

Cite this article as: Yao Dan, Wang Weiwei, Tong Ruixue. $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ Thin-Films with Tunable Metal – Insulator Transition Grown by Polymer-Assisted Deposition[J]. Rare Metal Materials and Engineering, 2021, 50(05): 1518-1522.

ARTICLE

$\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ Thin-Films with Tunable Metal – Insulator Transition Grown by Polymer-Assisted Deposition

Yao Dan¹, Wang Weiwei², Tong Ruixue³

¹ School of Mathematic & Physics, Anhui Jianzhu University, Hefei 230601, China; ² Department of Materials, Hefei Gotion High-Tech Power Energy Co., Ltd, Hefei 230011, China; ³ Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

Abstract: The epitaxial $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ ($x=0.5, 0.55, 0.6$, SNNO) thin films with (001)-oriented single-crystal LaAlO_3 substrates were fabricated by a chemical solution deposition technique, namely polymer-assisted deposition (PAD) under the ambient oxygen annealing. X-ray diffraction θ - 2θ scan, rocking curve measurement, φ -scan and scanning electron microscopy were used to study the SNNO characteristics. The results reveal the good crystallinity and heteroepitaxy of these SNNO films. Temperature dependence of the resistivity indicates that all the films show a clear Mott metal-insulator transition (MIT) and the transition temperature (T_{MI}) shifts to higher temperature with the increase of Sm content. The epitaxial $\text{Sm}_{0.55}\text{Nd}_{0.45}\text{NiO}_3$ thin films exhibit MIT near room temperature. The successful growth of high quality SNNO films with room temperature transition by economic and facile PAD method shows great potential in practical application of nickelate.

Key words: nickelate; metal-insulator transition; epitaxial film; polymer assisted deposition

Rare earth nickelate RENiO_3 attracts much attention because it provides a wide range of important functionality for applications in modulated sensors^[1], optoelectronic switches^[2], and thermochromic coatings^[3]. Furthermore, these materials also show temperature-driven metal-insulator transition (MIT) properties^[4]. Among the RENiO_3 , LaNiO_3 maintains a metallic conductivity until the temperature drops to 1.5 K, while RENiO_3 with $\text{RE}=\text{Pr}, \text{Nd}, \text{Sm}$ and Eu undergoes the MIT at 135, 200, 400, and 460 K, respectively^[4]. This systematical shift towards higher values is ascribed to the increasing deviation of Ni-O-Ni angles (180°) with reducing the RE ion size^[5,6]. Besides, the application of external pressure^[7], electrical field^[8] and substrate modification^[9] can also change the metal-insulator transition temperature (T_{MI}).

From the perspective of device application, the nickelate with a T_{MI} around room temperature is note-worthy^[10]. To alter the MIT temperature to the room temperature, epitaxial strain engineering through hetero-epitaxial growth and substitution of RE ions by alkaline earth metal ions or other RE ions are two major feasible ways. Ojha et al^[11] demonstrated that the

electronic and magnetic phase of ultrathin NdNiO_3 film can be engineered through various degrees of lattice mismatching between the film and substrate. Bruno et al^[12] observed that adding 1.0% compressive strain in SmNiO_3 thin film can dramatically decrease the T_{MI} by 200 K, while the addition of tensile strain does not increase the T_{MI} prominently. RE cation substitution with desired ratio alters the MIT as well. Shao et al^[13] observed that the solid solution of $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_3$ ($x=0.3, 0.4$) exhibits the tunable sharp MIT near room temperature. Xiang et al^[14] reported that 1wt%~2wt% Ca doped SmNiO_3 films of 30 nm in thickness deposited on LaAlO_3 (001) substrate shows a sharp MIT at room temperature. Similar room temperature MIT was achieved in $\text{Nd}_{0.7}\text{Eu}_{0.3}\text{NiO}_3$ films^[15]. For NdNiO_3 solid solution, the T_{MI} varies from 200 K to 400 K as Sm gradually substitutes for Nd and the $\text{Nd}_{0.45}\text{Sm}_{0.55}\text{NiO}_3$ displays a transition near room temperature. Ambrosini et al^[16] synthesized $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ (SNNO) films on (100) NdGaO_3 substrates and MIT occurs at room temperature when $x=0.6$. In addition, Lian et al^[17] prepared $\text{Sm}_{0.5}\text{Nd}_{0.5}\text{NiO}_3$ films on NdGaO_3 (100) substrates with MIT at about 300 K and illustrated that the deposi-

Received date: May 20, 2020

Foundation item: Natural Science Foundation of Anhui Jianzhu University (2019QDZ63)

Corresponding author: Yao Dan, Ph. D., Lecturer, School of Mathematic & Physics, Anhui Jianzhu University, Hefei 230601, P. R. China, E-mail: yaodan1212@ahjzu.edu.cn

Copyright © 2021, Northwest Institute for Nonferrous Metal Research. Published by Science Press. All rights reserved.

tion parameters such as oxygen pressure, substrate temperature and thickness should be well controlled to grow the film with sharp MIT transition. As for the studies above, the solid composites can only be obtained under sufficiently high pressure and high temperature, and the thin films are mainly synthesized under relatively mild conditions by pulsed laser deposition (PLD) technique. However, the high-cost and inability to coat the large area with uniform films restrict the techniques for application. In order to widen the applications, it is desirable to prepare nickelate films under ambient pressure using soft method. The ability to grow high quality epitaxial RENiO_3 thin films can also provide additional possibilities for exploring the mechanism of MIT as well as the opportunity to incorporate the functionality into new device application. There are some reports about the preparation of LaNiO_3 ^[18] and NdNiO_3 films using chemical solution deposition. However, there is few relevant reports on nickelate epitaxial films with smaller RE ions. Recently, a novel method named polymer-assisted deposition (PAD)^[19] offers a great opportunity for achieving scalable high-quality metal oxide films. In the process of PAD technique, a mixture of metal precursor and soluble polymer were used to form the aqueous solution. A solution sample with desired viscosity without gelling is then spin-coated on the smooth substrate. After anneal at proper temperature, the hybrid polymer coating decomposes to form the metal oxide films. The main advantage of this approach is that the polymer actively binds with the metal ion to prevent premature precipitation and yield a very stable and homogeneous solution. A great amount of high-quality metal oxide films can be successfully prepared using this low-cost and simple technique^[20].

In this research, epitaxial $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ ($x=0.5, 0.55, 0.6$) films on single crystal LaAlO_3 substrates were fabricated by this simple PAD method. The obtained epitaxial $\text{Sm}_{0.55}\text{Nd}_{0.45}\text{NiO}_3$ thin films exhibit not only desired crystal structure but also expected MIT near room temperature on LaAlO_3 substrates. The successful growth of high quality SNNO films with room temperature transition by PAD method shows great potential in practical application of nickelate.

1 Experiment

High purity (>99.9%) $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were employed as starting materials for SNNO precursor solution. The metal salts with stoichiometric amount were dissolved into 5 mL distilled water and stirred until clear solution was obtained. Appropriate amounts of citric acid and polyethyleneimine (PEI) were added slowly to the solution. Then the precursor solution was heated through oil bath with constant stirring until its volume was 5 mL. Finally, the solution was aged for 24 h to confirm its stability avoiding any kind precipitation and/or particle agglomeration.

The homogeneous solutions were spin-coated on (001)-oriented single-crystal LaAlO_3 (LAO) substrates with 5000 r/min. The resultant coatings were thermally heated at 800 °C for 12 h with a ramping rate of 1 °C/min under ambient atmosphere. X-Ray diffraction (XRD) using Cu K α 1 radiation (Panalytical

X'pert, $\lambda=0.15406$ nm, 40 kV and 20 mA) was used to characterize the crystal structure of the films. The thickness of the SNNO film was measured by direct observation of the field emission scanning electron microscope (FE-SEM, JSM-6700F). The electrical resistivity of the films as a function of temperature (50~325 K) was measured by standard four-probe technique.

2 Results and Discussion

2.1 Microstructure of as-prepared films

Fig. 1 shows the surface morphologies of SNNO ($x=0.55$) films grown on LAO substrate. The surfaces of these films obtained by PAD method are smooth, dense, and uniform without large voids or cracking on the substrates. Also, the thickness of the SNNO films is about 80 nm, which is characterized by cross-section SEM micrographs.

Fig. 2 shows the typical XRD θ - 2θ scan results of SNNO films grown on a LAO(001) substrate and annealed at 800 °C. The patterns confirm that no secondary phase or epitaxial growth of (001)-oriented SNNO on LAO substrate occurs. According to Vegard's rule, the expected pseudocubic lattice parameter of SNNO solid solution can be calculated from $x \times a_p(\text{SmNiO}_3) + (1-x) \times a_p(\text{NdNiO}_3)$, where the pseudocubic lattice parameter a_p for bulk SmNiO_3 and NdNiO_3 is 0.379 90 and 0.380 80 nm^[1], respectively. Therefore, the a_p for SNNO should be close to 0.380 35, 0.380 31 and 0.380 26 nm when $x=0.5, 0.55, 0.6$, respectively. The relatively small mismatch between films and substrates ($a=0.379$ 20 nm) results in coherent growth of films, which leads to the appearance of small bulges along the substrate peaks. The insets in Fig. 2 show the

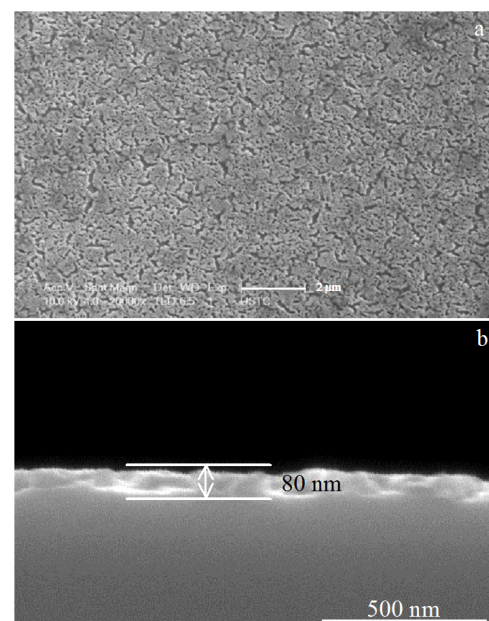


Fig.1 SEM morphologies of SNNO ($x=0.55$) films on LAO substrate (a) and the corresponding cross-section (b)

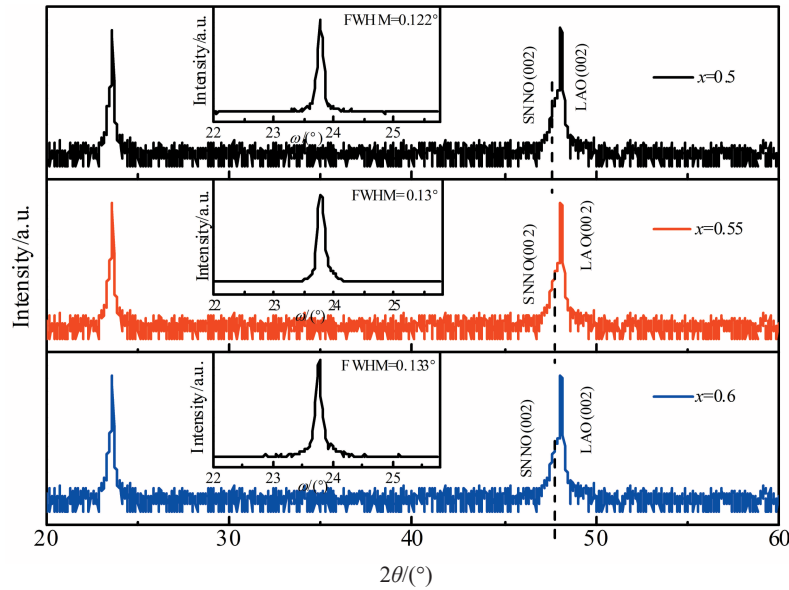


Fig.2 XRD patterns of θ - 2θ scan for $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ ($x=0.5, 0.55, 0.6$) films grown on LAO substrates (insets are related rocking curves of (002) ω -scan results; FWHM-full width at half-maximum)

rocking curves of (002) reflection of the SNNO films. The values of the full width at half-maximum (FWHM) are 0.122° , 0.130° and 0.133° when $x=0.5, 0.55, 0.6$, respectively, suggesting good crystallization of the films.

To further confirm the epitaxial property of the obtained films, representative XRD φ -scans of reflections of SNNO {110} and LAO {110} are shown in the Fig. 3. The film is aligned with the four-fold symmetry in plane. The heteroepitaxial relationship between the SNNO films and the LAO substrates can be described as (001)SNNO// (001)LAO and (110)SNNO// (110)LAO, which is consistent with the films measured by other techniques. Considering the results of θ - 2θ scans, rocking curves, and φ -scans, it can be concluded that the epitaxial SNNO films successfully grow under the compressive strains by the simple PAD method.

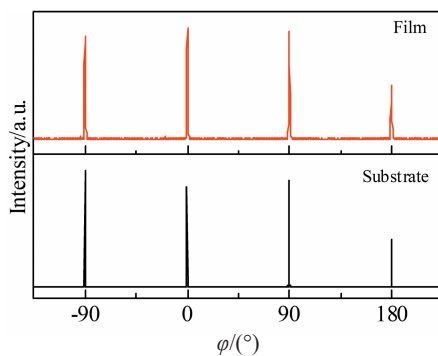


Fig.3 XRD patterns of φ -scan for (101) plane reflection of SNNO ($x=0.55$) film on LAO substrate

2.2 Electrical properties of the films

Fig.4a shows the three epitaxial thin films carried out by the standard four-probe technique with silver paste contact. The films exhibit a positive temperature coefficient of resistivity at high temperature with the metallic behavior. Below the transition temperature, all the samples exhibit temperature-dependent semiconducting behavior. Their behavior is quite similar to that of reported bulk samples^[21] and films^[16] with a clear Mott MIT. Fig.5 shows the relationship between T_{MI} and Sm content of these films. The value of T_{MI} is the temperature corresponding to the change of the slope of resistivity. T_{MI} of the solid solution increases linearly as the Sm concentration increases. It is generally accepted that T_{MI} is sensitive to the changes of Ni-O bond length ($d_{\text{Ni-O}}$) and Ni-O-Ni bond angle ($\theta_{\text{Ni-O-Ni}}$), which are modified by the lattice mismatch strain and Sm substitution. Gradual substitution of Nd by Sm decreases the Ni-O-Ni bond angles and increases the bandwidth due to the smaller radius of the Sm^{3+} ion, resulting in the insulating state. Furthermore, as to $\text{Sm}_{0.55}\text{Nd}_{0.45}\text{NiO}_3$, compared with the T_{MI} of bulk solid counterparts ($\sim 305\text{ K}$)^[21], the decrease of T_{MI} under compressive strain for the film is obvious. It is claimed that the in-plane compressive stress imposed by the LAO substrate leads to the increase of out-of-plane $\theta_{\text{Ni-O-Ni}}$, and the in-plane $\theta_{\text{Ni-O-Ni}}$ is unchanged, resulting in the stabilization of metallic phase and decrease of T_{MI} ^[22,23]. Meanwhile, the compressive strain shrinks the Ni-O bond distance which also stabilizes the metallic state. Therefore, the combined effect of variation of Ni-O-Ni angle and Ni-O distance leads to a lower T_{MI} for the films under compressive strain.

Specially, the $\text{Sm}_{0.55}\text{Nd}_{0.45}\text{NiO}_3$ film displays a transition near room temperature, indicating that this material can be used for technical applications, such as thermochromic coatings or sensors.

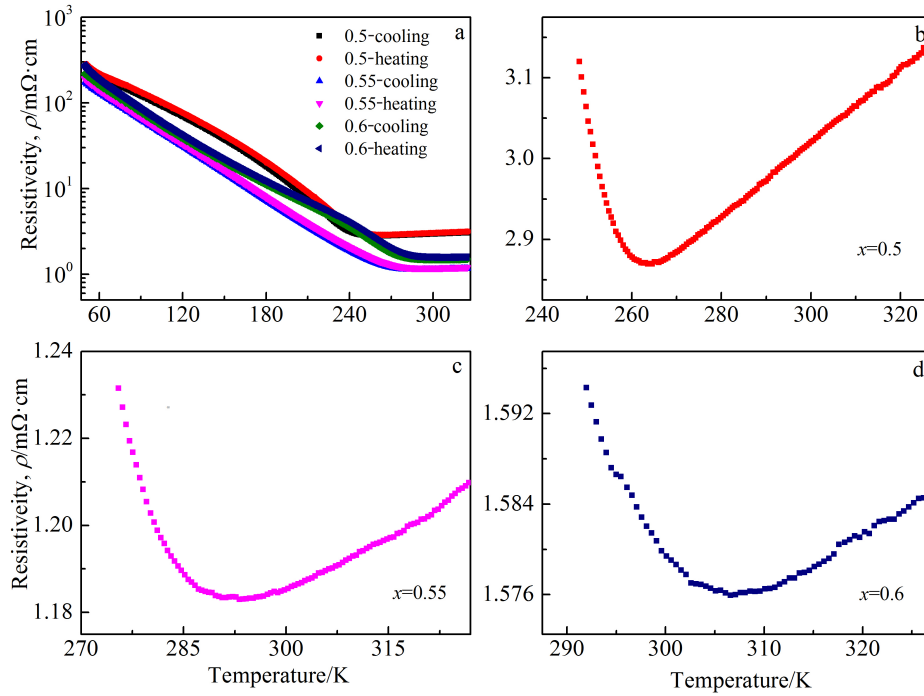


Fig.4 Resistivity versus temperature plots of SNNO ($x=0.5, 0.55, 0.6$) thin films in the temperature range of 50–325 K (a) and partial enlarged plots around the transition temperature for different SNNO films of $x=0.5$ (b), $x=0.55$ (c), and $x=0.6$ (d)

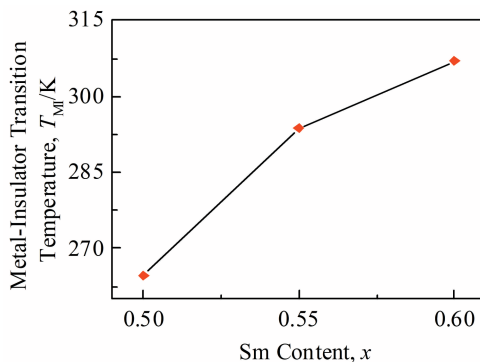


Fig.5 Relationship between MIT temperature T_{MI} and Sm content of SNNO films

The films were also deposited on SrTiO₃ (001) substrates by PAD method, but the experiment failed. The reasons need to be studied further. Currently, the oxidation state of nickel changing from 3⁺ to 2⁺ in the SmNiO₃ film under tensile strain shows great possibility as the determinable cause^[24].

3 Conclusions

1) Sm_xNd_{1-x}NiO₃ ($x=0.5, 0.55, 0.6$) thin films on single-crystal (001) LaAlO₃ substrates can be successfully fabricated by polymer-assisted deposition technique.

2) The metal-insulator transition temperature shifts to higher temperature with the increase of Sm content for

Sm_xNd_{1-x}NiO₃ thin films.

3) The Sm_{0.55}Nd_{0.45}NiO₃ film grown on LaAlO₃ substrate shows metal-insulator transition near room temperature, which offers a promising suitability for application of the thermochromic coatings.

References

- 1 Bruno F Y, Boyn S, Fusil S et al. *Advanced Electronic Materials* [J], 2016, 2(3): 1 500 245
- 2 Wang Le, Chang Lei, Yin Xinmao et al. *Applied Physics Letters* [J], 2017, 110(4): 43 504
- 3 Kiri P, Hyett G, and Binions R et al. *Advanced Materials Letter* [J], 2010, 1(3): 86
- 4 Catalano S, Gibert M, Fowlie J et al. *Reports on Progress in Physics*[J], 2018, 81(4): 46 501
- 5 Torrance J B, Lacorre P, Nazzari A I et al. *Physical Review B*[J], 1992, 45(14): 8209
- 6 Medarde M, Fontaine A, García-Muñoz J L et al. *Physical Review B*[J], 1992, 46(23): 14 975
- 7 Ramos A Y, Piamonteze C, Tolentino H C N et al. *Physical Review B*[J], 2012, 85(4): 45 102
- 8 Scherwitzl R, Zubko P, Lezama I G et al. *Advanced Materials* [J], 2010, 22(48): 5517
- 9 Catalan G. *Phase Transitions*[J], 2008, 81(7-8): 729
- 10 Meijer G I. *Science*[J], 2008, 319(5870): 1625
- 11 Ojha S K, Ray S, Das T et al. *Physical Review B*[J], 2019,

- 99(23): 235 153
- 12 Bruno F Y, Rushchanskii K Z, Valencia S et al. *Phys Rev B*[J], 2013, 88(19): 195 108
- 13 Shao Tao, Qi Zeming, Wang Yuyin et al. *Applied Physics Letters* [J], 2015, 107(2): 21 904
- 14 Xiang P H, Asanuma S, Yamada H et al. *Applied Physics Letters* [J], 2010, 97(3): 32 114
- 15 Hamet J F, Ambrosini A, Retoux R. *Journal of Applied Physics* [J], 2003, 93(9): 5136
- 16 Ambrosini A, Hamet J F. *Applied Physics Letters*[J], 2003, 82(5): 727
- 17 Lian X K, Chen F, Tan X L et al. *AIP Advances*[J], 2013, 3(6): 62 133
- 18 Chen S T, Wang G S, Zhang Y Y et al. *Journal of the American Ceramic Society*[J], 2007, 90(11): 3635
- 19 Zou G F, Zhao J, Luo H M et al. *Chemical Society Reviews*[J], 2013, 42(2): 439
- 20 Yao D, Shi L, Zhou S M et al. *Journal of Applied Physics*[J], 2016, 119(3): 35 303
- 21 Frand G, Bohnke O, Lacorre P et al. *Journal of Solid State Chemistry*[J], 1995, 120(1): 157
- 22 Xiang P H, Zhong N, Duan C G et al. *Journal of Applied Physics* [J], 2013, 114(24): 243 713
- 23 Yao D, Shi L, Zhou S M et al. *Journal of Physics D: Applied Physics*[J], 2016, 49(12): 125 301
- 24 Ha S D, Aydogdu G H, Ramanathan S. *Applied Physics Letters* [J], 2011, 98(1): 12 105

高分子辅助沉积法制备 $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ 外延薄膜

姚丹¹, 汪伟伟², 童瑞雪³

(1. 安徽建筑大学 数理学院, 安徽 合肥 230601)

(2. 合肥国轩高科动力能源有限公司 工程研究总院, 安徽 合肥 230011)

(3. 中国科学技术大学 合肥微尺度物质科学国家研究中心, 安徽 合肥 230026)

摘要: 采用高分子辅助沉积法制备掺杂不同钐 (Sm) 含量的 $\text{Sm}_x\text{Nd}_{1-x}\text{NiO}_3$ 外延薄膜 (钐掺杂量 $x=0.5, 0.55, 0.6$)。X 射线衍射 (特征 θ - 2θ 扫描、摇摆曲线和 φ -scan) 和扫描电子显微镜的测试结果表明, 制备的薄膜结晶性和外延性良好, 与衬底的 (001) 取向保持一致。电阻率-温度曲线表明制备的外延薄膜均表现出金属绝缘体转变现象。随着 Sm 掺杂量的提高, 金属绝缘体转变温度逐渐升高; 当 $x=0.55$ 时, 外延薄膜的转变温度在室温附近。并且高分子辅助沉积法可以简单有效地制备热致变色外延薄膜。

关键词: 镍酸盐; 金属绝缘体转变; 外延膜; 高分子辅助沉积法

作者简介: 姚丹, 女, 1989年生, 博士, 讲师, 安徽建筑大学数理学院, 安徽 合肥 230601, E-mail: yaodan1212@ahjzu.edu.cn