

Characterizations of nickel oxide thin films prepared by reactive radio frequency magnetron sputtering

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ABSTRACT: The NiO thin films were prepared by reactive radio frequency magnetron sputtering method on glass substrates. The influence of sputtering power on the crystal structure, surface morphological, optical and electrical properties was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible spectrophotometer (UV-VIS) and Hall effect tester, respectively. The as-prepared NiO thin films are polycrystalline with preferred orientation growth along (200) plane and have very high optical transmittances more than 60 %. All samples have a columnar structure with growth perpendicular to the film surface, and are dense, and homogeneous. With the increase of the sputtering power, a growth mode transformation appears from island growth to layer growth. The lowest resistivity of 2.4 $\Omega \cdot \text{cm}$ could be obtained in our samples. An optimization electrical properties of the films can be achieved by the variation of crystal quality arises from the sputtering power.

Introduction

Recently, nickel oxide (NiO) has received a lot of attention due to its excellent optical, electrical and magnetic properties as well as good chemical stability. It is a promising material for various applications such as anti-ferromagnetic layers, functional layers for solar cells, p-type transparent conductive thin films, a part of functional sensor layers in chemical sensors, material for electrochromic devices, and the p-type layer for UV detectors [1-6].

NiO is a typical p-type transparent oxide semi-conductor with intrinsic p-type conductivity and wide band gap energy range from 3.6 to 4.0 eV [7]. Although stoichiometric NiO is an insulator, it has been reported that the resistivity of NiO can be lowered by increasing Ni³⁺ ions, being ascribed to doping of monovalent atom such as Li, Na, K or Ni vacancies and interstitial oxygen in NiO crystallites [8-10]. The p-type conductivity of Li-doped film can be as high as 1.41 $\text{S} \cdot \text{cm}^{-1}$ [11]. However, the properties of NiO thin films for the p-type transparent conductive films is low until now. It is evident that the improvement of the material properties can be reached by the optimization of the preparation conditions.

In recent years, there are several methods could be used to prepare NiO thin films, which involve magnetron sputtering, plasma-enhanced chemical vapor deposition, electron beam evaporation, spray pyrolysis, sol-gel deposition, chemical bath deposition, atomic layer deposition (ALD), pulsed laser deposition, etc [12-17]. Among these methods, magnetron sputtering has been most widely useful technique having high deposition rates, uniformity over large areas of the substrates and easy control over the composition of the deposited films. The films properties depend on various deposition process parameters such as substrate temperature, sputtering power, oxygen partial pressure, sputtering pressure, substrate bias voltage and post deposition conditions. In this work, we report on the deposition of NiO thin films by reactive radio frequency magnetron sputtering system at room temperature and investigate the influence of sputtering power on the crystal structure, surface morphology, optical and electrical properties of NiO thin films.

Experimental

Preparation of NiO thin films

The NiO thin films were deposited on Corning 1737 glass substrates by reactive radio frequency magnetron sputtering method from a metallic nickel target (size: 60 mm in diameter with a thickness

of 3 mm) of 99.99 % purity. The chamber base pressure was approximately 8×10^{-4} Pa. Pure argon was used as sputter gas and oxygen as reactive gas.

All substrates were ultrasonically cleaned with acetone, ethanol and deionised water. In addition, the target was pre-sputtered for 10 min to remove the surface oxide layers if any on the surface of the target. The distance between the target and the substrate was approximately 70 mm. Sputtering deposition was performed under a gas pressure of 2 Pa. The parameters during the deposition are listed in Table 1.

Table 1. Deposition conditions of the reactive radio frequency magnetron sputtered NiO thin films

Sample	T/(oC)	Power/W	Gas flow/sccm		Time/h
			O2	Ar	
P-50	25	50	10	20	2
P-80	25	80	10	20	2
P-120	25	120	10	20	2
P-150	25	150	10	20	2

Measurements and characterizations

The structural properties of the NiO thin films were analysed by Bruker Advance D8 X-ray diffractometer, using Cu K α radiation ($\lambda=0.1546$ nm). The surface morphology of the films was characterized by scanning electron microscopy of JEOL JSM-6700F. The thickness of the films were measured by Aquila NKD7000V thin film analysis system. For the optical properties of the films, the transmittance measurements were carried out by using Purkinje General TU-1901 ultraviolet-visible spectrophotometer with a wavelength resolution better than ± 0.1 nm. The electrical properties of the NiO thin films were measured by Ecopia HMS-3000 Hall system. All the measurements were performed at room temperature.

Results and disussion

Crystal Structure

To investigate the crystal quality of the NiO thin films prepared at different sputtering power , X-ray diffraction measurements were performed on NiO thin films, shown in Fig. 1. The crystal structure of the films is identified to be polycrystalline and retained the cubic structure (JCPDS data No. 78-0643). From the XRD patterns, it could be seen that all samples have the only one sharp peak corresponding to the diffraction of NiO (200) plane except the sample of P-50, indicating a strong (200) orientation and good quality of crystallinity. With the increase of sputtering power, the intensity of (200) diffraction peak become stronger, which indicates the better crystallinity.

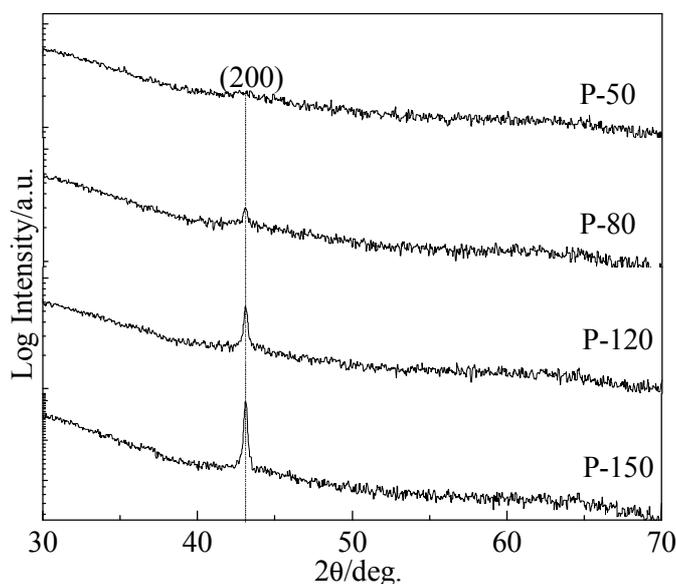


Figure 1. XRD patterns of the NiO thin films deposited on glass substrates at various sputtering power

Surface morphology

The surface morphology variation of NiO thin films with sputtering power was observed by SEM, shown in Fig. 2. All samples had a columnar structure with growth perpendicular to the film surface, and was dense, and homogeneous. With the increase of sputtering power, the grain gradually increases from a size of 10 to 50 nm. When sputtering power increase to 150 W, a smoother surface was obtained. It may be attributed to the transformation of thin film growth mode [18]. When the sputtering power is low, the basic unit of film growth is less, film growth appears to island growth mode. With the increase of the sputtering power, the basic unit required for film growth also increased, and the islands on substrate gradually increases. When the sputtering power increases to a certain extent, the islands on substrate contact others, and gradually merge into a larger grain. This process results in a growth mode transformation from island growth to layer growth. The thickness of NiO thin film deposited at various sputtering power was given in Fig. 3. We observed that the thickness of NiO thin films linearly increases with the increase of sputtering power.

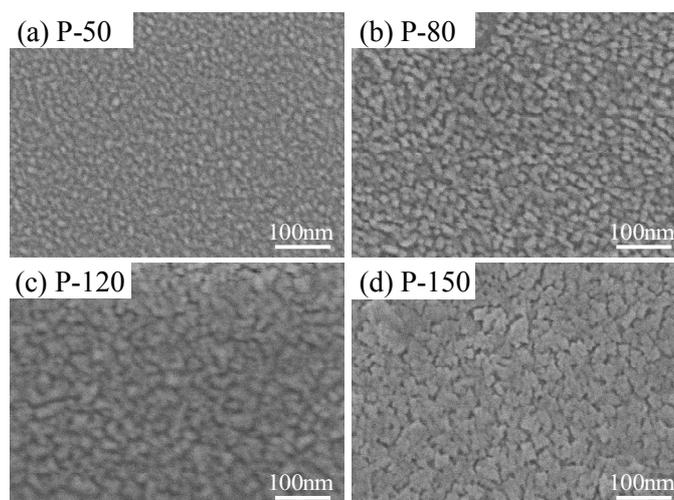


Figure 2. SEM images of the NiO thin films deposited on glass substrates at various sputtering power

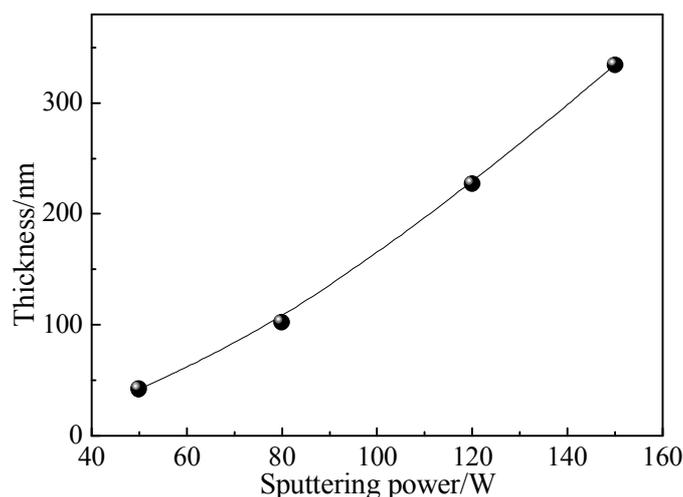


Figure 3. Thickness of the NiO thin films deposited on glass substrates at various sputtering power

Optical and electrical properties

The optical transmittance of all as-prepared NiO thin films is more than 60 % at the visible range, shown in Fig.4. The transmittance of the films decreased from 90 % to 65% with the increase of sputtering power from 50 to 150 W. There are two ways for the optical loss in thin film transmission, light absorption and scattering, respectively [19]. The light absorption mainly depends on the film thickness, while the light scattering is related to the defects of the film. The thickness difference of the as-prepared samples is relatively large, The influence of light absorption caused by the thickness dominates the transmittance of the film.

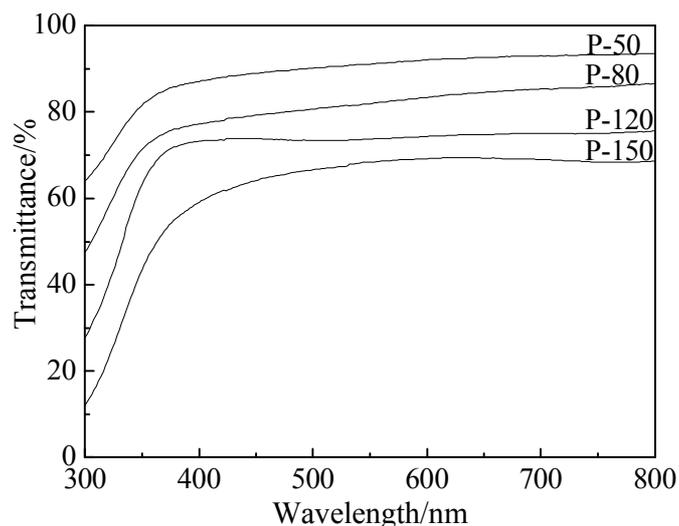


Figure 4. Transmittance of the NiO thin films deposited on glass substrates at various sputtering power

The resistivity of the NiO thin films prepared at different is shown in Fig. 5. It was clear that the electrical properties of NiO thin films are greatly affected by sputtering power, and the resistivity of the NiO thin films decreases with the increase of sputtering power. The films showed high electrical resistivity of 4.1 $\Omega \cdot \text{cm}$ at sputtering power of 50 W. The electrical resistivity of the films decreased to 2.4 $\Omega \cdot \text{cm}$ with increasing the sputtering power to 150 W. The electrical resistivity of NiO thin films has a strong dependence on the microstructural defects existing in NiO crystallites, such as nickel vacancies and interstitial defects [20].

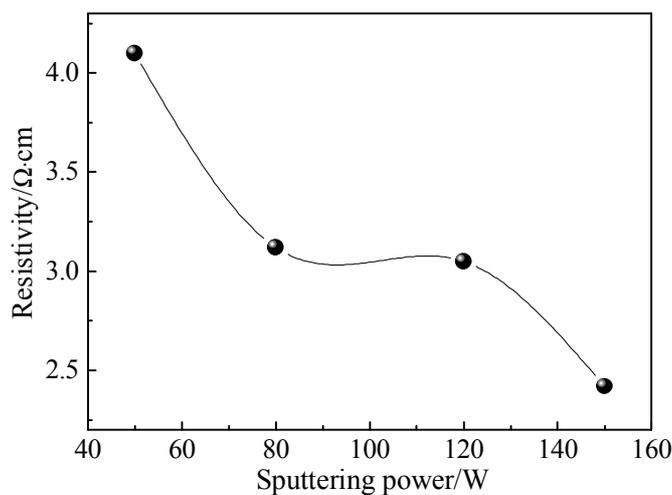


Figure 5. Resistivity of the NiO thin films deposited on glass substrates at various sputtering power

Conclusions

The NiO thin films have been prepared by reactive radio frequency magnetron sputtering method on glass substrates. The influence of sputtering power on the crystal structure, surface morphological, optical and electrical properties was investigated. The as prepared NiO thin films were polycrystalline with preferred orientation growth along (200) plane and very high optical transmittances more than 60%. All samples had a columnar structure with growth perpendicular to the film surface, and was dense, and homogeneous. With the increase of the sputtering power, a growth mode transformation appears from island growth to layer growth. The lowest resistivity of 2.4 $\Omega \cdot \text{cm}$ could be obtained.

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