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A study of the electronic states of $Ni_xMn_{3-x}O_{4+\delta}$ thin films using scanning tunneling microscopy and current imaging tunneling spectroscopy

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Abstract

$Ni_xMn_{3-x}O_{4+\delta}$ ($0.4 \leqslant x \leqslant 1$) are a series of spinel structured materials exhibiting negative temperature coefficient of resistance (NTCR) characteristics. Thin films were produced on <100> silicon substrates using rf magnetron sputtering in an oxygen/argon atmosphere (2.5% oxygen). Following deposition, the films were annealed at 800 °C in air and the crystalline structure studied using X-ray diffraction. Scanning tunneling microscopy (STM) was used to study the topology of the layers in both the as-deposited and annealed states. Annealing resulted in a more uniform and ordered structure. Tunneling conductance (dI/dV vs V) and normalised tunneling conductance $\{(dI/dV)/(1/V)$ vs $V\}$ characteristics were measured and used to generate conductance maps $\{dI/dV\ (x,y,eV)\}$ and to study the local density of states (LDOS) of the film surface. The tunneling conductance maps showed islands of bright contrast in an otherwise relatively uniform background of dark contrast. There were substantially fewer bright contrast islands in annealed films and they appear to bear no relation to any topographical features. The distribution of the LDOS in the bright regions was similar to that normally associated with metallic behaviour, while in the regions of dark contrast, the LDOS was more characteristic of semiconductors (LDOS ~0 at Fermi level). The resistance–temperature characteristics were measured and found to be consistent with conduction models based on electron hopping.

Keywords: Nickel manganate; NTCR; Spinel; STS; Variable range hopping

1. Introduction

Nickel manganese oxides with the general formula $Ni_xMn_{3-x}O_{4+\delta}$ ($0.4 \leqslant x \leqslant 1$), owing to their large temperature dependent resistivity,[1] have been used as temperature sensors and other thermistor based devices for over thirty years. $Ni_xMn_{3-x}O_{4+\delta}$ are cubic spinel structured materials and the electrical conductivity is believed to be dependent on electrons hopping from Mn^{3+} to Mn^{4+} in the octahedral lattice sites. Consequently the conductivity is dependent on the ratio of the trivalent and tetravalent manganese ions in the material. The conductivity,[2] optical[3] and physical[4] properties of such material have been widely studied in bulk and to a lesser extent, in thin film forms but the electronic structure has remained largely unresearched. Recently Basu et al.[5] reported the parabolic nature of the distribution of the LDOS of the material using scanning tunneling spectroscopy (STS). In the present work thin films of $Ni_xMn_{3-x}O_{4+\delta}$ were produced by rf magnetron sputtering and electronic states were studied using STS.

2. Experimental

Thin films of $Ni_xMn_{3-x}O_{4+\delta}$ were deposited on <100> silicon using a custom built rf magnetron sputtering system fitted with a 33mm diameter MiniMak cathode. The target was made by mixing nickel and manganese oxide precursors in the molar ratio of 1:1.22. The powder was pressed into a 2–3 mm thick disc of 35 mm diameter, which was then sintered at 1200 °C for 24 h, annealed at 800 °C for 40 h and quench cooled to room temperature. The procedure is described in greater detail elsewhere[6] The sputtering was carried out in an argon/oxygen (2.5% oxygen) ambient with a pressure of $\sim 5 \times 10^{-2}$ mbar at a substrate temperature of 35 °C and

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with a substrate to target distance of 35 mm. The films were then annealed in an air oven at 800 °C for 1 h and subsequently quenched to room temperature. The film topography and the STS measurements were carried out in an ultra-high vacuum using an Omicron VT-AFM/STM. The measurements were carried out on every pixel over an area of 300×300 nm^2, which was divided into 256×256 pixels. Tips were prepared by mechanically sectioning a platinum/iridium wire. The experimental parameters chosen for the STS measurements were 1V bias and 0.2nA tunneling current and the energy range of the spectroscopy was $+/-$ 2eV. In current imaging tunneling spectroscopy (CITS), the (I/V) curves were recorded simultaneously in a constant current mode by the interrupted-feed-back-loop technique.[7] Based on these measurements the first derivative (dI/dV) was calculated. Normalisation of the spectra were carried out using the method proposed by Feenstra,[8] where the differential conductance is divided by the total conductance $\{(dI/dV)/(I/V)\}$. Both the normalised curves and the conductance map, which is a representation of the local density of states at a particular energy, are presented. The resistance versus temperature (R–T) measurements was carried out in air ranging from room temperature up to 200 °C in a custom-built furnace using a Microcal temperature controller. The resistance was measured using a Kiethley 617 electrometer. Contacts were fabricated by evaporating aluminium on to the surface. These were then covered with silver paste.

3. Results and discussion

The topology of an as-deposited sample is shown in Fig. 1(a) and the corresponding conduction map at Fermi level is shown Fig. 1(b). At Fermi level the brighter regions (b) represent areas with higher LDOS compared to that of the darker areas (a) and would therefore be expected to be more conductive. The map clearly shows that the electronic structure of the film surface was not homogeneous. Comparison of Figs. 1(a) and (b) also indicates that the inhomogenity cannot be attributed to any topological feature of the surface and it must be assumed that the bright contrast regions are either due to surface defects or to the different stoichiometry of the material. Topology and conductance maps of films annealed at 800 °C are shown in Fig. 2(a) and (b) respectively. Again the conductance maps show regions with bright and dark contrast, but the areas

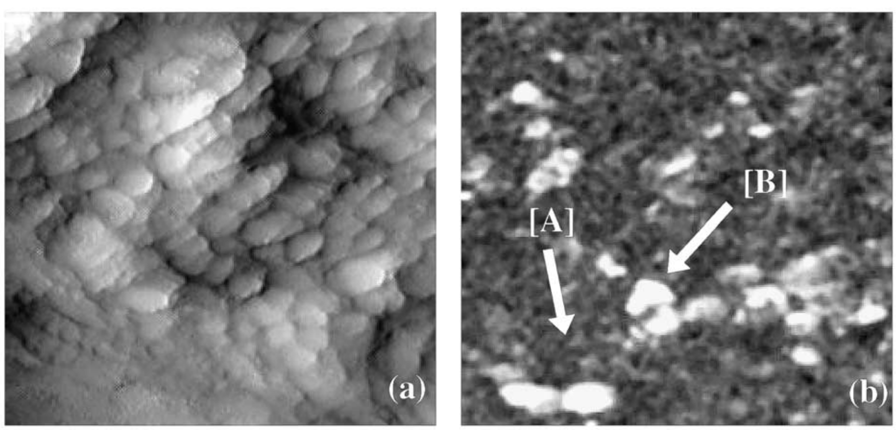

Fig. 1. (a) Topology of as-deposited film (300×300 nm); (b) conductance map of as-deposited film (300×300 nm).

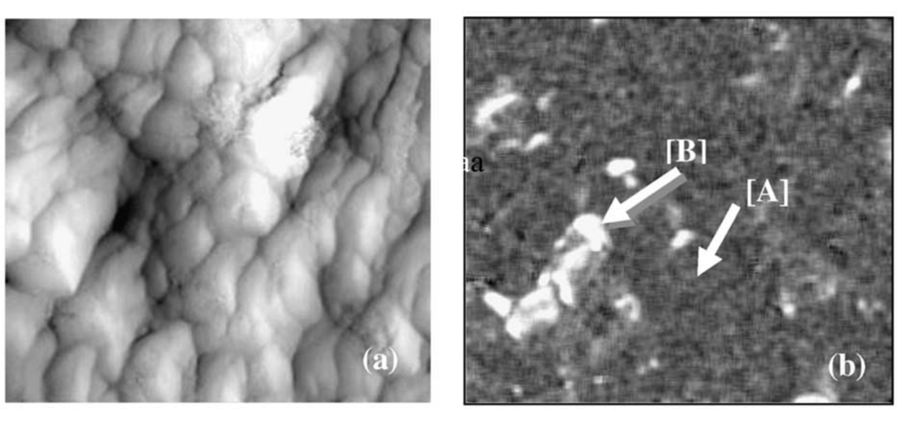

Fig. 2. (a) Topology of film annealed at 800 °C (300×300 nm);(b) conductance map of annealed film (300×300nm).

with bright contrast are far less abundant than in the as-deposited films. Although the results presented here are for a very small area (300×300 nm), they were representative of the whole surface. Different parts of the films were investigated and similar results were found. The topography of the films after annealing changed to a more ordered structure, but no significant grain growth was observed. X-ray diffraction studies indicated that annealing resulted in a monophase cubic spinel material compared to a rather amorphous/nanocrystalline structure in the as-deposited state.

The normalised conductance spectra, which show the shape of the LDOS of the material, are given in Fig. 3(a) for an as-deposited layer and in Fig. 3(b) for an annealed layer with [B] representing the dark regions and [A] the bright islands of the film. The shape of the LDOS of the bright regions in the conductance maps in Figs. 3(a) and (b) showed a high Fermi level LDOS, characteristic of metals. In contrast, the shape of the LDOS for the dark regions showed a typical semi-conducting behaviour where the LDOS at Fermi energy was almost zero. The higher contribution of bright (high density of states) regions in the as-deposited layers would suggest that these films should have been the more conducting. That they were not so, as confirmed from $R-T$ measurements, implies that the bright regions were not contiguous (i.e. percolation paths) and/or that there were some potential barriers to current flow between the two types of surfaces. The shapes of the LDOS of the as-deposited and film annealed at 800 °C were different. The shape of the LDOS was much narrower for annealed film compared to the film in the as-deposited state. Additionally, different features could be seen in the dark region spectra of both types of layer. In the as-deposited films, this took the form of a small minimum located just above the Fermi energy, which after annealing became a small maximum at approximately the same energy. The significance of these features is as yet unknown, but is the subject of continuing study.

The resistance of the films was measured in air as a function of temperature (T) and shows typical NTCR characteristics. In both instances conduction can be described by the variable range hopping model[9] where the resistivity of the material is expressed by

$$\rho = \rho_0 T \exp(T_0/T)^{0.5} \quad (1)$$

where $T_0 = \beta_1 e^2/k_b \kappa a_0$, ρ_0 is a scaling factor, $\beta 1$ is a numerical factor and is given as 2.8,[9] e is the charge of an electron, k_b is Boltzmann constant, κ describes the

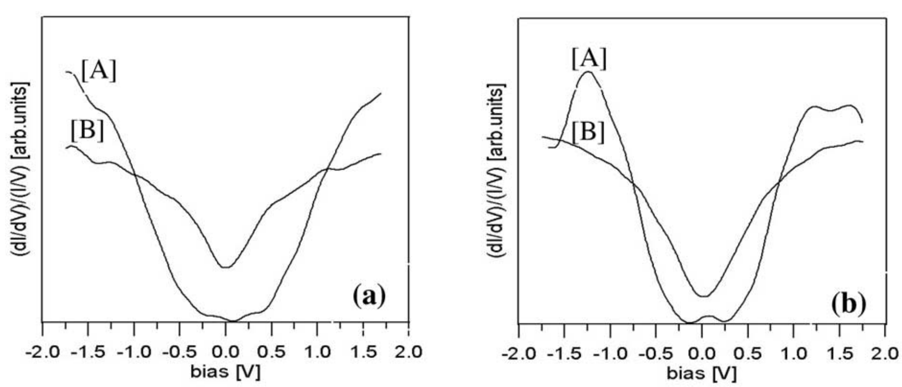

Fig. 3. (a) STS spectra of as-deposited film; (b) STS spectra of annealed film.

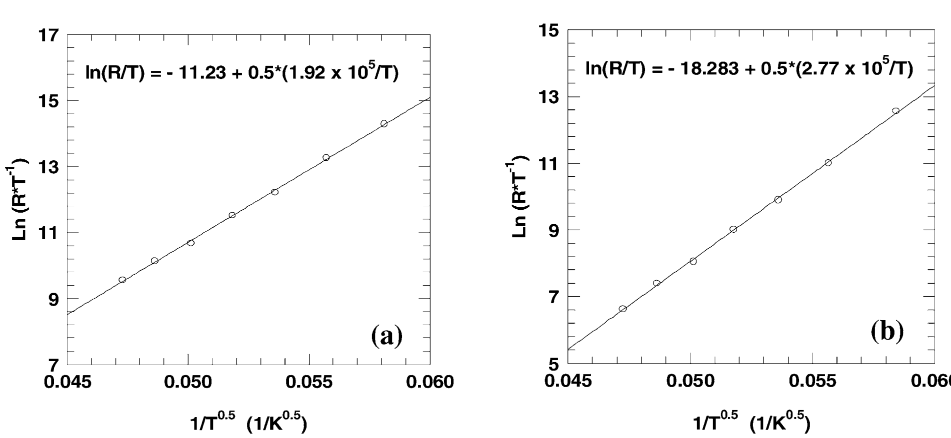

Fig. 4. (a) R–T data of as-deposited film; (b) R–T data of annealed film.

coulomb interaction between the electrons and a_0 is the Bohr's radius of hydrogen atom. The data in both as-deposited and annealed states fitted the model as shown in Figs. 4(a) and (b). The T_0 value increased after annealing, implying a reduction in the $\kappa^* a_0$ product, the effective radius.

The resistivity of the films decreased from ~2900 ohm cm at 50 °C in the as-deposited state to ~310 ohm cm after annealing.

4. Conclusions

Films of $Ni_xMn_{3-x}O_{4+\delta}$ have been produced using rf magnetron sputtering in an oxygen (2.5%)/argon ambient. The electronic structure of the film surface appeared to be inhomogeneous with some areas displaying metallic behaviour and others more semiconducting characteristics. Annealing at 800 °C in air made the material more uniformly semiconducting but some inhomogenity can be still observed. Since the inhomogenity cannot be correlated with topological features, it is assumed that they are associated with variations in the stoichiometry induced during the deposition process. The shape of the LDOS and *R–T* measurement suggested that the conductivity of the semiconducting parts was higher in the case of annealed films. The *R–T* data could be fitted to a variable range hopping model, where the T_0 value increases after annealing The shape of the LDOS was parabolic in agreement with the Shklovskii and Efros variable range hopping model.

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