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Letter

Highly transparent conductive F-doped ZnO films in wide range of visible and near infrared wavelength deposited on polycarbonate substrates

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ABSTRACT

Highly transparent fluorine-doped ZnO thin films in the visible and near infrared region with/without ZnO buffer layers were prepared by magnetron sputtering on flexible substrates at room temperature. Structural, electrical, and optical properties of FZO/PC films were investigated as a function of sputtering pressure ranging from 0.1 to 1 Pa. Lowest resistivity of $7.66 \times 10^{-2}\ \Omega$ cm, with carrier concentration of $1.31 \times 10^{20}\ cm^{-3}$ and Hall mobility of $0.62\ cm^2\ V^{-1}\ s^{-1}$, was achieved at 0.3 Pa. Importantly, an average optical transmittance of above 80% was achieved for all doped films in the spectrum range of 300–2000 nm. With a ZnO buffer layer, the electrical resistivity of FZO/ZnO/PC films reduced to $5.82 \times 10^{-3}\ \Omega$ cm with Hall mobility improved from $0.618\ cm^2\ V^{-1}\ s^{-1}$ to $8.08\ cm^2\ V^{-1}\ s^{-1}$, as the crystal quality was significantly improved.

1. Introduction

Zinc oxide (ZnO) transparent conductive thin films, with unique electrical and optical properties, have been used extensively in thin film solar cells, light-emitting diodes, flat panel displays and various optoelectronic devices [1–5]. The resistivity of undoped ZnO films is usually high due to the low carrier concentration [6–8]. Therefore, a suitable dopant should be taken into consideration in order to obtain a relatively high electrical property. Most of the previous studies were carried out with metallic cation dopants such as B, Al, Mn, Ga, and In [9–13]. However, fluorine has a similar ionic radius compared to oxygen (O^{2-}, 1.38 Å; F^-, 1.31 Å), which makes it a potential candidate for anion dopant in ZnO [14,15]. Besides, if oxygen is substituted by fluorine, the electronic disturbance will be mainly limited in the valence band and the scattering of conduction electrons will be reduced, which could lead to high electron mobility as well as low absorption loss [16]. In addition, fluorine is not an electrically active element, while active elements such as Al, Ga, will diffuse into the *a*-Si:H film, resulting in the decrease of the solar cell performance [17]. Moreover, compared with metal doped films, FZO films usually have higher carrier mobility and lower carrier concentration with similar electrical resistivity [18–20], and hence result in a better transmission in the near infrared region. It suggests that the FZO films are more appropriate for the application in *a*-Si:H thin film solar cells.

Especially, transparent conducting oxide thin films deposited on flexible substrates have attracted a lot of attentions because they have many advantages such as light duty, low cost, small volume, and promising applications on flexible electronic devices [21–25]. But they have several defects as well, weak mechanical strength, low thermal resistance and huge mismatch in thermal expansion coefficient between ZnO films and polymer substrates [26]. Moreover, flexible substrates have a trend of absorb moisture and gas. In order to reduce diffusion of vapor and oxygen and obtain high electrical performance, a buffer layer is necessary when the films are deposited on polymer substrates [7,27,28].

Many researchers have studied Al-doped ZnO (AZO) and Ga-doped ZnO(GZO) thin films on polymer like polyethylene naphthalene (PEN), terephthalate (PET), and polycarbonate (PC), but still, there are only less reports about FZO thin films on flexible substrates [29–32].

In this paper, we prepared F-doped ZnO thin films on PC substrates by RF magnetron sputtering at room temperature to investigate the effect of different sputtering pressures on these thin films. Besides, in order to improve the photovoltaic properties of the films, a ZnO buffer layer was added. FZO films with/without the ZnO buffer layer deposited at the optimal parameter were compared.

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2. Experiments

F-doped ZnO thin films and FZO/ZnO bilayer films were deposited onto polycarbonate substrates (with thickness of 0.25 mm) by radio frequency magnetron sputtering. The ZnO target was fabricated using high-purity ZnO (99.99%) powders. The FZO target was fabricated by high-purity ZnO (99.99%) and ZnF_2 (99.99%) powders, and the atomic ratio of Zn/F was 0.97:0.03.

Firstly, as the flexible substrates would be fused at a relatively high temperature, the FZO films with a thickness of about 120 nm were grown at room temperature (RT). The sputtering pressure varied from 0.1 Pa to 1 Pa while the output power and deposition time kept at 120 W and 60 min, respectively.

Then, an undoped ZnO buffer layer was deposited onto the PC substrates before the FZO layer, in order to increase the film's photovoltaic performance. Then, we compared the presence of the performance of thin film with and without buffer layer.

Electrical properties of the films were measured by Hall measurements in the van der Pauw configuration (BIO-RAD HL5500PC) at room temperature. The crystal structure was analyzed by X-ray diffraction (XRD) using a XPERT-PRO system with a Cu Kα (λ = 1.5406 Å) source. The FZO films had an approximate film thickness of 110 nm, which was measured by a spectroscopic ellipsometers. In addition, a UV-4100 spectrometer was used to measure the optical transmission.

3. Results and discussion

3.1. Influence of the sputtering pressure on the properties of FZO films

The XRD patterns of the FZO thin films grown at different sputtering pressure are shown in Fig. 1. All the films exhibit a strong (002) peak and a weak (004) peak, suggesting that all the films are polycrystalline with hexagonal wurtzite ZnO structure. No fluorine-related compounds such as ZnF_2 can be found from the XRD patterns, which indicates that fluorine replaces the position of oxygen to contribute extra free electrons. Besides, the intensities of (002) peak increases when the sputtering pressure changes from 0.1 Pa to 0.3 Pa, then decreases gradually with increasing the pressure. The film prepared at 0.3 Pa has a Full-Width Half-Maximum (FWHM) of 0.295, presenting the best crystal quality in all the films. It is due to that if the pressure is too low (0.1 Pa), the mean free path of the electrons will be relatively large, thus some electrons reach the anode with less collision with Ar ions, leading to the instable glow discharge. The increase of the collision between the sputtered ions and the Ar ions at high pressure (0.5, 0.8, 1 Pa) causes more energy loss when the sputtered ions arrive at the substrates, degrading the crystallinity of the films [33,34].

Fig. 2 summarizes the variation of resistivity (ρ), carrier concentration (n), and Hall mobility (μ) as a function of sputtering pressure for FZO films. As the sputtering pressure increases from 0.1 Pa to 0.3 Pa, the resistivity of the films decreases to a minimum value of $7.66 \times 10^{-2}\ \Omega$ cm, with carrier concentration of $1.31 \times 10^{20}\ cm^{-3}$ and Hall mobility of $0.62\ cm^2\ V^{-1}\ s^{-1}$. As the sputtering pressure further increases, the increase of the resistivity is due to both the decrease of the Hall mobility and the carrier concentration, corresponding to the damage of crystallinity shown in the XRD patterns. In addition, the voltage applied between target and substrate decreases with the pressure increasing [35]. So, few sputtered F ions can reach the substrate and participate in doping, leading to the increase of resistivity. The concentrations of dopant F are 1.16% (0.1 Pa), 1.34% (0.3 Pa), 0.99% (0.5 Pa), 1.02% (0.8 Pa) and 0.83% (1 Pa), respectively, measured by XPS. It is clear that the concentration is consistent with the electrical properties of the films.

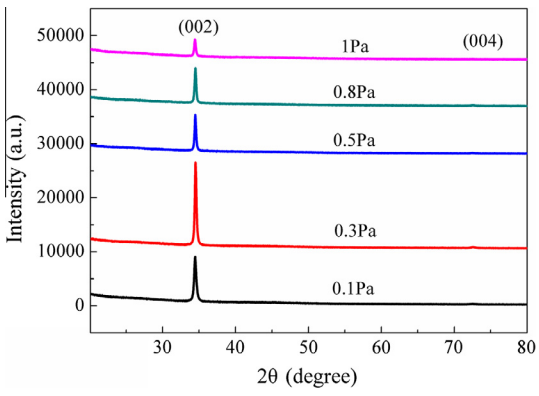

Fig. 1. XRD patterns of F-doped ZnO films grown at different sputtering pressures.

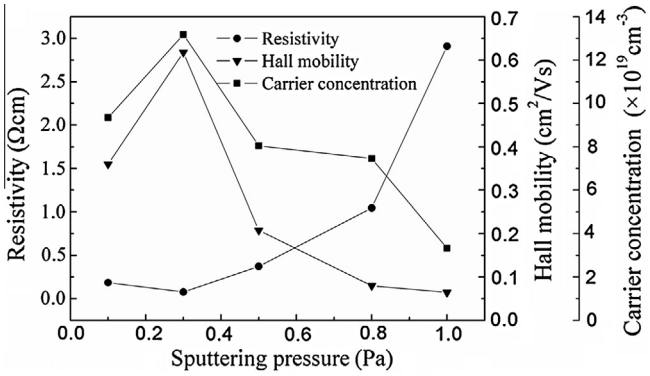

Fig. 2. Resistivity, carrier concentration, and Hall mobility as a function of sputtering pressure for FZO films.

Fig. 3 shows the optical transmittance in the wavelength range of 300–2000 nm for FZO films deposited at various sputtering pressures. The inset of Fig. 3 is a locally-magnified figure in the wavelength range of 300–400 nm. It can be seen that all the films have a sharp absorption edge in the ultraviolet range, which shifts to the longer wavelength as the working pressure increases. All the films exhibit an average optical transmittance of higher than 80% in both visible and near infrared region, while the transmittance of a typical metal doped ZnO films, such as AZO and GZO, have fallen down after 1000 nm. The plasma frequency for the conduction electrons in a transparent conductor, which increases approximately with the square root of the conduction-electron concentration, divides the optical properties [16]. Like most metal doped ZnO films, AZO has a plasma frequency at about 1300 nm. In the range 300–1200 nm, the reflectance of AZO films varies little and the films behave as a transparent dielectric for the electrons cannot respond, while in the near infrared region, the transmittance decreases as the films reflect and absorb incident light [36,37]. However, FZO films are highly transparent in the near infrared region for their corresponding plasmonic wavelength at 2000 nm.

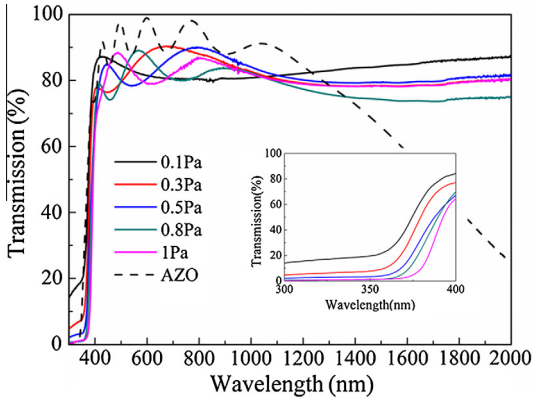

Fig. 3. Transmission spectra of the FZO thin films grown at different sputtering pressures in the spectra of 300–2000 nm. The inset shows a enlarge figure in the wavelength range of 300–400 nm.