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COMMUNICATIONS

PROPERTIES OF SPUTTERED NiO THIN FILMS

Ivan Hotovy * — Jozef Liday * — Helmut Sitter ** — Peter Vogrinčič *

Nickel oxide (NiO) thin films were deposited on unheated Si substrates by reactive d.c. magnetron sputtering. A pure metallic nickel target was sputtered in a mixture of argon and oxygen. The oxygen content in the gas mixture was changed in the range from 20 to 44 %. After deposition the prepared NiO films were annealed at 500 °C for 8 hours in dry air. The films were characterized by X-ray diffraction (XRD), Auger electron spectroscopy (AES), and atomic force microscopy (AFM). Only as-deposited films in the metal-sputtering mode are crystalline. Annealing in dry air gives rise to crystalline phases in all samples. All examined NiO films were semiconductors and their conductance increased by four orders of magnitude between 25 and 350 °C.

K e y w o r d s: nickel oxide, thin films, reactive magnetron sputtering

1 INTRODUCTION

Interest in nickel oxide thin films is growing fast due to their importance in science and technology. NiO is an attractive material for use as antiferromagnetic layers [1], p-type transparent conducting films [2], in electrochromic devices [3] and as a functional sensor layer for chemical sensors [4]. In the bulk, NiO has a cubic (NaCl-type) structure with a lattice constant of 0.4195 nm. Also, NiO is a good candidate for p-type semiconductor films due to its wide band gap energy from 3.6 to 4.0 eV. Thin films of NiO have been fabricated by various physical and chemical vapour deposition techniques such as reactive sputtering and plasma-enhanced chemical vapour deposition. The obtained layers showed chemical stability as well as excellent optical and electrical properties. It is well known that the structural properties, composition and surface morphology of materials in thin film form depend on the used deposition techniques, deposition conditions and post-deposition processing. These properties for metal oxide films have become of great interest in the last few years. In particular, the field of gas sensors has benefited from the production of materials characterized by a high surface to volume ratio [5]. The gas-sensing properties of metal oxides are more or less related to the material surface, its high porosity and the microstructure with smaller particle size.

In this paper the influence of the oxygen content in the gas mixture and of the post-deposition annealing on the structural properties, composition, surface morphology and conductance of NiO thin films is studied. Throughout these investigations, the aim was to find the correlation between process parameters and physical properties of NiO layers.

2 EXPERIMENTAL DETAILS

The NiO films were deposited by DC reactive magnetron sputtering from a Ni target (101.2 mm in diameter, thickness of 3 mm, and 99.95 % pure) in a mixture of oxygen and argon onto unheated Si substrates. The distance between the target and the substrate was approximately 75 mm. The apparatus was evacuated to a pressure below 5×10^{-4} Pa before deposition. A sputtering power of 600 W was used. Both argon inert flow and oxygen reactive flow were controlled by mass flow controllers. The relative partial pressure defined as $\xi = p(O_2)/p(O_2 + Ar)$ was varied from 20 to 60 %. The total gas pressure was kept at 0.5 Pa. NiO films were prepared in two operation modes: metal-sputtering mode and oxide-sputtering mode. Details of these modes have been given elsewhere [6]. Before deposition, the target was pre-sputtered to remove contaminants. The sputtering conditions are listed in Tab. 1.

The film thicknesses under the above conditions were 100–150 nm and were measured by a Talystep. The films were annealed in the furnace at temperature 500 °C in dry air for 8 hours. The crystal structure was identified with a Theta 2 Theta Diffractometer D 5000 with a Goebel mirror into Bragg-Brentano focusing with Cu K_α radiation. The homogeneity of the depth distribution of elements and the purity of NiO layers were studied by Auger electron spectroscopy (AES). The analysis was carried out in a Varian system equipped with a CMA. A primary electron beam was used with energy 3 keV, diameter about 10 μm and angle of incidence 15° to the sample normal. The energy of the Ar^+ ion beam employed to sputter-etch the sample was 1 keV, energy resolution of the CMA was 0.3 %. The surface morphology

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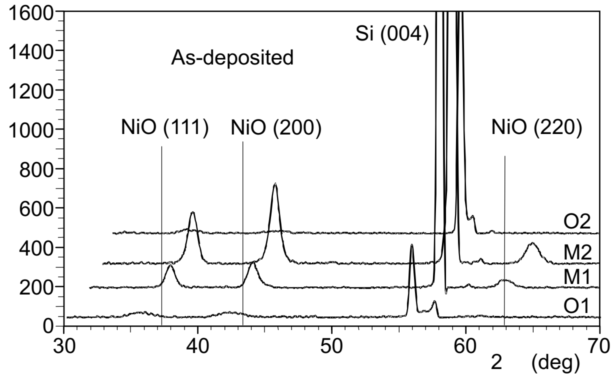

Fig. 1. XRD patterns of as-deposited NiO films prepared in the metal-sputtering mode (M1 and M2) and the oxide-sputtering mode (O1, O2).

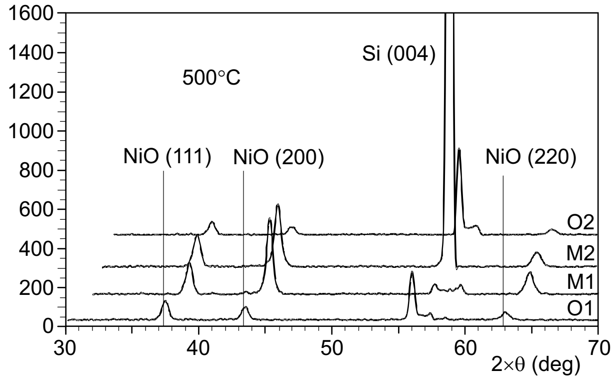

Fig. 2. XRD patterns of NiO films prepared in the metal-sputtering mode (M1, M2) and the oxide-sputtering mode (O1, O2) and annealed at 500 °C for 8 hours in dry air.

was observed by atomic force microscopy (AFM) using a Topometrix Discover TM 2000 under normal air conditions in contact mode. In our case a 70 μm x, y, z linear scanner with a minimal z-resolution of 0.2 nm was used. For electrical measurements the films were deposited on an alumina substrate containing previously deposited and annealed interdigitated Pt electrodes.

3 RESULTS AND DISCUSSION

Figure 1 presents the XRD diffraction patterns of the samples that were prepared at different oxygen contents in the working gas. The three diffracting peaks in Fig. 1 for nickel oxide films are at $2\theta = 36.76$, 42.91 and $61.19°$, respectively. From XRD spectra of as- deposited NiO films it was found that the NiO films prepared had both amorphous and polycrystalline structures. In the diffraction pattern from as-deposited samples in the oxide- sputtering mode (O1, O2) no diffraction peaks were observed. These films are X-ray amorphous. On the other hand, the diffraction patterns from samples M1, M2 prepared in the metal-sputtering mode show the presence of diffraction peaks from the (111), (200) and (220) lattice planes of the NiO lattice. Peak positions are present at angles smaller by around 0.7–1.2, which means a bigger distance between the lattice planes than expected in theory. We suggest that the observed amorphous structure in the oxide-sputtering mode and the polycrystalline structure in the metal-sputtering mode are connected with the NiO deposition conditions. As we can see in Tab. 1, the metal-sputtering mode is characterized by high target voltages (329 and 366 V), while low target voltages (299–309 V) correspond to the oxide-sputtering mode. However, different results have also been reported. Wang *et al* [2] prepared NiO nano-size thin films with (200) preferred orientation on Si (111) substrates by a pulsed ultrasonic spray pyrolysis method. Y.M. Lu *et al* [3] observed that NiO films deposited by r.f. reactive magnetron sputtering had weak and broadened (111) diffraction peaks, which implies poor crystallinity. These different results indicate that the NiO film structure depends on the oxygen content as well as on the deposition method.

The effect of annealing on the structure of films is as follows. Figure 2 shows the diffraction intensities measured after annealing at 500 °C. The samples prepared in metal-sputtering mode became fully polycrystalline but the structure of the samples formed in oxide-sputtering mode changed from amorphous to polycrystalline (fcc NiO phase). It was found that the samples prepared in metal-sputtering mode have a strong (200) diffraction peak that indicates a preferred orientation along [100] direction and its intensity increased. On the other hand, samples prepared in oxide-sputtering mode show a strong (111) diffraction peak and its intensity also increased.

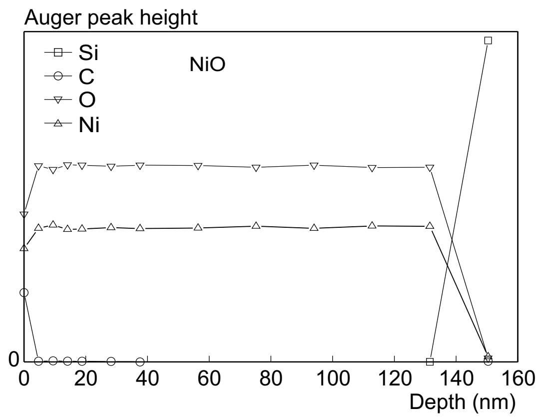

Fig. 3. AES depth profiles for NiO film (M1) prepared in the metal-sputtering mode as deposited.

A typical depth distribution of elements in NiO layers represented by sample M1 prepared in the metal-sputtering mode as-deposited is shown in Fig. 3. One can see a relatively homogeneous depth distribution of the main constituents, Ni and O. Similar homogeneity of elemental depth distribution was characteristic for all as-deposited NiO films prepared in both modes. Besides the main constituents, NiO layers revealed impurities, namely

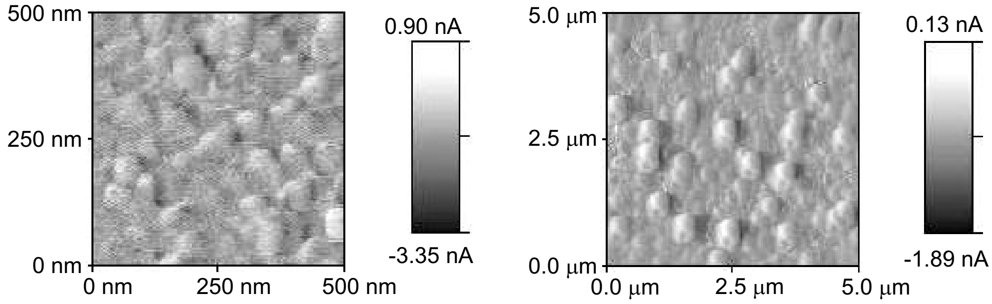

Fig. 4. AFM images showing the surface for sample M1 prepared in metal-sputtering mode and for sample O1 prepared in oxide-sputtering mode after annealing at 500 °C.

C, N, S and Cl at the surface and subsurface region and also C at layer/substrate interfaces. With exception of a relatively large carbon surface coverage, the content of impurities at the subsurface region and at the interface was rather small, less than 0.2 at%.

Table 1. Sample preparation conditions

Sample	M1	O1	M2	O2
Sputtering mode	Metal	Oxide	Metal	Oxide
Pumping speed (l/s)	275	275	136	136
Oxygen flow (sccm)	50	70	20	30
Oxygen content in working gas (%)	20	30	36	44
Average target voltage (V)	329	299	366	301

The AFM topography of the as-deposited NiO films prepared in both modes reveals that the film surface is rather smooth and compact. We found that the mean roughness R and the root mean square RMS of these samples, as deduced from AFM analysis, are similar, $R = 0.15\ \ 0.26$ nm, $RMS = 0.21$–0.33 nm. AFM observations (Fig. 4) show clear grains after annealing at a temperature of 500 °C. The AFM results also show that, in the metal-sputtering mode, the grain size and surface roughness are higher than in the oxide-sputtering mode.

The conductance of the prepared films under study was about 10^{-7} S at room temperature. The temperature variation of the conductance in air has been measured between 25 and 350 °C. Figure 5 shows a representative temperature dependence of the conductance for NiO films prepared at different oxygen contents. It is seen that the film conductance increases by four orders of magnitude between 25 and 350 °C. All NiO films investigated were p-type semiconductors in the temperature range between 25 and 300 °C. The analysis of the electrical conductance showed a similar behaviour for all samples. The values of activation energy calculated from the slope of Arhenius curves are 0.45–0.81 eV and 0.35–0.40 eV in the 225–300 °C and 25–100 °C temperature ranges, respectively.

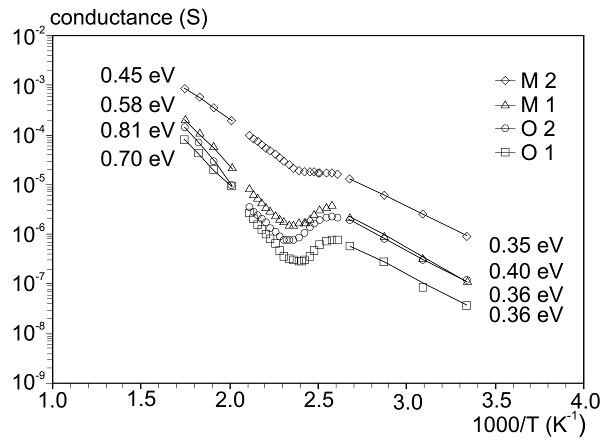

Fig. 5. The conductance of different NiO films in air as a function of inverse temperature (between room temperature and 350 °C). The calculated values E_a according to the fit function $\sigma \approx \exp(-E_a/kT)$ are given in the graph.

4 CONCLUSIONS

NiO films have been deposited on Si substrates by dc reactive magnetron sputtering using a metallic nickel target at different oxygen contents in the working gas mixture (from 20 to 60 %). Only the as-deposited films in the metal-sputtering mode are crystalline. Annealing in dry air also gives rise to crystalline phases in all samples. The resulting films prepared in the metal-sputtering mode have a higher surface roughness. All examined NiO films were semiconductors and their conductance increased by four orders of magnitude between 25 and 350 °C.

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