Effects of discharge power on the structural and optical properties of TGZO thin films prepared by RF magnetron sputtering technique*

GU Jin-hua (顾锦华)[1,2]**, **LU Zhou** (陆轴)[2], **ZHONG Zhi-you** (钟志有)[2,3], **LONG Lu** (龙路)[2], and **LONG Hao** (龙浩)[2]

1. Center of Experiment Teaching, South-Central University for Nationalities, Wuhan 430074, China

2. College of Electronic Information Engineering, South-Central University for Nationalities, Wuhan 430074, China

3. Hubei Key Laboratory of Intelligent Wireless Communications, South-Central University for Nationalities, Wuhan 430074, China

(Received 18 December 2015)

The transparent semiconductors of Ti and Ga-incorporated ZnO (TGZO) thin films were prepared by radio frequency (RF) magnetron sputtering onto glass substrates. The effects of discharge power on the physical properties of thin films are studied. Experimental results show that all nanocrystalline TGZO thin films possess preferential orientation along the (002) plane. The discharge power significantly affects the crystal structure and optical properties of thin films. When the discharge power is 200 W, the TGZO thin film has the optimal crystalline quality and optical properties, with the narrowest full width at half-maximum (*FWHM*) of 1.76×10^{-3} rad, the largest average grain size of 82.4 nm and the highest average transmittance of 84.3% in the visible range. The optical gaps of thin films are estimated by the Tauc's relation and observed to increase firstly and then decrease with the increase of the discharge power. In addition, the optical parameters, including refractive index, extinction coefficient, dielectric function and dissipation factor of the thin films, are determined by optical characterization methods. The dispersion behavior of the refractive index is also analyzed using the Sellmeier's dispersion model.

Document code: A **Article ID:** 1673-1905(2016)03-0188-4

DOI 10.1007/s11801-016-5265-5

Ga-doped ZnO (GZO) is a promising transparent semiconductor film material for applications as transparent electrodes in photovoltaic cells (PVCs)[1], random access memory (RAM)[2], superficial acoustic waves[3], touch screens[4] and gas sensitive devices. Besides high conductivity and optical transmittance in the visible region, the GZO thin films have a lot of advantages, such as non-toxicity, low cost, high abundance and high stability under hydrogen plasma, compared with Sn-doped In_3O_2 (ITO) thin films. For the preparation of GZO thin films, there are many deposition techniques currently in use, for example, direct-current (DC) magnetron sputtering, radio frequency (RF) magnetron sputtering[5-7], hydrothermal process[8], molecular beam epitaxy, reactive plasma deposition and pulsed laser ablation (PLA). Among all these methods, conventional RF magnetron sputtering is promising in preparing transparent semiconductor GZO thin films, due to the low cost of the source materials, the high growth rates and the simplicity of the growth process required.

In the present study, the transparent semiconductor thin films of Ti-doped GZO (TGZO) were deposited on glass substrates by RF magnetron sputtering technique at different discharge powers. The structural, optical and dielectric properties of the deposited films are studied in detail.

Commercial plane glasses (CSG Holding Co., Ltd.) were cut into 30 mm×30 mm plates and used as substrates in this experiment. Prior to their use, the glass substrates were successively washed in an ultrasonic bath with acetone, alcohol and deionized (DI) water, each for 12 min, and then dried in a high-purity nitrogen gas jet. The TGZO transparent semiconductor films were deposited on the previously cleaned glass substrates by RF magnetron sputtering system (KDJ-567) using a sintered ceramic target with a diameter of 50 mm. The following compositions were chosen: 97% (weight percentage, the same below) ZnO, 1.5% Ga_2O_3, 1.5% TiO_2. Raw materials were ZnO, Ga_2O_3 and TiO_2 powders (99.99% in purity). Before deposition, the chamber was evacuated to

* This work has been supported by the National Natural Science Foundation of China (No.11504436), the Natural Science Foundation of Hubei Province (No.2015CFB364), and the Fundamental Research Funds for the Central Universities (Nos.CZW14019 and CZW15045).

** E-mail: jinhwagu@163.com

an ultimate background pressure of 5.2×10^{-4} Pa using a turbo molecular pump. Then high-purity (99.99% in purity) argon gas was introduced into the chamber at a fixed flow rate of 20 mL/min, and the argon pressure was maintained at 0.5 Pa. Then 10 min pre-sputtering with the glass substrate covered by a closely mounted shutter was employed to clean contamination on the target surface, followed by true sputtering. During deposition, the substrate temperature was fixed at 600 K, and the distance between the target and the substrate was kept at 70 mm. In order to investigate the effects of discharge power on the properties of TGZO thin films, the discharge power was changed from 170 W to 260 W.

The X-ray diffraction (XRD) patterns of the deposited films were recorded with a Bruker advanced D8 diffractometer using standard Cu Kα radiation (λ=0.154 06 nm). The scan range is 10°—80° with 0.016 4° steps. The crystallite phase was evaluated with the data of Joint Committee on Powder Diffraction Standards (JCPDS). The optical transmission spectra were measured at room temperature (RT) in the wavelength range of 350—800 nm using a TU-1901 ultraviolet-visible (UV-Vis) spectrophotometer. Based on the measured transmittance spectra, the optical constants of the films can be obtained.

Fig.1 shows the XRD patterns of the TGZO thin films deposited at different discharge powers. Note that all the samples exhibit a dominant (002) peak with slight (004) peak in the displayed 2θ region, which indicates that the TGZO thin films have highly preferred orientation with their crystallographic *c*-axis perpendicular to the substrates, irrespective of discharge power. Neither metallic Ti or Ga characteristic peaks nor TiO_2 or Ga_2O_3 peaks are observed from the XRD patterns, which implies that the dopants do not destroy the ZnO structure and act as typical dopants. Corresponding to the discharge powers of 170 W, 200 W, 230 W and 260 W, the intensity ratios of (004) peak to (002) peak ($I_{(004)}/I_{(002)}$) and the intensities of (002) peak ($I_{(002)}$) for the samples can be found from the insets of Fig.1 to be 0.84%, 1.13×10^6 cycles per second, 0.81%, 1.43×10^6 cycles per second, 0.83%, 1.32×10^6 cycles per second, and 0.85%, 1.22×10^6 cycles per second, respectively. Clearly, the values of $I_{(004)}/I_{(002)}$ and $I_{(002)}$ are observed to rise initially and then fall with the increase of the discharge power. The TGZO thin film deposited at 200 W has the minimum $I_{(004)}/I_{(002)}$ and the maximum $I_{(002)}$. To assess the quality of the deposited films, the full-width at half-maximum (*FWHM*) of (002) peak and the average grain size (L_{av}) are used. The L_{av} is determined by the Scherrer formula[9,10]:

$$L_{av} = K\lambda/(\beta\cos\theta), \quad (1)$$

where λ is the wavelength of X-rays used, β is the *FWHM* in radian, θ is the Bragg's diffraction angle at peak position in degrees, and *K* is a constant that depends on crystallites shape (*K* is equal to 0.90 in this work). The values of β and L_{av} as a function of discharge power are presented in Fig.2(a) and (b), respectively. With increasing discharge power from 170 W to 200 W, β decreases while L_{av} increases, suggesting that the crystalline quality of the films becomes better. However, with further increasing discharge power from 200 W to 260 W, β increases while L_{av} decreases, indicating that the crystalline quality deteriorates. It is obvious that the TGZO thin film prepared at the discharge power of 200 W shows the best multicrystal structure. From Fig.2, the average grain size along the *c*-axis is found to range from 61.6 nm to 82.4 nm. The TGZO sample deposited at 200 W has the narrowest *FWHM* (1.76×10^{-3} rad) and the largest crystal grain (82.4 nm). The results indicate that the crystalline quality of TGZO thin films depends on the discharge power significantly.

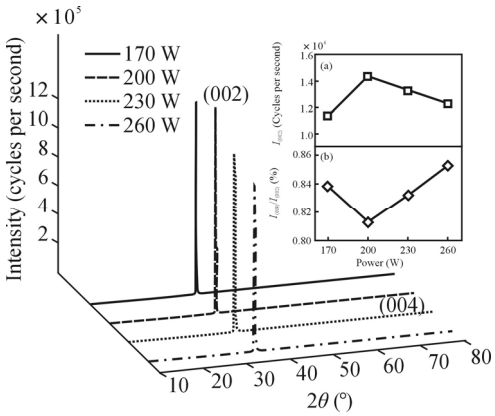

Fig.1 XRD patterns of all the TGZO samples with (a) the intensity of (002) peak and (b) the intensity ratio of (004) peak to (002) peak

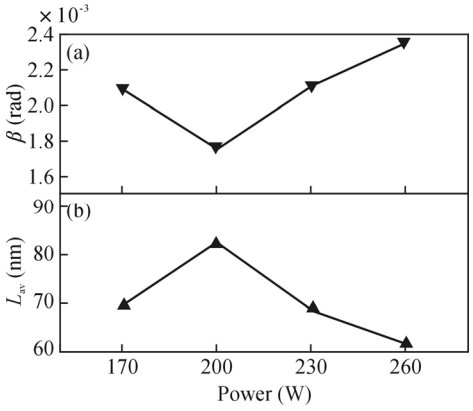

Fig.2 (a) β and (b) L_{av} of all the TGZO samples

Fig.3 presents the optical transmittances (*T*) of the TGZO thin films deposited on the glass substrates (film/substrate system) prepared at different discharge powers, using air as reference. The well oscillating transmittance curves can be observed for all the samples, indicating their low surface roughness and good homogeneity. The average optical transmittance in the visible range (T_{vis}) exceeds 82.8% for all the samples regardless

of the discharge power. The highest T_{vis} of 84.3% is obtained for the TGZO sample prepared at the discharge power of 200 W. Near the absorption edge of the transmission spectra, the absorption coefficient (α) is related to the optical gap (E_{opt}) following the power-law behavior of Tauc[11,12]:

$$(\alpha h\nu)^m = B(h\nu - E_{opt}), \quad (2)$$

where $h\nu$ is the photon energy, B is an energy-independent constant, and m is an index which can assume values of 1/3, 1/2, 2/3 and 2 depending on the nature of the electronic transitions responsible for the optical absorption (m=2 and 2/3 for direct allowed and forbidden transitions, respectively; m=1/2 and 1/3 for indirect allowed and forbidden transitions, respectively). The E_{opt} of the thin films can be estimated by plotting curves of $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the straight line portion of the curves to the energy axis, as shown in the inset of Fig.3. The obtained E_{opt} values of TGZO samples are in the range of 3.411—3.489 eV, larger than that of pure ZnO (3.270 eV). The widening of optical band gap may be attributed to Moss-Burstein shift[13]. Similar results have been reported previously by Tsay et al[14] and Aghdaee et al[15].

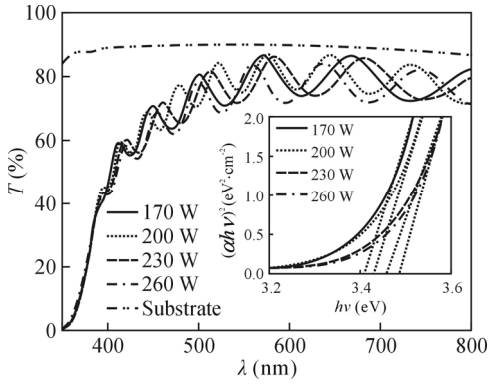

Fig.3 Transmittance curves of all the TGZO samples (The inset shows $(\alpha h\nu)^2$ versus $h\nu$.)

From the measured optical transmittance data, the refractive indices (n) and the extinction coefficients (k) of the deposited films are determined by the method of optical spectrum fitting. Fig.4 displays n and k of the thin films as a function of wavelength (λ). As can be seen, the k values of the samples are very small at long wavelengths, indicating that the thin films are highly transparent. In addition, the curves of k are fairly flat above 550 nm and rise rapidly at shorter wavelengths. Similar to the curves of k, the n values decrease linearly with increasing λ for the thin films, indicating the typical shape of the dispersion curve near an electronic interband transition. At λ=530 nm, corresponding to the discharge powers of 170 W, 200 W, 230 W and 260 W, n and k of the samples are 2.199, 1.959×10^{-3}, 2.143, 2.046×10^{-4}, 2.169, 2.661×10^{-3}, and 2.101, 4.123×10^{-3}, respectively, which are close to the previous results[16].

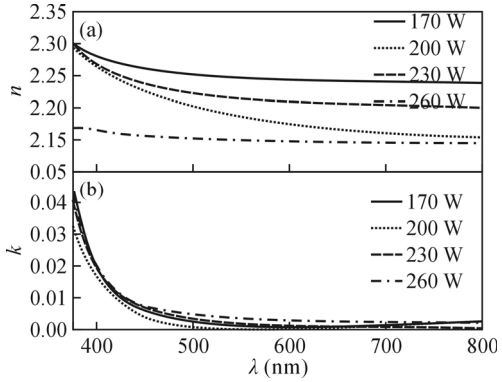

Fig.4 (a) Refractive indices n and (b) extinction coefficients k of all the TGZO samples

The n data of the films are analyzed by the Sellmeier's dispersion formula[17,18]:

$$n^2 - 1 = S_o\lambda_o^2 \Big/ \left(1 - \lambda_o^2/\lambda^2\right), \quad (3)$$

where S_o is the average oscillator strength, and λ_o is the average oscillator position. The curves of $(n^2-1)^{-1}$ versus λ^{-2} for all the samples are plotted in Fig.5, and the data are fitted into straight lines. The results indicate that the Sellmeier's dispersion model is applicable to the TGZO thin films in our work.

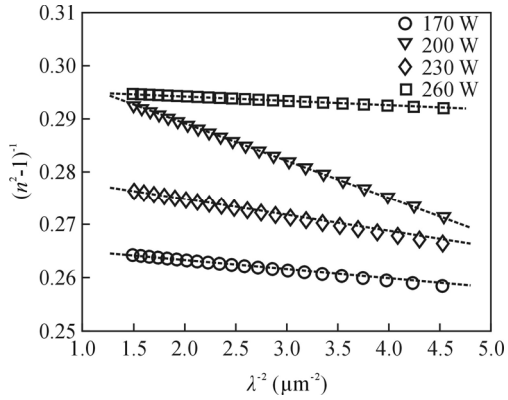

Fig.5 $(n^2-1)^{-1}$ versus λ^{-2} curves of all the TGZO samples

The complex dielectric constant (ε^*) and the dissipation factor ($\tan\delta$) of the deposited films are determined by the following relations[19]:

$$\varepsilon^* = \varepsilon_r - i\varepsilon_i, \quad \tan\delta = \varepsilon_i/\varepsilon_r, \quad (4)$$

where ε_r and ε_i are the real and imaginary parts of ε^*, respectively, and $\varepsilon_r=n^2-k^2$, $\varepsilon_i=2nk$. Fig.6 illustrates ε_r, ε_i and $\tan\delta$ of the deposited films as a function of λ. ε_r, ε_i and $\tan\delta$ are observed to decrease with the increment of λ, and ε_r is significantly higher than ε_i for all the samples. At λ=540 nm, for the samples deposited at 170 W, 200 W, 230 W and 260 W, the ε^* values are 4.841−i0.072 4, 4.574−i0.010 1, 4.695−i0.296 1 and 4.405−i0.809 2, and the corresponding $\tan\delta$ values are 0.014 9, 0.002 2, 0.063 1 and 0.183 7, respectively.

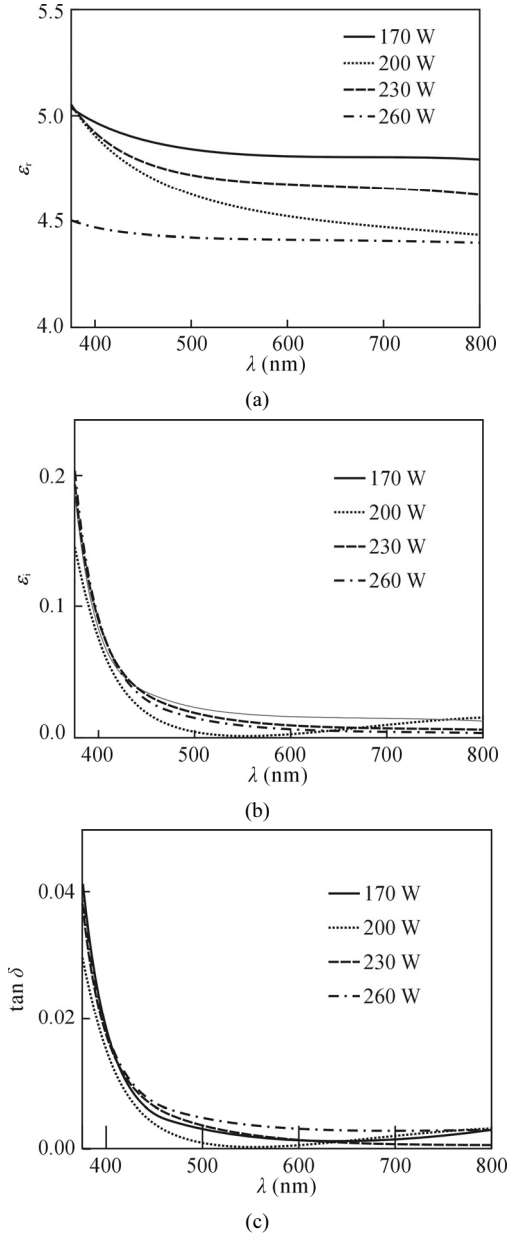

Fig.6 (a) ε_r, (b) ε_i and (c) tanδ of all the TGZO samples

In summary, the transparent TGZO semiconductor thin films were fabricated by RF magnetron sputtering method. The discharge power dependence of the structural, optical and dielectric properties of the samples is investigated by XRD and optical characterization methods. XRD patterns confirm that the deposited films have polycrystalline nature. The average grain sizes of the films are found to be in the range of 61.6—82.4 nm. The optical gaps of the films are determined and observed to be larger than that of undoped ZnO due to Moss-Burstein effect. The refractive index dispersion curves obey the Sellmeier's dispersion model. The results demonstrate that the crystal quality, optical and dielectric properties of the thin films are subjected to the discharge power. The TGZO thin film deposited at the discharge power of 200 W exhibits the optimal crystallinity and optical properties.

References

[1] Owen J, Son M S, Yoo K-H, Ahn B D and Lee S Y, Appl. Phys. Lett. **90**, 033512 (2007).

[2] Kinoshita K, Okutani T, Tanaka H, Hinoki T, Agura H, Yazawa K, Ohmi K and Kishida S, Solid-State Electron. **58**, 48 (2011).

[3] Wang Y, Tang W and Zhang L, J. Mater. Sci. Technol. **31**, 175 (2015).

[4] Tsay C Y, Fan K S and Lei C M, J. Alloy. Compd. **512**, 216 (2012).

[5] Kim S K, Kim S H, Kim S Y, Jeon J H, Gong T K, Choi D H, Son D I and Kim D, Ceram. Int. **40**, 6673 (2014).

[6] Zhou J and Zhong Z Y, Cryst. Res. Technol. **47**, 944 (2012).

[7] He X and Xiong L, J. South-Cent. Univ. Nationalities (Nat. Sci. Ed.) **30**, 70 (2011). (in Chinese)

[8] Ramalingam R J and Chung G S, Mater. Lett. **68**, 247 (2012).

[9] Huang T, Li C, Wu J, Zhou Z, Chi Q and Liu H, J. South-Cent. Univ. Nationalities (Nat. Sci. Ed.) **32**, 5 (2013). (in Chinese)

[10] Zi Xing-fa, Ye Qing, Liu Rui-ming and He Yong-tai, Journal of Optoelectronics·Laser **26**, 883 (2015). (in Chinese)

[11] Gu J H, Long L, Lu Z and Zhong Z Y, J. Mater. Sci.: Mater. Electron. **26**, 734 (2015).

[12] Li Cui-ping, Yang Bao-he, Qian Li-rong, Xu Sheng, Dai Wei, Li Ming-ji, Li Xiao-wei and Gao Cheng-yao, Optoelectron. Lett. **7**, 0431 (2011).

[13] Liu Jie-ming, Chen Xin-liang, Tian Cong-sheng, Liang Jun-hui, Zhang De-kun, Zhao Ying and Zhang Xiao-dan, Journal of Optoelectronics·Laser **25**, 2114 (2014). (in Chinese)

[14] Tsay C Y, Wu C W, Lei C M, Chen F S and Lin C K, Thin Solid Films **519**, 1516 (2010).

[15] Aghdaee S R, Soleimanian V and Tayebi B, Superlattice Microst. **51**, 149 (2012).

[16] Gu J, Long L, Lan C and Zhong Z, J. South-Cent. Univ. Nationalities (Nat. Sci. Ed.) **33**, 78 (2014). (in Chinese)

[17] You Z Z and Hua G J, J. Alloy. Compd. **530**, 11 (2012).

[18] Aksoy S, Caglar Y, Ilican S and Caglar M, J. Alloy. Compd. **512**, 171 (2012).

[19] Pankove J I, Optical Processes in Semiconductors, New York: Dover Publications, 1975.