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Rapid communication

Tailoring of textured ZnO: Al film via hydrogen

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ABSTRACT

In this present study, textured hydrogen and aluminum co-doped ZnO (HAZO) films were directly prepared on glass substrates through a pulsed DC magnetron sputtering technique. The influence of hydrogen flow rate on the morphological, optical, and electrical properties of HAZO films was investigated. With increasing hydrogen flow rate, surface morphology changed from pyramid-like to crater-like, feature size increased, and light trapping ability improved. The change in micro-structure of the HAZO films showed that hydrogen suppresses the more complex peaks and optimizes the dominant (002) and (004) peaks. In our experiment, optimal HAZO film properties were achieved at a hydrogen flow rate of 8 sccm, showing higher light trapping ability than commercial textured SnO_2: F (FTO).

Transparent and conductive oxides (TCO) are widely used as a front contact element in thin film silicon solar cells [1]. Among TCO films, ZnO thin films doped with group III elements (B, Al, and Ga) have attracted more attention in recent years due to their low cost, low resistivity, and high transparency in the visible wavelength range; they are non-toxic and also stable in a hydrogen plasma environment [2–4]. In addition to high transparency and high electrical conductivity, the morphological characteristics of the TCO layer are essential when applied as a front electrode for superstrate (p–i–n type) thin film silicon solar cells.

Textured ZnO films are fabricated by various methods, for example: low pressure chemical vapor deposition (LPCVD) [5], metal-organic chemical vapor deposition (MOCVD) [6], and magnetron sputtering of flat AZO films followed by wet-chemical etching [7]. Although magnetron sputtering shows several advantages in comparison with other deposition methods, such as low process temperature, high deposition rate, and good adhesion to the substrate, the additional wet-chemical etching step required to realize effective light trapping increases production cost. As a result, direct magnetron sputtered textured ZnO film without etching may be preferable. Some attempts have been made to directly deposit self-textured zinc oxide films by magnetron sputtering. Necessary modifications have included adding water-vapor to the reactor chamber during sputtering [8] or using high gas pressures (>2 Pa) [9]. However, the electrical properties of these films are limited. One investigation has reported that, during ZnO film fabrication, incorporation of hydrogen not only improves the optical and electrical properties, but also modifies the morphological properties [10]. However, the inherent influence of hydrogen on micro-structural properties of AZO films was not reported at that stage.

In this paper, we report the preparation of textured hydrogen and aluminum co-doped ZnO (HAZO) films by magnetron sputtering technology. The effect of H_2 flow rate on the morphological, optical, and electrical properties of AZO film was systematically investigated. Finally, surface-textured HAZO film with a sheet resistance of 4.7 Ω/cm was fabricated, possessing higher light trapping capacity than commercial textured SnO_2: F (FTO) film (Asahi-U type).

The HAZO films were prepared on Eagle XG glass by pulsed DC magnetron sputtering using a 1 wt.% Al_2O_3 doped ZnO (ZnO:Al_2O_3) ceramic target. Glass substrates were ultrasonically cleaned with detergent followed by deionized water and dried with nitrogen gas. They were then positioned 50 mm from the target. Before film deposition, the chamber was pumped to 5×10^{-5} Pa. During deposition, substrate temperature was maintained at 300 °C. High purity (99.999%) Ar and H_2 gases were introduced through separate mass flow controllers. Sputtering power was fixed at 460 W. In order to understand conditions leading to an optimal self-textured HAZO film, samples were processed in two series of different

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treatments. In the first series, total flow rates of H_2 and Ar were kept at 55 sccm and the pressure is maintained at 5 mTorr. During deposition, H_2 flow rate was increased from 0 sccm to 8 sccm, while Ar was concurrently changed from 55 sccm to 47 sccm, maintaining constant flow. In the second series, the H_2 and Ar flow rates were kept at 8 sccm and 47 sccm, respectively, and the deposited film thickness was increased from 980 nm to 1400 nm.

The surface morphology of the HAZO films was characterized by field emission scanning electron microscopy (FE-SEM, ZEISS Supra-55vp) and atom force microscopy (AFM, NanoNavi-SPA400). Structural analysis was carried out by X-ray diffraction (XRD, Rikaku, ATX-XRD) using Bragg–Bretano ($\theta/2\theta$) geometry, and a scan range from 20° to 80°. Electrical properties of the HAZO films were measured at room temperature using the van der Pauw method in an HL5500 Hall System. Film thickness was measured by a surface profilometer (Veeco Dektak 150). Optical properties, such as total transmittance (TT) and specular transmittance (ST), were measured in the range of 300–1100 nm using a UV–Vis–NIR spectrophotometer (Cary 5000) and an integrating sphere. The haze value was calculated from the difference of TT and ST value ((TT − ST)/TT × 100%).

Fig. 1(a)–(d) shows SEM images of textured HAZO films deposited at different H_2 flow rates. A rough textured surface is clearly seen for the as-grown HAZO thin films. Fig. 1(a) shows pyramid-like surface morphology with a feature size of ~150 nm, and was fabricated in a pure argon atmosphere. When the H_2 flow rate increased from 0 sccm to 4 sccm and 6 sccm, the surface appearance of HAZO film changed from single pyramid-like to a combination of both pyramid-like and crater-like features, and the crater size increased with H_2 flow rate. From Fig. 1(d) it is seen that, when the H_2 flow rate was further increased to 8 sccm, the pyramid-like features disappeared and the surface completely changed to a crater-like topography.

To explore the micro-structural mechanism for surface topography changes of HAZO films, XRD was conducted. Fig. 2 shows XRD patterns of HAZO films produced at different H_2 flow rates. For pure AZO film (0 sccm of H_2), in addition to the dominant (002) and (004) diffraction peaks, many other peaks such as (100), (101), (103), and (200) were observed. This structural property is consistent with the self-textured ZnO films prepared by LPCVD [5] and ultrasonic spray pyrolysis (USP) [11] methods. The presence of

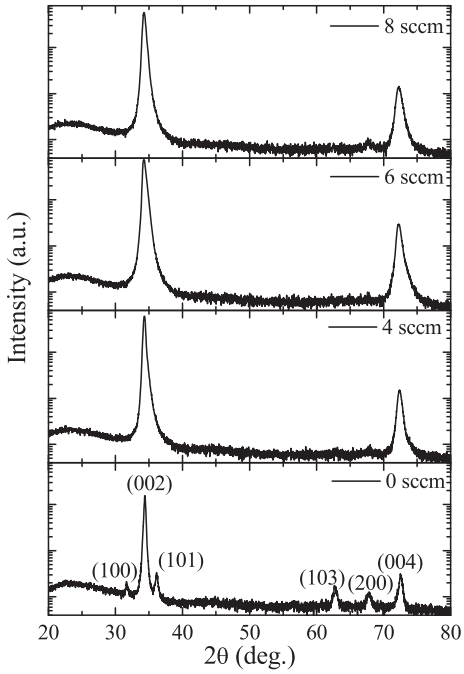

Fig. 2. X-ray diffraction (XRD) patterns of HAZO films deposited at different hydrogen flow rates.

other peaks is related to the production of a pyramid-like surface morphology. In our experiments, the AZO films changed from the pyramid-like surface morphology mode to a crater-like surface topography with the incorporation of H_2. For the AZO films considered in this study, O^{2-} ions bombarding the substrate surface with high energy, cause more damage to the (002) plane than to other loosely packed planes such as (101) [12]; there are also many dangling bonds produced on the growing film surface [13]. Thus, crystallites having orientations normal to the (101) plane can grow relatively undisturbed and serve as seeds for further growth. However, with incorporation of hydrogen, the dangling bonds are terminated, so the sputtered atoms are able to travel further and the crystal quality improved [13]. As the (002) crystal plane has the

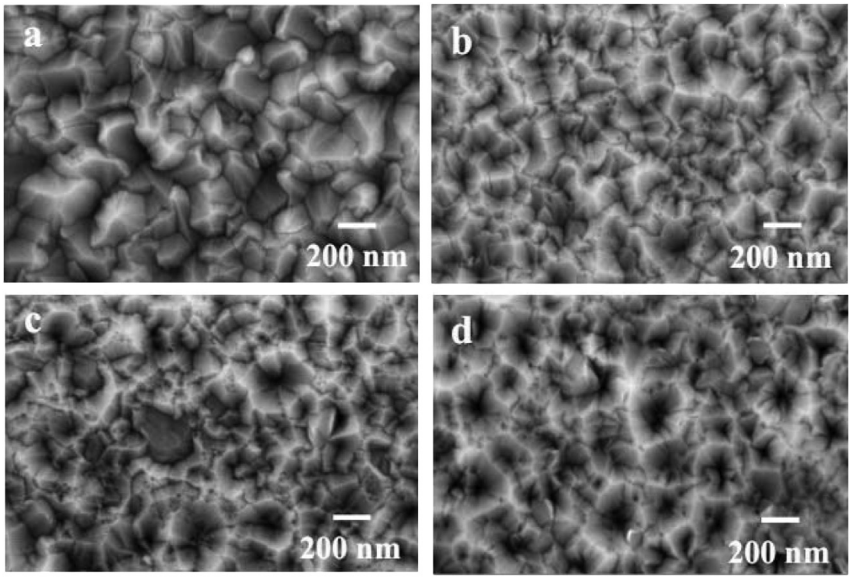

Fig. 1. SEM images of self-textured HAZO films deposited at various H_2 flow rates: (a) 0 sccm, (b) 4 sccm, (c) 6 sccm, and (d) 8 sccm.