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Surface textured ZnO:Al thin films by pulsed DC magnetron sputtering for thin film solar cells applications

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ABSTRACT

Transparent conducting thin films of ZnO:Al (Al-doped ZnO, AZO) were prepared via pulsed DC magnetron sputtering with good transparency and relatively lower resistivity. The AZO films with 800 nm in thickness were deposited on soda-lime glass substrates keeping at 473 K under 0.4 Pa working pressure, 150 W power, 100 μs duty time, 5 μs pulse reverse time, 10 kHz pulse frequency and 95% duty cycle. The as-deposited AZO thin films has resistivity of 6.39×10^{-4} Ω cm measured at room temperature with average visible optical transmittance, T_{total} of 81.9% under which the carrier concentration and mobility were 1.95×10^{21} cm^{-3} and 5.02 cm^{2} V^{-1} s^{-1}, respectively. The films were further etched in different aqueous solutions, 0.5% HCl, 5% oxalic acid, 33% KOH, to conform light scattering properties. The resultant films etched in 0.5% HCl solution for 30 s exhibited high T_{total} = 78.4% with haze value, H_T = 0.1 and good electrical properties, $\rho = 8.5 \times 10^{-4}$ Ω cm while those etched in 5% oxalic acid for 150 s had desirable H_T = 0.2 and relatively low electrical resistivity, $\rho = 7.9 \times 10^{-4}$ Ω cm. However, the visible transmittance, T_{total} was declined to 72.1%.

1. Introduction

Transparent conducting oxides (TCOs) films are prerequisite for most photovoltaic applications and have been subjected to a very large number of investigations for several decades [1,2]. The most widely used and studied n-type TCOs are based on Zn, In, Sn and Cd owing to their superior optoelectronic properties, and especially, has widely applications in the front electrodes for most thin film solar cells [3–5]. Practically, indium-tin-oxide (ITO) thin films are the widely used TCOs. Nevertheless, the limited indium supply as well as the increasing price promotes the development of ITO alternatives [6]. Zinc oxide is a direct, wide bandgap (∼3.37 eV) semiconductor material with many promising properties for optoelectronics, electronics, spintronics and sensor applications [7]. It was shown that Al, Ga and In-doped ZnO films have great chemical stability and excellent electrical conductivity as well as visible transmittance which has made it one of the most promising TCOs owing to its non-toxicity, less expensive, more resistant to defect, impurity doping, hydrogen plasma reduction [8] and can be deposited at lower temperature [9,10].

As a satisfactory front contact materials for photovoltaic applications, the TCOs films has to be highly conductive for good current transport to obtain low series resistance and highly transparent for the incident sunlight to reduce the absorption losses [11]. Moreover, an adapted surface topography for better light scattering and subsequent light trapping inside the silicon based solar cells is necessary. Surface textured TCO with light-trapping structures can facilitate optical reflection, refraction, and scattering by a suitably rough surface to scatter the incident light [12,13]. The light scattering capability of the TCO front electrode depends on the dimensional features and surface morphology [14–16]. Polycrystalline ZnO films are readily etched in many acidic and alkaline solutions [7,14–18]. Up to now, there is no theoretical model to predict the wet-chemical etching behavior of polycrystalline AZO films as functions of processing parameters. However, a systematic approach to elucidate the properties of textured AZO films by different wet-chemical solutions was quite rare. In this study, a comprehensive study for the surface textured Al-doped ZnO films by wet etching with three different mediums was illustrated. The influence of structural, electrical and optical properties of the resultant films as a function of texturing medium and time period was investigated to obtain the desirable front electrodes materials with good light-trapping properties for thin film silicon solar cells applications.

2. Experimental

All films were deposited onto soda-lime glass substrate by pulse DC magnetron sputtering using a ceramic AZO target 76 mm

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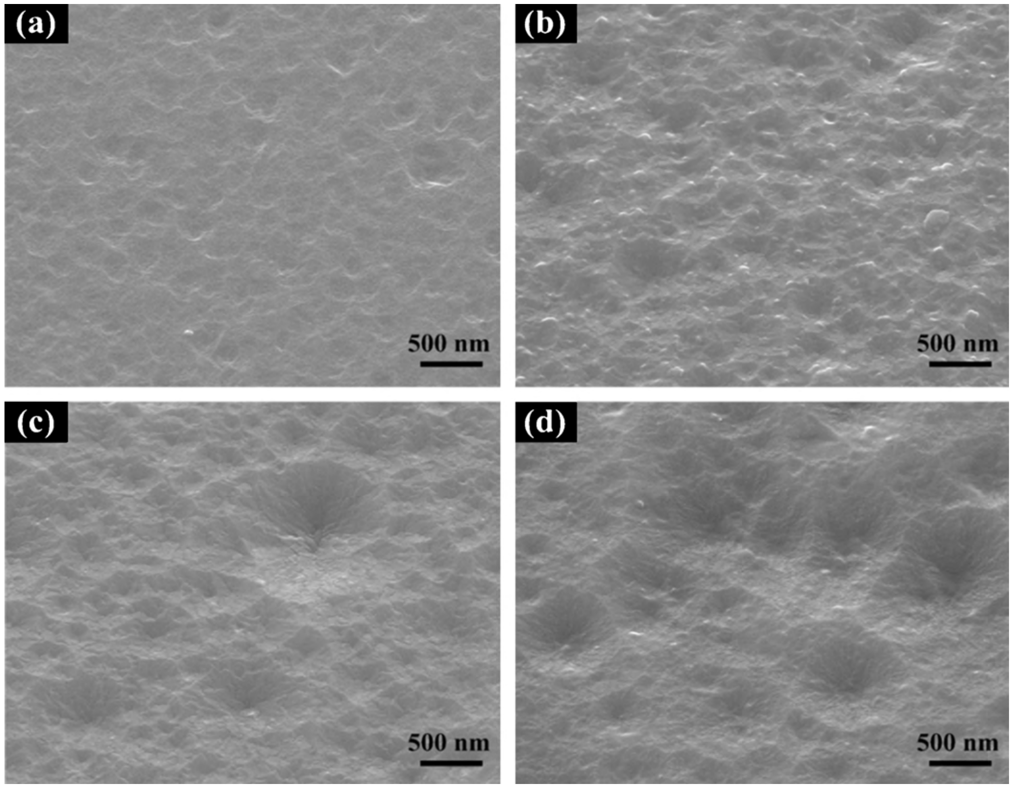

Fig. 1. SEM micrographs of textured AZO films as function of etch time in 0.5% HCl solution. (a) As-deposition; (b) etched for 15 s; (c) etched for 30 s and (d) etched for 45 s.

in diameter, $ZnO:Al_2O_3$ (2.0 wt.%). The sputtering chamber was pumped down to 6.65×10^{-6} Pa by cryogenic pump in which the AZO target was exposed to Ar plasma for 5 min to clean the target surface. Since the optoelectronic properties of the films are very sensitive to the deposition conditions, the fine-tuned optimal parameters turned to be that: substrates temperature keeping at 473 K, working distance between the target and the substrate was 5.5 cm, pulse frequency 10 kHz by modulating pulse sputter process parameters such as: power 150 W, working pressure 0.4 Pa and duty cycle 95%, respectively. All of the films used in the following wet-chemical etch have identical deposition parameters, if without further notification. After baseline calibration, the deposition rate and thickness were determined by α-step (Kosaka Laboratory Ltd., ET3000). The films morphology was characterized by FE-SEM (JEOL JSM 7000F) and atomic force microscope (AFM, Q-Scope 350). X-ray diffraction (XRD, Cu Kα, λ = 1.54052 Å, Shimadzu XD-6000) was used to analyze the crystalline structure of the deposited film. A typical θ–2θ scan by Brag–Brentano geometry gives valuable information in both the crystallinity and grain size of the deposited thin films [13,14,17,18]. The intensity of XRD patterns has been normalized to the film thickness as the absorption depth of X-ray was considered. The electrical properties of the films were examined using Hall-effect measurements (ECOPIA HMS-2000). Only the films with lowest resistivity and optical transmittance greater than 78% in every batch were choose for further investigation. Quantitatively, the light scattering can be evaluated by the so-called haze value, i.e. the ratio of diffuse to total light transmission as defined by Eq. (1).

$$\text{Haze} = \frac{T_{\text{diffuse}}}{T_{\text{total}}} \tag{1}$$

$$T_{\text{total}} = T_{\text{diffuse}} + T_{\text{specular}} \tag{2}$$

The total transmittance (T_{total}) and specular transmittance (T_{specular}) defined in Eq. (2) was measured by the angle-adjustable and multifunctional optical characterization system (Hong-Ming MFS-630) with wavelength 400–800 nm. Wet-chemical etching experiments were conducted at 300 K and compared separately in three different etching solutions: The etch time was: (1) 0.5% HCl_{aq} for 15, 30 and 45 s, (2) 5% oxalic acid (HOOC–COOH) solution for 75, 150 and 225 s, and (3) 33% $KOH_{aq.}$ for 45, 90 and 135 s which corresponding to film thickness of 800 (initial), 700, 600 and 500 nm, respectively.

3. Results and discussion

3.1. Etched in 0.5% HCl solution

We developed the surface morphology of AZO films which etched in 0.5% $HCl_{(aq)}$ at 300 K with different etch time. Fig. 1 shows the SEM images of the as-deposited films (a) and after different etching (b–d). The tilt angles for the SEM observation are ~40° to the horizontal. The as-deposited film is quite smooth as a whole with typical root-mean-square roughness, δ_{rms} less than 3 nm as measured by AFM. In addition, wet-chemical etching in dilute hydrochloric acid leads to a rough surface with regularly distributed craters typically with lateral feature size of 200–300 nm which was characteristic of the anisotropic etch behavior for all the etching time. In our system, the surface topography of AZO films etching in dilute hydrochloric acid is generally applicable by applying the Berginski's description [12] in which there is three different topography of texture-etched AZO as function of target alumina concentration (TAC) and substrate temperature (T_{sub}). The as-deposited AZO films in our study comprise a compact smooth topography with a small δ_{rms} value of 2.7 nm. For those slightly texturing surfaces as shown in Fig. 1b, a rough surface with a δ_{rms} value of 21.3 nm is developed in Fig. 2b. The topography of this film belongs to the type I surface by Berginski's definition. This result is somewhat contradict to what is predicted by Berginski under the