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Structural and optical properties of $Mg_xZn_{1-x}O$ thin films prepared by the sol–gel method

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Abstract

A series of $Mg_xZn_{1-x}O$ thin films were successfully fabricated by the sol–gel method on n-type Si (0 0 1) and quartz substrates. The structural and optical properties were studied using XRD and the transmittance spectrum. The $Mg_{0.05}Zn_{0.95}O$ and $Mg_{0.15}Zn_{0.85}O$ alloys with wurtzite structure show high thermal stability up to 1000°C. However, when x is 0.36, phase separation will occur at 800°C. The optical band gap of $Mg_xZn_{1-x}O$ alloys ($0 \leqslant x \leqslant 0.36$) ranges from 3.4 to 3.93 eV. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been great interest in wide-band-gap semiconductors because of the strong commercial desire to produce efficient and lasting blue light-emitting diodes (LED) and short-wavelength laser diodes. Recently, ZnSe- and GaN-based diodes have achieved this aim [1]. As a member of the II–VI semiconductors, zinc oxide (ZnO) is known to have a wide range of technological applications such as transparent conducting electrodes in solar cells, flat panel displays, surface acoustic wave devices, and chemical sensors. Since 1997, ZnO has been paid considerable attention because it can be applied to light-emitting devices in the ultraviolet region, and it is considered the next generation in LED materials [2–4].

To obtain high-performance LED devices, one of the key techniques is to construct a heterojunction to realize double confinement actions for both electrons and photons. Modulation of the band gap while keeping the lattice constants similar to each other is essential for this purpose [5]. Because the ionic radius of Mg^{2+} (0.57 Å) is similar to that of Zn^{2+} (0.60 Å), a wide-ranging solubility of Mg in the zinc blende could be obtained in the film [6]. Recently, thin films of $Mg_xZn_{1-x}O$ alloys with larger band gaps than ZnO were obtained by pulsed laser deposition (PLD), laser ablation MBE and rf magnetron sputtering on (0 0 0 1)-sapphire substrates [7–9]. The films retained the ZnO

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hexagonal structure for x value as high as 0.36. The band gap could range from 3.36 to 4.00 eV.

The sol–gel deposition technique is a more convenient and cheaper way to fabricate thin films [10,11]. The components of the film are changed easily by adjusting the different ion proportions in the sol. High-quality ZnO thin films doped with aluminum were prepared by this deposition method. In this study, $Mg_xZn_{1-x}O$ alloy thin films were successfully made by the sol–gel method on n-type Si (1 0 0) and quartz substrates. The structural and optical properties were also studied.

2. Experimental procedure

The sol was composed of $Zn(CH_3COO)_2$, $Mg(CH_3COO)_2$ and polyvinyl butyral (PVB) in an ethanol solution. The total concentration of metal ions was controlled at 0.1 mol/l. The concentration of Mg^{2+} was adjusted to 0.01, 0.02, 0.04, 0.05 and 0.08 mol/l. The films were spin-coated on Si (1 0 0) and quartz substrates at 2500 r/min. The average thickness of a single layer is 200 nm examined by a scanning electron microscope (SEM). After the deposition, the substrates were first heated to 100°C in air for 10 min to evaporate the solvent, then at 350°C in O_2 for half an hour to eliminate the organic component in the film. This process may be repeated many times to reach the desired thickness (about 800 nm). The sample was cut into several pieces for use in different experiments and thermal annealing was performed for 1 h in an O_2 environment at different temperatures ranging from 500°C to 900°C in order to crystallize the zinc oxide film. The infrared spectrum was measured by a BIO-RAD FTS-3000 spectrophotometer having a resolution of $4\,cm^{-1}$ in the range $400–4000\,cm^{-1}$, and indicted that there was no organic component in the film above 350°C.

To determine crystal structure, the XRD pattern was measured by a D/max-rA X-ray diffractometer (Rigaku) using Cu K_α of 1.5418 Å. A UV-360 Spectrophotometer (Shimadzu) was used for the optical characterization. The Mg and Zn contents were obtained using energy-dispersive X-ray (EDX) analysis.

3. Result and discussion

To find the optimum temperature for the formation of the wurtzite structure, the thin film of $Mg_{0.05}Zn_{0.95}O$ was heated to different temperatures. Fig. 1 shows the XRD spectra of $Mg_{0.05}Zn_{0.95}O$ thin films heated to temperatures of 350°C, 500°C, 600°C, 700°C, 800°C and 900°C. From Fig. 1, it is found that the films are almost amorphous in structure for temperatures below 500°C. When the temperature is as high as 600°C, three peaks appear corresponding to the (1 0 0), (0 0 2) and (1 0 1) directions of the ZnO wurtzite structure. The film is well oriented to the c-axis without any peaks related to MgO. As the temperature is further increased, the orientation along (0 0 2) of the hexagonal crystal structure becomes stronger and stronger.

Based on the above experiment, a series of $Mg_xZn_{1-x}O$ thin films were fabricated at 700°C. The Mg^{2+} content of the film corresponding to that in the solution is shown in Fig. 2. The content of Mg^{2+} in the film is proportional to the concentration of Mg^{2+} in the solution, but it is a little lower in the film than in the solution when the component of Mg^{2+} is less than 50%. This difference can be attributed to the fact that the coordinated ability of the Zn^{2+} ion is larger than that of the Mg^{2+} ion. Thus, more Mg^{2+} ion has been out of the substrate during the spin-coating process [12]. The XRD patterns of these films are shown in Fig. 3. The $Mg_xZn_{1-x}O$ alloy keeps the ZnO wurtzite structure when the value of x is less

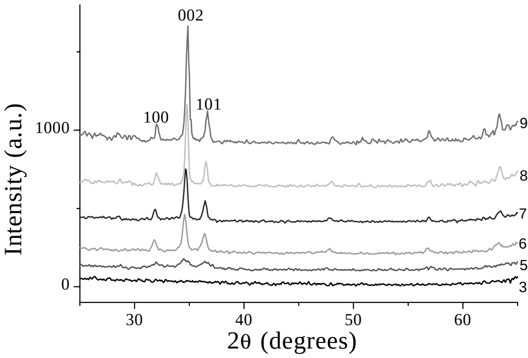

Fig. 1. The X-ray diffraction pattern of $Mg_{0.052}Zn_{0.948}O$ thin films annealed at different temperatures.

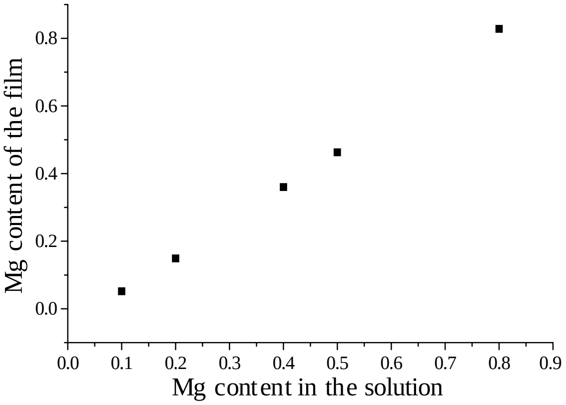

Fig. 2. Mg content in the $Mg_xZn_{1-x}O$ thin films as a function of that in the solution.

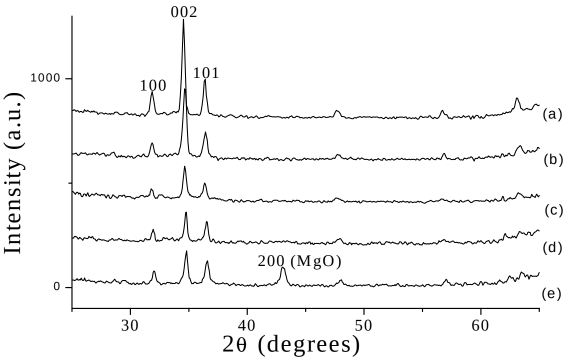

Fig. 3. The XRD spectra of the $Mg_xZn_{1-x}O$ thin films with different x. (a) ZnO, (b) $x = 0.05$, (c) $x = 0.15$, (d) $x = 0.36$, (e) $x = 0.46$.

than 0.36. The c-axis orientation becomes weak with an increase of the Mg^{2+} content in the film. If the x value exceeds 0.36, a peak appears at about 43°. This belongs to the (2 0 0) direction of the MgO cubic structure. Thus, in order to keep the hexagonal crystal structure, the content of the doped Mg^{2+} should not be more than 0.36. This is in good agreement with the result obtained by another group [7].

The surface morphology of the films was examined by SEM (not given in the article). Only some large clusters which consisted of lots of the ZnO crystallite can be seen on the surface of all the films.

The thermal stability of the $Mg_xZn_{1-x}O$ alloys was also studied. The $Mg_{0.05}Zn_{0.95}O$ and $Mg_{0.15}Zn_{0.85}O$ thin films present high stability up to 1000°C, while the $Mg_{0.36}Zn_{0.64}O$ alloy is not as stable. Fig. 4 shows the XRD spectra of the $Mg_{0.36}Zn_{0.64}O$ thin film annealed at 600°C, 700°C and 800°C. From Fig. 4 it is observed that the film was almost a wurtzite phase at low temperature. However, at 800°C an impurity peak appears at 43° which is attributed to the (2 0 0) direction of the MgO cubic structure. This phenomenon indicates that the hexagonal crystal structure of $Mg_{0.36}Zn_{0.64}O$ is a metastable phase. When the heating temperature is higher than 800°C, the phase separation will occur.

These films were also deposited on a quartz substrate to allow transmittance spectra measurement. The optical properties of the alloy thin films were studied from the transmittance spectra at room temperature, as shown in Fig. 5. All the samples were highly transparent in the visible region from 400 to 800 nm and have a sharp absorption band in the UV region. From Fig. 5 it is clearly seen that the absorption edge is a function of x when $x \leqslant 0.36$, but it is saturated at higher Mg concentrations. These results are in good agreement with the appearance of the MgO impurity phase detected by XRD. The excitonic nature of the films is clearly apparent in the spectra. Because the exciton binding energy is almost the same as that of ZnO (≈ 60 eV) in the $Mg_xZn_{1-x}O$ alloy thin films, the exciton peak remains present for all alloy

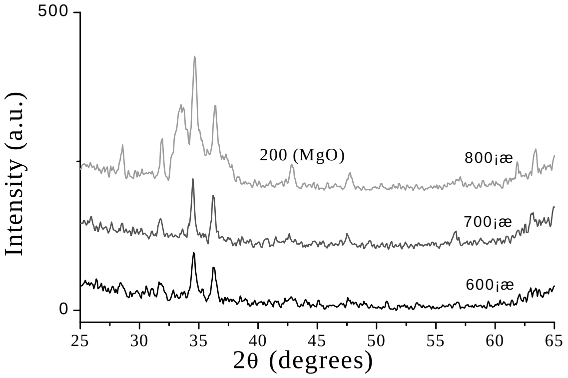

Fig. 4. The XRD pattern of $Mg_{0.36}Zn_{0.64}O$ thin film annealed at different temperatures.

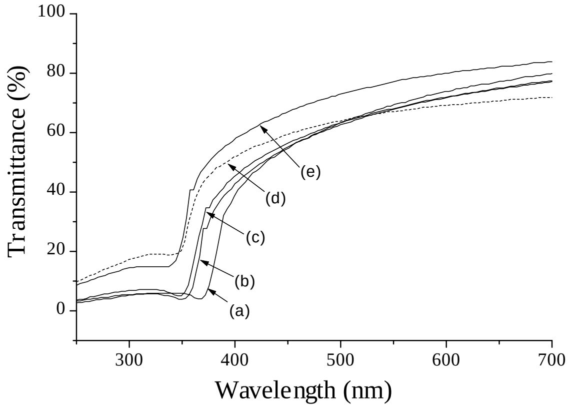

Fig. 5. The transmittance spectra of $Mg_{0.36}Zn_{0.64}O$ thin films: (a) ZnO, (b) $x = 0.05$, (c) $x = 0.15$, (d) $x = 0.36$, (e) $x = 0.46$.

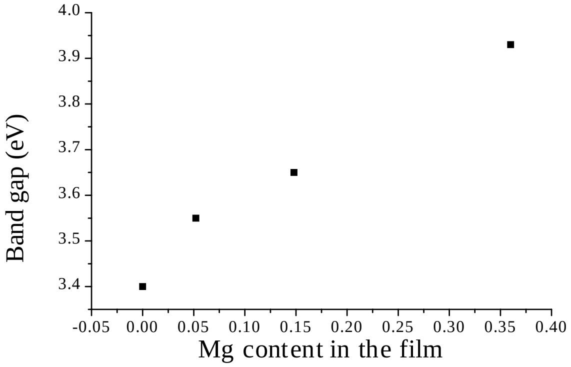

Fig. 6. The band gap (Eg) determined from the transmittance spectra by considering exciton effect.

compositions with increasing Mg concentration. By considering the exciton effect, the band gap (Eg) of these alloy films is estimated. The band gap is shown as a function of x in Fig. 6. The Eg increases almost linearly up to 3.93 eV for $0 \leqslant x \leqslant 0.36$, which indicates that $Mg_xZn_{1-x}O$ is a suitable material for potential barrier layers in ZnO-based devices. Because the $Mg_xZn_{1-x}O$ ($0 \leqslant x \leqslant 0.36$) alloy has the same structure as ZnO with a higher Eg, good-quality ZnO/$Mg_xZn_{1-x}O$ heterojunctions could be fabricated.

In conclusion, $Mg_xZn_{1-x}O$ alloy thin films with wurtzite structures and wide band gaps were successfully fabricated by the sol–gel method. These films could be used as ultraviolet light emission material or to fabricate new photoelectronic devices.

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