Scanning tunneling microscopy and spectroscopy of La$_{0.67}$Ca$_{0.33}$MnO$_3$ thin films grown on LaAlO$_3$(100)

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Abstract

Thin films of La$_{0.67}$Ca$_{0.33}$MnO$_3$ have been deposited at room temperature on LaAlO$_3$(100) substrates by dc magnetron sputtering. The as-deposited films are amorphous and become polycrystalline on annealing ex situ at 800°C in oxygen ambient. Topographic and tunneling spectroscopic features of annealed films have been studied by a scanning tunneling microscope at room temperature in air. The main micro structural features in these films are the presence of fish-scale or slate like plates, terraces of integer multiple of unit cell or half-unit cell parameter height and oblate shaped grains. Grain boundaries have been identified from the orientation of terraced grains with respect to the substrate plane. Such a planar growth accompanied by grain boundaries may enhance magnetoresistance both at and below ferromagnetic transition temperature. An average barrier height of 4.0 eV of La$_{0.67}$Ca$_{0.33}$MnO$_3$ has been obtained from current-voltage measurements. A band gap of 0.2 eV has been found from the existence of states near the Fermi level in the density of states spectrum.

Keywords: Colossal magnetoresistance; Scanning tunneling microscopy; Tunneling spectroscopy; Thin film

1. Introduction

Lanthanum-based manganite perovskites of the type La$_{1-x}$A$_x$MnO$_3$ (where A is a divalent metal like Ca) exhibit colossal magnetoresistance (CMR) [1-5]. They are potential candidates for the fabrication of magnetoresistive sensors. These materials exhibit interesting transport properties. La$_{0.67}$Ca$_{0.33}$MnO$_3$ (LCMO) has intrinsically perovskite type layered crystal structure. The a-b plane consists of alternating layers of La(Ca)-O and Mn-O, stacked along the c-axis. The Mn-O layer is ferromagnetically ordered in a-b plane maintaining antiferromagnetic order along the c-axis, with a non-magnetic La(Ca)-O layer in between two Mn-O layers below the Neel temperature [6]

Step flow growth has been observed in (La,Ca)MnO$_3$ thin films grown on SrTiO$_3$(001) substrate has shown terraces and island edges of either one-unit-cell or half-unit-cell height [8]. Chung et al. [9] have examined highly oriented La$_{0.84}$Sr$_{0.16}$MnO$_3$ perovskite films deposited on SrTiO$_3$, MgO and yttria stabilized zirconia by STM and observed either layer by layer growth or apparent spiral of steps coupled with a two-dimensional growth process. Overlapping platelets have been found in Nd$_{0.2}$Sr$_{1/3}$MnO$_3$ epitaxial film on LaAlO$_3$ substrate [10]. Yeh et al. [11] have mainly reported the step flow growth mode of CMR films in their STM investigation.

Recently, a number of spectroscopic studies have been carried out on this perovskite system [12-20]. Electronic structures have also been computed by several workers [21-23]. It has been found that [13] there exists a gap even in metallic phases of these compounds at high temperatures, indicating the survival of gap on doping in charge excitation. Both the end materials, LaMnO$_3$ and CaMnO$_3$, are insulators. With gradual substitution of La by Ca in LaMnO$_3$, the Jahn-Teller split Mn(3d) e$_g$ occupied band becomes empty. Its
complete depletion occurs for CaMnO$_3$ and the substituted intermediate compounds become conductors [22].

Topographic features along with energy and spatial variation of the electronic density of states (DOS) are helpful to obtain an insight into the local surface nature of these layered oxide materials [24]. The exact role of crystallinity of these compounds on CMR is not so clear [25]. Since the magnetotransport properties of CMR materials are significantly controlled by the local structural order, the growth nature of films is expected to influence the CMR properties. We report here on the investigation of growth morphology and tunneling spectroscopy (TS) of LCMO thin films by STM. Efforts have been made to understand the structure of DOS near the Fermi level ($E_F$) and to estimate the band gap at room temperature.

2. Experimental details

LCMO thin films were deposited on LaAlO$_3$(100) substrates at room temperature by dc magnetron sputtering. The films were ex situ annealed at 800°C in oxygen ambient for 30 min. The surface morphology of the annealed films was studied using an STM in air at room temperature. Electrochemically etched tungsten tips were used for topographic studies. Topographic features were obtained at a tunneling current of 400 pA and a gap bias-voltage of 400 mV.

The tunneling spectra were acquired by freezing the tip position corresponding to a tunneling current of 100 pA and different tip-sample separation voltages ($V_s$). Each separation voltage $V_s$ corresponded to a particular tip to sample distance. The current-voltage ($I-V$) data were acquired, with the feedback loop interrupted by the sample and hold circuit [24,26]. The signals were averaged over ten spectra at each sample point. Sample sites were mainly chosen on planar regions, away from grain boundaries and step edges. Reproducibility was checked by acquiring data at different locations and at different tip to sample distances using tungsten and mechanically cut platinum-iridium tips.

We studied tunneling spectroscopy of an electron beam evaporated tungsten thin film [W/Si$_3$N$_4$/Si(100)] with both electrochemically etched tungsten and mechanically cut platinum-iridium tips to obtain information on the nature of electronic DOS of the tip material.

3. Results

As deposited films were amorphous and insulating. On annealing they became polycrystalline and semiconducting at room temperature. The resistivities of the annealed films at room temperature were found to be about 30 mfl cm and showed a peak in resistivity at 173 K with magnetoresistance (MR) of 22% at 142 K in the presence of 0.35 T magnetic field.

Surfaces of annealed films were found to be stable in air for about 6 h. A gradual surface degradation was noticed on prolonged exposure to air giving arbitrary and obscure surface features, indicating the presence and formation of some sort of insulating or semiconducting layer, as observed by others [10].

Surface topography of annealed films exhibited an overall planar growth. Step-like terraces have been seen to extend over areas of more than a square micron (Fig. 1(a)) and are not always straight having curved or ragged edges (Fig. 1(b)). The step-heights are either integer or half-integer multiples of unit cell parameter (a≈7.7 Å). Fig. 1(c) shows a line profile of height variation of the surface steps from sites A to site B. The growth-step planes are more or less parallel to the substrate and are aligned at angles ranging between 2° and 6° to the substrate plane. It varies from place to place. The line scan, AB shows this angle to be 2.3°, while CD makes an angle of 5.4° with the substrate surface. But the steps of Fig. 1(a) maintain almost a constant value of 4.3°. RMS roughness of these films is found to be 33 Å over an area of 1 x 1 μm.

Another mode of layered growth is shown in Fig. 2(a) and (b). It exhibits fish-scale type plates. These plates are 100 nm in width and 300-400 nm in length. Sometimes slate like planes are very clear as shown in a smaller area scan of Fig. 2(b). A mixture of three-dimensional and two-dimensional growth modes has been observed occasionally in a few places (Fig. 2(c)). Oblate shaped platelets together with steps (lower left corner of the topograph) have been found to be about 300 nm across.

Fig. 3(a) shows a set of I-V tunneling characteristic curves taken for different $V_s$. Corresponding tunneling conductivities are shown in Fig. 3(b). The electronic nature of the film is obscure due to overlapping of the tunneling parameter with the electronic DOS of the sample. The bias dependence of the tunneling parameter is evident from the monotonic increase of conductance with applied bias voltage. Fig. 3(c) shows DOS of the film surface. The value of current changes abruptly after a voltage of about 0.1 V for both positive and negative biasing of the sample. The inflection points correspond to the valence band and the conduction band edges, respectively. These are very prominent in Fig. 3(c). The existence of a band gap is clear from the appearance of states at about 0.1 eV and — 0.1 eV near the Fermi level (0 eV) implying a band gap of ~ 0.2 eV only. Such a small band gap indicates the material to be semiconducting at room temperature.

It is possible to get an idea about the value of barrier height from the I-V characteristics for a dynamical range of tip-sample spacing following the method de-
scribed by Stroscio et al. [27-29]. In this method, the I-V measurements at different gap-bias voltages can be normalized to certain common voltage by multiplying the observed current by \[ \exp(1.025\sqrt{1/2}Ad) \], where \( \Phi \) is the barrier height and \( Ad \) is the known change in vertical tip position. \( Ad \) can be obtained from a measurement of Z-position vs. gap bias-voltage, at 100

![Fig. 1. Surface morphology of annealed LCMO/LaAlO\(_3\) (100) thin films.](image1)

![Fig. 2. Growth platelets of LCMO/LaAlO\(_3\) (100) thin films: (a) fish-scale shaped appearance and (b) slate like appearance and (c) a typical region of the film surface showing a transition from island to planar growth.](image2)

\( \Phi \) is a constant current. For example, if the relative tip-sample separation for \( V_s = 0.4 \) V is considered to be zero, then the four \( V_s \) 0.4, 0.6, 0.8 and 1 V correspond to \( Ad \) of 0, 0.5, 1.3 and 19 Å, respectively. We have normalized all the curves for \( V_i = 1 \) V considering various values for \( \Phi \). The best overlapping of I-V characteristics and hence the optimum normalization have been obtained for a value of \( \Phi = 4.0 \) eV, indicating a barrier height to be close to 4.0 eV. The normalized curves for this value of \( \Phi \) have been plotted in Fig. 4 on a semilogarithmic scale to highlight the features near \( E_F \). We identify three regions labeled by VB, EG,
and CB, which stand for valence band, energy gap and conduction band region, respectively.

Fig. 5 shows the I-V curve and corresponding DOS of the freshly cleaved sintered LCMO pellet surface of our earlier measurements on bulk manganites [30]. One noticeable feature in the DOS curve is the existence of kinks near the Fermi level at around the same positions as they are in the corresponding curve for the film (Fig. 3(c)), suggesting that the band gap in the film is of the same order as in sintered pellets. Electronic DOS of tungsten thin film studied by both tungsten and platinum-iridium tips is shown in Fig. 6. With respect to LCMO, the flatness of metallic DOS is clear from these studies.

4. Discussion

4.1. Topographic aspects

The change from amorphous to crystalline phase of thin films on thermal annealing is a complex process of solid-solid phase transformation. Both granular and planar growth features have been observed in our samples prepared under the same growth conditions. Planar growth dominates most of the cases. In Fig. 2(c), a transition from granular to planar growth can be noticed. This indicates that the growth mechanism of these films involves a three-dimensional island to a two-dimensional planar growth transformation. Such a growth mode has also been observed in perovskite barium-strontium-titanate thin films [31].
In an STM image, it is difficult visually to identify the grain boundaries in planar growth structures. They can be recognized from the alignment of planes of two adjacent grains, as shown in Fig. 1(b) by the line scans AB and CD. The depressed grey line EF is a grain boundary, though it merely appears to be a step. Planar growth of LCMO films is an indication of intrinsically layered structural nature of the complex perovskite oxides like high $T_c$ oxide superconductors. A similar type of growth mode has also been observed in those materials [24].

A number of researchers have studied the effects of microstructural aspects on magnetoresistance [11,32-34]. Grains having planar structure may have great impact on magnetotransport properties of such materials, where the transport properties are explained by double exchange, since it is greatly influenced by its local order [33]. Individual large planar grains enhance MR, as single crystallinity is the primary requirement of the CMR effect [5]. However, at temperatures below $T_c$, growth defects such as dislocations and grain boundaries, help in enhancing MR and broadening the magnetoresistance peak.

4.2. Spectroscopic aspects

Electron tunneling from the occupied states of the tip to the unoccupied conduction band states of the samples arises when a positive bias is applied to the sample. In negative bias electrons tunnel from occupied valence band states of the sample to the unoccupied states of the tip. Analysis of the tunneling spectroscopy becomes difficult due to the unknown DOS of the tip and unknown bias dependence of the tunneling probability, as the obtained I-V is a convolution of the tunneling probability and the DOS of both tip and sample [24,26]. Dependence on tunneling probability is compensated by normalizing the differential conductance $dI/dV$ to the total conductance $I/V$ [35]. Though the electronic structure of the tip is unknown, it can be assumed to be constant (Fig. 6), contributing a constant background to DOS [24]. The constant DOS of the tip has been confirmed by taking tunneling spectra of the tungsten film in the energy range of our interest.

$I-V$ spectroscopy (Fig. 3(a)) of the films exhibits semiconducting behavior, similar to that of the bulk. The curves are asymmetric implying the trapezoidal nature of barrier potential, expected for metal-insulator-semiconductor junctions [12]. The observed bias dependence of conductivity is a typical behavior of semiconducting oxide materials [36], which is evident from $dI/dV$ vs. $V$ curves (Fig. 3(b)). The features of DOS in films (Fig. 3(c)) are not so prominent as in the sintered pellets (Fig. 5). This is possibly due to two important contributions in thin films: one is from the effect of scattering of electrons and the other from the effect of surfaces itself [37]. Existence of other energy states is also noticeable in the figure. Though most of the peaks corresponding to different $V_t$ coincide, non-coincidence of few of them can be due to a change in the nature of the tip-sample interaction, local surface inhomogeneity, piezo drift or thermal drift of the sample.

From various spectroscopic studies on (La,Sr)MnO$_3$ [13,14] and LCMO [18] and local-density approximation (LDA) calculations [21-23], it has been evident that the spectral weight appears in the in-gap region with Sr or Ca doping. Biswas et al. [12], in their tunneling spectroscopy study at 77 K, have shown the appearance of states at approximately 0.1, 0.35 and 0.6 eV with respect to $E_F$. The reported values of band gap measured by different techniques in these manganite systems are found to vary over a wide range from about 0.03 to 2.3 eV [13,14,21,38-42]. We have obtained activation energies of LCMO from the temperature variation of resistivity measurement. It is found to be 0.1 eV in sintered pellets whereas it is 0.14 eV in films. The band gap 0.2 eV obtained from our tunneling measurement is in fair agreement with those mentioned above.

According to LDA and LDA + U (U is Coulomb energy) calculations [22] and experimental evidence [13,14], the contribution to DOS in the occupied states may arise from all Mn(3d) $e_g$, $t_{2g}$, and O(2p) bands in the energy region of our TS measurement. In the unoccupied region the DOS surface states may arise from the contribution of all these states. So it is very difficult to find out any correspondence between these energy states and the observed peaks in Fig. 3(c). The appearance of spectral weight in this region is a convolution of a number of overlapping energy states. In the occupied region the first peak may correspond to the $e^+$ state, electrons in which are responsible for conduction mechanism in these materials. Saitoh et al. [14] have suggested that the electronic structure near the Fermi level is not of rigid band type. Therefore, it can be said that either there exists negligibly small density of states near the Fermi level due to the band edge tails or it has a small band gap at room temperature. The tailing of band gap edges may also represent the existence of surface states mainly arising from the surface contamination which is unavoidable while working in air.

5. Conclusions

LCMO/LaAlO$_3$(100) films deposited by dc magnetron sputtering are amorphous but subsequent ex situ annealing converts them to the polycrystalline phase. At the annealing temperature of 800°C, film grows in
step flow mode. Microstructural features like oblate shaped grains, fish-scale like platelets and slaty like layers have been observed which indicate that an island to planar growth transformation is likely to occur during annealing. Terraces of integer multiples of unit or half-unit cell parameter height have also been found. Grain boundaries have been identified from the orientation of terraced grains with respect to the substrate plane. A barrier height of about 4.0 eV has been determined from TS measurements on the films. The films are semiconducting with a band gap about 0.2 eV at room temperature having no states at the Fermi level. In the occupied region the first peak most probably corresponds to the Mn(3d) e_g^1 state.

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References