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Pulsed laser deposition of (110) oriented semiconductive $SrFeO_{3-x}$ thin films

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Abstract. The semiconductive perovskite-type oxide $SrFeO_{3-x}$ ($x < 0.16$) (SFO) thin films have been directly fabricated on (001)$SrTiO_3$ and (001)$LaAlO_3$ single crystal substrates by pulsed laser deposition(PLD) under high oxygen partial pressure of 100 Pa. The SFO thin films were (110) oriented. The x-ray photoelectron spectroscopy (XPS) analysis showed that the surface of SFO thin film has strong gas absorption capability. The resistance versus temperature has been measured in the temperature range from 77 K to 300 K. The SFO thin film showed typical semiconductive property. Dependence of resistance of SFO thin film on oxygen pressure was measured and result showed that the SFO thin film had better oxygen sensitive property.

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Recently perovskite-type oxides with electrical conductivity have attracted much attention because of their technologically useful electric and magnetic properties. Among them, $LaCrO_3$–$SrCrO_3$ and $LaFeO_3$–$LaSrO_3$ have been investigated for electrode materials in MHD generators, fuel cells and thermal-processing applications [1], while La–Sr–Co–O(LSCO), Y–Ba–Cu–O(YBCO), $LaNiO_3$(LNO) have been used as bottom electrodes in ferroelectric random access memories (FRAM) to fabricate high quality ferroelectric thin films and to solve the fatigue problem [2–4]. The stoichiometrically compositional $SrFeO_3$ has a simple cubic perovskite structure (a = 3.85 Å) [5, 6]. Ceramic bulks of this material are conductive (the resistivity is 10^{-5} Ω.m) and their temperature dependence exhibits characteristic of metallic conduction [6]. It is a possible candidate of electrode material. But preparation of stoichiometric $SrFeO_3$ is difficult because the higher oxidation state of iron (Fe^{4+}) is instable at the necessary temperature for solid state reaction [5, 6] S. Shin et al. have found that $SrFeO_{3-x}$ (x stands for oxygen deficiency) significantly absorbs NO gas in its lattice above 100°C [7]. Since $SrFeO_{3-x}$ ($x < 0.16$) (SFO) has p-type semiconductive property [6, 8], it has the possibility to be used as gas sensitive material. In this application, thin film has the obvious advantages of rapid responsibility, high sensitivity and possibility to be integrated with Si-integrated circuit. In the last few years, pulsed laser deposition (PLD) has been successfully used to prepare thin films of the oxide materials [9, 10]. Comparing with the other thin film deposition techniques, PLD showed some advantages of possibility of preparing high quality films and higher compositional consistency between the film and target [10]. To our knowledge, the research on $SrFeO_{3-x}$ thin film had not been reported, so it is meaningful to prepare $SrFeO_{3-x}$ ($x < 0.16$) conductive thin films by PLD at higher oxygen partial pressure. In this paper we first report on the preparation of conductive $SrFeO_{3-x}$(SFO) thin films by PLD method under higher oxygen pressure on (001) $SrTiO_3$ (STO) and (001) $LaAlO_3$ (LAO) single crystal substrates. The X-ray photoelectron spectroscopy (XPS) analysis implied that the SFO thin film has strong gas absorption capability. The resistance versus temperature measurement have been used to characterize the electrical conductivity of SFO thin films.

The PLD processes were performed by using Lambda Physik LPX205i KrF excimer laser system with the 248 nm radiation in wavelength, 30 ns in pulse width and 5 Hz in pulse frequency. In our experiment, the average laser pulse energy density was 200 mJ/mm^2. The SFO target used in our experiment was prepared by heating a stoichiometric mixture of Fe_2O_3 and $SrCO_3$ at 900 °C for 24 h and then at 1200 °C for 2 h in air. The target was light black in color and conductive. During laser deposition, the substrates were mounted on a resistively heated stage whose temperature could be varied from 25 °C to 800 °C. The target and the substrate stage were set inside the deposition chamber with a background vacuum of 2×10^{-5} Pa. The SFO thin films were fabricated on STO and LAO single crystal substrates at 700 °C under 100 Pa oxygen pressure for 30 min. After deposition, the films were post annealed in 0.6 atm oxygen for 30 min and then cooled to room temperature at a rate of about 10 °C/min. The films were shiny dark in color and conductive. The typical thickness of the film was 300 nm. When the oxygen pressure decreased to 30 Pa during laser deposition (the

Fig. 1. The scanning electron micrograph of SFO/STO surface

other deposition conditions did not change), the films were light brown in color and transparent, but they were not conductive. Although these films changed into gray and conductive after annealed at 600 °C for 6 h in air or 1 atm oxygen, their resistances were much higher than those of the films which were directly deposited by PLD under higher oxygen pressure.

The scanning electron micrograph (SEM) of the surface of conductive SFO thin film deposited on STO under 100 Pa oxygen pressure is shown in Fig. 1. It shows that there are a lot of particles on the surface. J.P. Gong et al. have investigated the precipitate formation on laser-ablated YBCO thin films and believed that the particles observed on the thin film originated from two sources. One is the droplets which directly dislodged from the target and the other is the precipitates segregated from the thin film matrix. The particles originated from droplets can be easily excluded by adjusting PLD conditions [11]. In our experiment, much fewer particles could be observed on SFO film surface in SEM photograph when the oxygen pressure decreased to 30 Pa during PLD process (the other deposition conditions did not change). We can say that the particles observed in Fig. 1 are mainly droplets come from the target. The chemical analysis of the SFO thin film was carried out by the energy dispersion analysis of X-ray (EDAX) studies. The atomic ratio Sr : Fe = 1.00 : 0.99, which was close to 1 : 1 within the experimental error of 1.4%.

These films were then characterized by X-ray diffraction (XRD) using CuK_α radiation on a Rigaku diffractometer. In Fig. 2, we showed the XRD pattern of (a) SFO target, (b) SFO/STO and (c) SFO/LAO. The peaks of XRD pattern of SFO target in Fig. 2(a) have been labelled according to JCPDS card (No. 33–678). Fig. 2(a) reveals that the SFO target is in the oxygen sufficient state (Sr : Fe : O is close to 1.00 : 1.00 : 2.83). This is consistent with the good conductivity and black color of the target. In Fig. 2(b) and (c), the (110) peak of SFO thin film is dominant, this indicated that the SFO thin films were (110) textured or oriented grown on STO and LAO substrates. In a physical vapor deposition process such as PLD, there exists the competition between thermo-

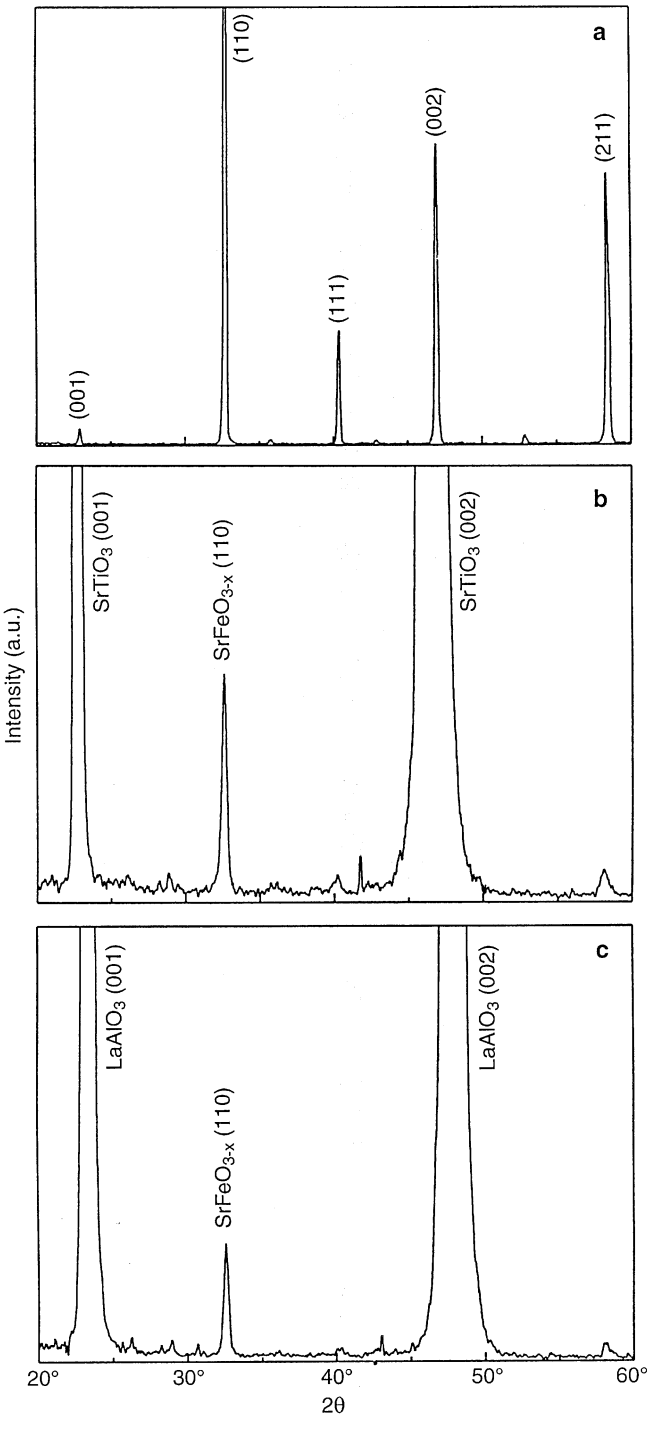

Fig. 2. The XRD pattern of **a** SFO target, **b** SFO/STO and **c** SFO/LAO

dynamics and kinetics [11]. Considering the structure of SFO is similar to that of STO or LAO, (001) oriented SFO thin films should be grown on (001) STO or (001) LAO substrates within an ideal thermodynamic equilibrium condition. The (110) orientation of the SFO films implys that kinetics is dominant during our PLD process. In this case, the growth conditions such as high oxygen partial pressure and laser energy, which could strenghten the effect of kinetics, maybe strongly influence the SFO thin

film crystallinity and orientation [12]. In fact, it has been reported that some perovskite thin films prefer (110) orientation in PLD process [13]. In additional, the defects on the substrate surface are maybe another reason for the (110) orientation of SFO thin films.

X-ray photoelectron spectroscopy (XPS) analysis was performed by using AlK_{α} radiation to characterize the surface of SFO thin film. In XPS analysis, the SFO film surface was first cleaned by Ar^{+} ion bombardment. Fig. 3 (a) is the wide scan result and Fig. 3(b) is the narrow scan spectrum of O1 s peak of SFO thin film on STO substrate. All the binding energies at various peaks were calibrated by using the binding energy of C1s (284.6 ev). Fig. 3(a) showed that the film was composed of Sr, Fe and O elements. The quantitative analysis using Sr3d, Fe2p and O1s peaks revealed that the Sr : Fe : O atomic ratio was 1.00 : 1.23 : 2.82. Because the depth of XPS analysis is limited (< 2 nm), this result gave the chemical composition near the surface of the film. In Fig. 3(b) two peaks can be found. One peak of lower binding energy ($E_b = 529$ eV) corresponds to the lattice oxygen in SFO thin film. Another peak of higher binding energy ($E_b = 531.5$ eV) arises from the chemical adsorptional oxygen on the SFO thin film surface [14, 15]. In general, the peak of adsorptional oxygen is much weaker than that of lattice oxygen in XPS spectra of ABO_3 type of oxide films [14, 16, 18]. But in Fig. 3(b), our result is opposite, i.e. the peak of adsorptional oxygen is higher than that of lattice oxygen. This result implied that the SFO thin film surface has strong gas absorption capability. This would be a favourable property for SFO thin film to be used as gas sensitivity material.

In order to characterize the electrical conductive property of SFO thin films, the resistance versus temperature for SFO/STO and SFO/LAO was measured by the standard DC four-point probe method below 300 K. Four thin film electrodes of Pt spaced 2 mm were deposited by PLD on each SFO thin film. The results of logR versus 1000/T for SFO/LAO and SFO/STO were plotted in Fig. 4 (a) and (b) respectively. A resistivity of 0.75 Ω.m of SFO thin films was obtained at room temperature. In our experiment, the resistance of SFO thin films increased exponentially with temperature down to 80 K. This result indicated that the SFO thin film showed typical semiconductive property. In Fig. 4(a), from 80 K to 250 K, the logR versus 1000/T plot was reasonably linear, with an activation energy of 0.056 ± 0.005 eV [17]. In Fig. 4(b), from 80 K to 120 K, the plot was linear, with the same

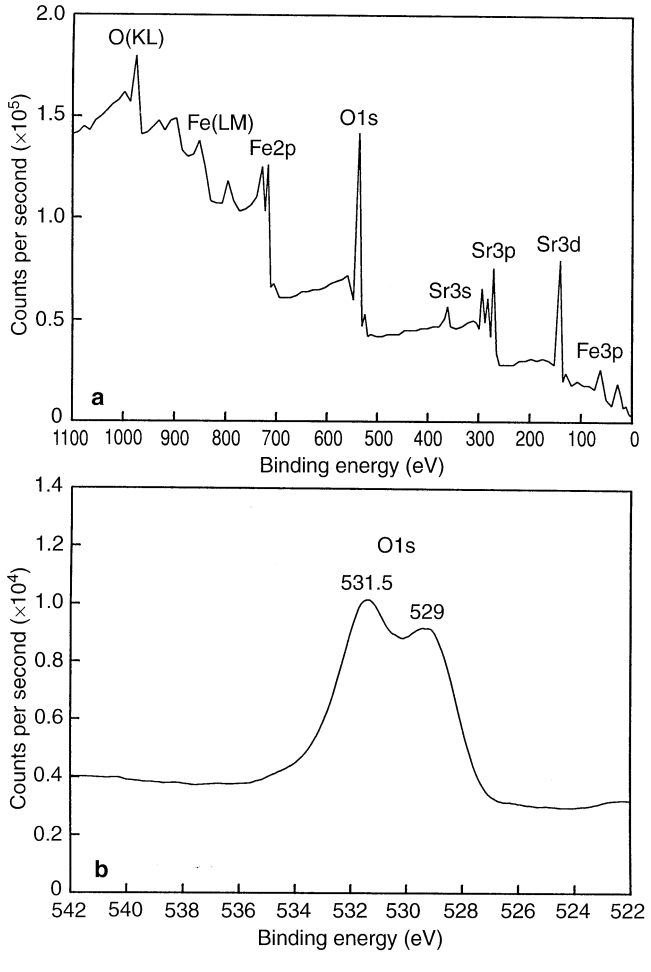

Fig. 3. **a** The wide scan XPS spectrum of SFO thin film deposited on STO. **b** The narrow scan XPS spectrum of the O1s peak of SFO thin film on STO substrate

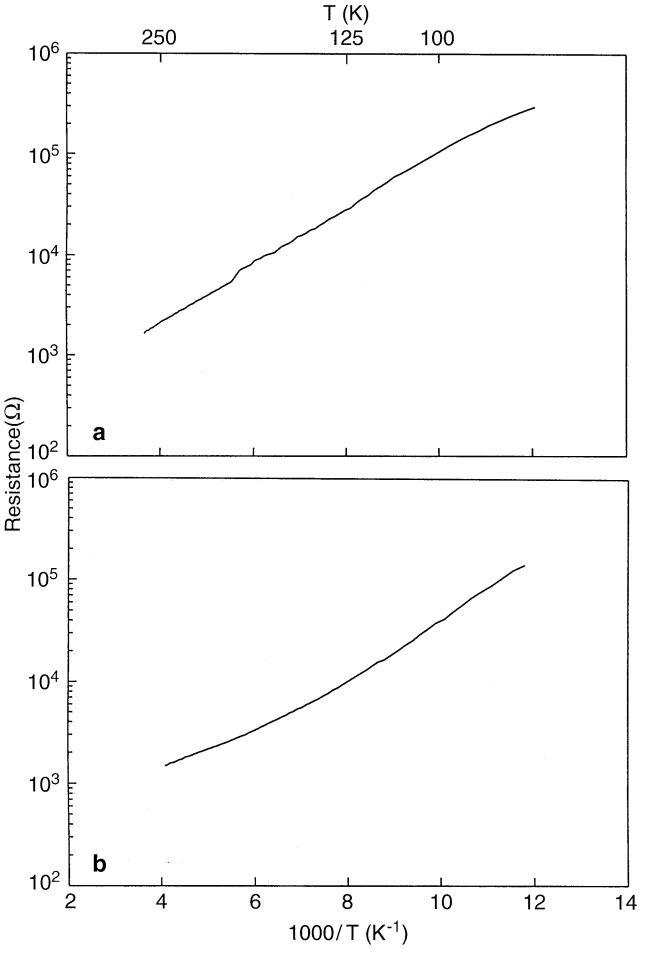

Fig. 4. The logR versus 1000/T plot for **a** SFO/LAO and **b** SFO/STO

activation energy as that in Fig. 4(a). Since this experiment was performed in same atmospheric condition, this phenomenon would not come from the difference of the surface gas absorption capability of the SFO films. But this result possibly implied that there was slight structural difference between the SFO thin film on STO and the SFO on LAO substrate with the change of temperature.

The oxygen sensitive property of SFO thin film was measured in our experiment. The SFO/LAO sample was mounted on a resistively heated stage in a chamber with a background vacuum of 2×10^{-5} Pa. Then the SFO/LAO was kept at 300 °C and 350 °C, the resistance of SFO thin film was measured by standard DC four-point probe method under different oxygen pressure. The result was plotted in Fig. 5. In Fig. 5, the resistance decreased with the oxygen pressure increasing, especially when the oxygen pressure increased from 0.2 to 2 kPa, the resistance of SFO thin film dropped a lot. This result shows that the SFO thin film has better oxygen sensitivity, especially under the oxygen pressure range from 0.2 to 2 kPa. This result is probably related to the oxygen adsorption process on the SFO thin film surface. To explain this result in detail needs to do further research work.

In summary, the semiconductive SFO thin films have been deposited on STO and LAO substrates by PLD at 700 °C under 100 Pa oxygen partial pressure. The SFO thin films were (110) oriented grown on the substrates. The SFO thin film showed typical semiconductive property down to 80 K. The strong gas absorption capability of the SFO thin film was found by XPS analysis Our experiment implied that semiconductive SFO thin film would be a possible candidate of gas sensor.

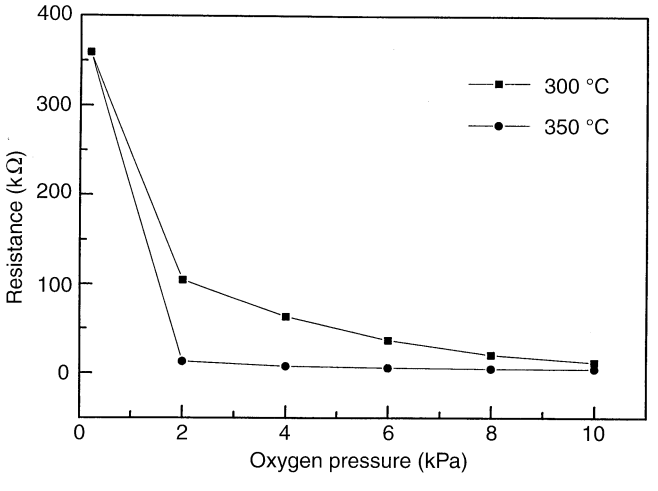

Fig. 5. Dependence of resistance of SFO thin film on oxygen pressure at temperature of 300 °C and 350 °C

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