STUDY ON FLUORINATION AND HYDROGENATION IN TRANSPARENT CONDUCTING ZINC OXIDE THIN FILMS[#]

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Abstract. Fluorination and hydrogenation are known as two methods for enhancing crystalline structural and electrical properties of ZnO material. The ZnO thin films normally require a low resistivity and a high transmittance for using as high-performance transparent electrodes in optoelectronic applications. In this study, we report successful preparation of fluorinated and hydrogenated ZnO thin films (FZO and HFZO) by using d.c. magnetron sputtering technique. The hydrogenation was carried out by depositing the films in hydrogen plasma atmosphere, while a highly-sintered body of ZnO and ZnF_2 compound was employed as a sputtering target for the fluorination. The results showed that the strong improvements in carrier concentration, mobility and resistivity of the FZO and HFZO films as compared to the pure ZnO films. The carrier concentration increased to 2×10^{20} cm^{-3} which is mainly due to the hydrogenation. The effect combination of the fluorination and the hydrogenation was responsible for enhancing the mobility up to 43 cm^2/Vs. These results gave rise to two-order reduction in resistivity, from 0.06 Ωcm (ZnO) to 7.5×10^{-4} Ωcm (HFZO), which could be a good choice for thin-film electrode application. In addition, the crystalline structure and optical transmission of the films are also discussed.

Keywords: transparent conducting oxide, ZnO thin films, fluorination, hydrogenation, magnetron sputtering.

Classification numbers: 2.1.3, 2.5.2, 2.5.3.

1. INTRODUCTION

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Currently, transparent conducting oxides (TCOs) play an important role in optoelectronic devices, especially, transparent electrodes in solar cells, flat panel displays, etc. [1]. To be alternative for the high-cost ITO, known as one of the best TCOs, other oxides such as CdO, SnO_2 and ZnO have been considered as promising candidates. Among them, ZnO becomes prominent semiconductor due to its safety, rich abundance and potential optoelectronic properties [2]. However, the most disadvantage of the ZnO thin films is high electrical resistivity, which limits ZnO-based applications. Doping foreign elements into ZnO lattice is a simple solution to reduce the resistivity. The effect of dopants can be classified into two groups, *i.e.* increasing carrier concentration and enhancing mobility. The latter is more effective than the former, because of decreasing simultaneously the resistivity and free-carrier absorption in the near IR region [3].

Fluorination is known as an n-type dopant in the ZnO structure when it substitutes O^{2-} sites. Owing to the similar ionic radii of F^- (1.36 Å) and O^{2-} (1.40 Å), the O^{2-} substitution of F^- causes less lattice distortion, which contributes to increase the mobility [4]. There have been some reports which suggest the possibility of fluorination in reducing resistivity and improving mobility interval of $10 - 30$ cm^2/Vs [5–7]. Also, hydrogenation is indicated as another way to enhance strongly mobility. Thanks to passivation ability of hydrogen on vacancy-related defects, the mobility of ZnO-based thin films can increase more than 30 cm^2/Vs, but resistivity is still high [8–10].

From these remarks, the combination of fluorination and hydrogenation is expected to increase carrier concentration to a medium degree, especially, enhance mobility more than 40 cm^2/Vs for low-resistivity and high-transmittance ZnO thin films. In this study, the fluorinated and hydrogenated ZnO (HFZO) thin films were sputtered from a $ZnO+ZnF_2$ compound target in the H_2+Ar mixture gas. The comparisons in crystalline structure, electrical and optical properties of the ZnO, FZO and HFZO films are discussed.

2. MATERIALS AND METHODS

The 3 inch-FZO sputtering target was produced from high-temperature annealed compound of ZnF_2 powder (99.999 %, Alfa Aesar) and ZnO (99.99 %, Merck) with F atomic ratio of 0.25 %. After ball-milling process, the powders mixture was pressed by using a hydraulic compressor, and then was sintered at high temperature (1400 ^oC) in air. The FZO thin films were deposited from the target and were hydrogenated by adding H_2 gas into sputtering atmosphere with partial pressure ratio $H_2/(H_2+Ar)$ = 1.7 %. An Univex-450 sputtering system (Leybold, Germany) with a DC-source gun was used to deposit the films. The thickness of the ZnO, FZO and HFZO films were maintained at 600 nm. The substrate temperature, sputtering power, base and working pressures were fixed at 200 ^oC, 60 W, 6×10^{-6} torr and 3.5 mtorr, respectively. Every kind of the films was fabricated at least three times to verify accuracy and repetition of experimental results.

The crystalline structure of the films was analyzed by using an X-ray diffraction system (Bruker D8 Advanced, US) with Cu Kα source (λ = 0.154 nm). The carrier concentration, mobility and resistivity were determined from Hall measurement (Ecopia HMS-3000, Korea). The optical transmission of the films was recorded by a UV-Vis spectrophotometer (Jasco V530, Japan).

3. RESULTS AND DISCUSSION

Figure 1 shows the variations of carrier concentration, mobility, resistivity and sheet resistance of the ZnO, FZO and HFZO thin films. It is seen that the carrier concentration of the films increased as doping, especially co-doping fluorine and hydrogen. It is explained in terms of donor formation from O^{2-} substitution of F^- [11] and from interstitial H^+ and substituted H^+ at V_O sites [12, 13]. While the carrier concentration increases fivefold from 0.4×10^{20} cm^{-3} (ZnO) to 2×10^{20} cm^{-3} (HFZO), the mobility enhances fivefold from 2.2 cm^2/Vs (ZnO) to 10.1 cm^2/Vs (FZO), especially by 20 times to 43 cm^2/Vs (HFZO). As a result, the resistivity reduces dramatically from 5.8×10^{-2} Ωcm (ZnO) to 1.6×10^{-2} Ωcm (FZO) and to 7.5×10^{-4} Ωcm (HFZO). It corresponds to sheet resistance of ~990, ~250 and 12.3 Ω/sq. for the ZnO, FZO and HFZO films. Consequently, the results suggest that the increased mobility contributes mainly to the reduced resistivity of the films.
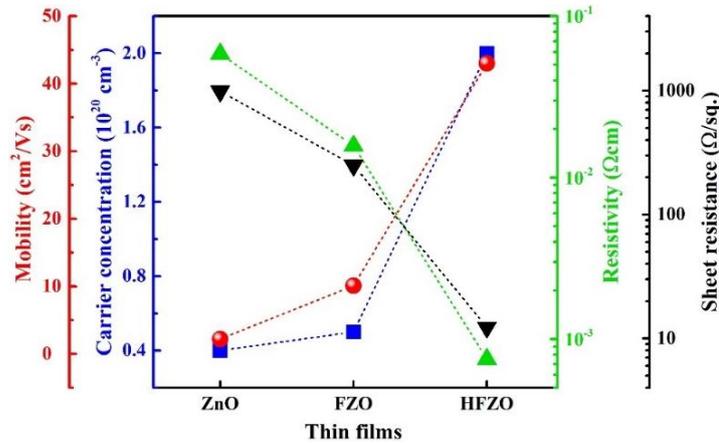

Figure 1. Electrical parameters of the ZnO, FZO and HFZO thin films.

To confirm the presence and effect of the dopants on the mobility of the films, the crystalline structure of the ZnO, FZO and HFZO films was investigated as shown in Figure 2.
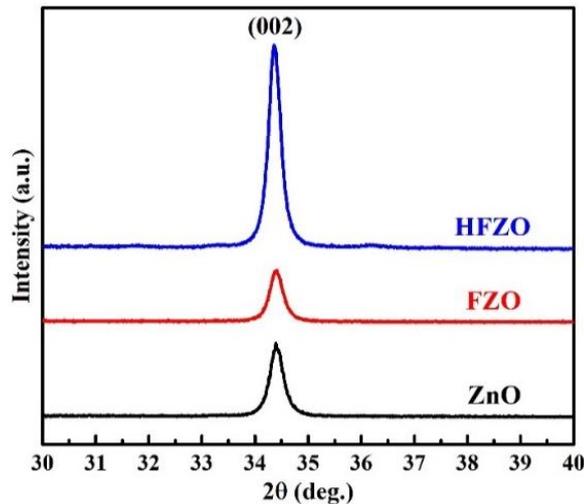

Figure 2. XRD patterns of the ZnO, FZO and HFZO thin films.

Table 1. Crystallographic information of the ZnO, FZO and HFZO thin films.

Thin films	2θ (deg.)	FWHM (deg.)	D (nm)	MFP (nm)
ZnO	34.39	0.2922	28.4	0.2
FZO	34.42	0.2970	28.0	1.0
HFZO	34.37	0.2721	30.5	5.1

There is only one peak in all XRD patterns of the films, which is associated with the c-oriented (002) plane of the hexagonal ZnO structure. The XRD intensities of the ZnO and FZO films are similar, while the strongest intensity is observed for the HFZO films. It could suggest much higher number of crystals in the HFZO thin films. To estimate fully crystallinity of the films, however, it is necessary to consider value of full-width half maximum (FWHM) of the (002) peak, as listed in Table 1.

The combination of the FWHM and 2θ values allowed to calculate mean crystal size (D) which was according to the Scherrer formula as given by $D = 0.9\lambda/(FWHM \cos\theta)$, where $\lambda = 0.154$ nm is the X-ray wavelength. It is seen that the highest value of mean crystal size is obtained for the HFZO films, which is in agreement with the highest XRD intensity. Nevertheless, this variation of the mean crystal size is insignificant, with only a very small deviation of 2 nm. It indicates that the crystallinity is mainly attributed to the number of crystals in the films. Therefore, the highest crystallinity was obtained for the HFZO films. In aim to understand effect degree of the crystallinity on the mobility of the films, mean free path (MFP) of electrons in the films was evaluated by [3]:

$$MFP = \frac{h}{2\pi e}\left(3\pi^2 n\right)^{1/3}\mu$$

From the MFP results in Table 1, it could be seen that the MFP values are very much smaller than the corresponding mean crystal sizes of the films. Consequently, the mobility depends on intra-crystalline quality, which the electronic scattering occurred mainly inside crystalline grains, instead of at the grain boundaries. It shows that the passivation of hydrogen and fluorine on dangling bonds, vacancy-related defects could enhance the mobility of the films, which is also suitable with the references [11, 14, 15]. Considering the 2θ value, the (002) peak position of the FZO films tends to shift towards larger angle (34.42°) as compared to that of the ZnO films (34.39°). It is associated to the decrease of interplanar spacing (d_{002}), according to the Bragg's law [16]. The O^{2-} (1.40 Å) substitution effect of the smaller ionic F^- (1.36 Å) could be recognized. After doping hydrogen, however, the (002) peak position of the HFZO films tends to shift towards smaller angle (34.37°), which corresponds to the expansion of interplanar spacing. The reason could be related to the interstital H at Zn–O bonds [15, 17].

Another verification of the impact of fluorination and hydrogenation on the grain size of the films could be observed through FESEM images, as shown in Figure 3. The surface morphology of the films is not uniform, with grain size interval of 50 – 300 nm. The arrangement of crystalline grains is close-packed structure. Furthermore, the morphology of the ZnO, FZO and HFZO films changes insignificantly, which is in agreement with the above calculation of average crystal size. Consequently, the effects of hydrogenation and fluorination on the crystalline structure of the ZnO thin films are verified. The results also indicated that the enhanced mobility of the films could be attributed to the intra-crystalline quality which is improved by the incorporation of hydrogen and fluorine into the ZnO lattice structure.
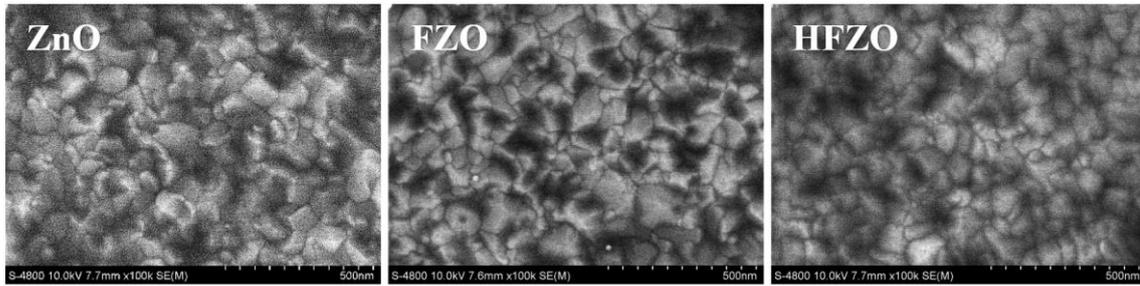
Figure 3. XRD patterns of the ZnO, FZO and HFZO thin films.

Figure 4 displays the optical transmission spectra of the ZnO, FZO and HFZO thin films in the wavelength region from 300 to 1100 nm. All the films have higher average transmittance than 83 % in the broad spectrum. The spectra of the FZO and HFZO films show clear interference fringes and sharp absorption edge, which indicates the good crystallinity, as mentioned in the XRD analyses. The absorption edge of the HFZO films has the largest blue-shift, followed by the FZO films, as compared to the ZnO films. It is in accordance with the increase of carrier concentration of the films due to the Burstein-Moss effect [18].
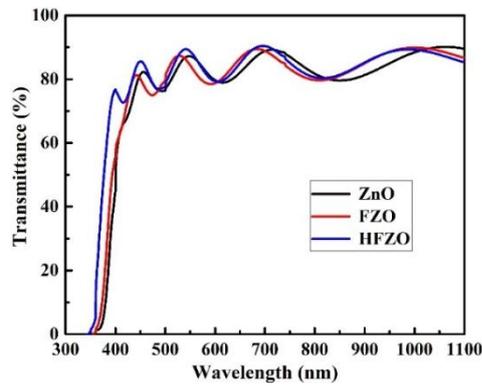

Figure 4. Optical transmission spectra of the ZnO, FZO and HFZO thin films.
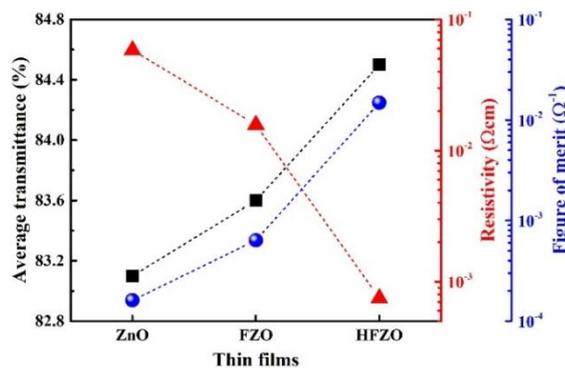

Figure 5. Relationship between resistivity, average transmittance and figure of merit of the films.

Normally, the increases of electrical conductivity and average transmittance have opposite trends, which depend strongly on the carrier conentration. In this work, the reduced resistivity of

the films is mainly due to the enhanced mobility. Therefore, to estimate optoelectronic performance of the films, the figure of merit (FOM) as given by FOM = $T^{10}/R_S = T^{10}t/\rho$, where T is the average transmittance in range of 400–1100 nm, t is the thickness of the films (600 nm), R_S and ρ are the sheet resistance and resistivity, respectively [19]. The variation in the FOM value of the ZnO, FZO and HFZO thin films was depicted in Figure 5.

Figure 5 shows evolutions of the average transmittance, resistivity and FOM values of the films. The highest FOM value is observed for the HFZO films (0.015 Ω^{-1}), followed by the FZO (6.4×10^{-4} Ω^{-1}) and ZnO (1.6×10^{-4} Ω^{-1}) films. From the above discussions, it is a result of (i) the reduction of resistivity due to the enhanced mobility, and (ii) the increase of average transmittance due to the improved intra-crystalline quality. As compared to the literature, our result of FOM value was also better than, for example, 0.0125 Ω^{-1} [3], 0.01 Ω^{-1} [12], 0.005 Ω^{-1} [20], etc. In the next study, we will adjust the fabrication conditions to optimize the FOM value for the good-performance HFZO thin films.

4. CONCLUSIONS

In this work, we report the successful deposition of fluorinated and hydrogenated ZnO thin films by using d.c. magnetron sputtering technique. The HFZO achieved the high mobility of 43 cm^2/Vs, carrier concentration of 2×10^{20} cm^{-3} and low resistivity of 7.5×10^{-4} Ωcm. From the XRD analyses, the increased mobility is attributed to the improvement in intra-crystalline quality of the HFZO films. Thanks to the highest average transmittance and the lowest resistivity, the HFZO films obtained the highest figure of merit, as compared to the FZO and ZnO films. Consequently, the positive effect of fluorination and hydrogenation on improving the performance of the ZnO thin films was recognized. It opens a tendency for high-mobility and good-performance TCO-ZnO thin films.

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