# Effects of Mg doping on the properties of highly transparent conductive and near infrared reflective $Zn_{1-x}Mg_xO$:Ga films

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## Abstract

Highly transparent conductive and near infrared (IR) reflective Gallium-doped ZnMgO ($Zn_{1-x}Mg_xO$:Ga) films with Mg content from 0 to 10 at% were deposited on glass substrate by DC reactive magnetron sputtering. X-ray diffraction shows all the ZnMgO:Ga films are polycrystalline and have wurtzite structure with a preferential $c$-axis orientation. Hall measurements indicate that the resistivity of these films obviously increases with the Mg concentration increasing. The average transmittance of $Zn_{1-x}Mg_xO$:Ga films is over 90% in the visible range. All the $Zn_{1-x}Mg_xO$:Ga films have low transmittance and high reflectance in the IR region.

## 1. Introduction

Transparent conductive oxide (TCO) films have been extensively investigated with respect to their applications in optoelectronic devices, liquid crystal displays, heat mirrors, and multiplayer photothermal conversion systems. Among the different materials belonging to this category, ZnO has attracted attention as a TCO because of large band gap (3.3 eV), high conductivity, ease in doping, chemical stability in hydrogen plasma, thermal stability when doped with III group elements, abundance in nature, and non-toxicity. However, investigations of IR reflective property of doped ZnO films or the films with mixture of ZnO have received less attention though transparent conductive doped-ZnO films have been studied extensively in recent years due to their good electrical and optical properties.

All the transparent conductive doped-ZnO films provide excellent UV shielding due to the absorption edge on the short wavelength side ($\lambda\sim300$ nm) [1]. Besides, high reflectance in the IR region can make this film a good candidate for application as the coating for IR reflecting mirror or heat reflector and smart coating on architectural glasses, as well as in other fields of technology [2,3]. All these applications require films with good uniformity, high electrical conductivity and high electron concentration simultaneously with high transmittance to visible light and high reflectance to near-IR light [4,5].

From many reported investigations of the doping effect of impurities on ZnO, Ga doping seems to be the most successful and promising due to its advantages, such as the rather similar atomic radius compared to Zn, which could result in only small ZnO lattice deformations even for the case of high Ga concentrations [6,7]. Also, Ga is less reactive and more resistive to oxidation compared to Al [8,9]. Therefore, Ga doping can produce higher electron concentration than Al doping, which may be more useful for improving the reflective behavior of transparent conductive ZnO films according to Drude theory. At present, the study on high IR reflective property of Ga-doped ZnO (ZnO:Ga) films and Ga-doped ZnMgO (ZnMgO:Ga) films has not been reported. Moreover, it is known that incorporating Mg into ZnO can increase the band gap of ZnO [10]. Furthermore, $n$-ZnMgO transparent

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conductive films can be used as barrier layer to realize efficient electron-hole recombination in ZnMgO homostructures, presented for ZnO-based ultraviolet light-emitting diodes (LEDs) [11,12]. But few researchers pay attention to the study of $n$-ZnMgO films for LEDs. We expect to incorporate Mg into ZnO:Ga films to synthesize Ga-doped ZnMgO ($Zn_{1-x}Mg_xO$:Ga) films to increase the bandgap of ZnO-based films and also study the IR reflective behavior of transparent conductive $Zn_{1-x}Mg_xO$:Ga films.

In the present work, $Zn_{1-x}Mg_xO$:Ga films were deposited by DC reactive magnetron sputtering. A systematic study of structural, electrical, and optical properties of $Zn_{1-x}Mg_xO$:Ga films deposited with different Mg content from 0 to 10 at% have been investigated.

## 2. Experimental procedure

Highly transparent conductive and near-IR reflective $Zn_{1-x}Mg_xO$:Ga films were synthesized on glass substrate by DC reactive magnetron sputtering. $Zn_{1-x}Mg_xGa_{0.03}$ ternary metal alloy of 99.999% purity with $x = 0.01$, 0.03, 0.05, and 0.1 was used as sputtering target. The deposition chamber was initially evacuated to a base pressure of $10^{-3}$ Pa and a mixture of Ar (99.999%) and $O_2$ (99.999%) was then introduced as the sputtering gas. The $Ar/O_2$ ratio is 4:1. The total pressure during sputtering was maintained at 1.0 Pa. The substrate temperature was controlled at 300 °C. Before deposition, the alloy target was pre-sputtered in $Ar + O_2$ atmosphere for about 5 min to remove contaminants from the surface. The sputtering power was controlled at 140 W.

The crystal quality of the films was analyzed by X-ray diffraction (XRD) using a Bede D1 system with a Cu$K\alpha$ ($\lambda = 0.1541$ nm) radiation (The counting step and time are 0.05° and 0.3 s, respectively.). The film thickness was assessed using scanning electron microscopy (FE-SEM SIRION). The depth profile of ZnMgO:Ga film was carried out by a CAMECA IMS-3f secondary ion mass spectrometer (SIMS). Surface chemical state analysis was investigated by Thermo ESCALAB 250 X-ray photoelectron spectrometer (XPS) using a 1486.6 eV Al$K\alpha$ source. Hall measurements were performed using Van der Pauw technique at room temperature. The optical transmission and reflection spectra were measured with a U-4100 Spectrophotometer.

## 3. Results and discussion

The XRD patterns of the $Zn_{1-x}Mg_xO$:Ga films with different Mg contents are shown in Fig. 1. All the film thickness is around 500 nm. Only the peaks indexed to hexagonal (0 0 2) and (0 0 4) ZnO were observed in these patterns. No peak from other compounds such as $Ga_2O_3$ and MgO or Mg, etc. appeared even though when the Mg content increases up to 10 at%, indicating that the $Zn_{1-x}Mg_xO$:Ga films are polycrystalline and possess
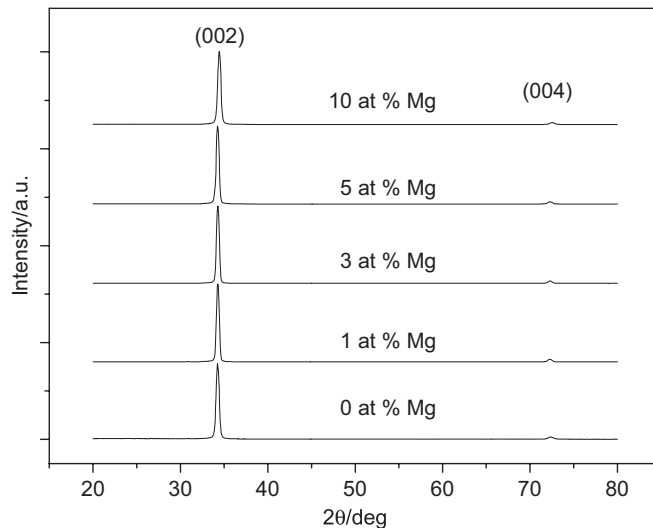


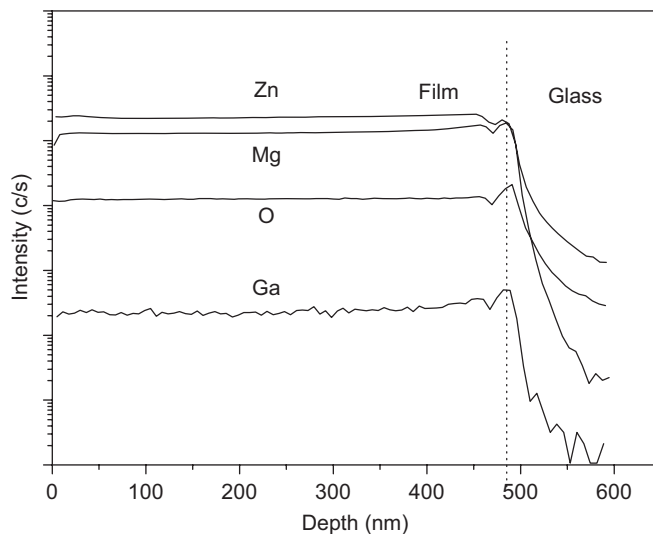Fig. 1. XRD patterns of the $Zn_{1-x}Mg_xO$:Ga films with different Mg content.



Fig. 2. SIMS depth profile of the $Zn_{1-x}Mg_xO$:Ga film with Mg content of 3 at%.

hexagonal wurtzite structure with a preferential $c$-axis orientation.

The depth profile of the $Zn_{0.97}Mg_{0.03}O$:Ga thin film was investigated by SIMS measurements, and the result is shown in Fig. 2. The distribution of Zn, Mg, O, and Ga is uniform in the whole film. Fig. 3 shows the cross-section SEM picture of the $Zn_{0.97}Mg_{0.03}O$:Ga film. The thickness of the film is about 490 nm. The image shows the film is very dense.

In order to investigate surface chemical state of Ga and Mg, XPS measurements on the $Zn_{1-x}Mg_xO$:Ga films were performed. Fig. 4(a) shows the $Ga_2P_3$ peaks of $Zn_{1-x}Mg_xO$:Ga films with different Mg concent. The peaks of the $Ga_2P_3$ can be fitted by one Gaussian peak, which indicates that only one chemical state of Ga is
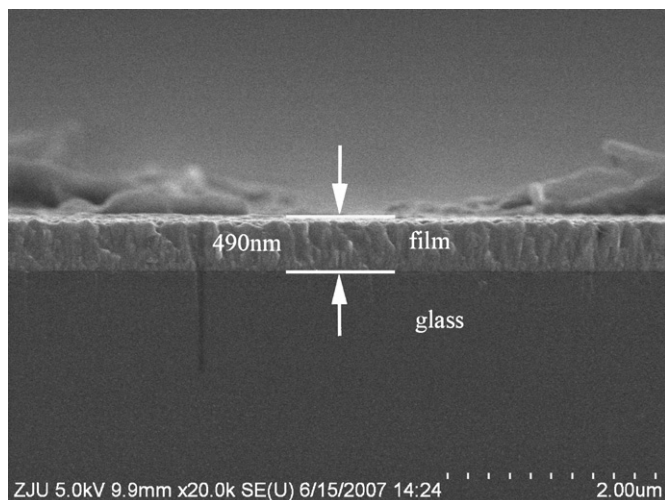
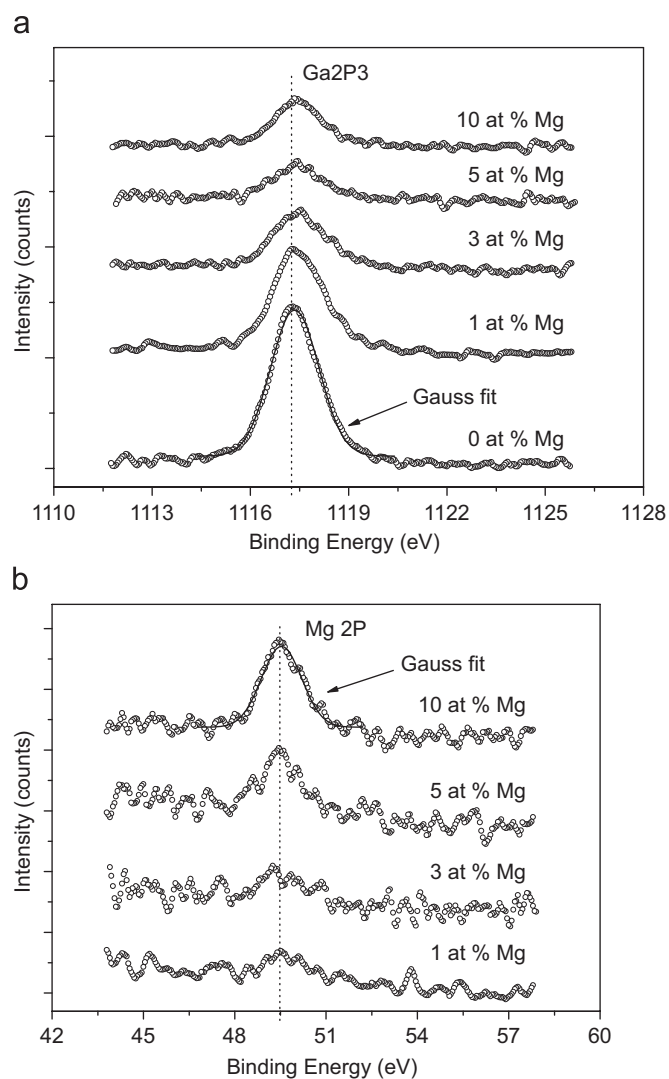Fig. 3. The cross-section SEM picture of the $Zn_{0.97}Mg_{0.03}O$:Ga film.

a



b



Fig. 4. XPS spectra of the $Zn_{1-x}Mg_xO$:Ga films with different Mg content: (a) $Ga_2P_3$ peaks of the $Zn_{1-x}Mg_xO$:Ga films and (b) Mg 2P peaks of the $Zn_{1-x}Mg_xO$:Ga films.

present in the $Zn_{1-x}Mg_xO$ films. The peak at 1117.4 eV is attributed to Ga–O bonding [13]. Mg 2P peaks of $Zn_{1-x}Mg_xO$:Ga films is shown in Fig. 4(b). From Fig. 4(b), it is seen that the intensity of the Mg 2P peaks becomes more intense with Mg content increasing. Only one peak appears around 49.7 eV, which is considered as the Mg–O bonding because no Mg phase has been found from XRD patterns [14]. The Zn, Mg, and Ga atomic concentrations for the $Zn_{1-x}Mg_xO$:Ga films are listed in Table 1. The data of atomic concentration is determined by XPS. It is different from the starting alloy used for sputtering.

Fig. 5 illustrates the electrical properties of the $Zn_{1-x}Mg_xO$:Ga films measured at room temperature. Hall measurements indicate that the resistivity of these films obviously increases with the Mg concentration increasing, accompanied with a reduction in carrier concentration and Hall mobility. It is known that incorporating Mg into ZnO can increase the band gap of ZnO. One reason of the generally higher resistivities for $Zn_{1-x}Mg_xO$:Ga films is the deepening of Ga-donor level in the band gap of ZnMgO films due to Mg doping [15], which makes both mobility and electron carrier concentration decrease. The other reason for the conductivity decrease of $Zn_{1-x}Mg_xO$:Ga films may be resulted from lower doping efficiency with increasing Mg content. Assuming a hydrogenic donor dopant model, the donor activation energy also increases with the effective mass increasing due to the increase of Mg content compared to ZnO, $m^* = 0.38m_e$, and this would

Table 1
Zn, Mg, and Ga atomic concentrations for the $Zn_{1-x}Mg_xO$:Ga films

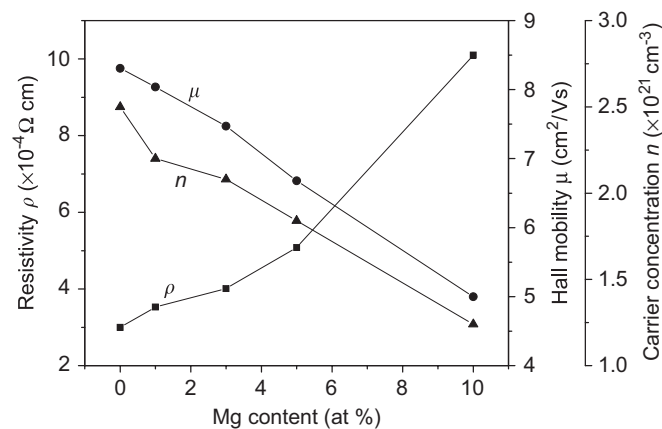| Sample | Zn content (at%) | Mg content (at%) | Ga content (at%) |
|---|---|---|---|
| ZnO:Ga | 93.9 | 0 | 6.1 |
| $Zn_{0.99}Mg_{0.01}O$:Ga | 91.9 | 3.2 | 4.9 |
| $Zn_{0.97}Mg_{0.03}O$:Ga | 87.9 | 7.6 | 4.5 |
| $Zn_{0.95}Mg_{0.05}O$:Ga | 88.3 | 7.9 | 3.8 |
| $Zn_{0.9}Mg_{0.1}O$:Ga | 74.2 | 22.4 | 3.4 |



Fig. 5. Resistivity, Hall mobility, and carrier concentrations as a function of Mg content for $Zn_{1-x}Mg_xO$:Ga films.

decrease doping efficiency [16]. Alternatively, the formation of magnesium gallate may prevent Ga from acting as an electron donor, according to the equation

$$Mg_{Zn}^{X} + 2Ga_{Zn}^{*} + 2e^{-} + 3O_{O}^{X} + \tfrac{1}{2}O_{2(g)} \Leftrightarrow MgGa_2O_4. \quad (1)$$
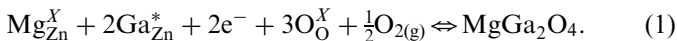
Note that magnesium gallate clusters might be present at very low levels so that they would not be easily detected by XRD. Therefore, the electron concentration of the $Zn_{1-x}Mg_xO$:Ga films decreases with increasing Mg content, the same as the Hall mobility. However, the increase of Mg content will lead to the scattering centers increase in the films, which hinders the movement of the electrons and results in the decrease of the mobility.

For optical applications $Zn_{1-x}Mg_xO$:Ga film with high transmittance in the visible range and high reflectance in the near-IR region is very important. Fig. 6 shows the transmittance and reflectance spectra of the $Zn_{1-x}Mg_xO$:Ga films as a function of wavelength in the range of 300–2500 nm. Both the transmittance and reflectance are with substrate deduction. It is observed that in the visible region the films are highly transparent, and their spectra are like those of dielectrics regardless of Mg content. In the IR region the films behave like metals and have high reflectance. The crossover between these two behaviors is at the plasma wavelength, which moves to shorter wavelength as the electron concentration in the films increases. The film without Mg has the lowest transmittance and the highest reflectance in near-IR range. Its transmittance is below 10% when the wavelength is longer than 1500 nm and the reflectance reaches 72% at the wavelength of 2500 nm. The near-IR reflective property of the as-deposited film without Mg is much better than that of the most reported IR-reflective ZnO:Al films [17–21] whose reflectance is below 60% at 2500 nm. The good IR-reflective property makes $Zn_{1-x}Mg_xO$:Ga films of interest as IR reflector—window coating or heat reflector.

The IR reflective behavior of transparent conductive films originates from the plasma resulted from the high-electron concentration [22]. In the model of Drude, it is predicted that the electron concentration $N_e$ is related to the plasma frequency, that is, the plasma wavelength by the following relation [23]:

$$\lambda_p = 2\pi c_0 (N_e e^2 / \varepsilon_0 \varepsilon_\infty m_e^* - \gamma^2)^{-1/2}, \quad (2)$$

where $\varepsilon_\infty$ is the high-frequency dielectric constant, e is the electron charge, $m_e^*$ is the effective mass of the electron in the conduction band, $\gamma$ is the Drude scattering frequency given by the relation

$$\gamma = e/m_e^* \mu, \quad (3)$$

and $\mu$ is the mobility of the electrons. The values of $\varepsilon_\infty$ and $m_e^*$ are 4 and $0.38m_e$ [24]. The plasma wavelength $\lambda_p$ of the films without Mg doping can be calculated to be 850 nm by the above equations (Eqs. (2) and (3)). This is in good agreement with that determined from the transmission spectra. It is seen that the plasma wavelength relies on electron concentration $N_e$ significantly. The IR transmission cut-off wavelength (the plasma wavelength) of the films shifts toward the lower wavelength with the electron concentration increasing. As demonstrated from Fig. 6 the film with higher electron concentration and higher mobility has the higher near-IR reflectance. However, Mg doping is not useful to improve near-IR reflective behavior of $Zn_{1-x}Mg_xO$:Ga films although the band gap of the films can be increased by the addition of Mg.

## 4. Conclusions

In summary, we have prepared highly transparent conductive and near-IR reflective ZnMgO:Ga films on glass substrate via DC reactive magnetron sputtering method. All the $Zn_{1-x}Mg_xO$:Ga films are polycrystalline and show a single phase wurtzite structure with a preferential *c*-axis orientation. The resistivity of these films obviously increases with the Mg concentration increasing, accompanied with a reduction in carrier concentration and Hall mobility. The average transmittance of $Zn_{1-x}Mg_xO$:Ga films is over 90% in the visible range. All the $Zn_{1-x}Mg_xO$:Ga films have low transmittance and high reflectance in the IR region. The novel IR reflective property of the films will significantly contribute to the application of near-IR reflecting mirror and heat reflector. Further investigations on highly transparent conductive and near-IR reflective $Zn_{1-x}Mg_xO$:Ga films are in progress. This method is considered as an ideal approach in producing highly transparent conductive and near-IR reflective $Zn_{1-x}Mg_xO$:Ga films with large-area.
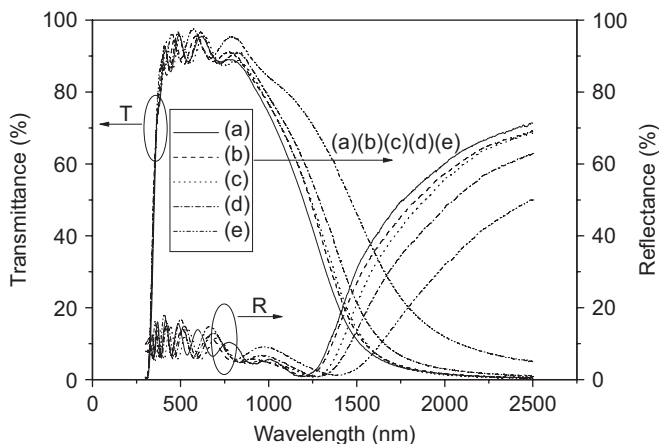
Fig. 6. Transmittance and reflectance spectra of $Zn_{1-x}Mg_xO$:Ga films measured in the wavelength range of 300–2500 nm: (a) 0 at% Mg, (b) 1 at% Mg, (c) 3 at% Mg, (d) 5 at% Mg, and (e) 10 at% Mg.

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