# Radio Frequency Sputter Deposition of Ga and F Co-Doped ZnO Thin Films: Effects of Substrate Temperature

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**Abstract.** Doped zinc oxide (ZnO) thin films can be used as transparent conducting electrodes for various optoelectronic device such as flat panel displays andphotovoltaic cells. The present study investigates the effect of substrate temperature on Ga and F co-doped ZnO (GFZO) thin films.The GFZO thin films were deposited on glass substrates by RF magnetron sputtering in $CF_4$/Ar atmosphere with a ZnO:$Ga_2O_3$ (3 wt%) target. The structural, electrical, and optical properties of the samples have been observed and analyzed by x-ray diffraction, field emissionscanning electron microscopy, Hall measurements, and UV-visible spectrophotometry. All the GFZO thin films showed the highly c-axis-oriented phase and their average visible transmittances were over 91%. The electrical resistivity of the samples significantly decreased by an order of magnitude to $6.47\times10^{-4}\Omega$-cm as the substrate temperature raised from room temperature to 200 ℃. The maximum carrier concentration of $6.10\times10^{20}$ $cm^{-3}$ and Hall mobility of 15.4 $cm^2$/V-s were obtained at the optimum substrate temperature at 200 ℃. The optical bandgap of the GFZO films has been widened from 3.388 to 3.620 eV with the increase of the substrate temperature. The findings show the developed GFZO thin filmprepared at the higher substrate temperature haveeffectively improved optoelectronic properties andare potentially able to applications in variousoptoelectronic devices.

## 1. Introduction

Transparent conducting oxide (TCO) films have been extensively used in solar cells, light-emitting diodes, liquid crystal displays, and other optoelectronic devices. [1]ZnO is a wide band gap (~3.4 eV) semiconductor with high exciton binding energy (~60 meV) and the existence of shallow donor states, and thus can be a suitable TCO material.[1–2] Most of the studies on impurity-doped ZnO films were made using single cation or anion dopant such as aluminum, gallium, indium, and fluorine. [2–6] Recently, co-doped ZnO films have attracted much attention, such as Al–Ru, [7] Al–Co, [8] Al–Sn, [9] Al–Nv, [10] Al–Ga, [11] Al–F, [12] and In-F. [13] Ga–F co-doped ZnO thin films are an interesting alternative because the co-doping provides double dopants in which the cationic $Ga^{3+}$ substitutes $Zn^{2+}$, and anionic $F^-$ substitutes $O^{2-}$ in the ZnO film. In this study, GFZO thin films were deposited on glass substrates by RF magnetron sputtering in $CF_4$/Ar atmosphere with a ZnO: $Ga_2O_3$ (3 wt %) target. Effects of substrate temperature on the structural, optical, and electrical properties ofGFZO thin films were studied.

## 2. Experimental details

The ceramic target fabricated by Ultimate Materials Tech. Co. consists of 97 wt% ZnO (99.99%) powders and 3 wt% $Ga_2O_3$ (99.99%) powders. The GFZO thin films were prepared on glass substrates

(Corning 1737 glass) in an RF magnetron sputtering system (Syskey Tech. Co.) using the GZO target in $CF_4$/Ar atmosphere. The flow rates of $CF_4$ (99.999%) and Ar(99.999%) gas were 20 sccm and 0.04 sccm, respectively, and the flow rate ratio of $CF_4$/Ar was kept at 0.2%. The GFZO films with a thickness of about 330 nm were deposited with a fixed RF power of 100 W and the substrate temperatures of RT, 100 ℃, and 200 ℃. The base/working pressure was $6.67\times10^{-4}$ Pa/$6.67\times10^{-1}$ Pa ($5\times10^{-6}$Torr/$5\times10^{-3}$ Torr).The structure of the film was examined by X-ray diffraction (XRD) (PANalytical) analysis with Cu-Kα radiation (λ = 1.54056 Å, θ–2θ scan mode). The morphology of the films was observed using a field emission scanning electron microscope (FE-SEM) (JEOL, JSM-6700). The resistivity, Hall mobility, and carrier concentration were measured using the Van der Pauw method (Ecopia, HMS-300) at room temperature. The optical transmittance was measured by a UV/VIS/NIR spectrophotometer (Thermo Evolution 220) in the 300–1100 nm wavelength range.

## 3. Results and discussion

### *3.1. Structural properties*

Figure 1 exhibits θ–2θ XRD patterns of the GFZO films prepared at different substrate temperatures. All the GFZO films possessed a sharp (002) preferred orientation, regardless of substrate temperature. It is attributed to GFZO thin films having lowest surface energy at (002) crystal orientation and thus the continuous growing of the films along this orientation. Moreover, (002) peak intensity increased with the increasing substrate temperature, indicating that the film had better crystallinity at the higher substrate temperature. The 2θ angle of (002) peak slightly shifted from 34.48 ° to 34.50 °as the substrate temperature raised to 200 ℃, suggesting a small decrease of the lattice constant of the film. It is due to that cationic $Ga^{3+}$ substitutes $Zn^{2+}$, and anionic $F^-$ substitutes $O^{2-}$ in the film at the high substrate temperature. The full width at half maximum (FWHM)of(002)diffraction peaks gradually decreased with the increasing substrate temperature, revealing that the grain size of the films increased. The grain size is calculated from the FWHM of the (002) peak using the Scherrer's formula.[2] The largest grain size of 27.0 nm was reached at the substrate temperature of 200 ℃.

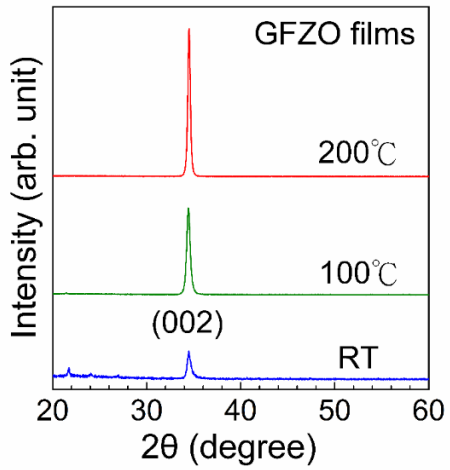


**Figure 1.** XRD patterns of the GFZO thin films prepared at different substrate temperatures

The field emission scanning electron microscopy (FESEM) images of GFZO thin films were taken to evaluate their surface morphology and film thickness. The film thickness estimated from cross-section images was about 330 nm for these samples. Figure2 shows plan-view micrographs of the GFZO thin films prepared at different substrate temperatures. The micrographs showed that the surface morphology changed from sphere-like shape to dense and rough surface as the substrate temperature increased to 200 ℃. It can be attributed to that high substrate temperature enhances grains growth in the GFZO thin films.

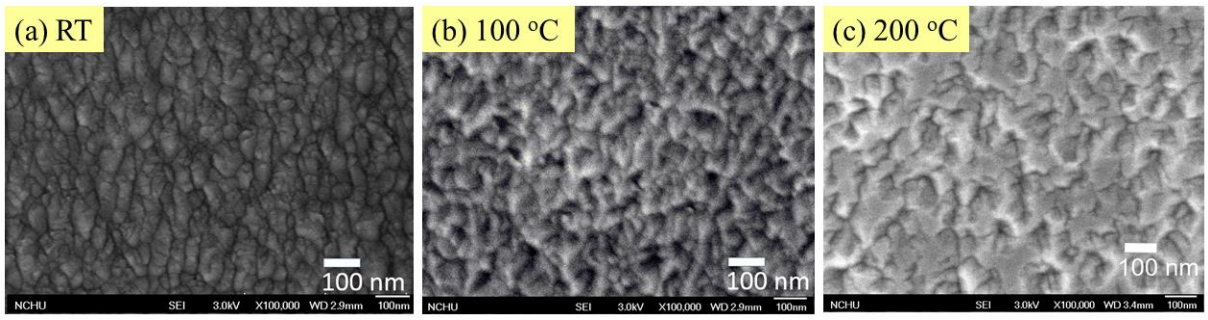


**Figure 2.** Plan-view micrographs of the GFZO thin films prepared at different substrate temperatures: (a) RT, (b) 100 ℃, and (c) 200 ℃

*3.2. Optical properties*

Figure 3 shows the optical transmittance spectra of the GFZO thin films deposited at different substrate temperatures. All samples had high transmittances in the visible region (400–800 nm) and a strong absorption in the UV region. The average transmittances of the as-deposited films slightly increased from 91.12% to 92.63% as the substrate temperature rose to 200 ℃. The increase of optical transmittance with increasing substrate temperature can be attributed to the weakening of scattering and absorption of light because of improved crystallinity. In addition, the absorption edge for the sample prepared at a high substrate temperature shifted toward the short wavelength side (as the inset shows), revealing a band gap widening effect.

The optical band gap energy ($E_g$) of the GFZO thin film can be estimated by dependence of optical absorption coefficient (α) on photon energy (*hv*).[14]Figure4shows the graph of $(\alpha hv)^2$ vs. photon energy (*hv*)for the prepared GFZO thin films. The calculated $E_g$ values increased from 3.388 to 3.620 eV after raising the substrate temperature to 200 ℃. The film deposited at a higher temperature exhibited a stronger band gap widening phenomenon. The broadening in the band gap was known as the Burstein–Moss effect [15], which will be discussed in the following section.

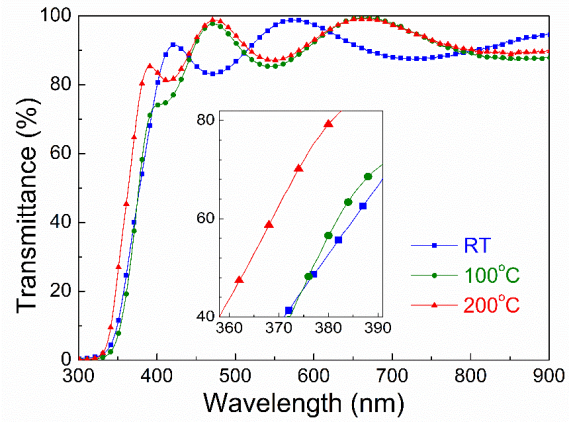


**Figure 3.** Optical transmittance spectra of the GFZO films at different substrate temperatures

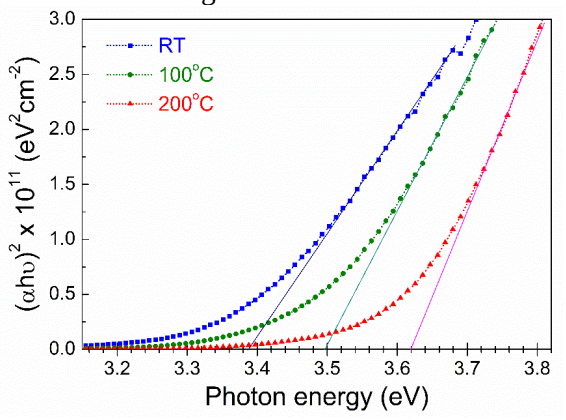


**Figure 4.** Plot of $(\alpha hv)^2$ vs. photon energy (hv) for the sputtered GFZO thin films

*3.3. Electrical properties*

Figure 5illustrates the dependence of the electrical properties of the as-deposited GFZO thin films with various substrate temperatures. The Hall mobility of the samples increased by 2.7 times to 15.4 $cm^2/V$-s, and the carrier concentration increased by 2.2 times to $6.10\times10^{20}$ $cm^{-3}$ as the substrate temperature raised from RT to 200 ℃. These improvements are due to more generated donors and better crystallinity at a higher substrate temperature. In depth the increase in carrier concentration may be due to $Ga^{3+}$ or $F^-$ in substitution for $Zn^{2+}$ and $O^{2-}$, and desorption of adsorbed negatively charged oxygen species, which increases shallow donors and free electrons in the films. [16–17] The increase in mobility may be attributed to increased grain size and decreased the number of. defects at grain

boundaries, which decreases the barrier potential and grain boundary scattering. [18] The resistivity is the combined result of the Hall mobility and the carrier concentration. Therefore, the resistivity of the film decreased from 6.89 (RT) to 0.647 mΩ-cm (200 ℃). That is, the film conductivity increased by 9.7 times (from 145 to 1545 S/cm) when the substrate temperature increased from RT to 200 ℃.

Thebroadening band gap with the increasing carrier concentration is known as the Burstein–Moss effect. [15]The following equation shows that the band gap widening ($\Delta E_g$) is related to carrier concentration ($n_e$) in a degenerate semiconductor:

$$\Delta E_g = \frac{h^2}{8m^*}\left(\frac{3}{\pi}\right)^{2/3} n_e^{2/3}, \quad (1)$$

where $h$ is Planck's constant and $m^*$ is the electron effective mass in conduction band. Eq. (1) indicates that the band gap increases with the increasing carrier concentration. Figure6 displays the variation of band gap as a function of carrier concentration. It can be observed that $\Delta E_g$ increases linearly with the carrier concentration. These results approximately agree with the eq. (1).

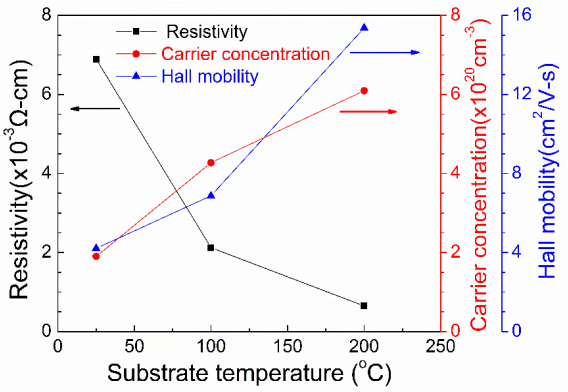


**Figure 5.** Electrical properties of the GFZO thin films with various substrate temperatures

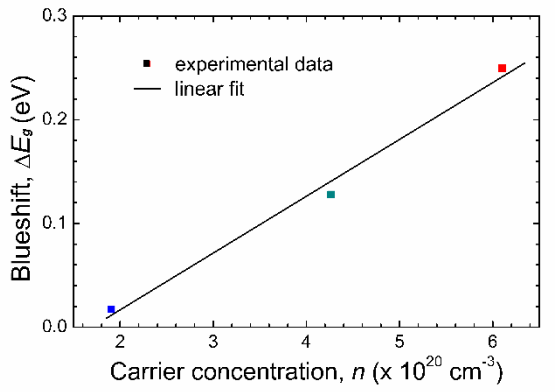


**Figure 6.** Blueshift as a function of carrier concentration for GFZO thin films

The substrate temperature effect on optoelectronic properties of the GFZO thin films can be examined more clearly by calculating the figure of merit (FOM). Haacke defined the quantitative measure for the FOM by $T^{10}/R_S$, where T is the average optical transmittance and $R_S$ is the sheet resistance of films.[19]Figure7 exhibits the FOM for the GFZO thin films with different substrate temperature. The optimal FOM value, $2.37\times10^{-2}$ $\Omega^{-1}$, was obtained for the 200 ℃-deposited sample, which is nearly twelve times larger than RT-deposited one. This result indicates that sputtering at high substrate temperatureis very effective in improving optoelectronic properties of the developed GFZO thin films.

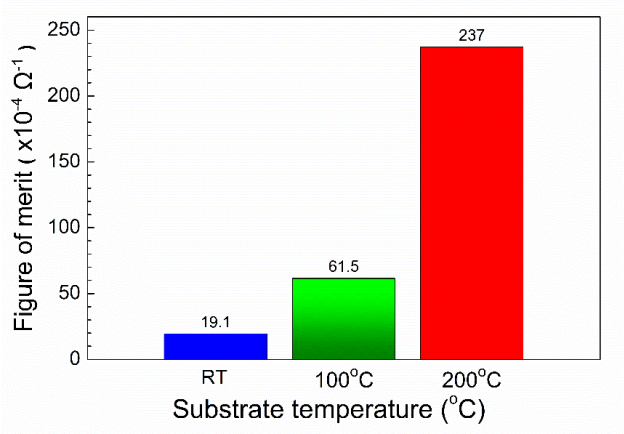


**Figure 7.** Figure of meritof GFZO thin films with different substrate temperatures

## 4. Conclusions

The transparent conducting GFZO thin films were deposited by RF magnetron sputtering using a ZnO: $Ga_2O_3$ (3 wt%) target in $CF_4$/Ar atmosphere. Influence of substrate temperature on physical properties of the GFZO films was studied. The high substrate temperature effectively enhanced the crystallinity and optoelectronic properties of the prepared GFZO thin films.The electrical conductivity, and figure of merit increased by 9.7 and 12 times, respectively, as the substrate temperature raised from RT to200 ℃. The largest grain size of 27.0 nm, the lowest resistivity of 0.647 mΩ-cm, and the highest average transmittance of 92.63% were achieved at the substrate temperature of200 ℃. These improvements on properties of GFZO films are owing to enhanced grain growth and substitution of $Ga^{3+}$ and $F^-$ for $Zn^{2+}$ and $O^{2-}$, respectively. Such a GFZO thin film can be suitable for various optoelectronic device applications because of their low resistivity combined with high transmittance in the visible range.

## 5. Acknowledgments

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## 6. References

[1] Morag A and Jelinek R 2016 J Colloid Interface Sci. 482 267 – 89.
[2] Wang F H and Chang C L 2016 Appl. Surf. Sci. 370 83 – 91.
[3] Kim B G, Kim J Y, Lee S J, Park J H, Lima D G and Park M G 2010 Appl. Surf. Sci. 257 1063.
[4] Wang F H, Kuo H H, Yang C F and Liu M C, 2014 Materials 7 948–62.
[5] Zebbar N, Kechouane M, Aida M S and Trari M 2016 Vacuum 605 57.
[6] Wang F H, Yang C F, Liou J C and Chen I C 2014 J. Nanomater. 857614.
[7] Houng B, His C S, Hou B Y and Fu L 2008 J. Alloys Compd. 456 64.
[8] Sheta S, Ahnc K S, Deutscha T, Wanga H, Nuggehallib R, Yana Y, Turnera J and Al-Jassim M 2010 J. Power Sources 195 5801.
[9] Pan Z, Tian X, Hu G, Xiao C, Wei Z, Wu S, Li Z and Deng J 2013 Mater. Sci. Semicond. Process. 16 587.
[10] Ismailn A and Abdullah M J 2013 Ceram. Int. 39 S441.
[11] Lee W, Shin S, Jung D R, Kim J, Nahm C, Moon T and Park B 2012 Curr. Appl. Phys. 12 628.
[12] Pan Z, Xiao Y, Tian X, Wu S, Chen C, Deng J, Xiao C, Hu G and Wei Z 2014 Mater. Sci. Semicond. Process. 17 162.
[13] Hadri A, Taibi M, Loghmarti M, Nassiri C, SlimaniTlemçani T and Mzerd A 2016 Thin Solid Films 601 7.
[14] Onuk Z, Rujisamphan N, Murray R, Bah M, Tomakin M and Shah S I 2017 Appl. Surf. Sci. 396 1458.

[15] Burstein E 1954 Phys. Rev. 93 632.
[16] Ohashi N, Wang Y G, Ishigaki T, Wada Y, Taguchi H, Sakaguchi I, Ohgaki T, Adachi Y and Haneda H 2007 J. Cryst. Growth 306 316.
[17] Wang F H, Chang H P, Tseng C C and Huang C C 2011 Surf. Coat. Technol. 205 5269 –77.
[18] Fang G, Lia D and Yao B L 2003 Vacuum 68 363.
[19] Haacke G, New figure of merit for transparent conductors, 1976 J. Appl. Phys. 47 4086 –89