Thin Solid Films 520 (2012) 4678–4684

Contents lists available at SciVerse ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Development of two-step etching approach for aluminium doped zinc oxide using a combination of standard HCl and NH_4Cl etch steps

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ARTICLE INFO

Available online 10 November 2011

Keywords:
ZnO:Al
Etching method
NH4Cl
Scattering properties
Silicon thin solar cells

ABSTRACT

An etching method for ZnO:Al films deposited by radio-frequency sputtering is presented. The method is developed to achieve appropriate surface morphology for efficient light scattering. This etching method consists of a first step where the sample is dipped in standard diluted HCl (0.5 wt.%) for 40 s (the "standard Jülich" etch process) and a subsequent step where a NH_4Cl aqueous solution with concentrations ranging from 2 to 20 wt.% is used. The introduction of the second step leads to a slight modification of the surface feature shape and an increase in the surface roughness of up to around 37% in relation with that obtained using only the first step. High haze values are also obtained, reaching up to 93% at 550 nm and strong light scattering into angles above 50° at 632 nm. On the other hand, the resistivity of the textured films remains low enough for cell application, being ranged from 6 to 13 Ω/sqr depending on the NH_4Cl concentration used. Finally, in order to assess the role of the features obtained on the surface as effective light trapping, the textured films are applied as front contact in silicon thin film solar cells.

1. Introduction

Transparent conductive oxides (TCOs) play an important role in the thin film silicon solar cells, having a huge influence on the device efficiencies [1]. As integral part of these devices, TCOs can be used as a front electrode in p-i-n (superstrate) configuration or as part of back side reflector. In the first case, the TCO should fulfil two conditions: to show favourable physico-chemical properties for the posterior growth of the silicon and to provide the enhancement of the light scattering within the solar cell. In this sense, among the most common TCOs used, magnetron-sputtered aluminium-doped zinc oxide (ZnO:Al) presents several advantages such as high stability against hydrogen plasma and adequate post-deposition textured surface using wet-chemical etching [2]. It has to be pointed out that there are growth techniques, such as plasma enhanced chemical vapour deposition (PECVD), that permit to obtain well textured ZnO material suitable for silicon solar cell applications [3]. However, the advantage that the post-deposition etching processes present is the possibility to separate the light scattering behaviour from the optoelectronic properties. For this post-deposition texturization, the single or mixed acids usually used are the hydrochloric acid (HCl), hydrofluoric acid (HF), ammonium chloride (NH_4Cl), nitric acid (HNO_3) and phosphoric acid (H_3PO_4) [4–8]. The optimised textured etched films obtained using these acids normally provide an effective light trapping in silicon thin film solar cells [9]. It has to be realised that the light scattering properties depend on the shape and size of the features obtained after the etching process. Hence, to achieve appropriate features, it has to be considered on one hand, the strong influence of the film deposition parameters on the surface morphology [10–12] and on the other hand, the etching mechanism and the behaviour that the acids exert on the surface. As example, low deposition pressures lead to steep and sharp features, appropriate for light scattering. However granular features are obtained on the layer surface when increasing the sputtering deposition pressure, thus leading to bad light scattering properties [10,13,14]. Regarding the used etchant, and also as example, the features obtained with HF are much more homogeneous and in a higher number than etching with HCl [7], demonstrating the huge effect of HF on the final surface morphology.

In this work, an etching process using a combination of two acids, HCl and NH_4Cl, has been developed to etch approximately 800 nm-thick ZnO:Al films. Films are firstly etched with HCl (0.5 wt.%) for 40 s, parameters previously optimised for this material [15], and secondly etched with NH_4Cl. The effect that the second step based on NH_4Cl has on the size and the shape of the surface features obtained after upon the first step based on HCl has been studied, analysing also the effect of the whole process on the electrical and optical properties of final textured films. This surface morphology achieved could result an appealing option to improve the solar cell performance. In order to evaluate the surfaces obtained upon the approach and trying to distinguish the effect on each chemical etchant used in it, they have been compared with those obtained using only NH_4Cl. Finally, a comparison

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doi:10.1016/j.tsf.2011.10.190

Table 1
Description of the final thicknesses obtained together with the RMS and ΔA values, calculated from $10\times10\ \mu m^2$ AFM images, and the sheet resistances as function of the wet-chemical process performed. The initial layers used here are approximately 800 nm-thick ZnO:Al films deposited on Corning glass. For comparison, the parameters from "standard Jülich" textured ZnO:Al films and the commercial substrate, labelled as ASAHI-U, are also included.

Sample	Wet-chemical etching		Thickness (nm)	RMS (nm)	ΔA (%)	R_{sheet} (Ω/sq)
	Process	Time				
ASAHI-U	–	–	–	35.6	13.4	10.5 ± 0.2
As-deposited ZnO:Al	–	–	798	13.4	2.2	3.33 ± 0.04
Standard Jülich	HCl (0.5%)	40 s	650	118.4	22.9	6.2 ± 0.1
A	NH_4Cl (5%)	20 min	714	21.7	9.8	4.34 ± 0.03
B	NH_4Cl (10%)	10 min	644	83.4	43.1	4.2 ± 0.1
C	NH_4Cl (10%)	15 min	566	92.1	28.4	6.2 ± 0.2
D	NH_4Cl (15%)	4 min	704	41.7	17.8	3.50 ± 0.05
E	NH_4Cl (15%)	8 min	608	82.8	22.3	5.5 ± 0.2
F	NH_4Cl (20%)	4 min	668	103.6	27.5	5.4 ± 0.2
G	NH_4Cl (20%)	6 min	602	109.7	31.5	5.9 ± 0.2
H	NH_4Cl (15%) + NH_4Cl (5%)	(4 + 20) min	745	85.9	27.0	6.4 ± 0.5
I	NH_4Cl (20%) + NH_4Cl (5%)	(4 + 20) min	735	117.6	30.2	6.7 ± 0.5

between the properties of the etched ZnO:Al films and those shown by commercially textured SnO_2:F (Asahi-U type)/glass substrates has been established. a-Si:H/μc-Si:H tandem solar cells have been fabricated to evaluate the suitability of the light scattering properties of the different textured glass/ZnO:Al substrates.

2. Experimental details

The 800 nm-thick polycrystalline ZnO:Al films were deposited on a cleaned (10×10) cm^2 glass substrate (Corning Eagle XG) using RF magnetron sputtering in a vertical in-line system (VISS 300, VON ARDENNE Anlagentechnik GmbH, Dresden, Germany). A ceramic target consisting of ZnO with 1 w/w% Al_2O_3 (Cerac Inc., Milwaukee, WI, USA) was used. The deposition was carried out at the substrate temperature of 300 °C, a discharge power density of 2 W cm^{-2}, and an Argon working pressure of 0.1 Pa. Details about the sputtering deposition process and material properties can be found elsewhere [16].

Regarding the wet chemical process used in this work, the chemical solution of 0.5 wt.% HCl has been prepared by dilution of p.a. grade HCl (25 wt.%, Merck, Darmstadt, Germany) with deionised water (ρ> 16 MΩ-cm) from a Elix 10 water purification system (Millipore Co., Schwalbach, Germany) at room temperature (RT). On the other hand, the NH_4Cl aqueous solution has been prepared by dissolving NH_4Cl powder with a purity of 99.5% in deionised water (ρ> 18 MΩ-cm) at RT. The range of NH_4Cl concentrations and the etching times studied are from 2 to 20 wt.% and from 4 to 25 min, respectively. The etching mechanism of ZnO in diluted NH_4Cl solution can be found in Ref. [8]. The choice of the both acids used in the etching process proposed in this work was based in their different acidy and the possible difference in the shape of the features that could be found because of that. Firstly, the surface would be etched in an aqueous solution of a strong acid (HCl), and hence, its effect on the surface is sharp. Secondly, when the main facets are defined, the sample is dipped into an aqueous solution of a weak acid (NH_4Cl) which effect on the surface is to obtain a double feature within the main one.

The surface morphology was evaluated by an atomic force microscope (AFM) (Multimode SPM, Veeco-Digital Instruments) operated in tapping mode and using antimony-doped silicon AFM tips (TESPSS tip from Veeco). The roughness of the films was quantified by the average value of the root mean square (RMS) deviation of the AFM measured height from the mean data plane in AFM $10\times10\ \mu m^2$ images. Another statistical parameter ΔA was also used to quantify the surface morphology in the XY-plane after the etching. It can be defined as the ratio between actual scanned surface area (SA) and the area of its projection on the XY plane (PA) following the formula

$$A=(SA-PA)/PA\times100(\%). \tag{1}$$

The error bar in ΔA calculation is about 10%.

The specular and total optical transmittance spectra were performed by a Perkin-Elmer Lambda 1050 UV/Visible/NIR spectrophotometer with an integrating sphere of 60 mm, illuminating from the glass substrate side. From these measurements, the transmitted haze parameter $H_T(\lambda)$ was determined by the ratio of diffuse to total transmittance ($T_{diffuse}/T_{total}$). The transmittance angular distribution function (ADF_T), defined as the intensity distribution of scattered light as function of the angle at which it is scattered, was also determined. For this measurement, a He-Ne laser operating at the wavelength of 635 nm was used as light source. The laser emission is chopped to enhance the signal/noise ratio of the measurement. The intensity of the scattered light from the sample was detected with a Silicon photodetector with an aperture of 1 mm^2 area by changing the angle between the detector and the incident laser beam with a step of $\Delta\varphi=2°$. The optical signal is measured by a lock-in amplifier using an integration time of 1 s. After measurement, the signal measured by the detector was normalised in order to obtain the relative angular dependency of the scattered light. The electrical sheet resistance R_s was determined from the four-point probe method using a commercial Veeco Instrument system. The thickness of the etched films was measured using a surface profiler.

The resulting textured ZnO:Al films were applied as substrates in tandem p-i-n-p-i-n amorphous/microcrystalline silicon (420 nm a-Si:H/ 1.25 μm μc-Si:H) solar cells. The Si films were deposited by plasma enhanced chemical vapour deposition (PECVD) in a (30×30) cm^2 reactor. Details of the PECVD Si deposition process have been described elsewhere [17,18]. The back contact consisted of sputter-deposited ZnO:Al from the same system as the front contacts and silver deposited by thermal evaporation through a mask to determine a cell area of (1×1) cm^2. To ensure comparability, all cells have been prepared in the same deposition process. Solar cells were characterised with a Wacom WXS 140 S solar simulator (Wacom Electric Co., Saitama, Japan) under standard test conditions (AM1.5, 100 mW cm^{-2}, 25 °C). The external quantum efficiency (EQE) was measured by differential spectral response at zero bias.

3. Results and discussion

3.1. As-deposited and reference samples

The as-deposited 800 nm-thick ZnO:Al films presented a surface roughness of around 13.4 nm, a high transmittance in the visible range (~80%), a sheet resistance of 3.33 ± 0.04 Ω/sq and a resistivity as low as 2.6×10^{-4} Ω cm. After the optimised etch process labelled in this work as "standard Jülich", HCl (0.5 wt.%) for 40 s, the etched films showed RMS values of 118.4 nm, a deterioration of the sheet resistance up to 6.2 ± 0.1 Ω/sq and haze values at the wavelength of 550 nm and 800 nm of 70% and 35%, respectively. On the other hand, the commercially textured SnO_2:F (Asahi-U type)/glass substrate also used here