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COMMUNICATION

Organic-acid texturing of transparent electrodes toward broadband light trapping in thin-film solar cells

Woojin Lee[a], Taehyun Hwang[a], Sangheon Lee[a], Seung-Yoon Lee[a], Joonhyeon Kang[a], Byungho Lee[a], Jinhyun Kim[a], Taeho Moon[b,*], Byungwoo Park[a,**]

[a]*WCU Hybrid Materials Program, Department of Materials Science and Engineering, and Research Institute of Advanced Materials, Seoul National University, Seoul 151-744, Republic of Korea*
[b]*Department of Materials Science and Engineering, Dankook University, Cheonan, Chungnam 330-714, Republic of Korea*

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Abstract
Regardless of the great importance of light trapping towards the breakthrough in the saturated photoconversion efficiencies of Si thin-film solar cells, much research on the surface texturing of transparent conducting oxides (TCOs) has been focused more on the nanostructural control during thin film growth. Herein, an organic acid for the surface texturing of ZnO:Al is introduced as an alternative to the conventional HCl etchant, making more efficient light scattering by TCO. The texturing behavior by oxalic acid is investigated in terms of vertical roughness and lateral correlation length, and a mass-transport model is developed to explain the etching evolution mechanisms. Texturing with oxalic acid results in superior light-scattering performance (by ~8% more haze at λ=1000 nm) with maintaining the transparency and resistance, compared to the etching with HCl. This fascinating behavior is explained by utilizing the light-scattering haze model with the extracted two surface parameters. Significantly, this straightforward and reproducible texturing tactic extends tunability for the desirable TCO morphology, enabling efficient light trapping, and therefore appears potentially applicable for the large-scale photovoltaic devices in industry.

*Corresponding author.
**Corresponding author.
E-mail addresses: taehom@dankook.ac.kr (T. Moon), byungwoo@snu.ac.kr (B. Park).

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Introduction

The key challenges for the solar-cell developments lie in the improvement of power-conversion efficiency and the reduction of fabrication cost [1-9]. For enhancing the power-conversion efficiency, much research has been focused on the light trapping to fully utilize broadband light with minimum optical losses [10-13]. Novel light-trapping methods using photonic structures or plasmonic effects are being continuously reported [14,15]. However, these methods require additional steps or materials inducing cost concerns, inevitably questioning the possibility of the large-scale manufacturability.

Especially for Si thin-film solar cells with a superstrate configuration, light-trapping capability is mainly determined by the surface texturing of the front TCO [16-20]. The scattering by the rough surface increases the optical-path lengths, leading to high absorption in the active semiconductor layers, thereby enhancing the power-conversion efficiency [21,22]. Compared to the conventional SnO_2:F, ZnO-based TCOs have received strong attention because of the large feature size from the surface texturing by wet-chemical etching, enabling more efficient light scattering [22-29].

The surface morphology by wet etching largely depends on the nanostructures of TCO. In manufacturing, however, the nanostructural control of TCO is pretty limited due to the consideration of electrical conductivity, transparency and high throughput. Therefore, the tunability of surface texturing by etching process for the synthesized TCO nanostructures offers a great merit widening the strategy of TCO development for superior light-scattering performance.

In this paper, an organic acid for the surface texturing of ZnO-based TCO is introduced as an alternative to the conventional HCl. The enhancement of light scattering by oxalic acid is demonstrated without any deterioration of transparency or resistance. We believe that the organic-acid texturing can be easily adopted into the manufacturing process via simple substitution of the wet etchant, which is a cost effective light-trapping technique toward high efficiency solar cells.

Experimental procedure

The ZnO:Al films with a thickness of 1.8 μm were deposited on glass substrates (Corning 1737) by RF magnetron sputtering using a ZnO:Al target (1 wt% Al_2O_3). Sputtering was performed at 400 °C under an Ar atmosphere with an operating pressure of 5 mTorr. The sheet resistance of ~11 Ω/□ was measured by 4-point probe. The as-deposited films were surface-textured by wet-chemical etching using oxalic acid (0.02 M) or HCl (0.5 vol%) at room temperature. The surface morphology and etched thickness of the textured films were obtained by scanning electron microscopy (SEM, JSM-6330F: JEOL), and the surface morphology was evaluated by atomic force microscopy (AFM, SPA-400: Seiko Instrument). The normal and total transmission spectra were obtained by a UV–vis spectrometer (Lambda 35: Perkin Elmer) equipped with an integrating sphere, and the haze was determined by the ratio of diffused to total transmittance ($T_{diffused}/T_{total}$).

Results and discussion

In Si thin-film solar cells, oxalic acid, as an alternative to the conventional HCl, makes a highly scatterable surface morphology of ZnO:Al by wet etching (Fig. 1(a)). Without sacrificing the electrical properties, the increase of optical paths within the absorber layers by multiple scattering can simply enhance the power-conversion efficiency. Here we discuss how organic acid texturing can induce the distinctive surface morphology, based on the statistically straightforward quantification of two surface parameters during the crater evolution. Also, superior light-scattering performance is facilely explained by utilizing the light-scattering haze model with the extracted two surface parameters. First of all, the textured morphology by oxalic acid and conventional HCl etching were compared by SEM (Figs. 1 (b) and (c)), confirming notably different crater profiles. Relatively large and smoothly-textured craters are clearly observed from oxalic acid. Smooth craters (i.e., low steepness) intuitively suggest that oxalic acid has the larger lateral etching rate compared to the vertical etching for the crater formation. More meaningful comparison of the crater morphologies between the two etchants is difficult by SEM imaging. Therefore, as we will discuss in detail later, two surface-roughness parameters are statistically determined for the crater morphologies.

Figures 1(d) and (e) shows the total transmittance and haze characteristics for the films textured by oxalic acid and HCl, respectively, at different etching times. The haze data are determined from the ratio of diffuse to total transmittance ($T_{diffused}/T_{total}$). Even though no significant differences in the total transmittances are observed, the haze values increase with the etching time due to the crater evolution. Interestingly, the textured ZnO:Al films by oxalic acid show higher haze over the whole wavelength range compared to those by HCl. Particularly at the long wavelength region, the haze increase becomes more significant. Electrical performance (sheet resistance) also changed by etching, therefore the performances of TCOs textured by different etchants should be considered in the aspects of both optical and electrical properties. Figure 1(f) shows haze (at λ=1000 nm) vs. sheet resistance for two systems. The clear trend showing superior light-scattering performance by oxalic acid is confirmed, and the absolute haze increase of ~8% is observed at the same sheet resistance.

Through AFM (Fig. 2(a)), the craters can be characterized by vertical roughness and lateral correlation length (lateral roughness) [30,31]. The vertical roughness σ_{rms} is given as follows:

$$\sigma_{rms}^2 = <z(x,y)^2> - <z(x,y)>^2, \quad (1)$$

where $z(x,y)$ is the surface-height distribution. The lateral correlation from rough surfaces can be easily obtained by the autocorrelation function [24-27]:

$$C(\tau_x,\tau_y) = \lim_{L_x,L_y\to\infty} \frac{1}{4L_xL_y\sigma_{rms}^2} \int_{-L_y}^{L_y} \int_{-L_x}^{L_x} z(x,y)z(x+\tau_x,y+\tau_y)dxdy, \quad (2)$$