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Growth of high-quality Ga–F codoped ZnO thin films by mid-frequency sputtering

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Abstract

Ga and F codoping was applied by mid-frequency magnetron sputtering on glass substrates at room temperature to prepare ZnO-based thin films with excellent opto-electrical properties. The effects of deposition parameters including sputtering power and pressure were investigated by varying them from 200 W to 2300 W and from 0.1 Pa to 1.0 Pa, respectively. The as-deposited films had a polycrystalline structure and a strong preferred *c*-axis orientation. The strain state of the films was also determined by XRD analysis, and a residual stress of −1.08 GPa was obtained at 1300 W. A resistivity of as low as $6.4 \times 10^{-4}\ \Omega$ cm was achieved for the film deposited at 1300 W and 0.1 Pa. The optical performance of Ga–F-codoped ZnO films significantly improved compared with Al-doped ZnO films, exhibiting a high transmittance of $> 90\%$. Hall effect measurements showed that Ga and F addition led to increased carrier concentration for ZnO-based thin films.

Keywords: ZnO film; Ga and F codoping; Carrier concentration; Optical performance; Electrical resistivity

1. Introduction

As attractive transparent conductive oxide materials, ZnO-based thin films have been investigated for several years [1]. Most studies have focused on Al-doped ZnO (AZO) films because of their good opto-electrical properties and low cost. However, the application of AZO films is limited especially when used as an anode in flat panel displays compared with traditional tin-doped In_2O_3. In recent years, Ti, Ag, or In have been used as dopants to enhance the opto-electric performances of ZnO-based films [2–6]. However, the resistivity and transparency of ZnO films are unsatisfactory. To improve the properties of transparent conductors, codoping strategies are used. For example, Jiang et al. [7] prepared Al–Ti codoped ZnO films by RF sputtering and obtained highly conductive films with a minimum resistivity of $7.96 \times 10^{-4}\ \Omega$ cm. The most notable result is obtained for Al–Co codoped ZnO films prepared by a sol–gel method, in which resistivity as low as $3.5 \times 10^{-4}\ \Omega$ cm and high mobility as high as 50 cm^2/V s are reported [8]. However, these codoping strategies are limited by low transparency or complicated preparation processes.

Apart from metal dopants, fluorine is considered as a proper anion dopant for ZnO-based films. Several studies have reported the preparation of high-performance Al–F codoped ZnO films [9,10]. Results demonstrate that cation–anion codoped ZnO films are promising TCO materials [11,12]. However, these codoped ZnO films show poor transparency when prepared by magnetron sputtering. Thus, other new and high-performance ZnO films including deposition technics are worthy of further research. The ionic size of Ga^{3+} is close to that of Zn^{2+}, and the bond length of Ga–O is similar to that of Zn–O. Using Ga is expected to produce less strain and local lattice distortion than Al; thus, better opto-electrical properties can be obtained. Sato et al. [13] prepared 200 nm-thick Ga-doped

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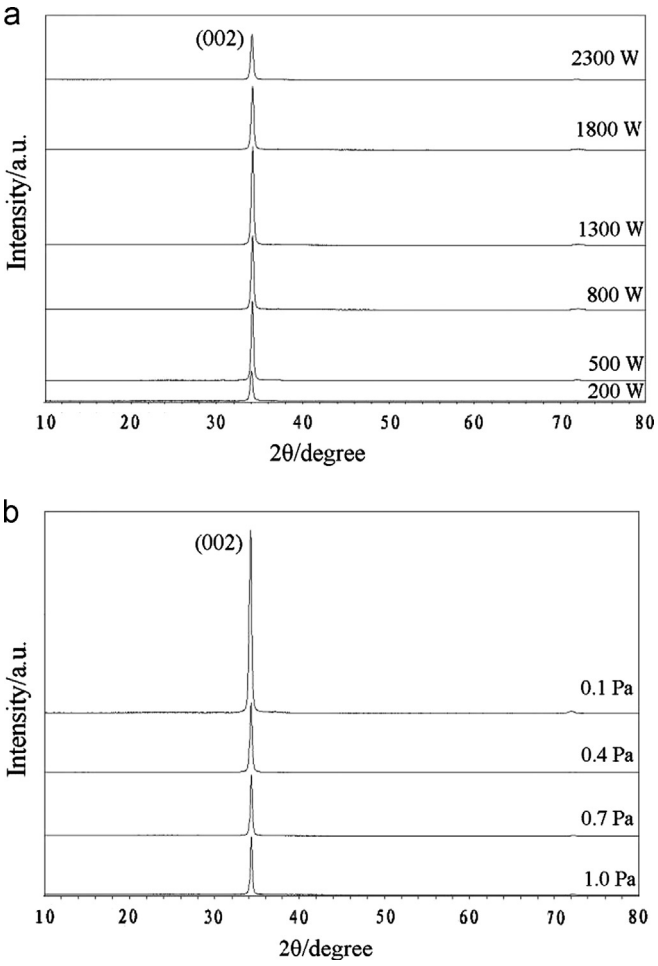


Fig. 1. XRD patterns of Ga–F codoped ZnO films deposited at different (a) sputtering powers and (b) pressures.

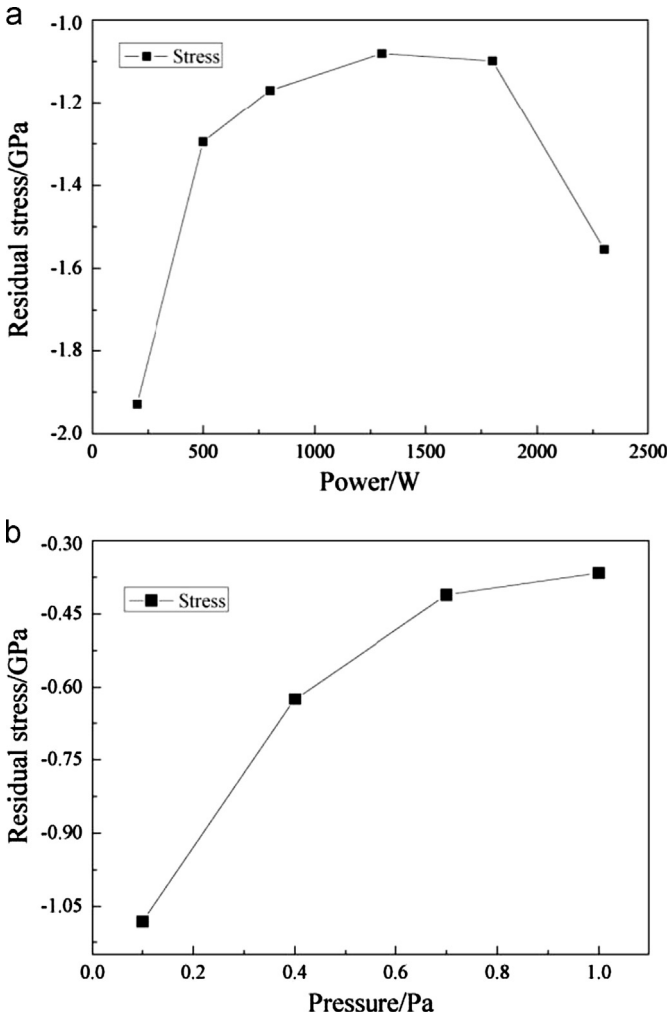


Fig. 2. Residual stress of Ga–F codoped ZnO films deposited at different (a) powers and (b) pressures.

ZnO films deposited by ion plating using DC arc discharge. They found that the films had an electrical resistivity of $3.5 \times 10^{-4}\ \Omega$ cm and an optical transmittance of 80% in the visible region. Therefore, Ga and F codoping is supposed to lead to higher performance than Al and F codoping in ZnO films.

This study aimed to investigate the growth of Ga–F codoped ZnO (GFZO) films and improve the opto-electrical properties of ZnO-based films. To the best of our knowledge, this work was the first to investigate the properties of GFZO films. The structural, optical, and electrical properties of GFZO films deposited by mid-frequency (MF) magnetron sputtering were optimized by varying the sputtering parameters, such as MF power and working pressure. The purpose was to achieve the best transparent and conducting films at room temperature. To determine the feasibility of preparing GFZO films, the properties of traditional AZO films prepared by the same parameters were considered.

2. Experimental

Transparent conductive GFZO films were deposited on glass substrates by MF magnetron sputtering (SHENGPU sputtering source consisting of two cathodes operated at 40 kHz). Glass substrates were ultrasonically cleaned sequentially with distilled water, acetone, and ethanol. ZnO containing 3 wt% Ga_2O_3 and 2 wt% ZnF_2 with dimensions of 300–75 mm was used as a sputtering target. Chamber vacuum was evacuated to a base pressure of 4×10^{-3} Pa. Films were grown within the pressure range of 0.1–1.0 Pa in Ar atmosphere, and the sputtering power was varied from 200 W to 2300 W. These ranges were determined from a previous study and the boundary condition of a sputtering equipment [14]. To achieve uniform film thickness, the deposition duration was changed from 5 min to 15 min based on sputtering power. Before deposition, the substrates were plasma etched for 5 min with an ion source at 300 W power and 800 V bias voltage. Comparison samples were prepared at 1300 W and 0.1 Pa using a target of ZnO with 3 wt% Al_2O_3.

The structure of the as-deposited films were examined by X-ray diffraction (XRD) using a Philips X'pert MPD diffractometer. Stress of the films was also estimated from XRD measurements. For a hexagonal lattice, the film stress (σ_{film}) can be estimated by the biaxial strain model $\sigma_{film} = -233\varepsilon$ [15]. The strain along the c-axis can be calculated using: $\varepsilon = (c_{film} - c_{bulk})/c_{bulk}$, where c_{bulk}

is the lattice constant of bulk ZnO and c_{film} is the lattice constant of ZnO films as measured by XRD. Surface morphology was assessed by field-emission scanning electron microscopy (SEM) on a Nova NanoSEM 430. Transmission electron microscopy (TEM) and electron diffraction analyses were performed using a PHILIPS CM200FEG TEM system with a field-emission gun and 160 kV acceleration voltages. Optical measurements were made using an SP-752PC spectrophotometer and photon wavelengths ranging from 300 nm to 800 nm. The resistivity, carrier concentration, and mobility were obtained by the four-probe van der Pauw method using a four-point probe instrument and Hall-effect measurement system (HL5500).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of GFZO films deposited at different powers. Only one diffraction peak at $2\theta = 34^\circ$ can be observed, and this peak corresponds to the (002) orientation of ZnO with a hexagonal wurtzite structure. The absence of additional peaks in the XRD patterns excluded the possibility of any impurity phase in the films. No significant change was observed in the location of the measured diffraction peaks with increased MF power. The (002) peak became more intense and sharper with increased sputtering power from 200 W to 1300 W. A small drop was observed with further increased sputtering power, delivering a maximum at 1300 W. This finding confirmed the collision effects of sputtered species on film growth as previously reported [14]. Fig. 1(b) shows the XRD results of GFZO films deposited at different sputtering pressures. The films exhibited a strong (002) peak, revealing that the *c*-axis was predominantly oriented perpendicular to the substrates. However, the (002) texture was linearly suppressed with increased sputtering pressure, indicating a crystal deterioration of films. These results have also been observed for Ga-doped ZnO [16]. Deterioration of crystal growth at high pressures was due to low energy particles that arrived on the substrate surface, leaving a lower dynamism for surface diffusion. The (002) texture improved with decreased sputtering pressure, confirming the enhancement of film properties under the working pressure.

Previous studies have indicated a close relationship between physical properties and stresses in ZnO thin films [17]. Thus, residual stress in films must be determined to adjust the film conductivity and optical properties. The effects of sputtering power on residual stress are shown in Fig. 2(a). With increased sputtering power from 200 W to 2300 W, a minimum residual stress of −1.08 GPa was obtained at 1300 W. This finding indicated higher crystal quality allowed films to release residual stress. In addition, the decreased residual stress was related to increased surface mobility of high-energy particles [18], and stress increased with decreased sputtering pressure, as shown Fig. 2(b). The bombarding energy decreased with increased pressure because of the shorter mean free path. Consequently, the strain in the films was released at high working pressures. The same effect has been observed in AZO films by other researchers [19].

Fig. 3 shows surface morphology of GFZO films deposited at pressures of 0.1, 0.4, 0.7, and 1.0 Pa. Notably, the sputtering pressure markedly influenced the surface structure. The film underwent inhomogeneous growth and became closely compact with a smooth surface at low pressures. With increased sputtering

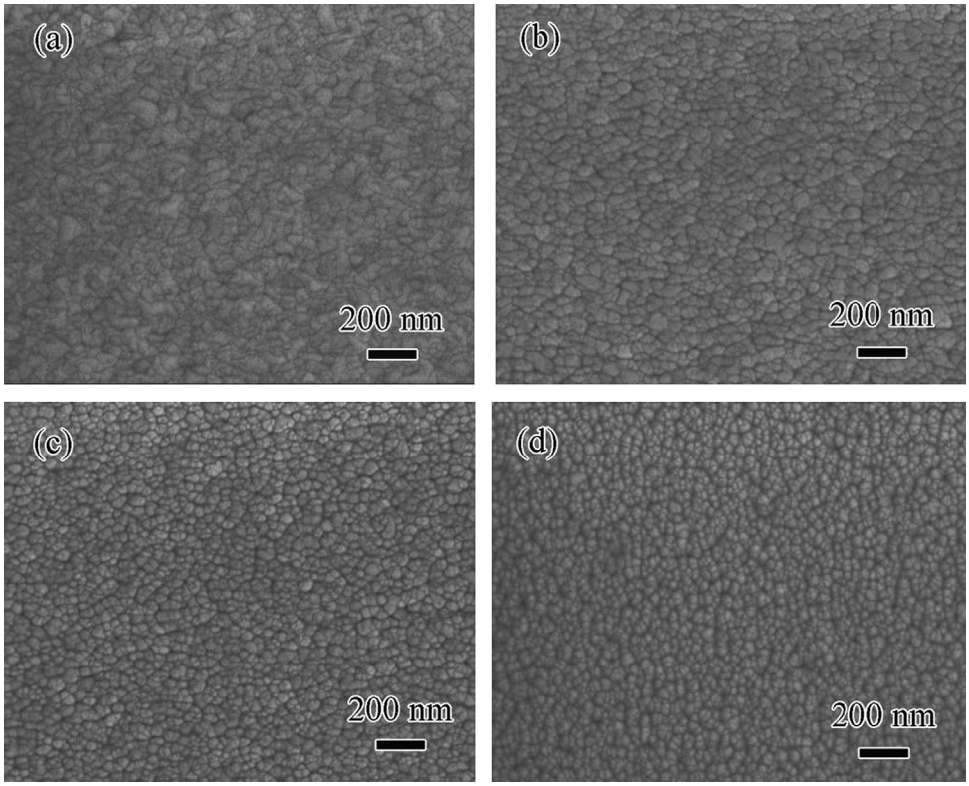
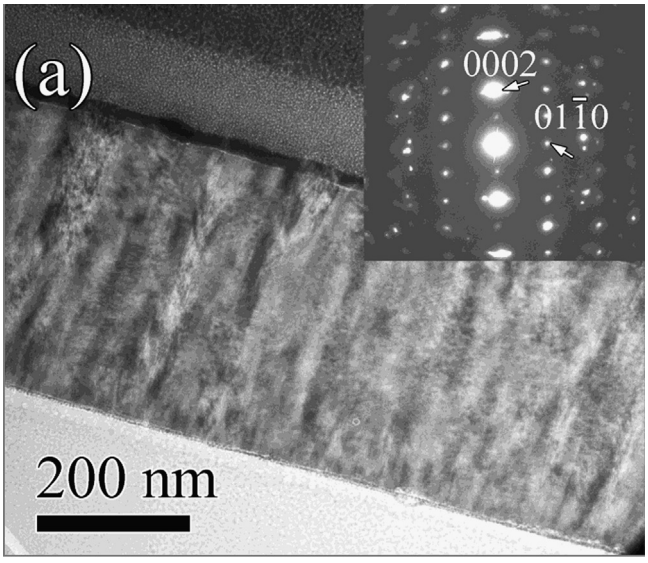


Fig. 3. SEM images of Ga–F codoped ZnO films deposited at different pressures: (a) 0.1, (b) 0.4, (c) 0.7, and (d) 1.0 Pa.

pressure over 0.7 Pa, the grains began to grow loosely and acquire clear grain boundaries, as shown in Fig. 3(c) and (d). Decreased grain size and a rugged surface were clearly observed. The morphology deterioration of GFZO films was due to the variation in energetic particles arriving at the substrates [20].

To gain a deep insight into structure and morphology of GFZO films, selected specimens were subjected to TEM and high-resolution TEM (HRTEM) analysis. Fig. 4(a) displays a low-magnification view of a GFZO film deposited at 0.1 Pa. The observed cross-section microstructure showed a dense and well-defined columnar morphology. Obviously, the film grew perpendicular to the substrate and the thickness was around 340 nm. The width of the columns was smaller near the substrate surface and grew larger on the top without obvious grain boundaries, indicating the presence of relatively small defects in the crystals. The SAED pattern comprised regular spots corresponding to the (0002) and (01-10) ZnO planes.



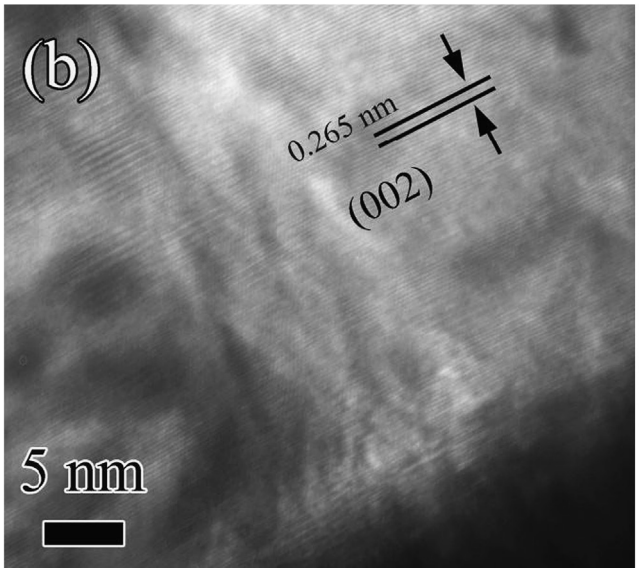


Fig. 4. TEM images of (a) the cross-section and associated diffraction patterns, and (b) HRTEM image of Ga–F codoped ZnO films deposited at 0.1 Pa.

Arched ZnO reflections were observed and considered to be structural strain, as similarly observed by Gabás [21]. Fig. 4(b) is an HRTEM image of the GFZO lattice near the substrates. Lattice fringes perpendicular to the substrate were clearly observed, and the measured interplanar spacing was 0.265 nm. The fringes corresponded to the (0002) plane, which was slightly larger than $d_{(002)}=0.260$ nm in the standard spectrum of ZnO. The increase in d was possibly induced by the compressive stress along the substrate.

Fig. 5 shows the transmission spectra of GFZO films prepared at different powers and pressures. The average transmittance of all films was $>90\%$ within the visible wavelength region of 400–800 nm regardless of power and pressure. The transparency was better than 82–85% for AZO, illustrating that Ga and F codoping can improve the optical properties of ZnO-based films [22]. The spectra showed a shift in the absorption edge to higher energies, and the largest band gap of 3.67 eV was obtained under the sputtering conditions of 1300 W and 0.1 Pa compared with the ZnO intrinsic band gap of 3.3 eV [23].

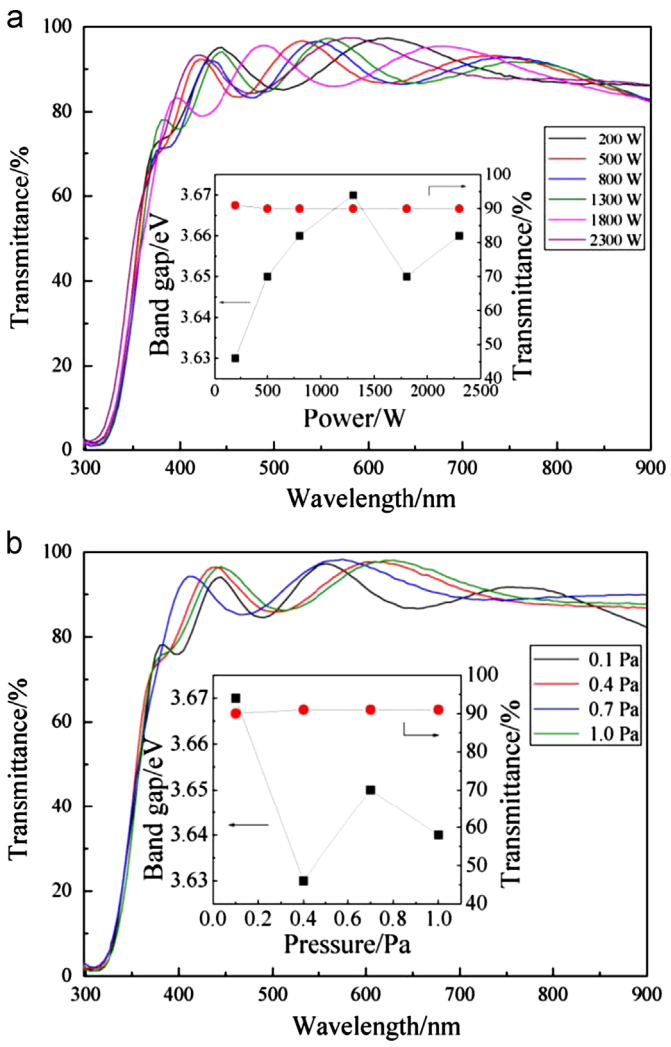


Fig. 5. Transmission spectra of Ga–F codoped ZnO films deposited at different (a) sputtering powers and (b) pressures. The inset shows the band gap and transmittance of the samples.

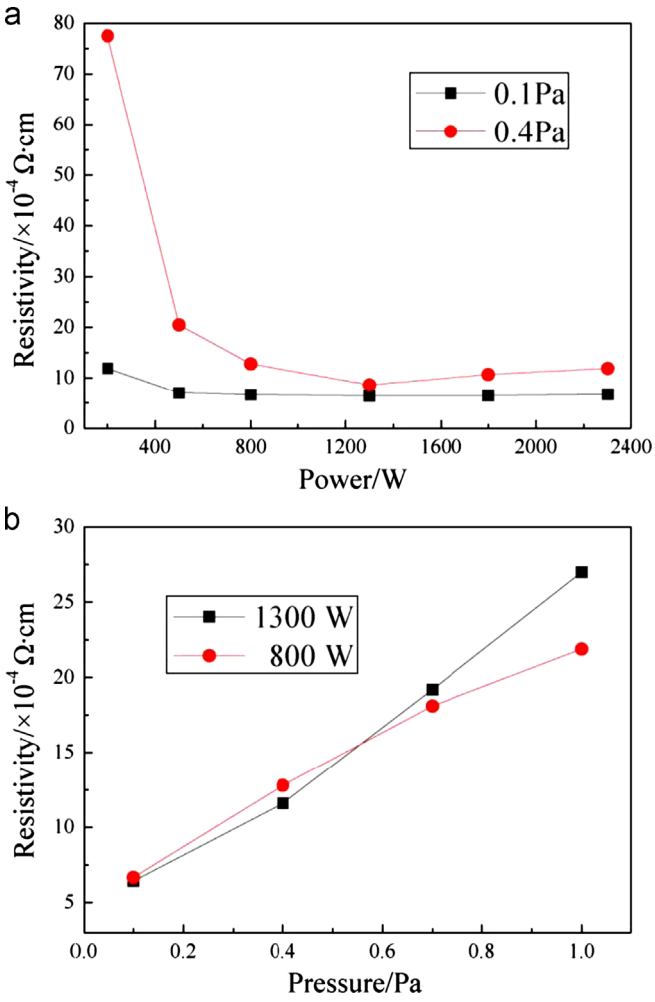


Fig. 6. Resistivity of Ga–F codoped ZnO films deposited under different conditions as a function of (a) sputtering power and (b) pressure.

The resistivity of the GFZO films as a function of power and pressure is given in Fig. 6. A poor resistivity value of 1.19×10^{-3} Ω cm was obtained at a low sputtering power of 200 W. With increased power to 2300 W, the order of resistivity magnitude decreased to 10^{-4} Ω cm, reaching the minimum of 6.4×10^{-4} Ω cm at 1300 W. Different from MF power, the resistivity of the GFZO films linearly increased as a function of working pressure. The largest resistivity of 2.7×10^{-3} Ω cm was achieved at 1.0 Pa. As expected, the decrease in working pressure led to the enhancement of structural properties, which improved the electrical properties as previously shown by XRD analysis.

Considering the possible influence of pressure on sputtering power, the variation in resistivity at 0.1 and 0.4 Pa as a function of sputtering power was determined, and the result is shown in Fig. 6(a). The resistivity values decreased by an order of magnitude with increased working pressure from 0.1 to 0.4 Pa. The possible influence of sputtering power as a function of pressure on the resistivity is given in Fig. 6(b). The resistivity values were similar to one another; a slight increase was observed at a high power of 1300 W, and the increase became more obvious at high sputtering pressures. Thus, the best preparation parameter of GFZO films was under the conditions of 1300 W and 0.1 Pa.

Table 1
Opto-electric properties of the GFZO and AZO films deposited on glass substrates.

Sample	Hall mobility (cm^2/V s)	Carrier concentration (cm^{-3})	Resistivity (Ω cm)	Transmittance (%)
AZO	16.2	4.8×10^{20}	8.4×10^{-4}	83
GFZO	13.4	6.8×10^{20}	6.7×10^{-4}	90

Based on the above analysis, we considered that the electrical properties were related to grain growth and residual stress [24,25]. Stress evolution generated more defects in the films, which led to poor electric performance. In addition, the present results also revealed that electrical properties also depended on crystal growth. Fig. 2(b) shows that the highest residual stress was obtained at a low working pressure of 0.1 Pa and was accompanied by the lowest resistivity. This finding can be explained by the crystal growth according to XRD and TEM results. A high-intensity diffraction peak was obtained at 0.1 Pa, indicating small structural disorders and crystal defects at the (002) orientation. Accordingly, the properties of GFZO films can be deduced to be governed by the combined effects of stress and crystal growth, in agreement with previous studies [26,27].

For comparison, AZO films were prepared under the same deposition conditions. Results suggested that Ga and F codoping benefited the optical and electrical performances of ZnO-based films compared with Al doping, as shown in Table 1. The transparency of GFZO and AZO film was 90% and 83%, respectively. The carrier concentration and hall mobility of the GFZO films deposited at 1300 W and 0.1 Pa were 6.8×10^{20} cm^{-3} and 13.6 cm^2/V s, respectively. For comparison, AZO films were prepared at same deposition parameters but a lower carrier concentration of 4.5×10^{20} cm^{-3} was obtained. A similar mobility of 16.2 cm^2/V s was observed. These results indicated that more free electrons can be provided by Ga and F codoping. A high carrier concentration also helped to improve the electric resistivity and transparency because more free electrons existed in the conduction band. Simultaneously, the presence of cation and anion dopants prevented the sudden suppression of electron mobility. Further investigation including post-annealing treatment may be necessary to improve the electrical properties of GFZO films. Initial results showed a promising tendency toward increased conductivity.

4. Conclusion

ZnO films codoped with Ga and F were successfully grown on glass substrates by MF sputtering, and the effects of sputtering power and pressure on the structural, morphological, and optical properties of these films were investigated. Results showed that Ga and F codoping improved the electrical properties of ZnO-based films, and the best deposition parameter was set as 1300 W and 0.1 Pa. In the visible region, $>90\%$ transparency of GFZO films was achieved regardless

of sputtering conditions. Compared with AZO films, a high carrier concentration of $6.8 \times 10^{20}\,cm^{-3}$ was obtained and considered to be an important reason for the improvement of opto-eletric properties by Ga and F codoping.

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