thin films had not been addressed prior to 1986, the year of the discovery of the HTS cuprates. The role of the substrates in the efforts exploring the epitactic growth of ceramic thin films has been treated so far

simply as that of a mechanical support combined with chemical stability and compatibility with the prerequisites given by the epitaxy relations. In order to pave a new way for all-oxide electronics and novel device concepts an advanced oxide epitaxy technology is required based on nanoscale substrate engineering as well as on atomic layer control of oxide films. Furthermore, the opportunities buried in tailoring the substrate surface morphology have to be explored in order to intentionally modify growth conditions and defect arrangements.

2. The "Perfect" Film on a "Perfect" Substrate

The film growth in general is determined by the relative importance of surface energies of film, substrate and interface, respectively, supersaturation and substrate temperature. A specific balance of the thermodynamic and kinetic is required to achieve single-crystal type ceramic thin films. Supersaturation and substrate temperature are the most important variables in the film growth process, they determine whether the nucleation is dislocation controlled or island growth controlled. Substrates for the growth of ceramic thin films are more than just a mechanical support for the film. The ideal substrate has to fulfill the requirements of perfect lattice match to ensure epitaxy, match of the thermal

expansion coefficients to avoid cracking, lack of structural phase transition between deposition temperature and operating temperature to prevent additional stress, chemical inertness with respect to the film forming species and, finally, lack of interdiffusion. The misfit between the substrate and the film at epitaxial growth temperature not only affects the selection of the epitaxy relations it also influences the surface nucleation and growth modes. Misfit reduces the step-flow regime and enhances two-dimensional nucleation. Additionally, the stored elastic energy in the pseudomorphically grown layer adjacent to the substrate acts as a driving force for several relaxation mechanisms ranging from the generation of misfit dislocations, stacking faults to cluster formation. Misfit acts in the same direction as supersaturation. If these mechanisms cannot relieve the strain, cracking may occur. The difficulties in achieving the "perfect" ceramic thin film are connected with problems of the phase stability and oxygen supply superimposed to the peculiarities of the kinetically controlled thin film growth process and the substrate related effects. Nevertheless, using optimized preparation conditions for film deposition in the temperature pressure and supersaturation parameter space, nearly perfect single crystal ceramic films can be produced. In Fig. 1a TEM cross section micrograph of a $La_{0.9}Sr_{0.1}MnO_3$ thin film is given showing the perfect epitaxy on the $SrTiO_3$ substrate [10].

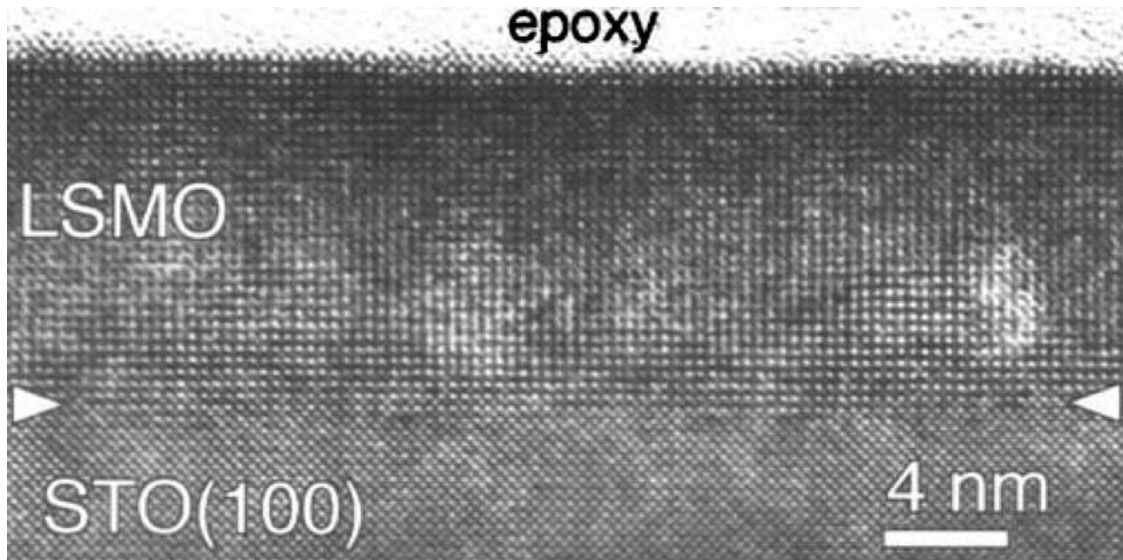*Fig. 1*. High resolution cross-sectional TEM of a 9 nm $La_{0.9}Sr_{0.1}MnO_3$ film.

3. Tailoring Epitaxial Strain in HTS Thin Films

It is a well known phenomenon that a lattice mismatch between substrate and film will result in a pseudomorphically strained layer with subsequent stress relieve by different accommodation mechanisms generation of misfit dislocations, stacking faults or undulations of the lattice planes or a combination of these. As a rule of thumb, a lattice mismatch in the order of 1–2% is accommodated by the generation of stressed pseudomorphically grown films up to a critical thickness, t_c, which decreases with increasing lattice mismatch. For $YBa_2Cu_3O_7$ deposited onto $LaGaO_3$ single crystal substrates, t_c has been determined to be around 50 nm [11]. A careful analysis of the pressure and strain dependence of T_c for different HTS materials by Locquet et al. [8] shows that in most cases the uniaxial dT_c/dp values have different signs and thus add up to an increase of T_c for compressive strain and a decrease of T_c for tensile strain. Indeed, Locquet et al. could demonstrate, that biaxial strain in $La_{1.9}Sr_{0.1}CuO_4$ (LSCO) thin films pushes T_c up from the bulk value of 25 to 50 K.

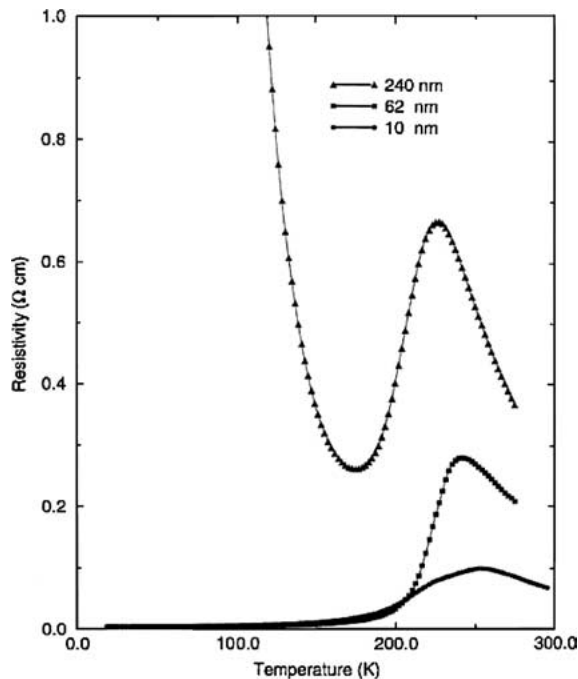In the case of manganite thin films compressive strain can cause an even more dramatic effect on the temperature dependence of resistivity. In Fig. 2 the $\rho(T)$ curves $La_{.88}Sr_{.1}MnO_3$ thin films of different thickness are represented. Whereas the thick film (240 nm) shows the bulk-like behavior with a metal-insulator transition, T_{MI}, at 220 K followed by a transition to a charged ordered insulator at 170 K, charge ordering is destroyed in homogeneously strained thin films. Compressive epitaxial strain causes here the transition from a ferromagnetic insulator to a ferromagnetic metal [4].

4. YBCO Thin Films Deposited on Vicinal Cut SrTiO₃ Single Crystals

When (001)-oriented $SrTiO_3$ substrates with an intentional miscut (angle $\alpha < 15°$) towards the [010] direction are annealed at $950°C$ a regular step and terrace structure is generated with the step height of typically one unit cell of $SrTiO_3$ ($a = 0.3905$ nm) and a step width corresponding to $w = a/\tan\alpha$. In contrast to films grown onto closely lattice matched (001)-oriented perovskite-type oxide substrates the films deposited onto the vicinal cut substrates show a terrace-like surface morphology with steps along the [100] direction, indicating a change from the usual Stranskit–Krastanov growth to a step-flow growth mode. In $YBa_2Cu_3O_{7-x}$ the substrate-mediated modification of the growth mode $YBa_2Cu_3O_{7-x}$ influences the microstructure of the films and causes an artificially introduced anisotropy of their transport and pinning properties. We find a close correlation between the film morphology and the film properties as revealed by transport measurements and Raman spectroscopy. In Fig. 3 the surface of a 10° miscut $SrTiO_3$ surface clearly demonstrates a remarkable nanoscale terrace structure as a result of the UHV annealing. Along the [010] direction regularly spaced terraces with a period of 2.3 nm and a step height of ≈ 0.39 nm corresponding to one unit cell of $SrTiO_3$ is found. The terrace-like structure is basically preserved after $YBa_2Cu_3O_{7-x}$ film deposition, indicating a change of the usual Stranskit–Krastanov island growth a step-flow growth for $YBa_2Cu_3O_{7-x}$. Compared to the substrate, the terraces of the film are wider by roughly a factor of three (≈ 7 nm). The step heights, however, are multiples of 0.2 nm, deviating from the full integer of the unit cell height of 1.2 nm of $YBa_2Cu_3O_{7-x}$. This implies that the unit cells grown on the upper and the lower part of a single unit cell step of the substrate can be shifted vertically forming an antiphase boundary (APB). The planar APBs are
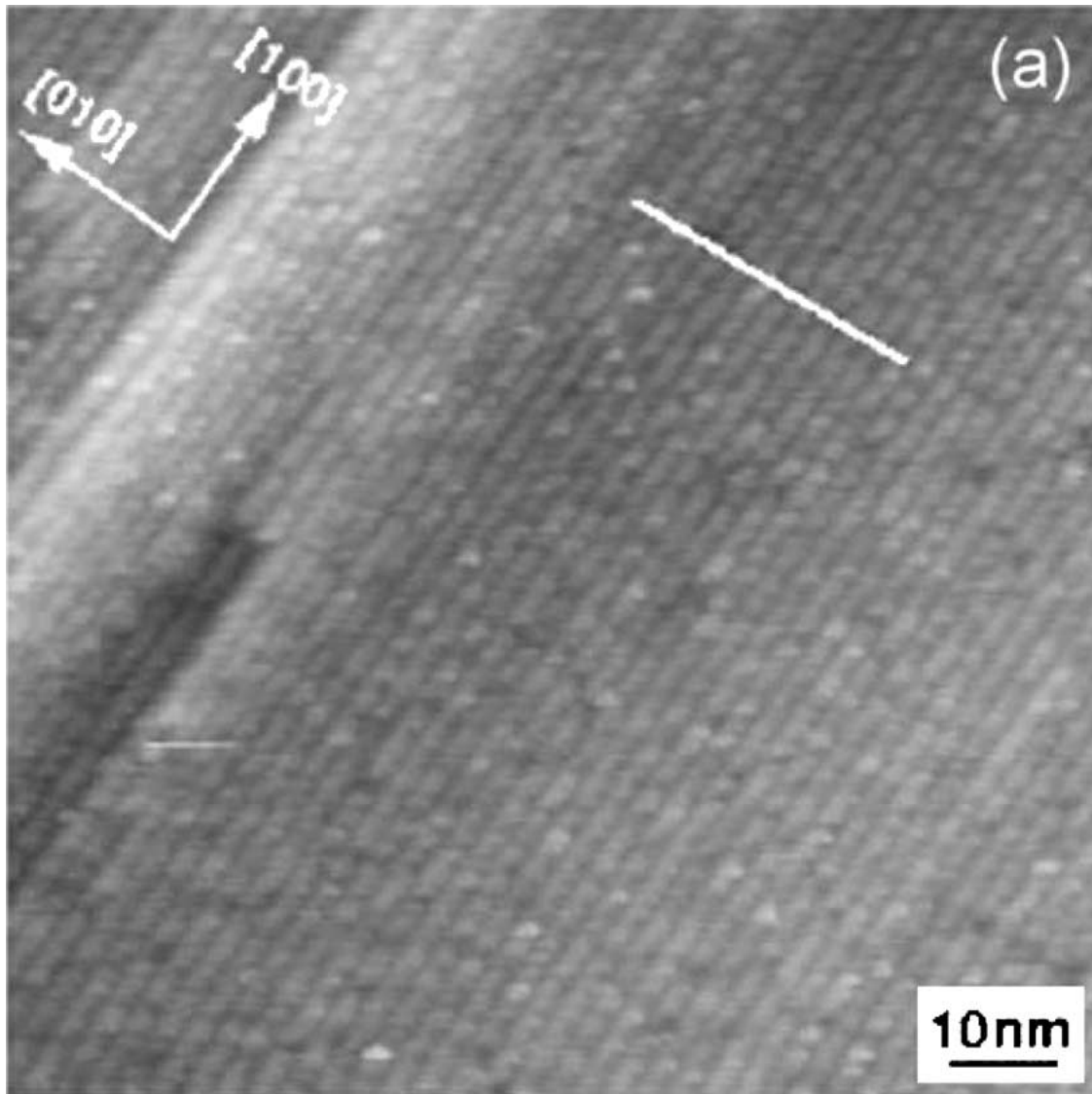

Fig. 2. Temperature dependence of resistivity of $La_{.88}Sr_{.1}MnO_3$ thin films of different thickness.

Fig. 3. STM image of a 10° vicinal cut SrTiO₃ single crustal substrate after UHV annealing.

oriented perpendicular to the film plane forming a regular nanoscale array with an APB distance of around 7 nm. A detailed analysis of the defect structure due to the nanoscale surface step structure of the substrate and its implications to transport properties and flux pinning is given by Haage et al. [12]. The predominant modifications of the properties of such films are summarized as follows [13]: (i) Strong anisotropy of the electrical dc resistivity; (ii) thickness dependent enhancement of the critical current; (iii) partial detwinning of the films with a better perfection of the CuO chains along the step edges; (iIV) anisotropy of the dimensionality of the fluctuation conductivity above T_c with a large temperature range for the 3-dimensional fluctuations along the step edges and a small range for 3-dimensional fluctuations perpendicular to the step edges.

Similarly, manganite thin films grown on vicinal cut SrTiO₃ substrates show an in-plane magnetic anisotropy with the easy axes along the substrate steps. Over a large angular range the angular dependence of the magnetic switching field is found to obey the $1/\cos\varphi$ law, indicatiing that the magnetic reversal is completed

by a 180° domain nucleation and sweeping along the easy axis [14].

5. Conclusions and Outlook

The experiments described above demonstrate the new possibilities in ceramic thin film research if the substrate is not only treated as a support material for the films but also additionally regarded as a functional integrated part of the system film/substrate. Making use of epitaxial strain opens the possibility to externally affect the atom arrangement and thus the properties of the films. Modifying the growth mode from Stranskit–Krastanov to step flow in the case of the vicinal cut substrates is a new possibility for tailoring the defect structure and thus flux-line pinning sites in cuprates and in-plane magnetic anisotropy in manganites. Recently, a further technique for controlled substrate surface modification has been introduced using either ion implantation with a focused ion beam microscope [15] or laser surface treatment to regularly etch μm scale grooves or trenches into the substrate. The physical concept behind these experiments is the search of matching effects in HTS flux-line pinning, fabrication of flux guides and formation of regular arrays of manganite ferromagnetic quantum dots for in plane spin valve devices.

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