Fabrication of polycrystalline LNO/STO/Si(100) electrode by PLD

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Abstract

Polycrystalline $LaNiO_3/SrTiO_3/Si(100)$ conducting substrates (LSS) were fabricated by pulsed laser deposition (PLD) technique. STO buffered (LSS) conducting substrate is a potential candidate for the multiferroic materials to be used as bottom electrode. X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM) and electrical resistivity were employed to characterize the crystal structure, surface topography/morphology and electrical properties of the STO and LNO layers. STO buffer layer deposited at 700°C exhibited smooth, crack free and bicrystalline [(100), (110)] structures on the Si(100) substrate confirmed by XRD patterns. Deposition of epitaxial LNO as conductive layer followed the buffer layer at 600°C substrate temperature. The role of oxygen partial pressure during deposition affecting the crystallinity and resistivity of the STO and LNO films was also explored in detail. Atomic force microscopy revealed the films grown have smooth surfaces desirable for functional devices. Resistivity of the conducting film (LNO) was ~10^{-4} Ω.cm at room temperature. Thus it is demonstrated that LNO/STO/Si(100) is a suitable conducting substrate for growth of the multiferroic functional materials.

Keywords: Functional materials, Polycrystalline, Pulsed laser ablation, Buffer layer, Multiferroic, Conductive electrode

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1. Introduction

In recent years, multiferroic materials have received considerable attention for their potential applications in integrated circuits and other functional devices [1]. These applications require fabrication of high quality ferroelectric and magnetic thin films on suitable electrodes, such as metal or conducting oxides. Electrodes are required to have certain properties, such as high metallic conductivity, sufficient resistance against oxidation and good adhesion to the films [2]. Therefore, platinum (Pt), one of the few metals satisfying these requirements, has been used as a bottom electrode in high dielectric constant thin film capacitors [3]. However, Pt as an electrode poses a challenge to obtain a good quality thin film due to its large lattice mismatch with most of the perovskite oxide materials. Moreover, Pt electrodes often result in the formation of hillocks, which may lead to the degradation

of dielectric properties. Also the electrical properties of capacitors (like Pt/PZT/Pt) easily degrade in a hydrogen-containing or plasma environment [4].

As an alternative material, conducting perovskite oxides such as LaSrMnO (LSMO), $La_{0.5}Sr_{0.5}CoO_3$ (LSCO), $YBa_2Cu_3O_7$ (YBCO), $SrRuO_3$ (SRO) and $LaNiO_3$ (LNO) have been tried as bottom electrode [5-8] for the determination of electrical properties of the multiferroic thin films. Among all these conductive oxides $LaNiO_3$ (LNO) is the most attractive candidate for electrode material due to its simple crystal structure, easy synthesis at low temperatures compared to other metal oxides. For multilayers containing LNO, the diffusion of ions into the material (YBCO) during fabrication may be smaller than with the multilayers of other materials and finally, LNO has only two metal ions in it and its composition is thus easier to reproduce. It has a pseudo-cubic perovskite crystal structure with lattice parameter a = 3.84 Å and electrical resistivity $<10^{-3}$ Ω.cm at room temperature [9]. LNO has been used as the bottom contact for the study of ferroelectric materials $BaSrTiO_3$ (BST), $Pb(ZrTi)O_3$ (PZT), $BaTiO_3$ (BTO) [10-13]. The (100) and/or (110) oriented LNO bottom electrode could result in the ferroelectric materials grown in the similar orientation and they exhibit good electrical properties [14].

Significant understanding of LNO has been developed through numerous experimental and theoretical analyses [15-17]. PLD has been applied [18-20] to grown LNO and/or multiferroic/superconducting films on $SrTiO_3$ (STO), MgO and $LaAlO_3$ (LAO) single crystal substrates. However, their growth on silicon substrate is still a challenge due to large lattice mismatch. This paper focuses on the fabrication of conductive LNO thin film on Si(100) substrate. The complexity of lattice mismatch between LNO and Si is addressed by introducing a buffer layer of STO. Here we report the structural, topographic/microstructural and electrical properties of LNO and STO films deposited on silicon (100) substrates using PLD. The LNO/STO/Si (100) would be used as a bottom contact to study the overgrown $BiFeMnO_3$ thin films at a later stage. To the best of our knowledge this is the first attempt to fabricate a bottom contact (LNO/STO/(Si(100)) for the growth of multiferroic ($BiFeMnO_3$) materials by PLD technique.

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2. Experimental

Pulsed laser deposition (PLD) technique was employed to deposit $LaNiO_3$ (LNO) on $SrTiO_3$ (STO) buffered Si (100) substrate. KrF excimer laser (λ = 248 nm) in the energy range of (200-250) mJ/pulse was used with the frequency of the pulse was (f = 3-4 Hz). Laser beam was focused on the off centered ceramic targets by a quartz lens. During ablation, the target was rotated (30 rpm) in order to reduce non-uniform erosion and to get the homogeneous films.

The dense and crack free polycrystalline target samples (ϕ = 15 mm) of $SrTiO_3$ and $LaNiO_3$ were prepared by conventional powder metallurgy technique. The detail of preparation technique is given in the Table 1. Before deposition native oxide layer on the silicon substrates was removed. Furthermore, before deposition of STO the silicon substrate was heated at 715°C for 15 minutes under vacuum. Various deposition parameters like target to substrate distance, oxygen partial pressure and substrate temperatures were optimized. The optimum deposition conditions for STO buffer layer and LNO conductive layer are given in Table 2. In the film growth sequence, STO

film as a buffer layer was first deposited and then LNO was deposited as the conductive layer. For first 200 laser pulses the STO deposition was carried out at lower oxygen partial pressure then pressure was increased gradually. STO films were deposited under different oxygen partial pressures ranging from ($8x10^{-1}$ Torr) to ($1x10^{-4}$ Torr) at $700^{o}C$ for 25 minutes. After deposition, STO films were slowly cooled to room temperature under high oxygen pressure in order to maintain the oxygen stoichometry.

Perovskite $LaNiO_3$ conductive thin films were deposited on STO buffered Si (100) substrate under varied conditions and the optimum conditions for LNO conductive layer are summarized in Table 2. LNO film was deposited under various oxygen partial pressures ranging from ($1x10^{-1}$ Torr - $7x10^{-1}$ Torr) to achieve good conducting film. Post deposition in-situ annealing at $600^{o}C$ was carried out to avoid oxygen vacancies and maintain the phase stoichometry of the conductive film. This is required to further improve the electrical conductivity of the LNO films [21]. The film was then cooled slowly to room temperature. The phases and structures of STO and LNO thin films were examined by X-ray diffraction with Cu-Kα radiation. The cross sectional view, surface morphologies and topography of films (STO and LNO) were observed by the FE-SEM and AFM. The electrical properties were measured by four-probe technique.

3. Results and discussion

The crystallographic phases and orientations of STO buffer layer and LNO conductive thin films deposited on Si (100) were identified by XRD patterns taken at room temperature. The effects of oxygen partial pressure on the phase formation and resistivity of STO and LNO films were studied. Figure 1 shows the formation of various STO phases as identified in the XRD patterns deposited at $700^{o}C$ under various oxygen partial pressures. STO films grown at low oxygen partial pressure, i.e., ($1x10^{-4}$ Torr) are shown in Figure 1 (a). The peaks are labeled by comparing the XRD pattern with the available literature and standard JCPD card of PDF # 84-0444 (ICSD # 201257). Two major peaks (111) and (110) along with the peak from Si substrate were observed. So under low oxygen partial pressure the growth conditions are not favorable for the preferred phase of STO (100), which is absent. Contrary to this STO films grown at relatively higher oxygen partial pressures ($1x10^{-2}$ Torr), three peaks (100), (110 and (200) were recorded in the XRD patterns as shown in Figure 1(b). Thus increase in oxygen partial pressure played a key role for the formation of desired phase of STO. Figure 1(c) shows the XRD pattern of the STO film deposited at ($1x10^{-1}$ Torr) oxygen partial pressure, where (100) peak is now suppressed and an extra peak from (111) plane is reappeared. STO deposition under rather higher oxygen partial pressure ($8x10^{-1}$ Torr) results in the peak pattern as shown in Figure 1(d). Here (100) peak is again absent and a major unidentified peak at 44.78^{o} appeared along with some other unwanted peaks like (111) and (211). It is observed that the oxygen partial pressure range is very narrow for the development of preferred STO phase. Thus, the STO film deposited at $700^{o}C$ under ($1x10^{-2}$) Torr oxygen partial pressure was best suited as the buffer layer as at other pressures, other phases of STO become prominent, which would affect the quality of the interface. The preferential crystallographic orientation of thin film is supposed to minimize the surface and interface energies. Figure 2 is a comparison of XRD patterns of

STO film deposited on Si(100) substrate, bulk target sample and Si(100) substrate. The FWHM of the (110) peak for the STO film deposited under optimum conditions for twenty five minutes is 0.2^o. This value is comparable to that of reported by others [22-23]. This shows that the film is well crystallized. This peak is bit shifted as compared to the one usually observed in the bulk samples and is possibly due to the strains developed between the film grains and the substrate surface during the film growth but not becoming a big concern.

LNO films on STO/Si(100) were deposited at 600^oC for 45 minutes under various oxygen partial pressures and their XRD scans are shown in Figure 3. In the case of LNO films deposited on STO/Si(100) substrate, it was observed that oxygen partial pressure has a little effect on the crystallinity of the deposited LNO film. Deposition of LNO at $3x10^{-1}$ Torr oxygen partial pressure results in the sharper and intense LNO peaks as can be seen in Figure 3(b). The XRD patterns in Figure 4 show that LNO film epitaxially followed the same peak patterns as was optimized for the STO buffer layer. Only two reflections from the planes (100) and (110) with major reflection coming from (110) plane are recorded from LNO film. Thus it can be concluded that epitaxial growth of LNO thin film under optimized conditions follows the biycrystalline STO buffer layer grown on Si(100) substrate. $LaNiO_3$ (LNO) has a perovskite structure like STO and hence under suitable deposition conditions follow the lattice-coherently growth mode.

For film thickness measurement and surface topography, FE-SEM and AFM studies of individual films deposited under optimized conditions were employed. Figure 5 shows the cross-sectional view in a FE-SEM micrograph of the STO (60 nm thick) and LNO films (437 nm thick) deposited on Si(100) substrate. It is deduced that STO and LNO films were 60 nm and 437 nm thick, respectively. The image also shows the top layer of multiferroic (BiFeMnO) film. Figure 6 is the (2x2) μm^2 tapping mode AFM right scans of the STO and LNO film. The variation in the surface smoothness is around 7 ± 1 nm as determined from the AFM images for STO and LNO thin film. Root mean square (R_{rms}) values of the surface roughness for the STO and LNO films were 1.50 nm and 2.51 nm respectively. The AFM images also show that the STO and LNO films grown are dense, crack free and packed with regular spherical grains. The average grain size of STO and LNO films was 125 nm and 200 nm respectively. It can be clearly seen that the particles or grains are almost identical in shape in both films. This observation is quite consistent with XRD (θ-2θ) patterns, that the LNO film deposited on STO buffer layer epitaxially follow it. This shows that films have smooth surfaces and homogeneous particle distribution. Therefore LNO films could be used as bottom electrode layer. Figure 7 represents their three dimensional (3D) views of the dense, flat, crack free surface as well as low level of porosity on the surface. These are critical and affects the various film related properties as has been reported earlier [24]. It can also be seen that there are no droplet formation as could be the case in PLD, since the particle sizes are much smaller than those droplets [25].

The electrical resistivity of the LNO films deposited on STO/Si(100) substrate at different oxygen partial pressures were deduced from standard four-probe method and Figure 8 shows the electrical resistivity behavior of the LNO film as a function of oxygen partial pressure during its growth. It is evident that at low oxygen partial pressure the

LNO film is highly resistive and then becomes conductive with increase in oxygen partial pressure. From these measurements, LNO films deposited at high oxygen partial pressure, i.e., around ($3x10^{-1}$ Torr) were highly conductive ($\rho \cong 10^{-4}$ Ω.cm). The values of resistivity of these films are as good as obtained by other techniques, such as CSD, sputtering and radio frequency magnetron sputtering [26-28]. These electrical measurements also highlights the key role of oxygen partial pressure to obtain good electrical conducting LNO films on STO buffered silicon substrate. As already discussed, variations in oxygen pressure for LNO deposition strongly affect the electrical properties of the film but this was not observed in XRD patterns. It had already been suggested that stoichometry of the $LaNiO_3$ phase and oxygen vacancies play an important role for conductivity of the LNO films [19, 29]. Here we have demonstrated that the use of STO as a buffer layer improves the crystallinity of the LNO film and without modifying the crystal structure, its electrical properties can be tailored by varying the oxygen partial pressures. Thus, it is proposed here that conducting thin films of LNO deposited by using STO as buffer can be produced by controlling oxygen partial pressures during growth and can be an excellent starting point for fabrication of multiferroic devices. This system also allows the growth of buffer and electrode in a single step.

4. Conclusion

PLD has proven to be a viable technique for the preparation of multilayer structures of conductive oxides and functional materials. The highly conducting $LaNiO_3$ (LNO) thin films have been successfully fabricated on $SrTiO_3$ (STO) buffered Si(100) substrate by PLD technique. STO exhibited bicrystalline growth on Si(100) substrate. This growth mode decreases the interfacial energy by reducing the lattice mismatch between STO and LNO films. The AFM images reveal that the STO and LNO films have atomically smooth surfaces with dense and extremely homogeneous grain distribution, which are highly desirable for an electrode template layer. It is demonstrated that the resistivity of LNO film strongly depends on the oxygen partial pressure during deposition without affecting the crystal structure. The magnitude of electrical resistivity of LNO film deposited on STO/Si(100) substrate under optimized oxygen pressure is suitable to be a bottom electrode for ferroelectric or dielectric materials and can replace traditional metal/oxide electrodes.

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Figure captions

Figure 1 XRD patterns of $SrTiO_3$ (STO) thin films deposited at 700°C on Si(100) substrate by PLD under oxygen partial pressure (a) $1x10^{-4}$ Torr (b) $1x10^{-2}$ Torr (c) $1x10^{-1}$ Torr and (d) $8x10^{-1}$ Torr.

Figure 2 XRD patterns of (a) Si(100) substrate (b) STO bulk target sample (c) STO buffer layer deposited at 700°C under $1x10^{-2}$ Torr oxygen partial pressure on Si(100) substrate.

Figure 3 XRD patterns of the LNO thin films deposited at 600°C under various oxygen partial pressures (a) $1x10^{-1}$ Torr (b) $3x10^{-1}$ Torr (c) $7x10^{-1}$ Torr.

Figure 4 XRD patterns of the (a) STO/Si(100) substrate (b) LNO conductive layer deposited on STO/Si(100) substrate at 600°C under $3x10^{-1}$ Torr oxygen partial pressure.

Figure 5 Field emission scanning electron microscopic image showing cross sectional view of the LNO/STO/Si(100) conductive substrate.

Figure 6 Atomic force microscopic (AFM) images of the (a) STO buffer layer and (b) LNO conductive layer deposited under optimum deposition conditions.

Figure 7 3D-AFM image of the (2x2) μm^2 (a) STO buffer layer (b) LNO conducting layer deposited under optimum deposition conditions.

Figure 8 Electrical resistivity as a function of oxygen partial pressure of the LNO/STO/Si(100) substrate prepared under optimum conditions.

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