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Natively textured surface hydrogenated gallium-doped zinc oxide transparent conductive thin films with buffer layers for solar cells

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ABSTRACT

Natively textured surface hydrogenated gallium-doped zinc oxide (HGZO) thin films have been deposited via magnetron sputtering on glass substrates. These natively textured HGZO thin films exhibit rough pyramid-like textured surface, high optical transmittances in the visible and near infrared region and excellent electrical properties. The experiment results indicate that tungsten-doped indium oxide (In_2O_3:W, IWO) buffer layers can effectively improve the surface roughness and enhance the light scattering ability of HGZO thin films. The root-mean-square roughness of HGZO, IWO (10 nm)/HGZO and IWO (30 nm)/HGZO thin films are 28, 44 and 47 nm, respectively. The haze values at the wavelength of 550 nm increase from 7.0% of HGZO thin film without buffer layer to 18.37% of IWO (10 nm)/HGZO thin film. The optimized IWO (10 nm)/HGZO exhibits a high optical transmittance of 82.18% in the visible and near infrared region ($\lambda \sim 400$–1100 nm) and excellent electrical properties with a relatively low sheet resistance of 3.6 Ω/□ and the resistivity of 6.21×10^{-4} Ωcm.

1. Introduction

Transparent conducting oxides (TCOs) based on impurity-doped zinc oxide (ZnO) have been used in various applications such as channel layers and electrodes in transparent thin film transistors, light-emitting diodes and thin film solar cells [1–3]. Although aluminum-doped ZnO (ZnO:Al, AZO) has been widely investigated over the last decade, gallium-doped ZnO (ZnO:Ga, GZO) has drawn much attention due to its advantages over AZO including lower reactivity of Ga than Al and the Ga-O bond length of 1.92 Å, shorter than the Al-O bond length of 1.97 Å, that enables smaller lattice distortion on doping as compared to AZO [4,5]. Furthermore, highly doped GZO thin films also exhibit better electronic stability than that of AZO when exposed to moisture [6,7]. Additionally, first-principles calculations based on density functional theory and infrared spectroscopy measurements have indicated that hydrogen impurities can act as shallow donors in ZnO. It forms a strong bond with oxygen (H-O) and provides a free carrier to improve the electrical characteristics of ZnO thin films [8–12].

In order to improve conversion efficient and stability, textured surface ZnO-TCO thin films with good light-scattering capability are necessary for Si-based thin film solar cells. The light scattering capability of textured ZnO-TCO layers depends on the dimensional features and surface morphology. Polycrystalline ZnO films are readily etched in many acidic and alkaline solutions, such as diluted HCl, HF, HNO_3, CH_3COOH, KOH, NaOH and NH_4Cl aqueous solutions [13–18]. It has been extensively reported that sputtering and post wet-etching treatments combining ~0.1–2.0% (v/v) diluted HCl solution with etching time ~10–100 s are the main techniques to obtain rough-textured surface ZnO-TCO thin films [19–22]. Recently, some researchers have introduced two-step etching methods to modify the surface structures by wet-etching process [23,24]. However, there may be some risks and uncertain factors on fabricating large-area thin film production for application in photovoltaic module. If natively textured sputtered ZnO-TCO thin films can be used to fabricate high efficiency Si-based thin film solar cells, the savings in terms of time and equipment would be beneficial for industrial processing. There has been relatively little research focused on natively textured surface hydrogenated Ga-doped ZnO (HGZO) grown by magnetron sputtering for thin film solar cells.

In this work, natively textured surface HGZO TCO thin films for solar cells were directly deposited by using pulsed direct current (DC) magnetron sputtering and the influences of tungsten-doped indium oxide (In_2O_3:W, IWO) buffer layers on the micro-structural, electrical and optical properties of HGZO films were investigated in detail.

2. Experimental details

HGZO thin films were deposited by pulsed ($f = 30$ kHz) DC magnetron sputtering on borosilicate glass substrates using ZnO ceramic target with low Ga concentration (ZnO:Ga_2O_3, 0.5 wt.% Ga_2O_3). The

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sputtering power was controlled at 450 W (0.96 W/cm^2), and the target-to-substrate distance was 45 mm. Before sputtering, the vacuum chamber was evacuated to a base pressure of about 3×10^{-4} Pa. The sputtering pressure was maintained at 0.57 Pa and the substrate temperature was maintained at 553 K. High purity (99.999%) Ar and H_2 gases were introduced through separate mass flow controllers. The Ar flow rate was set at 50.0 sccm and the H_2 flow rate was set at 2.0 sccm with other conditions remaining unchanged, respectively. The deposition periods are 30 rounds and each round will last one minute and thirty seconds. The HGZO thin films were deposited on the IWO buffer layer (buffer layer thickness: 10 and 30 nm) coated glass substrates. Note that the IWO buffer layers were fabricated by electron beam deposition technique [25,26]. The growth structure of textured surface IWO/HGZO thin films was shown in Fig. 1.

The film thicknesses were measured with a step profilometer (Ambios XP-2). Surface morphology and root-mean-square (RMS) roughness for the ZnO films were characterized by scanning electron microscopy (FE-SEM, Zeiss Supra-550p) using a 30.0-kV operating voltage and atom force microscopy (AFM, Seiko SPA 400) using the same pyramidal Si_3N_4 tip in contact mode, respectively. Carrier concentrations, sheet resistances and electron mobilities were determined by Hall measurement (Accent HL5500 PC) using the van der Pauw configuration. Optical transmittances, including the specular and total, were recorded with a double beam spectrometer with an integrating sphere (UV-Vis-NIR spectrometer, Varian Cary 5000). The haze ratio was calculated as haze = diffuse T (DT)/total T (TT) (total T (TT) = (diffuse T (DT) + specular T (ST)) × 100%), where T was transmittance.

3. Results and discussion

3.1. Structural properties

Fig. 2(a)–(c) show the typical SEM images of HGZO thin films with and without IWO buffer layer. These HGZO thin films exhibit pyramid-like surface morphology.

This may result from the etching process of hydrogen plasma. A postulated etching mechanism may involve in the removal of O by means of H and subsequent elimination of Zn in its metallic state, although the elimination of Zn via the formation of ZnH_2 cannot be excluded [27]. Therefore, pyramid-like surface morphology has been formed in the HGZO thin film growth process. On the other hand, there could be some large particles sputtered from ZnO ceramic targets existing in the thin film surface and thus they act as nucleation center for subsequent thin growth.

The HGZO thin film without IWO buffer layer has the feature size of ~200–500 nm, as shown in Fig. 2a. When applied the IWO buffer layer into the HGZO thin films, the pyramid-like feature size is increased, ~400–600 nm, as shown in Fig. 2b and c. It is speculated that the IWO buffer layer could form the nucleation centers and thus accelerate the crystallization of ZnO thin films. In addition, ZnO thin film grown on In_2O_3 layer will benefit from a small lattice

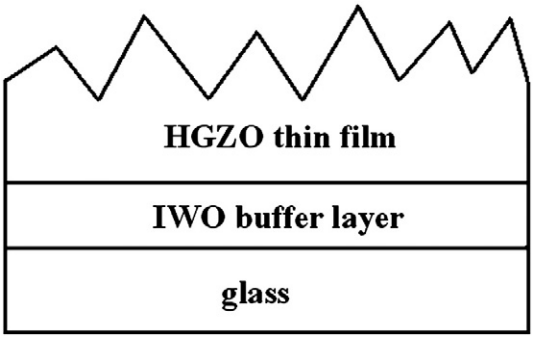

Fig. 1. Growth structure of textured surface IWO/HGZO thin films.

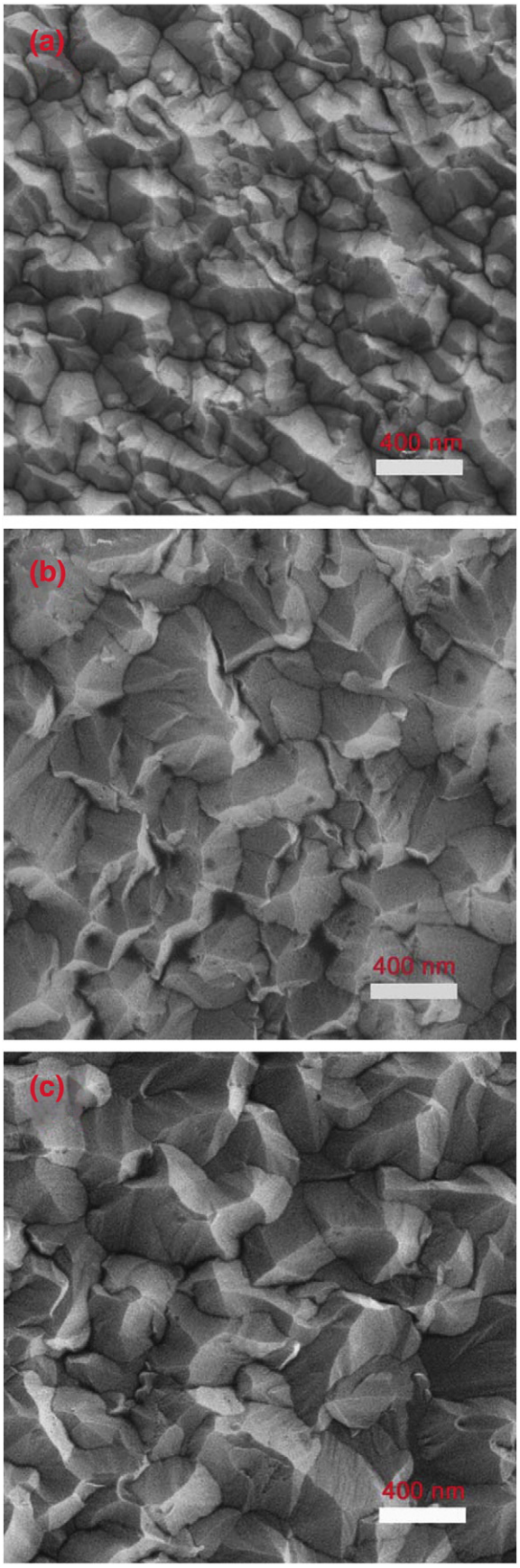

Fig. 2. Typical SEM images of the natively textured surface HGZO and IWO/HGZO thin films: (a) HGZO, (b) IWO (10 nm)/HGZO and (c) IWO (30 nm)/HGZO.