Fabrication and optical properties of $Mg_xZn_{1-x}O$ thin films*

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(Received 10 June 2009; revised manuscript received 29 June 2009)

$Mg_xZn_{1-x}O$ ($x \leq 0.3$) thin films have been prepared on silicon substrates by radio frequency magnetron sputtering at room temperature. The thin films have hexagonal wurtzite single-phase structure and a preferred orientation with the *c*-axis perpendicular to the substrates. The Mg content in the films is slightly larger than that in the targets. The refractive indices of $Mg_xZn_{1-x}O$ films measured at room temperature by spectroscopic ellipsometry (SE) on the wavelength 632.8 nm are systematically decreased with the increasing of Mg content. Optical band gaps of $Mg_xZn_{1-x}O$ films are determined by the transmittance spectra. With increasing Mg content, the absorption edges of $Mg_xZn_{1-x}O$ films shift to higher energies and band gaps linearly increase from 3.24 eV at $x = 0$ to 3.90 eV at $x = 0.30$.

Keywords: semiconductor, thin films, alloys, optical properties
PACC: 8115C, 8160C, 7820D

1. Introduction

In the past several years, a great deal of research efforts on wide band gap semiconductors have resulted in the commercialization of GaN-based blue lasers, light emitting diodes, and ultraviolet photodetectors.[1−3] As an alternative to the GaN material system, ZnO and its alloys are of substantial interest.[4,5] The exciton binding energy of ZnO is about 60 meV and results in extremely efficient emission with room temperature optically pumped lasing reported in thin films and microcrystallites.[6−8] In optoelectronic device applications the modulation of the optical constant and band gap energy of the constituent layers while their lattice constants keep close to each other is important for constructing appropriate heterostructures. $Mg_xZn_{1-x}O$ has been considered as an appropriate ternary alloy system that can construct efficient heterojunctions with ZnO.[9] Alloying ZnO films with MgO facilitates band gap engineering for heterostructure device design and the replacement of Zn by Mg is not expected to induce a significant change in the lattice constants.

There are only few studies on the refractive indices of $Mg_xZn_{1-x}O$ films, which are essential for design and analysis of ZnO-based optoelectronic devices. Spectroscopic ellipsometry (SE) has widely been used as a nondestructive technique to investigate the optical response of semiconductors. Refractive indices can be obtained accurately by fitting SE data (ψ, Δ) to a theoretical model. In this paper, we describe the results of three kinds of methods performed on $Mg_xZn_{1-x}O$ films prepared on silicon substrates with a testing wavelength of 632.8 nm. The dependence of optical band gaps of $Mg_xZn_{1-x}O$ films on the Mg content is also investigated by the transmittance spectra.

2. Experimental

The $Mg_xZn_{1-x}O$ films were deposited on silicon substrates in a JPGF-450 model radio frequency magnetron sputtering system with a base pressure of 4×10^{-3} Pa. A power supply was operated at a crystal-controlled frequency of 13.56 MHz. The sintered ceramic targets with a mixture of ZnO (purity 99.99%) and MgO (purity 99.99%) were employed as source material. A mixture of Ar (99.999%) and O_2 (99.999%) was used as a sputtering gas. The separation between the substrate and target was 5 cm. During film deposition, the argon and oxygen partial pressure were maintained at 0.5 Pa, respectively. The sputtering power was 200 W and deposition time was 60 min.

The Mg contents of the $Mg_xZn_{1-x}O$ films were

*Project supported by the National Found for Fostering Talents of Basic Science (NFFTBS) of China (Grant No. J0730318) and the Natural Science Foundation of Shandong Province, China (Grant No. Y2007F02).
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determined with a JXA-8800R electronic probe and a 1.7 MV Tandem Accelerator (RBS). The structural properties were determined with a Bede QC200 Double Crystal Diffractometer (XRD). The refractive indices of $Mg_xZn_{1-x}O$ films were achieved by the prism-coupling method (Metricon Model 2010 Prism Coupler, laser wavelength 632.8 nm) and SE measurements. The SE measurements were carried out with a wavelength of 632.8 nm using an SGC-2 auto spectroscopic ellipsometer and a J. A. Woollam Co. model M88 spectroscopic ellipsometer at an incident angle of 70°. The optical transmittance measurements were performed with a TV-1900 UV double beam spectrophotometer.

3. Results and discussion

Figure 1 shows the Mg content in the films as a function of that in the targets. The Mg content in the films was systematically larger than that in the targets by a factor of 1.3. If the substrate temperature is very high, this difference can be attributed to the fact that the vapour pressure of ZnO and Zn is much larger than that of MgO and Mg at the substrate temperature.[10] But our samples were deposited at room temperature, so we consider that the difference can be caused by the effect of charge accumulating during electronic probe testing.

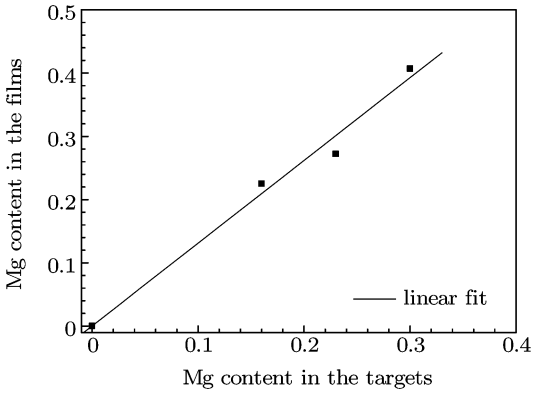


Fig. 1. Mg content (atomic ratio) in the $Mg_xZn_{1-x}O$ films as a function of target Mg content.

Rutherford backscattering (RBS) was also used to estimate the Mg content of the alloys. This was done by simulating the random yield using a range of compositions to find the best fit to the actual data. The Mg content in the films is only slightly larger than that in the targets. Figure 2 shows the RBS spectrum of $Mg_xZn_{1-x}O$ ($x = 0.23$) film.

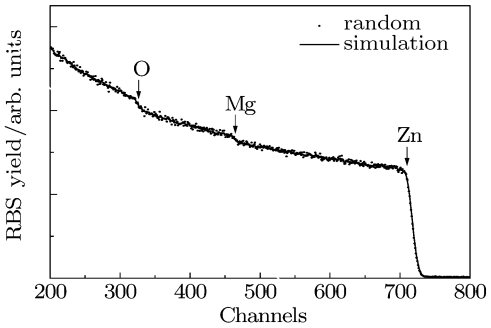


Fig. 2. RBS spectrum of $Mg_xZn_{1-x}O$ ($x = 0.23$) film.

An in-plane (0002) ω scan of an $x = 0.23$ film is shown in Fig. 3. The full width at half maximum (FWHM) value of the (0002) rocking curve was 0.33°. According to the FWHM value of the (0002) peak, the average grain size of $Mg_xZn_{1-x}O$ ($x = 0.23$) film was estimated to be 29 nm by the Scherrer formula. All the thin films have hexagonal wurtzite single-phase structure and a preferred orientation with the c-axis perpendicular to the substrates. There was no significant formation of a separated MgO phase in $Mg_xZn_{1-x}O$ film. The thermodynamic solubility limit of MgO in ZnO has been reported to be less than 4 mol%, according to the phase diagram of the ZnO–MgO binary system.[11] So the $Mg_xZn_{1-x}O$ film reported here can be considered as metastable phase. Radio frequency magnetron sputtering is a suitable growth method for fabricating such metastable phase films because of the high energy of the sputtering ions. The target material particles arrive at the substrate surface with high energy and are rapidly cooled, finally crystallizing at the low substrate temperature. The nonequilibrium nature of this crystal growth enabled us to fabricate solid solution films above the thermodynamic solubility limit.

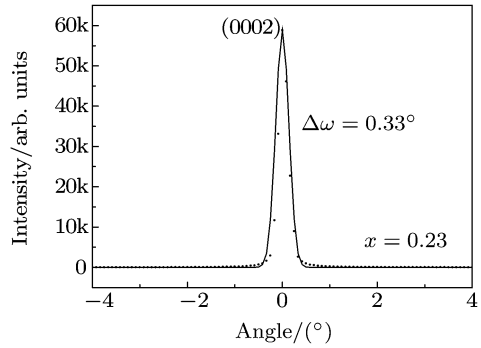


Fig. 3. X-ray diffraction rocking curve showing (0002) ω scan of a $Mg_xZn_{1-x}O$ ($x = 0.23$) film.

The measurements of refractive indices of $Mg_xZn_{1-x}O$ films were achieved by the prism-coupling method and SE measurements. The TM and TE in Fig. 4 were achieved by a Metricon Model 2010

Prism Coupler with a laser wavelength of 632.8 nm. In birefringent materials such as $Mg_xZn_{1-x}O$, the ordinary (TE) and extraordinary (TM) indices are obtained by performing the experiment for transverse electric and transverse magnetic polarization, respectively. The SE measurements were carried out at a wavelength of 632.8 nm using an SGC-2 auto spectroscopic ellipsometer (SE1) and a J. A. Woollam Co. model M88 spectroscopic ellipsometer (SE2) at an incident angle of 70°. Obviously, the refractive indices of $Mg_xZn_{1-x}O$ films linearly decrease with the increasing of Mg content. The data of SE1 and SE2 are about the same while the data of TM and TE are a little larger. The results indicate that the refractive index of $Mg_xZn_{1-x}O$ film for $x = 0.3$ decreased by about 6% compared to pure ZnO whatever methods were used. This is of advantage in preparing optical waveguides.

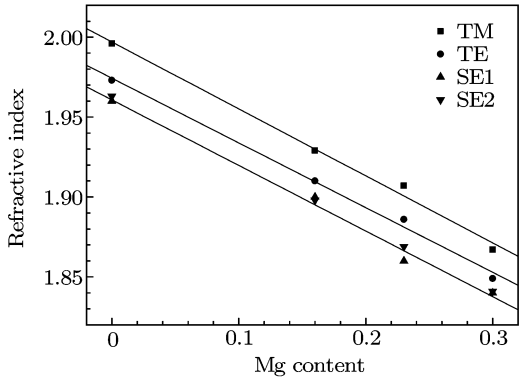


Fig. 4. Refractive indices of $Mg_xZn_{1-x}O$ films versus Mg content.

Figure 5 shows the transmittance spectra of the $Mg_xZn_{1-x}O$ films deposited on sapphire substrates with different Mg content. Transmittances of all $Mg_xZn_{1-x}O$ films are highly transparent in the visible region from 400 to 800 nm and have a sharp absorption edge in the UV region. The absorption edge shifted to shorter wavelength as the Mg content increased, which indicates that the band gap of $Mg_xZn_{1-x}O$ films became wider as the Mg content increased. The dependence of the band gap energy on the Mg content in these films is shown in the inset. It can be seen that the band gap energy of $Mg_xZn_{1-x}O$ films widened linearly from 3.24 to 3.90 eV when the Mg content of $Mg_xZn_{1-x}O$ films increased from $x = 0$ to $x = 0.30$. The results demonstrate that the band gap can be modulated within this region. Because the $Mg_xZn_{1-x}O$ films ($0 \leq x \leq 0.30$) have the same structure as ZnO films with a wider band gap, $Mg_xZn_{1-x}O$ is a suitable material for potential barrier layers in ZnO based devices.

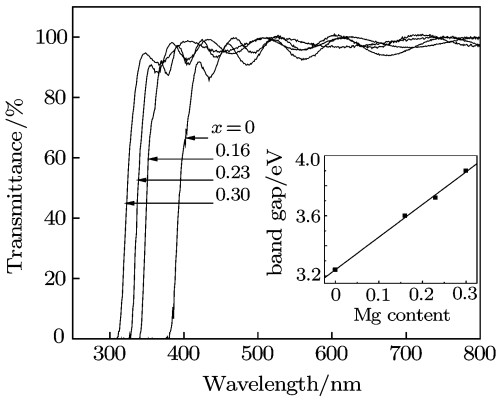


Fig. 5. Transmittance spectra of $Mg_xZn_{1-x}O$ films measured at room temperature.

4. Conclusions

$Mg_xZn_{1-x}O$ thin films have been prepared by radio frequency magnetron sputtering at room temperature. The thin films have hexagonal wurtzite single-phase structure. The Mg content in the films is slightly larger than that in the targets. The refractive indices of $Mg_xZn_{1-x}O$ films systematically decrease with increasing Mg content. With increasing Mg content, the absorption edges of $Mg_xZn_{1-x}O$ films shift to higher energies and band gaps linearly increase. These results provide important information for the design and modelling of $ZnO/Mg_xZn_{1-x}O$ heterostructure optoelectronic devices.

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