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The catalytic effect of iron(III) on the etching of ZnO:Al front contacts for thin-film silicon solar cells

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ABSTRACT

Sputter-deposited ZnO:Al thin films, used as front contact in thin-film Si solar cells, were etched in diluted HCl containing catalytic amounts of Fe(III) salts. The Fe(III) effectively catalyzes the HCl-based etch process, leading to a crater-like morphology that is qualitatively similar to the one generated by the uncatalyzed etching process at the same HCl concentrations. Utilizing this catalyzed process, an increase of the etching rate by a factor of approximately 1.8–2.6 was observed. This allows for a well-controllable tuning of the etch duration without changing HCl concentration or temperature. The process has been evaluated with a selection of Fe(III) salts at different concentrations of the acid and of the catalyst. Optical, electrical and scanning force microscopic characterization of such catalytically etched ZnO:Al films has shown that the catalytical process leads to slightly smaller morphological features on the film compared to the uncatalyzed etching, accompanied by a shift of light scattering intensity to higher angles. This etching behavior may be used beneficially for light trapping in thin-film Si solar cells. In addition to these application-oriented aspects, this approach provides a deeper insight into the mechanistic details of the ZnO thin-film dissolution.

1. Introduction

The front contact in thin-film Si solar cells has to fulfil three criteria: (i) it has to be highly transparent, (ii) a low series resistance is necessary, and (iii) it has to provide a certain roughness for light management in the device, thus helping to trap the light within the absorber layer stack by total internal reflection. The first two aspects are given for many doped, transparent conductive oxides (TCO) like SnO_2:F, In_2O_3:SnO_2, ZnO:Al, ZnO:B, or ZnO:Ga [1–6]. The latter criterion, however, necessitates further texturing in the case of some TCO materials that are smooth in the as-deposited state. Sputter-deposited, polycrystalline ZnO:Al, for example, may be artificially roughened by an etching step in diluted HCl [7–10] (e.g., leading to the '*standard Jülich*' type material [11,12]), HF [13], NH_4Cl [14–16], other acids in liquid [7–10,17,18], gaseous [19], or vaporized state [20], by electrochemical means [21], or by a combination of such processes [13,22–26]. The variety of possible etching methods together with a model for the etching of polycrystalline ZnO:Al has been addressed in a recent review [27].

Besides the texture, one parameter of significant industrial relevance is the duration of the etching step. For inclusion of such a process into in-line production systems, adjustable etch times are desirable. This can be done to a certain extent by changing the concentration of the etchant or the temperature. However, the resulting morphology is changed significantly by such alterations as well [22,28]. Readily applicable methods for the adjustment of the etch time are hence not at hand.

One general option for accelerating chemical reactions is the utilization of catalytic processes. It is well known that catalysis is a concept of utmost relevance for chemical industry because of its ability to initiate, accelerate, or steer chemical reactions. Although the exact nature of the interfacial processes during acidic etching of ZnO:Al thin films is still not completely understood [27], it can be expected that this process is accelerated by suitable, catalytically active agents, similarly to what has been known for In_2O_3:SnO_2 thin films since many years [29].

In this study, we evaluated the potential of Fe(III) salts to catalyze and accelerate the etching of sputter-deposited ZnO:Al thin films in diluted HCl. A catalytic mechanism is proposed that is strongly supported by experimental evidence. Electrical measurements, angle-resolved scattering (ARS), and scanning force microscopy (SFM) were used to quantify the surface morphologies resulting from the catalyzed etching. This new process renders very suitable morphologies for light scattering at increased etch rates, and their suitability for thin-film Si photovoltaic devices is demonstrated.

2. Experimental

2.1. ZnO:Al thin-film preparation

Approximately 800–850 nm thick, polycrystalline ZnO:Al films were deposited on a (10×10) cm^2 glass substrate (Corning Eagle XG)

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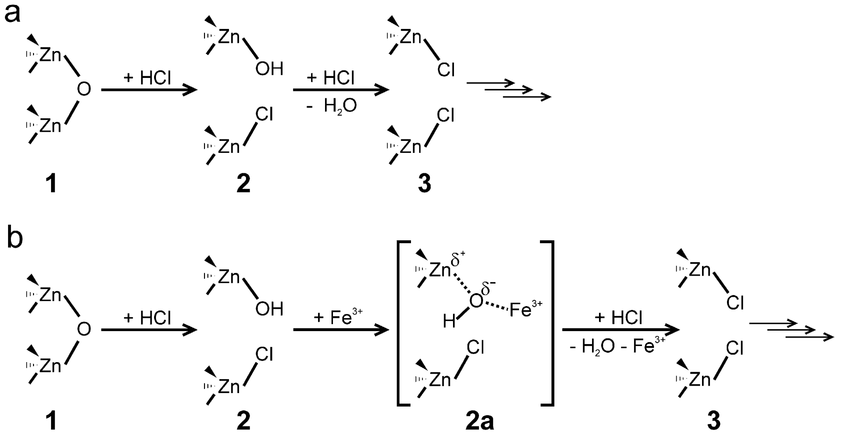

Fig. 1. Proposed mechanism for the acidic dissolution of ZnO (a) without catalyst and (b) with Fe^{3+} as a catalytically active species.

using radio frequency magnetron sputtering in a vertical in-line system (cf. Fig. 1 in Ref. [30]) from a ceramic target consisting of ZnO with 1 w/w% Al_2O_3 (Cerac Inc., Milwaukee, WI, USA). The deposition was carried out at a substrate temperature of 300 °C, a discharge power density of $2\,W\,cm^{-2}$, and an Ar pressure of 0.1 Pa. Details about the process and ZnO:Al film properties are reported elsewhere [12].

2.2. Etching process and chemicals

All solutions were prepared with deionised water ($\rho > 16\,M\Omega\,cm^{-1}$) from an Elix 10 water purification system (Millipore Co., Schwalbach, Germany). HCl, $FeCl_3$, $Fe(NO_3)_3$, $K_3[Fe(CN)_6]$, $FeCl_2$ (all Merck KGaA, Darmstadt, Germany), and $Fe_2(SO_4)_3$ (Sigma-Aldrich Chemie GmbH, Munich, Germany) were of analytical grade and were used without further purification. The temperature was kept constant at 25 ± 0.5 °C during all etching experiments. After etching, substrates were rinsed with copious amounts of deionized water to remove salt residues originating from the etching solution.

Special care has to be taken when an acid is added to a compound containing hexacyanidoferrate because very toxic HCN may be generated. Such experiments therefore have to be carried out with proper personal protective equipment in a closed fume hood and with a very small amount of CN-containing compounds only.

2.3. Film characterization

Film thicknesses d have been measured with a Dektak 3030 surface profiler (Veeco Instruments Ltd., Santa Barbara, CA, USA), taking into account those points where the films have got the highest thickness. To correct for inhomogeneities in the initial measured film thickness, this initial thickness has been determined by taking the maximum measured d value for each etch series as initial value instead of taking the measured values at each individual etching spot. SFM images have been recorded utilizing a NANOStation 300 (S.I.S. GmbH, Herzogenrath, Germany) in non-contact mode with NCHR-POINTPROBE Si cantilevers (NanoWorld AG, Neuchâtel, Switzerland). Image post-treatment was performed with the software SPIP, version 5.1.6 (Image Metrology A/S, Hørsholm, Denmark). A linear background was subtracted from the images for removal of the sample tilt. A four-point probe was utilized for determining the sheet resistance R_{sh} of the films. ARS measurements in transmission were performed in a home-built system at an optical wavelength of $\lambda = 550$ nm.

2.4. Solar cell preparation and characterization

Roughly 1 μm thick μc-Si:H films for single junction solar cells were deposited in a $(40 \times 40)\,cm^2$ in-line plasma-enhanced chemical vapor deposition (PECVD) system [31]. Si films for 420 nm a-Si:H/1.25 μm μc-Si:H tandem p-i-n solar cells were prepared by PECVD in a $(30 \times 30)\,cm^2$ reactor. Details of the Si PECVD process can be found elsewhere [32,33]. The back contact consisted of sputter-deposited ZnO:Al and Ag from the same deposition system as the front contact films. A lab-scale laser patterning system (ROFIN-SINAR Laser GmbH, Hamburg, Germany) was used to determine a cell area of $(1 \times 1)\,cm^2$. Solar cells were characterized with a Wacom WXS 140 S solar simulator (Wacom Electric Co., Saitama, Japan) under standard test conditions (AM1.5 spectrum, $100\,mW\,cm^{-2}$, 25 °C). External quantum efficiencies EQE were measured in a home-built system by differential spectral response (DSR) at zero bias voltage. The crystallinity I_C^{RS} of the Si absorber was determined from the back side of the cells via Raman measurements with an excitation wavelength of 647 nm which leads to information depths roughly of the thickness of the μc-Si:H absorber. In the case of the tandem devices, the measured crystallinity of the bottom component cell $I_{C,bottom}^{RS}$ is also influenced by the top component cell. This is due to the penetration depth of the Raman measurement and leads to an underestimation in $I_{C,bottom}^{RS}$ compared to the real crystallinity of the bottom component cell. To access the Si, the ZnO:Al/Ag back contact has been removed at selected spots close to the measured cells with a wet-etching process. Details about the Raman setup [34] and the determination of the crystallinity [35] can be found in the respective references.

3. Results and discussion

3.1. Mechanistical considerations

van den Meerakker et al. [29] used Fe(III) species to catalyze the etching of In_2O_3:SnO_2 thin films in halogen acids. Taking into account the nature of the wurtzite-type ZnO:Al material, their proposed mechanism for the uncatalyzed [36] as well as for the catalyzed etching of In_2O_3:SnO_2 [29] may be adapted (Fig. 1). When etching ZnO in an aqueous, diluted HCl solution (Fig. 1a), a Zn–O–Zn bond (**1**) is attacked by an HCl moiety. This leads to the formation of one Zn–OH and one Zn–Cl bond. The resulting surface intermediate (**2**) reacts with a second HCl moiety in a condensation reaction to form two Zn–Cl bonds (**3**) and H_2O. This process is repeated, yielding $ZnCl_2$ and H_2O as the reaction products.

If Fe^{3+} is present in addition to HCl (Fig. 1b), the Fe^{3+} ion interacts with one electron pair of the oxygen atom in **2**, leading