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Effect of growth ambient on the structure and properties of $Mg_xZn_{1-x}O$ thin films prepared by radio-frequency magnetron sputtering

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Abstract

$Mg_xZn_{1-x}O$ thin films were grown by the radio-frequency magnetron sputtering technique in $Ar + N_2$ and $O_2 + N_2$ ambient with different nitrogen partial pressure ratios on quartz substrates at 773 K. The correlations between the growth ambient and the resultant films properties were discussed. It is found that Mg concentration, structure and band gap of the MgZnO film can be tuned by increasing the nitrogen partial pressure ratio of the $Ar + N_2$ ambient, but cannot be tailored by changing the nitrogen partial pressure ratio of the $O_2 + N_2$ ambient. X-ray diffraction shows that the $Mg_xZn_{1-x}O$ films grown in the $Ar + N_2$ ambient consist of wurtzite phase at the nitrogen partial pressure ratios from 0% to 50%, a mixture of wurtzite and cubic phases at the ratios of 78–83%, and a cubic phase at 100%, whereas such structure transformation did not exist in the $Mg_xZn_{1-x}O$ film deposited in the $O_2 + N_2$ ambient by changing the nitrogen partial pressure ratio. The Mg concentration increases linearly with the increasing nitrogen partial pressure ratio of $Ar + N_2$, but does not vary with the increasing nitrogen partial pressure ratio of $O_2 + N_2$. The band gap increases linearly from 3.64 to 4.02 eV for the wurtzite $Mg_xZn_{1-x}O$ deposited in the $Ar + N_2$ ambient as nitrogen partial pressure ratio increases from 0% to 50%, but the band gap of the $Mg_xZn_{1-x}O$ film deposited in the $O_2 + N_2$ ambient keeps a constant of 3.63 eV with oxygen gas and reaches 6.30 eV abruptly in pure nitrogen ambient (without oxygen gas). The $Mg_xZn_{1-x}O$ films, which are grown in the $Ar + N_2$ and $O_2 + N_2$ ambient at nitrogen partial pressure ratio from 50% to 100% and 83% to 100%, respectively, show p-type conduction after annealing.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

ZnO, a wide-band gap ($E_g = 3.37$ eV) semiconductor oxide, has attracted considerable attention in recent years for its promising potential applications in ultraviolet (UV) optoelectronic devices, such as light-emitting diodes (LED), laser diodes and photodetectors [1–6]. The band gap engineering for the growth of heterostructures and quantum wells is one of the key issues that need to be addressed in applications of UV optoelectronics. It is well known that alloying ZnO with MgO can tune the band gap from 3.37 to 7.8 eV depending upon the Mg concentration [7–9]. Moreover, the substitution of Zn^{2+} by Mg^{2+} does not induce a significant change in the lattice constant because the ionic radius of Zn^{2+} (0.60 Å) is close to that of Mg^{2+} (0.57 Å). Therefore, the $Mg_xZn_{1-x}O$ films have been suggested as one of the promising barrier materials of ZnO for band gap engineering as well as heterostructure device design.

There are a number of reports on the growth and properties of the $Mg_xZn_{1-x}O$ thin films. Ohtomo *et al* have prepared the

$Mg_xZn_{1-x}O$ films by changing the Mg content in the target by pulsed laser deposition and investigated the effect of Mg content in the target on the structure and properties of the $Mg_xZn_{1-x}O$ films [10]. It was found that the Mg content in the films was systematically larger than that in the targets by a factor of 2.5. The band gap of the $Mg_xZn_{1-x}O$ film would be increased to 3.99 eV at $x = 0.33$. By studying the effect of substrate temperature on the $Mg_xZn_{1-x}O$ films, Bhattacharya *et al* grew the $Mg_xZn_{1-x}O$ films with the substrate temperature from 773 to 1023 K [11]. The $Mg_xZn_{1-x}O$ films have wurtzite phase at 500 and 600 °C, a mixture of wurtzite and cubic phases at 650 °C and a cubic phase at 750 °C. The effect of the Mg/Zn flux ratio on the growth of the $Mg_xZn_{1-x}O$ films was demonstrated by Vashaei *et al* [12]. They fabricated the $Mg_xZn_{1-x}O$ films over a wide composition range of $0.0 \leqslant x \leqslant 0.97$ by plasma-assisted molecular-beam epitaxy with different Mg/Zn flux ratios. Besides the substrate temperature, Mg content of the target and the Mg/Zn flux ratio, the growth ambient is also a very important factor for the $Mg_xZn_{1-x}O$ films growth. However, there is no detailed study on the effect of growth ambient on the structure and properties of the $Mg_xZn_{1-x}O$ thin films.

In this work, the $Mg_xZn_{1-x}O$ films were grown by radio-frequency (rf) magnetron sputtering in the $Ar+N_2$ and O_2+N_2 ambient with different nitrogen partial pressure ratios. The Mg concentration, structure and band gap of the $Mg_xZn_{1-x}O$ films were changed with the increase in the nitrogen partial pressure ratio in the $Ar + N_2$ ambient, but did not vary with the nitrogen partial pressure ratio of the $O_2 + N_2$ ambient. The effect of the growth ambient on the structure and properties of the $Mg_xZn_{1-x}O$ thin films was discussed in this work.

2. Experimental procedures

Predetermined amounts of ZnO (99.99%) and MgO (99.99%) powders were mixed and sintered at 1273 K for 10 h in ambient air to form a compact ceramic target with a nominal component of $Mg_{0.18}Zn_{0.82}O$. This target was used to grow the $Mg_xZn_{1-x}O$ films, where x is the atomic fraction, on quartz substrates by rf magnetron sputtering. Before deposition, the quartz substrates were cleaned in an ultrasonic bath with acetone, ethanol and deionized water at room temperature, and then washed using deionized water. The distance between the target and the substrate was fixed at 6 cm. The growth chamber was initially evacuated to 5×10^{-4} Pa, and then filled to 1.0 Pa with 99.99% pure $Ar + N_2$ or $O_2 + N_2$ background gas with nitrogen partial pressure ratio changing from 0% to 100%. We defined the nitrogen partial pressure ratio, R_{N_2} = nitrogen partial pressure/the total pressure of 1.0 Pa. The gas pressure ratio can be tuned by controlling flow rates of nitrogen, argon or oxygen. Here, we denoted the nitrogen partial pressure ratio of $Ar + N_2$ and $O_2 + N_2$ as R_{N_2} and R'_{N_2}, respectively. All the $Mg_xZn_{1-x}O$ films were grown on the quartz for 1 h at a substrate temperature of 773 K, and then annealed for 30 min at 873 K under 10^{-4} Pa in a tube furnace. In order to prevent pollution, a quartz tube was inserted into the furnace and the films were placed in a quartz boat.

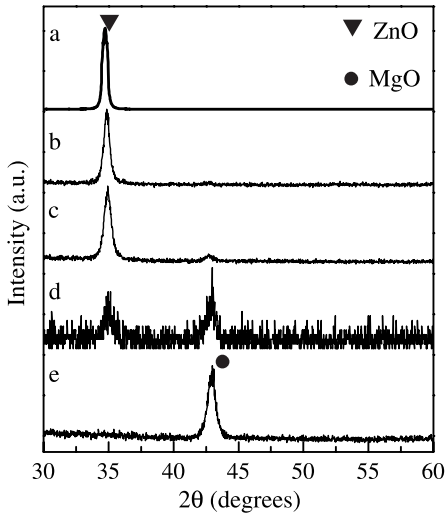

Figure 1. XRD patterns of the annealed $Mg_xZn_{1-x}O$ films deposited in the $Ar + N_2$ ambient under various nitrogen partial pressure ratios: (a) 0%, (b) 50%, (c) 78%, (d) 83%, (e) 100%.

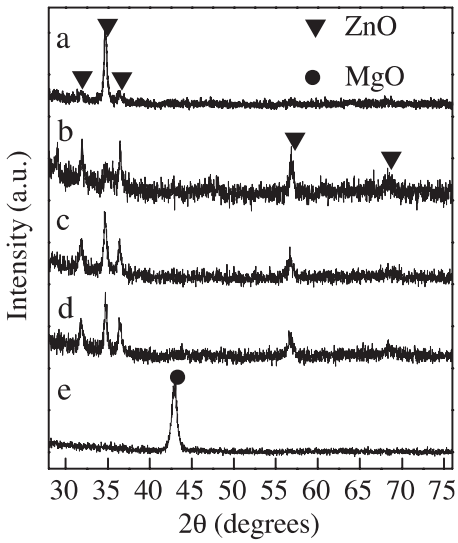

Figure 2. XRD patterns of the annealed $Mg_xZn_{1-x}O$ films deposited in the $O_2 + N_2$ ambient under various nitrogen partial pressure ratios: (a) 0%, (b) 50%, (c) 78%, (d) 83%, (e) 100%.

The structure of the films was characterized by x-ray diffraction (XRD) with Cu K_α radiation ($\lambda = 0.15406$ nm). The electrical properties were investigated by Hall measurement in the Van der Pauw configuration at room temperature (Lakershore HMS 7707). The composition of the $Mg_xZn_{1-x}O$ film was detected by using an energy dispersive x-ray (EDX) analyzer. The room temperature absorbance measurement was performed using an UV–Vis–NIR spectrophotometer (Shimadzu).

3. Results and discussion

Figures 1 and 2 illustrate the θ–2θ XRD patterns of the annealed $Mg_xZn_{1-x}O$ thin films grown in the $Ar + N_2$ and $O_2 + N_2$ ambient with various R_{N_2} and R'_{N_2}, respectively. The single-phase of $Mg_xZn_{1-x}O$ films having wurtzite structure

were prepared at nitrogen partial pressure ratio of $Ar+N_2$ (R_{N_2}) up to 50%, as shown in figures 1(*a*) and (*b*). When R_{N_2} increased to 78%, as shown in figure 1(*c*), besides the (0 0 2) diffraction of the wurtzite $Mg_xZn_{1-x}O$, a small peak due to (2 0 0) diffraction of cubic $Mg_xZn_{1-x}O$ was detected. This indicates that phase segregation occurs in the film when R_{N_2} is larger than 50%. The (0 0 2) peak of the wurtzite $Mg_xZn_{1-x}O$ completely disappeared with a further increase in R_{N_2} to 100% (pure nitrogen ambient) and only a (2 0 0) diffraction peak was observed at 42.91° (see figure 1(*e*)), which is smaller than the (2 0 0) diffraction angle of pure MgO (42.98°), implying that some Zn^{2+} ions occupy the lattice site of Mg^{2+} and a single cubic $Mg_xZn_{1-x}O$ was obtained. The $Mg_xZn_{1-x}O$ films deposited in Ar + N_2 undergo structure transformation from the wurtzite phase at $0\% \leqslant R_{N_2} \leqslant 50\%$ to the mixture of the wurtzite and cubic phases at $78\% \leqslant R_{N_2} \leqslant 83\%$, and to cubic phase at $R_{N_2} = 100\%$. However, as can be seen from figure 2, such structure transformation was not observed for the $Mg_xZn_{1-x}O$ film grown in the O_2 + N_2 ambient by changing the R'_{N_2}. Figures 2(*a*)–(*d*) show all the diffraction peaks are of the wurtzite structure $Mg_xZn_{1-x}O$. No peaks related to MgO are detected, implying that the $Mg_xZn_{1-x}O$ films deposited at $0\% \leqslant R'_{N_2} \leqslant 83\%$ are of a single wurtzite phase. No structure transformation occurred when increasing the nitrogen partial pressure ratio of O_2+N_2 with the existence of oxygen gas except the single cubic structure $Mg_xZn_{1-x}O$ at $R'_{N_2} = 100\%$ without oxygen gas. In addition, as shown in figures 1 and 2, the wurtzite structure $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient are highly *c*-axis oriented, while the wurtzite structure $Mg_xZn_{1-x}O$ films grown in the O_2+N_2 ambient do not have the *c*-axis preferential orientation. This can be attributed to the low energy of deposited atoms. During the deposition process, the sputtered atoms of Mg and Zn will combine with O-related species of plasma, which are of opposite move direction compared with sputtered Mg and Zn atoms, thus leading to the decrease in the energy of the deposited atom. So the deposited atoms do not have sufficient time to undergo surface diffusion to thermodynamically stable sites of the *c*-axis direction before being covered by the next layer of atoms. As a result, the films deposited with O_2 do not show preferred orientation.

Figure 3 reveals the variation of Mg concentration of the $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 and O_2 + N_2 ambient with various R_{N_2} and R'_{N_2}. The Mg concentration of the $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient increases linearly with increasing R_{N_2}, as shown in figure 3(*a*). However, figure 3(*b*) shows that the Mg concentration of the $Mg_xZn_{1-x}O$ films grown in the O_2 + N_2 ambient remains nearly constant at about $x = 0.23$ by increasing R'_{N_2} from 0% to 83%, and it abruptly increases to $x = 0.83$ at $R'_{N_2} = 100\%$ without oxygen gas. It is concluded that without O_2, the Mg concentration of the $Mg_xZn_{1-x}O$ films can be tuned by changing the nitrogen partial pressure ratio, but with O_2, the Mg concentration is invariable when changing the nitrogen partial pressure ratio. The variation of Mg concentration with the increasing nitrogen partial pressure ratio without O_2 is attributed mainly to the loss of the limited O and Zn atoms, which are supplied only by the target, the former is induced by a reaction between

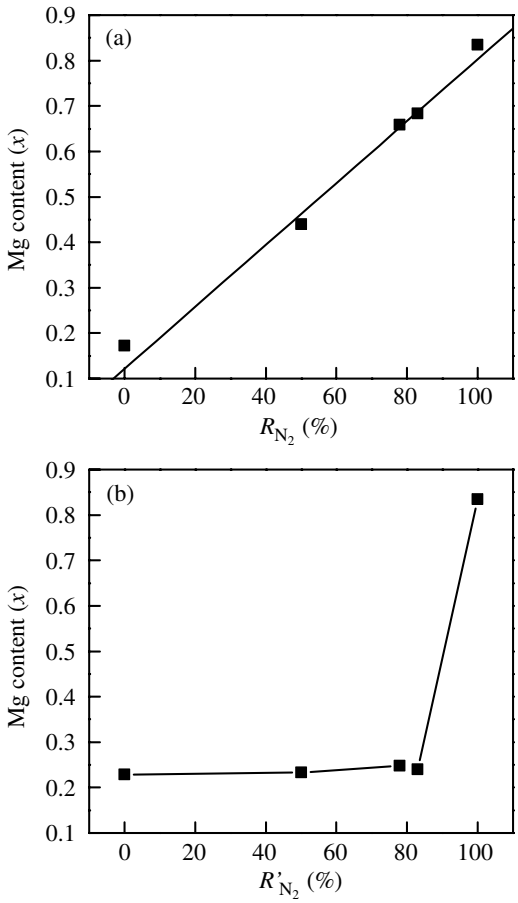

Figure 3. Variation of the Mg concentration of the $Mg_xZn_{1-x}O$ films as a function of nitrogen partial pressure ratio: (*a*) grown in Ar + N_2, (*b*) grown in O_2 + N_2 ambient.

the N and O, and the latter results from some excessive Zn atoms, which are re-evaporated as they deposit on the substrate due to a high substrate temperature and expelled from the chamber. The mechanism of the effect of nitrogen partial pressure ratio without O_2 on the Mg concentration has been discussed in detail in our previous work [13]. The invariable Mg concentration as the nitrogen partial pressure ratio with O_2 can be attributed to the loss of O atoms from the target due to the reaction with N atoms, which can be compensated by ionization of O_2 in the mixed gases, so that there are enough O atoms to react with Mg and Zn to form $Mg_xZn_{1-x}O$ alloy in the growth process.

Figures 4 and 5 show room temperature absorbance spectra and band gaps of the $Mg_xZn_{1-x}O$ films deposited in the Ar + N_2 and O_2 + N_2 ambient with various R_{N_2} and R'_{N_2}, respectively. The band gap (E_g) of the wurtzite and cubic $Mg_xZn_{1-x}O$ is evaluated by employing $(\alpha h\upsilon)^2$ $(h\upsilon - E_g)$ relationship, where α is the absorption coefficient and $h\upsilon$ is the photon energy. For the $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient, only one absorption edge is observed in the films fabricated at $R_{N_2} \leqslant 50\%$, and the edge shifts to a short wavelength direction as R_{N_2} increases. When R_{N_2} increased to 78%, two absorption edges were observed, as shown in figure 4(*c*). According to the XRD result of figure 1, it is concluded that the appearance of the two absorption edges is due to the phase segregation and that

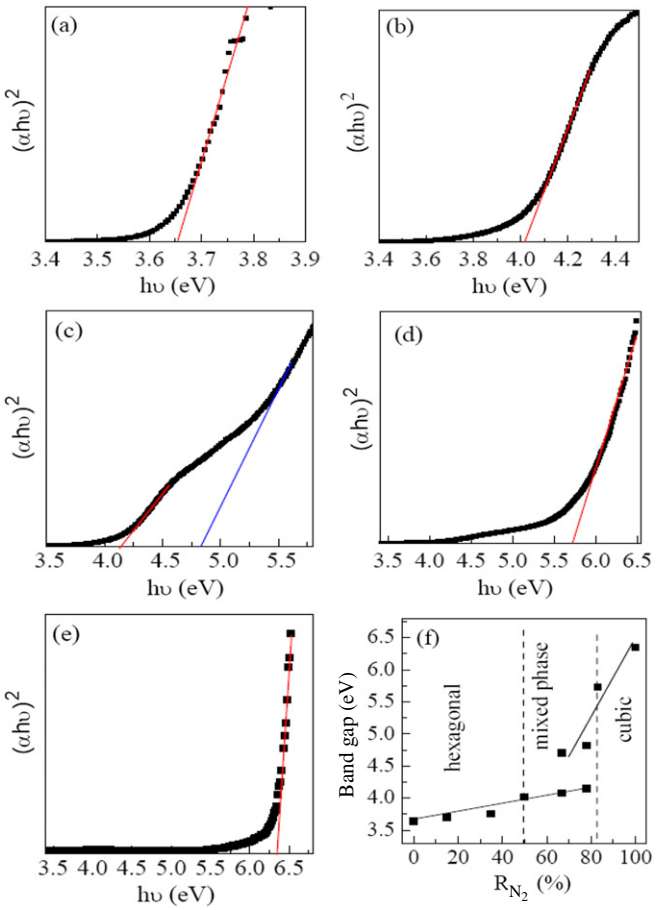

Figure 4. Dependence of energy band gap of the annealed $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient at different nitrogen partial pressure ratios: (*a*) 0%, (*b*) 50%, (*c*) 78%, (*d*) 83%, (*e*) 100% and (*f*) the plot of band gap of the $Mg_xZn_{1-x}O$ films as a function of nitrogen partial pressure ratio.

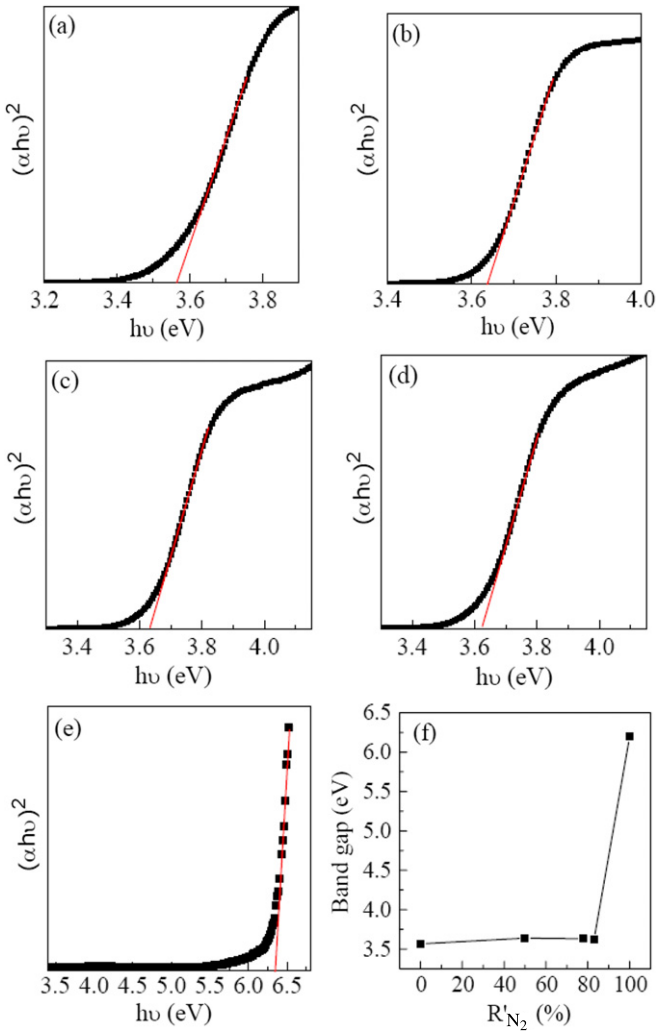

Figure 5. Dependence of energy band gap of annealed $Mg_xZn_{1-x}O$ films grown in the O_2 + N_2 ambient at different nitrogen partial pressure ratios: (*a*) 0%, (*b*) 50%, (*c*) 78%, (*d*) 83%, (*e*) 100% and (*f*) the plot of band gap of the $Mg_xZn_{1-x}O$ films as a function of nitrogen partial pressure ratio.

the absorption edge at low photon energy is for the wurtzite $Mg_xZn_{1-x}O$ and the absorption edge at high photon energy is for cubic $Mg_xZn_{1-x}O$. The absorption edge at low photon energy becomes unclear when R_{N_2} increased to 83%, which is attributed to the band tail absorption caused by heavy doping of Mg. As R_{N_2} reached 100%, only one absorption edge, which is for cubic $Mg_xZn_{1-x}O$ based on the result of figure 1(*e*), is observed, as shown in figure 4(*e*). The E_g is plotted as a function of R_{N_2} in figure 4(*f*). The E_g increases linearly from 3.64 to 4.09 eV for the single wurtzite $Mg_xZn_{1-x}O$ as R_{N_2} increases from 0% to 50%. For the films deposited in the O_2 + N_2 ambient, only one absorption edge was observed, as shown in figures 5(*a*)–(*e*), which is in agreement with the XRD results (figure 2) of which the structural phase transition is abrupt as the R'_{N_2} changes from 0% to 100%. The film is either of the single wurtzite structure or of the single cubic structure, there is no mixed phase. The band gap is 3.56 eV at $R'_{N_2} = 0\%$, it remains constant at about 3.63 eV at $50\% \leqslant R'_{N_2} \leqslant 83\%$, and it increases abruptly to 6.35 eV for $R'_{N_2} = 100\%$, as shown in figure 5(*f*). The band gap of the films deposited at $50\% \leqslant R'_{N_2} \leqslant 83\%$ is 70 meV larger than that of the film deposited at $R'_{N_2} = 0$ (pure oxygen ambient). This may be the result of the defects related to nitrogen doping. The reasons were unclear and should be studied further. The above results indicate that the absorption edge (or band gap) of the wurtzite and cubic $Mg_xZn_{1-x}O$ can be tuned by changing the nitrogen partial pressure ratio of the Ar + N_2 ambient, but cannot be controlled by varying the nitrogen partial pressure ratio of the O_2 + N_2 ambient.

The Hall measurement results for the annealed $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 and O_2 + N_2 ambient with various R_{N_2} and R'_{N_2} are listed in tables 1 and 2, respectively. Table 1 shows that the annealed film grown in the Ar + N_2 ambient at $R_{N_2} = 0\%$ displays high resistivity, while the annealed films grown at $50\% \leqslant R_{N_2} \leqslant 100\%$ show p-type conduction. The films deposited in O_2 + N_2 at $0\% \leqslant R'_{N_2} \leqslant 78\%$ show n-type, they becomes p-type conduction when the nitrogen partial pressure ratio increases to 83%. It is noted that the annealed films with the p-type conductivity were all grown by sputtering gas containing nitrogen, implying that the p-type conductivity of the $Mg_xZn_{1-x}O$ films is related to nitrogen doping. We deduce that some N atoms substitute for O atoms in the wurtzite or cubic $Mg_xZn_{1-x}O$ to form shallow acceptors during the growth process. These acceptors

Table 1. Room temperature electrical properties of the annealed $Mg_xZn_{1-x}O$ films deposited in the Ar + N_2 ambient under various nitrogen partial pressure ratios (R_{N_2}).

R_{N_2} (%) ($Ar + N_2$)	Phase	Type	Mobility $cm^2\,V^{-1}\,s^{-1}$	Resistivity (Ω cm)	Concentration (cm^{-3})
0	H	HR			
50	H	P	1.177	2.1×10^4	2.9×10^{14}
78	H + C	P	0.197	2.9×10^3	1.1×10^{16}
83	H + C	P	0.095	9.9×10^3	7.0×10^{15}
100	C	P	0.633	2.0×10^4	5.3×10^{15}

Table 2. Room temperature electrical properties of the annealed $Mg_xZn_{1-x}O$ films deposited in the $O_2 + N_2$ ambient under various nitrogen partial pressure ratios (R'_{N_2}).

R'_{N_2} (%) ($O_2 + N_2$)	Phase	Type	Mobility ($cm^2\,V^{-1}\,s^{-1}$)	Resistivity (Ω cm)	Concentration (cm^{-3})
0	H	n	5.879	1.1×10^0	1.0×10^{18}
50	H	n	0.878	7.3×10^0	9.9×10^{17}
78	H	n	15.359	3.2×10^3	1.5×10^{14}
83	H	p	1.460	1.5×10^3	3.4×10^{15}
100	C	p	0.633	2.0×10^4	5.3×10^{15}

overcome compensation of other possible native donor defects and make the $Mg_xZn_{1-x}O$ conduct in p-type. However, the films grown at $50\% \leqslant R'_{N_2} \leqslant 78\%$ containing nitrogen show n-type. This can be attributed to the fact that there are not enough N atoms as a substitute for O atoms to form shallow acceptors at low nitrogen partial pressure ratio because some N atoms will react preferentially with ionized O atoms of O_2.

4. Conclusions

In conclusion, we have observed that the Mg concentration, structure and band gap of the $Mg_xZn_{1-x}O$ film can be tuned by increasing the nitrogen partial pressure ratio of the Ar + N_2 ambient, but cannot be tailored by changing the nitrogen partial pressure ratio of the O_2 + N_2 ambient. The $Mg_xZn_{1-x}O$ films deposited in Ar+N_2 undergo structure transformation from the wurtzite phase at $0\% \leqslant R_{N_2} \leqslant 50\%$ to a mixture of wurtzite and cubic phases at $78\% \leqslant R_{N_2} \leqslant 83\%$, and to the cubic phase at $R_{N_2} = 100\%$. The structural phase transition is not abrupt. However, the structural phase transition is abrupt as the nitrogen partial pressure ratio in the O_2+N_2 ambient changes from 0% to 100%. The film is either of single wurtzite structure or of single cubic structure, there is no mixed phase. The wurtzite structure $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient are highly *c*-axis oriented, while the wurtzite structure $Mg_xZn_{1-x}O$ films grown in the O_2 + N_2 ambient do not have the *c*-axis preferential orientation. This can be attributed to the low energy of deposited atoms in O_2 + N_2 ambient. The band gap and the Mg concentration increase with the nitrogen partial pressure ratio in the Ar + N_2 ambient, but they are invariable with the nitrogen partial pressure ratio in the O_2 + N_2 ambient containing O_2. The Mg concentration in the $Mg_xZn_{1-x}O$ films grown in the Ar + N_2 ambient can be precisely controlled by the nitrogen partial pressure ratio due to the linear increase with the increasing nitrogen partial pressure ratio of Ar + N_2. The variation of the structure and band gap can be attributed to the increase in the Mg concentration in the film while the variation of Mg concentration is attributed mainly to the loss of the O and Zn atoms based on reactive thermodynamics. This study also indicates a possibility of band gap engineering of the $Mg_xZn_{1-x}O$ films by varying the nitrogen partial pressure ratio in the Ar + N_2 ambient but not in the O_2 + N_2 ambient.

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