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Textured surface structures formed using new techniques on transparent conducting Al-doped zinc oxide films prepared by magnetron sputtering

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ABSTRACT

Surface-textured Al-doped ZnO (AZO) films formed using two new techniques based on magnetron sputtering deposition were developed by optimizing the light scattering properties to be suitable for transparent electrode applications in thin-film silicon solar cells. Scrambled egg-like surface-textured AZO films were prepared using a new texture formation technique that post-etched pyramidal surface-textured AZO films prepared under deposition conditions suppressing c-axis orientation. In addition, double surface-textured AZO films were prepared using another new texture formation technique that completely removed, by post-etching, the pyramidal surface-textured AZO films previously prepared onto the initially deposited low resistivity AZO films; simultaneously, the surface of the low resistivity films was slightly etched. However, the obtained very high haze value in the range from the near ultraviolet to visible light in the scrambled egg-like surface-textured AZO films did not contribute significantly to the obtainable photovoltaic properties in the solar cells fabricated using the films. Significant light scattering properties as well as a low sheet resistance could be achieved in the double surface-textured AZO films. In addition, a significant improvement of external quantum efficiency in the range from the near ultraviolet to visible light was achieved in superstrate-type n-i-p μc-Si:H solar cells fabricated using a double surface-textured AZO film prepared under optimized conditions as the transparent electrode.

1. Introduction

Recently, transparent and conductive impurity-doped ZnO thin films have attracted much interest for transparent electrode applications in thin-film $CuIn_{1-X}Ga_XSe_2$ and Si solar cells [1–20]. For impurity-doped ZnO thin films to be suitable for transparent electrode applications in thin-film Si solar cells, the textured surface structure formed on the films must induce a significant scattering of incident sunlight. As an example, pyramidal texture surface structures were formed by post-etching c-axis oriented impurity-doped ZnO films deposited by magnetron sputtering deposition (MSD) [4–20]. In addition, crater-like texture structures were formed during the crystal growth of films deposited by direct current MSD (dc-MSD) or low-pressure metalorganic chemical vapor deposition under conditions suppressing c-axis orientation [1,21–24]. It has been reported recently that a doubly textured surface structure formed on impurity-doped ZnO thin films can effectively scatter the incident visible and near-infrared light [17–19]. In addition, we have recently reported that a textured surface structure with larger crater diameters formed by extensively post-etching c-axis oriented impurity-doped ZnO films deposited by radio frequency power superimposed dc-MSD (rf + dc-MSD) can effectively scatter the incident visible and near-infrared light [17–19]. Thus, the development of transparent conducting impurity-doped ZnO thin films that would be appropriate for applications as transparent electrodes in thin-film Si solar cells will necessarily involve investigating the deposition conditions and methods used in MSD [25–28] as well as using new formation techniques.

In this paper, we describe the light scattering properties in surface-textured Al-doped ZnO (AZO) films formed using new two techniques based on MSD. In addition, the suitability of the surface-textured AZO films formed for transparent electrode applications was evaluated by fabricating superstrate-type n-i-p hydrogenated microcrystalline silicon (μc-Si:H) solar cells.

2. Experimental

The transparent conductive AZO films were prepared on glass (OA-10, Nippon Electric Glass Co., Ltd.) substrates by dc-MSD and rf + dc-MSD methods, using different magnetron sputtering apparatuses with appropriate oxide targets [25,28]. Commercially available high-density-sintered AZO targets prepared with an Al_2O_3 content of 2 wt.% were used as the targets. We used two surface texture formation techniques: (a) post-etching pyramidal surface-textured AZO films that had been deposited by MSD directly onto glass substrates under conditions suppressing c-axis orientation and (b) post-etching pyramidal

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surface-textured AZO films that had been deposited by dc-MSD under conditions suppressing c-axis orientation onto c-axis oriented AZO films deposited by either dc-MSD or rf + dc-MSD (onto glass substrates), as shown in Fig. 1. The deposition by dc-MSD under conditions suppressing c-axis orientation was carried out by controlling the sputter Ar gas pressure at a substrate temperature of 350 °C, with the films then heat treated in a H_2 gas atmosphere for 30 min. C-axis oriented AZO films that exhibited a low resistivity on the order of 10^{-4} Ω cm were prepared at an Ar sputter gas pressure of 0.6 Pa and a substrate temperature of 350 °C by dc-MSD or 0.2 Pa and 200 °C by rf + dc-MSD. The deposition conditions in these MSD methods are shown in Table 1. The post-etching was always carried out using a wet-chemical etching in a 0.1% HCl solution at 25 °C [25,26]. Subsequently, observations of the surface morphology and measurements of the optical transmittance and the diffusive component of the surface-textured thin films were performed using a scanning electron microscopy (SEM) and spectrophotometer (Hitachi U-4100), respectively. Film thickness was measured using a conventional surface roughness detector with stylus (Tokyo Seimitsu Surfcom MD-S69 A). The electrical properties were measured using the van der Pauw method (Accent HL-5500PC). To evaluate the suitability of the light scattering characteristics, superstrate-type single-junction silicon solar cells were fabricated on surface-textured AZO films formed by using the above techniques [17,29,30]. The μc-Si:H and hydrogenated nanocrystalline silicon oxide (nc-SiO_x:H) films were deposited by conventional plasma-enhanced chemical vapor deposition (PECVD) [29,30]. The photovoltaic properties of the solar cells were evaluated under AM1.5G solar illumination (100 mW/cm^2) at 25 °C.

Table 1
Deposition conditions of dc-MSD and rf + dc-MSD.

(a) Direct current (dc)-MSD	
Target	AZO (Al_2O_3 2 wt.%) (150 mm ϕ)
Sputter gas	Ar
Gas pressure (Pa)	0.6–12
Temperature (°C)	350
dc Power (W)	160
Film thickness (μm)	1–3.8
(b) Radio frequency (rf)+dc-MSD	
Target	AZO (Al_2O_3 2 wt.%) (127 mm × 275 mm)
Sputter gas	Ar
Gas pressure (Pa)	0.2
Temperature (°C)	200
dc Power (W)	570
rf (13.56 MHz) Power (W)	700
Film thickness (μm)	1

3. Results and discussion

3.1. Formation by post-etching pyramidal surface-textured films

To obtain surface-textured AZO films exhibiting a large haze value over the range from near ultraviolet to near infrared light, we used a new formation technique that post-etched pyramidal surface-textured AZO films prepared by dc-MSD, as shown in Fig. 1(a). The pyramidal surface-textured AZO films were formed during the crystal growth of AZO films prepared by dc-MSD under deposition conditions that suppressed c-axis orientation, based on our previous report [22,23].

Fig. 2 shows the wavelength dependence of haze value as a function of the sputter gas pressure for as-deposited (dashed lines) and post-etched (solid lines) AZO films prepared by dc-MSD at a substrate temperature of 350 °C with a thickness of 3.5 μm. The surface-textured AZO films formed by post-etching as-deposited AZO films exhibited a haze value that clearly increased as the sputter gas pressure was increased. The post-wet-chemical etching (in a 0.1% HCl solution at 25 °C) was carried out to produce an AZO film thickness of approximately 1 μm. The obtained etching rate in the post-etching was strongly dependent on the sputter gas pressure, in particular, increasing dramatically as the pressure was increased from approximately 3 to 9 Pa, as shown in Fig. 3.

Examinations confirmed that as-deposited AZO films prepared with a thickness of approximately 1 μm at a sputter gas pressure above approximately 6 Pa exhibited a pyramidal textured surface structure [22,23]. In addition, the obtained resistivity in as-deposited AZO films increased significantly as the pressure was increased from approximately 3 to 6 Pa, even after being post-annealed in a H_2 gas atmosphere.

Consequently, the sheet resistance in post-etched AZO films (thickness of 1 μm) significantly increased when using films that had a pyramidal surface-texture resulting from a deposition at or above a pressure about 3 Pa, as shown in Fig. 3. In addition, the obtained haze value in these 1-μm-thick AZO films reached the maximum value of 100% at wavelengths shorter than approximately 800 nm; that is, the incident light was completely scattered by the post-etched AZO films. In contrast, the post-etching haze value did not significantly increase for AZO films deposited with a pressure up to approximately 3 Pa.

SEM images of typical textured surface structures formed by etching the as-deposited AZO films prepared at 0.6, 6 and 12 Pa are shown in Fig. 4. The observed rough-textured surface for post-etched AZO films prepared at a pressure above approximately 6 Pa features a scrambled egg–like structure with an average texture size larger than the pre-etching pyramidal shapes. In contrast, the surface of AZO films formed by post-etching the as-deposited AZO films prepared at a pressure below approximately 6 Pa exhibited a crater-like texture structure. Note that the scrambled egg–like texture structure was formed with a higher etching rate than that of the crater-like texture structure, as seen in Fig. 3. Thus, the increase in haze value obtained in post-etched

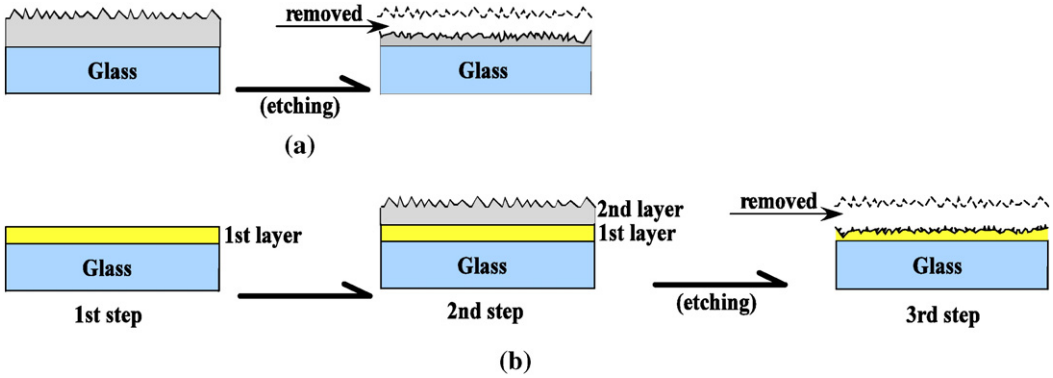

Fig. 1. Schematic diagrams (pre- and post-etching) of two surface texture formation techniques: (a) post-etching pyramidal surface-textured AZO films that had been deposited by dc-MSD under conditions suppressing c-axis orientation and (b) post-etching pyramidal surface-textured AZO films that had been deposited by dc-MSD under conditions suppressing c-axis orientation onto c-axis oriented AZO films deposited by either dc-MSD or rf + dc-MSD.