MICROSTRUCTURE, ELECTRICAL, AND OPTICAL PROPERTIES OF NON-STOICHIMETRIC P-TYPE NICKEL OXIDE FILMS BY RADIO FREQUENCY RECTIVE SPUTTERING

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Introduction

NiO film is a promising material for applications in electrochromic display devices, gas sensors, p-type transparent conductive film etc, due to its excellent chemical stability, electric and optical properties. Because its wide band gap in the range of 3.6 to 4.0 eV, the NiO compound exhibits transparent properties. On the other hand, the electric resistivity (ρ) of NiO films can be reduced significantly by adding monovalent atoms or creating nickel vacancies and forming interstitial oxygen atoms in NiO crystallites [1].

NiO films have been fabricated by various kinds of techniques, including spray pyrolysis [2], plasma enhanced chemical vapor deposition [3], and sputtering [4] etc. The ρ value of NiO film could be decreased significantly when the O_2 gas is introduced during deposited NiO films [4]. However, the influence of different flow rate ratio of O_2 to Ar on microstructure of NiO film is still not clear. In this work, the NiO films are deposited on glass substrates by radio frequency (rf) reactive sputtering to investigate the effect of O_2 partial pressure on microstructure, electrical, and optical properties of NiO films.

Experimental

The NiO films with 100nm thickness were deposited onto Corning 1737F glass substrates by sputtering NiO target using rf magnetron sputtering in Ar+O_2 gas mixture with various O_2 partial pressures ($\frac{O_2}{O_2+Ar}$) at ambient temperature. The O_2 partial pressures were adjusted to be 0, 10, 30, 50, 70, and 100%.
The crystal structure of the NiO films deposited in various O_2 partial pressures was examined by X-ray diffraction (XRD) using Cu-Kα radiation. The surface morphologies were analyzed by atomic force microscope (AFM). The electrical properties were measured by four point probe and Hall effect. The transmittance of NiO films was determined by ultraviolet-visible spectrometer (UV-VIS). The microstructures of the NiO films were investigated by a high resolution transmission electron microscope (HR-TEM). The chemical composition of the NiO films was determined by energy disperse spectrum (EDS) and electron probe X-Ray microanalyzer (EPMA). The thicknesses of the films were measured by α-step and AFM.

Results and Discussion

Fig.1 shows the relation between electric resistivity (ρ) of NiO films and O_2 partial pressure. The electric resistivity decreases as O_2 partial pressure is increased. An ultra high ρ value is obtained and can not be detected by four-point probe measurement when the NiO film is sputtered in pure Ar atmosphere without introducing O_2 gas. The ρ value is reduced significantly to 0.45 Ω-cm as O_2 partial pressures of 10 % is introduced during deposition. It is decreased continuously from 0.45 to 0.01 Ω-cm as the O_2 partial pressure is further enhanced from 10 to100 %.

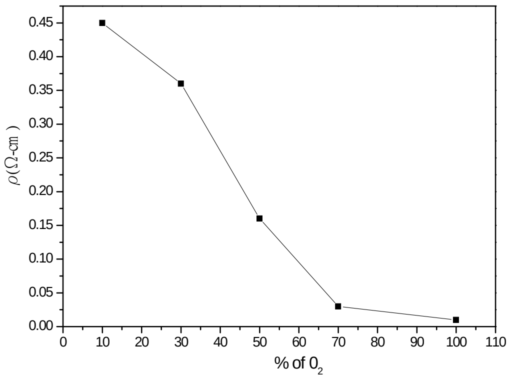

Fig.1 Resistivity of NiO films which deposited in different oxygen partial pressures.

The variation of transmittances of NiO films with O_2 partial pressure is shown in Fig.2. The transmittance of NiO films in the visible range decreases as the partial pressure of oxygen is increased. The transmittance for NiO film deposited in pure Ar gas is as high as 96.33 % and it reduces greatly to 72.58 % as 10 % O_2 partial pressures is introduced during sputtrting. Further increasing the partial pressure of oxygen to 30, 50, 70, and 100 %, the transmittance of NiO films are decreased further to 62.77 %, 47.85 %, 40.15 %, and 32.93 % respectively. The interstitial O atoms in non-stoichiometric O-rich NiO films will cause to scatter or absorb the incident light that results in the reduction in transmittance of NiO films [5] as the partial pressure of oxygen is increased.

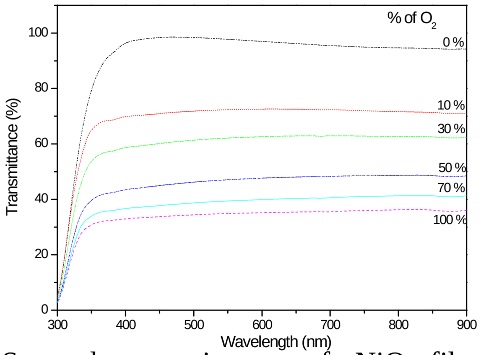

Fig.2 Spectral transmittance of NiO films which deposited in different oxygen partial pressures.

Table 1 is the result of Hall measurement for the NiO films sputtered in various O_2 partial pressures. The result shows that the carrier concentration are all positive, indicating that all the NiO films deposited in Ar+O_2 gas mixture exhibit p-type conduction. It is also found that the carrier concentration increases with increasing the O_2 partial pressure. The concentration of NiO film deposited in 10 % O_2 partial pressure is 6.95×10^{15} cm^{-3}. It is increased continuously from 6.95×10^{15} to 1.29×10^{20} cm^{-3} as the O_2 partial pressures are enhanced from 10 to 100 %. Therefore, the decrease in electric resistivity of NiO films with increasing the partial pressure of oxygen is due to the increase of hole carrier concentration.

Table1 Hall measurement of NiO films which deposited in different oxygen partial pressures.

oxygen partial pressure (% of O_2)	Carrier mobility ($cm^2V^{-1}sec^{-1}$)	Carrier concentration (cm^{-3})
10%	24.46	$+6.95\times10^{15}$
30%	35.41	$+1.27\times10^{16}$
50%	78.57	$+5.19\times10^{16}$
70%	3.62	$+3.61\times10^{19}$
100%	3.51	$+1.29\times10^{20}$

The XRD patterns of NiO films sputtered in various O_2 partial pressures are shown in Fig.3. The diffraction peaks of NiO(111) and NiO(200) appear at 37.02° and 43.02° respectively as NiO film is deposited in pure Ar atmosphere. Both peaks shift significantly to lower angle and the crystallization of the films decreases as the NiO films are deposited in Ar+O_2 gas mixture. The variation of lattice parameter of NiO films with O_2 partial pressures is shown in Fig. 4, which is calculated from the peak of NiO(111) in Fig.3 by Bragg's law. The lattice parameter of NiO film deposited in pure Ar atmosphere is 0.420 nm. It enlarges obviously to 0.425 nm as 10 % O_2 partial pressure is introduced. The lattice parameters of NiO films are further increased to 0.426, 0.428, 0.430, and 0.431 nm respectively as the O_2 partial pressures is enhanced to 30, 50, 70, and 100 %.This result confirms that the existence of interstitial O atoms in NiO lattice to expand lattice parameter and reduce transmittance of NiO film as O_2 gas is introduced to deposit NiO film.

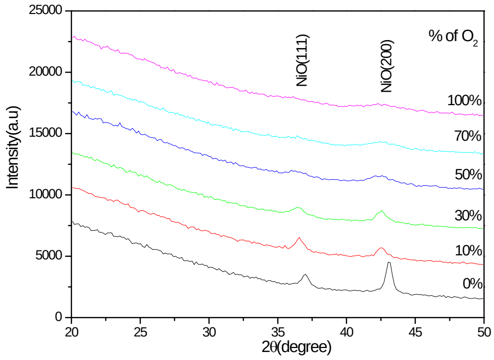

Fig.3 XRD patterns of NiO films which deposited in different oxygen partial pressures.

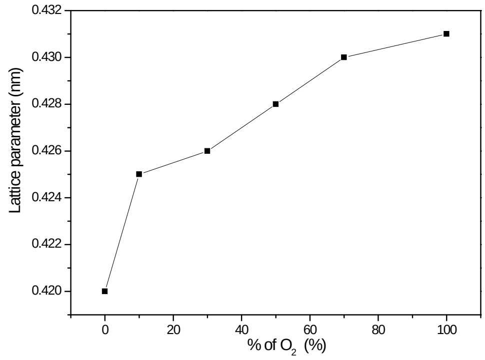

Fig.4 Lattice parameter of NiO films which deposited in different oxygen partial pressures.

Conclusion

The non-stoichiometric p-type NiO films are achieved by introduction of O_2 into Ar atmosphere to sputter NiO target. Both the electric resistivity and transmittance of NiO films are decreased as O_2 partial pressure is increased, but the crystallization of the films becomes worse.

References

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