Novel etching method on high rate ZnO:Al thin films reactively
sputtered from dual tube metallic targets for silicon based solar cells

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Abstract

Highly transparent and conductive aluminum doped zinc oxide thin films (ZnO:Al) were reactively sputtered from metallic targets at high rate of up to 90 nm·m/min. For the application as transparent light scattering front contact in silicon thin film solar cells, a texture etching process is applied. Typically, it is difficult to achieve appropriate etch features in hydrochloric acid, as the deposition process must be tuned and the interrelation is not well understood. We introduce a novel two step etching method based on hydrofluoric acid. By tuning the etch parameters we varied the surface morphology and achieved a regular distribution of large craters with the feature size of 1-2 μm in diameter and about 250 nm in depth. Microcrystalline silicon single junction solar cells (μc-Si:H) and amorphous/microcrystalline (a-Si:H/μc-Si:H) tandem solar cells with high efficiency of up to 8.2% and 11.4%, respectively, were achieved with optimized ZnO:Al films as light scattering transparent front contact.

Key words: ZnO:Al films, chemical wet etching, surface structure, silicon thin-film solar cells
1. Introduction

High conversion efficiency silicon-based thin film solar cells strongly rely on light scattering typically introduced by rough TCO front contacts [1-4]. Sputter deposited and texture etched aluminum doped zinc oxide (ZnO:Al) films with optimized surface structures could supply a good light trapping effect to improve the short circuit current ($J_{sc}$) [5]. ZnO:Al films deposited at low growth rate from planar ceramic targets were successfully applied in silicon based thin films solar cells with high conversion efficiency. With the development of industry and demand for low cost solar modules, cost-effective preparation techniques are required. Some researchers focused on high deposition technologies like sputtering deposition with high discharge power from ceramic targets [5, 6] and reactive magnetron sputtering technologies from metallic targets [7-9]. Other groups focused on improvement of target utilization employing tube targets instead of traditional planar targets [10, 11]. However, after a chemical wet etching in HCl etching these cost-effective high growth rate ZnO:Al films showed poor light trapping due to relatively flat surface structures with a few large and shallow craters. Recently, Hüpkes et al. introduced a new two step etching method to modify the surface structures by the etch process rather than tuning the deposition process [12]. In this study, we employed this etching method on our high rate ZnO:Al films reactively sputtered from metallic tube targets. We studied the etching behavior, light scattering properties and surface structures of the rough ZnO:Al films. Optimized films with high transparency and high conductivity were applied in μc-Si:H solar cells and a-Si:H/μc-Si:H tandem solar cells as light scattering front contacts.

2. Experimental details

ZnO:Al films were reactively sputtered on glass substrates (Corning, Eagle XG) in a vertical in-line sputtering system (VISS 300, by von Ardenne Anlagentechnik, Dresden, Germany). The system is typically under a base pressure of $6 \times 10^{-4}$ Pa. Rotatable dual magnetron cathodes (RDM) with metallic Zn:Al tube targets (0.5 wt%) were operated at discharge power of 10 kW with mid-frequency excitation of 40 kHz to achieve a growth rate of up to 90 nm/min. The process pressure, Argon gas flow and substrate temperature were respectively 0.96 Pa, 200 sccm and 350°C as measured via heat radiation prior to deposition. The working point was controlled via plasma emission monitor (PEM) in the transition mode at PEM intensity of 35 % and average oxygen gas flow of 160 sccm. More details on PEM control can be found in literature [9, 13]. A related paper provides more detailed information on ZnO:Al film properties [14]. As-grown ZnO:Al films with low resistivity of less than $4 \times 10^{-4}$ Ω·cm were used for etching experiments followed in this study. ZnO:Al films were etched in aqueous solutions of diluted hydrofluoric (HF 1%) or hydrochloric (HCl 0.5%). As reference material we used a ZnO:Al film sputtered at low rate from ceramic tube targets in the same deposition system, as such ZnO:Al films could achieve excellent light trapping upon HCl etching in silicon based thin film solar cells [11]

The thicknesses were measured with surface profiler. The electrical properties of the films were investigated by 4-point probe and Hall effect measurement using van der Pauw method. The morphologies of as-deposited and etched ZnO:Al films were evaluated by atomic force microscopy (AFM, Nanoscope system from Veeco). Optical transmission and reflection of surface textured thin films were carried out with a double beam spectrometer equipped with an integrating sphere (Perkin Elmer Lambda 19). An index matching fluid (CH₂I₂) was used to avoid systematic
measurement errors due to light scattering of the rough films during optical measurement for absorption determination [15].

Standard single junction p-i-n microcrystalline silicon solar cells (μc-Si:H) as well as a-Si:H / μc-Si:H tandem solar cells were prepared using plasma enhanced chemical vapor deposition (PECVD). For all solar cells, the μc-Si:H absorption layer thickness (i-layer) was about 1.1 μm. For a-Si:H/μc-Si:H tandem solar cell, the thickness of top cells (a-Si:H) was about 320 nm. A ZnO:Al / Ag double layer served as a back reflector for all solar cells. Solar cell J-V characteristics were measured using a class A sun simulator under standard test conditions at 1x1 cm² cells. Quantum efficiency measurement was carried out in the range of 300-1100 nm at 25ºC to confirm the measured currents. Since we observed some deviations for tandem solar cells, here the short circuit current densities (Jsc) were extracted from quantum efficiency measurement.

3. Results and discussion

We studied the ZnO:Al film properties after etching. Fig.1 shows the variation of thickness and sheet resistance as well as root mean square (RMS) roughness of ZnO:Al films after two-step etching first in HF (120 sec) and then in HCl. The values given at negative times correspond to the as-grown ZnO:Al film. The etch times correspond to the second etch step in 0.5 % HCl. Thickness (solid square) first decreases by about 150 nm by etching in HF solution for 120 s, and then decreases gradually from 720 nm to 550 nm with the increase of etching time in HCl solution. Sheet resistance (solid circle) increases with the decrease of thickness from about 3.8 Ω to 9 Ω. RMS roughness (solid triangle) rises from about 10 nm to about 90 nm by the first etching step. During the second etching step the RMS roughness shows a maximum of about 100 nm at 8 s and then decreases again for long etch times. In addition, the data of ZnO:Al film is shown, that was etched only by a single etching in HCl solution for 60 s. The sheet resistance is about 4.5 Ω due to its relatively high thickness (800 nm). The depth of large craters of these films is about 200 nm. Even though the films are etched for long time in HCl solution, the RMS roughness cannot be raised above 60 nm. Upon a longer etching time the films would suffer from holes that are etched to the glass.

Fig. 2 shows the morphologies of high rate ZnO:Al films from Fig. 1 before (a) and after etching (b-f). The respective duration for HF and HCl etching are given in the caption. The as-grown ZnO:Al film surface (Fig. 2(a)) shows tiny craters with lateral feature size of 100-200 nm. A first etching step in HF solution develops steep craters with lateral sizes between 300 nm and 500 nm as shown in Fig. 2(b). Subsequent etching in HCl solution widens the sharp craters continuously with etching time (see Fig. 2(c-e)). Fig. 2(f) shows the surface structure of the ZnO:Al film after a single step etch only in HCl solution for 60 s. The surface is relatively flat with only a few large craters on the surface. This surface structure was previously categorized as type III surface [16]. Most of the surface is covered by small and shallow craters. To conclude the effect of the two-step etching, the first etch step in HF creates a high density of craters that are enlarged by the second HCl etching to achieve strong light scattering.

Fig. 3 shows the transmission and absorption of ZnO:Al films discussed before. All films show a high average transmission of more than 85% in visible wavelength region. Even in the
infrared they also show high transmission and low absorption owing to low carrier concentration of \(3.6 \times 10^{20} \text{cm}^{-3}\) in the as-grown state (for more details see Zhu et al. [14]). The slight variations in transmission and absorption are mainly dominated by thickness effects by the etching as shown in Fig. 1. However, they show different light scattering properties i.e. haze as shown in Fig. 4. For as-grown films, they only show nearly no light scattering effect in the whole wavelength region due to their very flat surfaces. After the first etching step in HF solution for 120 s, the films show a great increase in diffuse transmission and haze. With the increasing etching time in HCl solution from 2 s to 16 s, the diffuse transmission and haze have a very small increase over the whole spectrum. Thus the haze of films with the second etching in HCl for 2 s and 16 s are shown here. The haze of more than 30% at 700 nm was achieved. The light scattering properties depend not only on the diameter of craters but also on their depth. Thus the small changes of haze can be understood by the rather narrow variation of RMS roughness with duration of the second etch step in HCl (see Fig. 1). The film etched with single step in HCl solution for 60 s shows relatively low haze since there are only a few large but shallow craters on the surface.

Since there is no model available with predictive power for the solar cell performance from light scattering characteristics we prepared solar cells and studied their properties in detail. Optimized and reference ZnO:Al films were applied as front contacts in \(\mu\text{c-Si:H}\) single junction solar cells A-D and G as well as a-Si:H/\(\mu\text{c-Si:H}\) tandem solar cells E, F and H, respectively. The \(J/V\) parameters such as efficiency, fill factor (FF), open circuit voltage (V\(_{OC}\)) and short circuit current density (J\(_{sc}\)) as measured by sun simulator are shown in Table 1. Additionally, total or top and bottom cell currents were determined from QE data. Possible deviations of J\(_{sc}\) values between the two measurements are mainly related to the actual spectrum and are discussed in literature [17]. Moreover, the last column of the Table 1 lists the solar cell types as well as details on ZnO:Al films and applied etch steps. Cell A, which was grown on the ZnO:Al films only etched in HF solution for 120s, shows a high J\(_{sc}\) of up to 22.5 mA/cm\(^2\) but a relatively low FF of 68% and low V\(_{OC}\) of 500 mV. Conversely, cell D grown on ZnO:Al films that were etched in only diluted HCl solution for 60 s, shows a low J\(_{sc}\) of 19.1 mA/cm\(^2\) but the highest FF and V\(_{OC}\) within this study. These \(J/V\) results are strongly related to the surface structure of corresponding etched ZnO:Al films. Relatively flat surfaces with a few large craters are good for electrical cell performance while rough surface structures improve optical performance. By double etching method on high rate ZnO:Al films, high conversion efficiency \(\mu\text{c-Si:H}\) solar cells C and D were achieved due to combination of high short circuit current density and rather good electrical performance. Both solar cells with high efficiencies of up to 8.2% and 8.1% have high J\(_{sc}\) of up to 22.8 mA/cm\(^2\) and high FF of up to 71%. In addition, a-Si:H/\(\mu\text{c-Si:H}\) tandem solar cells E and F with initial conversion efficiency of up to 11.4% were prepared on the same ZnO:Al films etched with the two-step etch. We estimate the efficiency to stabilize after light induced degradation at a level above 10 %. The short circuit currents of 11.0 mA/cm\(^2\) for a-Si:H/\(\mu\text{c-Si:H}\) tandem solar cells E and F were extracted from quantum efficiency measurements as shown in Fig. 5. The short circuit currents have a good match between top cells (a-Si:H) and bottom cells (\(\mu\text{c-Si:H}\)) for both tandem cells. Good solar cell results prove that rather larger and relative shallow craters are good for light trapping effect. It proves further that our novel etching method works well on high rate ZnO:Al films reactively sputtered from metallic tube targets.
4. Discussion

As we have reported [11], low rate ZnO:Al films deposited from dual tube ceramic targets had achieved good surface structures upon etching in diluted HCl for μc-Si:H solar cells with high conversion efficiency of 8.5%. The RMS of this etched low rate ZnO:Al film was up to 180 nm. The feature sizes of craters on the surface are 1-2 μm in diameter and about 450 nm in depth. The diameter of craters is similar to that of craters on high rate ZnO:Al films reactively deposited from metallic targets after etching by the two-step etch. However, the depth of craters on low rate ZnO:Al films is almost factor of two deeper than that of rough high rate ZnO:Al films. The haze of etched low rate ZnO:Al films at 700 nm is about 60%, which is much higher than that of etched high rate ZnO:Al films with two steps etching in this study as shown in Fig. 4. This is also reflected by the higher RMS roughness of the low rate ZnO:Al films. Note that they show similar transmission and absorption (not shown here). Even though low rate ZnO:Al films from ceramic targets and high rate ZnO:Al films from metallic after the two-step etching here display different light scattering properties, the corresponding silicon thin films solar cells show comparable conversion efficiencies as shown in Table 1. J/V test results of cells G (μc-Si:H ) and cells H (a-Si:H/μc-Si:H), which were co-deposited on etched low rate ZnO:Al films, are listed below the dot-dash line in the Table 1. It indicates that not only large and deep craters but also large and relatively shallow craters work well in a similar way for improving Jsc and keeping high FF. This supports the observation, that haze and RMS roughness are not sufficient to describe the surface structure as both are related to vertical feature size [18] The lateral size and corresponding scattering angles are important as well and might play an even major role for the light scattering [19, 20]. The new double etching reveals the possibility to tune the surface structures of etched ZnO:Al films by the etch process rather than by the deposition conditions as it is done in state-of-the-art optimization. We are able to improve the uniformity of the crater distribution and could vary the crater density and size. In general, regular distribution of the surface features is necessary for high efficiency silicon based solar cells. In particular, large features are favorable for effective scattering of red and near infrared light.

5. Conclusions

Highly conductive and transparent ZnO:Al films were reactively sputtered from metallic targets at high deposition rates. We applied a novel chemical wet etching method based on two-step etching in diluted HF and HCl. The new etch process enables to tune the surface structures of ZnO:Al films for effective light scattering. Optimized films lead to high haze and effective light trapping in silicon based thin film solar cells utilizing the etched ZnO:Al films as light scattering transparent front contact. High efficiency μc-Si:H solar cells and a-Si:H/μc-Si:H tandem solar cells were achieved with high efficiencies of up to 8.2% and 11.4%, respectively. These solar cells are comparable to that grown on low rate rough ZnO:Al films from ceramic targets.

6. Acknowledgements

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References


Captions

**Fig. 1** Variations of thickness and sheet resistance as well as RMS roughness of high growth rate ZnO:Al films upon etching: Negative etch times correspond to initial values before etching, the values at 60 s correspond to single step etching in HCl; all other values correspond to the second HCl step after a first HF etch.

**Fig. 2** Morphologies of high rate films etched with one step in HF solution or HCl solution or with two steps first in HF solution and then in HCl solution. The HF etching time / HCl etching time are: (a) 0 s/0 s, (b) 120 s/0 s, (c) 120 s/4 s, (d) 120 s/8 s, (e) 120 s/16 s, (f) 0 s/60 s.

**Fig. 3** Total transmission and absorption spectra of high rate ZnO:Al films etched with one or two step etches as shown in **Fig. 1**.

**Fig. 4** Spectral haze of selected high rate ZnO:Al films etched with one step in HF solution or in HCl solution or with two steps i.e. first in HF solution and then in HCl solution. Haze of the low rate ZnO:Al film, deposited from dual tube ceramic targets after etching in diluted HCl etchant (0.5%), is also added here for comparison (dash-dot-dot line).

**Fig. 5** Quantum efficiency is plotted as function of wavelength for tandem solar cells E, F and H (details are given in **Table 1**)

**Table 1** J/V results and QE cell currents of silicon based thin films solar cells with different etched ZnO:Al films as front contacts. A to F correspond to the high growth rate ZnO:Al films while G and H correspond to the low growth rate ZnO:Al films used here as a reference.
Zhu_Fig. 1
Zhu_Fig. 2
Zhu Fig. 3

![Graph showing transmission and absorption vs. wavelength for different HF/HCl etching times.]

- Transmission (%) on the y-axis.
- Absorption (%) on the right y-axis.
- Wavelength (nm) on the x-axis.
- Different etching times are indicated by various line types and colors.

Legend:
- 0s / 0s
- 0s / 60s
- 120s / 0s
- 120s / 2s
- 120s / 4s
- 120s / 8s
- 120s / 16s
null
Zhu Fig. 5

- Cell E: $J_{sc} = 10.97 \text{ mA/cm}^2$, $J_{sc} = 11.34 \text{ mA/cm}^2$
- Cell F: $J_{sc} = 11.03 \text{ mA/cm}^2$, $J_{sc} = 11.14 \text{ mA/cm}^2$
- Cell H: $J_{sc} = 11.05 \text{ mA/cm}^2$, $J_{sc} = 11.08 \text{ mA/cm}^2$
### Zhu_Table 1

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