Effects of oxygen partial pressure on optical properties of NiO_x films deposited by reactive DC-magnetron sputtering

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The influence of oxygen partial pressure on the optical properties of NiO_x thin films deposited by reactive DC-magnetron sputtering from a nickel metal target in a mixture gas of oxygen and argon was presented. With the oxygen ratio increasing, the reflectivity of the as-deposited films decreased, and optical band gap increased. Thermogravimetric analysis (TGA) showed that the decompose temperature of the films was above 250 °C. After annealed at 400 °C, only films deposited at 5% O_2/Ar ratio showed high optical contrast which was about 52%. Scanning electron microscope (SEM) results revealed that the changes of surface morphology were responsible for the optical property variations of the films after annealing. Its thermal stability and high optical contrast before and after annealing made it a good potential write-once optical recording medium.

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In the early 1980s, non-stoichiometric or sub-oxide thin films such as GeO_x, TeO_x, and SbO_x with oxygen content lower than the stoichiometric composition were proposed as promising, stable, and highly sensitive media for optical recording[1]. Among them, TeO_x thin films were found to be sufficiently sensitive to the diode laser beam and have excellent stability[2]. Unfortunately, the optical changes of TeO_x films under laser-pulse irradiation required several minutes to be completed[3], thus limiting the quick data transfer, and Te itself is toxic. Therefore, TeO_x thin films were hard to be applied in write-once blue-ray recording.

Recently, NiO_x films have attracted a great deal of attention due to their specific features such as excellent stability, low material cost, and large span optical density[4]. Using NiO_x films as the recording materials of optical disc is one of their new applications. Some previous literatures have discussed the feasibility of using the NiO_x films as the recording medium of write-once discs[5,6]. It is well known that the properties of films depend on various process parameters such as oxygen component, working pressure, and substrate temperature[7]. Therefore, it is necessary to investigate the influence of these parameters based on the optical recording. In this letter, we focus on the effects of the oxygen partial pressure on the optical properties of NiO_x films.

Single-layer NiO_x films were deposited on K9 glass substrates by reactive DC-magnetron sputtering using a 99.99% pure nickel target in a mixture of argon-oxygen environment. The flow rates of argon and oxygen were individually controlled using a mass flow meter, and O_2/Ar ratios were 5%, 10%, 20%, 30%, respectively. The background vacuum was typically 7.0×10^{-4} Pa, the sputtering pressure was 0.6 Pa, and the sputtering power was 250 W. Some samples were annealed at 400 °C for 30 min in air.

The thickness of the films was determined by an Alpha-step 500 surface profilometer (Tencor, America). Thermal properties of NiO_x films were analyzed by a thermogravimetric analysis (TGA) system with a SDT Q600 V5.0 Build 63 from 100 to 700 °C at a heating rate of 5 °C/min. Scanning electron microscope (SEM) micrographs were measured using a JSM-6360LA SEM. The reflectivity and transmittance of the films were measured by a Perkin-Elmer Lambda (900UV/VIS/NIR) spectrophotometer in the wavelength range of 350—700 nm. The bonding configurations of sputtered NiO_x thin films were surveyed by using a RBD upgraded PHI-5000C ESCA X-ray photoelectron spectroscopy (XPS) with Mg Kα emission at 1253.6 eV.

In optical recording, the signal to noise ratio (SNR) ultimately determines the storage density of the media. If the thermal and shot noises in the readout channel are negligible, the SNR is theoretically proportional to optical contrast. To achieve a SNR greater than 45 dB, optical contrast is required to be higher than 6% and the optical contrast can be calculated as[8]

$$C = 100\% \times (R_\mathrm{a} - R_\mathrm{i})/(R_\mathrm{a} + R_\mathrm{i}), \quad (1)$$

where C is the optical contrast, R_i is the reflectivity of the as-deposited films, R_a is the reflectivity of the films annealed at 400 °C.

Figure 1 shows the deposition rate of the NiO_x film as

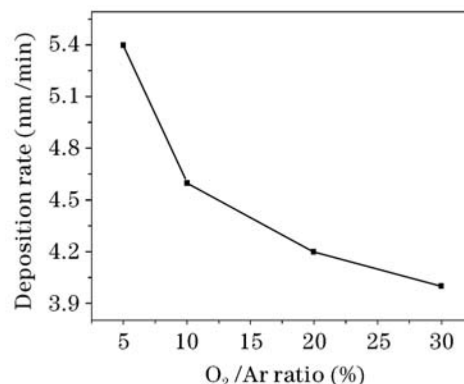

Fig. 1. Deposition rate of the NiO_x film as a function of oxygen partial pressure.

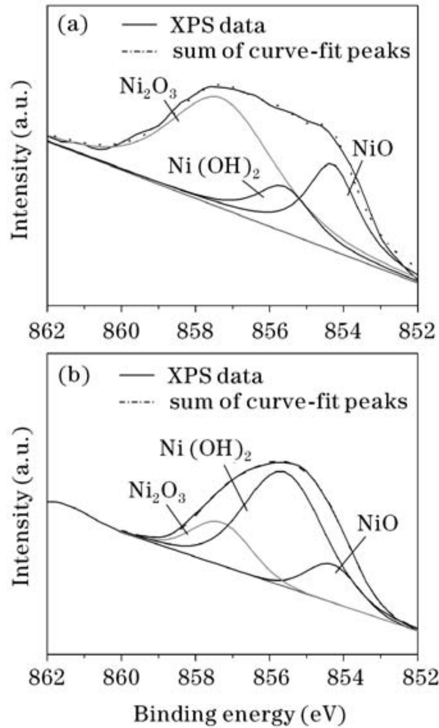

Fig. 2. XPS spectra of $Ni2p_{3/2}$ peaks for the as-deposited NiO_x films. (a) Deposited at 5% O_2/Ar ratio; (b) deposited at 20% O_2/Ar ratio.

a function of oxygen partial pressure. The deposition rate decreased from 5.4 to 4.0 nm/min as the O_2/Ar ratio increasing from 5% to 30%. The thicknesses of the films deposited at 5%, 10%, 20% and 30% O_2/Ar ratio are 27, 23, 21, and 20 nm, respectively. This can be explained by the fact that the oxide layer was formed on the target surface and the sputtering yield of nickel metal was higher than that of nickel oxide[9]. Figure 2 shows the XPS spectra of $Ni2p_{3/2}$ peak for the as-deposited NiO_x films. The XPS analysis showed that the as-deposited NiO_x films contained both Ni^{2+} and Ni^{3+}. This was related to that many Ni^{2+} vacancies existed in the NiO_x films, and to keep the charge near the Ni^{2+} vacancies neutral, some of the Ni^{2+} were oxidized to Ni^{3+}[10]. In addition, the NiO_x films deposited at 5% O_2/Ar ratio contained more Ni^{3+} than the films deposited at 20% O_2/Ar ratio. Therefore, more vacancies may exist in the films deposited at 5% O_2/Ar ratio. In the experimental process, the color of the as-deposited films changed from dark brown to straw yellow as O_2/Ar ratio increasing from 5% to 20%. The reason was that more Ni^{3+} ions which were produced as color centers in NiO_x films[11] existed in the films deposited at 5% O_2/Ar ratio. TGA curves of the NiO_x films deposited at 5% and 20% O_2/Ar ratios are shown in Fig. 3. According to TGA curves, it was observed that the weight decreased slowly in the range from 100 to 260 °C. In general, thermal stability at high temperature over 250 °C is necessary for write-once optical recording. This revealed that the NiO_x thin films had an excellent thermal stability. As the temperature increasing, TGA curves exhibited a sharp decomposition temperature at about 263 °C for the NiO_x films deposited at 5% O_2/Ar ratio, and about 300 °C for the films deposited at 20% O_2/Ar ratio, respectively, which

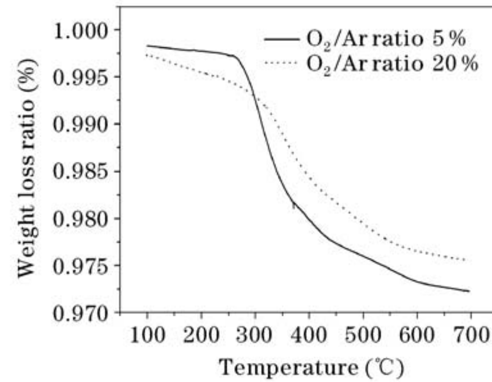

Fig. 3. TGA curves of NiO_x films deposited at 5% and 20% O_2/Ar ratios.

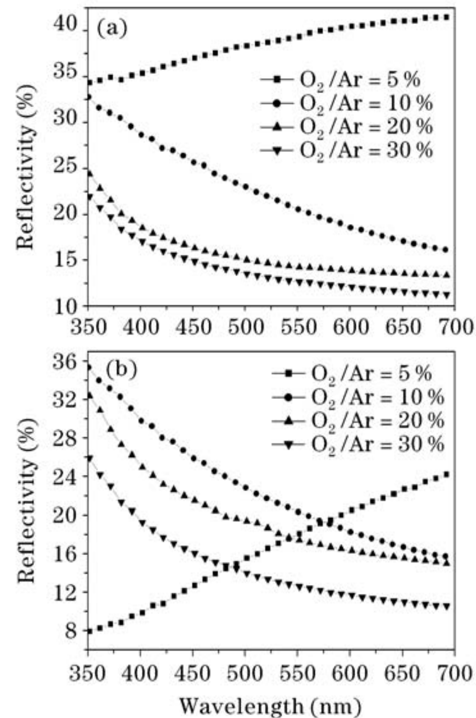

Fig. 4. Reflection spectra of NiO_x films. (a) As-deposited films; (b) 400 °C annealed films.

was because that the reaction $NiO_x \rightarrow NiO+O_2$ releases O_2, leading to the weight loss. Therefore, the annealing temperature was determined at 400 °C.

Reflectance spectra of both the as-deposited and 400 °C annealed NiO_x films are shown in Fig. 4. It was observed that the reflectances of the as-deposited films decreased with O_2/Ar ratio increasing. Figure 5 shows transmission spectra of both the as-deposited and 400 °C annealed NiO_x films. The optical absorption coefficient (α) was calculated from the optical transmittance (T) and reflectance (R) using the relation[12]

$$\alpha = (1/d)\ln[(1-R)/T], \tag{2}$$

where d is the film thickness. The direct or indirect nature of optical transition between parabolic bands can be studied using the relation[13]

$$\alpha h\nu = B(h\nu - E_{\rm g})^{\gamma}, \tag{3}$$

where B is the quality factor depending on the transition

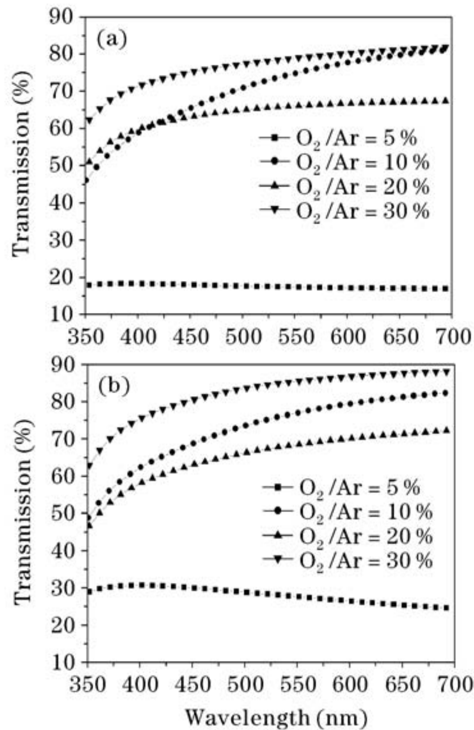

Fig. 5. Transmission spectra of NiO_x films. (a) As-deposited films; (b) 400 °C annealed films.

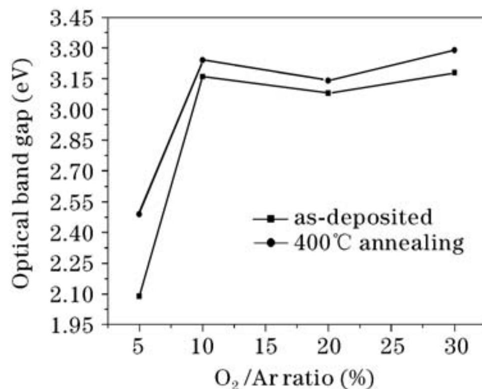

Fig. 6. Optical band gaps of both deposited and annealed NiO_x films at various O_2/Ar ratios.

probability, $h\nu$ is the photo energy, and the power term γ is an index which characterizes the optical absorption process. γ can take values of 2, 3, 1/2 or 3/2 depending on the nature of electronic transitions. In the present study, the variation of absorption coefficient with photo energy followed the above relation for $\gamma = 1/2$ indicating that the transition must correspond to direct allowed transition. Figure 6 shows optical band gaps of both the as deposited and annealed NiO_x films at various O_2/Ar ratios. The optical band gap of the as-deposited films increased from 2.09 to 3.18 eV with the increase of the O_2/Ar ratio. Hong *et al.*[14] have reported that the optical band gap of ZnO films increased with increasing O_2/Ar ratio clearly. This can be related that the NiO_x films deposited at low O_2/Ar ratio existed more vacancies and these vacancies decreased the optical band gap. After annealing, the optical band gap of samples deposited at different O_2/Ar ratios increased. The reason is that the gradual annealing out of the unsaturated bonds produces a large number of saturated bonds. The reduction in the number of unsaturated bonds decreased the density of localized states in the band structure, consequently increased the optical band gap[15].

The refractive index n was calculated from the reflectance spectra of the films[16]. The extinction coefficient k was determined by the relation of $k = \alpha\lambda/4\pi$. Figure 7 shows the optical constant of both the as-deposited and annealed films at different O_2/Ar ratios. The optical constant of the films deposited at 5% O_2/Ar ratio was different from that at the other O_2/Ar ratios apparently. The extinction coefficients of the films deposited at 10%, 20%, and 30% O_2/Ar ratios were consistent with those in the previous literature[5], and the refractive indices of the films were larger than that in the previous literature[5]. The difference of the refractive index could come from the different thicknesses of the films, the different sputtering conditions and calculated methods without considering intervene effect.

From Fig. 8, it was observed that only the films deposited at 5% O_2/Ar ratio have high optical contrast which was about 52% at 405 nm. The results were consistent with the experimental phenomena. The as-deposited films deposited at 5% O_2/Ar ratio exhibited a dark brown color, after annealing at 400 °C, the films become translucent. Little color changes have been observed for the films deposited at other O_2/Ar ratios after annealing.

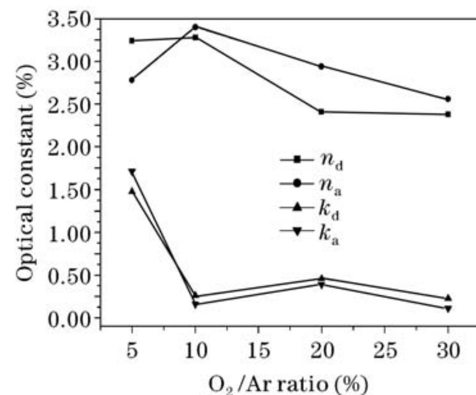

Fig. 7. Optical constants at 405 nm of both the as-deposited and annealed NiO_x films at various O_2/Ar ratios (n_d, n_a and k_d, k_a are refractive indices and extinction coefficients of the films in the deposited and annealed states, respectively).

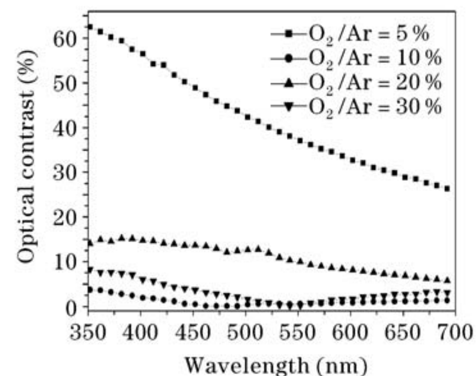

Fig. 8. Optical contrast of NiO_x films deposited at various O_2/Ar ratios.

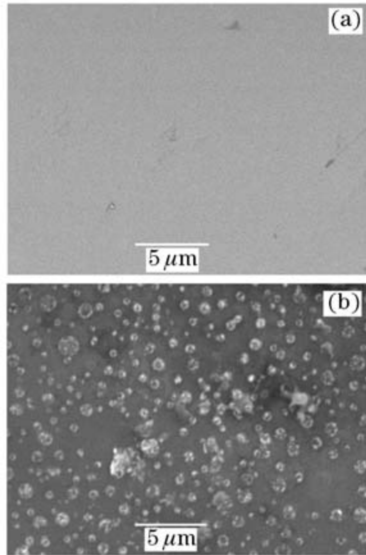

Fig. 9. Surface morphologies of the NiO_x films deposited at 5% O_2/Ar ratio. (a) As-deposited films; (b) 400 °C annealed films.

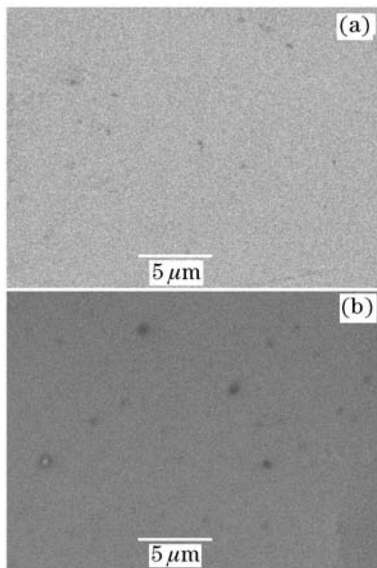

Fig. 10. Surface morphologies of the NiO_x films deposited at 20% O_2/Ar ratio. (a) As-deposited films; (b) 400 °C annealed films.

Figures 9 and 10 show the surface morphologies of both the as-deposited and annealed films with 5% and 20% O_2/Ar ratios. It was found that the surface morphologies of the as-deposited films with different O_2/Ar ratios were smooth and compact. After annealing, the surface morphology of the films deposited at 5% O_2/Ar ratio changed obviously and became very rough due to the decomposition of NiO_x films. Meanwhile, the surface morphology of the films deposited at 20% O_2/Ar ratio changed slightly, therefore, the optical contrast of the films was small. It can be obtained that the changes of surface morphology were responsible for the variation of the optical contrast of the films after annealing.

In summary, the different oxygen partial pressures strongly influence the optical properties of NiO_x films deposited by reactive DC-magnetron sputtering. The deposition rate decreased from 5.4 to 4.0 nm/min as the O_2/Ar ratio increasing from 5% to 30%. The reflectance of the as-deposited films decreased, and the optical band gap increased with the increase of O_2/Ar ratio. The reason may be that vacancies exist in NiO_x films. The optical constant of the films deposited at 5% O_2/Ar ratio was different from the films deposited at the other O_2/Ar ratios apparently. After annealed at 400 °C, the optical band gaps of all the films deposited at different O_2/Ar ratios increased. However, only the films deposited at 5% O_2/Ar ratio showed high optical contrast that was about 52% at 405 nm. It was large enough to be used as an optical recording medium. The SEM results revealed that the changes of surface morphology were responsible for the reflectance variation of the films after annealing.

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