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Formation of F-doped ZnO transparent conductive films by sputtering of ZnF_2

Yu-Zen Tsai *, Na-Fu Wang, Chun-Lung Tsai

Department of Electronic Engineering, Cheng Shiu University, Kaohsiung 83347, Taiwan, ROC

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ABSTRACT

Fluorine-doped ZnO transparent conductive thin films were successfully deposited on glass substrate by radio frequency magnetron sputtering of ZnF_2. The effects of rapid thermal annealing in vacuum on the optical and electrical properties of fluorine-doped ZnO thin films have been investigated. X-ray diffraction spectra indicate that no fluorine compounds, such as ZnF_2, except ZnO were observed. The specimen annealed at 500 °C has the lowest resistivity of 6.65×10^{-4} Ω cm, the highest carrier concentration of 1.95×10^{21} cm^{-3}, and the highest energy band gap of 3.46 eV. The average transmittance in the visible region of the F-doped ZnO thin films as-deposited and annealed is over 90%.

1. Introduction

Transparent conducting oxide thin films have been widely applied as transparent electrodes for light-emitting diodes, flat-panel displays and solar cells [1]. In most cases, indium tin oxide (ITO) thin films deposited by direct current magnetron sputtering are in practical use. In recent years, zinc oxide (ZnO) has attracted more attention because of its numerous advantages such as low material cost, non-toxicity, and the stability under the hydrogen plasma compared to ITO [2]. Most of the studies on the properties and preparation of doped ZnO thin films were made using trivalent cation dopants such as Al, Ga, and In [3–5]. Fluorine, the radius of which is similar to that of oxygen, may be an adequate anion doping candidate due to lower lattice distortion compared to Al, Ga or In, but comparatively few studies on F-doped ZnO can be found in the literature.

F-doped ZnO thin films have been deposited by many methods such as spray pyrolysis [6,7], chemical vapor deposition [8], vacuum arc plasma evaporation [9], and sputtering [10]. Most of the studies on F-doped ZnO thin films were done by using spray pyrolysis, but the electrical properties of the films were far from satisfactory [6]. On the contrary, magnetron sputtering is a useful method for the formation of high quality thin films, offering the advantages of low growth temperature, high deposition rate, and large area preparation in different growth ambients [11]. The difficulty of preparing F-doped ZnO thin films by magnetron sputtering is also well known [9]. Lately, ZnO thin films doped with Al and F were deposited by radio frequency (RF) magnetron co-sputtering of ZnO target containing Al_2O_3 and ZnO target containing ZnF_2 [10]. To our best knowledge, there is no report on F-doped ZnO thin films prepared by magnetron sputtering of ZnF_2 target in the literature. It is more advantageous in process control compared with co-sputtering.

In this study, F-doped ZnO thin films were grown on glass substrate by RF magnetron sputtering of ZnF_2 target and further annealed. The effects of rapid thermal annealing on the structural, electric, and optical properties of F-doped ZnO thin films were investigated.

2. Experimental

F-doped ZnO thin films were deposited on glass substrate by reactive RF magnetron sputtering of a ZnF_2 (purity of 99.99%) ceramic target. Prior to deposition, a vacuum chamber was pumped down to base pressure of 0.25 mPa and the target was pre-sputtered for about 10 min. The RF power was fixed at 90 W and the substrate temperature was kept at 150 °C. High purity (99.999%) Ar and O_2 were introduced into the chamber with total pressure maintained at 0.67 Pa. The thickness of the deposited thin films was approximately 200 nm. After deposition, the samples were annealed for 10 min at 300 °C, 400 °C, and 500 °C, in vacuum by using a rapid thermal annealing furnace.

X-ray diffraction (XRD, Siemens D5000) analysis with Cu Kα radiation (wavelength = 1.5418 Å) was performed to investigate the crystallographic structure of F-doped ZnO thin films. The surface morphology of the films was observed by field-emission scanning electron microscopy (FE-SEM, LEO1530). The optical transmittance of the films was measured using a spectrophotometer (HITACHI U-4100) in the spectral range 240–800 nm. The electrical resistivity, Hall mobility, and carrier concentration were obtained by Hall effect

* Corresponding author. Tel.: +886 7 7310606 3231; fax: +886 7 7331758.
E-mail address: naive@csu.edu.tw (Y.-Z. Tsai).

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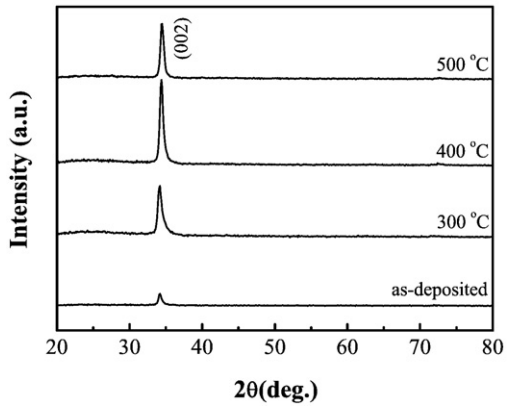

Fig. 1. XRD patterns of F-doped ZnO thin films as-deposited and annealed at various temperatures.

measurements (HL 5500 IU) using van der Pauw's method at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of F-doped ZnO thin films as-deposited and annealed at various temperatures. Only ZnO (002) diffraction peak can be found in the XRD patterns, indicating that all of the films obtained have a preferred orientation with the c-axis perpendicular to the substrate surface. No extra phases involving fluoride compounds, such as ZnF_2, were observed, even for the as-deposited thin film. This can be attributed to high volatility of fluorine [12]. Nakanishi et al. also pointed out that ZnF_2 was oxidized to ZnO by residual O_2 gas at a pressure of about 0.13 mPa [13]. In this study, ZnF_2 is more likely to be oxidized to ZnO because of the introduction of O_2 gas into the reaction chamber in the sputtering process. In addition, the intensity of (002) diffraction peak increases with the increasing of annealing temperature and reaches a maximum value at 400 °C. The 2θ values of (002) diffraction peak for the F-doped ZnO thin films as-deposited and annealed at 300 °C, 400 °C, and 500 °C are 34.2°, 34.2°, 34.4°, and 34.5° respectively. The little peak shifting of F-doped ZnO thin films as-deposited and annealed at 300 °C is due to the interstitial occupation of fluorine. Similar result can be found in DC reactive sputtering deposition of ZnO:Al thin film on glass [14].

Table 1
Hall data of F-doped ZnO thin films as-deposited and annealed at various temperatures.

Annealing temperature °C	Resistivity Ω cm	Mobility $cm^2\ V^{-1}\ s^{-1}$	Carrier concentration cm^{-3}
As-deposited	N/A	N/A	N/A
300	N/A	N/A	N/A
400	4.96×10^{-3}	6.4	2.07×10^{20}
500	6.65×10^{-4}	4.8	1.95×10^{21}

The SEM micrographs in Fig. 2 show the surface morphology of F-doped ZnO films. The magnification of the micrographs is the same. The surface of the as-deposited F-doped ZnO film is compact and smooth. No grain large enough can be found in Fig. 2(a). After 10 min annealing at 300 °C, the agglomeration of small grains gives rise to elongated secondary grains and makes the grain size distribution wide as shown in Fig. 2(b). When the annealing temperature is higher than 400 °C, the grain size distribution narrows and the images of Fig. 2(c) and (d) show smooth surface with sphere-like shape grains (~30 nm in diameter).

Shown in Table 1 are the results of Hall measurements of F-doped ZnO thin films as-deposited and annealed at various temperatures. The films as-deposited and annealed at 300 °C show high sheet resistance and no data can be obtained from Hall effect measurement due to the interstitial occupation of fluorine. The result is consistent with little peak shifting of XRD patterns of F-doped ZnO thin films as-deposited and annealed at 300 °C. As can be seen in Table 1, the lowest resistivity of 6.65×10^{-4} Ω cm and the highest carrier concentration of 1.95×10^{21} cm^{-3} were obtained for the F-doped ZnO thin film annealed at 500 °C. The increasing of carrier concentration with the increasing of annealing temperature can be ascribed to the activation of fluorine. The slight decreasing of Hall mobility of F-doped ZnO thin film annealed at 500 °C may be caused by worse crystallinity, inferring from the intensity of (002) diffraction peak.

Fig. 3 shows the optical transmission spectra of F-doped ZnO thin films as-deposited and annealed at various temperatures. The average transmittance in the visible region is above 90% and a marked absorption band edge can be found in the vicinity of 360 nm for all specimens. The band gap of ZnO is about 3.4 eV [15] and the band gap of ZnF_2 is about 7–8 eV [13]. Therefore, the absorption band edge in the vicinity of 360 nm should be attributed to excitation caused by the absorption of ZnO. No characteristic absorption related to ZnF_2 was found in optical transmission spectra, indicating no existence of ZnF_2

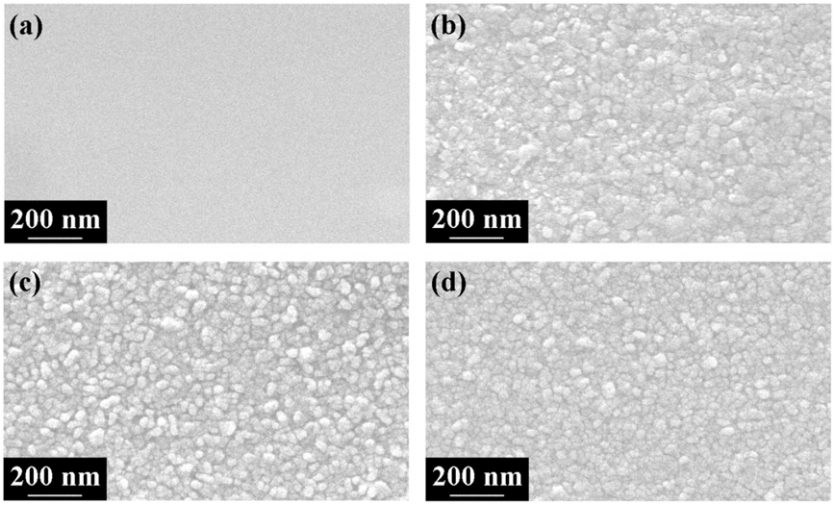

Fig. 2. SEM micrographs of F-doped ZnO thin films (a) as-deposited and annealed at (b) 300 °C, (c) 400 °C, and (d) 500 °C.

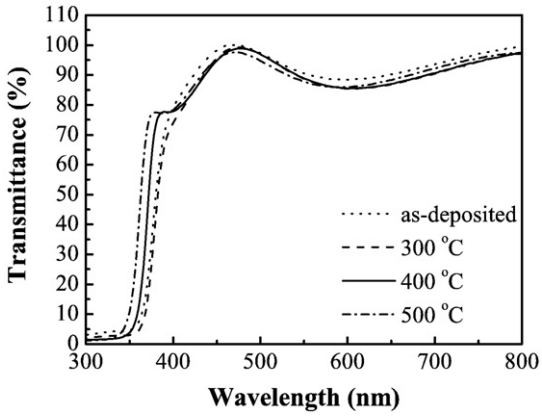

Fig. 3. Optical transmission spectra of F-doped ZnO thin films as-deposited and annealed at various temperatures.

phase in the thin films as-deposited and annealed. XRD patterns shown in Fig. 1 come to the same conclusion. The optical band gap, Eg, of the films can be obtained by plotting $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the linear portion of this plot to the energy axis, where $h\nu$ is photon energy and α is absorption coefficient [16]. As obtained Eg values are 3.28, 3.28, 3.37, and 3.46 eV for F-doped ZnO thin films as-deposited and annealed at 300 °C, 400 °C, and 500 °C respectively. The specimen annealed at 500 °C has the highest Eg value as expected by the Burstein–Moss shift [17].

4. Conclusions

Fluorine has been successfully incorporated into ZnO by reactive RF magnetron sputtering of ZnF_2 target. Highly conducting and transparent F-doped ZnO thin films were achieved by post-deposition annealing in vacuum. The specimen annealed at 500 °C has the best electrical properties: the lowest resistivity of 6.65×10^{-4} Ω cm and the highest carrier concentration of 1.95×10^{21} cm^{-3}. The average transmittance in visible region for all prepared samples is over 90%. Reactive RF magnetron sputtering of ZnF_2 target might be a feasible method for deposition of transparent conducting F-doped ZnO thin films with high performance.

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