Thin Solid Films 555 (2014) 138–142

Contents lists available at ScienceDirect

Thin Solid Films

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

Potential of high-mobility sputtered zinc oxide as front contact for high efficiency thin film silicon solar cells

B. Stannowski [a,*], F. Ruske [a], S. Neubert [a], S. Schönau [a], S. Ring [a], S. Calnan [a], M. Wimmer [a], O. Gabriel [a], B. Szyszka [b], B. Rech [a], R. Schlatmann [a]

[a] Helmholtz-Zentrum Berlin für Materialien und Energie, PVcomB, 12489 Berlin, Germany
[b] Technische Universität Berlin, Einsteinufer 19, 10587 Berlin, Germany

ARTICLE INFO

Available online 11 October 2013

Keywords:
Aluminum-doped zinc oxide
Post deposition treatments
Thin film silicon solar cell
Amorphous silicon
Transparent conducting oxides

ABSTRACT

For thin film silicon solar cells with high conversion efficiency and low production costs transparent conducting oxide (TCO) substrates with a high performance are required. TCO layers must have excellent conductivity and high transparency over a wide range in the VIS/NIR wavelength spectrum. Moreover, an advanced light trapping scheme has to be implemented, generally obtained by TCO surface texture. For low production costs it is favorable to keep the TCO and silicon layers as thin as possible. We present methods that accomplish all of these requirements. Tandem solar based on amorphous and microcrystalline silicon deposited on DC magnetron-sputtered zinc oxide (ZnO:Al) coated substrates, which have been capped with silicon and subsequently annealed at 500 °C, result in an efficiency improved by 0.4% reaching 12.4%. This is due to the increased carrier mobility, reaching up to 70 cm^2/Vs, and improved transparency of the ZnO:Al. The high TCO conductivity allows for reducing the layer thickness significantly. In order to demonstrate the potential of combining this improved TCO with alternative light scattering concepts, we show results of a tandem cell on substrates comprising ZnO:Al sputtered on sol–gel coated light-scattering layers with dielectric particles having excellent light trapping properties. Combining both methods will allow for thin film silicon solar cells with high efficiency and potentially low production costs.

1. Introduction

Manufacturers of photovoltaic (PV) modules are facing tremendous pressure to reduce production costs significantly. For PV modules based on thin film solar cells, moreover, the conversion efficiency has to be increased to be competitive with modules based on c-Si wafers. For example, for modules based on a tandem structure of amorphous silicon (a-Si:H) and microcrystalline silicon (μc-Si:H) the module conversion efficiency in production has to be increased from currently 9–10% to 12% and more. In the last years much effort has been put in the development of better transparent conducting oxide (TCO) materials with high transparency and excellent light scattering properties. The latter allows for very thin silicon absorber layers, and, hence, a reduction of production costs. Oerlikon Solar (now: TEL Solar) claims very low production costs at stabilized module efficiencies up to 10.8% [1] using a total Si absorber thickness of only about 1 μm. Boron-doped zinc oxide deposited by low-pressure chemical vapor deposition is implemented as TCO for the front and back contact with typical thicknesses of 1.5–2.5 μm each [1–3]. It is obvious that the TCO contributes significantly to the total material costs. Thus, thinner TCO layers can help to reduce production costs even further.

Magnetron sputtered aluminum doped zinc oxide (ZnO:Al) has been developed as an alternative TCO material for high efficiency a-Si:H/μc-Si:H tandem solar cells [4–7]. Layers are typically sputtered at a thickness of 0.8 μm in order to obtain the desired sheet resistance of about 10 Ω. To obtain a rough, light scattering surface the as-deposited smooth ZnO:Al layer is usually texture-etched, e.g. in diluted hydrochloric acid. Recently, it has been shown, that high-rate sputtered and texture-etched ZnO:Al can be produced on production scale [8] yielding 1.4 m^2 modules with a stabilized efficiency above 10% [9].

Recently, the “cap + annealing” process has been developed to improve the opto-electrical properties of ZnO:Al even further [10–12]. In this process, ZnO:Al layers are capped with a-Si:H and subsequently annealed at temperatures above 500 °C, resulting in an increase of the charge carrier mobility (μ_{Hall}) from 30–40 cm^2/Vs to 70 cm^2/Vs [10]. In addition to a reduced free carrier absorption (FCA) in the near-infrared (NIR) spectrum it was found that also the transmission in the short wavelength spectrum (UV/VIS) is increased. This is due to a reduced absorption for photon energies close to the ZnO:Al band gap energy at 3.5 eV where the density of defect-related band tails is reduced [11]. While initially demonstrated on RF sputtered ZnO:Al

* Corresponding author at: Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, PVcomB, Schwarzschildstr. 3, 12489 Berlin, Germany. Tel.: +49 30 806215491; fax: +49 30 806215677.
E-mail address: bernd.stannowski@helmholtz-berlin.de (B. Stannowski).

0040-6090/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.tsf.2013.10.014

layers on lab scale, it could also be shown that ZnO:Al layers produced with high-rate DC sputtering in industrial processes on large-area float glass can be improved by this procedure [12].

In this paper we briefly describe the effects of annealing on optical and electrical properties of ZnO:Al layers and present ideas for explaining the microscopic origins of the observed changes. Furthermore, we apply texture-etched ZnO:Al films improved by the cap + annealing procedure [13] as front TCO to a-Si/μc-Si silicon solar cells and present the beneficial effect of the improved optical properties. In general two routes are possible to benefit from the higher carrier mobility while keeping the TCO sheet resistance constant: either by reducing the charge carrier density or by reducing the TCO thickness. In this paper we first present solar cells applying the first route. Later, we discuss the possibilities of the second route, which is promising for very thin (<400 nm) ZnO:Al front TCO layers for yielding solar cells with high efficiency at reduced costs. To circumvent the difficulty of texture etching very thin ZnO:Al layers, approaches to obtain textured surfaces for efficient light trapping, alternative to the texture etching, are briefly discussed. We assess the potential of implementing high mobility ZnO:Al together with light-scattering structures for high-efficiency and low-cost a-Si/μc-Si PV modules.

2. Experimental details

The process for high-mobility ZnO:Al films by cap + annealing has been originally established with ZnO:Al films deposited by RF sputtering from ceramic planar ZnO targets with 1 wt.% Al_2O_3 [10,11]. Corning Eagle XG or Schott Borofloat glass was used as substrates. Results on these layers are discussed in the "High-mobility sputtered ZnO:Al layers" section. For deposition of tandem solar cells as reported later in this paper, ZnO:Al substrates from large-scale production using DC magnetron sputtering from ceramic tube targets on 3.2 mm thick low-iron float-glass coated with a diffusion barrier were used. Such TCO substrates, cut down from 5.7 m^2 to 30 × 30 cm^2 substrates, are also used for the baseline thin film silicon tandem cell process at PVcomB. The advantage of these TCO substrates is that the sample-to-sample variation and the non-uniformity can be neglected, allowing the optimization of the solar cell process and reliable comparison of effects of annealing procedures over a large number of runs. For the silicon capping 50–100 nm thick plasma-enhanced chemical vapor deposited (PECVD) a-Si:H layers were applied. Subsequently, the samples were annealed at temperatures of 500–650 °C in a nitrogen atmosphere. The samples were slowly heated up, kept at the set-point temperature for several hours, and then slowly cooled down. The maximum annealing temperature was limited by the glass transition temperature of the substrate. In our case this means, that maximum annealing temperatures of 650 °C were applied for films on Corning or Schott Borofloat glass substrates, while a maximum annealing temperature of 500 °C had to be used for the industrial TCO substrates on float glass. For characterization and solar cell deposition on annealed ZnO:Al films, the silicon capping layer was removed by plasma etching using SF_6 or NF_3 as etching gas.

For solar cells, prior to annealing the ZnO:Al samples were etched in a 0.5% HCl solution for 75 s to obtain a surface texture for light scattering. Subsequently, the TCO layers were treated as described by Wimmer et al. [12], namely, films were first heated in a furnace under nitrogen flow *without* capping. The presence of residual oxygen is assumed as the effect of this pre-annealing is a reduction of the charge carrier density by a factor of ten. It was carried out at 500 °C with a plateau time of 6 h. After this pre-annealing the cap + annealing process as described above was carried out with parameters identical to those of the pre-annealing step. As a result the carrier density recovers partially. This 2-step annealing procedure was done to increase the mobility and, at the same time, reduce the charge carrier density, as a result, keeping the TCO sheet resistance constant. While carrier mobility was increased from about 30 to 60 cm^2/Vs the carrier density was decreased from about 3 to 1.5 cm^{-3}. More details and TCO properties can be found in [12,13].

For tandem solar cells a stack of an a-Si:H and a μc-Si:H p-i-n cell was deposited in a PECVD cluster system (AKT1600 from Applied Materials) on 30 × 30 cm^2 substrate area. The typical layer stack of such a solar cell is shown in Fig. 1. The same system was used for the deposition and the removal of the silicon capping layers. The intrinsic layer thickness of top and bottom cells was 290 nm and 1750 nm, respectively. All doped p- and n-type layers are based on microcrystalline silicon oxide (μc-SiO_x:H). The back contact was deposited by DC sputtering and consisted of a 80 nm thick ZnO:Al layer and a 200 nm thick Ag layer. Solar cells with an area of 1 cm^2 were defined by laser patterning.

Current–voltage parameters of the solar cells under standard test conditions were measured with a dual-source class AAA solar simulator (Wacom WXS-155S-L2). Total reflection measurements and external quantum efficiency measurements using blue and red bias light and DC bias voltage were carried out on selected 1 cm^2 solar cells.

3. Results and discussion

3.1. High-mobility sputtered ZnO:Al layers

In this section the effect of the cap + annealing procedure on various sample series as described in Refs. [10–12] is reviewed and the major

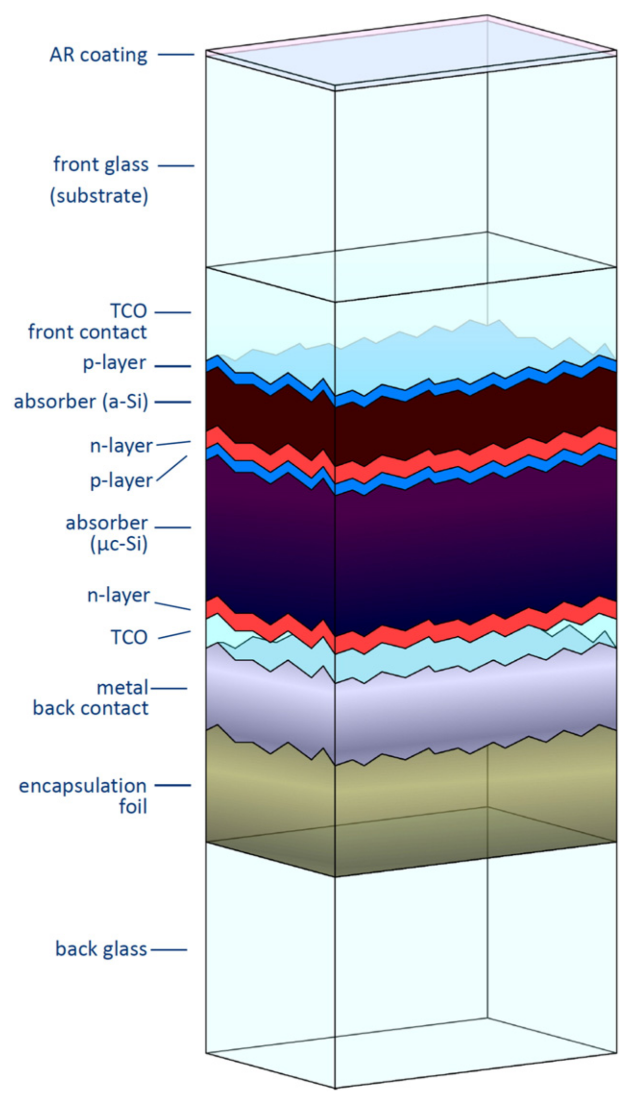

Fig. 1. Schematic drawing of the layer structure of an a-Si:H/μc-Si:H tandem solar cell in superstrate (pin/pin) configuration.