Influence of sputtering pressure on band gap of $Zn_{1-x}Mg_xO$ thin films prepared by radio frequency magnetron sputtering

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$Zn_{1-x}Mg_xO$ thin films were deposited onto quartz glass substrates using a radio frequency magnetron sputtering at various deposition pressures. It was found that the Mg concentration in the $Zn_{1-x}Mg_xO$ thin films significantly increased by decreasing the deposition pressure from 9 to 1 Pa, which contributed to an increase in the band gap of the ZnMgO films. In addition, the $Zn_{1-x}Mg_xO$ thin films, which had a hexagonal wurtzite structure when obtained by high pressure deposition (7 and 9 Pa) at $x \leq 0.478$, had a cubic rock-salt crystal structure when deposition pressure was decreased to 1–5 Pa at $x \geq 0.482$. These results show that the band gap of the ZnMgO thin films could be easily modulated only by adjusting of the deposition pressure during the radio frequency sputtering process. © *2011 American Vacuum Society*. [DOI: 10.1116/1.3622316]

I. INTRODUCTION

Zinc oxide (ZnO) has attracted considerable attention in optoelectronic applications, such as light emitting devices and laser diodes. This interest is due to its promising properties, including a wide band gap of 3.37 eV at room temperature, a large excitation binding energy of 60 meV, chemical stability, and transparency, etc.[1–3] For commercial applications of ZnO-based semiconductors, an important issue is the realization of band gap engineering in a wide range. One can modulate the band gap of ZnO by alloying it with a semiconductor that has a different band gap to form a ternary compound. $Zn_{1-x}Mg_xO$ has been widely investigated because its band gap can be modulated from 3.37 (for wurtzite ZnO) to 7.9 eV (for rock-salt MgO). The similarity of the ionic radius between Mg^{2+} (0.57 Å) and Zn^{2+} (0.60 Å) allows them to be substituted for one another without causing significant changes in a lattice structure.[4] So far, ZnMgO films have been prepared by various techniques such as pulsed laser deposition,[5,6] molecular beam epitaxy,[7,8] and radio frequency (RF) sputtering.[9,10] Among these deposition techniques the RF magnetron sputtering is considered as the most convenient method to deposit reproducible and homogeneous ZnMgO thin films over a large-area substrate at a lower deposition temperature. Han *et al.*[11] achieved a high Mg concentration of between 0.70 and 0.84 by changing the RF power. Li *et al.*[12] have investigated the effects of thermal annealing on Mg concentration ($0.10 \leq x \leq 0.14$) in $Zn_{1-x}Mg_xO$ films. Although the RF sputtering method is extensively applied for modulating Mg concentration in a ZnMgO film, there are few reports on the effects of deposition pressure on structural and optical properties of $Zn_{1-x}Mg_xO$ thin films deposited at a low temperature. In this research, $Zn_{1-x}Mg_xO$ thin films were prepared by RF magnetron sputtering at a variable deposition pressure based on the extensive experience of thin film fabrications in our group.[13,14] The effects of deposition pressure on the structural and optical properties of ZnMgO thin films were investigated.

II. EXPERIMENT

$Zn_{1-x}Mg_xO$ films (500 nm in thickness) were deposited onto quartz glass by a RF (13.56 MHz) magnetron sputtering system using a 4-inch ZnO/MgO (70/30 wt.%) ceramic target. The substrate on an anode was heated and kept at 200°C before and during deposition and the chamber was evacuated to 8×10^{-5} Pa with a turbomolecular pump. During the sputtering process, the RF power was set consistently at 180 W. A mixture gas of oxygen and argon was introduced at a flow ratio of $Ar/O_2 = 10$ sccm/30 sccm, controlled by mass flow controllers. In order to investigate the effects of deposition pressure on the properties of $Zn_{1-x}Mg_xO$ films, the deposition pressure was varied from 1 to 9 Pa, in graduations of 2 Pa.

The crystal structure of the $Zn_{1-x}Mg_xO$ films were characterized using an x-ray diffraction system (Rigaku ATX-G diffractometer), performed in $2\theta/\omega$ sweeping from 30° to 50° in 2θ with a step width and a scan speed of 0.01° and 0.5°/min, respectively, employing a Cu $K\alpha$ ($\lambda = 0.154178$ nm) radiation (50 kV, 300 mA). Rutherford backscattering/ion channeling techniques were used to determine the chemical composition of the films. Rutherford backscattering (RBS) was taken using a probe beam of 2.0 MeV He^+ ions, with a surface barrier detector positioned at 165°. Optical transmission spectra measurements were performed using an UV–visible spectrophotometer (U-4100, Hitachi Corp.). All measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

Figure 1 shows the influence of deposition pressure on deposition rate. It is observed that the deposition rate of the $Zn_{1-x}Mg_xO$ thin films decreases from 4.50 to 2.06 nm/min when the deposition pressure is increased from 1 to 9 Pa,

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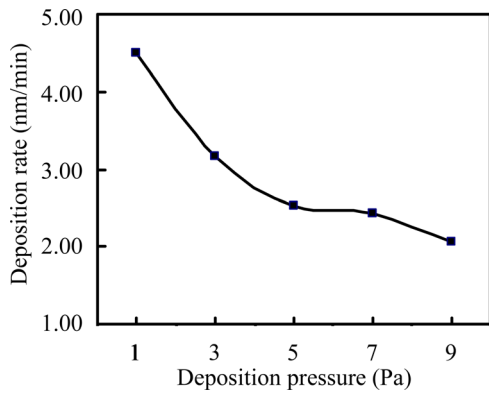FIG. 1. (Color online) Dependence of the deposition rate of the Zn$_{1-x}$Mg$_x$O films on the deposition pressure.

which might be due to the fact that the bombardment effect of sputtering ions is weakened by increasing sputtering pressure.[15,16]

Figure 2 shows the XRD patterns of the Zn$_{1-x}$Mg$_x$O thin films prepared under different deposition pressures. The ZnMgO films exhibit single cubic rock-salt structure and only MgO (200) peak can be observed in the films deposited at a low pressure (1–5 Pa). With an increase in the deposition pressure, the MgO (200) peak shifts slightly to a lower diffraction angle coupled with a decrease of the intensity of the peak. It can also be seen that the cubic rock-salt structure is converted into hexagonal wurtzite structure when the deposition pressure is increased from 5 to 7 Pa, whereas the MgO (200) peak disappears and only one weak ZnO (002) peak is observed in the ZnMgO film. When the deposition pressure is increased further to 9 Pa, only the ZnO (002) peak is observed in the as-deposited film. Meanwhile, the ZnO (002) peak slightly shifts toward a lower diffraction angle with an enhanced intensity, which indicates that the ZnMgO alloy exhibits dominated ZnO hexagonal wurtzite structure and crystallinity of films is improved. The XRD results demonstrated that 7 Pa deposition pressure is a turning point at which the crystal structures of hexagonal wurtzite are con-
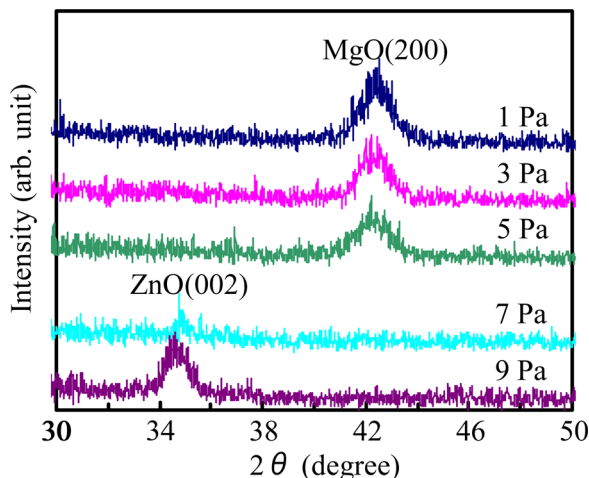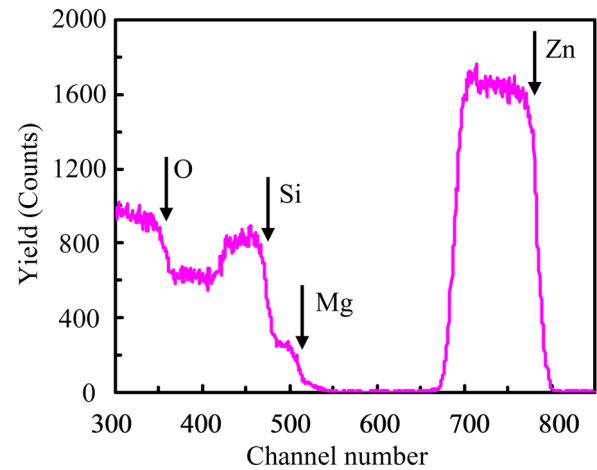

FIG. 3. (Color online) RBS spectra of the Zn$_{1-x}$Mg$_x$O thin films deposited under different pressures.

verted from cubic rock-salt under the high-pressure RF sputtering process. Therefore, the crystal structure of ZnMgO thin films can be modulated by adjusting the deposition pressure.

Figure 3 shows the typical RBS spectra of the Zn$_{1-x}$Mg$_x$O thin film. The Zn$_{1-x}$Mg$_x$O films are composed of O, Zn, and Mg. The composition of the films is then determined from the Mg/Zn peak height ratios in RBS spectrum by quantitative analysis.[17] Figure 4 shows the calculated atomic ratios of Mg concentration x as a function of the deposition pressure. The RBS results reveal that the Mg concentration in the Zn$_{1-x}$Mg$_x$O thin films gradually decreases from 0.531 to 0.482 as the deposition pressure increases from 1 to 5 Pa, and then further decreases to 0.478 and 0.467 as the deposition pressure increases to 7 and 9 Pa, respectively. The RBS results demonstrate that the Mg concentration in the ZnMgO films is modulated by varying the deposition pressure.

The decrease in the Mg concentration in the ZnMgO thin films with the increase in the deposition pressure might attribute to the scattering effect.[18] Under a lower sputtering pressure the ejected species, including the sputtered adatoms and ion clusters from the target, experience fewer collisions and scatterings with the sputtering gas atoms prior to
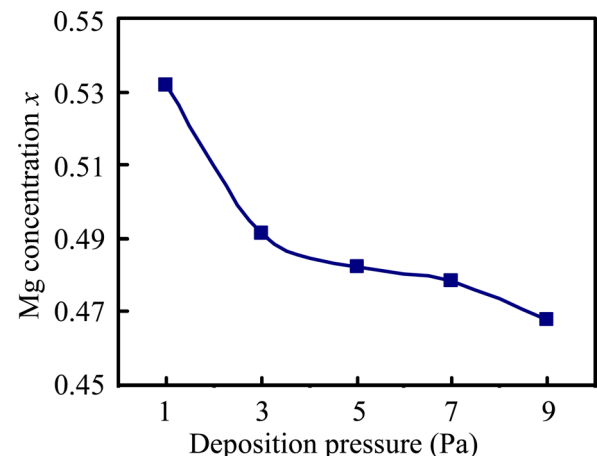

FIG. 2. (Color online) XRD spectra of the Zn$_{1-x}$Mg$_x$O thin films prepared on the quartz substrates under the deposition pressure from 1 to 9 Pa.

FIG. 4. (Color online) Calculated Mg concentration of the Zn$_{1-x}$Mg$_x$O films on the deposition pressure.

reaching the substrate, leading to higher deposition rate. It is confirmed with RBS measurement that the Mg concentration is 0.531 at the deposition pressure of 1 Pa, which is higher than Zn concentration in as-deposited ZnMgO film. In addition, the ejected species suffered fewer collisions with higher kinetic energy, the result being that Zn^{2+} ions are substituted by Mg^{2+} ions. This is due to the fact that Mg–O (531.2 eV) has a higher bond strength than Zn–O (530.2 eV), and therefore ZnMgO films exhibit better crystallization with the higher Mg concentration. However, with the deposition pressure increases, the collision and scattering effects are enhanced. Mg related species can be scattered more easily than Zn related species in the sputtering gas ambient, because the relative atomic mass of Mg (24.31) is lighter than that of Zn (65.39). Consequently, there is less Mg occupation of the position of Zn, corresponding to reduction in Mg incorporation efficiency. Mg concentration therefore gradually decreases until it is less than Zn concentration in the films after the pressure increase over 3 Pa, as shown in Fig. 4. This result correlates well with the result of XRD measurement.

The transmittance spectra of the Zn$_{1-x}$Mg$_x$O films prepared at different deposition pressures are shown in Fig. 5. The transmittances for all the ZnMgO films on the quartz glass are ∼85% in the visible region. The absorption edge of the ZnMgO films shifts to higher wavelengths with the decrease in Mg concentration. It is observed that the slope becomes less acute near the absorption edges as the deposition pressure becomes lower than 5 Pa. However, the films deposited under higher pressure (7 and 9 Pa) have a sharp absorption edge in the UV region. The absorption edge of ZnMgO films deposited from 5 to 7 Pa shifts from the average wavelength of 260 to 290 nm, indicating that the phase transformation also is observed from the transmittance spectra. Further, the Mg concentration in ZnMgO films decreases as deposition pressure increases, which is consistent with the XRD results.

The absorption edge can be used to evaluate the band gap of the Zn$_{1-x}$Mg$_x$O films. The relationship between the
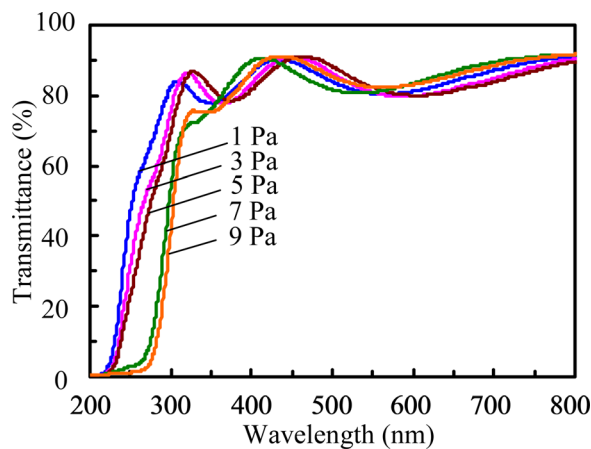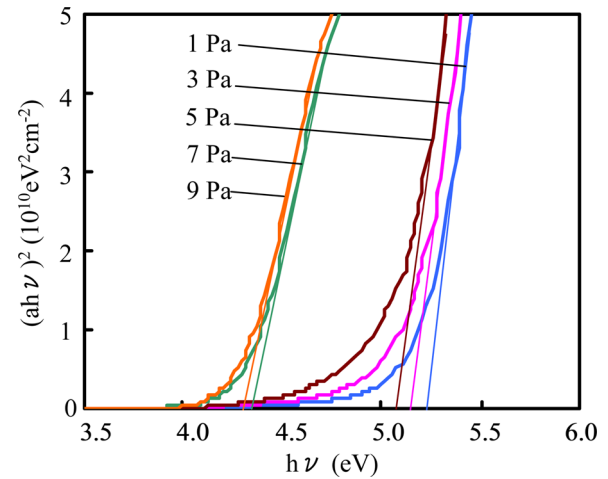

FIG. 6. (Color online) Variation of $(\alpha h\upsilon)^2$ of the Zn$_{1-x}$Mg$_x$O thin films as a function of the photon energy ($h\upsilon$).

absorption coefficient and the photon energy can be expressed as follows[12]:

$$(\alpha h\upsilon)^2 = A\left(h\upsilon - E_g\right), \tag{1}$$

where A and E_g represent the constant and the band gap of a film. The absorption coefficient (α) could be obtained from the transmittance $T = A\exp(-\alpha d)$, where A and d are a constant and the thickness of the film, respectively. The band gap (E_g) is determined by extrapolation of the linear portion to the photon energy axis at $(\alpha h\upsilon)^2 = 0$.

Figure 6 shows $(\alpha h\upsilon)^2$ plots of the ZnMgO films as a function of the photon energy ($h\upsilon$). The evaluated band gaps of the Zn$_{1-x}$Mg$_x$O thin films are 5.23, 5.16, 5.10, 4.33, and 4.30 eV corresponding to the deposition pressure of 1, 3, 5, 7, and 9 Pa, respectively. These results indicate that the band gap energy of the ZnMgO thin films decreases with increasing deposition pressure. The band gap change in the Zn$_{1-x}$Mg$_x$O thin films prepared under different deposition pressures is in correlation with the crystallite phase transformation from cubic to wurtzite structure obtained from the XRD measurement. Therefore, modulation of the band gap of the ZnMgO thin films can be achieved by controlling the deposition pressure during the RF sputtering process.

IV. CONCLUSIONS

The deposition pressure was found to be an important parameter influence on the structural and optical properties of Zn$_{1-x}$Mg$_x$O films prepared on quartz substrates by RF magnetron sputtering. The Mg concentration in the ZnMgO thin films increased by decreasing deposition pressure from 9 to 1 Pa. Correspondingly the crystal structure was converted from hexagonal wurtzite to cubic rock-salt when Mg concentration $x \geq 0.482$. Further, the band gap of the ZnMgO films was significantly increased from 4.30 to 5.23 eV, whereas the deposition pressure decreased. Therefore, it is possible to control the crystalline structure and the band gap of the ZnMgO films by simply adjusting the deposition pressure in the RF magnetron sputtering process.

FIG. 5. (Color online) Transmittance spectra of the Zn$_{1-x}$Mg$_x$O thin films prepared under different deposition pressures.

ACKNOWLEDGMENTS

[1]T. Aoki, Y. Hatanaka, and D. C. Look, Appl. Phys. Lett. **76**, 3257 (2000).

[2]U. Ozgur, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S.-J. Cho, and H. Morkoç, J. Appl. Phys. **98**, 041301 (2005).

[3]D. C. Look, B. Claflin, Ya. I. Alivov, and S. J. Park, Phys. Status Solidi A **201**, 2203 (2004).

[4]R. D. Shannon, Acta Crystallogr. Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 51 (1976).

[5]F. K. Shan, B. I. Kim, G. X. Liu, Z. F. Liu, J. Y. Sohn, W. J. Lee, and B. C. Shin, J. Appl. Phys. **95**, 4772 (2004).

[6]C. Yang, X. M. Li, X. D. Gao, X. Cao, R. Yang, and Y. Z. Li, J. Cryst. Growth **312**, 978 (2010).

[7]H. Tanaka, S. Fujita, and S. Fujita, Appl. Phys. Lett. **86**, 192911 (2005).

[8]S. C. Su, Y. M. Lu, Z. Z. Zhang, B. H. Li, D. Z. Shen, B. Yao, J. Y. Zhang, D. X. Zhao, and X. W. Fan, Appl. Surf. Sci. **254**, 4886 (2008).

[9]T. Minemoto, T. Negami, S. Nishiwaki, H. Takakura, and Y. Hamakawa, Thin Solid Films **372**, 173 (2000).

[10]J. Y. Moon, J. H. Kim, H. Kim, H. S. Lee, Y. Y. Kim, H. K. Cho, and H. S. Kim, Thin Solid Films **517**, 3931 (2009).

[11]S. Han, D. Z. Shen, J. Y. Zhang, Y. M. Zhao, D. Y. Jiang, Z. G. Ju, D. X. Zhao, and B. Yao, J. Alloys Compd. **485**, 794 (2009).

[12]H. Li, Y. Z. Zhang, X. J. Pan, T. Wang, and E. Q. Xie, J. Alloys Compd. **472**, 208 (2009).

[13]C. Y. Li, T. Matsuda, T. Kawaharamura, H. Furuta, M. Furuta, T. Hiramatsu, T. Hirao, Y. Nakanishi, and K. Ichinomiya, J. Vac. Sci. Technol. B **28**, C2B51 (2010).

[14]M. Furuta, T. Hiramatsu, T. Matsuda, H. Furuta, and T. Hirao, Jpn. J. Appl. Phys. **46**, 4038 (2007).

[15]V. Assuncao, E. Fortunato, A. Marques, H. Aguas, I. Ferreira, M. E. V. Costa, and R. Martins, Thin Solid Films **427**, 401 (2000).

[16]H. Zhu, J. Hupkes, E. Bunte, A. Gerber, and S. M. Huang, Thin Solid Films **518**, 4997 (2010).

[17]L. C. Feldman and J. W. Mayer, *Fundamentals of Surface and Thin Film Analysis* (Elsevier, North-Holland, 1986), Chap. 3.

[18]P. Misra, P. Bhattacharya, K. Mallik, S. Rajagopalan, L. M. Kukreja, and K. C. Rustagi, Solid State Commun. **117**, 673 (2001).