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Improvement of haze ratio of DC (direct current)-sputtered ZnO:Al thin films through HF (hydrofluoric acid) vapor texturing

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ABSTRACT

The textured ZnO:Al films are used to enhance light trapping in thin film solar cells. The wet etch process is used to texture ZnO:Al films by dipping in diluted acidic solutions such as HCl (hydrogen chloride acid) or HF (hydrofluoric acid). During this process, the acidic solution can damage the glass substrate, which could then be difficult to apply for the inline mass production process since this process needs to be performed outside the chamber. In this paper we report a new technique to control the surface morphology of DC-sputtered ZnO:Al films. The ZnO:Al films are textured with vaporized HF formed by mixing the HF with an H_2SiO_3 solution. We achieved a high haze value of 74.6% at a 540 nm wavelength by increasing the etching time and HF concentration. A haze value of about 58% was achieved at a 800 nm wavelength when vapor texturing was used. The ZnO:Al film texture by HCl had a haze ratio of about 9.5% at 800 nm and less than 40% at 540 nm. In addition to a low haze ratio, in the texturing by HCl it was very difficult to control etching and to keep reproducibility due to its very fast etching speed.

1. Introduction

Al-doped ZnO (ZnO:Al) thin films are one of the promising TCO (transparent conductive oxide) films which can be applied to thin film Si solar cells. Moreover, as it is very strong against hydrogen plasma, it can be adopted to microcrystalline Si solar cells (μc-Si:H) [1,2].

The sputtered ZnO:Al films deposited in the conditions of low pressure and high temperature are more compact and dense than those deposited at relative high pressure and low temperature. The sputtered ZnO:Al films are usually textured by diluted HCl (hydrogen chloride acid) solution (0.5–1 Vol%) despite the low etching efficiency [4]. It is well known that the surface morphology of the ZnO:Al films etched by HCl solution strongly depends on the film properties which are determined by the deposition conditions such as pressure and temperature [5]. Although these films can be etched efficiently in the HF (hydrofluoric acid) solution [3], the surface of the films textured by HF solution has sharp and small structures, leading to a low haze ratio. Furthermore, the surface of the glass substrate might be damaged by HF during the wet etching process.

In the present work, we investigated a new vapor texturing technique to control the surface morphology and improve the haze ratio of the sputtered ZnO:Al. The HF vapor generated by the reaction of HF and silica hydrous gel (H_2SiO_3) solutions was used to texture the sputtered ZnO:Al films. It effectively etched only one side where the ZnO:Al film was deposited. The surface of the ZnO:Al textured by the vapor had pillar-like irregular and sharp structures compared to that of the films textured typically and the haze ratio increased dramatically for both long and short wavelengths.

2. Experimental

ZnO:Al (Al_2O_3 2 wt.% doped) films were deposited on the corning glass by a DC (direct current) magnetron sputtering system. The deposition temperature, argon gas flow rate, working pressure, power density, substrate rotation, the inter electrode distance between the target and substrate, and the thickness of ZnO:Al films during sputtering were fixed at 267 °C, 15 sccm, 2 mtorr, 2.74 W/cm^2, 5 rpm, and 13.6 cm and 1 μm, respectively. Prior to deposition,

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Table 1
Symbolization of samples according to HF concentration and etching time.

	A	B	C	D	E
HF concentration [%]	40	40	45	45	50
Etching time [sec]	60	120	120	180	180

glass substrates were cleaned ultrasonically in acetone and IPA (isopropyl alcohol) for 10 min to remove surface impurities. The substrates were finally rinsed with DI (deionized) water, and dried in high purity N_2 (nitrogen) gas. Initially, the sputtering chamber was evacuated to a base pressure of 1×10^{-6} Torr. Pre-sputtering was performed for 10 min to remove target surface contamination. High purity (99.99%) Ar gas was introduced to the chamber as the carrier gas and deposition was performed in an Ar ambient controlled by a MFC (mass flow controller).

The ZnO:Al films were textured using the vaporized HF by a mixture of HF and H_2SiO_3 solutions. The experiment configuration for HF vapor texturing of ZnO:Al films was based on the published literature [6]. During vapor texturing, the H_2SiO_3 solution was fed into the HF acid solution every 30 s to avoid abrupt reaction that resulted in a non-uniform surface. We fabricated the textured ZnO:Al film samples from A to E with different etching times and HF concentrations. Table 1 shows the conditions of HF concentration and etching time for each sample.

For comparison, the ZnO:Al film was also textured with HCl solution. The concentration of HCl solution was 0.5% and the etching time was continued for 35 s. Transmittance measurements of ZnO:Al films were performed using UV–VIS spectroscopy before texturing (Model: SCINCO S-3100). The total and diffused transmittances after texturing were measured using the integrating sphere mode to obtain the haze value of the films by a QE (quantum efficiency) measurement system (Model: QEX10, PV Measurements, Inc.,). The surface morphology of the films was investigated by FE-SEM (field emission scanning electron microscopy) (Model: JMS-7600F, JEOL). The surface roughness was measured using AFM (atomic force microscopy).

3. Results and discussion

HF vapor texturing for ZnO:Al films was carried out with varying etching times and HF concentrations at room temperature using a

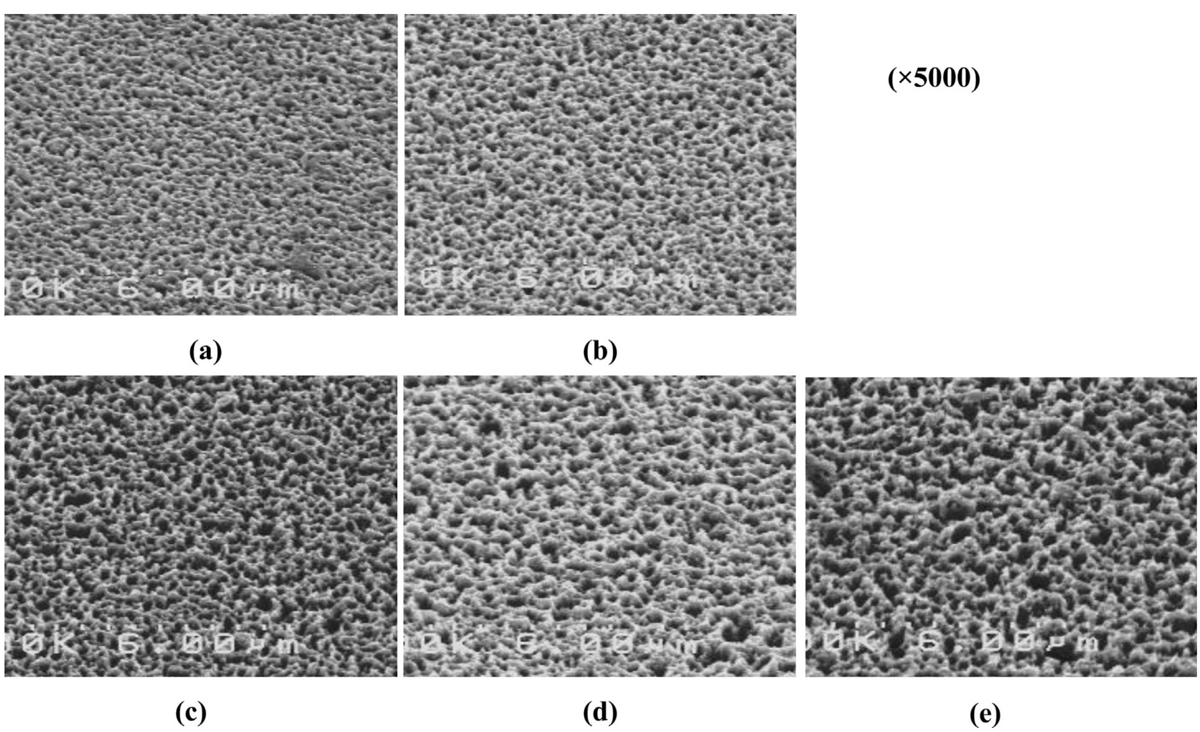

Fig. 1. Surface images of ZnO:Al films after HF vapor texturing under different conditions by FE-SEM. (a) sample A, (b) sample B, (c) sample C, (d) sample D, and (e) sample E).

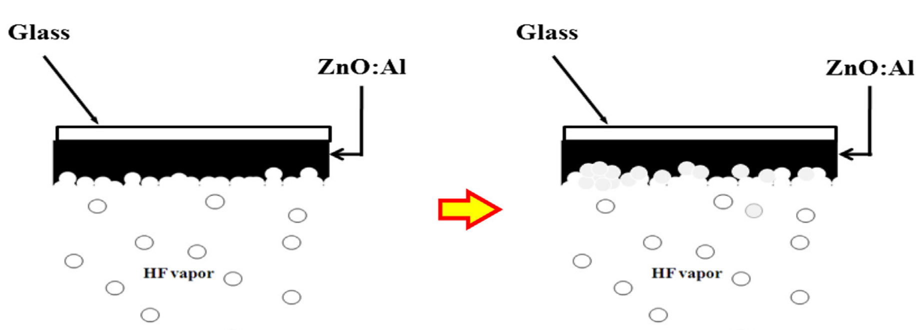

Fig. 2. The schematic diagram of vapor texturing process.