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Control of structure, conduction behavior, and band gap of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films by nitrogen partial pressure ratio of sputtering gases

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$\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were grown by radio-frequency reactive magnetron sputtering using mixture of nitrogen and argon as sputtering gases. It was found that Mg concentration, structures, electrical properties, and band gaps of the films can be tuned by changing nitrogen partial pressure ratio of the sputtering gases. The $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ film consists of wurtzite phase at the ratios from 0% to 50%, mixture of wurtzite and cubic phases at the ratios of 78% to 83%, and cubic phase at 100%. The Mg concentration increased linearly with increasing the ratio. The band gap increases from 3.64 eV at $x=0.172$ to 4.02 eV at $x=0.44$ for the wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ and reaches 6.30 eV for cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with $x=0.84$. All the as-grown $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films show high resistivity at room temperature, but transform into p -type conduction after annealing at 600 °C for 30 min under 10^{-4} Pa, except for the film grown at the ratio of zero. © 2006 American Institute of Physics.

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ZnO has long been touted as candidate material for ultraviolet (UV) light-emitting diodes (LEDs) and laser diodes, due to wide band gap of 3.37 eV and exciton binding energy of 60 meV at room temperature.¹ Recently, electroluminescence (EL) of p - n homojunction ZnO was reported by many groups.²⁻⁵ However, the EL emissions are not in an UV but visible wavelength region. In order to realize UV EL, it is crucial to develop LEDs with active layers of ZnO-based superlattices or quantum wells, which need suitable ZnO-based potential barrier material. More recently, a LED with active layer of Be-Zn-O quantum wells was fabricated and emitted UV light.⁶ However, because Be is a poisonous metal, it may be very difficult to fabricate the Be-Zn-O alloy safely.

Another potential barrier material, Mg-Zn-O alloy was proposed and has been investigated widely in recent years. Ohtomo *et al.*⁷ and Vashaei *et al.*⁸ reported that $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with different Mg contents and structures were obtained by changing the Mg content of targets. Bhattacharya *et al.*⁹ obtained $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with different Mg concentrations and structures by changing the substrate temperatures from 500 to 750 °C. These Mg-Zn-O alloys mentioned above usually shows n -type conduction and are prepared easily. However, it has been proven that fabrication of p -type Mg-Zn-O is difficult. Only phosphor doping, nitrogen doping and N-Al codoping p -type $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were reported up to now.¹⁰⁻¹² Preparation of stable p -type Mg-Zn-O alloy has become a very important issue for UV LEDs with active layers of quantum wells.

Differing from literatures previously reported, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films are prepared by using radio-frequency (rf) magnetron sputtering technique and mixture of argon and

nitrogen as sputtering gas in the present work, and the Mg concentration, structure, and conduction behavior of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were tuned by adjusting nitrogen partial pressure ratio of the sputtering gases.

A $\text{Mg}_{0.18}\text{Zn}_{0.82}\text{O}$ target was prepared by sintering mixture of 99.99% pure MgO and ZnO powders at 1000 °C for 10 h in air ambient. The quartz substrates were cleaned in an ultrasonic bath with acetone, ethanol, and de-ionized water at room temperature, and then washed using de-ionized water. The growth chamber was evacuated to a base pressure of 5×10^{-4} Pa, and then filled to 1.0 Pa with mixed gases of 99.99% pure nitrogen and argon, in which the nitrogen partial pressure ratio, R_{N_2} =nitrogen partial pressure/the total pressure of 1.0 Pa, changes from 0% to 100%. $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were grown on the quartz for 1 h at substrate temperature of 500 °C by rf magnetron sputtering, then annealed for 30 min at 600 °C under 10^{-4} Pa in a tube furnace.

The structures of the films were characterized by x-ray diffraction (XRD) with Cu $K\alpha$ radiation ($\lambda=0.15406$ nm). The room temperature absorbance measurement was performed using an UV-Vis-NIR spectrophotometer (Shimadzu). Electrical properties were measured in the van der Pauw configuration by a Hall effect measurement system at room temperature. The composition was detected by energy dispersive x-ray analyzer.

Figure 1 shows the XRD patterns of the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ thin films grown at various R_{N_2} . They are basically the same as that of as-grown $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films (not shown here), except that the diffraction angles 2θ of the as-grown films are smaller than that of annealed films due to tensile stress in the as-grown films, indicating that the structure of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films are stable. As shown in Figs. 1(a) and 1(b), only one diffraction peak was observed at 34.72° and 34.94°, respectively, for the films deposited in pure argon ambient ($R_{\text{N}_2}=0$) and at $R_{\text{N}_2}=50\%$, indicating

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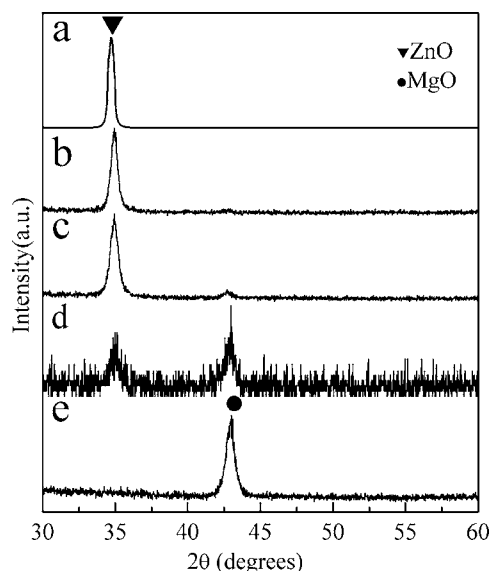


FIG. 1. XRD patterns of annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films deposited under various nitrogen partial pressure ratios: (a) 0%, (b) 50%, (c) 78%, (d) 83%, and (e) 100%

that both films are of wurtzite structure with (002) preferential orientation, and the lattice constant c was evaluated to be 5.168 and 5.135 Å, respectively, smaller than the value of 5.209 Å of ZnO powder sample. Since the ionic radius of Mg^{2+} (0.57 Å) is smaller than that of Zn^{2+} (0.60 Å), the decrease of the c axis lattice constant implies substitution of some Mg for Zn in the films.

When R_{N_2} increased to 78%, the XRD of the film showed two diffraction peaks, as shown in Fig. 1(c). The strong peak located at 34.93° corresponds to (002) diffraction of wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, and the weak peak located at 42.75° to (200) diffraction of cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, implying that phase segregation occurs in the film. As the R_{N_2} goes up, as shown in Fig. 1(d), the (002) diffraction peak intensity decreases, while the (200) diffraction peak intensity increases, indicating that the concentration of wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ in the film decreases with increasing R_{N_2} while the concentration of cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ increases. The annealed films grown at $78\% \leq R_{\text{N}_2} \leq 83\%$ consist of wurtzite and cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$.

For the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ film grown in pure nitrogen ambient ($R_{\text{N}_2} = 100\%$), only a (200) diffraction peak was observed at 42.91° [see Fig. 1(e)], which is smaller than the (200) diffraction angle of pure MgO (42.98°), implying that some Zn^{2+} ions occupy the lattice site of Mg^{2+} and a single cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ was obtained.

The Mg concentration as a function of R_{N_2} is plotted in Fig. 2 for the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$, showing that the Mg content increases linearly with increasing R_{N_2} . Combining the results of Figs. 1 and 2, it is concluded that the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ consists of a single wurtzite structure in the Mg content from 0.17 to 0.44, wurtzite and cubic structures between 0.66 and 0.68, and a single cubic structure at $x = 0.84$. Exactly, the Mg concentration should be between 0.44 and 0.66 for occurrence of the phase segregation and between 0.68 and 0.84 for formation of single cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$.

It is known that some Mg, Zn, and O atoms escape from the ZnMgO target in a state of atom or ion when the target is sputtered by the Ar and N_2 mixed gases. The O atoms or ions

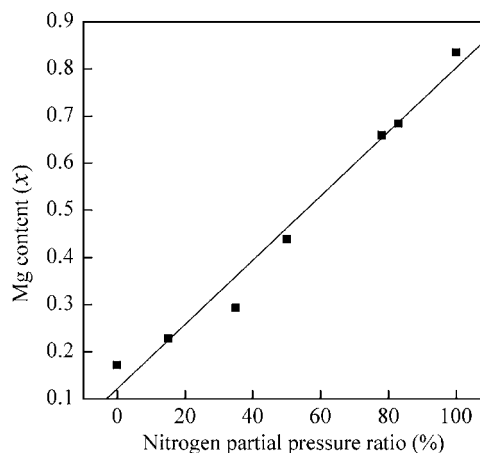


FIG. 2. Plot of Mg concentration as a function of nitrogen partial pressure ratio.

react with the N atom and ions produced by ionization of the N_2 in the mixed gas to form NO or NO_2 , which will be expelled from the growth chamber by pump soon. This reaction results in the fact that the O atoms or ions decrease in the chamber and the (Mg,Zn) to O ratio is much larger than the stoichiometric ratio of 1:1; that is, there are many excessive Mg and Zn atoms. Since Mg is more active than Zn, all Mg but one part of Zn atoms react with the O to form Zn-MgO alloy, while another part of Zn atoms do not. These unreacted excessive Zn atoms are deposited on the substrate hardly due to reevaporation induced by high substrate temperature (500°C) and will be expelled from the chamber finally. As a result, the Mg concentration in the as-grown ZnMgO is larger than in the ZnMgO target and increases with increasing the N partial pressure. According to thermodynamics, the structure of ZnMgO changes from wurtzite phase to existence of wurtzite and cubic phases and to cubic phase finally with increasing Mg concentration, in agreement with our results. Therefore, the changes of the Mg concentration and the structure of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with R_{N_2} are mainly attributed to the loss of the O and Zn atoms induced by the reaction between the N and O as well as high substrate temperature.

In the recent years, Zn-Mg-O alloys were produced by many methods and techniques. For example, Ohtomo *et al.*⁷ fabricated $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with different structures and Mg concentrations by changing the Mg content in the targets and obtained single wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ at $x \leq 0.25$. Vashaei *et al.*⁸ obtained a single wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloy at Mg concentration $x \leq 0.34$ and a single cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ at $0.65 \leq x \leq 0.97$. Bhattacharya *et al.*⁹ prepared the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with different Mg concentrations and structures by changing the substrate temperature. Differing from the results reported previously, in the present work, the structure and Mg concentration of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ film were tuned by nitrogen partial pressure ratio. The largest Mg concentration of the single wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ is larger than 0.44, which is much larger than the values reported previously.⁷⁻⁹ This implies that the wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with larger band gap can be obtained using the present method. This method provides a technique for the preparation of $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ with different Mg concentrations and structures.

Hall measurement results for the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films are listed in Table I, which gives that the annealed film

TABLE I. Room temperature electrical properties of annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films deposited under various nitrogen partial pressure ratios (R_{N_2}). (Note: H, hexagonal; C, cubic.)

R_{N_2} (%)	Phase	Type	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Resistivity (Ωcm)	Concentration (cm^{-3})
0	H	High resistivity	...	...	...
50	H	<i>p</i>	1.177	2.1×10^4	2.9×10^{14}
78	H+C	<i>p</i>	0.197	2.9×10^3	1.1×10^{16}
83	H+C	<i>p</i>	0.095	9.9×10^3	7.0×10^{15}
100	C	<i>p</i>	0.633	2.0×10^4	5.3×10^{15}

grown at $R_{\text{N}_2}=0$ shows high resistivity, while the annealed films grown at $50\% \leq R_{\text{N}_2} \leq 100\%$ show *p*-type conduction. It is noted that the annealed films with *p*-type conductivity were grown by sputtering gas containing nitrogen, implying that the *p*-type conduction of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films is related to nitrogen doping. This conclusion is confirmed by our other experiments, where $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were grown using mixture of Ar and O_2 , and no *p*-type $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ was obtained after annealing at 600°C . So, we deduce that some N atoms substitute for O atoms in the wurtzite or cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ to form shallow acceptors during the growth process. These acceptors overcome compensation of other possible native donor defects and make the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ conduct in *p* type. A similar result was found in N-doped Zn-Mg-O film.¹² The mobility of the films decreased as the R_{N_2} increased from 50% to 84% and then increased as the R_{N_2} increased from 84% to 100%. The former is attributed to degradation of crystalline quality of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films due to phase segregation and latter to improvement of the crystalline quality. That can be confirmed by the change of full width at half maximum (FWHM) of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films, as shown in Fig. 1. The FWHM increases as the R_{N_2} increases from 50% to 83%, which corresponds to the structure transformation of the films from single wurtzite phase to the coexistence of wurtzite and cubic phases, and decreases as the R_{N_2} increases from 83% to 100%, which corresponds to the structure transformation from the coexistence of the two phases to single cubic phase.

Absorbance measurement of the annealed $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ was performed at room temperature, and the band gap (E_g) was evaluated by using $(\alpha h\nu)^2 \propto (h\nu - E_g)$ relationship, where α is the absorption coefficient and $h\nu$ is the photon energy. The E_g is plotted as a function of R_{N_2} in Fig. 3. All the E_g values of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ are larger than E_g of ZnO (3.37 eV), implying that ZnO alloying with MgO is feasible to enlarge the band gap of ZnO. The E_g increased linearly from 3.64 to 4.09 eV for the single wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ as the R_{N_2} increases from 0% to 50% (or Mg concentration increases from 0.17 to 0.44), as shown in the Fig. 3, indicating that the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ alloy is a suitable potential barrier layers of ZnO-based quantum well or superlattices.

In conclusion, $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films with different Mg concentrations and structures were prepared by rf magnetron sputtering through varying R_{N_2} . Highly (002) oriented and

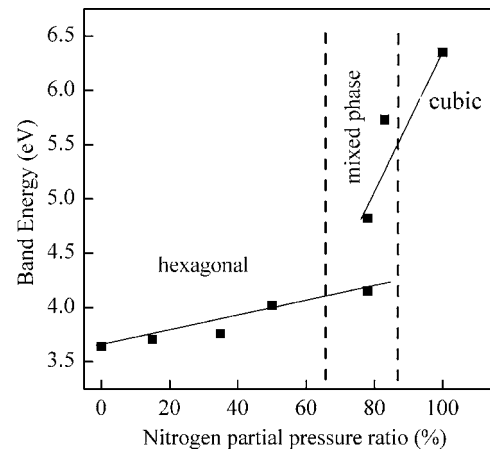


FIG. 3. Plot of band gap of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films as a function of nitrogen partial pressure ratio.

single wurtzite $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films were obtained at $0 \leq R_{\text{N}_2} \leq 50\%$, and their band gap is in the range of 3.64–4.02 eV. A stable cubic $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ film with band gap energy of 6.3 eV was prepared in pure nitrogen ambient. The structure, Mg concentration, and band gap of the $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ can be tuned easily by nitrogen partial pressure ratio. The $\text{Zn}_{1-x}\text{Mg}_x\text{O}$ films grown at nitrogen partial pressure ratio from 50% to 100% shows *p*-type conduction after annealing at 600°C for 30 min under 10^{-4} Pa, which is related to nitrogen doping.

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