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Spectroscopic ellipsometry study of thin NiO films grown on Si (100) by atomic layer deposition

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Thin NiO films are grown at 300 °C on Si (100) using atomic layer deposition. The dependence of annealing temperature on the optical properties of NiO films has been investigated using spectroscopic ellipsometry in the spectral region of 1.24–5.05 eV. It is found that the refractive index and thickness of NiO films are affected by high temperature annealing. The optical band gap of the as-deposited thin NiO film is determined to be 3.8 eV, which is almost independent of the annealing temperature. The indirect band gap of NiO film shifts toward lower photon energy with an increase in annealing temperature. © *2008 American Institute of Physics*.
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NiO films have various interesting properties, such as excellent chemical stability, good crystallinity, transparency with low resistivity, and controllable transmittance for incident visible light.[1,2] All these desirable properties have rendered NiO film an attractive material for use as the antiferromagnetic layers of spin valve films, *p*-type transparent conducting films, and electrochromic devices.[3] In addition, NiO films have also shown good resistance switching, such as large resistance change, induced by external electric fields.[4,5] Therefore, the growth of nickel oxide films has recently received great attention due to their potential applications for nonvolatile resistance random access memory devices. In spite of these applications, very few reports have so far been published on optical properties of NiO films. In this letter, spectroscopic ellipsometry (SE) has been employed to investigate the influence of thermal annealing on optical properties of thin NiO films grown by atomic layer deposition (ALD).

Thin NiO films were deposited at 300 °C on *n*-type Si (100) by alternate pulsing $Ni(Cp)_2$ (Cp=cyclopentadienyl, C_5H_5) and O_3 in an ALD F-120 (ASM-Microchemistry, Ltd.) reactor. Before being loaded into the ALD reactor, the Si substrates were first cleaned using SC-2 ($HCl:H_2O_2:H_2O=1:1:5$, 85 °C, 10 min) solutions and then dipped into a dilute HF solution ($HF:H_2O=1:50$) to produce H-terminated surfaces. Inside the reactor, $Ni(Cp)_2$ were evaporated from an open boat at a source temperature 40 °C. The oxygen source O_3 was generated from O_2 (99.999%) in an ozone generator and fed into the reactor at a mass flow flux of 400 SCCM (SCCM denotes cubic centimeter per minute at STP). After deposition, some prepared NiO samples were then subjected to a rapid thermal annealing (RTA) at temperatures ranging from 500 to 700 °C for 60 s in nitrogen ambient.

Optical properties of thin NiO films were characterized by SE method. A spectroscopic ellipsometer (J. A. Woollam, Co., M-2000) was used to acquire spectra in the visible-UV range from 1.24 to 5.05 eV. The ellipsometric angle ψ and phase difference Δ were recorded at an incidence angle of 75°. The Tauc–Lorentz (TL) dispersion function[6,7] is employed to characterize the dielectric function of the NiO films, which is expressed as follows:

$$\varepsilon_2(E)=\begin{cases}\dfrac{AE_0C(E-E_g)^2}{(E^2-E_0^2)^2+C^2E^2}\dfrac{1}{E}, & (E>E_g)\\ 0, & (E\leqslant E_g)\end{cases} \quad (1)$$

and

$$\varepsilon_1(E)=\varepsilon_\infty+\frac{2}{\pi}P\int_{E_g}^{\infty}\frac{\xi\varepsilon_2(\xi)}{\xi^2-E^2}d\xi, \quad (2)$$

where A is the amplitude, E_0 is the peak transition energy, C is the broadening term, and E_g is the band gap. A simple four-phase model consisting of substrate/SiO_2 interfacial layer/thin NiO film/surface rough layer has been used to represent the sample. The surface rough layer is modeled by the Bruggeman effective medium approximation[8] of 50% NiO and 50% voids. The variables in the fitting procedure include the layer thickness and all TL parameters. The fitting quality

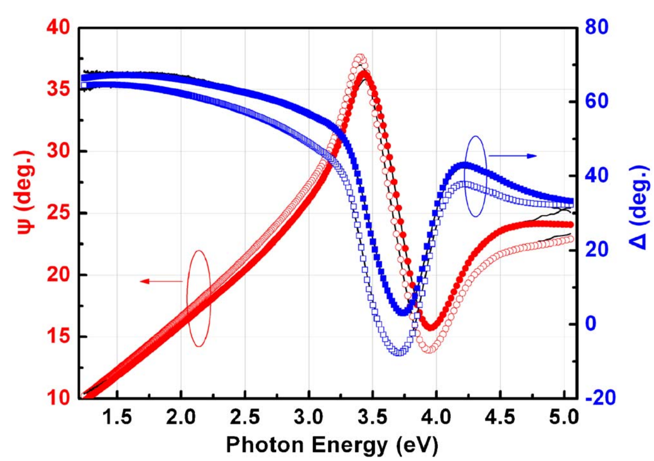

FIG. 1. (Color online) Experimental (solid curves) and fitted (symbols) ellipsometric data, Δ and ψ, of thin NiO films: (open) as-deposited and (filled) 700 °C annealed.

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TABLE I. Compilation of the fitted results for all the samples using double Tauc–Lorentz dispersion function. t_f, t_s, and t_{IL} are the thicknesses of NiO film, surface rough layer, and SiO_2 interfacial layer with units of nanometers, respectively. σ is an unbiased estimator.

Sample	t_f	t_s	t_{IL}	ε_∞	A_1	E_{g1}	E_{01}	C_1	A_2	E_{g2}	E_{02}	C_2	σ
As-deposited	27.08	2.08	2.68	2.50	111.89	3.30	3.96	0.82	59.10	2.53	5.09	5.83	1.32
500 °C	26.86	1.56	2.73	2.07	117.09	3.31	3.97	0.82	77.47	2.58	5.27	7.46	1.61
600 °C	26.65	1.02	2.92	1.24	121.79	3.33	3.96	0.79	70.41	2.29	6.70	9.47	1.48
700 °C	25.99	0.70	3.25	0.84	141.88	3.36	3.95	0.79	66.89	2.05	8.17	11.56	2.25

is poor when simple TL dispersion function is used, indicating that more than one single type of electronic transition dominates the optical absorption in the ultraviolet region for NiO films. Double TL dispersion function is then applied to fit the measured ellipsometric data in the present work.

Figure 1 shows the experimental (solid curves) and fitted (symbols) spectroscopic spectra of ψ and Δ as a function of the photon energy for as-deposited and 700 °C annealed NiO films. The similar spectra for the samples annealed at 500 and 600 °C are not shown here. It can be seen that a good agreement between the experimental and fitted spectra is obtained except in the range of 4.75–5.05 eV. This means that the double TL dispersion function works well and the physical and optical properties of the NiO films can be exactly determined by the best-fitted results. Table I summarizes all of the layer thicknesses and the TL parameter values obtained from data fitting with a 90% confidence limit.

The extracted optical constants n and k for as-deposited and annealed NiO films are presented in Fig. 2. The energy dependence of n and k is similar to those reported for NiO single crystal[1] and films.[9,10] The value of n is 2.37 at the photon energy of 2 eV for as-deposited sample, which is in good agreement with the value reported by Powell and Spicer.[1] The n values of NiO film annealed at 500 °C are similar to those of as-deposited sample. For the samples annealed at temperature above 500 °C, it is found that n values decrease by around 0.2 in the photon energy region from 1.2 to 3.3 eV. The refractive index of a thin film is proportional to the film density. In general, the film density (and thus the refractive index) increases with increasing annealing temperature. This is contrary to the behavior shown in our case. On the other hand, it is observed that the thickness of thin NiO film decreases from 27.08 to 25.99 nm with the increase in annealing temperature, as listed in Table I. The decrease in n values and film thickness with increasing RTA temperature may be attributed to the change in film composition when thin NiO films are annealed at and above 600 °C. X-ray photoelectron spectroscopy (XPS) is then employed to determine the film stoichiometry and chemical state of samples under RTA processes. It has been demonstrated by XPS (not shown here) that the formation of Ni cluster and decrease in oxygen contents occur slightly in the 600 and 700 °C annealed NiO samples. The outdiffusion of oxygen in the annealed sample increases the porosity of the film, resulting in the decrease in refractive index and thin film thickness. A similar behavior was reported by Sasi and Gopchandran.[11] In addition, the surface roughness of as-deposited NiO film is determined to be 2.08 nm and it decreases as the annealing temperature increases from 500 to 700 °C. The decrease in NiO film surface roughness is ascribed to the increase in mobility of film surface atoms or molecules at high annealing temperature.

A slight variation of extinction coefficient induced by RTA is observed in the annealed NiO films (see Fig. 2). The absorption coefficients α of sample can be obtained via $\alpha=4\pi k/\lambda$, where λ is wavelength of the incident light. The spectral variation of α as a function of the photon energy for as-deposited and annealed NiO films is shown in Fig. 3. It is observed that α abruptly rises, reaching values of 10^5 cm^{-1} in the UV region, which is attributed to band gap absorption in NiO sample. Based on the optical absorption spectra, the nature of optical transition can be determined. The optical band gap E_g can be calculated using the following:[12]

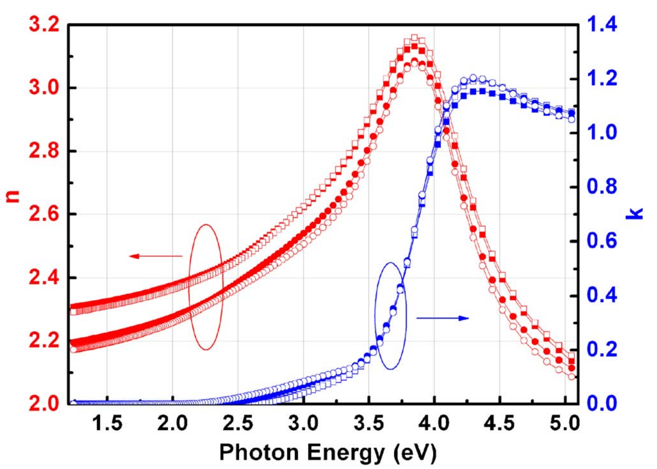

FIG. 2. (Color online) Spectra of refractive index (n) and extinction coefficient (k) for thin NiO films: (■) as-deposited, (□) 500 °C annealed, (●) 600 °C annealed, and (○) 700 °C annealed.

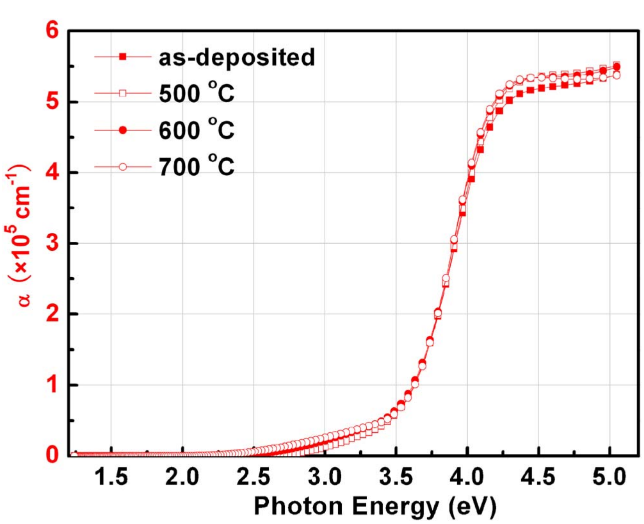

FIG. 3. (Color online) The absorption coefficient (α) vs photon energy for as-deposited and annealed thin NiO films.

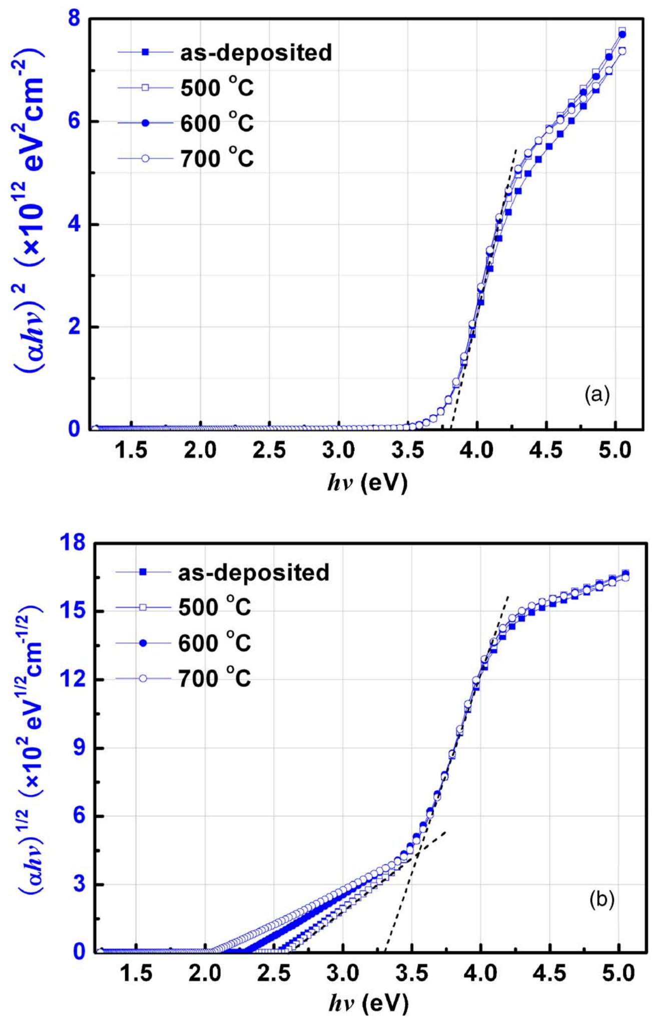

FIG. 4. (Color online) Plots of $(\alpha h\nu)^2$ (a) and $(\alpha h\nu)^{1/2}$ (b) vs $h\nu$ for as-deposited and annealed thin NiO films.

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \tag{3}$$

where A is a constant and $h\nu$ is the incident photon energy. The variation of $(\alpha h\nu)^2$ versus $h\nu$ for all the NiO samples is shown in Fig. 4(a). The nature of the plots indicates the existence of direct interband transition in thin NiO films. The E_g values are determined from the energy intercept by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ to $\alpha=0$. The E_g for the as-deposited NiO film is estimated to be 3.8 eV, which is in good agreement with the results (3.6–4.0 eV) reported by Adler and Feinlieb[13] and Kamal *et al.*,[14] and is larger than the value (3.25 eV) for NiO films deposited by solution growth technique.[15] It is noted that the E_g is almost independent of the annealing temperature.

The optical absorption data are also analyzed for evidence of indirect allowed transitions by the following:[16]

$$\alpha h\nu = B(h\nu - E_{\text{gind}} \pm E_p)^2, \tag{4}$$

where B is a constant, E_{gind} is the indirect energy gap (minimum gap between conductor band and valance band), and E_p is the energy of the absorbed (+) or emitted (−) phonons. Figure 4(b) shows the plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for as-deposited and annealed NiO films. Each plot can be resolved into two distinct straight line portions. One is in the lower photon energy region corresponding to phonon absorption and has an intercept with the photon energy axis at $(E_{\text{gind}} - E_p)$. The other straight line portion corresponds to a phonon energy emission process and has an intercept $(E_{\text{gind}}+E_p)$. From the energy intercepts, the values of E_{gind} and E_p for all NiO samples have been calculated. The E_{gind} is found to be about 2.92 eV for the as-deposited NiO film, and moves to 2.91, 2.80, and 2.69 eV for films annealed at 500, 600, and 700 °C, respectively. It is evident that the E_{gind} obtained for the indirect allowed transition shifts toward lower energy when the annealing temperature increases. The variation in E_{gind} with annealing temperature may be attributed to the changes in homogeneity, crystallinity, and composition of NiO samples treated by RTA.

In conclusion, the effect of annealing temperature on optical properties of ALD grown thin NiO films has been investigated by SE. The results show that the refractive index of NiO films decreases as the annealing temperature increases. The thickness of as-deposited NiO film is 28.7 nm, which decreases to 25.9 nm as the annealing temperature increases to 700 °C. The estimated optical band gap is 3.8 eV for as-deposited NiO film and is not affected by high temperature annealing. The indirect band gap is found to decrease as the annealing temperature is increased from 500 to 700 °C.

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