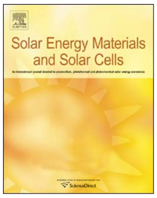
Solar Energy Materials and Solar Cells 174 (2018) 196–201

Contents lists available at ScienceDirect

Solar Energy Materials and Solar Cells

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



Versatility of doped nanocrystalline silicon oxide for applications in silicon thin-film and heterojunction solar cells

Alexei Richter[a,*], Vladimir Smirnov[a], Andreas Lambertz[a], Keita Nomoto[b], Katharina Welter[a], Kaining Ding[a]

[a] *Institute of Energy and Climate Research 5-Photovoltaik, Forschungszentrum Jülich GmbH, 52425 Jülich, Germany*

[b] *School of Aerospace, Mechanical and Mechatronic Engineering, Faculty of Engineering and Information Technologies, The University of Sydney, Sydney, Australia*

ARTICLE INFO

Keywords:
Nanocrystalline silicon oxide
Silicon heterojunction solar cells
Multi-junction thin-film solar cells
Atom probe tomography
Photon management

ABSTRACT

To optimize the optical response of a solar cell, specifically designed materials with appropriate optoelectronic properties are needed. Owing to the unique microstructure of doped nanocrystalline silicon oxide, nc-SiO_x:H, this material is able to cover an extensive range of optical and electrical properties. However, applying nc-SiO_x:H thin-films in photovoltaic devices necessitates an individual adaptation of the material properties according to the specific functions in the device. In this study, we investigated the detailed microstructure of doped nc-SiO_x:H films via atom probe tomography at the sub-nm scale, thereby, for the first time, revealing the three-dimensional distribution of the nc-Si network. Furthermore, n- and p-type nc-SiO_x:H layers with various optical and electrical properties were implemented as a window, back contact, and an intermediate reflector layer in silicon heterojunction and multi-junction thin-film solar cells with a focus on the key aspects for adapting the material properties to the specific functions. Here, nc-SiO_x:H effectively reduced the parasitic absorption and opened new possibilities for the photon management in the solar cells, thereby, demonstrating the versatility of this material. Remarkably, using our adapted nc-SiO_x:H layers in distinct functions enabled us to achieve a combined short circuit current density of 15.1 mA cm^{-2} for the two a-Si:H sub-cells in an a-Si:H/a-Si:H/μc-Si:H triple-junction thin-film solar cell and an active area efficiency of 21.4% was realized for a silicon heterojunction solar cell.

1. Introduction

Hydrogenated nanocrystalline silicon oxide (nc-SiO_x:H), often also called microcrystalline silicon oxide (μc-SiO_x:H), attracts significant attention as a material for photovoltaics [1–6]. The unabated interest in doped, both n- and p-type, nc-SiO_x:H prevails mainly due to its remarkable variability. Particularly, the optical and electrical properties of this material can be varied in a broad range, providing a tunable refractive index, a low absorption coefficient in the relevant energy range, and a sufficient electrical conductivity. This is made possible by its characteristic microstructure, which is usually described as comprising of well conducting filaments or pearl-chain like arrangements of nanocrystalline silicon (nc-Si) embedded in a highly transparent, oxygen rich amorphous silicon oxide (a-SiO_x:H) matrix as indicated by TEM investigations [1,2,7,8]. As a result, nc-SiO_x:H is widely applicable as a window, back contact (BC) or intermediate reflector (IR) layer in various solar cell concepts. So far, nc-SiO_x:H has been utilized in photovoltaic devices like thin-film (TF) silicon solar cells [3,9–11], multi-junction solar cells [12–14], crystalline silicon solar cells with diffused emitters [6], and silicon heterojunction (SHJ) solar cells [15–18]. Each of these applications requires specific optoelectronic properties in order to improve the overall spectral utilization and the response of the solar cell. In this study, we investigate the microstructure of device relevant nc-SiO_x:H n- and p-type nc-SiO_x:H films by atom probe tomography (APT) revealing the three-dimensional network structure of nc-Si in nc-SiO_x:H for the first time. Furthermore, we present our most recent results on SHJ and triple-junction TF solar cells employing n- and p-type nc-SiO_x:H films.

2. Materials and methods

The n- and p-type nc-SiO_x:H TFs described in this study were deposited on Corning Eagle 2000 glass substrates via plasma enhanced chemical vapor deposition (PECVD) at a plasma frequency of 13.56 MHz (RF). While the substrate temperature was around 185 °C and the power density was fixed at around 300 mW cm^{-2}. The deposition pressure was set to 4 mbar. Silane (SiH_4), hydrogen (H_2), methane (CH_4), and carbon dioxide (CO_2) served as precursor gases and

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* Corresponding author.
E-mail address: ale.richter@fz-juelich.de (A. Richter).

http://dx.doi.org/10.1016/j.solmat.2017.08.035
Received 28 April 2017; Received in revised form 17 July 2017; Accepted 29 August 2017

the n- and p-type doping of the films were achieved by adding phosphine PH_3 or trimethylborane $B(CH_3)_3$, respectively. The composition of the gas mixture during the deposition was characterized by the silane concentration SC and the CO_2 gas flow ratio r_{CO2}, defined by $SC = \frac{[SiH_4]}{[H_2]+[SiH_4]}$ and $r_{CO_2} = \frac{[CO_2]}{[CO_2]+[SiH_4]}$, respectively.

To evaluate the properties of the nc-SiO_x:H films, the thickness was measured using a Vecco DEKTAK 6 M Stylus Profiler. Here, the thickness of the deposited films ranged from 0.3 to about 1 µm. The electrical performance was evaluated by determining the lateral dark conductivity σ_D with coplanar silver contacts. To describe the optical properties of the films, the spectral transmittance and reflectance were obtained using a Perkin Elmer LAMBDA 950 spectrometer. Afterwards, the spectral absorption coefficient $\alpha(\lambda)$ was evaluated [19] to determine the optical band gap E_{04} at $\alpha = 10^4\,\mathrm{cm}^{-1}$. Furthermore, the refractive index $n(\lambda)$ was determined using the Fresnel equation. Additionally, photo thermal deflection spectroscopy (PDS) was employed to determine the E_{04} and n of highly transparent films.

Specimen for the Atom Probe Tomography (APT) investigations were prepared by using a Zeiss Auriga focused ion beam electron microscope (FIB-SEM). Before, a 300 nm layer of Pt was deposited on the films to prevent damage from Ga ions during the FIB milling. More details on the sample preparation can be found in [20]. The measurements were performed on a CAMECA LEAP 4000Xsi with a pulsed 355 nm laser (250 kHz, 50 pJ) and an overall detection efficiency of 57%. During the APT measurements the sample holder was cooled to 40 K at a chamber pressure below 10^{-9} Pa. In the last step, CAMECA's IVAS software was used for reconstruction and analysis of the sample data.

All wafers used for the SHJ solar cells were cleaned by sulfuric acid and hydrogen peroxide (96% and 30%, respectively) in a ratio of 2:1 for 10 min followed by a 2 min dip in 1% hydrofluoric acid (HF) prior to deposition. The cells were deposited on (100)-oriented wet chemically textured CZ silicon wafers (170 µm, 1–5 Ω cm). After cleaning, 5 nm of intrinsic a-Si:H layers were deposited via PECVD to passivate the wafer surface at a substrate temperature of 140 °C and a deposition pressure of 1 mbar, using SiH_4 and H_2 as process gases, the power density was set to 18 mW cm^{-2} with an electrode distance of 23 mm at 13.56 MHz. The deposition was followed by a thermal annealing step in ambient air at 220 °C. After a short HF dip, the n- and p-type nc-SiO_x:H layers were deposited at the conditions outlined above. Then, the area of each cell on the wafer was defined by sputtering indium tin oxide (ITO) through a shadow mask on each side at a substrate temperature of 125 °C. An ITO target with 5 wt% SnO_2 was used at a deposition pressure of 50 mPa. Following the ITO deposition, silver grids were evaporated onto the cells through shadow masks. On the back side a full area silver contact was evaporated for each cell. Lastly, the cells were thermally annealed in air for 2 h at 220 °C. The full layer stack of the SHJ solar cells has been described in [21].

For the TF silicon solar cells SnO_2:F coated glass from the Asahi Glass company was used as a substrate to deposit cells in a p-i-n configuration. The schematic layer stack is depicted in Fig. 1b). The exact deposition parameters for the a-SiC: H, a-Si:H and µc-Si:H layers can be found in [9,10,13,22].

To characterize the solar cells, a double source AM1.5 solar simulator (Class A) was used at standard test conditions (AM1.5 G, 1 kW m^{-2}, 25 °C). Furthermore, external quantum efficiency *EQE* spectra were measured using a differential spectral response (DSR) setup. More details on the measurement of the multi-junction solar cells can be found in [13]. Additionally, by convoluting the *EQE* spectra with the AM1.5 G solar spectrum in the range from 350 to 1150 nm, the active area short circuit current density J_{sc} was calculated. The reflectance R was measured using the Perkin Elmer LAMBDA 950 spectrometer.

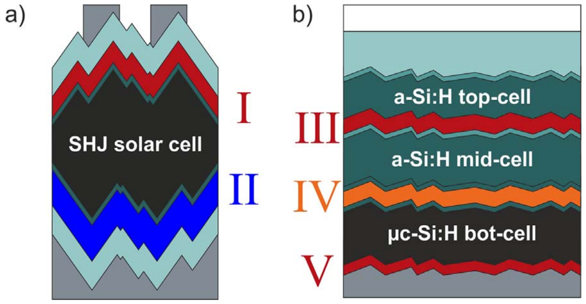

Fig. 1. Schematic layer stacks for (a) a silicon heterojunction (SHJ) and (b) a Si thin-film (TF) triple-junction solar cell with indicated potential applications of nc-SiO_x:H layers. These are: (I) front surface field (FSF)/front-emitter layer, (II) back surface field (BSF)/rear-emitter layer, (III) first interlayer, (IV) intermediate reflector (IR), and (V) back contact (BC) layer.

3. Results

Various possible applications of nc-SiO_x:H layers in silicon heterojunction (SHJ) and Si thin-film (TF) solar cells are sketched in Fig. 1a) and b), respectively. At the illuminated side of a SHJ solar cell layers of nc-SiO_x:H can be used as front-emitter or front surface field (FSF) layers ("I" in Fig. 1a)). The main focus in this application is to reduce the parasitic absorption at the front of the solar cell due to the high transparency of nc-SiO_x:H layers in comparison to a-Si:H [8,15,21]. At the same time, the conductivity of the employed layers has to be sufficient to maintain a high fill factor (*FF*) in the device. Furthermore, nc-SiO_x:H can be used at the rear of SHJ solar cells to serve as a rear-emitter layer [21] or a back surface field [23] ("II" in Fig. 1a)). Here, a high conductivity and a low contact resistance towards the transparent conductive oxide (TCO) are paramount.

In multi-junction Si TF solar cells nc-SiO_x:H layers can be applied at the back of the top sub-cell ("III" in Fig. 1b)) as a first interlayer, which mainly serves to reduce the parasitic absorption of light at this part of the solar cell. A well-balanced trade-off between a high transparency and a sufficient conductivity is required for these films similarly to the application as a FSF or a front-emitter layer. An intermediate reflector ("IV" in Fig. 1b)) is another possible application of nc-SiO_x:H layers in multi-junction Si TF solar cells. By using specifically optically tuned nc-SiO_x:H layers, these allow to match the generated current between the adjoining sub-cells in a multi-junction solar cell by introducing an abrupt change in n [24,25]. Furthermore, nc-SiO_x:H layers can reduce the parasitic absorption at the rear of Si TF solar cells when applied as back contact layers (BC, "V" in Fig. 1b)) [10]. Here, the nc-SiO_x:H layer reduces the parasitic absorption by surface plasmons in the metal contact [26,27] and a well-balanced compromise between a low refractive index n and a high electrical conductivity has to be found.

In order to fulfill the mentioned requirements for each application, the properties of the nc-SiO_x:H layers have to be tuned. Fig. 2 summarizes the development of a wide variety of nc-SiO_x:H films. In detail, the dark electrical conductivity (σ_D) is presented versus the refractive index n in Fig. 2a) and versus the optical band gap E_{04} in Fig. 2b). The n values achievable in these layers ranged from 3.6 to 1.9. Similarly, E_{04} could be varied from about 1.9 eV to almost 2.9 eV. All the while, σ_D changed by many orders of magnitude from $10^{-12}\,(\Omega\,\mathrm{cm})^{-1}$ close to $10^2\,(\Omega\,\mathrm{cm})^{-1}$. Typically, an increase in E_{04}, accompanied by a lowered n, leads to a decrease in σ_D. Furthermore, Fig. 2 shows that improved optoelectronic properties could be achieved with n-type nc-SiO_x:H films as compared to p-type nc-SiO_x:H, resulting in a higher E_{04} at any given σ_D or vice versa. Three films of nc-SiO_x:H are highlighted in this plot as stars to indicate layers that were suitable to serve as a FSF layer, an emitter layer, a BC layer, or an IR in Si TF or SHJ solar cells. Please note that the σ_D of the thin nc-SiO_x:H films used in solar cells is expected to be lower than the value determined from thicker (several hundred nm) films [28]. Nevertheless, the properties determined on thicker films