



Stable metal–insulator transition in epitaxial SmNiO₃ thin films

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ABSTRACT

Samarium nickelate (SmNiO₃) is a correlated oxide that exhibits a metal–insulator transition (MIT) above room temperature and is of interest for advanced electronics and optoelectronics. However, studies on SmNiO₃ thin films have been limited to date, in part due to well-known difficulties in stabilizing the Ni³⁺ valence state during growth, which are manifested in non-reproducible electrical characteristics. In this work, we show that stable epitaxial SmNiO₃ thin films can be grown by rf magnetron sputtering without extreme post-deposition annealing conditions using relatively high growth pressure (> 200 mTorr). At low growth pressure, SmNiO₃ is insulating and undergoes an irreversible MIT at ~430 K. As pressure is increased, films become metallic across a large temperature range from 100 to 420 K. At high pressure, films are insulating again but with a reversible and stable MIT at ~400 K. Phase transition properties can be continuously tuned by control of the sputtering pressure.

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1. Introduction

There is growing interest in investigating complex transition metal oxides for advanced electronics, such as neuromorphic circuits, nanoelectronics, and solid-state energy conversion. Among these materials, correlated oxides that exhibit a temperature-induced metal–insulator phase transition (MIT) are currently being studied. The family of rare-earth nickelates (RNiO₃, R=La, Nd, Gd, etc.) displays MI transitions for all R≠La, where the MIT temperature (T_{MIT}) increases with increasing R atomic number (decreasing cation radius) [1]. The distorted perovskite-structure RNiO₃ is insulating below and metallic above T_{MIT} , with a change in resistivity that can be several orders of magnitude around T_{MIT} . Recent work suggests that the MIT is caused by charge disproportionation ($2Ni^{3+} \rightarrow Ni^{3+\delta} + Ni^{3-\delta}$) below T_{MIT} , which opens a charge transport gap [2,3]. In the RNiO₃ series, SmNiO₃ (SNO) is the first material to have T_{MIT} above room temperature (400 K in the bulk) and, therefore, has potential for incorporation into existing semiconductor platforms.

It is known that the entire RNiO₃ series is difficult to synthesize, with high pressure oxygen annealing (> 100 bar, > 1000 K) typically required to achieve stoichiometric powders [1]. The difficulty arises because the stoichiometric Ni³⁺ valence state in RNiO₃ is metastable, with Ni²⁺ more likely to form. Pure RNiO₃, synthesized under high oxygen pressure, decomposes in air into R₂O₃ and NiO at temperatures that decrease with decreasing R cation radius (1123 K for SNO) [4]. Thin film growth by rf sputtering is also challenging, with very high sputtering background pressure (~200 mTorr) or

high pressure oxygen post-annealing required to stabilize the MIT, for example, in the related compound NdNiO₃ [5,6]. In contrast, sputtering pressures for most materials are generally in the tens of mTorr range. Stabilized SNO thin films grown by sputtering have not been demonstrated to date, to the best of our knowledge. Low pressures typically used for sputtering growth lead to an irreversible MIT in SNO, in which resistivity increases continuously for temperatures above T_{MIT} due to oxygen loss [7]. This limits interest for many applications that require recovery of the initial resistance state and further complicates fundamental physical studies. A reversible phase transition is needed for many devices, such as switches, sensors, oscillators, and photonic applications [8]. Studying the detailed physics of the MIT in thin films requires stable film properties as well. Here, we disclose high pressure (> 200 mTorr) growth of epitaxial SNO thin films with stable MIT properties. We show that modifying the deposition pressure can alter the electrical characteristics of SNO from insulating at low pressure to metallic at moderate pressure to insulating again at high pressure. In addition, we demonstrate that stable MIT characteristics of SNO, such as T_{MIT} and resistivity ratio, can be widely tuned at high pressures. Synthesis of stable SNO with straight-forward deposition procedures may contribute to greater research of fundamental physics in correlated oxides and advance exploration towards room-temperature correlated electronics.

2. Experimental

SmNiO₃ thin films were grown by rf magnetron sputtering from a sintered ceramic target in a flow of Ar and O₂ gas. The deposition temperature and target rf power were maintained at

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923 K and 200 W respectively for all deposition runs. The sputtering gas background pressure was varied from 10–400 mTorr. Film thicknesses varied from 10–100 nm, depending on sputtering pressure. Films were cooled in ambient, and no post-deposition annealing was performed. All films were grown on (001)-oriented single crystal LaAlO₃ (LAO) substrates purchased from MTI Corporation. LAO was chosen because SNO is known to grow epitaxially on LAO, thereby reducing experimental uncertainty from polycrystalline phases [9].

X-ray diffraction (XRD) was performed on a Bruker D8 Discover diffractometer system with Cu K α radiation. X-ray reflectivity (XRR) was used to calibrate film thickness. Atomic force microscopy (AFM) images were measured on an MFP-3D system from Asylum Research. Resistivity measurements were made in the van der Pauw geometry using an MMR Variable Temperature Hall System. Sputtered Pt was photolithographically patterned to define square electrical contacts.

3. Results and discussion

3.1. SmNiO₃ vs. sputtering pressure

We have measured 2θ - θ XRD patterns of SNO films grown at three different sputtering pressures from 10 to 250 mTorr. Only features related to SNO or LAO were observed from $2\theta=20^\circ$ to 80° , indicating phase purity. In Fig. 1a, we focus on the (002) pseudocubic reflection of SNO, which appears near the (002) pseudocubic reflection of LAO. In the bulk, both reflections occur at $\sim 48.0^\circ$, but due to in-plane compressive strain ($\sim -0.15\%$) in thin films, the SNO peak appears at lower 2θ angle, corresponding to higher out-of-plane lattice constant [10,11]. As a point of reference, the bulk pseudocubic c -axis lattice constant of SNO is 3.784 Å. It is clear that as deposition pressure is increased, the out-of-plane lattice constant decreases (see Table 1). Aside from epitaxial strain, the lattice constant is also affected by stoichiometry, which is a function of sputtering pressure. As oxygen content is reduced, the valence state of Ni is modified from $3+$ to $2+$, corresponding to a larger Ni ionic radius and expansion of the unit cell. Indeed, it has been reported in NdNiO_{3- δ} bulk samples that all unit cell parameters increase with increasing δ [12]. Therefore, we hypothesize that the reduction in out-of-plane lattice parameter with increasing sputtering pressure is due to an increase in oxygen concentration and increase in ratio of Ni³⁺ to Ni²⁺. The stabilization of the Ni³⁺ valence state at high sputtering pressures agrees well with the requirement of high oxygen pressure annealing for bulk powder synthesis [1].

Resistivity for each sample is plotted as a function of temperature in Fig. 1b. It can be seen that the sample grown at 10 mTorr is insulating at low temperatures and appears to exhibit a phase transition with increasing temperature at 430 K. However, upon cooling, the resistivity increases monotonically and does not follow the heating curve. This behavior cannot be characterized as hysteretic because the final resistivity after cooling is larger than the initial resistivity and is stable for days. The initial resistivity is irrecoverable. We have shown previously that this change in resistivity is due to irreversible oxygen loss induced by the MIT and that it occurs because of low oxygen concentration in films grown at 10 mTorr [7]. If the temperature is held above T_{MIT} , oxygen reduction will continue for some time and resistivity will continuously increase. In this regard, the metallic phase cannot be regarded as stable.

From Fig. 1b, films grown at 190 mTorr display markedly different electrical characteristics than films grown at 10 mTorr. Over the temperature range 200–420 K, the ρ - T plot is metallic and reversible in nature with no signature of a phase transition.

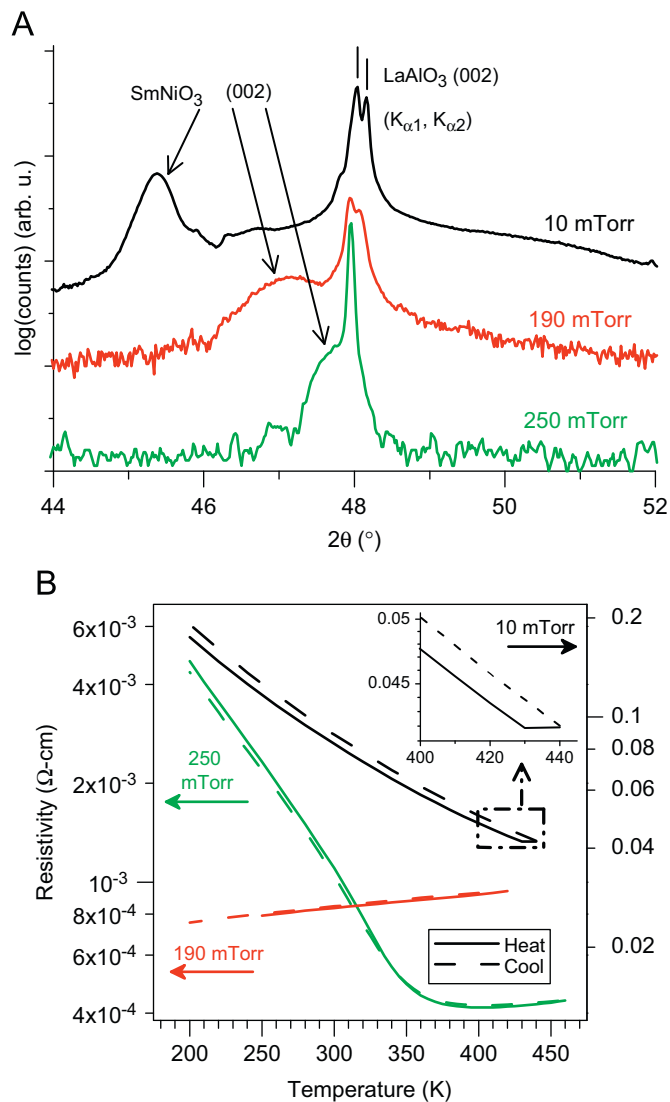


Fig. 1. (A) XRD patterns of the (002) pseudocubic reflection of SmNiO₃ films as a function of rf sputtering pressure. Plots offset for clarity. Two peaks from the (002) pseudocubic reflection of LaAlO₃ are due to contributions from Cu K α_1 and K α_2 lines. (B) ρ - T measurements of SmNiO₃ films as a function of sputtering pressure. The topmost curve corresponds to films grown at 10 mTorr and is referenced to the right hand ordinate axis. The 190 and 250 mTorr films are referenced to the left hand ordinate axis. Solid lines are data recorded during heating and dashed lines are data recorded during cooling.

Table 1

Structural and electrical properties of SmNiO₃ films as a function of sputtering pressure. Lattice constant in reference to pseudocubic structure. Transition temperature is defined as point at which $d\rho/dT$ changes sign.

Growth pressure (mTorr)	Oxygen partial pressure (mTorr)	Out-of-plane lattice constant (Å)	Electrical characteristics
10	5	4.00	Irreversible MIT at 430 K
190	38	3.86	Metallic from 100 to 420 K
250	50	3.81	Reversible MIT at 405 K

The films remain metallic down to 100 K from electrical transport measurements (see Fig. 4). The room temperature resistivity of the film grown at 190 mTorr ($8.35 \times 10^{-4} \Omega\text{-cm}$) is about 2 orders

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