Characteristics of Quaternary Flexible Mg and Ga Co-Doped ZnO Thin Films Fabricated Using RF Magnetron Sputtering

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ABSTRACT

Mg and Ga co-doped ZnO (MGZO) thin films with transparent conductive characteristics and low resistivity have been fabricated using a radio frequency (RF) magnetron sputtering process. Doped ZnO thin films with 0.5 at.% Mg and 0.3 at.% Ga were grown based on our previous investigation on polyethylene terephthalate substrates (PET) using different sputtering powers from 50 to 150 W. The influence of the various sputtering powers on the structural, morphological, compositional, optical and electrical properties of the MGZO thin films were investigated. X-ray diffraction patterns show that all of the films had a hexagonal wurtzite ZnO structure with a c-axis preferential growth. The MGZO thin films had directional uniform morphologies. The optical properties of the MGZO thin films demonstrated a high transmittance of approximately 80% and a band gap energy of 3.58 eV. The resistivity, the mobility and the carrier concentration of the MGZO thin films varied gradually from $2.4 \times 10^{-2}$ to $3.7 \times 10^{-3}$ Ωcm, 1.23 to 5.0 Cm²/Vs and 1.91 $\times 10^{-20}$ to 2.51 $\times 10^{-20}$/Cm³, respectively, with an increase in the sputtering power.

KEYWORDS: Transparent Conducting Oxide, Mg and Ga Co-Doped ZnO, Polymer Substrate, RF Magnetron Sputtering.

1. INTRODUCTION

Flexible electronic devices have attracted increased interest over the last decade for next generation applications, such as thin film solar cells, liquid crystal displays, organic light emitting diodes, electronic paper, and touch screen panels.¹,² In particular, flexible electronic devices are lightweight, mechanically robust and can be fabricated using a roll-to-roll process, which is a simple, facile, and low cost technique.³ To improve the performance and stability of flexible electro-optical devices, it is necessary to develop high quality transparent conducting oxide (TCO) thin films on flexible substrates. However, TCO thin films deposited on a flexible substrate presents certain challenges, such as the limitation of the substrate temperature, large difference in the thermal expansion coefficient between the TCO materials and the flexible substrate compared with TCO materials deposited on glass or on single crystal substrates.⁴,⁵ The most popular TCO material is Sn doped In₂O₃ (ITO) oxide, which has a band gap energy of 3.5 eV, a resistivity below $10^{-4}$ Ωcm, and a high transmittance in the visible region.⁶,⁷ Although ITO-based TCO materials have outstanding optical and electrical characteristics, the In is an expensive and scarce element and is unstable during the H₂ gas plasma process, which limits the use of In in the commercialization of electro-optical devices.⁸ Recently, ZnO-based TCO materials have been considered to be an alternative for ITO due to their low cost, relatively low deposition temperature, resistance to hydrogen-plasma-reduction and stability during plasma and chemical treatments.⁹–¹¹ However, un-doped ZnO-based electro-optical devices suffer from a relatively high resistivity of greater than $10^{-2}$ Ωcm and narrow band gap energy of 3.3 eV.⁷,¹² The optical and electrical properties of ZnO thin films can be controlled by doping with Mg and Ga.

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group III elements. Among the Group III elements, Ga doping in ZnO (GZO) resulted in the best characteristics compared with doping with other elements due to the following reasons:

(i) Ga has a better oxygen resistance than Al and In; (ii) The ionic radius of Ga is similar to Zn, which minimizes structural defects; and (iii) GZO films have shown good resistance to humidity and strong near-edge emission at room temperature.

Our group and other researchers have investigated the preparation and characterization of high quality GZO thin films with a low resistivity of $3.45 \times 10^{-4}$ $\Omega \cdot$cm and high transmittance ($\sim 80\%$) in the visible region. Although previous studies of GZO thin films showed outstanding optical and electrical characteristics, the optical band gap energy is limited to 3.6 eV.

Conversely, Magnesium oxide (MgO) is a promising dopant for band gap engineering of ZnO-based thin films. Previous studies have reported increases in the and the engineering of the band gap in the Mg doped ZnO (MZO) structural system prepared using various techniques. The optical band gap energy of MZO thin films was changed from 3.3 to 4.2 eV without changing the crystal structure by reducing the Mg doping concentration below 40 at.%. Although the optical band gap energy for ZnO thin films can be controlled by Mg doping, the high resistivity limits the practical use of Mg doping in electro-optical devices. More recently, our group reported the development of wide optical band gap energies and outstanding electrical characteristics for ZnO thin films that were constructed by introducing Mg and Ga elements to overcome the 3.6 eV band gap energy limitations while retaining low electrical resistivity. Shin et al. reported band gap engineering from 3.3 eV to 3.75 eV and a low resistivity of $6.89 \times 10^{-4}$ $\Omega \cdot$cm for Mg and Ga co-doped ZnO (MGZO) thin films prepared on glass substrates using a RF sputtering technique. These studies motivated the possibility of preparing flexible TCO thin films that include wider optical band gap energy and a lower electrical resistivity for use in high performance electro-optical devices. In this article, MGZO thin films were prepared on flexible PET substrates at room temperature using a RF sputtering system. The significant impact of sputtering power on the structural, morphological, electrical, and optical properties of the MGZO thin films is reported.

2. EXPERIMENTAL DETAILS

Flexible MGZO thin films were deposited on the PET substrate using a RF magnetron sputtering technique. The MGZO target was fabricated using a cold isotactic process (CIP) and sintered at 1100 °C for 3 h. Prior to deposition, the substrates were ultrasonically cleaned for 10 min using ethanol and deionized water and were dried with N$_2$ gas. For the sputtering process, Ar gas (99.999%) was used as a plasma source, and the gas flow rate was controlled at 40 sccm. The working pressure was maintained at 6 mTorr, and the temperature of the substrate was fixed at room temperature. The RF sputtering power varied from 50 to 150 W. The thickness of all of the samples was fixed at 600 nm.

The crystal structure and direction of the MGZO thin film growth was examined using high-resolution X-ray diffraction (XRD, X’pert PRO, Philips, Eindhoven, Netherlands) operated at 40 KV and 30 mA using Ni-filtered Cu-Ka radiation [\(\lambda = 1.54056\) Å]. The chemical binding energy was confirmed by X-ray photoelectron spectroscopy (XPS, VG Multilab 2000, ThermoVG Scientific, UK). The binding energy in the spectrometer was calibrated using the C 1s line at 285.0 eV. The surface morphology and roughness of the thin films were observed by field emission scanning electron microscopy (FE-SEM, JSM-6701F, JEOL, Japan) and atomic force microscopy (AFM, XE-100, Park System, Korea). The optical transmittance of the thin films was observed using UV-visible spectroscopy (Cary 100, Varian, Mulgrave, Australia). The electrical properties of the thin films were characterized by Hall Effect measurements in the Van der Pauw configuration (M/N #7707_LVWR, Lake Shore Crytronics Inc., USA).

3. RESULTS

Figure 1 shows the XRD patterns of the flexible MGZO thin films deposited at different sputtering powers. The XRD patterns of all of the deposited thin films showed a strong peak at 34.3° corresponding to the (0002) plane [JCPSD card No.: 89-1297 (ZnO)], which indicates that the deposited thin films exhibited a hexagonal wurtzite crystal structure. The MGZO thin film prepared at 150 W shows a weak and broad tiny peak of approximately 36.1°, which corresponds to the (10–11) plane. The deposited MGZO thin films were polycrystalline, with a highly

![Fig. 1. XRD diffraction patterns of the MGZO thin films deposited on the PET substrates as a function of the sputtering power (from 50 to 150 W).](image)
Figure 3 shows the FE-SEM images of the MGZO thin films deposited at different sputtering powers. All of the MGZO thin films showed a dense, uniform and crack-free microstructure and exhibited a columnar crystal structure that has a directional nature with a uniform thickness of approximately 600 nm. When the sputtering power was increased, the grain size of films was observed to increase in the images, and this result was confirmed using the Debye-Scherrer formula. Figure 4 shows the AFM images of the MGZO thin films at different sputtering powers: (a) 50 W, (b) 75 W, (c) 100 W, (d) 125 W, and (e) 150 W. All of the films showed relatively smooth surface morphologies without any cracks. The root mean square (RMS) roughness values, which represent the roughness degree of the MGZO thin films, are tabulated in Table I. The RMS values of the films varied from 6.941 nm to 9.415 nm and increased with an increase in the sputtering power. According to previous results, the reason the roughness of the MGZO thin films increased with an increase in the sputtering power can be explained by the ripening process in which ions can obtain more energy from the high sputtering power and move easily along the surface and interfaces. Therefore, large grains and interface energies can grow rapidly at the expense of small grains with high surface energies.

Table 1. Experimental results evaluated from the XRD patterns and the AFM of the MGZO thin films deposited on PET substrates as a function of the sputtering power (from 50 to 150 W).

<table>
<thead>
<tr>
<th>Sputtering power (W)</th>
<th>FWHM (°)</th>
<th>Grain size (nm)</th>
<th>RMS (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.38</td>
<td>42</td>
<td>6.941</td>
</tr>
<tr>
<td>75</td>
<td>0.34</td>
<td>48</td>
<td>7.35</td>
</tr>
<tr>
<td>100</td>
<td>0.30</td>
<td>54</td>
<td>7.412</td>
</tr>
<tr>
<td>125</td>
<td>0.28</td>
<td>58</td>
<td>7.822</td>
</tr>
<tr>
<td>150</td>
<td>0.24</td>
<td>68</td>
<td>9.415</td>
</tr>
</tbody>
</table>

- c-axis out-of-plane orientation and a random in-plane orientation. No peaks from secondary phases, such as Ga, Zn, GaO, MgO, or ZnGaO [JSCDS card No.: 45-0946 (MgO), 87-1901 (GaO), 86-0415 (Ga₂ZnO₄)], were found, regardless of the sputtering power. The peak intensity of the (0002) plane was significantly enhanced with an increase in sputtering power. However, a shift in the peak position of the (0002) plane was not observed.

The crystallite size of the MGZO thin film was calculated by using the Debye-Scherrer formula:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]

where \( K \) is the correction factor with a value of 0.9, \( \lambda \) is the X-ray wavelength, \( \theta \) is the Bragg diffraction angle, and \( \beta \) is the full width at half maximum (FWHM) value of the (0002) diffraction peak in the MGZO thin films. The variations in the FWHM and the grain size for the MGZO thin films versus the sputtering power is given in Table I. It is clearly observed that the FWHM decreases from 0.38° to 0.24° and the grain size significantly increases from 42 nm to 68 nm with an increase in the sputtering power. This result clearly indicates an improvement in the grain size caused by increasing the sputtering power, leading to an enhancement in the crystallinity.

The XPS characterization of the MGZO thin films was investigated to confirm the change in the chemical binding energy and the state of Mg and Ga elements in the MGZO system. Figure 2 shows the XPS measurement of the MGZO thin films prepared at 125 W. A typical survey spectrum of the MGZO thin films showed the presence of Mg, Ga, Zn, and O elements as well as the C reference (Fig. 2(a)). Figure 2(b) shows that the spectrum of the Ga 2p level peaks located at 1117.9 eV and 1144.9 eV coincide with the electronic state of Ga 2p₃/₂ and Ga 2p₅/₂ core levels respectively. Figure 2(c) shows that the peaks located at 50.6 eV and 47.2 eV can be assigned to the Mg 2p core levels. These characteristics indicate that all elements did not exist as metal, and the elements, such as Ga and Mg, were incorporated into the ZnO crystal structure by bonding with oxygen. Furthermore, only a single O1s peak was observed at 531.2 eV. This result indicates that Ga³⁺ and Mg²⁺ were successfully substituted by Zn²⁺ in the MGZO thin films.

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leads to nucleation and growth. This results in increasing the mean free path of electrons, which is attributed to the charge in the carrier mobility in the thin film. Furthermore, it is clear that the enhanced crystallinity decreases the grain boundary, which causes the free electrons to be trapped in the thin film, and this decreases the electron scattering.29

Figure 6 shows the UV-visible transmittance spectra (a), a plot of \((\alpha h v)^2\) versus the photon energy \((h v)\) (b) of the MGZO thin films at different sputtering powers, an image of the foldable PET substrate (c) and a plain substrate (d) deposited on a MGZO thin film. All of the MGZO thin films demonstrated a high transmittance in the visible region over 80%, regardless of the sputtering power. From Figures 6(c) and (d), the highly transparent MGZO thin films were observed to have been successfully deposited on the flexible PET substrates. The absorption edges of the MGZO thin films were quite sharp, which suggests that the surfaces of thin films were highly uniform and crystalline in structure.24 The x-axis of the \((\alpha h v)^2\) versus photon energy \((h v)\) plot, which corresponds to the optical band gap energy versus \(\alpha h v\) plot, was not nearly as varied in the range from 3.5 to 3.58 eV.28,30 These results agreed with the Burstein-Moss effect through the following equation.31

\[
\Delta E_g = \left( \frac{h^2}{8m^*} \right) \left( \frac{3n}{\pi} \right)^{2/3}
\]
Fig. 3. Tilt view FE-SEM images of the MGZO thin films deposited on the PET substrates as a function of the sputtering power (from 50 to 150 W). 50 W (a), 75 W (b), 100 W (c), 125 W (d) and 150 W (e).

where $m^*$ is the electron effective mass in the conduction band ($m^* = 0.27 m_0$). Figure 6 shows that there is not a significant difference between each films’ carrier concentration regardless of the sputtering power (from $1.91 \times 10^{-20}$ to $2.51 \times 10^{-20}$/Cm$^3$). This behavior was in good agreement with the band gap plots, which showed a distinction between each film. From the previous discussion, flexible MGZO thin films, which compare favorably to films deposited on the glass, were confirmed to be successfully fabricated with outstanding performance. With these characteristics, flexible MGZO thin films can be readily applied to opto-electronic devices.

4. DISCUSSION

In this article, flexible ZnO-based thin films were investigated by introducing Mg and Ga elements into the ZnO structure. The characteristics of the MGZO thin films improved due to an increase in the sputtering power. This tendency is explained below. When the sputtering power increased, the sputter species obtained more energy, which resulted in an increase in the sputter yield and in the amount of kinetic energy each sputtered species obtained. The sputtered species with a high kinetic energy has a greater probability of offering adatoms of the lowest energy state, which minimizes a mismatch of...
Fig. 4. The three-dimensional AMF images (1 μm × 1 μm) of the MGZO thin films deposited on the PET substrates as a function of the sputtering power (from 50 to 150 W). 50 W (a), 75 W (b), 100 W (c), 125 W (d) and 150 W (e).

Fig. 5. Electrical resistivity (△), carrier concentration (○) and mobility (□) of the MGZO thin films deposited on the PET substrates as a function of the sputtering power (from 50 to 150 W).

The crystal structure. Therefore, an increase in the sputtering power contributed to an increase in the deposition rate by increasing the quantity of sputtered species that are provided to the substrate and by providing kinetic energy to the sputter species. According to the thin film growth mechanism described above, it is clear that the crystallinity and the grain size of the thin film were enhanced with an increase in the sputtering power. Furthermore, the facts described above can be confirmed from the X-ray diffraction and SEM results. Additionally, the sputtering yield improved the crystallinity of the MGZO thin films. The increase in the sputtering yields can clearly be seen for the films deposited at a high sputtering power. Therefore, the high sputtering power resulted in a high sputter yield, which enhances the crystal quality. A high sputter yield at
a high sputtering power augments the crystal quality due to the effective formation of larger grains. 19

5. CONCLUSION

Mg and Ga co-doped ZnO (MGZO) thin films have been successfully prepared on PET substrates using an RF magnetron sputtering process. The properties of the MGZO thin films were investigated as a function of the sputtering power. The film properties depended strongly on the sputtering power. All of the films showed a c-axis preferred orientation and were transparent over 80% of the visible wavelength region. The lowest resistivity of 3.7 × 10⁻³ Ωcm and the widest optical band gap energy of 3.58 eV were obtained for MGZO thin films deposited at a sputtering power of 150 W. In this study, we have confirmed the high performance of quaternary compound TCO films on the polymer substrate as a promising candidate for flexible and foldable optoelectronic devices.

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References and Notes

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