Effects of Sputtering Parameters on Optical Constant of NiO_x Thin Films*

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Abstract: The effects of sputtering parameters on optical constant of NiO_x thin films prepared by reactive magnetron sputtering were studied by spectroscopic ellipsometry, XRD and XPS methods. The optical constant of the deposited films became smaller with O_2/Ar flow ratios increasing. After annealing, the refractive index shows an increase, especially at a high O_2/Ar flow ratio, while the extinction coefficient reduced by about 50%. The refractive index is greater for a higher sputtering power while smaller for a higher work pressure. It is related to the existence of interstitial oxygen and vacancy of Ni, the decomposition of NiO_x and compactness degree of NiO_x films, respectively.

Key words: Optical constant; NiO_x Thin films; Spurtting parameters

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0 Introduction

Nickel oxide has been studied extensively for the application in electrical, optical and write-once optical data storage industries during the past years. This NaCl-type antiferromagnetic oxide semiconductor owns some special features such as excellent durability and electrochemical stability, low material cost and large span optical density[1]. Nickel oxide thin films can also be prepared by various techniques including: vacuum evaporation, sol - gel[2], spray pyrolysis technique[3], pulsed laser deposition technique[4] and magnetron sputtering[5]. Electrochromic performance and optical properties of Nickel oxide has been studied by Bouessay, et al[6] and Franta, et al[7] respectively. NiO_x thin films used as recording material is one of its new applications[5]. Its recoding mechanism relates to releasing O_2 under the irradiation of pulse laser and forming pits.

Recently, investigation of the optical constant of NiO thin film prepared by different techniques using spectrophotometry and spectroscopic ellispometry were also started[2-5]. Adler and Powell had tried to interpretate the optical constant of NiO with energy band structure theory[8-9], but it is difficult. As we know, optical constant is very important for the study and application of NiO_x thin films. Reactive magnetron sputtering is an non-balance method to prepare non-stoichiometric compounds with nice homogeneity.[10] However, optical constant of NiO_x thin film prepared by reactive magnetron sputtering have not been completely reported. In this paper, we focus on the effects of sputtering conditions on optical constant (refractive index n and extinction coefficient k) of NiO_x thin films prepared by reactive magnetron sputtering. It will be the groundwork of our next work for numerical simulation of NiO_x as a recording materials.

1 Experiment

In a reactive DC-magnetron sputtering system using a high-purity Ni target (99.99%), a series of NiO_x thin films were deposited on single-crystal silicon (100) substrates at different O_2/Ar flow ratios. Before being loaded into the vacuum chamber, the substrates were treated chemically in a mixture of concentrated HF and H_2O to remove contaminants and the native SiO_2 layer on the silicon surface. Afterward, substrate was rinsed with anhydrous ethanol in a ultrasonic device and dried. The base vacuum was typically 7.0×10^{-4} Pa. The different working pressures and sputtering powers were used during sputtering. After deposition, some samples were annealed in vacuum ambience (20 Pa) at 400 ℃ for 30 mins.

The bonding configurations of NiO_x thin films deposited on single-crystal silicon (100) were surveyed by using a Kratos Axis Ultra DLD X-ray photoelectron spectroscopy (XPS) with Al Kα emission at 150 W. The reflectance of the films

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were measured by a Perkin-Elmer Lambda (900UV/VIS/NIR) spectrophotometer in the wavelength range of 300 ~ 700 nm. X-ray diffraction (XRD) (D/max2550V) with Cu Kα radiation was used to identify the structure of the as-deposited and annealed films.

The ellipsometric quantities of NiO_x thin films deposited on single-crystal silicon (100) were measured using a UVISEL/460-VIS-AGAS phase modulated ellipsometry within the spectral region 280-800 nm. As a non- destructive measurement technique with high accuracy in the study of thin films[11], ellipsometry measures two angles, Ψ and Δ, for the amplitude and phase of ρ ($\rho = r_p/r_s = \tan\Psi \times e^{i\Delta}$), the complex reflectance ratio of the p (parallel) and s (perpendicular) field components of the light beam defined with respect to the plane of incidence of the sample. Two parameters, I_s ($I_s = \sin(2\Psi) \times \sin\Delta$) and I_c ($I_c = \sin(2\Psi) \times \cos\Delta$), were fitted with differient fitting equations by using two-phase model between the air and the sample. Then the optical constant can be obtained when they all fit well between experimental and theoretic data. All spectra were taken at an angle of incidence of 70° and fixed polarizer angle of 45° from the plane of incidence and room temperature[12].

2 Results and Discussions

Fig. 1 shows the optical constant of the as-deposited and annealed films at different flow ratios of O_2/Ar. Before annealing, the refractive index and extinction coefficient have the same mutative trend, that is, optical constants of the as-deposited films get smaller with O_2/Ar flow ratios increasing.

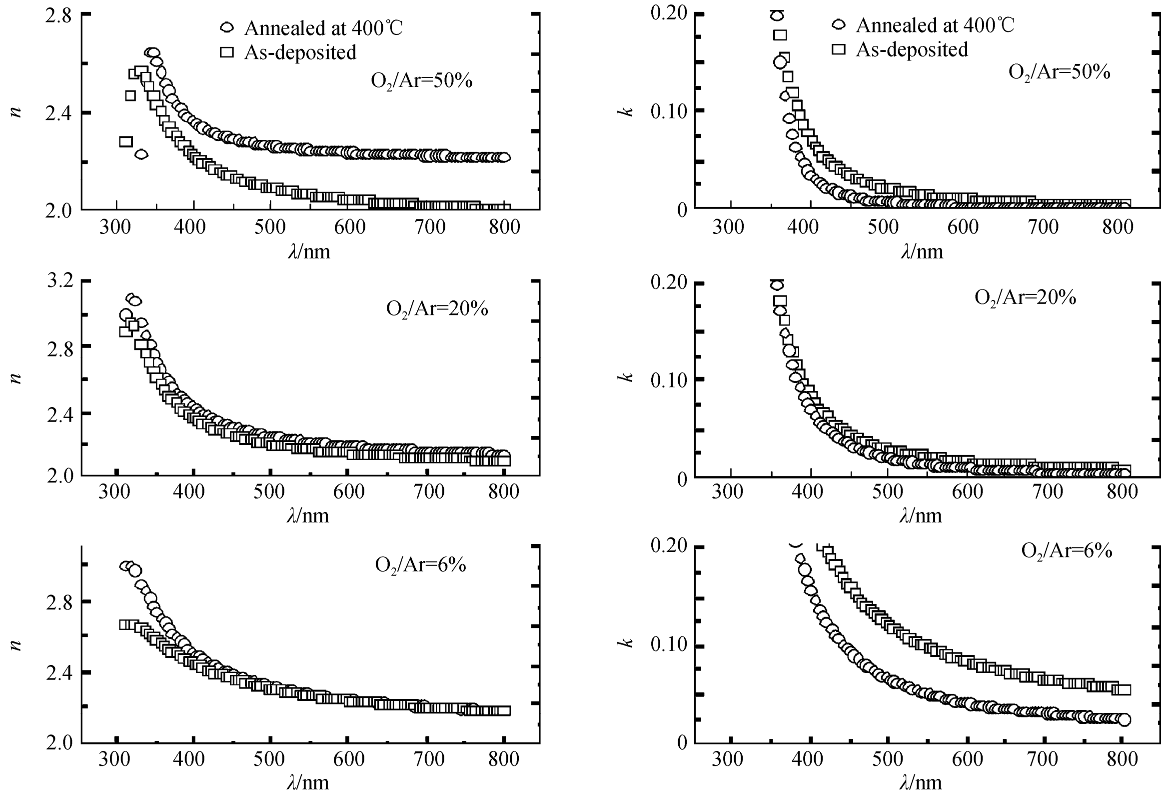

Fig. 1 Spectra of the refractive index of NiO_x samples at different sputtering flow ratios of O_2/Ar

This variation can be due to the different content of oxygen, which is imbedded in the films. After annealing, the refractive index and extinction coefficient show a contrary trend. The refractive index shows a increase, especially at a high O_2/Ar ratio, while the extinction coefficient change drastically, reduced by about 50%, which is accordance with reference [5]. The change of the complex refractive index can be attributed to the decomposition of NiO_x after annealing. Our measurement result is also accordance with reference [13] in which the refractive index n was calculated from the reflectance spectra of the NiO_x films.

In order to study the principle of optical constant change further, some samples were investigated by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis at room temperature. Fig. 2 demonstrates the XRD results of some NiO_x samples as-prepared at different O_2/Ar flow ratio.

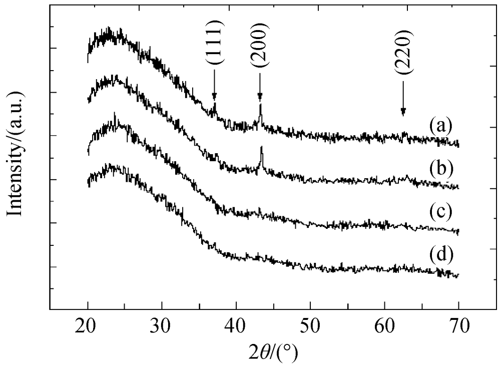

Fig. 2 X-ray diffractograms of NiO_x samples prepared at different O_2/Ar flow ratios

As shown in Fig. 2, (a) Stands for as-deposited of O_2/Ar flow ratio 6%, (b) Stands for annealed of O_2/Ar flow ratio 6%, (c) Stands for as-deposited of O_2/Ar flow ratio 50% and (d) stands for annealed of O_2/Ar flow ratio 50%. Crystalline diffraction peaks due to existence of cubic NiO are clearly evident for the sample deposited at an O_2/Ar flow ratio of 6%. However, It shows amorphous structure for the film deposited at the O_2/Ar flow ratio of 50%. The films like this were divided into two modes: metal-sputtering and oxide-sputtering modes in reference [14]. When O_2/Ar flow ratio is high during spurtting, there are much oxygen which is imbedded between grains. The execess oxygen in the film can be described by the reaction

$$\frac{1}{2}O_2+Ni\rightarrow O_i''+V_{Ni}''+Ni^{3+} \qquad (1)$$

Where V_{Ni}'' and O_i'' represent the vacancy of Ni and interstitial oxygen respectively. The vacancy of Ni and interstitial oxygen together make the films more loose. Therefore, the refractive index and extinction coefficient of as-deposited NiO_x sputtered at a high O_2/Ar flow ratio are smaller than that of sputtered at a low O_2/Ar flow ratio, as shown in Fig. 1.

There is no structure change after annealing at 400 ℃ for the films deposited at different O_2/Ar flow ratios, as shown in Fig. 2. However, the component of NiO_x films changes after annealing at 400℃, which is evident from following XPS spectra of NiO_x films.

Fig. 3 presents the XPS spectra of Ni $2p_{3/2}$ core levers for NiO_x films of 20% O_2/Ar flow ratio before and after annealing at 400 ℃. These samples contain two compounds, NiO and Ni_2O_3. The binding energy of Ni^{2+} of NiO and Ni^{3+} of Ni_2O_3 for the Ni $2p_{3/2}$ peak is located around 853.7 and 855.5 eV using the peak of the C 1s 284.8 eV as the standard , respectively . The result in our

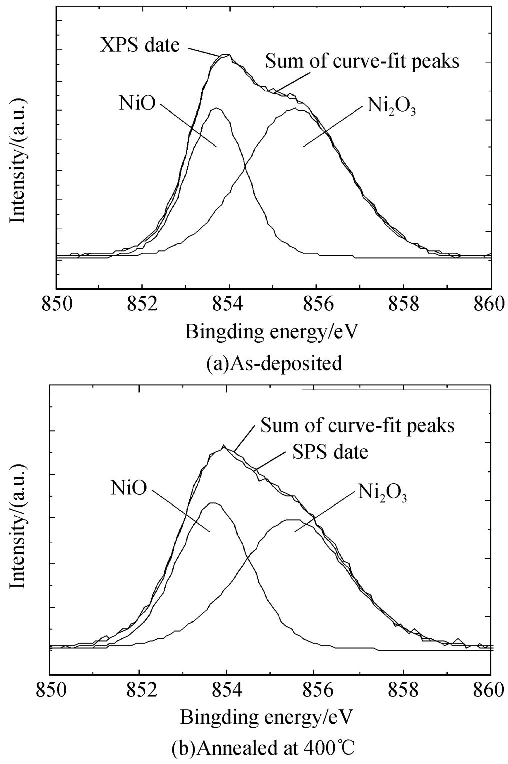

Fig. 3 XPS spectra of Ni $2p_{3/2}$ peaks for NiO_x samples prepared at O_2/Ar flow ratios 20%

measurement is slightly different from that reported by Yang, et al. [15]. A Shirly background was subtracted before performing the deconvolution. The Ni^{3+} / Ni^{2+} area ratio decreases from 1.67 to 1.36 after annealing in the main Ni $2p_{3/2}$ peaks. The XPS spectra for NiO_x films of 6% and 50% O_2/Ar flow ratio also shows the same character. It was concluded that the decomposition of NiO_x had taken place during annealing as the reaction

$$NiO_x\rightarrow NiO+O_2 \qquad (2)$$

causing releasing O_2. The decomposition of NiO_x in the films makes the thickness degressive and the whole film closer. The decrease of oxgen content caused by the decomposition of NiO_x after annealing causes the refractive index increase and extinction coefficient decrease as shown in Fig. 1.

Fig. 4 shows the spectra of the refractive index of as-deposited NiO_x samples at different sputtering powers and work pressures. The sputtering powers and work pressures have something to do with the refractive index of NiO_x samples. The refractive index is greater for a higher sputtering power. But it is smaller for a higher work pressures. This can be infered from the sputtering process. The higher the sputtering power is and smaller work pressure is, the more the particles from the target cross the space and reach the substrate at a certain time. According to the theory of molecular motion, when pressure decreases or work power increases, mean free path of molecular increases. The deposited particles gain more energy in the electric field and own high mobility on the surface of substrate. Then the particles can move to the places with lower energy and make the whole film compact[16]. The more compact NiO_x films causes the refractive index increasing. The increase of reflectence at high sputtering power and low work pressure can also confirm this (not shown here).

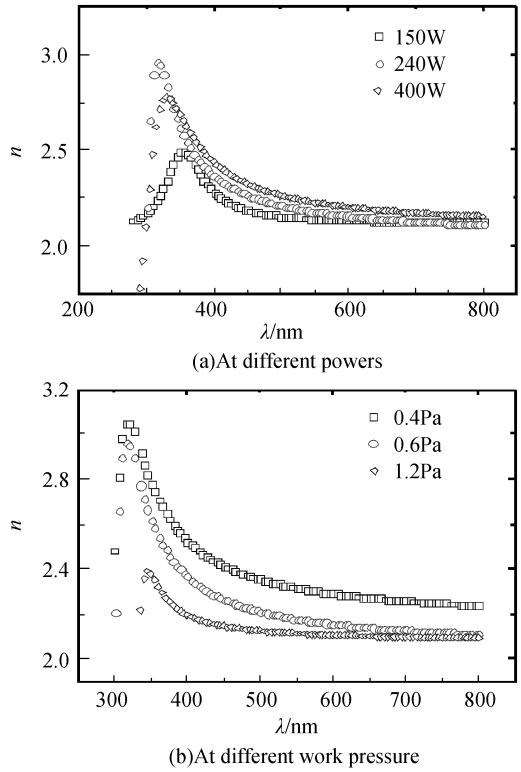

Fig. 4 Spectra of the refractive index of NiO_x samples at different sputtering powers and work pressures

3 Conclusion

Sputtering parameters strongly influence optical constant of NiO_x thin films prepared by reactive magnetron sputtering. For the NiO_x thin films as-deposited, the refractive index and extinction coefficient have the same mutative trend, that is, optical constant get smaller with O_2/Ar flow ratios increasing. After annealing, the refractive index shows an increase, especially at a high O_2/Ar flow ratio while the extinction coefficient reduced by about 50%. They are caused by the existence of interstitial oxygen and the decomposition of NiO_x, respectively. The refractive index is greater for a higher sputtering power while smallerer for a higher work pressure. It is caused by the difference of compactness degree of NiO_x films deposited at different sputtering conditions.

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磁控溅射参数对 NiO_x 薄膜光学常数的影响

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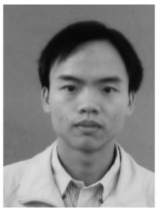
摘　要：采用反应性磁控溅射法制备了 NiO_x 薄膜，并结合椭圆偏振仪、XRD和XPS研究了溅射参量对其光学常量的影响. NiO_x 薄膜的光学常量随着 O_2/Ar流量比的增大而减小；热退火后，折射率增大而消光系数下降了50%；溅射功率越大折射率也越大，而工作气压越大折射率反而越小. 这些变化分别与薄膜中存在间隙O和Ni空位、NiO_x 分解以及 NiO_x 薄膜的致密度有关.

关键词：光学常数；NiO_x 薄膜；溅射参数



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