Structural and transport properties of epitaxial PrNiO$_3$ thin films grown by molecular beam epitaxy


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Abstract

Epitaxial single crystal films of praseodymium nickelate (PrNiO$_3$) have been grown by molecular beam epitaxy on LaAlO$_3$(001) substrates. In-situ electron diffraction and ex-situ X-ray diffraction techniques confirm an epitaxial relationship to the underlying substrate. Crystalline quality depends strongly on the substrate temperature and activated oxygen flux during growth with the highest quality films formed at 600°C under high oxygen plasma fluxes. The metal–insulator transition for PrNiO$_3$ films was suppressed as the crystalline quality of the layers was improved.

Keywords:
- A3. Molecular beam epitaxy
- B1. Perovskites
- B1. Rare earth nickelates
- B2. Metal–insulator transition

1. Introduction

Rare-earth nickelates (RENiO$_3$), with the exception of LaNiO$_3$, exhibit a first order Mott metal–insulator (MI) transition. With the decreasing size of the rare earth element’s ionic radius, the Goldschmidt factor is continuously decreased, which results in a stronger deviation of the Ni–O bond angle from 180°, causing the MI transition to shift to higher temperatures [1,2]. The ability to grow high quality epitaxial RENiO$_3$ thin films would provide additional possibilities for exploring the physics of the MI transition as well as the opportunity to incorporate the functionality into new device structures [3,4]. In particular, recent demonstrations of an electric field controlled MI transition in NdNiO$_3$ films [4] in combination with the known effects of bulk chemical doping [5,6] suggest it may be possible to eventually develop transistors with substantial on/off ratios and high switching speeds by either switching the MI transition directly [7] or through modulation doping [8].

Unfortunately most of the rare-earth nickelates are not stable under ambient conditions and require strong oxidizing conditions to synthesize the correct crystal structure in bulk [9]. LaNiO$_3$ is the most stable representative of the rare-earth nickelates, and has been successfully incorporated into perovskite heterostructures by molecular beam epitaxy (MBE) [10,11]. Since LaNiO$_3$ does not undergo a MI transition, it is necessary to develop compatible growth capabilities for some of the more difficult to form rare-earth nickelates. Of the RENiO$_3$ compounds exhibiting a MI transition, PrNiO$_3$ has the largest RE ion radius [12] and a transition temperature of 135 K in the bulk [1].

In epitaxial thin film growth, interfacial bonding with the underlying substrate lattice along with control over the surface termination leads to greater stability of RENiO$_3$ thin films compared to bulk [13]. Epitaxial growth of PrNiO$_3$ thin films by other methods like metal organic chemical vapor deposition [14] and pulsed laser deposition [15] have required relatively high oxygen pressures, around a few hundred millitorr and higher, to push oxygen into the films and keep the films stable during growth. However, when some of these films were annealed following deposition in 1 atm of O$_2$ at growth temperature, further oxidation of the films was obtained [14]. The MI transition of these films was also found to be shifted to lower temperatures and have a correspondingly smaller change in resistivity than for bulk materials [14,15]. This paper explores the growth conditions for thin single crystal epitaxial films of PrNiO$_3$ on LaAlO$_3$(001) substrates by MBE at chamber pressures ≤ $10^{-5}$ Torr and reports on the temperature dependent resistivity of the subsequent films.
2. Experimental

A VG V80 molecular beam epitaxy (MBE) system with a base pressure of $1 \times 10^{-10}$ Torr was used to grow epitaxial films of PrNiO$_3$ (PNO) on LaAlO$_3$(001) (LAO) substrates. The lattice mismatch between the pseudo cubic phase of PNO ($a_{pc} = 3.82 \, \text{Å}$) and the in-plane lattice of the LAO substrate ($a_{th} = 3.79 \, \text{Å}$) is $-0.8\%$. Substrates were chemically degreased and then backside coated with Ta for more efficient heating during growth. The substrates were loaded into the MBE where they were heated to growth temperature under an activated oxygen flux supplied by an SVT Associates RF-plasma source. The chamber pressure is controlled by the oxygen flow into the RF-plasma source and provides a relative measure of the activated oxygen flux. The RF-plasma source has a limited dynamic range and could only sustain a plasma for chamber pressures ranging from $10^{-6}$ to $10^{-5}$ Torr.

The growth window for PNO was initially investigated with e-beam evaporated Ni and then optimized with the deposition of Ni sublimed from a high-temperature effusion cell with a BeO crucible using alternate layer epitaxy. E-beam evaporation of Ni supports higher growth rates as the Ni can be molten during deposition and any oxide formation on the surface of the source material can simply be evaporated by the e-beam and the Ni flux adjusted accordingly before opening the shutter for deposition. Furthermore, the strong oxidizing environment results in premature failure of hot filaments and e-beam filaments are much simpler and cost effective to replace than traditional effusion cell filaments. However, better flux control and uniformity can be achieved with effusion cell sources. Pr was evaporated from an effusion cell using a Ta crucible.

Alternate atomic layers of Ni and Pr were sequentially grown and annealed in activated oxygen at an effective growth rate of $\sim 50 \, \text{Å} / \text{h}$ to imitate the layer-by-layer stacking of perovskite structure along the [001] growth direction. The surface of LAO(001) substrates can either be terminated by a La–O layer or by an Al–O$_2$ layer [16]. At the growth temperatures studied, the surfaces are believed to be terminated predominately by a La–O layer [17] so the growth of the nickelate film is initiated by depositing a Ni–O first in an attempt to maintain the continuity of the perovskite structure. An ion gauge was used to monitor the fluxes from the effusion cells and the flux from the e-beam source was monitored and controlled in real-time with an Inficon Sentinel III utilizing electron impact emission spectroscopy. Rutherford backscattering spectrometry was used to calibrate the elemental flux rates and the overall sample composition was confirmed in-situ by X-ray photoelectron spectroscopy. In-situ reflection high-energy electron diffraction (RHEED) was used to monitor the surface morphology and ordering of the films during growth. Nominal film thicknesses of 120 Å were deposited. The films were all capped with a thin AlO$_x$ layer before being removed from the vacuum system to limit any degradation of the films. The capping layers were deposited at the respective sample growth temperatures and resulted in the disappearance of any discernable RHEED pattern during growth indicating they were amorphous.

Electrical transport measurements were carried out in a Quantum Design PPMS. Ohmic contacts (20 nm Ni/300 nm Au) were evaporated in a Hall bar arrangement through a shadow mask onto $3 \times 10 \, \text{mm}^2$ pieces that were cut from each specimen.

3. Results and discussion

The growth of PrNiO$_3$ thin films require high fluxes of activated oxygen in order to suppress the formation of binary oxide phases. If the oxygen chemical potential is not sufficient, the binary oxides start to form instead of the rare-earth nickelate or in addition to other ternary phases [18]. Unfortunately for MBE growth, the levels of oxygen required are close to the limits of the growth technique. Operation at chamber pressures greater than $1 \times 10^{-5}$ Torr causes significant oxidation of source materials and rapidly decreases the useful lifetime of effusion cell and ion gauge filaments. Fig. 1 compares the $\theta-2\theta$ X-ray diffraction patterns from two Pr–Ni–O films deposited on LaAlO$_3$(001) substrates at the high ($10^{-5}$ Torr) and low ($10^{-6}$ Torr) range of the RF oxygen plasma source. Both films were grown at a substrate temperature of 700 °C and deposited with an e-beam source for Ni. The films deposited at lower oxygen pressures contain well-defined out-of-plane diffraction peaks corresponding to NiO and to Pr$_2$O$_{3n-2}$ ($n > 4$). The Pr–O system has a number of stable oxides with stoichiometry between Pr$_2$O$_3$ ($n=4$) and PrO$_2$ ($n \rightarrow \infty$) with similar c-axis planar distances [19] making it difficult to directly identify the specific phase or phases in the thin film from a $\theta-2\theta$ scan like the one in Fig. 1. As the oxygen plasma pressure is increased, the intensity of the binary oxide peaks decrease and the ternary phases become more stable.

With the activated oxygen pressure limited on the high end, further increases in oxygen incorporation required a reduction in the deposition temperature. Fig. 2 contains XRD patterns comparing the structure of films deposited under an activated oxygen plasma pressure of $10^{-5}$ Torr at various growth temperatures.
The out-of-plane lattice parameter for the PNO films, based on the position the (002) diffraction peak, was found to decrease from 4.07 Å at 700 °C growth, to 3.91 Å at 650 °C and 600 °C growth, and then increase again to 3.94 Å at 550 °C growth. From the position and width of the PNO (002) diffraction peak, the ideal growth temperature was found to be around 600 °C. The shift to larger angles for the PNO (002) peak (smaller lattice parameter) in 600 °C grown films suggests the oxygen concentration is moving closer to stoichiometry. Poor ordering of the films or low oxygen incorporation leads to larger lattice parameters due to the Coulomb repulsion of the ions. Further decreases in the substrate temperature below 600 °C produces a broadening of the PNO (002) peak and a shift back towards larger planar distances.

In an attempt to further improve the quality of the PNO films, an effusion cell was subsequently used for Ni under the high oxygen plasma flux and 600 °C substrate growth conditions. A typical XRD pattern corresponding to these PNO films is shown in Fig. 3. The out-of-plane lattice parameter was measured to be 3.88 Å, which is consistent with a PNO film grown under compression on an LAO substrate. Thickness fringes around the (002) peak confirm the improvement in film quality and are consistent with the deposited film thickness. In-situ RHEED patterns, shown in Fig. 4, also confirm these films are smooth and well ordered.

Fig. 4(a) shows the RHEED pattern obtained from the LAO substrate along the [010] just prior to growth of the nickelate. Alternating layers of Ni–O and Pr–O are deposited sequentially by opening and closing shutters in front of the Ni and Pr sources until the desired thickness is achieved. The PNO film can thus be terminated following either a Ni–O or a Pr–O layer. Fig. 4(b) and (c) show the RHEED images along the [010] of a completed PNO film at growth temperature for both a Ni–O termination and a Pr–O termination. Both terminations appear stable at growth conditions and show strong diffraction patterns. The Ni–O termination shows weak additional half order streaks in the RHEED indicating there is some form of 2 \times 2 surface ordering, which is not observed for the Pr–O surface termination.

Fig. 5 contains a plot of the PNO film resistivity versus temperature for three different growth conditions. The measurement temperature was swept in both directions with no hysteresis being observed. The lowest film resistivities correspond to the films with the smallest FWHM in the PNO (002) diffraction peaks. The best quality films have a room temperature resistivity of 2.5 \times 10^{-4} Ω cm and display metallic-like behavior with a resistivity falling to 8 \times 10^{-5} Ω cm at 4 K. This resistivity is slightly lower than values reported for bulk material [20] and is another indication the films are fully oxidized [21,22].

The film with the highest resistivity in Fig. 5 shows a minimum in the resistivity at 85 K consistent with what one might expect to occur at a MI transition. However, the XRD PNO (002) peak for this film has the largest FWHM of the three films and has the largest lattice spacing suggesting that it is poorly ordered or slightly off composition. It is possible that the upturn in resistivity at low temperature in this sample is due to disorder, rather than the Mott transition. The suppression of a MI transition for the highest quality films is attributed to the lattice distortions induced by the in-plane compressive strain due to the epitaxial alignment of the PNO films to the smaller underlying LAO substrate [20]. Unpinning the film from the substrate may enable a transition to be observed, if the perovskite structure can be stabilized; however, it may be possible to use appropriate substrates to manipulate the strain in rare-earth nickelates and
correspondingly the Ni–O bond angles to control the MI transition temperature.

Hall effect measurements on the films indicated p-type conduction dominates, as expected for PNO in the metallic state where a broadened oxygen p-like valance band closes the charge-transfer gap [23]. The magnitude of the Hall coefficient was found to increase from \(6.0 \times 10^{-5} \text{ cm}^2/\text{C} \) at room temperature to \(2.25 \times 10^{-4} \text{ cm}^2/\text{C} \) at 4 K. Direct interpretation of the Hall coefficient in terms of a single carrier density is not appropriate due to a complex Fermi surface of the RENiO\(_3\) compounds, which contain both electron- and hole-like regions [24]. However, similar trends in the temperature dependence of the Hall coefficient have been seen in sputter deposited metallic films of LaNiO\(_3\) [25].

4. Conclusions

Single crystal PrNiO\(_3\)(001) films have been grown by MBE on LaAlO\(_3\)(001) substrates using elemental sources. The quality of the films depends strongly on the substrate temperature and activated oxygen pressure with the highest quality films forming at 600°C under the most oxygen rich conditions the MBE system could withstand (\(< 5\) Torr background pressure). The resistivity of the PrNiO\(_3\) films decreased as their crystalline quality increased with the highest quality films demonstrating metallic behavior and a room temperature resistivity of \(2.5 \times 10^{-4} \Omega \text{ cm} \). A MI transition was not observed for epitaxial growth on LaAlO\(_3\)(001) substrates.

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