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Controlling surface texture of sputtered ZnO:Al using different acidic single- or multi-step etches for applications in thin-film silicon solar cells

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ABSTRACT

Magnetron-sputtered ZnO:Al is often used as a front contact in thin-film silicon solar cells due to its transparent conductive oxide (TCO) properties and its ability to be texturized by chemical etch processes to introduce light trapping. The transparency, conductivity, and surface texture after etching depend strongly on the sputtering conditions. Consequently, the typical preparation method is to find the right balance in TCO properties and light scattering, leading to a very narrow sputtering parameter window. It is preferable to separate the electro-optical optimization from that of texturization to allow for a larger process window and improve ZnO:Al film properties further. This paper presents some methods of controlling the surface features using various mixtures of HF and HCl, and two-step etching processes in aqueous solutions of both. Results include methods for controlling the density of craters, texturizing compact ZnO:Al films, and fabricating novel modulated surfaces with more than one characteristic feature size. The two-step etch process enables the creation of good surface textures even on high-rate material that, via state-of-the-art HCl etching, tend to lead to poor solar cell performance.

Introduction

Aluminium-doped zinc oxide (ZnO:Al) films, prepared by magnetron sputtering and surface textured by chemical etching, form a promising TCO for use as a front contact in amorphous and microcrystalline silicon thin-film solar cells [1,2]. Cost-effective processes are required for industrial application, including high-rate deposition using a high discharge power from ceramic targets [3], reactive sputtering from metallic targets [4], or more effective target usage from tube rather than planar targets [5]. Sputtering and subsequently etching ZnO:Al thin-films allows for the separate optimization of TCO properties and etch features.

However, the density and shape of resultant craters depend strongly on the ZnO:Al sputtering conditions used [1-3,5-7], and the two process steps (sputtering and etching) are not independent of each other. Thus, the current state-of-the-art is to tailor the deposition conditions of ZnO:Al to optimize electrical, optical, and the resultant etch features simultaneously. The best solar cell performance is achieved using ZnO:Al front contacts sputtered at low rates with radio frequency excitation from relatively expensive planar ceramic targets [8]. The transfer of this approach to other especially industrially-relevant processes has proved difficult in the past, even though the transparency and conductivity of these ZnO:Al films are well suited for solar cell application. If, however, the electro-optical optimization could really be separated from the texturization optimization, ZnO:Al thin-films that are better suited for solar cell applications could be prepared and industrially-relevant processes could be applied easily.

"The best solar cell performance is achieved using ZnO:Al front contacts sputtered at low rates with radio frequency excitation from relatively expensive planar ceramic targets."

It was recently shown that optimization of the etch process can lead to slightly different surface textures [9] and our group revealed that hydrofluoric acid (HF) texturizes sputtered ZnO:Al differently from hydrochloric acid (HCl), exhibiting small jagged and large smooth craters, respectively [10]. In this paper, the different etching properties of HF and HCl are used to:

1. vary the crater density on a given ZnO:Al film;
2. effectively texturize a compact ZnO:Al film that texturizes poorly under state-of-the-art HCl etching; and
3. fabricate a modulated (more than one feature size) surface texture for additional light trapping [11].

Experimental

The polycrystalline ZnO:Al thin-films used in this work were sputtered under two different conditions and will be referred to as low- or high-rate ZnO:Al. In both cases, the ZnO:Al was deposited using an in-line sputtering system (VISS 300, Von Ardenne Anlagentechnik) onto a cleaned glass substrate (CG, Corning, Eagle XG). Low-rate ZnO:Al substrates, which exhibit uniform crater coverage after HCl etching, were deposited on CG by radio frequency (RF) magnetron sputtering from a planar ceramic target at 13.56MHz. The ceramic target consisted of ZnO with a dopant concentration of 1 w/w% Al_2O_3; deposition was performed at a temperature, pressure, and discharge power of 300°C, 0.1Pa, and 1.5kW, respectively. The deposition rate for these sputtering conditions is 6nm m/min [6]. Details on film properties are available elsewhere [6].

High-rate ZnO:Al substrates, which exhibit relatively flat surfaces with a few large craters after HCl etching, were deposited on CG by mid-frequency dual magnetron sputtering from rotating ceramic targets at 40kHz. The rotatable ceramic targets consisted of ZnO with a dopant concentration of 0.5 w/w% Al_2O_3; deposition was performed at a temperature, pressure, and discharge power of 350°C, 1.5Pa, and 14kW, respectively. The deposition rate for these sputtering conditions is 100nm m/min [12]. Details on the ZnO:Al film properties are available elsewhere [12].

Varying crater density

Low-rate deposited ZnO:Al thin-films were etched in mixtures of HF and HCl, where the HF concentration was held constant at 1 w/w%, while the HCl concentration was varied from 0 to 1 w/w% in 0.125 w/w% steps. Etching times were adjusted so that approximately 150nm of the originally 800nm-thick film was removed, as determined by a surface profiler (Dektak 3030, Veeco). Surfaces were subsequently characterized by scanning electron microscopy (SEM, Supra 55VP SmartSEMTM, Carl Zeiss).

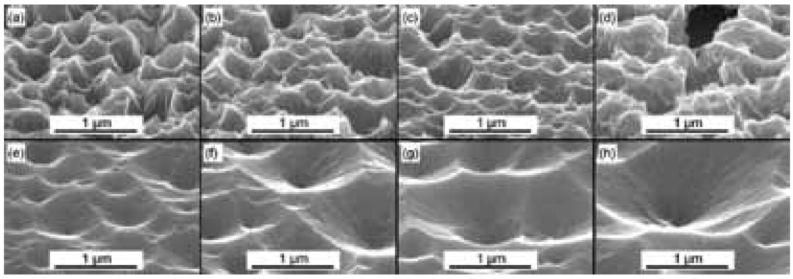

Figure 1. Low-rate ZnO:Al films etched in various mixtures of HF w/w%:HCl w/w%. Specifically, (a), (b), (c), (d), (e), (f), (g), and (h) were etched in 1:0, 1:0.25, 1:0.375, 1:0.5, 1:0.625, 1:0.75, 1:1, and 0:0.5, respectively.

Texturizing compact ZnO:Al films

High-rate deposited ZnO:Al thin-films were etched in 1 w/w% HF for 120 seconds. Following the HF etch, samples were etched in 0.5 w/w% HCl for 2, 4, 8, and 16 seconds. For reference, low- and high-rate ZnO:Al films were etched in 0.5 w/w% HCl for 40 and 50 seconds, respectively. The surface morphology was measured by atomic force microscopy (AFM, Nanostation 300, SIS), and the height and angular distributions were characterized using techniques described elsewhere [13]. Microcrystalline solar cells with a thickness of approximately 1.2µm were deposited by plasma-enhanced chemical vapour deposition (PECVD). Back contacts consisting of approximately 80nm of ZnO and 700nm of silver were deposited by RF sputtering and thermal evaporation, respectively. Test cells had an area of 1cm^2. The current density-voltage (I-V) characteristics of the solar cells were measured at 25°C under AM 1.5 illumination.

Fabricating modulated surfaces

Low-rate deposited ZnO:Al thin-films were etched in 0.5 w/w% HCl for 50 seconds. Following the HCl etch, samples etched in 1 w/w% HF for 5, 10, 20, or 40 seconds. Reference HCl- and HF-only surfaces were also made by etching in the respective solutions for 50 and 40 seconds. Thickness and morphology were determined by surface profiler and SEM, respectively. Reflection, total transmission, and diffuse transmission measurements were performed using an optical spectrometer with an integrating sphere (Lambda 950, Perkin Elmer). Diiodomethane was used for refractive index matching during total transmission and reflection measurements.

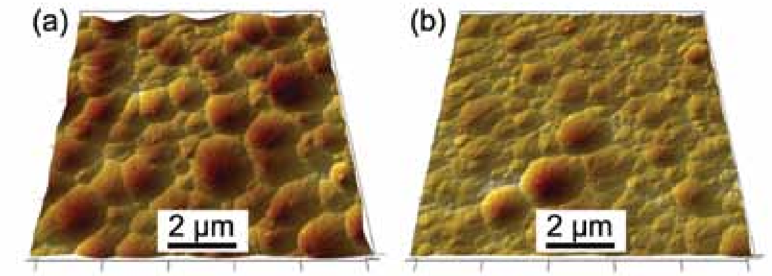

Figure 2. AFM images of (a) low-rate ZnO:Al etched in 0.5 w/w% HCl for 40 seconds; and (b) high-rate ZnO:Al etched in 0.5 w/w% HCl for 50 seconds.

Results and discussion

Varying crater density

Fig. 1 shows SEM images of the low-rate ZnO:Al films etched in various mixtures of HF and HCl. Notice that the feature sizes and shapes can be varied from large smooth craters of about 1-2µm in diameter as etched in HCl alone to small jagged craters of about 300nm in diameter as etched in HF alone. The transition, however, is not smooth and it appears that one etching process dominates the other. Specifically, Fig. 1 (b), (c), and (d) with HCl concentrations equal to or below 0.5 w/w% have features more similar to that of the HF etch alone as seen in Fig. 1 (a), while Fig. 1 (e), (f) and (g) with

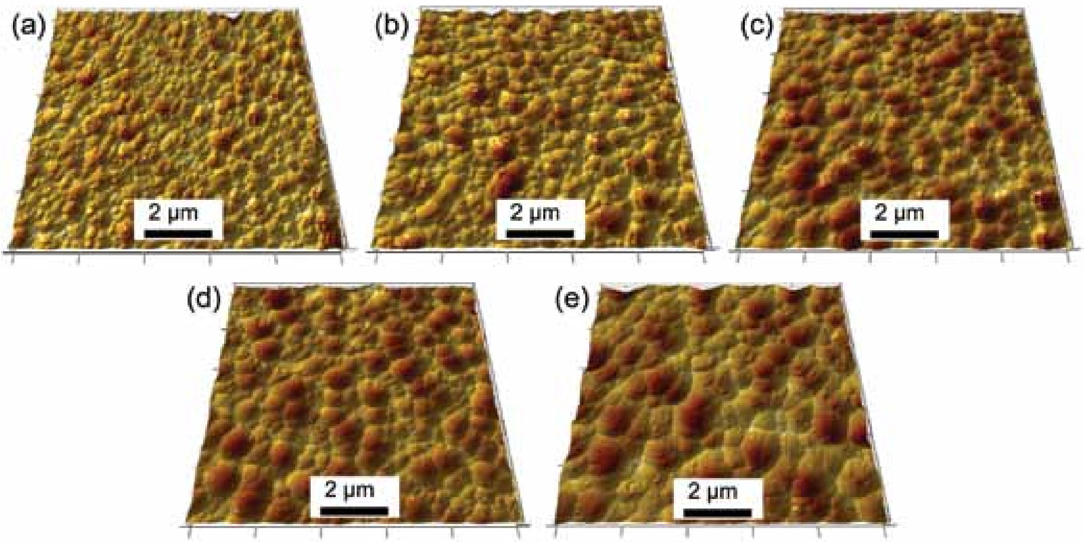

Figure 3. AFM images of high-rate ZnO:Al etched in 1 w/w% HF for 120 seconds then 0.5 w/w% HCl for (a) 0, (b) 2, (c) 4, (d) 8, and (e) 16 seconds.

HCl concentrations equal to or above 0.625 w/w% have features more similar to that of the HCl etch alone as seen in Fig. 1 (h).

The different etching behaviours of HF and HCl have been attributed to the different size and dissociation constants of the two acids [10]. HF with a smaller molecular size and much weaker dissociation constant is able to penetrate more grain boundaries before dissociating and etching [10]. By etching in mixtures of the two acids the density of craters can be somewhat controlled.

Texturizing compact ZnO:Al films

AFM images for the low-rate and high-rate reference etches in 0.5 w/w% HCl are shown in Fig. 2 (a) and (b), respectively. The low-rate deposited ZnO:Al exhibits homogeneous surface coverage with relatively large craters. This type of surface morphology has been shown to exhibit good light-trapping capabilities for microcrystalline solar cells [6]. The high-rate deposited ZnO:Al exhibits inhomogeneous texturization being mostly flat with a few large craters. Surfaces such as these exhibit low roughness [5,12], and poor light trapping due to their relatively flat nature.

AFM images of the high-rate ZnO:Al etched first in 1 w/w% HF for 120 seconds then 0.5 w/w% HCl for times between 0 and 16 seconds are shown in Fig. 3. The high-rate ZnO:Al etched only in HF is shown in Fig. 3 (a). Like the low-rate deposited ZnO:Al (Fig. 1 (a)), etching high-rate deposited ZnO:Al in HF leads to a higher density of craters [10]. AFM images of high-rate ZnO:Al etched in HF for 120 seconds followed by HCl for 2, 4, 8, and 16 seconds are shown in Fig. 3 (b), (c), (d), and (e), respectively. As the HCl etching time is increased, the diameter of the craters increases and the crater density decreases. After the longest HCl etching step (16 seconds, Fig. 3 (e)), relatively flat plateaus, like those observed on the high-rate deposited sample etched in only HCl (Fig. 2 (b)), begin to appear.

Height and angle distributions as calculated from the AFM images presented in Figs. 2 and 3 are given in Fig. 4. Median-centred height histograms, quantized into 10nm increments, are shown in Fig. 4 (a). Etching in only HCl yields broad and narrow distributions of feature heights for the low-rate (dashed black line) and high-rate (solid black line) deposited ZnO:Al substrates, respectively. The widths correspond to the different RMS roughness. Etching the high-rate ZnO:Al in only HF (red line) gives a slightly wider distribution of height values as compared to the HCl-only process (solid black line). The height distribution is widened further with the application of a second HCl-based etching step (orange, green, blue, and violet lines). Note, however, that the widest height distributions resulting from two-step etching are not as wide as the low-rate ZnO:Al reference. Thus, the RMS roughness and optical haze (diffuse transmission/total transmission) would remain smaller on these two-step textured surfaces than the low-rate HCl etch [14].

"As the HCl etching time is increased, the diameter of the craters increases and the crater density decreases."

Angular distributions of the surface segments quantized into one degree increments are shown in Fig. 4 (b). Etching in only HCl yields a broad distribution with a peak at 23° and a narrow distribution with a peak at 12° for the low- and high-rate deposited ZnO:Al substrates, respectively. Etching only in HF or the shortest additional HCl etching time (two seconds) yields sharp surface features as seen by the higher peak in angular distribution at 27° and 29°, respectively. Notice also that for these etches, a significant fraction of the surfaces is covered with very step angles (above 50°). For samples with a second etching step in HCl between 4 and 16 seconds, the angular distributions shift to a spectrum very similar to that of the low-rate ZnO:Al, with peak angular distributions between 20° and 24°. Like the low-rate ZnO:Al surface, there are close to zero very steep angles.

Microcrystalline silicon solar cells were deposited onto high-rate ZnO:Al etched in HCl, HF, and HF then HCl, as well as low-rate ZnO:Al etched in HCl. The average short-circuit current density (J_{sc}) of the five best cells on HCl texturized high- and low-rate ZnO:Al films were, respectively, 20.9 and 23.4mA/cm^2. Etching the high-rate ZnO:Al film in only HF increased average J_{sc} by 5% to 22.0mA/cm^2. Using a two-step etching process in HF then HCl increased the J_{sc} on the high-rate ZnO:Al by 11 % (as compared to the HCl etch) to 23.1mA/cm^2. Notice that the two-step etched high-rate ZnO:Al exhibits J_{sc} values almost as high as those observed on the low-rate ZnO:Al. The increase in J_{sc} directly increased the cell efficiency, and the cells on the two-step etched high-rate ZnO:Al rivalled those of the HCl etched low-rate substrate. Although the example given in this paper was made using ceramic targets, this process has also been successfully applied to reactively sputtered films [15] and industrial-type ZnO:Al on commercial float glass. From these results, we conclude that the two-step etching process is able to reliably produce surface texture with good light trapping on production-type sputter-deposited ZnO:Al films.

Fabricating modulated surfaces

SEM images of low-rate ZnO:Al textured with a single etching step in 0.5 w/w% HCl

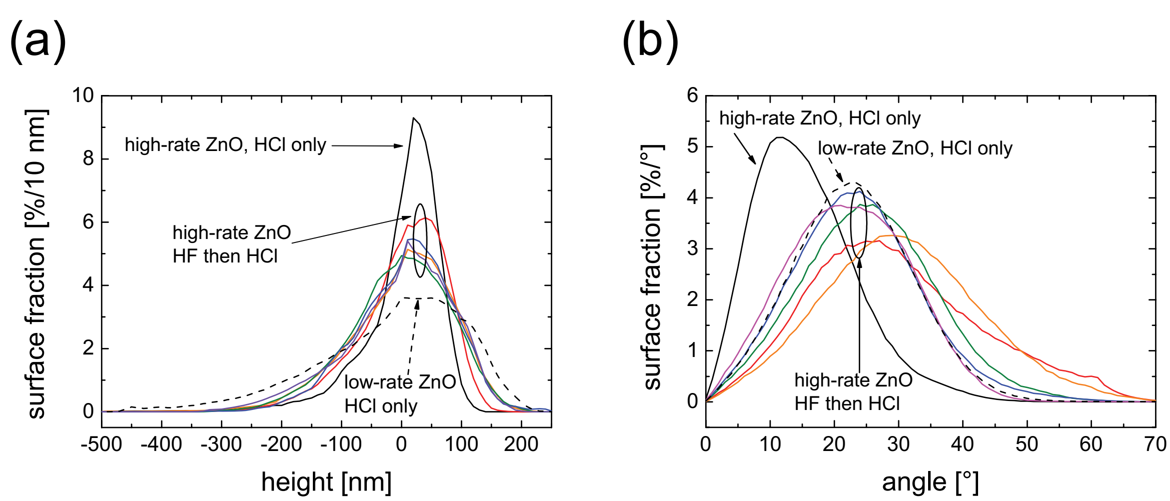

Figure 4. (a) Histograms of feature height in 10nm increments, and (b) surface angular distribution in one degree increments. The low-rate and high-rate reference surfaces are indicated by dashed and solid black lines, respectively. The 120 seconds HF etched followed by 0, 2, 4, 8, and 16 seconds of HCl etching are solid red, orange, green, blue, and violet lines, respectively.

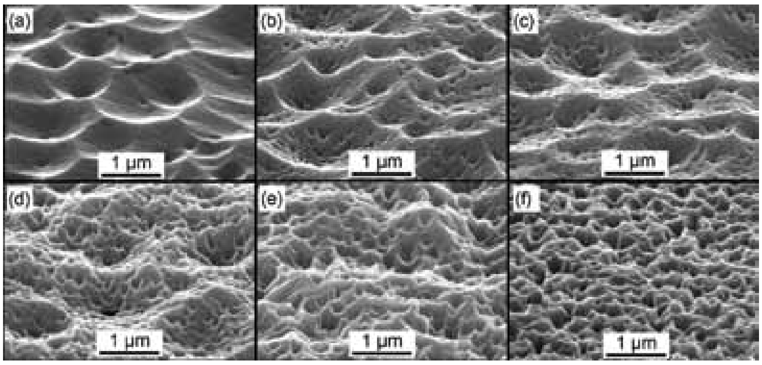

Figure 5. Low-rate ZnO:Al substrates etched in (a) 0.5 w/w% HCl for 50 seconds, 0.5 w/w% HCl for 50 seconds followed by 1 w/w% HF for (b) 5, (c) 10, (d) 20, and (e) 40 seconds, and (f) 1 w/w% HF for 40 seconds.

or 1 w/w% HF are shown in Fig. 5 (a) and (f), respectively. Fig. 5 (b-e) contain SEM images of modulated features etched into low-rate deposited ZnO:Al. The etching time for the first HCl-based etch was held constant at 50 seconds, while the second HF-based etch was varied; the 5, 10, 20, and 40 second etching times are shown in Fig. 5 (b), (c), (d), and (e), respectively. The first HCl-based etch yields large smooth craters, while the second HF-based etch introduces smaller jagged craters superimposed on the larger craters. As the duration of the second HF-based etch is increased, the small features deepen and the overall surface becomes more jagged.

The optical properties of the modulated and reference ZnO:Al samples are shown in Fig. 6. The total transmission, absorption, and reflection as a function of wavelength are shown in Fig. 6 (a). Transmission in the shorter wavelength region (400-600nm) is almost identical for the HCl-only and the modulated surfaces, while it is slightly reduced for the HF-only surface. In the longer wavelength region (700-1300nm), transmission generally increases with an increase in the duration of the second HF etching step. The only exception to this trend is the sample with a second HF etching time of 20 seconds, which exhibited higher total transmission than the sample with second HF etching step of 40 seconds. The HF-only etched surface also showed the lowest transmission values over this longer wavelength region. Since the reflection remained relatively constant, the absorption trends appeared inverse to those in total transmission.

"The first HCl-based etch yields large smooth craters, while the second HF-based etch introduces smaller jagged craters superimposed on the larger craters."

The haze measurements as a function of wavelength and etching method are shown in Fig. 6 (b). Like the total transmission, the haze generally increases with an increasing duration of the second HF-based etching step. Once again, the only exception was a second etching step of 20 seconds in HF, which had higher haze then that of 40 seconds. Like total transmission, the HF-only etch also showed the lowest haze values across the whole measured spectrum (400-1300nm), exhibiting an average value of 8%. The average haze value over the same range was 29 and 37% for the HCl-only and maximum modulated surface structures, respectively.

The increased absorption in the long and short wavelength regions by the ZnO:Al

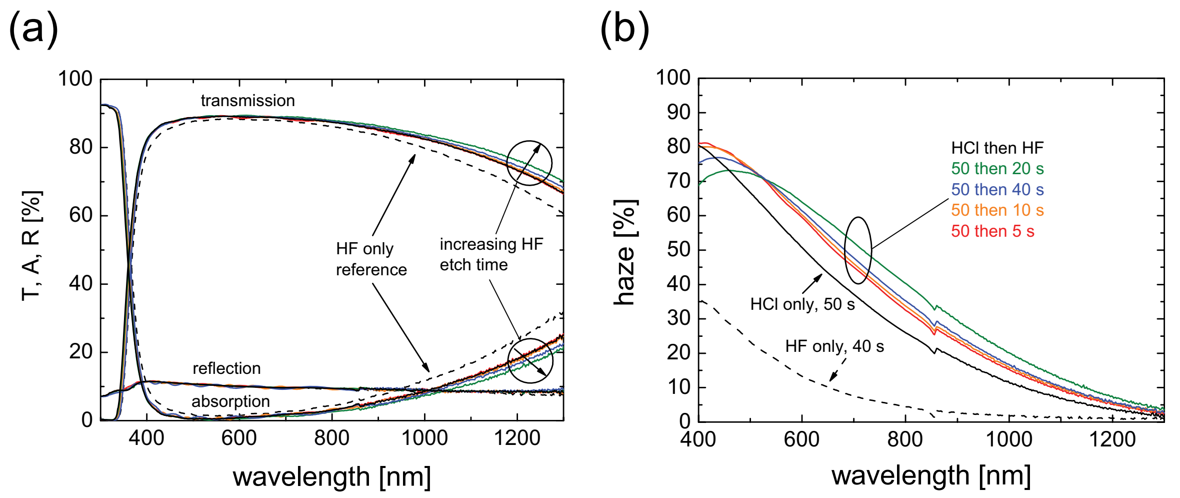

Figure 6. (a) Total transmission (T), absorption (A), reflection (R), and (b) haze as a function of wavelength for the various single and modulated etched surfaces.

sample etched only in HF is likely due to largest film thickness and thus largest free carrier absorption and steep angles causing strong internal light trapping, respectively. The decrease in absorption in the longer wavelength region with an increasing duration of the second HF-based etching step can be attributed to a decrease in film thickness, which was verified by surface profiler (with the 20-second HF modulated surface being thinnest).

The increase in haze observed from HF-only to HCl-only, and further with the modulated surfaces, is likely related to an increase in the ZnO:Al surface roughness [14]. The reduction in haze observed between the second HF-based etching step of 20 and 40 seconds is probably related to the loss of some of the underlying HCl-induced features. If allowed to progress too long (more than 20 seconds) the HF-induced features dominate and erase the HCl-induced features (see Fig. 5 (e)).

Conclusions and outlook

Using only different mixtures of and multiple etching steps in HF and HCl, we have demonstrated the ability to control the surface structures on sputtered ZnO:Al. Specifically, using various mixtures of HF:HCl, or two-step etching to create regular craters in HF and shaping them by HCl, the density of craters can be controlled. This may be especially applicable for surfaces that texturize poorly in HCl alone or amorphous silicon solar cells, where smaller feature sizes are desired. The two-step etching process was applied to high-rate ZnO:Al, which texturizes irregularly in HCl, and developed regular distribution of large craters. It closely mimics the surface texture of low-rate ZnO:Al. Solar cell prepared on a two-step texturized high-rate ZnO:Al showed similar light trapping and efficiencies as compared to a low-rate HCl textured surface.

Thus, this process is especially pertinent to industrial applications, where the deposition rates are high and common texturization methods are not ideal. This method provides a way to optimize the electro-optical properties and texture separately. Modulated surfaces were fabricated by etching low-rate ZnO:Al first in HCl then in HF. These surfaces have high haze and may be especially applicable in tandem solar cells, as they have both large and small surface features. Using a combination of these different approaches, it may be possible create modulated surfaces on the compact high-rate ZnO:Al films.

Acknowledgments

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