Available online at www.sciencedirect.com
SCIENCE DIRECT
ECERS
Journal of the European Ceramic Society 24 (2004) 1247–1250
www.elsevier.com/locate/jeurceramsoc

Effect of oxygen partial pressure on the NTCR characteristics of sputtered $Ni_xMn_{3-x}O_{4+\delta}$ thin films

A. Basu*, A.W. Brinkman, R. Schmidt

Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK

Abstract

$Ni_xMn_{3-x}O_{4+\delta}$ are ceramic materials with a spinel structure exhibiting a negative temperature coefficient of resistivity (NTCR). This inherent property makes this class of material ideally suited for temperature sensing applications. Films of $Ni_xMn_{3-x}O_{4+\delta}$ were deposited on oxide coated <100> silicon (SiO_x), using rf magnetron sputtering in an oxygen/argon atmosphere with different oxygen partial pressures (0.3, 1, 2.5, 5, 7.5, 10, 12.5, 15 percent oxygen). A first set of films were annealed in air at 800 °C for 1 h and quenched to room temperature. A second set of films were annealed in an atmosphere similar to that used during deposition (oxygen/argon), at 800 °C for 1 h and quench cooled to room temperature. The resistance versus temperature as measurements were done from room temperature up to 200 °C and the data fitted to a variable range hopping model where the resistivity can be expressed as $\rho_0 T\exp(T_0/T)$. The characteristic temperature T_0 (range $\sim 1.9\times10^5$–2.42×10^5 K) of the films was not noticeably different from the target material, with exception of the films deposited at low oxygen partial pressure, which showed higher values of T_0 ($\sim 3.1\times10^5$ K). The resistivity of the as-deposited films was dependent on the oxygen percentage in the ambient during sputtering, such that the resistance decreased with increasing oxygen. On annealing independent of the ambient, the resistivity of the films decreased considerably (~300 ohm cm). The films produced in ambients with higher oxygen had a resistivity in the as-deposited state similar to that of the annealed films and showed least variation on annealing.
© 2003 Elsevier Ltd. All rights reserved.

Keywords: Nickel manganate; NTC; Spinel; Sputtering

1. Introduction

Spinel structured $Ni_xMn_{3-x}O_{4+\delta}$ ($0.4\leqslant x\leqslant 1$) exhibits an exponential dependence of resistance on temperature, where the resistance of the material decreases with increasing temperature.[1] This negative temperature coefficient (NTCR) property makes it suitable to be used as temperature sensors (thermistor). The spinel structure is based on oxygen atoms forming a fcc structure containing tetrahedral and octahedral lattice sites.[2] The electrical charge transport in this material is believed to be by hopping of electrons between Mn^{3+} and Mn^{4+} ions present in the octahedral sites in the lattice.[3] Hence the resistivity (ρ) of the material is dependent on the ratio of the manganese ions in the octahedral sites and can be expressed as[4]

$$\rho = \rho_0 T^{2p}\exp\left(\frac{T_0}{T}\right)^p \tag{1}$$

where ρ_0 is a constant, T_0 is the characteristic temperature of the material and p is a constant, which is dependent on the initial assumption about the distribution of density of states around the Fermi level made in the electron hopping model. In this case $p=0.5$ following the variable range hopping model developed by Shklovskii and Efros,[5] assuming the distribution of LDOS to be parabolic as demonstrated by Basu et al.[6] using scanning tunnelling spectroscopic measurements. In this study, thin films of the material were deposited using rf magnetron sputtering at various argon/oxygen ambients, followed by annealing at 800 °C in different environments. The resistance of the films was measured as a function of temperature for both as-deposited and annealed films and the effect of the different growth conditions and annealing discussed.

2. Experimental

The films (~600 nm) were produced on thermally grown oxide on <100> silicon substrate, using a custom built rf magnetron sputtering system at various

* Corresponding author.
E-mail address: arnab.basu@durham.ac.uk (A Basu).

0955-2219/03/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/S0955-2219(03)00380-7

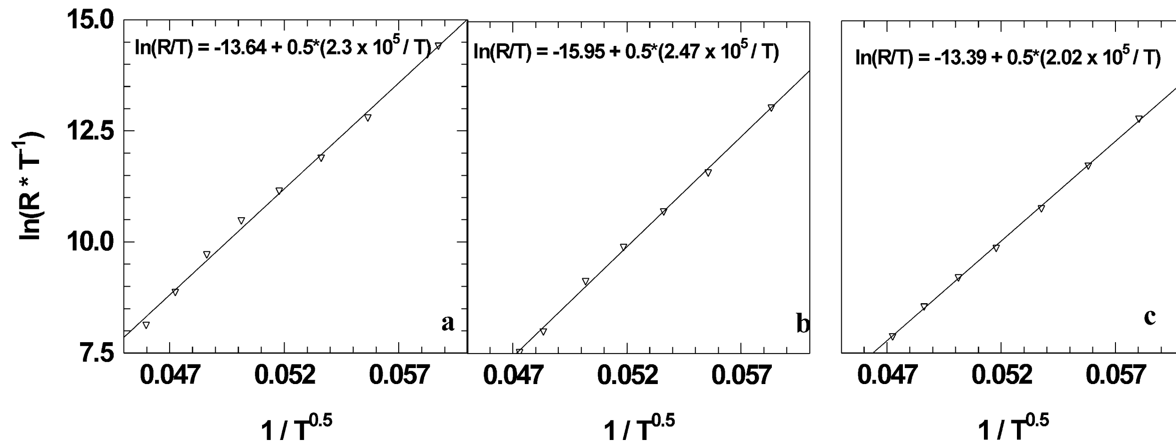

Fig. 1. R–T data fitted to the Shklovskii and Efros model of film deposited at 5% (a) as-deposited, (b) annealed in air and (c) annealed in nominally the same ambient as during sputtering.

argon/oxygen ambients (oxygen = 0.3, 1, 2.5, 5, 7.5, 10, 12.5 15%) with the substrate at a temperature of 35 °C and a power density of 3 W cm^{-2}. The oxide on the <100> silicon was produced by heating the silicon at 1100 °C for 15 h in a Lenton air oven. The oxygen percentage in the sputtering ambient was controlled using mass flow controllers and checked using an in-line Anacon oxygen sensor. The target was prepared from oxide precursors using conventional ceramic powder processing technique. One set of films was subjected to annealing at 800 °C in a Carbolite air oven for 1 h followed by quenching to room temperature. Another set of films were annealed at 800 °C for 1 h in a custom built furnace fitted with a Eurotherm 810 temperature controller, in the same ambient as that used during deposition, and quenched to room temperature. A pair of aluminium contacts was evaporated on the surface of the films and covered with silver paste to prevent oxidation. Resistance versus temperature (R–T) measurements were done in a furnace equipped with a Microcal temperature controller. The resistance was measured using a Kiethley 617 electrometer. An Alpha step profilometer was used to measure the thickness of the films.

3. Results and discussions

The R–T characteristics for all films were fitted to Eq. (1), with $p = 0.5$. Fig. 1 shows the plot of $\ln(RT^{-1})$ vs $T^{-0.5}$ for films deposited at 5% oxygen ambient; in the as-deposited state (a), after annealing at 800 °C in air (b) and after annealing at 800 °C in a nominally the same ambient as during sputtering (c). In this model T_0 is expressed as [5]

$$T_0 = \frac{B_1 e^2}{k_b \kappa a_o} \quad (2)$$

where $\beta_1 = 2.8 \pm 1.2$ is a numerical factor which is determined by solving the appropriate percolation problem, k_b is the Boltzmann constant, e is the charge on an electron, κ describes the Coulomb interaction between the electrons and a_0 is the Bohr radius. Here $\kappa = \varepsilon_0 \varepsilon_r 4\pi$, where ε_0 is the permittivity of free space and ε_r is the relative permittivity of the material. The product $a_0 * \varepsilon_r$ gives the effective radius of an atom of the material. T_0 values of films, in as-deposited and annealed states, deposited in different oxygen containing ambients are shown in Fig. 2 and listed Table 1. The results showed that the T_0 values of the films, irrespective of the deposition or annealing conditions, were similar to that of the target ($T_{0(\mathrm{Target})} = 2.12 \times 10^5$ K). The films annealed in air showed slightly higher values of T_0 whereas the films annealed in argon/oxygen ambient showed marginally lower values of T_0 compared to that of the target. This would imply that the

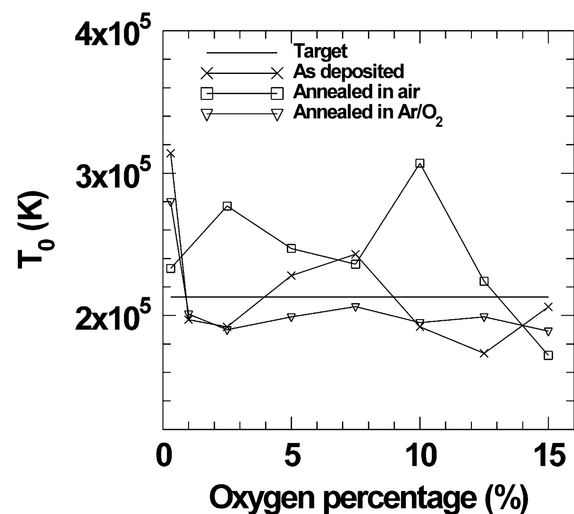

Fig. 2. Variation of T_0 of films deposited at various Ar/O_2 mixed ambients in as-deposited and annealed state.

Table 1
Values of T_0 of films in as-deposited and annealed state

Annealing conditions	To ($\times 10^5$ K) values of films sputtered at different oxygen containing ambient							
	0.3%	1%	2.5%	5%	7.5%	10%	12.5%	15%
As-deposited	3.13	2.01	1.92	2.27	2.42	1.91	1.72	2.05
Annealed in air	2.33	1.96	2.76	2.47	2.36	3.07	2.35	1.72
Annealed in ($Ar+O_2$) ambient	2.79	2.34	1.91	2.02	2.06	1.95	1.98	1.89

effective radius of the material of thin films is similar to that of the bulk $Ni_xMn_{3-x}O_{4+\delta}$. Films annealed in an ambient similar to that used during deposition, showed the least variation in T_0 with the deposition conditions (i.e. oxygen percentage in the ambient). Interestingly the films deposited in lower oxygen environments (0.3% oxygen) showed a higher value of T_0. The effect of the thickness variation on the electrical properties have not been investigated in the present study.

The resistivity of the films at 50 °C ($\rho_{(50)}$) was calculated using the film thickness and results are shown in Fig. 3. Following annealing in either air or in argon/oxygen mixed ambients, $\rho_{(50)}$ was nearly an order of magnitude lower than that of the target material ($\rho_{(50)\text{Target}}=1300$ ohm cm). The as-deposited films grown at lower oxygen percentages had higher resistivities ($\rho_{(2.5\%\ \text{Oxygen})}=2930$ ohm cm), though the as-deposited resistivity decreased with increasing oxygen percentage and at 12.5 and 15% their resistivity had become comparable to that of the annealed films. Films annealed at 800 °C in the same ambient as that used during sputtering, showed relatively little variation in resistivity with deposition and annealing environment, only increasing by a factor of ~2 as the oxygen fraction was increased from 0 to 15%. Dannenberg et al. [7] reported similar dependency of resistivity on the oxygen content (oxygen <0.1%) in the environment during sputtering, but did not carry out a post deposition annealing at the temperature used in this study.

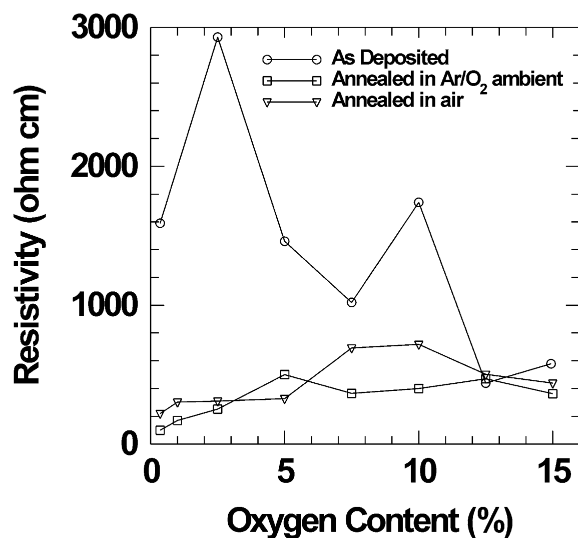

Fig. 3. Variation of resistivity at 50 °C of films deposited in different Ar/O_2 mixed ambients in as-deposited and annealed state.

The above results showed that the resistivity of the as-deposited films was strongly dependent on the percentage of oxygen in the sputtering environment. This was possibly due to a change in the oxygen stoichiometry of the films, resulting in an alteration of the ratio of Mn^{3+} to Mn^{4+} ions. Annealing in air or in an argon/oxygen mixed environment reduced the resistivity, which again implied a change in the oxygen stoichiometry, as loss of either nickel or manganese at such a low temperature was unlikely. Partial and/or inhomogeneous oxidation of the material in the as-deposited state was probably the cause of the higher resistivity of films deposited at lower oxygen percentages. On annealing oxygen diffused into the material, resulting in a more optimum ratio of Mn^{3+} to Mn^{4+}. However, annealing had very little effect on the resistivity of the films deposited at higher oxygen percentages, presumably there was sufficient oxygen present in the sputtering environment to ensure a more fully oxidised material. The films in general had a lower resistivity than the target which possibly could be due to a different ratio of the manganese ions in the octahedral sites or possibly due to the absence of porosity resulting in a better intergrannular contact. However neither of these could be confirmed within the scope of this study.

4. Conclusions

Thin films of $Ni_xMn_{3-x}O_{4+\delta}$ were produced which exhibited NTCR properties, with characteristic temperatures similar to that of the target material. Increasing the oxygen content in the sputtering environment reduced the resistivity of the material in the as-deposited state, indicating a variation of oxygen stoichiometry. Post deposition annealing in air or in an environment similar to that during sputtering, produced films with a resistivity that was less dependent on the growth environment. The resistivity of those films was nearly an order of magnitude lower than that of the bulk target, possibly due to the absence of porosity.

Acknowledgements

A Basu wishes to acknowledge the financial support provided by University of Durham and the provision of Overseas Research Scholarship (ORS)

References

1. Schmidt, R., Stiegelschmitt, A., Roosen, A. and Brinkman, A. W., Preparation and performance of thick film NTC thermistors. *Key Engineering Materials*, 2002, **206–213**, 1417–1420.
2. Koller, A., ed., *Structure and Properties of Ceramics. Materials Science Monographs 80*. Elsevier, Amsterdam, 1994.
3. Macklen, E. D., *Thermistors*. Electrochemical Publications, Glasgow, 1979.
4. Mansfield, R., Hopping conduction in III-V compounds. In *Hopping Transport in Solids*, ed. M. Pollak and B. Shklovskii. Elsevier Science, Amsterdam, 1991.
5. Shklovskii, B. I. and Efros, A. L., *Electronic properties of doped semiconductors. Solid State Sciences 45*. Springer-Verlag, Berlin, 1984.
6. Basu, A., Brinkman, A. W., Klusek, Z., Datta, P. K. and Kowalczyk, P., In situ study of the effect of temperature on the electronic structure of $Ni_xMn_{3-x}O_{4+d}$ thin films using scanning tunnelling spectroscopy. *Journal of Applied Physics*, 2002, **92**(7), 4123–4125.
7. Dannenberg, R., Baliga, S., Gambino, R. J., King, A. H. and Doctor, A. P., Resistivity thermopower and the correlation to infrared active vibrations of $Mn_{1.56}Co_{0.96}Ni_{0.48}O_4$ spinel films sputtered in an oxygen partial pressure series. *Journal of Applied Physics*, 1999, **86**(1), 514–523.