SUBSTRATE DEPENDENT MORPHOLOGIES
OF SELF-ASSEMBLED NANOCRYSTALLINE MANGANITE FILMS:
AN ATOMIC FORCE MICROSCOPY STUDY

S.N. Kale¹
Department of Electronic-Science, Fergusson College, F.C. Road, Pune 411004, India
and
The Abdus Salam International Centre for Theoretical Physics, Trieste, Italy,

J. Mona
Department of Electronic-Science, Fergusson College, F.C. Road, Pune 411004, India,

V. Ganesan, R.J. Choudhary and D.M. Phase
UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452017, India.

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¹ Regular Associate of ICTP. Corresponding author: sangeetakale2004@gmail.com
Abstract

Thin films of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) have been deposited on different substrates: Si (001), Al$_2$O$_3$ (AlO) (0001) and LaAlO$_3$ (LAO) (001), using a pulsed laser deposition system. 100 nm films have been deposited at substrate temperature of 700 ºC and oxygen partial pressure of 400 mTorr. X-Ray diffraction analysis shows a polycrystalline growth of both layers on Si and Al$_2$O$_3$ substrates, while a c-axis oriented growth on LAO substrate. Atomic force microscopy images exhibit interesting island-like morphology of grain size ~ 250 nm on Si substrate. Similar morphology with much smaller (~150 nm), closely packed islands are seen to grow on AlO substrate. Films on LAO show comparatively a smooth morphology with the grains size less than 100 nm, decorated by characteristic depressions at the grain boundaries. The formation of self-assembled nanostructures can be understood on the basis of film-substrate lattice misfit, strains in the systems and eventual growth of the films to attain energy minimization.
1. Introduction
The interaction between the electrons and lattice vibrations (phonons) in manganite perovskites is exceptionally strong, which provides an opportunity for them to be tuned over a wide range of electric and magnetic properties by variation of chemical composition, temperature, magnetic field and lattice strain induced by growth on lattice mismatched substrates. The influence of substrate-induced strain on structure, transport and magnetic properties has been intensively investigated due to its effects on magnetic anisotropy and transport. As is well known, manganite systems have been projected to have applications in possible devices [1–5], typically in read and write heads in magnetic storage devices, IR radiation sensors and diode-like structures [6-9]. For proper use of these in this microelectronics and measurement techniques, manganite films should be grown with very uniform morphological structures on the corresponding substrates, with good repeatability. The rigid bonding to the substrate, whose unit cell parameters and temperature coefficient of linear expansion may differ substantially from those of the grown layer, is one of the reasons for the generation of mechanical strains in the film, and hence morphological inhomogeneities. Though the influence of mechanical strains on the parameters of perovskite-like manganites has been the subject of many publications [10-12], a better control over the formed morphologies and better reproducibility is definitely called for.

In this work we report on the influence of strain on structure and surface morphology of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) thin films obtained onto silicon (Si) (001), Al$_2$O$_3$ (AlO) (0001) and LaAlO$_3$ (001) (LAO) substrates. The strain was seen to systematically change for different substrates, and was strongly related to substrate-film lattice misfit. The Pulsed laser deposition (PLD) technique (PerkinElmer, KrF excimer, 248 nm, pulse width = 20 ns) was used to synthesize these thin film structures. The film thickness was determined using tally step profilometer (Ambios Inc., USA). Structural analysis was done using the X-ray Diffraction (XRD) technique (Philips PW 1710 Diffractometer (Rigaku, Cu-Kα, 4 kW). Surface studies were done using Atomic force microscopy (AFM) (Nanoscope-E from Digital Instruments, USA. A 100 micron Si$_3$N$_4$ cantilever with a spring constant of ~0.57 N/m and images were taken in contact mode).

2. Experimental
The LSMO target used for the deposition was in the form of sintered pellets prepared by a citrate gel route [13]. The substrates were ultrasonically degreased, first in CCl$_4$, then in acetone, and, finally, in methanol for 5 min each. Thin film on Si, AlO and LAO substrates were deposited at 700 °C in the oxygen partial pressure of 400 mTorr, repetition rate of 10 Hz and energy density ~ 2 J/cm$^2$. The sample to substrate distance was 5 cm and the deposition time was 20 mins. The
deposited samples were cooled to room temperature in the oxygen ambient of 500 Torr pressure. The sample thickness was ~ 100 nm.

3. Results and Discussion

Fig. 1 shows the XRD patterns for LSMO on different substrates. From Fig. 1a and 1b, it was observed that on Si and AlO substrates, the growth of LSMO was polycrystalline in nature, with LSMO showing a perovskite pseudo cubic structure. The polycrystalline signatures of both materials could be due to their respective lattice and structural mismatches with their substrates (Si -cubic, \(a=5.43\) Å, AlO -hexagonal, \(a=3.905\) Å and LSMO -pseudo cubic, \(a=3.867\) Å). The polycrystalline growth on AlO can be well justified due to large lattice mismatch, inducing a tensile strain on the film growth, and deposition of the films at lower temperature, as has been reported by different groups [14-17]. Further, although Si does not have a high lattice mismatch, inherently grows a native oxide layer on the top, which is amorphous in nature, which can contribute to granular growth. However, LSMO and Si systems are essentially cubic, which should exhibit typical morphological growth as has been seen in AFM imaging. This is in comparison to the similar polycrystalline growth on AlO, wherein the lattice mismatch is high and the structures are different. This part is discussed in the coming paragraphs.

However, as shown in Fig. 1c, for the film on a LAO substrate, LSMO was seen to grow in c-axis oriented fashion. With the lattice and structural parameters of LSMO being similar to those of LAO (pseudocubic, \(a=3.786\) Å), the nature of growth was well expected. Additionally, a characteristic point which was noted in the XRD of LSMO on LAO substrate is the peak broadening and shoulder like doublet which is seen between 46-48°. The similar peculiarity is also observed between 22-24° as well as 72-74°. The inset shows expanded region between 2θ = 46-48°. One of the possible reasons for this peak-splitting is that probably the film grows in two phases, namely phase A and phase B. Though both the phases occur at almost similar values of 2θ , there is a slight mismatch. The lattice mismatches of \((a_{LSMO} - a_{LAO}) / a_{LAO}\) = +2.14 %, which suggests a compressive strain which is easy to distort the lattice. Phase A occurs due to the initial growth of the film, wherein, though the film tries to grow in an oriented fashion, due to slight compressive strain, the growth is initially strained and substrate-lattice-matched. At a later stage, the film relaxes to exhibit phase B. Such results of phase splitting have been observed before [18,19]. This peak splitting suggested that the compressive strain plus lattice mismatch is easy to distort the lattice. Evaluation of this strain is needed, because it is known that it affects the Colossal magnetoresistive (CMR) property of these perovskite manganites.

Figures 2 and 3 show the 2-dimensional and 3-dimensional AFM images of LSMO samples on different substrates. All images for a dimension are on the same scale and morphologies are clearly seen. As can be seen, films on Si and AlO showed island-like growth,
with the island size nearly mono-dispersed. The grain size ~ 250 nm was seen on Si substrate, while, much smaller (~150 nm), closely packed islands were seen on AlO substrate. This granular growth of manganites at lower deposition temperatures has been seen by various groups, and has been primarily assigned to the structural distortions and poor lattice-matching [14-16]. As has been discussed widely in the literature, upon adjusting substrate temperature, energy density and other deposition parameters, one can get uniform and smooth films as well. However, for applications of nanocrystalline high magneto-resistive (MR) materials, one requires uniformly grown nanostructures, which we can see on Si and also on AlO. Since the distortions and strain in the films on AlO are mostly due to structural as well as dimensional mismatch, smaller grains with larger grain boundaries are clearly seen in the AFM image. The overall growth-mode for the films on either substrate can be considered as Volmer-Weber type in which the energy relaxation takes place via the formation of 3D islands to minimize the energy. If the strain energy is large, the system will try to rearrange itself to find a lower energy state favoring the formation of 3D islands which may consist of self-assembled nanocrystalline particles. This parameter, if properly harnessed, can generate novel devices.

Figures 2c and 3c show the AFM images on LAO substrate. Clearly characteristic depressions were seen to decorate crystal grains on the surface of the manganite film. This can be evidenced also by comparing the contrast of the grain image as compared to the AFM images on Si and AlO. The grains are 80-100 nm in size. The reasons for grain boundary formation in epitaxial films of perovskite-like oxides grown coherently on single-crystal substrates have been analyzed in [19-20]. It has been noticed by Yu.A. Boikov and co-workers on their granular LCMO films grown on LAO plates, that the growth is primarily due to distortions in the stoichiometry of the phase adsorbed on the surface of the growing layer. The density of grain boundaries on the surface of LSMO films was seen to decrease with increasing thickness giving rise to the growth morphology contrast as is seen with granular and decorated regions. In fact, the AFM image also shows the phases as are seen in the corresponding XRD figure. The growth-mode can well be said to be Stranski-Krastanov mode, wherein the film creates a wetting layer to initially match the substrate and later tries to grow in a relaxed mode, which can be seen by a doublet in XRD and diffused-boundaries in AFM images.

Therefore, the growth of LSMO on various substrates is seen to be strained. The strain induced in all the systems, essentially depends upon the lattice misfits and also on the deposition conditions. If the lattice misfit is high, the polycrystalline growth with large grain boundaries and smaller grain size is seen to be dominating. As the lattice matching gets better, the growth struggles to get oriented, forming initially a wetting layer and then a relaxed phase. In addition, the orientation of films is closely related to the relationship of different energies such as surface energies, elastic energies, interface energies, and so on, which needs further advanced studies.
4. Conclusion
In conclusion, we have deposited thin films of LSMO on Si, AlO and LAO substrates using the pulsed laser deposition technique. X-ray diffraction analysis shows a polycrystalline growth of both layers on Si and AlO, while a c-axis oriented growth of LSMO on LAO with a phase-split. Atomic force microscopy images exhibit interesting island-like morphology of uniform grain size ~ 250 nm on Si substrate and ~150 nm on AlO substrate. Films on LAO show comparatively a smooth morphology with the grain size less than 100 nm, decorated by characteristic depressions at the grain boundaries. It has been proposed that growth mode for films on Si and AlO is of Volmer-Weber type, while films on LAO exhibit Stranski-Krastanov growth-mode.

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References


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Figure 1. X-Ray Diffraction patterns of LSMO film on Si (a) AlO (b) and LAO (c). The inset in Figure 1 (c) shows a region between $46^\circ$ to $48^\circ$ in expanded form. The arrows indicate broad signatures of LSMO growth exhibiting a split growth.
Figure 2. AFM images in two dimensions for LSMO film on Si (a) AlO (b) and LAO (c).

Figure 3. AFM images in three dimensions for LSMO film on Si (a) AlO (b) and LAO (c).