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Nanocrystalline thin film silicon solar cells: A deeper look into p/i interface formation

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ABSTRACT

The p/i interface plays a major role in the conversion efficiency of nanocrystalline silicon (nc-Si:H) solar cells. Under plasma-enhanced chemical vapor deposition (PECVD) of the intrinsic (i) nc-Si:H layer, ion bombardment can severely affect the underlying p-doped layer and degrade the solar cell performance. The core of the present work is to investigate the effect of light and heavy ion bombardment on the structural modifications of the p-layer during the p/i interface formation. The properties of the nc-Si:H materials deposited under distinct conditions are analyzed and correlated to the deposition rate and the resulting cell efficiency. To recreate the ion bombardment during the initial stages of the i-layer deposition on the p-layer, hydrogen plasma treatment was performed for 30 s (light ion bombardment), after which a flux of silane was introduced into the deposition chamber in order to initiate the heavy ion bombardment and growth of an ultra-thin (5 nm) i-layer. The structural changes of the p-type nc-Si:H layers were observed by spectroscopic ellipsometry. The obtained results confirm that detrimental structural modifications (e.g. partial amorphization of the sub-surface region and bulk) occur in the p-layer, caused by the ion bombardment. To minimize this effect, a protective buffer layer is investigated able to improve the performance of the solar cells fabricated under increased growth rate conditions.

1. Introduction

The efficiency of thin film silicon solar cells, both single- and multi-junction, has reached a plateau in previous decades [1] that needs to be surpassed in order for PV electricity to become a cost-competitive energy source. While the quality of the intrinsic and doped silicon thin films can hardly be improved further, new light trapping techniques [2–6], anti-reflective coatings [7] and better control over the cell interfaces [8] can still offer potential room for solar cell efficiency improvement.

The standard method of hydrogenated nanocrystalline silicon (nc-Si:H) deposition is by radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) with a high hydrogen dilution of silane [9]. To decrease the processing time and costs of nc-Si:H solar cells, it is desired to increase as much as possible the deposition rate of the intrinsic layer used as absorber in tandem or single junction nc-Si:H solar cells. The most typical method to achieve this is by increasing the RF power and simultaneously use very high frequency (VHF) plasma processes [10], which usually lead to poorly performing p–i–n solar cells. During the initial stages of the intrinsic nc-Si:H deposition, ion bombardment can easily damage a 20–30 nm thick doped layer, decreasing its crystalline volume fraction and conductivity [11,12]. This leads to solar cells with a degraded performance due to the large increase of defects at the p/i interface region, which is reflected by the increase of the series resistance, the recombination rate and, consequently, the decrease of the fill factor (FF) and efficiency.

For the purpose of improving the p/i interface of thin film Si p–i–n solar cells, some methods have been developed including the deposition of a buffer layer between the p-type and intrinsic layers [13]. It was reported that the insertion of a wide bandgap semiconductor layer, such as a-SiC:H, contributed to improve the blue response [14] and efficiency of a-Si:H solar cells [15,16]. Other groups used protocrystalline silicon (pc-Si:H) [17,18] or boron-doped microcrystalline silicon (p-μc-Si:H) [19] as buffer layers instead of a-SiC:H. Bugnon et al. explored SiO_x as buffer layer in microcrystalline (μc-Si:H) and amorphous (a-Si:H) solar cells [20], finding that a SiO_x buffer can limit boron cross-contamination and promote the nucleation of the i-layer; thus acting as buffer and seed layer simultaneously.

Concerning nc-Si:H solar cells, it was shown that wide bandgap buffer layers can enhance the V_{OC} and FF [21] due to a reduction of accumulated charges at the p/i interface, caused by the strengthened electric field at the interface [22,23]. These works employed an a-Si:H buffer layer;

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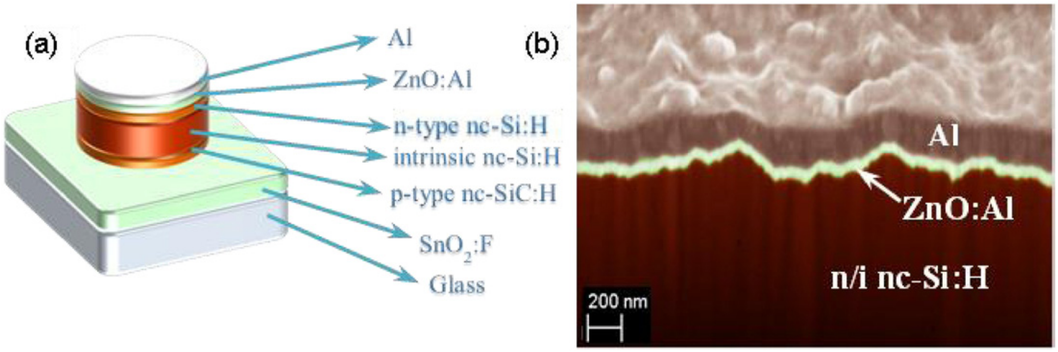

Fig. 1. Structure of the fabricated p–i–n nc-Si:H solar cells. a) Schematic representation of the solar cell structure after dry etching; b) SEM image showing a FIB cross section of one of the investigated solar cells. Colors are given as a guide for the eye.

however, nc-Si:H material as buffer has recently attracted a lot of attention since it can provide better optical transmission and electrical conductivity [24,25].

In this paper, we report an investigation of the effects of light and heavy ion bombardment on the p-layer, which occurs during the initial growth stages of the intrinsic layer deposition processed under VHF PECVD conditions. Based on this study, the beneficial effect of implementing an intrinsic nc-Si:H buffer layer at the p/i interface is then demonstrated for nc-Si:H p–i–n solar cells fabricated under increased growth rate conditions of the intrinsic layer.

2. Experimental details

Single junction nc-Si:H solar cells with p–i–n configuration were deposited on 3-mm-thick 10 × 10 cm^2 glass substrates, covered with 700 nm of SnO$_2$:F (Fig. 1), using a spider-configuration *Elettrorava* PECVD system. The 30-nm-thick p-type and 50-nm-thick n-type layers were deposited in separated RF-PECVD chambers, at a substrate temperature of 160 °C. All deposition parameters were previously optimized [10,26,27]. The intrinsic absorber and/or buffer layers were directly deposited on the p-layer at 160 °C in another VHF-PECVD chamber. To study the effect of the growth rate of the intrinsic nc-Si:H on the solar cells performance, various deposition conditions were used, labeled **i1**, **i2** and **i3** in Table 1.

All solar cells have a total i-layer thickness of about 2 μm, including the thickness of the buffer layer. The hydrogen dilution, D_H, defined as $D_H = (F_{H2} / (F_{H2} + F_{SiH4})) \times 100\%$, was varied from 96.10% to 97.01%. To promote the crystallinity of the i-layer, hydrogen plasma treatment (HPT) is applied to the as-grown p-layer while kept under vacuum. The flow of hydrogen (F_{H2}) and the deposition pressure were kept constant during the deposition and HPT. Back contacts of aluminium zinc oxide (AZO 75 nm) and Al (200 nm) were deposited by PVD methods using a mask with holes of 5 mm diameter, which define cell areas of 19.6 mm^2. After deposition of the top contacts, reactive ion etching (Trion Phantom III RIE ATCH system) with SF$_6$ plasma was applied to remove the remaining silicon around the top contacts, to avoid lateral side effects [28], resulting in the devices shown in Fig. 1. Finally, the cells were annealed at 160 °C under vacuum for 120 min, to reduce the dangling bonds impact caused by inhomogeneous microstructure [29].

Table 1
The deposition parameters of the nc-Si:H intrinsic layers by PECVD are the applied power (P), power density (P_d), frequency (f), inter-electrode distance (d_E), substrate temperature (T_{sub}), working pressure (p_w), gas fluxes (F_{SiH4} andF_{H2}) and hydrogen dilution (D_H).

Deposition conditions	P, W	P_d, mW/cm^2	f, MHz	d_E, mm	T_{sub}, °C	p_w, Torr	F_{SiH4}, sccm	F_{H2}, sccm	D_H, %
i1	20	139	75	13	160	1.0	10.0	246	96.10
i2	40	278	75	8	160	2.1	15.5	500	96.99
i3	58	403	75	8	160	2.0	15.4	500	97.01

To evaluate the influence of the ion bombardment on the p-layer, nanocrystalline p-type films were deposited on 1-mm thick glass substrates as described in Ref. [30]. Then, in order to simulate the initial stages of growth of the intrinsic nc-Si:H on top of the p-type layer, HPT was performed at different conditions ($f = 75$ MHz; $1.0 < p_w < 2.13$ Torr; $139 < P_d < 433$ mW/cm^2) for 30 s (light ion bombardment), followed by the introduction of a silane flux (according to the **i1**, **i2** or **i3** conditions of Table 1) into the deposition chamber to initiate the film growth (heavy ion bombardment). The deposition time was adjusted to grow only an ultra-thin (5 nm thick) i-layer.

The structural characterization of the p and i-type films was performed using Raman spectroscopy and spectroscopic ellipsometry (SE). Raman scattering experiments were performed at room temperature, in backscattering configuration, using a LabRam Horiba HR800UV spectrometer and a 532 nm laser.

SE was measured using a Horiba Jobin Yvon UVISEL ellipsometer, with a fixed 70° incidence angle in the 1.5–6.5 eV range, to determine the crystalline volume fraction, X_C, of the films and its variation with thickness.

The electrical properties of the films were studied via temperature dependent dark conductivity, from which the room-temperature conductivity, σ_d, and activation energy, E_a, were calculated. The linearity of the I (V) dependence was confirmed before each conductivity measurement. Low voltages (0.1–1 V) were used to reduce high-field effects, such as field-enhanced hopping transport. Chromium contacts (180 nm thick, 4 mm long and 1 mm apart) were deposited before the Si films by thermal evaporation. In order to determine the photosensitivity, σ_{ph}/σ_d, of the intrinsic layers, the photoconductivity, σ_{ph}, was measured under illumination (~100 mW/cm^2 at 300 K). The dark conductivity measurements were performed with a Deep Level Transient Spectroscopy (DLTS) system from Polaron equipped with a cryostat ranging from 200 K to 400 K.

The solar cells were characterized by current–voltage measurements at room temperature under AM1.5 illumination conditions (SPIRE SPI-Sun Simulator 240A). The external quantum efficiency (EQE) of the cells was determined in short-circuit condition in the wavelength range of 360 to 1100 nm using a home-made set up [3]. SEM observations were carried out using a Carl Zeiss AURIGA CrossBeam (FIB-SEM) workstation.

Table 2
Structural (crystalline volume fraction, $X_{C(RS)}$) and electrical (photosensitivity, σ_{ph}/σ_d, and activation energy, E_a) properties of the intrinsic layers deposited with the conditions of Table 1, resulting in different growth rates (r_d).

Deposition conditions	R_d, Å/s	$X_{C(RS)}$, %	σ_{ph}/σ_d	E_a, meV
i1	2.4	51 ± 2.5	8×10^3	571
i2	3.5	57 ± 2.8	7×10^3	554
i3	4.5	60 ± 2.9	2×10^2	528