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Influence of substrate on structural and transport properties of LaNiO_3 thin films prepared by pulsed laser deposition

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We report the structural and transport properties of LaNiO_3 thin films prepared by pulsed laser deposition technique. To understand the effects of film thickness, lattice mismatch and grain size on transport properties, various oriented substrates were used for deposition, including single-crystalline SrLaAlO_4 (001), SrTiO_3 (100) and LaAlO_3 (100). To achieve a high quality LaNiO_3 thin films, the vital parameters (such as laser fluence, substrate temperature, oxygen pressure, and deposition time) were optimized. The best quality films are found to be well textured samples with good crystalline properties. © 2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4971842>]

I. INTRODUCTION

In recent years, the study of nonvolatile memories for use in storage and ferroelectric random access memory (FeRAM) devices has gained a new impetus. Manufacturing of these types of devices requires bottom electrodes in the form of thin films with some specific properties such as a high metallic conductivity and good adhesion to the substrates. Among various oxides, including SrRuO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ and LaNiO_3 (LNO)¹⁻⁴ the use of perovskite-type conductive materials as bottom electrodes favors the growth of high quality ferroelectric thin films, such as BTO and PZT.^{5,6} From the remarkable family of perovskite oxides, lanthanum nickelate LNO is a rare example characterized by metallic behavior in a wide range of temperatures being at the same time structurally compatible with many active functional layers.⁷⁻¹⁰ LNO has attracted much attention due to its ability to drastically improve the ferroelectric fatigue problem.^{11,12} Its pseudocubic lattice structure (with a cell parameter of 3.84 Å) is compatible with that of silicon (and even PZT) showing resistivity as small as 225 $\mu\Omega$ cm at 300K.¹³ Several studies have been reported on LNO thin films grown by different deposition techniques using SrTiO_3 and LaAlO_3 as popular substrates.¹⁴⁻¹⁶ At the same time, very few systematical studies have been reported regarding deposition of LNO films on oriented SrLaAlO_4 substrates. The thermal expansion of single crystalline SrLaAlO_4 is around 7.38 ppm/°C at 462°C which is much less than that of other perovskite-type materials. Besides, the value of corresponding dielectric loss ($\sim 10^{-4}$) is equivalent to alumina¹⁷ thus making this substrate especially attractive for manufacturing FeRAM devices. A rather significant advancement of technology in recent years made it possible to fabricate devices on the nanometer scale. The main idea of our study is to investigate to what extent we can miniaturize (with

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respect to film thickness) the conductive layers of LNO maintaining good properties of its metallic behavior.

In this paper we present our results on fabrication and systematic study on structural characterization and transport properties of LNO thin films grown by pulsed laser deposition (PLD) technique on highly oriented substrates, SrLaAlO₄, SrTiO₃ and LaAlO₃. The structure of thin films deposited on these substrates was characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and atomic force microscopy (AFM). The electrical resistivity measurements as a function of temperature were used to verify and confirm the metallic behavior of our films.

II. EXPERIMENTAL

In order to provide high quality samples, PLD technique was used for deposition of thin films. When using the PLD technique for manufacturing thin films one should first obtain a target with high enough density because a compact and uniformly dense target is required to produce a laser plume with good quality and to have a consistent ablation of the surface of the target. The dense and crack-free LNO circular target with diameter of 5cm and thickness of 1.25cm was prepared from highly pure polymeric precursors by Pechini method¹⁸ using $La_2(CO_3)_3 \times H_2O$ (99.9% Aldrich) and $Ni(OCOCH_3)_2 \times 4H_2O$ (98% Aldrich). The calcination and sintering were performed in the air at 900°C for 4h and at 1200°C for 6h, respectively. The thin films were grown on SrLaAlO₄ (SLAO), SrTiO₃ (STO) and LaAlO₃ (LAO) substrates by PLD technique using a KrF excimer laser with 248 nm wavelength and 25 ns pulse duration and deposition rate of 4 Hz. The laser beam was focused at the angle of 45° on target of LNO with fluence ranging from 1.5 to 1.8 J/cm² depending on the type of substrate used. To reduce non-uniform erosion, the target was rotated during the ablation process and at the end of each deposition the target was sanded and polished before the next deposition. The distance between the target and the substrate ranged from 4.5 to 5 cm with deposition temperature between 610°C and 630°C. The temperature was controlled by a thermocouple placed immediately at the back side of the substrate. Before the start of the deposition, a base pressure was achieved in the deposition chamber using a turbo molecular pump. Thereafter, oxygen was injected into the deposition chamber and monitored by the mass flow control. In order to achieve preferred crystallographic orientation and good electrical conductivity, the oxygen deposition pressure of $P_{dep} = 0.2$ mbar was used. Post deposition in-situ annealing carried oxygen at a pressure of $P_{oxy} = 5 \times 10^2$ mbar for 1h to avoid formation of oxygen vacancies and maintain the phase stoichiometry of the films. This procedure is necessary to further improve the electrical conductivity of the LNO films. The values of the deposition parameters are summarized in Table I, where d_{t-s} is a distance between the substrate and the target, T_{dep} is a deposition temperature, Φ is the fluence given for a laser spot with dimensions of 1mm \times 6mm and P_{dep} is a deposition pressure. To study the effects due to film thickness, samples were manufactured with thickness ranging from 25 nm to 55 nm which has been controlled by the number of laser shots.

III. RESULTS AND DISCUSSION

XRD measurements of the films were carried out using a Shimadzu XRD-6000 diffractometer with CuK α radiation. The unit cell refinements were performed using the Le Bail method through the GSAS/EXPGUI code.^{19,20} The results shown in Fig. 1(a) revealed that, independent of the substrate, our films crystallize into a cubic perovskite structure with a space group symmetry Pm3m (221).

TABLE I. Optimized PLD parameters for bottom electrode of LaNiO₃ thin films for different types of substrates.

Substrate	d_{t-s} (cm)	T_{dep} (°C)	Φ (J/cm ²)	P_{dep} (mbar)
SrLaAlO ₄	4.5	610	1.50	0.20
SrTiO ₃	5.0	625	1.80	0.21
LaAlO ₃	5.0	630	1.75	0.21

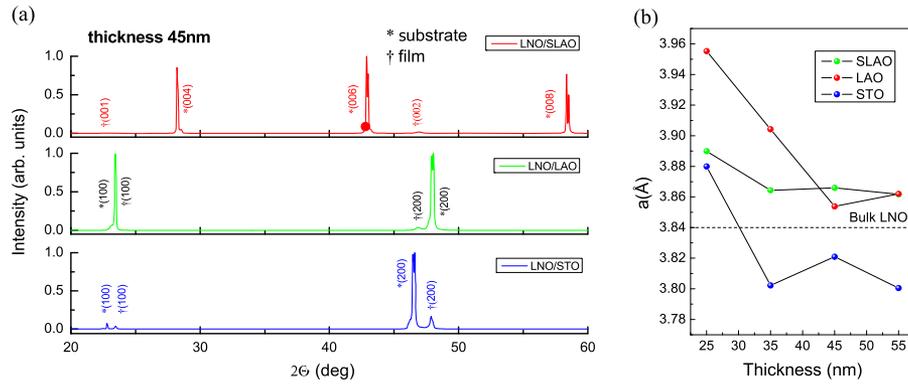


FIG. 1. (a) XRD patterns for LNO films deposited on different substrates; (b) relative variation of the lattice parameters with the thickness of the films.

For different substrates a similar behavior in the lattice parameter with the variation of the thickness was observed. In general, we may conclude that a degree of evolution of the lattice parameters is inversely proportional to the thickness of the films with a clear tendency toward the bulk lattice parameter for greater thicknesses. According to Fig. 1(b), the relative variation of the lattice parameters of our films is no higher than 0.1\AA for each substrate with the least variation (around 0.03\AA) observed in the films grown on SLAO. Also, it was confirmed that the growth of the films occurs in the (100) direction. The thicknesses of all films were measured by FEG-SEM (cross-sectional area) and their values were used for calculation of resistivity. Typical FEG-SEM images for LNO/STO, LNO/LAO and LNO/SLAO structures are shown in Fig. 2(a)–2(c). An image of silver contacts with

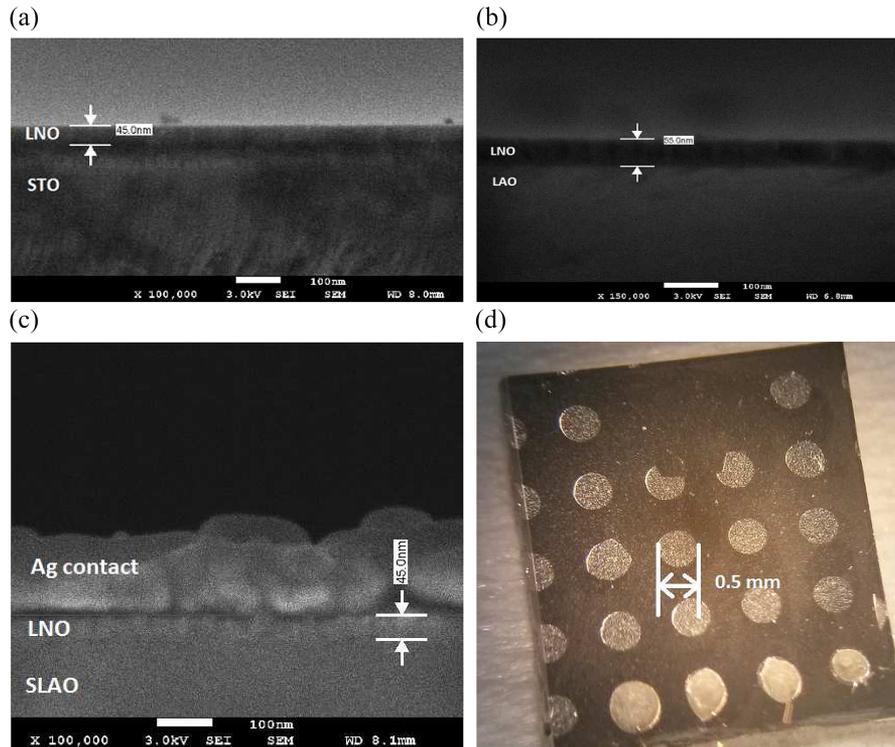


FIG. 2. Typical FE-SEM images of LNO thin films deposited on (a) STO substrate, (b) LAO substrate, and (c) SLAO substrate; (d) circular silver contacts with diameter of 0.5 mm used for electric measurements.

a diameter of 0.5 mm used for electric measurements is depicted in Fig.2(d). A silver pad was evaporated onto the surface of the heterostructure to form the top electrode. Several films have been prepared for this study but only the films with the thicknesses of 25, 35, 45 and 55nm were taken into account. The analysis based on FE-SEM images revealed no separation between LNO films and substrates, thus indicating a good adherence between the film and the substrate. Fig.2 depicts some typical FE-SEM images of LNO thin films deposited on (a) STO substrate, (b) LAO substrate, and (c) SLAO substrate; (d) circular silver contacts with diameter of 0.5 mm used for electric measurements. The resistivity measurements as a function of temperature were performed using the four-point method on as-deposited LNO thin film. The probed temperature region is ranging from 10 to 300 K. Fig.3(a)–3(c) presents typical resistivity data. The temperature dependence of the derivative $d\rho/dT$ shows a good metallic behavior for all samples. Fig.3(d) exhibits values of resistivity taken at 300 K compared to the thicknesses of thin films deposited on different substrates. The observed behavior for different types of substrates (an increase of the values of resistivity with decreasing the thickness of thin films) is quite similar to previously reported results.^{8–10} However, the LNO/STO heterostructure with thickness of 35 nm exhibits unusually small values of resistivity in comparison

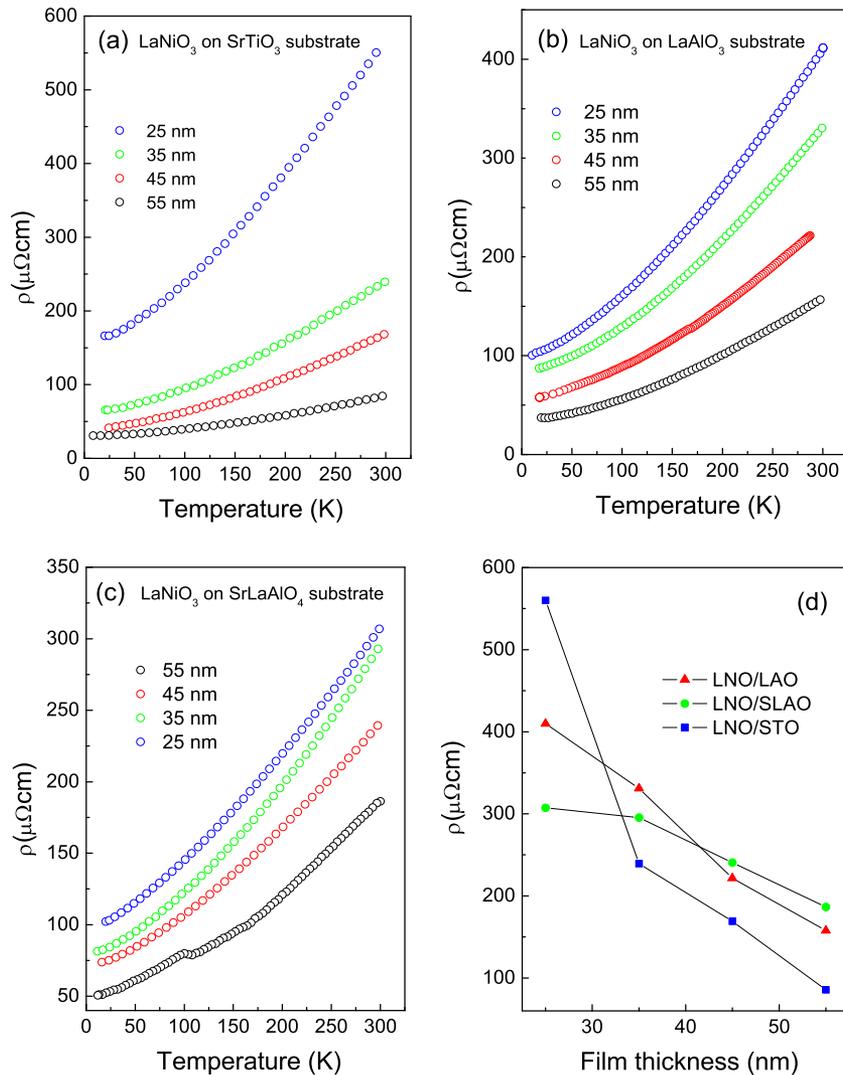


FIG. 3. The dependence of the measured resistivity ρ on temperature for LNO films deposited on (a) STO substrates, (b) LAO substrates, and (c) SLAO substrates; (d) values of resistivity taken at 300 K compared to the thicknesses of thin films deposited on different substrates.

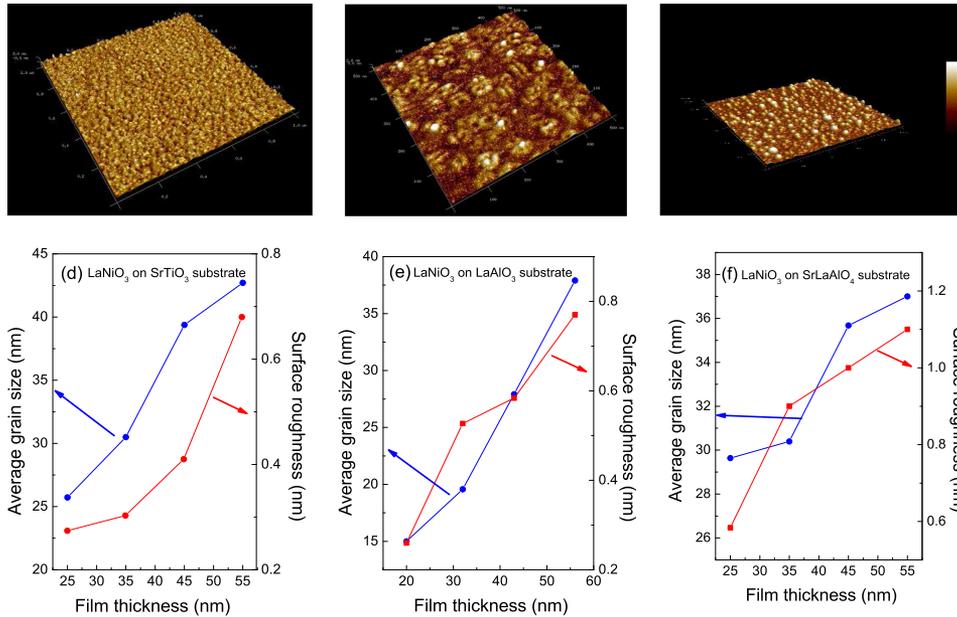


FIG. 4. Typical AFM images for LNO films deposited on (a) STO substrates, (b) LAO substrates, and (c) SLAO substrates; (d-f) dependence of the average grain size (left axis) and RMS roughness (right axis) on the thickness of the films deposited on different substrates (a-c).

with previous observations.^{15,21} The surface morphology of the films was checked by using atomic force microscopy (AFM). More precisely, the film roughness is defined by the root mean square (RMS) value. Typical AFM images for LNO films deposited on different substrates are shown in Fig. 4(a)–4(c). Measurements were made over the projected area of $1\mu\text{m} \times 1\mu\text{m}$. A much lower roughness (below 1.5 nm) has been observed in comparison with the results of the other groups^{22–25} making our films more suitable for their practical applications. Fig. 4(d)–4(f) represents the dependence of the average grain size (left axis) and RMS roughness (right axis) on the thickness of the films deposited on different substrates. The observed increase of RMS roughness with the increase of film thickness is probably due to a larger grain size formation as well as to an increase in the porosity of the films.

IV. CONCLUSION

In summary, highly oriented LNO thin films have been successfully fabricated using PLD technique on various substrates (SrLaAlO_4 , SrTiO_3 and LaAlO_3) with different thickness (25, 35, 45 and 55 nm). The structure probing methods (including FEG-SEM, XRD and AFM) and electrical measurements were used to determine the effect of crystallinity, orientation, and surface morphology of LNO thin films. The results obtained by electrical measurements indicate that LNO is a good conductor. AFM data show that the film roughness becomes larger with increasing the thickness. Based on our findings, we may conclude that the epitaxial LNO thin films deposited on oriented SLAO (001) substrates are very attractive for their use as bottom electrodes in the production of memory type devices.

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