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Electrical and optical properties of Ga-doped ZnO thin films deposited by DC magnetron sputtering

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Abstract: The electrical and optical properties of Ga-doped ZnO (GZO) thin film prepared by direct current (dc) magnetron sputtering were investigated. The GZO thin film was deposited on a glass substrate at a substrate temperature (Ts) of room temperature (RT), 150 °C, and 200 °C using DC power of 100 W and an Ar gas flow rate of 450 sccm. The thickness of films was maintained at about 200 nm by controlling the deposition rate of about 12.5 nm/minute. The result showed that the electrical properties improved with increasing Ts. The films deposited at Ts of 200 °C showed the lowest resistivity, highest hall mobility, and carrier concentration compared to other Ts. The average transmittance of the films in the visible range (380-750 nm) was approximately 86.04%. The value of the optical band gap (Eg) was approximately 3.8 eV. The results suggested that GZO films deposited by DC magnetron sputtering at Ts of 200 °C can be applied to transparent conducting oxide (TCO) as an electrode in optoelectronic applications such as solar cells, LEDs and display technology.

Keywords: *DC magnetron sputtering, electrical properties, GZO thin films, optical properties, transparent conducting oxide (TCO)*

Introduction

In recent years, there has been an interest in oxide materials such as ZnO. ZnO has a wurtzite structure that naturally acts as an n-type semiconductor. Doping to a semiconductor is important for practical application to control its properties according to its purpose. There are several n-type dopant candidates for ZnO, e.g. Group III elements (B [1], Al [2-3], Ga [4-7] and In [8]), Group IV elements (Ge [9], Si [10], and Sn [10]) and Group VII elements (F and Cl) [10].

Recent significant attention has been paid to transparent conductive oxides (TCOs) for use as transparent electrodes in optoelectronic applications such as thin-film photovoltaics [11], light-emitting diodes [12], flat panel displays [13], and gas sensor [3, 7]. Based on material from CdO and Sn-doped In_2O_3 (ITO) [14-15], the development of TCO materials has already begun in about 1950. Nowadays, the most commonly used TCO is ITO, but in the last decade, due to the scarcity of In and also toxicity problems with its processing, some alternatives to ITO were needed [16-17]. ZnO-based TCOs such as Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) have long been studied as transparent electrodes materials [16-17]. The resistivity of commercial ITO is approximately $1\text{-}3\times10^{-4}$ Ω.cm with a large optical band gap (~3.7 eV). GZO films are expected to have a higher transmittance in the visible wavelength range compared to ITO [18].

A variety of deposition methods such as magnetron sputtering (MSP), metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), ion plating (IP), vacuum arc plasma evaporation (VAPE), electrochemical, evaporation, and spray pyrolysis deposition can be used to prepare ZnO thin films [19]. MSP is one of the most effective methods for film deposition due to its low-temperature deposition with relatively high film quality and uniformity, homogeneous and relatively dense film, easy scalability to large area deposition, simplicity of the deposition process and also relatively simple control of film thickness [20].

The new candidate for high-quality TCO beside ITO which have disadvantages such as costly and toxicity issue is very important as mentioned above. The requirement of TCO properties such as electrical and optical properties is necessary to be investigated.

In this study, the electrical and optical properties of the GZO thin films deposited on the glass substrate by DC magnetron sputtering were demonstrated.

Method

The GZO films were prepared by DC magnetron sputtering with an excitation frequency of 13.56 MHz.

Before being used for sputtering deposition, the glass substrate was cleaned using two steps in the ultrasonic bath. First, to ensure that no organic material remains on the surface of the glass, the glass substrate was degreased with 2-propanol and then rinsed with deionized water for about 10 minutes. Then the substrate was dried with a nitrogen blow using a nitrogen gun.

The GZO films were deposited on alkali-free glass substrates (Corning, Eagle XG, the diameter of 50 mm) using a ZnO ceramic target containing 5.7 wt % Ga_2O_3 (AGC Ceramics, GZO). The target size was 76.2 mm in diameter and 6 mm in thickness. The distance from the substrate to the target was 100 mm. The base pressure of the deposition chamber was kept below 5×10^{-5} Pa, and the ultra-high purity of the Ar gas (99.9999 %) was introduced during the sputtering deposition at a flow rate of 450 sccm and a DC power supply of about 100 W. The substrates temperature (Ts) was RT, 150 °C and 200 °C. The thickness of the film was measured by a surface profiler (KLA Tencor, Alpha-Step IQ). The details of the experimental parameters and processes are given in **Table 1.**

Table 1. The detail of experimental parameter deposition and film thickness.

T_s (°C)	P_{DC} (W)	Ar flow rate (sccm)	Base pressure (Pa)	Deposition time (min)	Deposition rate (nm/min)	Film thickness (nm)
RT	100	450	2.6×10^{-6}	16.45	13.0	214
150	100	450	7.4×10^{-6}	16.46	12.2	200
200	100	450	9.8×10^{-6}	16.45	12.5	205

The electrical properties were characterized by a Hall Effect Measurement System (Accent, HL5500PC) with an HL5580 Buffer Amplifier. For practical characterization, the samples were cut to 1×1 cm^2 in size for each sample. Measurements of the Hall effect were carried out at room temperature using the van der Pauw method to obtain resistivity, carrier concentration, and the Hall mobility.

The optical properties were characterized by a spectrophotometer (Hitachi, U-4100) with wavelengths ranging from 200 nm to 2500 nm. Transmittance (T) and reflectance (R) measurements were performed with an angle of incidence for the light at 5°.

Results and Discussion

The film thickness of GZO thin films was about 200 nm as confirmed by surface profile meter. The results of electrical properties are shown in **Figure 1-4**. This figure displays the variation in sheet resistance (*Rs*), resistivity (ρ), Hall mobility (μ), and carrier concentration (*N*). The *Rs* in **Figure 1** showed a similar trend with ρ (**Figure 2**) because of the similarity of their properties. The *Rs* and ρ showed high for Ts of RT. The ρ is about 2.42×10^{-2} Ω.cm and decreased in Ts of 200 °C (1.38×10^{-3} Ω.cm). The order of ρ near to 10^{-4} after using Ts in higher than 150 °C.

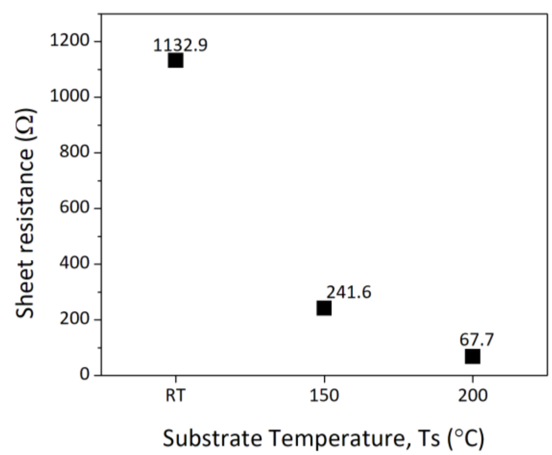

Figure 1. Sheet resistance (*Rs*) as a function of substrate temperature for the GZO thin films.

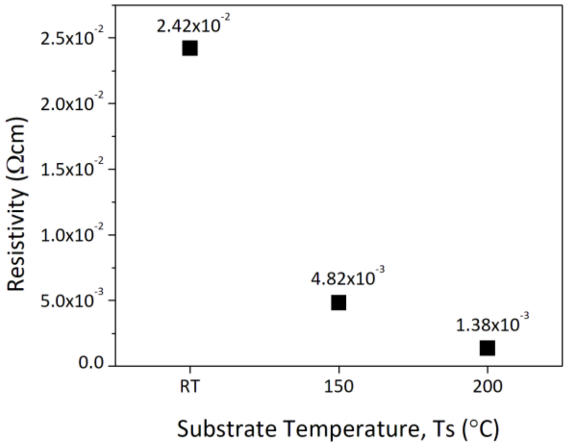

Figure 2. Resistivity (ρ) as a function of substrate temperature for the GZO thin films.

Figure 3 and Figure 4 show the tendency of hall mobility and carrier concentration. The μ and N were improved with increasing Ts. The μ and N at Ts of 200 °C were about 12.88 cm^2/Vs and 3.84×10^{20}, respectively. The N value in this result was comparable with the report by I. Shtepliuk et al. They reported that carrier density (N) increases up to ~4×10^{20} due to Ga doped ZnO [21]. It should be noted that the value of 3.84×10^{20} in our result can be obtained even only by using a glass substrate, not on GaN substrate.

In this result, the increase in N with increasing Ts can be clarified as annealing out of defects during deposition [22]. The increase in N could be provisionally attributed to a decrease in acceptor type defects such as interstitial oxygen (O_i) and/or zinc vacancy (V_{Zn}) [23].

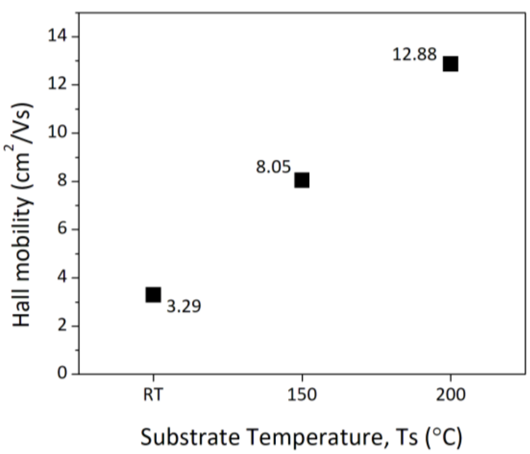

Figure 3. Hall mobility (μ) as a function of substrate temperature for the GZO thin films.

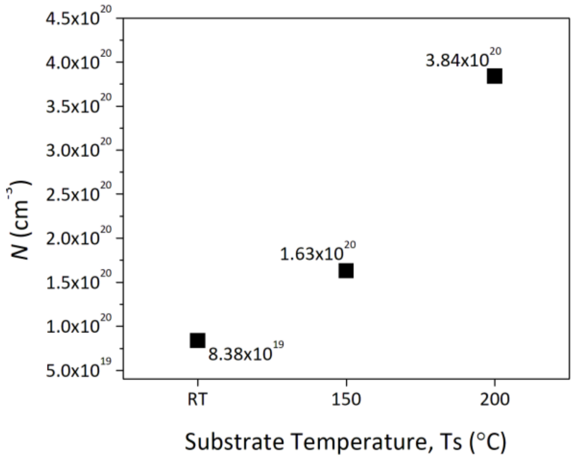

Figure 4. Carrier concentration (N) as a function of substrate temperature for the GZO thin films.

As a result of electrical properties, we then characterize the sample with Ts of 200 °C for optical properties. The optical properties of the film were shown in **Figure 5-8. Figure 5** shows the transmittance and reflectance in the wavelength range from 200 to 2500 nm. The reflectance increased in the near-infrared region, which affects the decrease in transmittance. This behavior was attributed to the free carrier absorption.

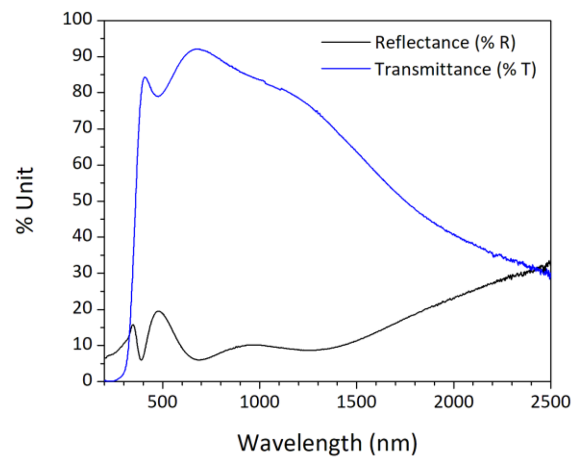

Figure 5. The transmittance and reflectance of GZO thin film as a function of wavelength.

Figure 6 displays the absorption spectra (in logarithmic / log 10 value) plotted as a function of wavelength (nm). The absorption coefficient, α, was calculated using the following equation [24]:

$$\alpha = \frac{1}{d} ln\left(\frac{100 - R}{T}\right) \tag{1}$$

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where *R* and *T*, respectively, are the percentage of reflectance and transmittance, and *d* is the film thickness. The increase in absorption greater than around 800 nm corresponds to free carrier absorption [25]. The absorption below 400 nm is known as the band gap absorption in the conduction band from the valence band to the Fermi level, whose exact energy level depends on the carrier concentration. Decreasing absorption in the visible region could be linked to annealing out of defects such as oxygen vacancy (V_o) [5].

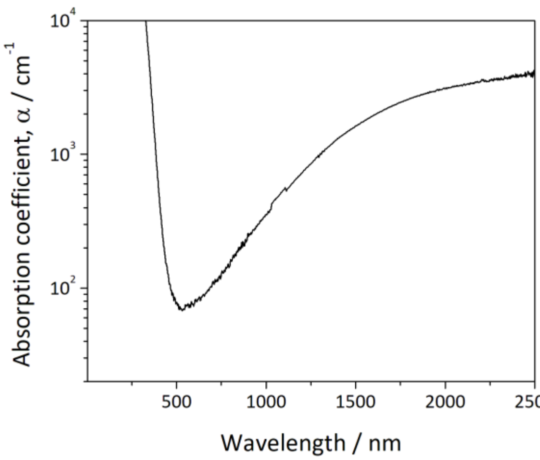

Figure 6. Optical absorption spectra, α, of GZO thin film as a function of wavelength.

Figure 7 shows the optical band gap (Eg) determined by the maximum of $d\alpha/dE$, where α and E are the absorption coefficient and photon energy. The method used to estimate the Eg of highly doped metal oxides followed the work by Sernelius and Hamberg et al. [26-27]. The figure showed the maximum of $d\alpha/dE$. The fitting of the maximum curve was estimated by the Voigt function model. The Voigt profile is a probability distribution based on the convolution of the Cauchy-Lorentz distribution and the Gaussian distribution. The optical band gap of the sample was approximately 3.82 eV (as shown in the figure as *xc*). This value is almost similar to the optical bandgap of the commercial ITO (~ 3.7 eV) commonly used for TCO.

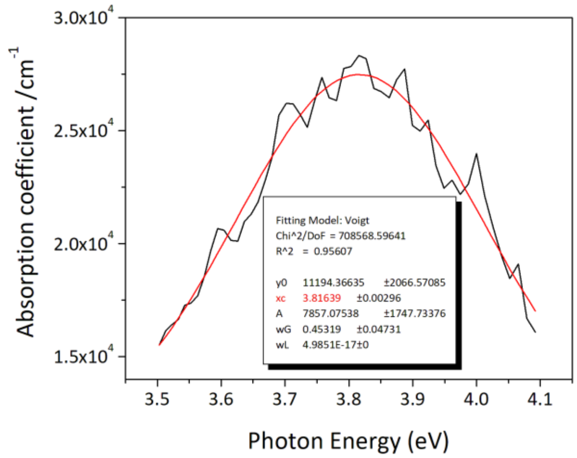

Figure 7. The fitting Voight model of GZO thin film from data of maximum of $d\alpha/dE$, where α and E are the absorption coefficient and photon energy, respectively.

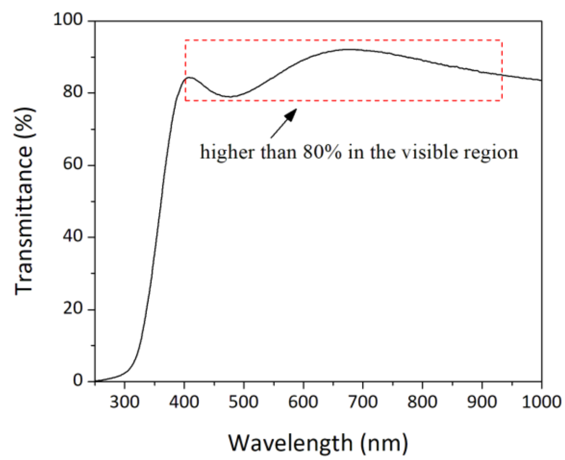

Figure 8. The transmittance of GZO thin film as a function of wavelength.

Figure 8 shows the transmittance of the film in the range of the visible region. The average transmittance in the range of 380-750 nm is approximately 86.04% (over 80%). The result showed that the sample was highly transparent and close to the properties of ITO [19]. This result was also comparable with previous reports (H. Cheng et al and N. Srinatha et al) [28, 29]. They reported on the case of GZO thin films on the ZnO buffer layer.

Conclusions

The electrical and optical properties of GZO thin film deposited by DC magnetron sputtering were investigated. Film properties at Ts of 200 °C showed similarity with the properties of commercial ITO. The ρ is about 1.38×10^{-3} Ω.cm (the order of ρ near to 10^{-4}). The resistivity of commercial ITO is about $1\text{-}3\times10^{-4}$ Ω.cm. The transmittance of film was higher than 80% in the visible region. The average of the transmittance in the range of 380-750 nm is about 86.04%. The optical band gap of this GZO thin film was about 3.82 eV (the ITO has a large optical band gap ~3.7 eV). The results suggest that this GZO thin film is promising for TCO application as an alternative of ITO.

Conflicts of interest

There are no conflicts to declare.

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