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Magneto-transport Properties in $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ Epitaxial Thin Film

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We investigated the magnetotransport properties in $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ epitaxial thin film synthesized by using pulsed laser deposition. X-ray diffraction (XRD) $\theta-2\theta$ and reciprocal space mapping scans showed strong peaks demonstrating high quality. The image of step and terrace at atomic force microscope scan image of the film showed a layer by layer growth mode of the thin film. The resistivity showed a significant decrease by applying magnetic field of 9 T, which could be described in terms of spin dependent scattering. The zero-field resistivity at low temperature (2 K-24 K) was fitted very well with a variable range hopping model. The observed negative magnetoresistance (T = 10 K, H = 9 T) was as high as ~20 %.

Keywords : epitaxial thin film, transport properties, oxygen vacancies, magnetoresistance

1. Introduction

Transition metal oxides with ABO_3 perovskite structure have been investigated extensively due to their various fascinating physical properties such as colossal magneto-resistance, resistance switching, and multiferroic properties [1-3]. The deformation and relative orientations of the octahedra, BO_6 crucially determines the magnetic, transport as well as band structure. $SrRuO_3$ (SRO) is a stoner ferromagnet due to its high density of states at the Fermi level. SRO shows some of its functional properties which include itinerant ferromagnetism, strong magneto crystalline anisotropy, extraordinary Hall Effect, and spin glass behavior [4-6]. For single crystal SRO, the resistivity shows a kink at the Curie temperature (160 K for bulk, 150 K for thin film) and a saturated of magnetization is around 1.6 μ_B/Ru [7]. The ferromagnetism (FM) in SRO comes from the narrow t_{2g} band of Ru^{4+} ion. The bandwidth in SRO can be varied by substituting A-site isovalent cation through the different bending angle of Ru-O-Ru bond. This suggests that doping at Ru site can also change the physical as well as magnetic properties considerably in SRO.

Different magnetic and non-magnetic ions were doped at Ru site to study the effect of doping on the physical properties of SRO [8]. Furthermore the substitution of magnetic cations except for Cr at Ru site was found to decrease remarkably the FM Curie temperature in SRO. The decrease in T_C is reported to be caused by the narrowing of the Ru 4d ($t_{2g}^4 e_g^0$) orbitals with the change in oxidation state of Ru. Fan *et. al.,* reported the suppression of ferromagnetism in lightly Fe-doped $SrRuO_3$ ($0.00 \leq x \leq 0.15$) polycrystalline samples [9]. They observed a decrease in ferromagnetism and an increase in magnetic crystalline anisotropy as Fe doping concentration increased.

In this work we have successfully grown $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ epitaxial thin film at higher O_2 partial pressure. The zero field resistivity down to low temperature showed large insulating behavior. The resistivity value decreased with increased magnetic field and we observed a higher value of – MR ~ 20 % at (T = 10 K, H = 9 T).

2. Experimental

Polycrystalline $SrRu_{1-x}Fe_xO_3$ target was prepared by using high-purity (99.999 %) of $SrCO_3$, RuO_2 and Fe_2O_3 as starting materials. Stoichiometric amounts of these chemicals were grinded and made into a pellet. The as prepared pellet was sintered at 1250 °C for 10 h. Fe doped $SrRuO_3$ epitaxial thin film on $SrTiO_3$ (001) substrates was grown by using pulsed laser deposition technique using a KrF excimer laser (35 mJ/cm^2, 4 Hz) with a wavelength λ = 248 nm. During the thin film growth the substrate temperature was maintained at 750 °C with oxygen partial pressure 175 mTorr. The film thickness was found to be 60 nm by using a surface profilometer. Surface morpho-

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logy of the thin film was studied by using an atomic force microscopy (AFM; XE-15, Park System). Crystal structure was characterized by using a high resolution X-ray diffraction (HRXRD; Bruker D8). The resistivity and magnetoresistance measurements were carried out using a cryogen free cryostat (CMag Vari9, Cryomagnetics Inc.) with a dual channel source-measure unit (Keithley 2612A Standard Measurement Unit).

3. Results and Discussion

Synthesis of bulk crystal of $Sr(Ru_{1-x},Fe_x)O_{3-\delta}$ with a single phase has been reported to be difficult [9]. In this report, we made thin film of $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$. Figure 1(a) shows the XRD pattern of $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ epitaxial thin film on the STO (001) substrate. The peak at the left side of STO (002) peak is the *SRFO* (002) film peak. The lattice constant and volume of the as-deposited $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ epitaxial thin film was found to be 3.955 Å and 60.31 $Å^3$

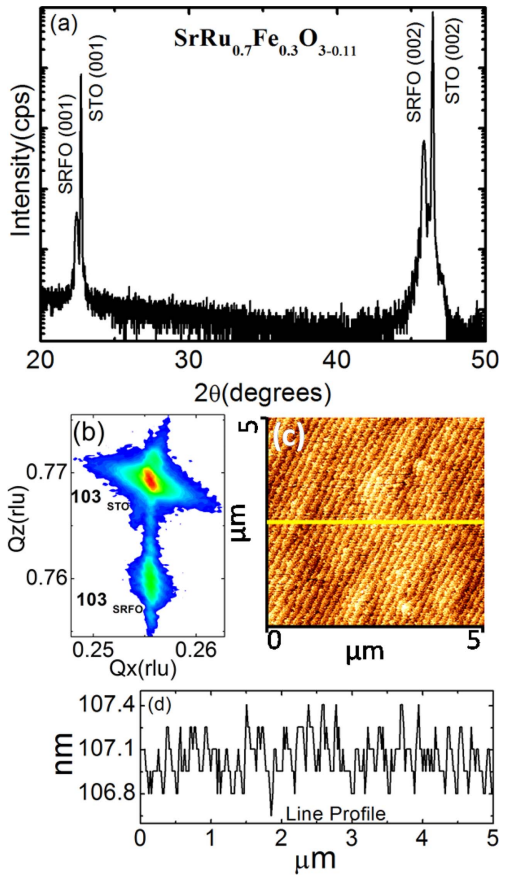

Fig. 1. (Color online) (a) HRXRD theta-2theta scan patterns of epitaxial $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin films on $SrTiO_3$ (001) substrate. (b) X-ray reciprocal space mapping around $SrTiO_3$ (103) planes. (c) Atomic force microscope image of the thin film. (d) Line profile analysis of AFM figure.

respectively. We roughly estimated the oxygen content in our thin film by using pseudo cubic unit cell volumes and linear estimation. It was found that the calculated chemical formula for $SrRu_{0.7}Fe_{0.3}O_{3-\delta}$ was $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$. We will use this notation ($SrRu_{0.7}Fe_{0.3}O_{3-0.11}$) in the later part of the manuscript.

X-ray reciprocal space mapping has been established as a powerful tool to investigate the symmetry, lattice strain, and structure of the epitaxial thin films. The vertical and horizontal axis of the reciprocal space mapping is referred to the in-plane lattice constant and out of plane lattice constant, respectively. Reciprocal space mapping around (103) reflection of STO was collected. Figure 1(b) shows the reciprocal space mapping of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ epitaxial thin film. The measured reciprocal space mapping shows substrate peak in upper side whereas the lower peak stands to the thin film peak. By seeing the mapping data it can be found that $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film was grown coherently with the same in-plane lattice constants as those of the underlying STO substrate [10, 11]. So the film is under compressive strain with tetragonal symmetry. Figure 1(c) shows the surface morphology of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film. The surface roughness was calculated and found to be 0.28 nm. The film displayed a nice step-and-terrace with minimal surface roughness. Figure 1(d) shows the line profile analysis of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film. From the analysis it clearly shows the step height and surface roughness of the film.

Figure 2(a) shows the $\rho(T)$ of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film measured across a wide range of temperature, 2 K-300 K. The ρ data was plotted in log scale. The ρ became higher as temperature decreased down to $T = 2$ K. Moreover the film did not show any kink or unusual behavior in the entire temperature range, which might be referred to the absence of any long range ferromagnetic order in the film. Bansal *et al*., studied $\rho(T)$ over a wide range of compositions ($0.00 \leq x \leq 0.1$) for Fe doped SRO polycrystalline samples [12]. At $x = 0.30$, the value of ρ for polycrystalline sample was found to be ~ 10^6 Ω·cm. They have reported that at higher concentration of Fe, the Ru^{4+} changed to Ru^{5+} state in order to compensate the valency of Fe^{3+}. They also found insulating behavior for 30 % Fe doped sample in the entire measured temperature range. Zhang *et al.*, studied $\rho(T)$ of Mn doped SRO polycrystalline material at a temperature range of 10-300 K. At $x = 0.27$, the value of ρ increased sharply at low temperature (down to 10 K) and found to be ~ 10^3 Ω·cm. They described the upturn of ρ at $x = 0.27$ in terms of variable range hopping model. It can be also found from their study that the Mn doping at Ru site disturbed itinerant character of Ru 4d electrons [13]. In order to

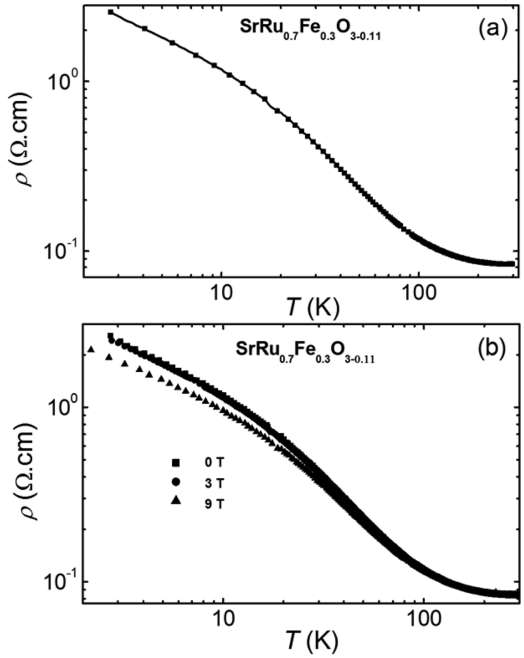

Fig. 2. (a) $\rho(T)$ of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film. (b) Temperature dependent resistivity $\rho(T)$ at various magnetic fields for $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film.

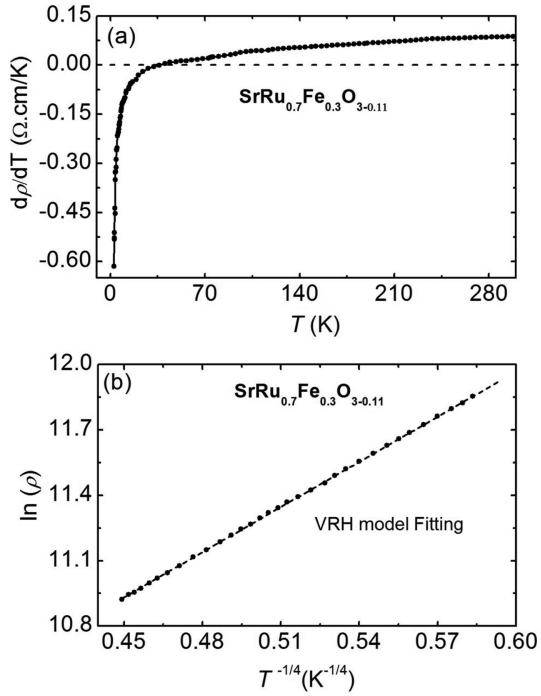

Fig. 3. (a) The $d\rho/dT$ of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ /$SrTiO_3$ (001) substrate. (b) Fitting based on three dimensional variable range hopping behavior within 8 K to 24 K.

find more for transport properties, the magnetic field dependence of resistivity for the $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ film was measured at 3 T and 9 T over a wide range of temperature (2 K-300 K) as shown in the Fig. 2(b). It can be observed from the figure that upon applying the magnetic field, the resistivity value of the film decreased. The systematic decrease in the film resistivity can be linked to the spin dependent scattering.

Figure 3(a) shows the $d\rho/dT$ plotted in a linear scale with temperature ranging from 2-300 K. The lack of any anomaly confirms the absence of long range ferromagnetic order in the material. Also it can be noticed that the sign of $d\rho/dT$ changed at $T \sim 20$ K [14]. We tried to explain the resistivity behavior in Fig. 3(b) in terms of variable range hopping mechanism where carriers were localized by random potential fluctuations. We have plotted the high temperature resistivity data with Mott's variable range hoping (VRH) mechanism and are given by the expression as follows [15-17]:

$$\sigma = \sigma_{0M} T^{-1/2} \exp\left[-\left(\frac{T_M}{T}\right)^{1/4}\right], \quad (1)$$

Where σ_{0M} and T_M are given by the following expression.

$$\sigma_{0M} = \frac{3e^2 \nu_{ph}}{(8\pi)^{1/2}} \left[\frac{N(E_F)}{\alpha k_B T}\right]^{1/2}$$

$$T_M = \left[\frac{\alpha^3}{k_B N(E_F)}\right]$$

Where T_M is a measure of the degree of disorder in the film, ν_{ph} ($\sim 10^{13}$), $\alpha = 18.1$ is a constant, $N(E_F)$ is the density of states at the Fermi level, k_B is the Boltzmann constant, and α is the inverse localization length of the localized states. The VRH model seems to be well fitted to the resistivity data over the temperature range 8 K < T < 24 K. Thus the conduction mechanism can be well established in the light of variable range hopping model.

Figure 4 shows the magnetization curve, M(T, H = 9 T)

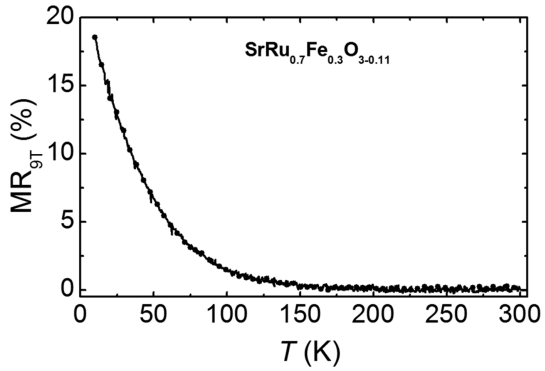

Fig. 4. MR (H = 9 T, T) for $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$/$SrTiO_3$ (001) substrate.

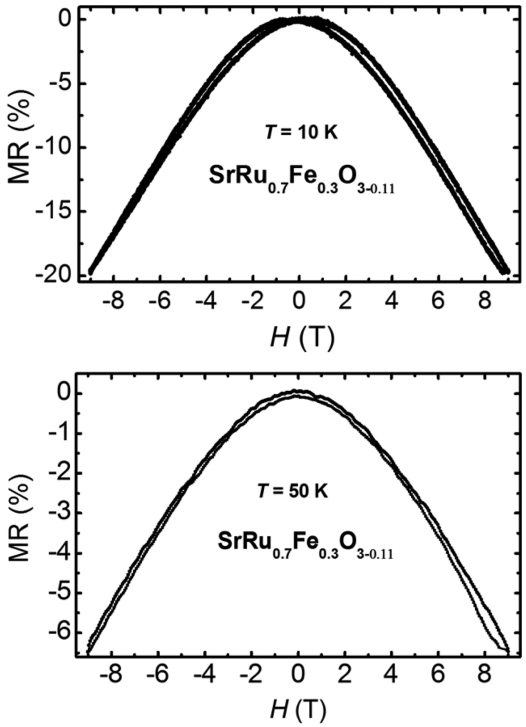

Fig. 5. (a) The MR (H, T = 10 K) for $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$/$SrTiO_3$ (001) substrate. (b) The MR (H, T = 50 K) for $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$/$SrTiO_3$ (001) substrate.

of $SrRu_{0.7}FeO_{3-0.11}$ thin film measured over a wide range of temperature (10-300 K). The value of MR decreased with increase in temperature and showed a linear approach down to higher temperature (> 150 K). The magneto-resistance of the film increased with decreased temperature. A large - MR (~ 20 %) was recorded at (T = 10 K, H = 9T). Similar behavior was also observed in $Sr_{0.7}La_{0.3}Ru_{0.7}Fe_{0.3}O_3$ polycrystalline material where larger MR (~ 40 %) was obtained at low temperature (T = 10 K, H = 9T) [18]. Unlike the SRO [19] whose MR has a peak near FM (T_C), we could not observe any such large MR at higher temperatures in our thin film.

Figure 5(a) shows the magnetic field dependence of magnetoresistance defined as MR ≡ [$\rho(H) - \rho(H=0)$]/ $\rho(H=0)$ × 100 %, measured at (H, T = 10 K) for $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ thin film, where $\rho(H)$ represents the resistivity at an applied magnetic field. The negative magnetoresistance obtained here was as large as ~ 20 % (H = 9 T, T = 10 K). The observed MR (~ 20 %) (T = 10 K, H = 9T) is quite higher than the MR of SRO (T = 10 K, H = 9T) [20]. We compared our epitaxial thin film with that of a polycrystalline sample. The higher value of MR in the polycrystalline sample at x = 0.30 might be attributed to the grain boundary and defects which are absent in our epitaxial thin film. Mamchik *et al*., reported that observed MR (H, T = 10 K) for $(Sr_{0.7}La_{0.3})(Ru_{0.7}Fe_{0.3})$ film was almost the same between the polycrystalline sample and the thin films deposited on STO (001) substrates made by themselves [18-21]. So they concluded that MR for their polycrystalline samples is an intrinsic property of the grains.

In polycrystalline material, the MR is believed to be associated with the grain boundary [22]. As we know, the transport property in polycrystalline material depends on the inter-grain whereas magnetic property depends on the grain itself. In case of epitaxial thin film, the presence of grain boundary is quite negligible. The origin of the large MR in our $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ film is not completely understood. The MR obtained in our current film is not associated with the Lorentz force as MR due to Lorentz force is always positive, which in turn contradicts our observation. The robust signature of negative MR reveals that this component is independent of Lorentz force and hence is not an orbital effect [20]. The appearance of strong negative MR at low temperature itself pointed to some form of magnetic scattering occurred in the material. As we know in ferromagnetic materials like SRO, the suppression of spin-flip scattering results in a negative MR. We speculate similar phenomena might occur in our $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ epitaxial thin film. Magnetic order may exist at short range scale while there is no long-range order in this sample.

4. Conclusions

In summary, we studied magneto-transport behavior of $SrRu_{0.7}Fe_{0.3}O_{3-0.11}$ epitaxial thin film prepared by using pulsed laser deposition. The zero filed resistivity curve shows higher value of resistance at low temperature. With increase in applied magnetic field, the film resistance decreased considerably. The resistance at low temperature T < 24 K was fitted very well with the variable range hopping mechanism. The temperature dependence of MR at 9 T showed a clear increase in MR with decrease in temperature. We observed a large magnetoresistance up to ~ 20% (H = 9 T, 10 K) with field parallel to the current direction. The MR value (~ 7 %) considerably decreased with increase in temperature (50 K).

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