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Nanoroughness control of Al-Doped ZnO for high efficiency Si thin-film solar cells

Seung-Yoon Lee [a, b], Taehyun Hwang [b], Sangheon Lee [b], Woojin Lee [b], Byungho Lee [b], Jinhyun Kim [b], Soohyun Kim [a], Hyun Lee [a], Heon-Min Lee [a], Byungwoo Park [b, *]

[a] LG Electronics Advanced Research Institute, Seoul, 137-724, South Korea
[b] WCU Hybrid Materials Program, Department of Materials Science and Engineering, Research Institute of Advanced Materials, Seoul National University, Seoul, 151-744, South Korea

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ABSTRACT

The Al-doped ZnO (ZnO:Al) front transparent conducting oxide (TCO) for high efficiency Si thin-film solar cell has been developed using RF magnetron sputtering deposition and chemical wet etching. Microscopic surface roughness of the as-deposited ZnO:Al film estimated by spectroscopic ellipsometry is closely related to the compactness of the TCO film, and shown to be a straightforward and powerful tool to optimize the deposition conditions for the proper post-etched surface morphology. Wet-etching time is adjusted to form the U-shaped craters on the surface of the ZnO:Al film without sharp etch pits that can cause the crack-like defects in the overgrown microcrystalline Si-absorbing layers, and deteriorate the V_{oc} and *FF* of the Si thin-film solar cells. That is to say, the nanoroughness control of the as-deposited TCO film with proper chemical etching is the key optimization factor for the efficiency of the solar cell. The *a*-Si:H/*a*-SiGe:H/μc-Si:H triple junction Si thin-film solar cells grown on the optimized ZnO:Al front TCO with anti-reflection coatings show higher than 14% conversion efficiency.

1. Introduction

Light management technologies for more light absorption have been intensively adopted in the Si thin-film solar cells, and transparent conductive oxide (TCO) front contact has one of the most important roles amongst them [1–7]. Aluminum doped zinc oxide (ZnO:Al) is a representative front TCO material, and has been researched significantly for the Si thin-film solar cells [8–13]. For the application of the front contact for the Si thin-film solar cells, ZnO:Al film should have both high optical transparency and haze level throughout the wide optical spectrum from visible to near infrared (NIR) region, and should also have proper sheet resistance of ~10 Ω/□ (depending on the module design). In order to satisfy these requirements, carrier mobility of the ZnO:Al film should be improved as high as possible, and surface morphology after wet etching should have uniform craters with approximately 1–2 μm lateral size to effectively scatter incident photons into the absorbing Si layers [1,2,8–10].

It has been proposed that the compactness of the deposited film is the key factor of the ZnO:Al film to satisfy both the high carrier mobility and the proper etched surface morphology with large craters [14,15]. Kluth et al. [14] showed that lower Ar pressure and higher temperature led to the formation of more compact nanostructures of the ZnO:Al films due to the enhanced mean free path and thermal energy of the incident adatoms, and hence resulted in both better conductivity and larger crater size. Hüpkes et al. [15] proposed that more compact TCO film means lower grain-boundary interfacial energies in which wet etching causes reduced crater densities (large crater sizes).

Another role of the front TCO is that it is a substrate for the growth of microcrystalline Si (μc-Si) absorption layer. There have been several researches in which the pyramidal-shaped rough surfaces can lead to crack-like defects in the over-grown μc-Si layers, and these defects deteriorate both the performance and stability of the Si thin-film solar cells [16,17]. Wet etching of the ZnO:Al film is known to be beneficial for the generation of crater-shaped surface morphologies.

In this article, process optimization of the ZnO:Al front TCO for the high efficiency Si thin-film solar cell was established in terms of the nanoroughness control of both the as-deposited and wet-

* Corresponding author.
E-mail address: byungwoo@snu.ac.kr (B. Park).

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etched films. At first, minimization of the microscopic surface roughness of the as-deposited compact ZnO:Al films, estimated by the straightforward spectroscopic ellipsometry, was confirmed to be a powerful tool to optimize the TCO deposition for the best Si thin-film solar cell performance. Then, wet-etching time was adjusted to form the U-shaped craters without sharp etch pits. Although it is not as severe as in the ZnO:B front TCO which have large pyramidal surface morphologies [16,17], occasional etch pits formed in the ZnO:Al front TCOs were shown to have detrimental effects on the performance of the solar cells. The *a*-Si:H/*a*-SiGe:H/*μc*-Si:H triple junction Si thin-film solar cells grown on the optimized ZnO:Al front TCO with anti-reflection coatings exhibited higher than 14% conversion efficiency.

2. Experimental procedure

The ZnO:Al films were deposited on Corning 1737 glass by a RF magnetron sputtering system using ZnO:Al_2O_3 target (with 0.5 wt. % Al_2O_3) at the deposition temperature of 200 °C. The RF sputtering power and target-to-substrate distance were adjusted to obtain both the minimum resistivity and uniformity of the ZnO:Al film. The Ar pressure during deposition was varied from 0.7 to 1.9 mTorr, in which the electrical resistivity was minimized. The electrical resistivity, mobility, and carrier concentration of the films were measured by the 4-point probe and Hall measurement system (BIO-RAD HL5500PC).

The film thickness and surface nanoroughness were estimated by a spectroscopic ellipsometry (J. A. Woollam M2000-U) with the Tauc-Lorentz model [18]. The thin-film structure was modeled as a surface roughness layer/ZnO:Al/glass stack, as shown in the inset of Fig. 1. Microscopic surface roughness was considered as a virtual layer including 50% ZnO:Al (50% void), and its real and imaginary dielectric constants were determined by the Bruggeman effective medium approximation (EMA) [19]. The modeling with the fitting process was supported by the software “VASE” (J. A. Woollam Co.).

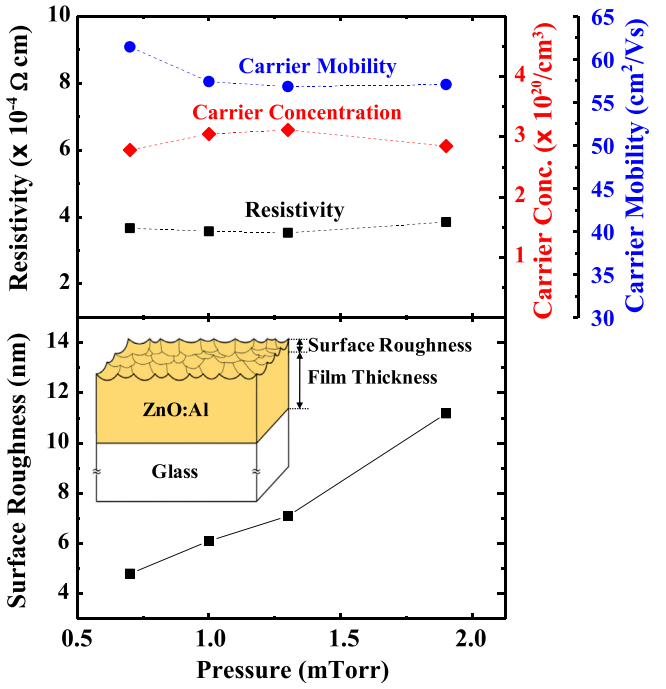

Fig. 1. For the as-deposited ZnO:Al (before the chemical etching), the resistivity, carrier concentration, and mobility (upper), and the microscopic surface roughness estimated by the spectroscopic ellipsometry (lower) in terms of the deposition pressure.

To obtain a textured surface, wet etching was carried out with the mixture of 0.5% diluted hydrochloric (HCl) acqueous solution and oxalic acid ($C_2H_2O_4$). Etching time was varied for the best haze level. The textured surface morphology was observed by scanning electron microscopy (SEM: JEOL JSM-6700F) and transmission electron microscopy (TEM: Philips CM20T/STEM). Transmittance (*T*) was obtained in the range from 350 to 1100 nm by spectrophotometer (Varian Cary5000), and haze values were evaluated with the ratio of the diffused transmittance over the total integrated transmittance. During the transmittance measurement, index matching liquid (CH_2I_2) with a cover glass was used to ensure that the diffuse transmittance induced by the textured TCO is not neglected.

The ZnO:Al films were utilized as front TCO substrates for single-junction *μc*-Si:H thin-film *p-i-n* solar cells and *a*-Si:H/*a*-SiGe:H/*μc*-Si:H triple-junction Si thin-film solar cells, prepared by plasma enhanced chemical vapor deposition (PECVD). For the triple junction solar cells, anti-reflecting coatings (ARCs) were prepared between ZnO:Al and glass, and between etched-ZnO:Al and PECVD-Si layers to reduce any reflection losses. Sputtered ZnO:Al/Ag/Al stack was used as a back reflecting electrode. Details of PECVD and cell preparation are described elsewhere [8,20,21]. Light *J-V* characterization of the solar cell was carried using a solar simulator (Wacom) at the standard test conditions (AM 1.5, 100 mW/cm^2 at 25°C).

3. Results and discussion

The electrical properties and surface roughness of the as-deposited ZnO:Al films as a function of Ar pressure (Fig. 1) are investigated for the high efficiency Si thin-film solar cells [12,13]. While the pressure dependence of the resistivity looks negligible, the microscopic surface roughness (as estimated by spectroscopic ellipsometry [19]) increases from ~5 to ~11 nm (before the chemical etching), which indicates the structural compactness (grain-boundary energies) for the chemical etching. As shown in Fig. 2 after wet etching, the ZnO:Al films deposited at 0.7 and 1.3 mTorr exhibit relatively large crater features (approximately 1–2 μm lateral size) than those of the 1.9-mTorr sample, consistent with the high haze levels. The haze ratio at the wavelength of 1000 nm is higher than ~30% which can induce enhanced light trapping and hence high photocurrent in Si thin-film solar cells [2]. From these results (Figs. 1 and 2), the microscopic surface roughness of the as-deposited ZnO:Al should be lower than ~10 nm by spectroscopic ellipsometry for the formation of a large surface texture after wet etching for the good light-trapping performance.

Wet-etching time of the front TCO was also optimized for the high-performance Si thin-film solar cell. The sheet resistance of the as-deposited film was ~3.2 Ω/□, and had quite uniform distribution (Fig. 3(a)). However, as etching proceeded, sheet resistance increased with broader distribution. Therefore, the etching time for the Si thin-film solar cell was chosen to be around 360–480 s in the consideration of sheet-resistance variations. Optically, transmittance trivially improved as etching time increased (Fig. 3(b)). However, the haze level kept similar from 360 to 600 s, indicating similar surface morphologies (upper SEM images in Fig. 4). The overall crater sizes are similar, corresponding to the similar haze levels. However, interestingly, the films etched for 360 and 480 s have etch pits with approximately 100–200 nm (lateral size), while the film etched for 600 s has reduced etch pits. Cross-sectional TEM images (Fig. 4) show crack-like defects in the overgrown *μc*-Si:H thin film along the TCO valley (especially with the 360-s etching time).

The etch-pit formation inside a crater can be explained by the etching mechanisms of sputter deposited polycrystalline ZnO films suggested by Hüpkes et al. [22]. Because the Zn-terminated (002)