



Room temperature DC magnetron sputtering deposition of hydrogenated aluminum doped zinc oxide thin films on polyethylene terephthalate substrates



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ABSTRACT

In this work, aluminum doped zinc oxide (AZO) and hydrogenated aluminum doped zinc oxide (HAZO) thin films were deposited on polyethylene terephthalate (PET) substrates at room temperature by DC magnetron sputtering. Hydrogenation improved the crystallinity and reduced surface roughness of the AZO thin films. The hydrogenated AZO films revealed improved electrical and optical properties comparing with the AZO films prepared under the same deposition condition: the resistivity decreased from $0.18 \Omega \text{ cm}$ to $3.0 \times 10^{-3} \Omega \text{ cm}$, which was mostly due to the increase of the carrier concentration from $1.5 \times 10^{19} \text{ cm}^{-3}$ to $2.3 \times 10^{20} \text{ cm}^{-3}$. The average transmittance in the visible range increased from 82.0% to 84.5%. This hydrogenated process may provide an easily realized method to fabricate high quality AZO films on flexible substrates at room temperature.

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1. Introduction

The deposition of transparent conductive oxides (TCOs) on flexible substrates has attracted increasing attention due to their applications in optoelectronic devices and thin-film solar cells [1–4]. Recently, many research groups have studied Al-doped ZnO films deposited on polymer substrates because the films combine attractive properties with low cost, nontoxicity, and stability in hydrogen plasma [5–8]. Comparing with other deposition techniques, magnetron sputtering is widely adopted in preparing the AZO films because of the excellent film properties and repeatability [5,9]. However, the low temperature process is not in favor of depositing high quality films, the resistivity of AZO films on polymer is too high to be adopted [10]. In order to improve the quality of films deposited at low temperature, an inorganic buffer layer was inserted between the AZO film and polymer substrate, which was reported by some researchers [7,10,11]. Apart from this approach, hydrogenated aluminum doped zinc oxide (HAZO) film may be an excellent option for low temperature deposition of high performance TCOs [12–15]. A low resistivity of $4.01 \times 10^{-4} \Omega \text{ cm}$ HAZO film deposited on glass at room temperature has been

reported [16]. Due to the physical, chemical and mechanical differences between the glass and polymer substrates, the effect of hydrogenation may be different for the AZO films on polymer and glass substrates [17]. The high quality hydrogenated AZO (HAZO) films on polymer has been rarely reported.

In this paper, hydrogen was added into sputtering gas with the aim to improve the properties of the AZO films. The effects of hydrogenation on the electrical, optical and structural properties of the AZO films on polyethylene terephthalate (PET) substrates were investigated.

2. Experimental details

AZO films were deposited on PET substrates from a home-made 1 wt% AZO ceramic target (99 wt% ZnO+1 wt% Al₂O₃). The substrates were cleaned in an ultrasonic bath with de-ionized water, and then blown dried with nitrogen gas before deposition. The distance between the target and substrate was fixed at 90 mm, while the base pressure in the chamber was kept below $5 \times 10^{-4} \text{ Pa}$ and sputtering pressure was 0.6 Pa. The sputtering process was carried out at room temperature in pure Ar and Ar+8 vol% H₂ atmosphere and the sputtering DC power was ranging from 40 W to 80 W.

The phase structure of the films was analyzed by X-ray diffraction (XRD) with Cu K α radiation in θ – 2θ Bragg–Brentano

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geometry (Bruker, AXS D8 Advance, USA). The thickness of the films was determined by a surface profilometer (Veeco, Dektak150, USA). The surface morphology was examined using an atomic force microscope (AFM, CSPM5500, China). The optical transmittance and reflection of the films were measured using an UV/visible/NIR spectrophotometer (Perkin-Elmer, Lambda 950, USA). The resistivity, carrier concentration and mobility of the films were measured using the Van der Pauw method by Hall measurements (Accent, HL5500PC, UK).

3. Results and discussion

Electrical properties: Fig. 1 shows the electrical properties of the AZO and HAZO films deposited on PET substrates at different DC powers. It was found that an optimum sputtering power of 60 W produced the lowest resistivity of $0.18 \Omega \text{ cm}$ for the AZO film. When hydrogen was added into the sputtering atmosphere, the electrical properties of the samples were remarkably improved. The resistivity of the film deposited at 60 W decreased from $0.18 \Omega \text{ cm}$ to $3.0 \times 10^{-3} \Omega \text{ cm}$. Correspondingly, the carrier concentration and the Hall mobility increased from $1.5 \times 10^{19} \text{ cm}^{-3}$ to $2.3 \times 10^{20} \text{ cm}^{-3}$ and from $2.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $8.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. When doping hydrogen into the AZO films, on one hand, the incorporated hydrogen acted as shallow donor, resulting in the increase of the carrier concentration [14,18–20]. On the other hand, the hydrogen atoms in the AZO films passivated defects at grain boundaries and/or acceptors, which improved the Hall mobility [14,18–20].

Optical properties: Fig. 2 shows the optical transmission and absorption spectra of the AZO and HAZO thin films deposited on PET substrates. When hydrogen was added to sputtering atmosphere, the average transmittance of the films in the visible range (400–800 nm) increased from 82.0% to 84.5%. It was noticed that the hydrogen introduction resulted in a drastic decrease in the transmittance of the AZO films in the near infrared range. Correspondingly, the absorption in the near infrared range of the

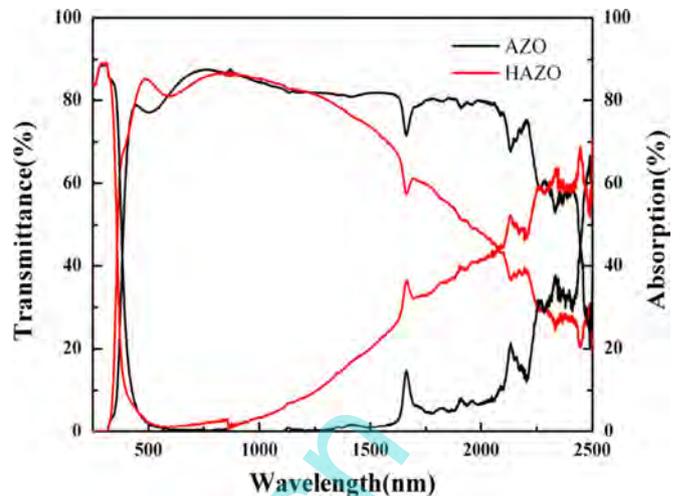


Fig. 2. Optical transmittance and absorption spectra of the AZO and HAZO films deposited on PET at 60 W.

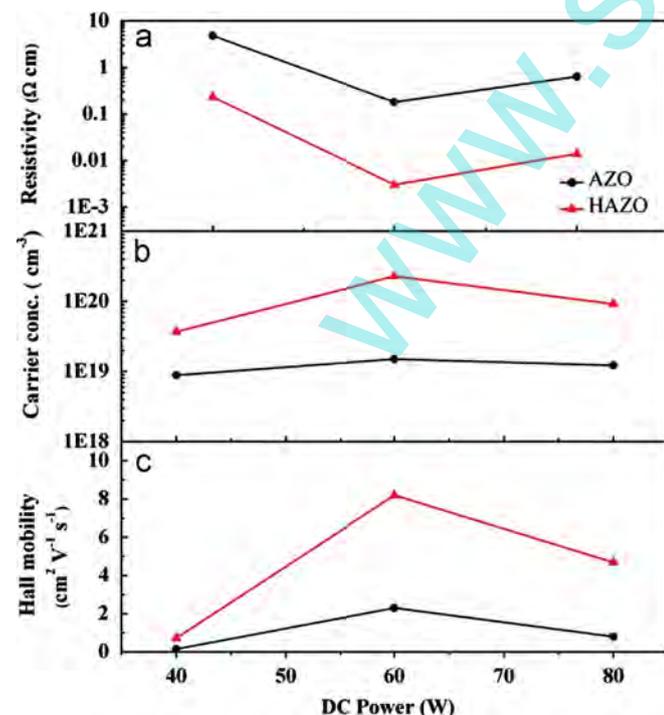


Fig. 1. (a) Resistivity, (b) carrier concentration and (c) Hall mobility of the AZO and HAZO films deposited on PET at different DC powers.

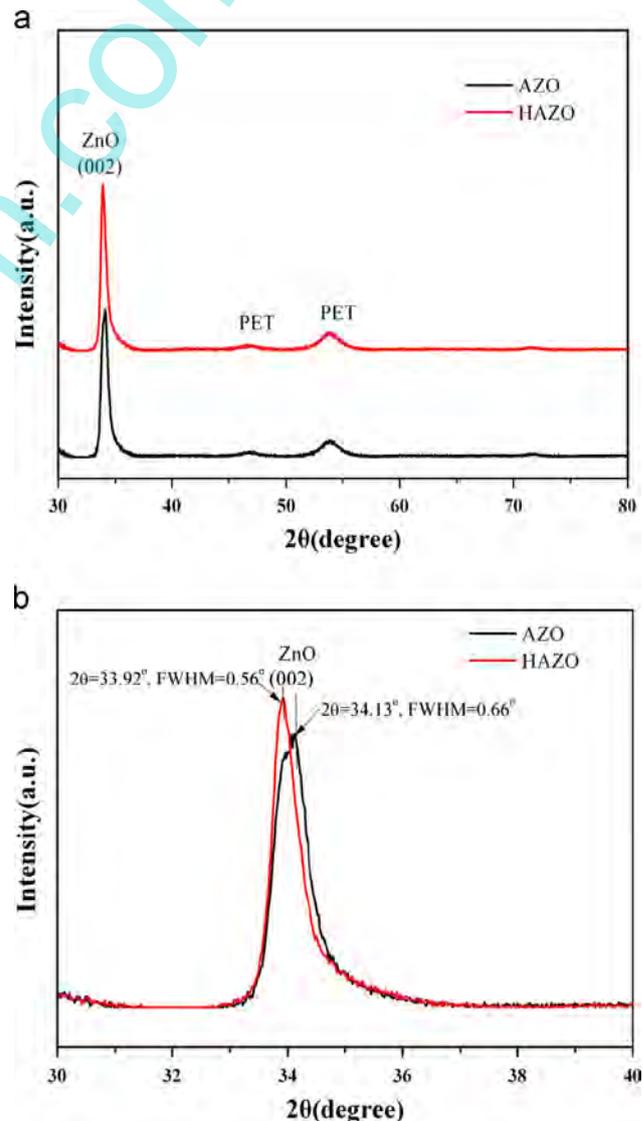


Fig. 3. (a) XRD patterns of the AZO and HAZO films deposited on PET at 60 W. (b) A narrow scan XRD profile.

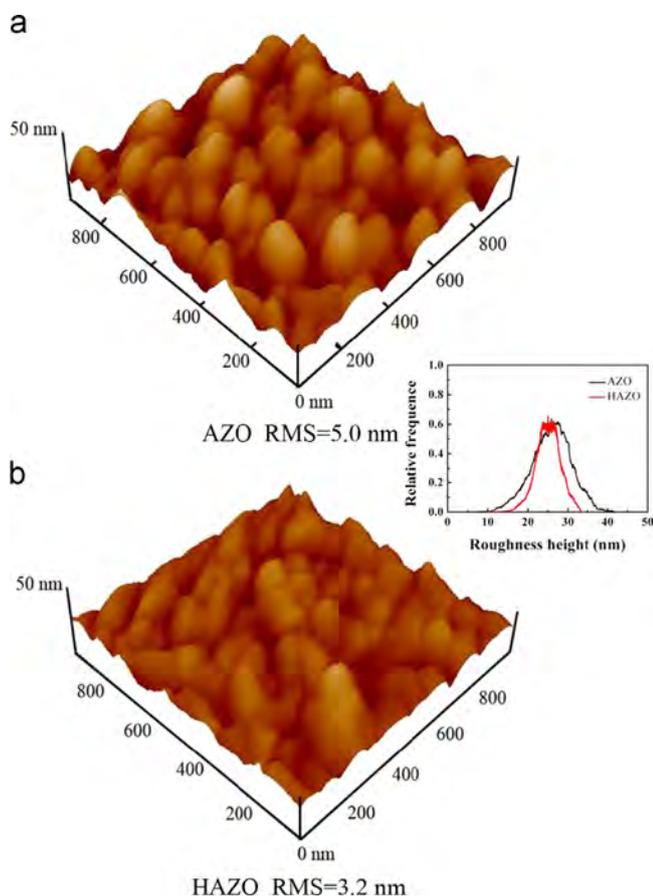


Fig. 4. AFM images of the (a) AZO and (b) HAZO films deposited on PET at 60 W. The inset is the roughness height histogram.

film remarkably increased after the hydrogen incorporation. The variations of optical transmission and absorption spectra in the near infrared range were caused by the free carrier absorption, which increased with the hydrogen incorporation. The fundamental absorption edge of HAZO film moved to the short wavelength region compared with that of the AZO film, which was also attributed to the increase in the carrier concentration. The band gap widening with increasing carrier concentration was due to the filling of the conduction band by electrons, which was known as the Burstein–Moss effect [21,22].

Structural properties: The crystal structures of the AZO and HAZO films deposited on PET substrates were also analyzed by XRD. The XRD spectra revealed strong preferred orientation (002) peaks as seen in Fig. 3(a), indicating that the films were orientated with their axes perpendicular to the substrate plane. Fig. 3(b) is a narrow scanned XRD profile. When hydrogen was incorporated into the AZO thin films on PET, the (002) peak position shifted from 34.13° to 33.92° . This implied that hydrogen incorporation in the AZO matrix induced further expansion of the crystal lattice. The full-width at half-maximum (FWHM) of the (002) peak for the thin films on PET decreased from 0.66° to 0.56° after hydrogenation, and the average crystallite size calculated according to the Scherrer equation increased from 12.5 nm to 14.7 nm. These results indicated the improvement of the crystallinity.

Surface morphologies: The AFM images of the AZO and HAZO films deposited on PET are shown in Fig. 4. The HAZO thin film showed a narrower roughness height distribution than that of the

AZO thin film. Correspondingly, the RMS roughness decreased from 5.0 nm to 3.2 nm after hydrogenation. The decrease in surface roughness might contribute to improve the electrical and optical properties [6,10,23].

4. Conclusions

In summary, highly transparent and conductive HAZO thin films were successfully deposited on PET substrates by DC magnetron sputtering of a ceramic target at room temperature. The hydrogenation improved the crystallinity and reduced surface roughness of the AZO thin films. After hydrogenation, the resistivity of the AZO thin films grown on PET decreased from $0.18 \Omega \text{ cm}$ to $3.0 \times 10^{-3} \Omega \text{ cm}$, and corresponding carrier concentration and mobility increased from $1.51 \times 10^{19} \text{ cm}^{-3}$ to $2.33 \times 10^{20} \text{ cm}^{-3}$ and from $2.28 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ to $8.94 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. The HAZO thin films revealed higher visible light transmission than that of the AZO thin films. This hydrogenated process may provide an easily realized method to fabricate high quality AZO films on flexible substrates at room temperature.

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