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Pulsed laser deposition of $NdNiO_3$ thin films

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Abstract

We report the structural and transport properties of $NdNiO_3$ thin films prepared via pulsed laser deposition over various substrates. The films were well textured and *c*-axis oriented with good crystalline properties. The electrical resistivity of the films undergoes a metal–insulator transition, depending on the deposition process. Well-defined first order metal–insulator phase transition (T_{MI}) was observed in the best quality films without high pressure processing. Various growth conditions such as substrate temperature, oxygen pressure and thickness were varied to see their influence on T_{MI}. Deposition temperature was found to have a great impact on the electrical and structural properties of these films. Further the films deposited on $LaAlO_3$ substrate were found to be highly oriented with uniform grain size as observed from X-ray diffraction and atomic force microscopy, whereas those on Si substrate were polycrystalline, dense and randomly oriented.

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1. Introduction

The study of the transition from the Mott-Hubbard (MH) insulating state to the metallic state [1] is called the metal–insulator transition (MIT), and is a topic of great current interest. The discovery of high temperature superconductivity and giant magnetoresistive effects has further renewed interest in the perovskite related transition metal oxides systems especially rare earth nickelates ($RNiO_3$) which show bandwidth controlled metal–insulator phase transition. The electronic properties of these systems have been associated with the degree of structural distortion. The critical temperature (T_{MI}) of the MI phase transition is dependent on the Ni–O–Ni bond angle. Straightening of this angle stabilizes the metallic state over the insulating one, hence lowering the value of T_{MI}, which can be achieved either by increasing the rare earth radius [2,3] or by applying external pressure [4–6].

Thin films of these materials have potential for various applications such as thermal switching, thermochromatic coatings, non-volatile memory, etc. Attempts have been made to deposit thin films of $RNiO_3$ by techniques such as sputtering [7,8], Pulsed laser deposition [9,15] and sol–gel methods [10]. These studies have shown that T_{MI} variation depends either on the preparation conditions or on the film/substrate misfit.

The maximum value of transition temperature reported for bulk $NdNiO_3$ is 200 K and in films prepared via sputtering on $LaAlO_3$ substrate by De Natale et al. [7] is 150 K. Catalan et al. [11] has reported transition temperature of 120 K with resistivity change of more than two order of magnitude for $NdNiO_3$ films prepared on $LaAlO_3$ substrate by using pulsed laser deposition technique. The lesser value of transition temperature observed by above

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said research groups in case of thin films as compared to $NdNiO_3$ bulk value was explained in terms of strain effect between epitaxial film and substrate [7,9].

In the present study we have successfully deposited in situ $NdNiO_3$ thin films on $LaAlO_3$ and Si substrates via pulsed laser deposition without high pressure annealing and tried to study the influence of substrate temperature, thickness and substrate effect on structural and electrical properties of these films.

2. Experimental

$NdNiO_3$ thin films were in situ grown by pulsed laser deposition using 30 mm diameter target. The target was prepared by mixing appropriate molar ratios of Nd_2O_3 and NiO powders, grinding and heating the mixed powder in air at 800 °C for 12 h. The powder was further reground and pressed into pellets under a pressure of about 80 MPa. Finally, it was sintered at 1000 °C for 12 h. The thickness of the films was in the range of 53–300 nm as measured from profilometer. A Siemens D 5000 four circle diffractometer with Cu K_α radiation was used to see the orientation and crystallinity of the films.

3. Results and discussions

3.1. Effect of substrate temperature on metal to insulator transition

Deposition temperature is found to have an important influence on resistivity of the $NdNiO_3$ films. Temperature dependence of film resistivity show that the films deposited on $LaAlO_3$ at lower temperature, i.e. at 400 and 500 °C are completely metallic with no T_{MI}. While the films deposited at higher substrate temperature, i.e. above 700 °C show better texture quality and undergoes sharp metal–insulator transition (T_{MI}). As shown in Table 1, the highest value of T_{MI} of 135 K (T_{MI} is defined by the change in sign of dR/dT on heating) has been observed for film deposited at 750 °C. With further increase in deposition temperature to 800 °C, the value of T_{MI} decreases. It is also interesting to note that the film resistivity ρ (250 K) deposited at 750 °C is highest, i.e. 588.6 μΩ cm. Either increasing or decreasing deposition temperature results in decreasing film resistivity, regardless of film quality.

Fig. 1 shows the resistance versus temperature curves (R–T) for $NdNiO_3$ films deposited on $LaAlO_3$ substrate at different deposition temperatures (600–800 °C). These curves indicate that the metal–insulator transition temperature (T_{MI}) increases with increase in deposition temperature. The films deposited at $T_s = 600$ °C (sample A) does not show any MI transition and the R–T curve of this film is more or less metallic throughout the temperature range. As the substrate temperature is increased to $T_s = 700$ °C (sample B), the metal to insulator transition is observed at 118 K as shown in Fig. 1. With increase in substrate temperature to $T_s = 750$ °C (sample C), the films show the sharp metal to insulator transition of 135 K. Further increase of substrate temperature to $T_s = 800$ °C (sample E) results in the decrease of the value of T_{MI} and the films show the more metallic phase as compared to an insulating phase (Table 1). The quality of metallic state and insulating state is calculated from normalized resistance slope at room temperature ($(1/R)(dR/dT)$ at 300 K) above and below T_{MI}, respectively. This could possibly be due to the fact that at higher deposition temperature $NdNiO_3$ phase get disassociated into Nd_2NiO_4 and NiO phase as reported by Demazeau et al. [12].

$$2NdNiO_{3-y} = Nd_2NiO_4 + NiO + (\tfrac{1}{2} - y)O_2$$

Zang et al. [13] observed the metal-to-metal transition in this phase. On dissociation of $NdNiO_3$ phase the oxidation state of Ni also changes from Ni^{3+} ($NdNiO_3$) to Ni^{2+} (Nd_2NiO_4).

The presence of NiO generally does not affect the electrical resistance because resistivity of NiO is very much greater than Nd_2NiO_4 phase. Therefore, percolation of electrical current is through Nd_2NiO_4 phase only which is in confirmation with our experimentally observed results for

Table 1
Various parameters of $NdNiO_3$ films deposited on $LaAlO_3$ substrate at different deposition temperatures

Sample	T_s (°C)	T_{MI} (K)	ρ (250 K) (μΩ cm)	ρ (20 K) (μΩ cm)	Quality of metallic state ($(1/R)(dR/dT)$ above T_{MI})	Quality of insulating state ($(1/R)(dR/dT)$ below T_{MI})	Ratio of insulating and metallic state	Hystresis (K)
A	600	–	197.6	434.5	2.19×10^{-3}	–	–	–
B	700	118	263.4	250.9	2.03×10^{-3}	2.84×10^{-3}	1.399	10
C	750	135	588.6	8860.6	2.69×10^{-3}	1.32×10^{-1}	48.88	16
D	780	129	355.4	2027.6	2.66×10^{-3}	6.88×10^{-2}	25.88	11
E	800	100	99.97	82.7	1.64×10^{-3}	1.65×10^{-3}	1.01	12

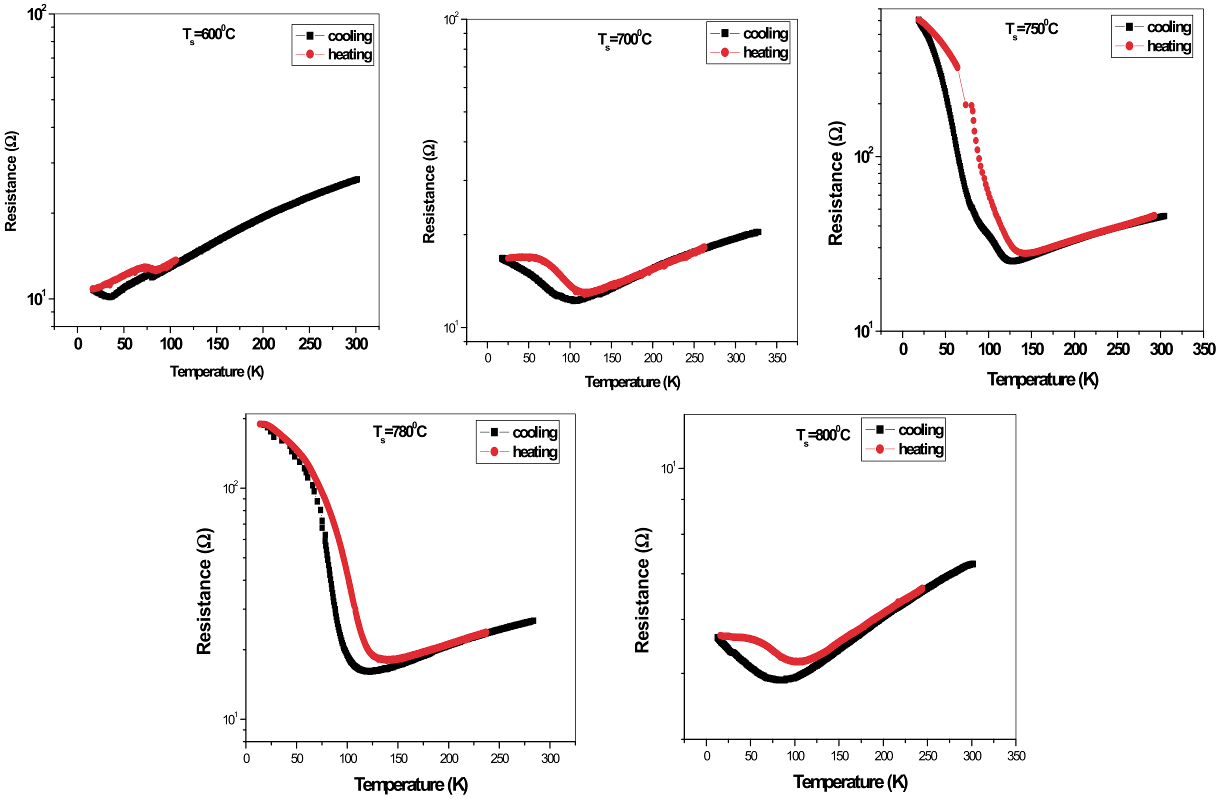

Fig. 1. Resistance versus temperature curves of $NdNiO_3$ films deposited on $LaAlO_3$ substrate at various deposition temperatures.

sample E showing more metallic phase as compared to insulating phase.

In order to understand the cause of the observed conductive properties, we investigated the structure of the $NdNiO_3$ films more accurately using XRD as shown in Fig. 2. It was found that the films deposited at low temperature are amorphous, and it began to crystallize at deposition temperature of 400 °C. The films are found to be polycrystalline at deposition temperature below 700 °C. Moreover multiple reflections with no preferred orientation has been observed in their XRD pattern. On the other hand the films deposited above 700 °C were *c*-axis textured and show only 00l reflection in their XRD patterns. The XRD pattern of sample A (deposited at 600 °C) shows only a broad (004) reflection. As we increase the deposition temperature to 700 °C (sample B), we obtain more intense peak of (004) reflection along with (002) reflection at $2\theta = 23.1°$ of $NdNiO_3$ phase. The film deposited at 750 °C shows best XRD pattern with preferred orientation. All the X-ray reflections from the $NdNiO_3$ film are observed only near the corresponding reflections from the substrate, which indicates that a single crystalline $NdNiO_3$ film is grown. No segregation of other phases was detected. With further increase in deposition temperature to 800 °C, the film quality degrades and NiO phase has been observed in the XRD pattern (Table 2).

The θ–2θ scans of (004) reflection of $NdNiO_3$ films display a clear difference in the film peak positions, as shown in Fig. 3. Firstly, we found that the films deposited at 500 or 600 °C shows a very broad peak, corresponding to

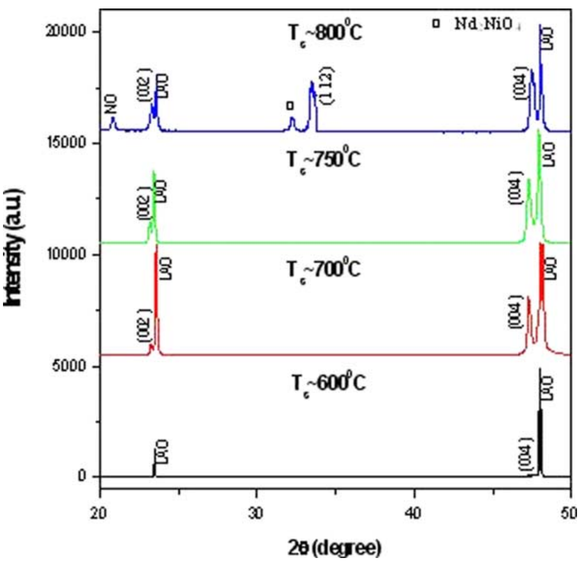

Fig. 2. X-ray diffraction patterns of $NdNiO_3$ films grown on $LaAlO_3$ substrate at various deposition temperatures.

Table 2
Comparative parameters of $NdNiO_3$ films grown on $LaAlO_3$ and Si substrates

Substrate	Optimum deposition temperature of best quality film (°C)	T_{MI} (K)	Lattice parameter (Å) substrate-film	Lattice mismatch (%)	Intensity ratio (I_{112}/I_{004})
$LaAlO_3$	750	120	3.788–3.841	−1.39	0
Si	675	–	5.431–5.38	0.7	1.89

a wide range of *c*-lattice constant. However, the peaks are much narrower for the *c*-axis oriented films deposited at 700 °C or higher deposition temperature and they shift to small angle values when the deposition temperature increases (corresponding to larger *c*-lattice constants as shown in Table 3). The value of *c*-lattice constant increases from 7.632 to 7.683 Å with increase in deposition temperature from 600 to 750 °C. Thus, the volume of $NdNiO_3$ unit cell increases with increase in deposition temperature. Further we found that the full width at half maximum (FWHM) for (004) reflection reduces from 0.37947 to 0.24644° when substrate temperature increases from 600 to 750 °C (Table 3). This indicates an improvement in film orientation. The crystallite size has been calculated using Debye Scherrer formula and found to vary in the range (39.55–60.82 nm). Out of plane pseudocubic lattice parameter for $NdNiO_3$ film deposited at $T_s = 750$ °C comes out to be 3.841 Å.

To get better insight we have done EDAX studies of these films. It has been observed that the films deposited at $T_s = 650$ and 700 °C have slightly lesser quantity of mole percentage of Ni as compared to Nd while the films deposited at $T_s = 750$ °C are found to be completely stoichiometric, i.e. with cationic ratio of Nd/Ni being equal to one. These results indicate that the non-stoichiometry of the films could be responsible for lowering of T_{MI} observed in the films deposited at substrate temperature lesser than 750 °C.

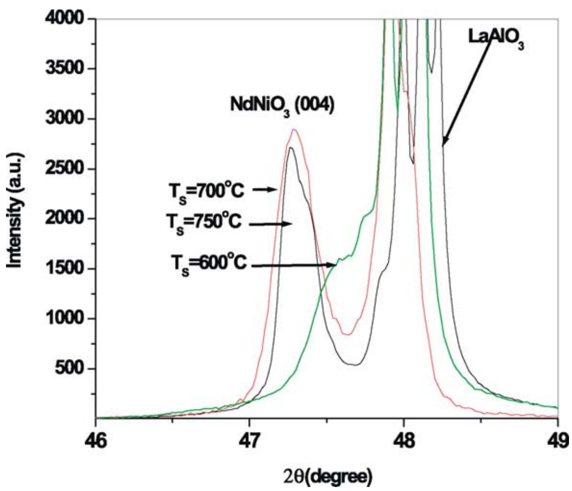

Fig. 3. θ–2θ scans of (004) reflection of $NdNiO_3$ films deposited at various deposition temperatures.

The hysteresis observed in (*R*–*T*) curves (as shown in Fig. 1) further confirm the presence of first order phase transition with the coexistence of high temperature metallic to low temperature semiconducting phase below T_{MI}. The cooling curves always display the lower resistivity. This fact signals the persistence of the nuclei of high temperature metallic phase below the onset of MI transition. In the lower temperature part of the metallic region, differences between the resistance in the cooling and heating process can be observed. The differences disappear at the higher temperature and are probably due to very subtle change in the ceramic structure caused by the phase transition and its cell volume changes. The transition hysteresis for these films is calculated from the difference between T_{MI} on heating and on cooling and is shown in Table 1.

The surface morphology of the films has been studied using scanning electron microscopy (SEM). As shown in Fig. 4, the film deposited at 600 °C looks partially crystallized, and has more amounts of amorphous phases. Even these films do not show any MI transition in their *R*–*T* curve and remain metallic throughout the temperature range. Where as those films deposited at higher substrate temperature (i.e. $T_s = 750$ °C) are well crystallized and consist of fine arranged network of grains. The best quality film (sample C) shows smooth surface with small roughness of 12 nm as measured with Atomic force microscopy. These films also show MI transition in their *R*–*T* curve.

3.2. Effect of substrate on metal to insulator transition

To understand the lattice mismatch effect we prepared various $NdNiO_3$ films at different substrate temperatures on

Table 3
Lattice parameters and FWHM (004) of $NdNiO_3$ thin films deposited on $LaAlO_3$ substrate

Sample no	Substrate temperature T_s(°C)	Lattice parameter (*c*) of the film (Å)	FWHM (004) (°)	Crystalline size (nm)
A	600	7.632	37947	39.55
B	700	7.679	26021	57.61
C	750	7.683	24644	60.82

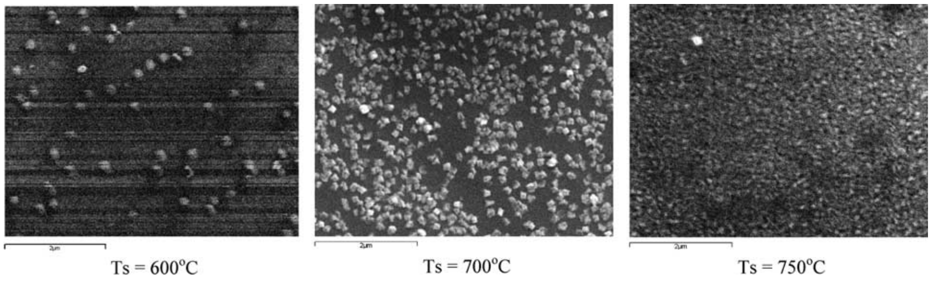

Fig. 4. SEM photographs of $NdNiO_3$ films deposited on $LaAlO_3$ substrate at (a) 600 °C (b) 700 and 750 °C.

Si and $LaAlO_3$ substrates. The optimum substrate temperature for growth of these films on Si and $LaAlO_3$ is found to be 675 and 750 °C, respectively. As we increase the deposition temperature to 750 °C in Si deposited film (shown in Fig. 5), the room temperature resistance increases and transition becomes more inferior. On the other hand the films deposited on $LaAlO_3$ at this temperature show the sharp metal to insulator transition with T_{MI} of 135 K.

XRD pattern of the best film deposited on Si is shown in Fig. 6(a). The highest intensity peak has been observed at $2\theta = 33.15°$, which is the most intense peak in bulk $NdNiO_3$. This reflection can be indexed as (020), (200) or (112) in the orthorhombic cell and (110) in the cubic perovskite. The peak corresponding to (004) reflection is also present in the XRD pattern; but is less intense as compared to the (112) reflection. This indicates that the $NdNiO_3$ films grown on Si are polycrystalline. The growth of $NdNiO_3$ films on Silicon is difficult as Si is covalent and $NdNiO_3$ being ionic. Moreover there is a high diffusivity of Si at deposition temperature ≥ 600 °C. In some cases we have also observed a diffraction peak at $2\theta = 44.6°$, which belong to Ni_2SiO_4 [14]. However, the observation of this impurity is not systematic and its actual formation and relationship with electrical properties still has to be confirmed. On the other hand XRD pattern of the best quality films deposited on $LaAlO_3$ are highly oriented as shown in Fig. 6(b). It reflects prominent 004 reflection of $NdNiO_3$ phase along with two intense peaks of $LaAlO_3$ substrate with no impurity peak. The lattice mismatch of $NdNiO_3$ films (Table 2) has been found to be −1.39% for $LaAlO_3$ and 0.7% for Si, respectively.

The films deposited on Si showed inferior switching characteristic. The metallic phase in these films almost disappear and show semiconducting behaviour in the whole temperature range. This is possible due to more lattice mismatching between film and substrate. On the other hand the best quality $NdNiO_3$ film (sample C) on $LaAlO_3$ substrate shows clear metal to insulator transition with T_{MI} of 135 K.

3.3. Effect of film thickness on metal to insulator transition

In order to further investigate the strain effect; $NdNiO_3$ films of various thicknesses in the range (53–300 nm) were grown on $LaAlO_3$ substrate. Film thickness was reduced by decreasing the deposition time. We observe the continuous change in phase transition behaviour with the thickness of the samples. When the film thickness is reduced, the relative impact of the strain generated at the film-substrate interface becomes increasingly important and result in the change of electrical properties of these films.

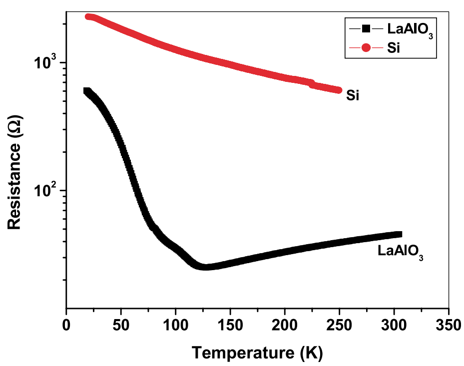

Fig. 5. Resistance versus temperature curves of $NdNiO_3$ films deposited on Si and $LaAlO_3$ substrate at $T_s = 750$ °C.

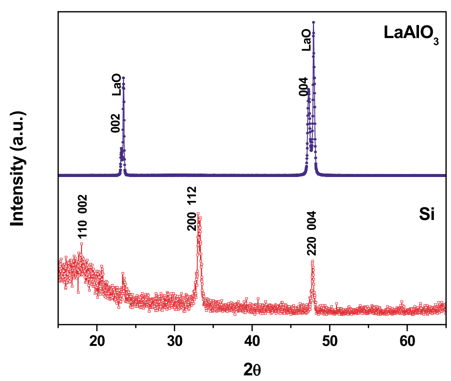

Fig. 6. X ray diffraction patterns of $NdNiO_3$ films deposited on Si and $LaAlO_3$ substrate at (a) 675 °C and (b) 750 °C, respectively.

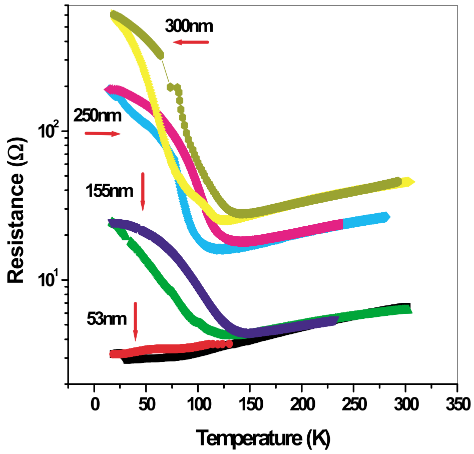

Fig. 7. Resistance versus temperature curves of $NdNiO_3$ films of various thicknesses grown on $LaAlO_3$ substrate at 750 °C.

Fig. 7 shows the temperature dependence of resistance (*R–T*) curve for four films of varying thickness of 53, 155, 250 and 300 nm. As the film thickness increases to optimum value of 300 nm, the change in resistance becomes larger and T_{MI} shifted towards higher temperature. The 53 nm thick film shows almost metallic behaviour in the whole temperature range. MI transition in this film is only signaled by hysteresis in the *R–T* curve. While 300 nm thick film shows clear metal to insulator transition with T_{MI} of 135 K. This is consistent with the fact that increased biaxial tensile strain produces between film and substrate with decreasing film thickness stabilizes the metallic phase by straining the in plane Ni–O–Ni bond angle in a similar fashion to the external pressure [6]. Considerable lowering of T_{MI} due to strain effect for $NdNiO_3$ films on $LaAlO_3$ has been reported by Denatale and Kobrin [7]. It is observed that with the increase of film thickness, the strain relaxes and transition temperature shifted towards higher temperature. As the metallic behaviour in $NdNiO_3$ is believed to be due to charge transfer interaction between Ni^{3+}–O (2p). The crucial structure parameter that influences the electrical properties in nickelates is Ni–O–Ni bond angle. It is believed that tilting of the NiO_6 octahedra is due to a mismatch of the rare earth size and the space between the corners sharing octahedral. The rare earths are too small to fill this space, therefore, causing the NiO_6 octahedra to tilt in order to make the space smaller. Pressure reduces the size of the space and consequently reduces the mismatch, resulting in the decrease of the NiO_6 octahedra's tilting and the straightening of the Ni–O–Ni angle. The strain produces between film and substrate shrink the volume that is analogous to the hydrostatic pressure effect and drives to metallic behaviour. In case of films with higher thickness, the strain relaxes and leads to MI transition as observed in present study.

4. Conclusions

In summary, we have successfully grown $NdNiO_3$ films on $LaAlO_3$ and Si substrates using PLD without high pressure annealing and have studied their structural and electrical transport properties. The temperature dependence of resistivity of the films was characterized in terms of deposition temperature, substrate and thickness. The best quality films grown on $LaAlO_3$ are well textured and *c*-axis oriented with good crystalline properties. The electrical resistivity of the films undergoes a clear metal–insulator transition, depending on the deposition process. Deposition temperature was found to have a great impact on the electrical and structural properties of these films. T_{MI} of the films decreases when the films are grown below or above optimum deposition temperature. The optimum substrate temperature for growth of these films on Si and $LaAlO_3$ is found to be 675 and 750 °C, respectively.

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References

[1] N.F. Mott, Metal Insulator Transitions, Taylor & Francis, London, 1990.
[2] J.L. Gracia-Munoz, et al., P. Lacorre, Phys. Rev. B 50 (1994) 978.
[3] J.L. Garcia-Munoz, et al., Phys. Rev. B 46 (1992) 4414.
[4] X. Obradors, et al., Phys. Rev. B 7 (1993) 12353.
[5] M. Medarde, et al., Physica B 234–236 (1997) 15.
[6] P.C. Canfield, et al., Phys. Rev. B 47 (1993) 12357.
[7] J.F. De Natale, et al., J. Mater. Res. 10 (1995) 2992.
[8] P. Laffez, et al., Thin Solid Films 354 (1999) 50.
[9] G. Catalan, et al., J. Appl. Phys. 87 (2000) 606.
[10] J.K. Vassiliou, et al., Solid State Chem. 81 (1989) 208.
[11] G. Catalan, et al., Phys. Rev. B 62 (2000) 7892.
[12] G. Demazeau, et al., J. Solid State Chem. 3 (1997) 582.
[13] Z. Zhang, et al., J. Solid State Chem. 117 (1995) 236.
[14] P. Laffez, et al., J. Magn. Magn. Mater. 211 (2000) 111.
[15] A. Venimadhav, et al., Mater. Res. Bull. 37 (2002) 201.