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⟨0 1 2⟩-oriented growth of the films $LaNiO_3/SiO_2/Si(1\,1\,1)$ by pulsed laser deposition

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The highly ⟨0 1 2⟩-oriented $LaNiO_3$ thin films were fabricated on SiO_2 coated Si(1 1 1) wafers by pulsed laser deposition at 690 °C with a well prepared target. The stability of the interface and the smoothness of the surface were confirmed by scanning electron microscopy and atomic force microscopy. The electrical resistivity of the films at 300 K is 2.6×10^{-5} Ωm. The results of this work suggest that the films can be applied to the bottom electrode of ferroelectric memory devices.

1. Introduction

In recent years, ferroelectric films such as lead zirconate titanate (PZT) have been widely investigated for their applications in nonvolatile random access memory (NVRAM) [1, 2]. Realization of a commercially viable ferroelectric memory technology has been hampered by some problems related to either the reliable performance of the ferroelectric capacitors or to the growth and processing of capacitors that translate to high density memory elements. Fatigue is one of the main problems. There is now a growing realization that the problem of fatigue can be overcome for all practical purposes through the use of metal oxide electrodes such as RuO_2, Y-Ba-Cu-O, La-Sr-Co-O and $LaNiO_3$ (LNO), etc. [3–7], instead of the conventional platinum electrode. Among these metal oxides, LNO is a most promising material because of its good conductivity, chemical composition simplicity and lattice matching with ferroelectric materials of perovskite structure, such as PZT, PLZT, etc.

$LaNiO_3$(LNO) is a perovskite-related metallic oxide. The primitive cell of LNO consists of two formula units. It is rhombohedral with lattice parameter a = 5.461A and the rhombohedral angle 60.41°. Pseudocubic "a" of this oxide is 3.83A. In this paper we report ⟨0 1 2⟩-oriented growth of LNO film on SiO_2/Si(1 1 1) substrate by pulsed laser ablation.

2. Experiments

2.1. Preparation of the target

We prepared LNO target in a chemical process. The starting materials used were lanthanum oxides (La_2O_3, 99.99%) and Ni metal powders (Ni, 99.9%). The chemicals taken stoichiometrically were dissolved in a minimum quantity of nitrate acid and distilled water in a beaker. Then citic acid (CA) was added to maintain a specific mole ratio of the metal ions to CA. The CA/metal solution was heated and stirred by a short magnetic rod on a hot plate. When the viscosity of the solution became so high that the magnetic rod could not stir the solution, the stirring was stopped. Then the temperature of the solution was kept at 70 °C until a dry, porous and puffed resin was obtained. Finally the resin was calcinated at 850 °C in a regular box furnace for 6 hours; thus we got the pure-phase powders of LNO. The purity of the powders was characterized by powder X-ray diffraction (XRD). In order to obtain a dense LNO target, a little 5% polyvinyl alcohol solution prepared by water-bath at 90 °C was added to the powders in the ratio of 1 : 95 (polyvinyl alcohol solution to the powders). The milled and screened uniform powders were pressed at 800 kg/cm^2 in a circular die into pellets. The pellets were sintered at 1200 °C for 6 hours in a regular box furnace. Thus we acquired the black dense LNO target. The density of the LNO target was 4.5 g/cm^3. The X-ray diffraction spectrum of the target was obtained in the range $20° < 2\theta < 80°$. The temperature dependence of the electrical resistivity of the target was investigated with a standard four-probe technique in a closed-cycle cryostat (APD Cryogenics, DE202) in the temperature range 45∼300 K.

2.2. Film deposition

LNO films were fabricated on SiO_2/Si(1 0 0) and SiO_2/Si(1 1 1) substrates by pulsed laser deposition. A Lambda Physik LPX300 excimer laser system with 2.5 J/cm^2 energy density per pulse of KrF (248 nm) radiation was used. The thin film depositions were carried out in the substrate temperature range of 650 °C∼750 °C, and the oxygen partial pressures in the chamber were 30Pa. In order to get a uniform thin film of LNO, the target and the substrates were rotated during the depositions. After the deposition the films were kept in the chamber with pure oxygen of 0.6 atm. pressure at the same temperature as that in the deposition procedure for 60 minutes. The X-ray diffraction spectra of the films were obtained in the range $20° < 2\theta < 80°$, and the chemical composition of the films was analyzed using

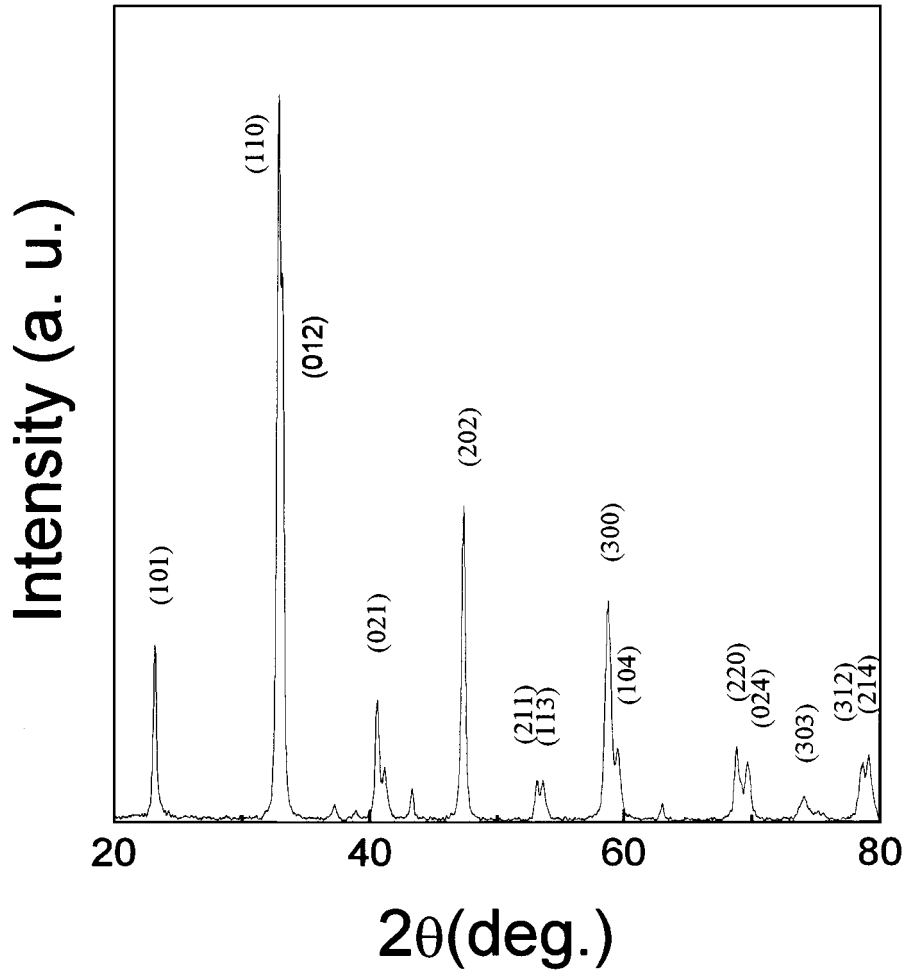

Figure 1 The X-ray diffraction spectrum of $LaNiO_3$ powders, indicating a pure-phase material.

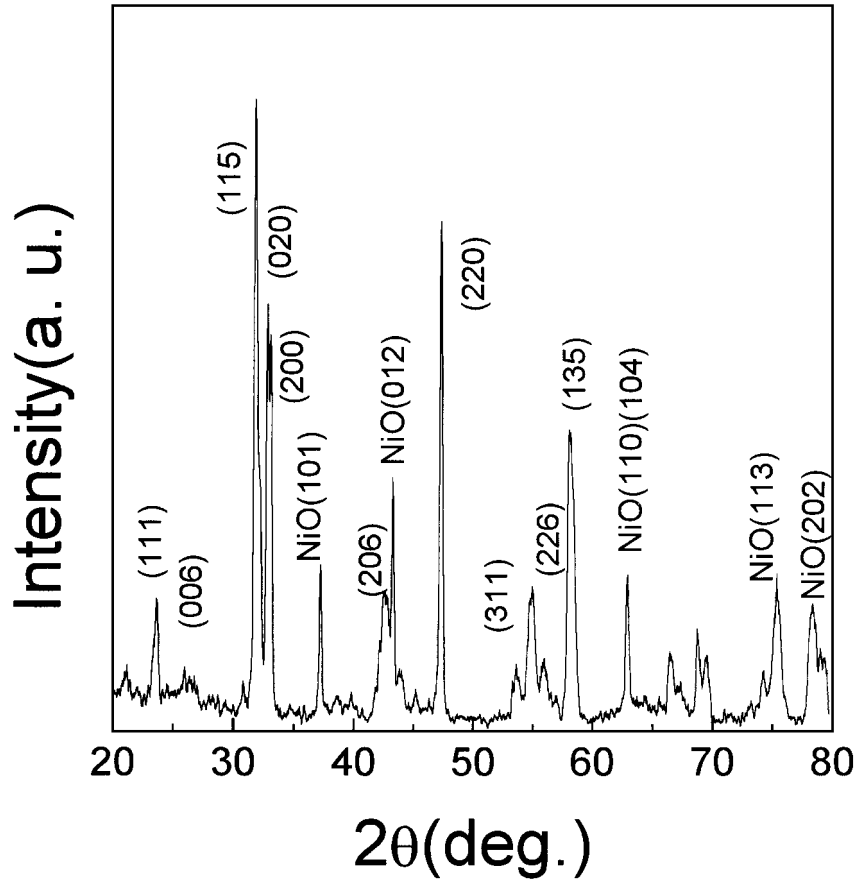

Figure 2 The X-ray diffraction spectrum of polycrystalline $La_3Ni_2O_7$ target.

an inductively coupled plasma quantometer (ICP). The thickness of the films was measured in an optical interference method; the typical thickness of the films was 4000 angstroms. The DC electrical resistivity of the films was studied in the temperature range 45∼300 K. The surface and cross-section morphology of LNO film was examined by scanning electron microscopy (SEM) and atomic force microscopy (AFM).

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern of LNO powders. It is obvious that LNO powders are of single phase. According to the empiric formula

$$D = K\lambda / B\cos\theta$$

where D is the average size of the grain, λ is the wavelength of CuKα ray, 1.5418, θ is the diffraction angle, B is the full width at half maximum (FWHM) and K is the Scherrer constant, 0.9∼1.1, we obtained that the average size of the grain of LNO powders was about 30 nm. The X-ray diffraction spectrum of the target is shown in Fig. 2. It demonstrates that the target contains polycrystalline $La_3Ni_2O_7$ and some NiO impurities. This is due to the instability of LNO above 1000 °C [8, 9, 10]. The temperature dependence of the electrical resistivity of the target is shown in Fig. 3, indicating that the target is a semiconductor, and that the electrical resistivity of the target at 300 K is about 7×10^{-4} Ωm, much smaller than that reported by K. Sceedhar *et al*. [11]. This is attributed to the denser target. The X-ray diffraction spectra of the films LNO/SiO_2/Si(1 0 0) deposited at 650∼750 °C are shown in Fig. 4. It follows from the figure that the crystalline phase formation began to appear at 650 °C, and that the relative intensity of (0 1 2)-peak became higher when the substrate temperature was increased. We can find that the 2θ angle position of (0 1 2)-peak was shifted right slightly when the substrate temperature was increased. This tendency can be seen clearly in Fig. 5, enlarged and reploted from Fig. 4. Fig. 6 shows the X-ray diffraction spectra of the films LNO/SiO_2/Si(1 1 1) deposited at 650∼750 °C. It is obvious that the film deposited at 690 °C is strongly grown with ⟨0 1 2⟩-orientation, and that the intensity of (1 2 2)-peak, the second strongest, is 8% of that of (0 1 2)-peak. We also observed the angle position shift of (0 1 2)-peak toward the right with the increase of the substrate temperatures, as shown in Fig. 7, enlarged and replotted from Fig. 6. We can reasonably conclude that the film LNO/SiO_2/Si(1 1 1) can be (orientedly) grown in a narrow operational window of the substrate temperature around 690 °C. The chemical composition analysis for the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C by an inductively coupled plasma quantometer (ICP) showed that one millilitre solution which dissolved LNO film

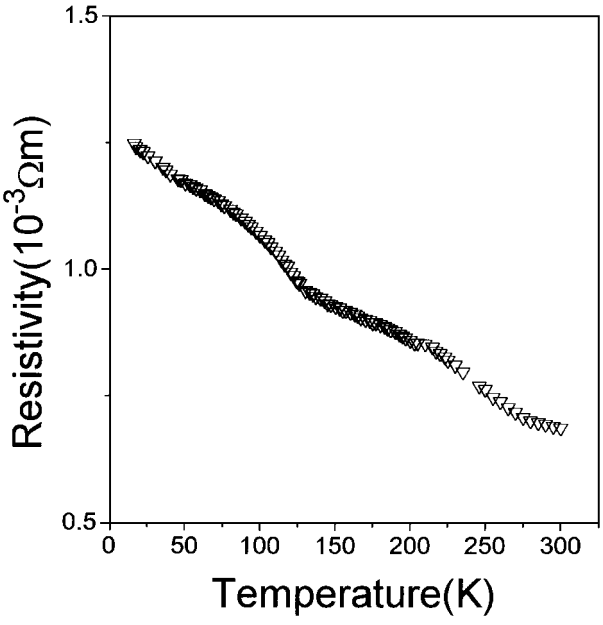

Figure 3 The temperature dependence of the electrical resistivity of polycrystalline $La_3Ni_2O_7$ target, showing a semiconductor behavior.

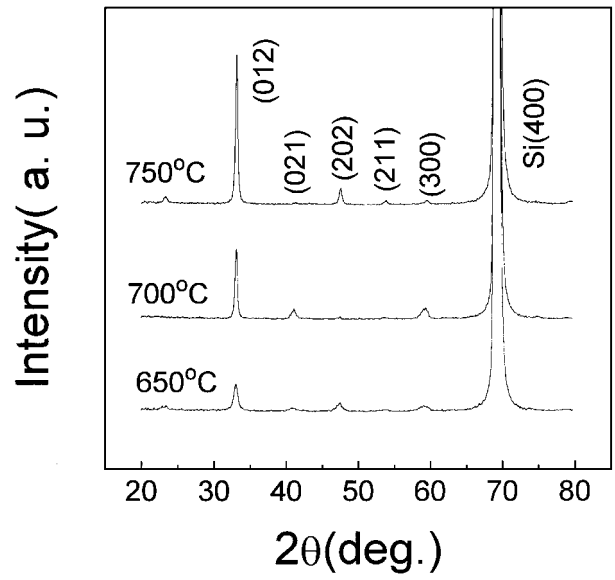

Figure 4 The X-ray diffraction spectra of the films LNO/SiO_2/Si(1 0 0) deposited in the range of the substrate temperatures 650∼750 °C.

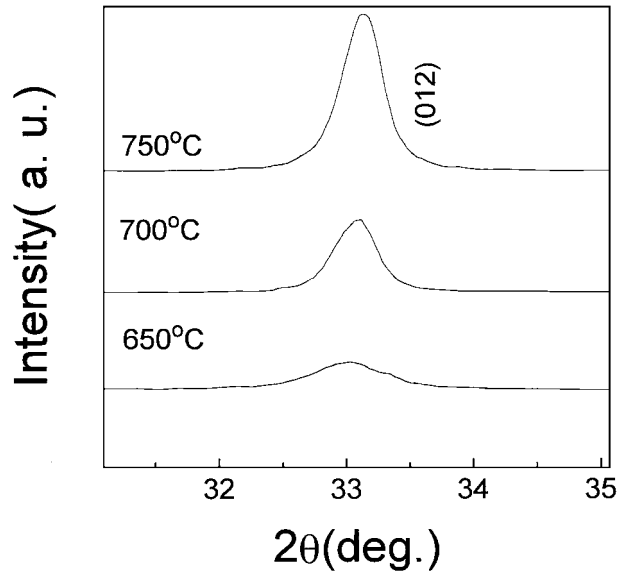

Figure 5 The X-ray diffraction spectra of the film LNO/SiO_2/Si(1 0 0) enlarged and replotted from Fig. 4, indicating angle position shift of (0 1 2)-peak slightly toward the right.

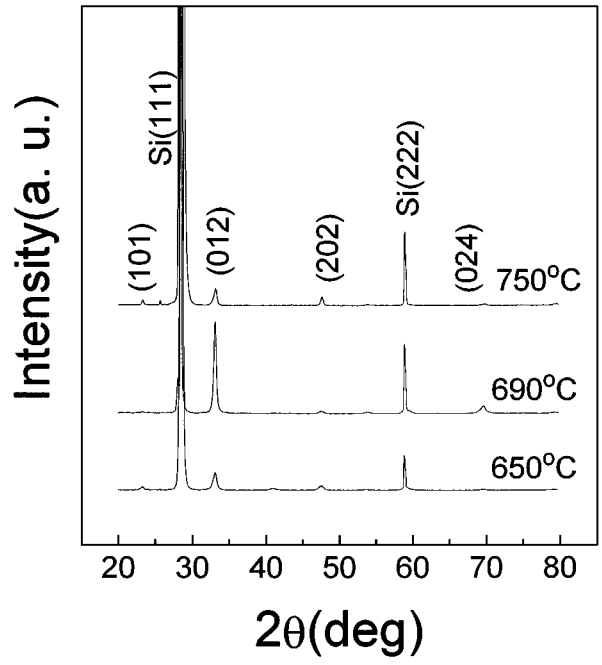

Figure 6 The X-ray diffraction spectra of the films LNO/SiO_2/Si(1 1 1) deposited in the substrate temperature range 650∼750 °C.

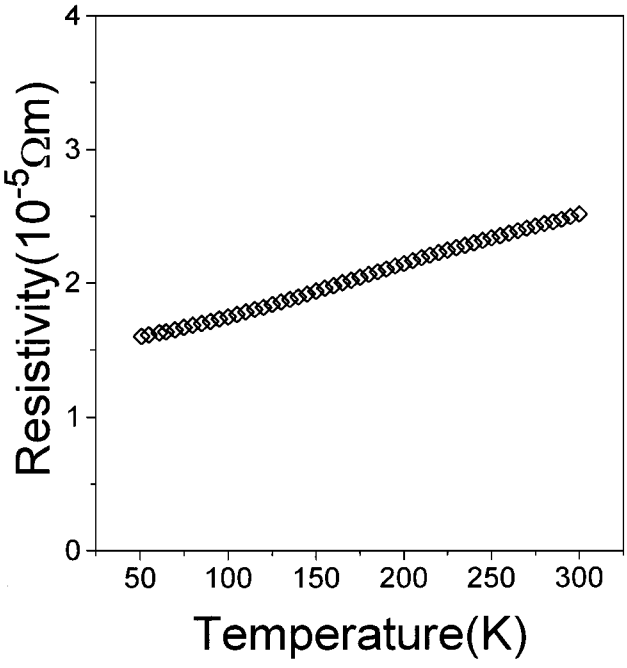

Figure 8 The temperature dependence of the electrical resistivity of the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C.

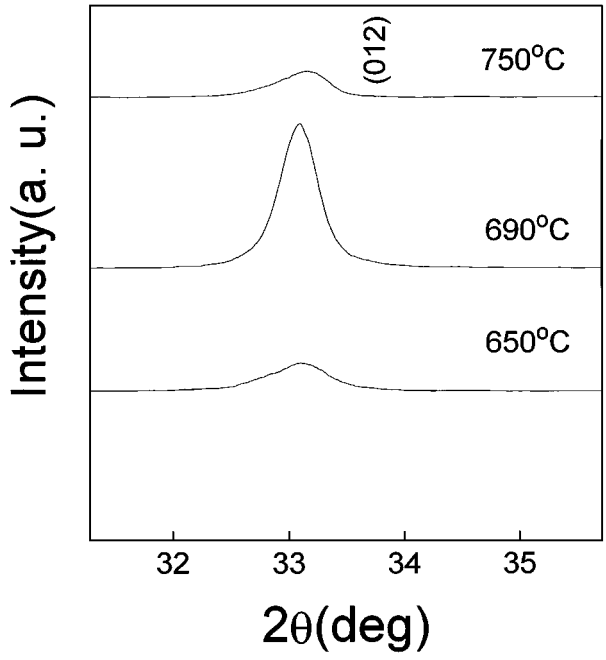

Figure 7 The X-ray diffraction spectra of the film LNO/SiO_2/Si(1 1 1) enlarged and replotted from Fig. 6, indicating angle position shift of (0 1 2)-peak slightly toward the right.

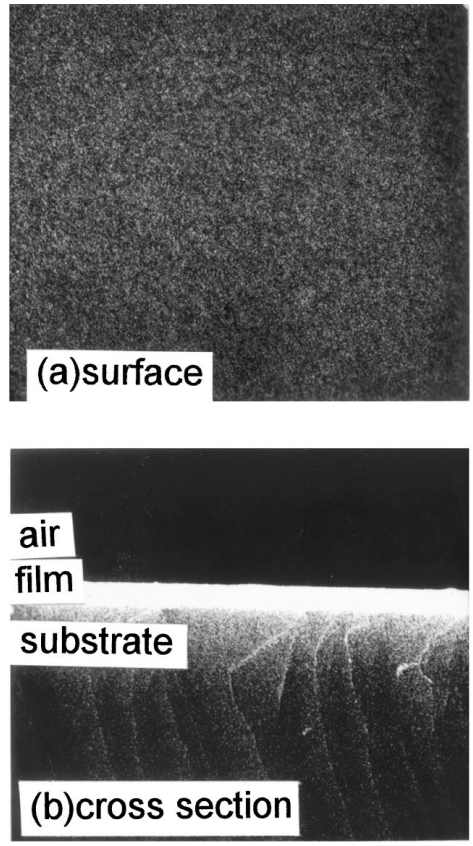

Figure 9 The SEM morphology of the surface and the cross section of the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C.

contained La of 32.6 μg and Ni of 13.8 μg, i.e., the mole ratio of La to Ni for the film is 1 to 1.002. This implies that the as-deposited LNO film is of pure phase. Fig. 8 shows the temperature dependence of the electrical resistivity of the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C. The electrical resistivity of the as-deposited film at 300 K is about 2.6×10^{-5} Ωm. The resistivity of the film is comparable to the epitaxial films $La_{0.5}Sr_{0.5}CoO_3$/MgO(1 0 0) and $La_{0.5}Sr_{0.5}CoO_3$/$SrTiO_3$(1 0 0)[12], so it is more valuable in view of application. Fig. 9 shows the SEM morphology of the surface and the cross section of the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C. The surface of the film is very smooth. No droplets were observed at this magnification. The interface of the substrate and LNO film is quite sharp, indicating that no obvious interdiffusion exists between Si(1 1 1) substrate and the film. Fig. 10 shows an AFM image of the as-deposited film. The trace of island growth can be observed clearly,

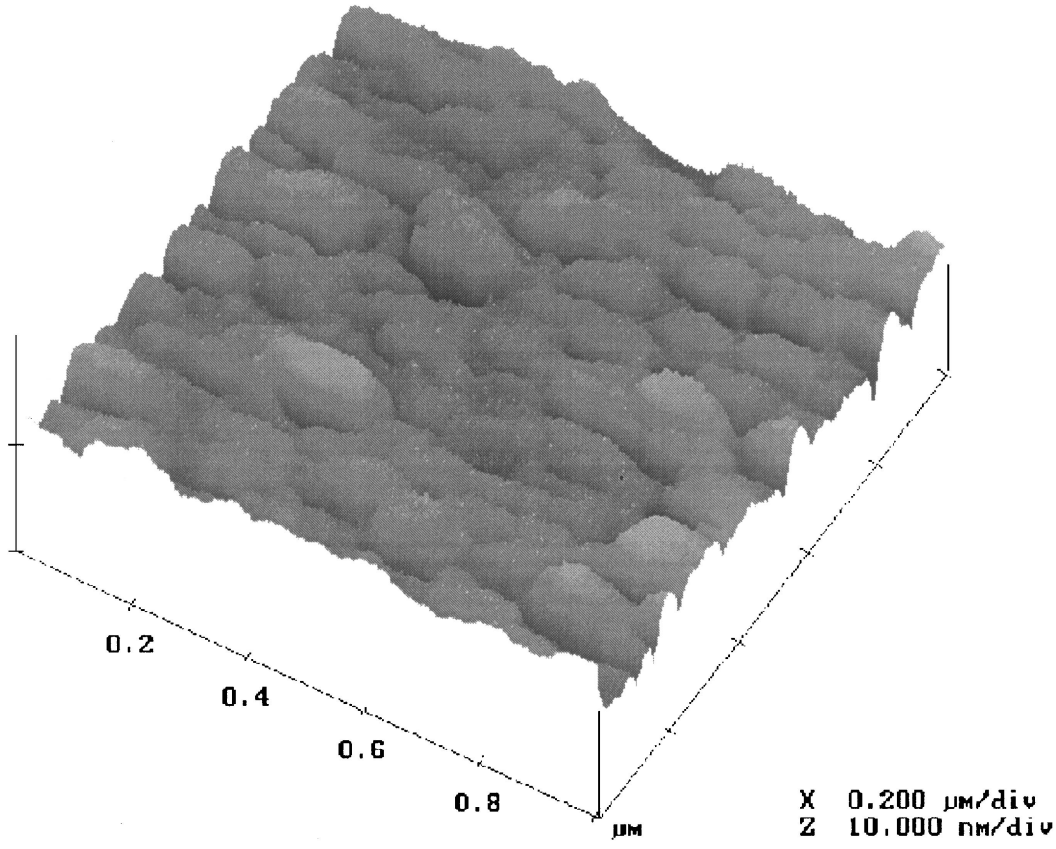

Figure 10 AFM image of surface of the film LNO/SiO_2/Si(1 1 1) deposited at 690 °C.

due to the substrate lattice mismatching with the film. Mean surface roughness can be estimated at 2 nm.

4. Conclusions

The film LNO/SiO_2/Si(1 1 1) of highly ⟨0 1 2⟩-textured was fabricated by pulsed laser deposition in a gas of oxygen of 30Pa at 690 °C using a well-prepared target. The resistivity of thin film with a thickness of 400 nm was 3.5×10^{-5} Ωm at 300 K. The surface of the film was quite smooth and the interface of the substrate and the film was very sharp. From the results of this work, LNO thin film is concluded to be a promising electrode for ferroelectric memory.

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