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Characterization of sputtered NiO thin films

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Abstract

Nickel oxide (NiO) thin films were deposited by RF magnetron sputtering process at different RF powers and substrate temperatures in a pure oxygen atmosphere. The structural, optical and electrical properties of NiO films were investigated using X-ray diffraction (XRD), visible spectrum and Hall effect measurements. The dependences of film properties on substrate temperature, crystalline structure and natural aging effect were studied. The results show that the resistivity increases as sputtering power increases from 100 to 200 W at constant temperature. The lowest resistivity and Hall coefficient obtained are 16.7 Ω cm and 1.99 cm^3/C, respectively, as the sputtering power is 100 W and substrate temperature is 350°. The highest carrier concentration obtained is 3.13×10^{18} cm^{-3} as the sputtering power is 100 W and substrate temperature is 350°. The crystal structure was analyzed by X-ray diffraction method. The preferred orientation of NiO film changes from (111) to (200) when the substrate temperature varies from unheated condition to 350°. Electrical properties of NiO films were unstable and show a natural aging effect. Resistivity of NiO films increases as the time of natural aging increases. Under the substrate-unheated condition, the transmittance of as-deposited samples is lower compared to the film prepared at substrate temperature of 350 °C. The change in transmittance may be due to the microstructural change in the material. It is suggested that the sputtering power affects the preferred orientation of NiO film. Higher substrate temperature induces larger grain size and more perfect crystalline structure, which lead to low resistivity of NiO film.

Keywords: Nickel oxide; Sputtering; Thin film; Hall effect; Natural aging

1. Introduction

Nickel oxide (NiO) is an attractive material due to its excellent chemical stability, as well as optical, electrical and magnetic properties. It has been used as antiferromagnetic material [1], material for electrochromic display devices [2] and functional layer material for chemical sensors [3]. Furthermore, it is considered to be a model semiconductor with p-type conductivity films due to its wide band-gap energy range from 3.6 to 4.0 eV [4]. These films have been fabricated by various physical and chemical vapor deposition techniques, which include spray pyrolysis [5], plasma-enhanced chemical vapor deposition [6] and reactive sputtering [3]. Among these methods, reactive sputtering has been most widely used. Many researches [6–10] have been carried out on the dependence of film properties on sputtering parameters. Many reference data and previous studies [6–10] show that superior electric and optical properties of NiO films can be obtained by reactive sputtering with sputtering pressure in the range of 10^{-3}–10^{-2} Torr and in a pure oxygen atmosphere with a heated substrate.

In this study, optima sputtering parameters, suggested in the reference [6–10], have been employed to reactively sputter NiO target in a pure oxygen atmosphere. The effects of sputtering parameters on the electrical and optical properties of NiO films, such as the crystalline structure, resistivity, transmittance and electrical stability were all investigated. It is also attempted to clarify the as-observed phenomena.

2. Experimental methods

Nickel oxide films were deposited on the Corning 1737 of 0.7 mm thickness glass substrate by an RF magnetron sputtering system from a NiO target of 99.99% purity in a

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pure oxygen atmosphere. The distance between the target and the substrate was approximately 80–85 mm. The chamber was evacuated to a pressure below 3×10^{-6} Torr before deposition. Sputtering deposition was performed at a gas pressure of 8×10^{-3}–1×10^{-2} Torr for 30 min. The power of target varied from 100 to 200 W. The substrate temperatures ranged from room temperature to 350 °C.

A conventional stylus surface roughness detector (Alpha-step 200) was used to measure the film thickness. The electrical properties of nickel oxide films, including resistivity, carrier concentration, mobility and Hall coefficient were measured by the Hall measurement system ("Lake Shore" model 7604 Hall effect measurement systems). The electric stability of NiO film was evaluated by natural aging process in the air atmosphere. The resistivity of the films was measured by a four-point probe system (Napson, RT-7) before and after natural aging process. The crystal structure of the deposited films was identified by the X-ray diffraction (XRD) technique. XRD patterns of the films were determined with Rigaku D/MAX 2500 multipurpose X-ray thin film diffractometer using monochromatic high-intensity CuKα radiation (λ=1.54060 Å). The transmittance was carried out at normal incidence in visible spectrum using HMT: OOIBase32 spectrometer. The surface morphology was observed by atomic force microscopy (AFM) using an NT-MDT/P47E10/P7LS dry type: contact mode under normal air conditions.

3. Results and discussion

3.1. Deposition rate and surface morphology

Fig. 1 shows deposition rate of NiO films produced at different sputtering power and substrate temperature. Fig. 2 shows the variations of surface roughness of NiO films measured by atomic force microscopy (AFM). The depend-

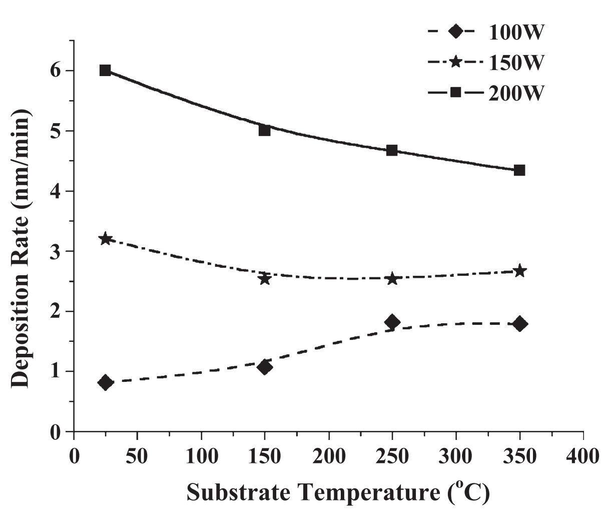

Fig. 1. Deposition rate of NiO films at different sputtering powers and substrate temperatures.

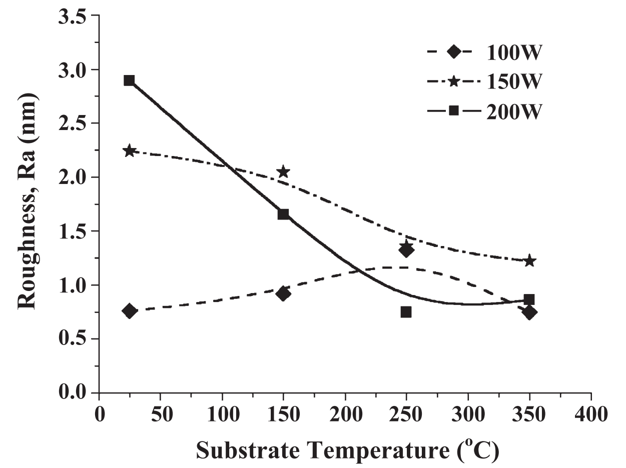

Fig. 2. Surface roughness of NiO films at different sputtering powers and substrate temperatures.

ence of deposition rate and surface morphology at various substrate temperatures can be reasoned as follows. Since more nickel atoms could be ejected from the target at higher RF power, the deposition rate increases with RF power increasing. The substrate temperature controls the mobility of the absorbed atoms on the surface. Depositing in cooler substrate has low atomic mobility and tends to form preferred crystallite structure, which leads to a rougher surface. Hence, the adsorbed atoms prefer to stack on the energetic favor crystalline plane site rather than random stacking. This result leads to a rougher surface. Increasing the substrate temperature, adsorbed atoms gain extrathermal energy and have the motivity to move to another preferred sites. The roughness decreases because of free atomic motion. On the other hand, the higher substrate temperature provides extrathermal energy for the adsorbed atoms and enhances atomic mobility that could minimize the preferred orientation and hence the roughness. At higher RF power and substrate temperature conditions, the sputtered atoms obtained more kinetic energy when they arrived at the substrate surface because of extrathermal energy provided by the heated substrate and high power. Hence, they have a higher probability to reach the equilibrium positions and leads to a more perfect crystalline structure. But the adsorpted atoms also have higher probability to desorb from the surface at higher substrate temperature because of the thermal energy. The roughness of surface is more probable to be reduced and lead to a dense structure at high RF power with elevated substrate temperature. Therefore, the deposition rate and surface roughness were reduced at 200 W RF power with elevated substrate temperature conditions.

3.2. Crystalline structure

Fig. 3 presents the XRD diffraction patterns of the samples prepared at different substrate temperature and constant RF power of 150 W. The (111) preferred

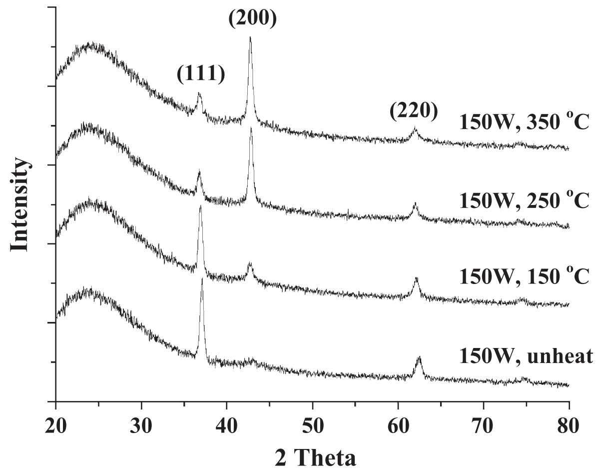

Fig. 3. XRD spectrum from the as-deposited NiO films prepared at RF power 150 W and different substrate temperatures.

orientation was obvious as NiO films prepared at unheated and 150 °C substrate temperature. The preferred orientation changes from (111) to (200) as substrate temperature increases to 250 °C and above. The variation of crystalline size calculated from Scherrer equation with sputtering conditions is shown in Fig. 4. The grain size increased from 11.42 to 18.17 nm with increasing substrate temperature.

3.3. Electrical properties—Hall effect measurement

Fig. 5 shows the results of Hall effect measurement of nickel oxide films at various RF power and substrate temperature. The value of resistivity, Hall coefficient and carrier concentration variation were dependent on substrate temperature and RF power. The results show that the lowest resistivity and Hall coefficient obtained are 16.7 Ω cm and 1.99 cm^3/C, respectively, as the sputtering power is 100 W and substrate temperature is 350° (Fig. 5a and b). The highest carrier concentration obtained is 3.13×10^{18} cm^{-3} as

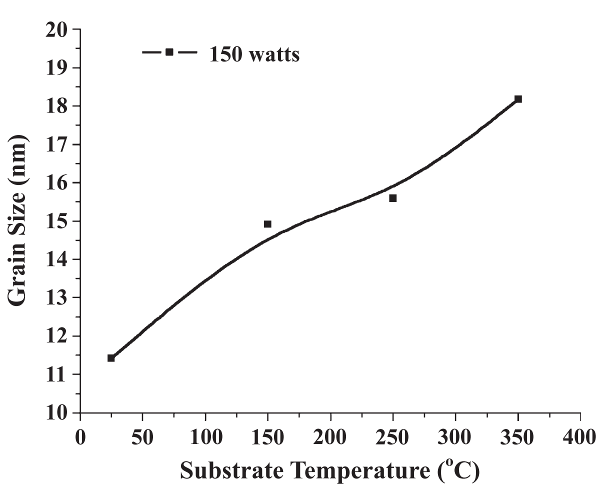

Fig. 4. The grain size of NiO films under various substrate temperatures at RF power 150 W.

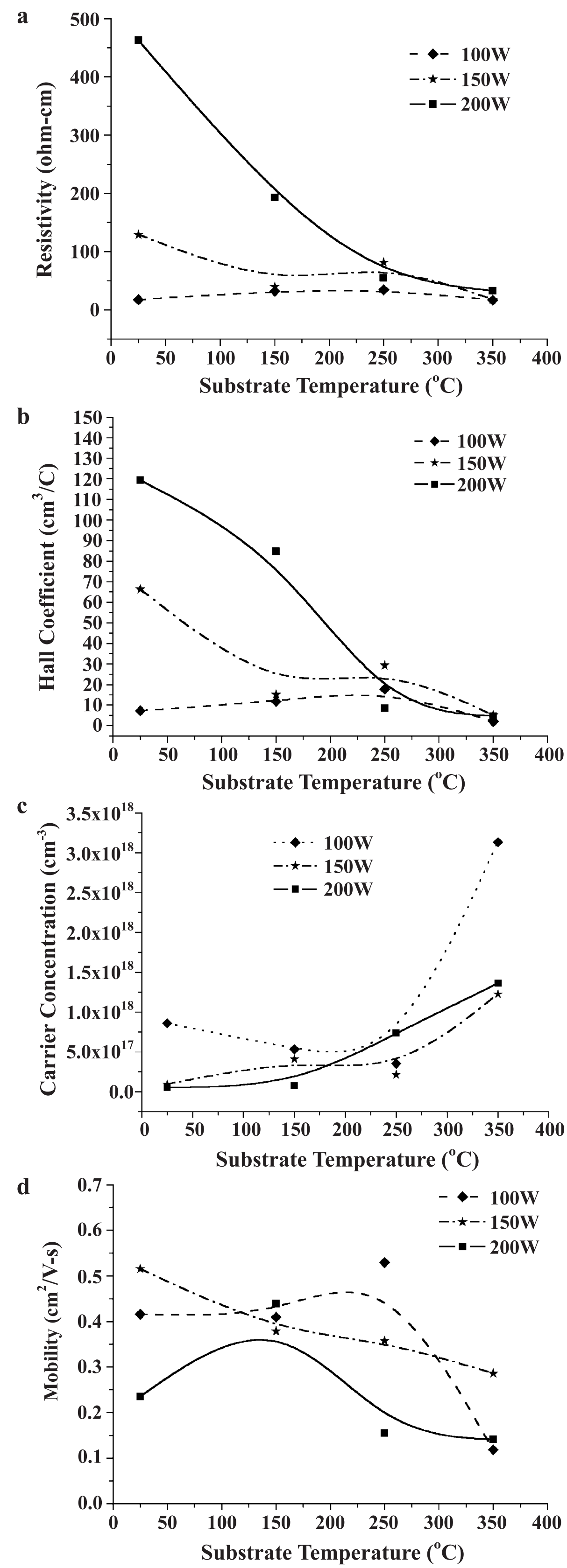

Fig. 5. Hall measurement of the nickel oxide films: (a) resistivity; (b) Hall coefficient; (c) carrier concentration; (d) mobility.

the sputtering power is 100 W and substrate temperature is 350° (Fig. 5c). The mobility variation of NiO films decreases progressively as a function of substrate temperature and target power (Fig. 5d).

The electrical conductivity of undoped NiO has a strong dependence on the microstructural defects existing in NiO crystallites, such as nickel vacancies and interstitial [6–10]. Furthermore, the microstructure and composition, as well as the deposition conditions and environment, are the main factors affecting the electrical properties of NiO film. Surface chemical reaction [11] may happen in pure oxygen atmosphere at elevated substrate temperature. Lu et al. [8,9] had discussed the variation of carrier concentration with substrate temperature and probable reaction on the surface. In our suggestion, the carrier concentration variation depends on both crystalline microstructures and surface chemical reactions during the sputtering process.

The drift velocity and mean free path of the charge carriers determine the value of mobility. Reducing the scattering by the lattice imperfections increases the mobility of carrier with larger grain means less grain boundaries existing, and the scattering effect at the grain boundary is reduced [9]. Nakahata et al. [12] prepared polycrystalline silicon films on glass by PECVD and have found that the Hall mobility depends strongly on either the grain size, their textures, the crystallinity and the fluctuation of grain orientation as well. Substrate heating and postannealing are the main factors affecting the structural properties and the surface morphology of NiO films. We suggest that the observed variation of carrier concentration and Hall mobility are associated with the NiO crystalline microstructure change and point defects as well.

3.4. Electrical stability in natural aging test

It is found that the electrical property of NiO films has a dramatic aging effect. The results of NiO resistivity

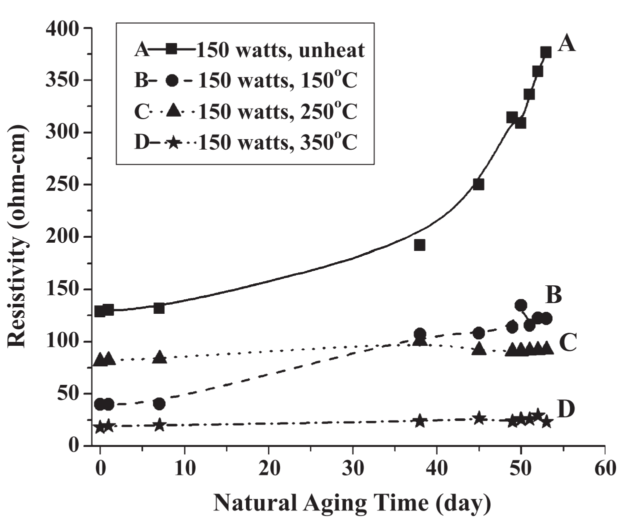

Fig. 6. The variation of resistivity of NiO films in natural aging test.

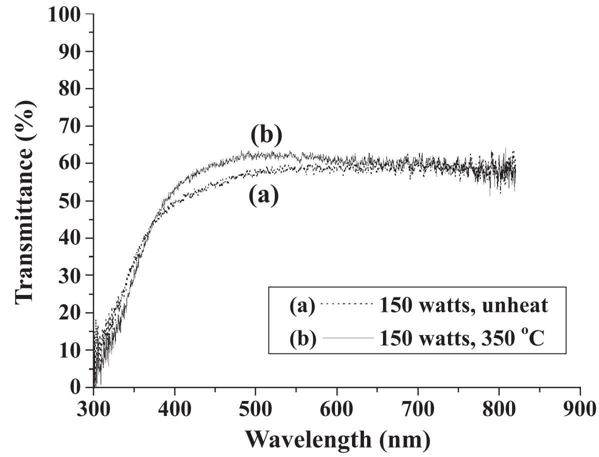

Fig. 7. The variation of spectral transmittance of the nickel oxide films at RF power 150 W and different substrate temperatures.

variation in natural aging test with respect to natural aging time (day) are shown in Fig. 6. The electrical property of NiO films was very unstable. The resistivity of NiO films increases dramatically after aging in natural atmosphere more than 35 days. The reason of dramatic change of resistivity, i.e., electrical aging effect in NiO film, is still ambiguous. It is thought that the residual stress, microstructural defect recovery and oxygen adsorption and desorption may be the reason for resistivity aging of NiO films.

3.5. Optical transmittance

The optical transmittance of as-deposited samples showed strong dependence on the substrate temperature [4,13]. Fig. 7 shows the spectral transmittance of nickel oxide films prepared at constant RF power (150 W) with different substrate temperature. The sample prepared at unheated substrate shows lower transmittance than the one prepared at 350 °C. The transmittance increases at elevated substrate temperature due to improving crystalline microstructure and leads to less defect scattering.

4. Conclusion

From the results of the study, some conclusions can be described below:

(1) The deposition rate and surface roughness were reduced at 200 W RF power with elevated substrate temperature conditions.
(2) The resistivity decreases with increasing the substrate temperature. The lowest resistivity obtained is 16.7 Ω cm in this study.
(3) The electrical property of NiO films is unstable during atmosphere aging.

(4) The transmittance of NiO films improves at higher substrate temperature. The highest transmittance obtained is about 60%.

Acknowledgments

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