Abstract

In this study we developed a hydrogenated nanocrystalline silicon oxide (p)nc-SiO$_x$:H as an emitter window layer for silicon heterojunction solar cells. We investigated the variation of refractive index and crystalline volume fraction at different growth conditions by Plasma Enhanced Chemical Vapor Deposition (PECVD) and we show that combining a low refractive index (n ~ 2.65) and low parasitic absorption the (p)nc-SiO$_x$:H emitter can replace the standard (p)a-Si:H, which leads to a short circuit current increase of up to 4%. We also show a method to reduce the incubation layer thickness in the initial stage of growth using a CO$_2$ plasma treatment of the intrinsic amorphous layer surface prior to the emitter deposition. Lifetime measurements prove that the plasma treatment and the emitter layer deposition did not compromise the passivation layer quality. Moreover, in order to improve the p-emitter/n-type TCO contact, a highly doped nc-Si:H layer is implemented on top of the emitter, which leads to lower series resistance ($R_{s,light}$) and higher fill factor (FF) without affecting the open circuit voltage ($V_{oc}$).

Keywords: HIT solar cell, nanocrystalline silicon oxide emitter, substrate effect, CO$_2$ plasma treatment, emitter/TCO tunnel contact.

* Corresponding author. Tel.: +49-30-8062-18158.
E-mail address: luana.mazzarella@helmholtz-berlin.de

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1. Introduction

Silicon wafer based heterojunction solar cells with thin intrinsic hydrogenated amorphous silicon ((i)a-Si:H) layers, the so-called HIT structure, have demonstrated a conversion efficiency of 24.7% [1]. The HIT device concept combines low-temperature fabrication processes, with silicon layer deposition done by plasma enhanced chemical vapor deposition (PECVD) leading to well passivated silicon surfaces. This permits to achieve open circuit voltages of up to 750 mV [1]. Further progress was recently achieved in an interdigitated back-contacted (IBC) configuration with a conversion efficiency of 25.6% [2].

Generally, such solar cells are based on an n-doped monocrystalline silicon wafer (c-Si) with an (i)a-Si:H and boron-doped (p)a-Si:H emitter stack deposited on the front illuminated side, to form the p/n junction, and an (i)a-Si:H and phosphorous-doped (n)a-Si:H layer forming the back surface field (BSF). Although an optimized (p)a-Si:H emitter layer is only a few nanometers thick (5-10 nm), it absorbs a significant amount of incoming light parasitically [3], hence its fabrication still remains challenging. In a previous study [4], we have shown that it is possible to reduce this parasitic absorption by using an improved emitter layer stack: The emitter is designed such that it forms a stack with the front transparent conducting oxide (TCO) with refractive index (n) that consecutively decreases from the silicon wafer to the ambient air (index grading), thus significantly minimizing the reflection losses.

The (p)a-Si:H refractive index is unfavorably close to the crystalline silicon one (~ 3.9), which contributes to an increased reflection at the front side. A material that has the potential to fulfill the above-mentioned tasks better than (p)a-Si:H is hydrogenated nanocrystalline silicon oxide (nc-SiO_x:H), deposited by PECVD, consisting of (doped) silicon nanocrystallites embedded in an amorphous silicon oxide matrix (often referred to as hydrogenated microcrystalline silicon oxide μc-SiO_x:H) [5]. Such a two phase system opens another degree of freedom for finding an optimum between electrical and optical properties that can be tuned over a wide range by varying growth conditions, doping type and alloying (i.e. with oxygen) [6-7].

Several issues have to be taken into account especially when nanocrystalline layers of a few tens of nanometers are used, which we address in this work: (a) the initial stages of growth, (b) bulk material electrical/optical trade-off and (c) contact to the front TCO. An amorphous incubation zone can develop between the substrate and the stationary nanocrystalline growth, and its thickness is strongly influenced by deposition conditions, nature and morphology of the substrate surface [8-9]. As compared to growing nanocrystalline films directly on a c-Si substrate, on top of the (i)a-Si:H passivation layer they are more prone to develop a thicker amorphous incubation layers [9-10]. Koh at al. [11] have reported about the dopant source gas effect on crystalline volumes fraction (F_c). They also found that the incubation layer thickness is further increased by employing trimethylboron (TMB) as dopant source gas, and that special strategies are required. Plasma treatments on the i-layer interface have been suggested to slightly change the substrate before depositing the nanocrystalline layer [11-13]. Harsh plasma conditions, usually used to stimulate crystalline growth, cannot be used here as they would damage the c-Si passivation and reduce cell Voc. While the H_2 plasma treatment effect is the insertion of hydrogen atoms into Si–Si bonds, which results in structural changes allowing a disorder-to-order transition within the a-Si:H film [14], the CO_2 plasma seems to favor the formation of Si-O by substitution of the weak Si-Si and/or Si-H bonds [13].

In this report, we show an approach to reduce the incubation layer thickness and reach a faster nanocrystalline growth in order to improve the p-doped nc-SiO_x:H emitter by means of CO_2 plasma on test structures and by analyzing the solar cell performances. The passivation quality is monitored by measuring Quasi Steady States Photo Conductance decay (QSSPC) both for standard a-Si:H and nc-SiO_x:H emitters. Then we investigate the refractive index and crystalline volume fraction at various PECVD growth conditions for the bulk (p)nc-SiO_x:H emitter. Finally, the interface between the (p)nc-SiO_x:H emitter and the front TCO is changed by inserting a (p)nc-Si:H contact layer with variable thickness in order to address the poor fill factor issue.

2. Experimental

The p-doped nc-SiO_x:H layers are deposited by RF PECVD technique (Applied Material AKT1600 cluster tool, electrode area 2000 cm²) using SiH_4, H_2, TMB and CO_2 as process gases.
For layer characterization, the emitter materials are deposited as 150–450 nm films on glass substrates and characterized by means of spectrophotometry and Raman spectroscopy. For the RF power (P) and the gas pressure (p), the range investigated are 330-700 W and 5-9 Torr, respectively. The CO$_2$, TMB gas flow ratios are kept constant ($r_{CO2}=40 \%$ and $r_{TMB}=0.5 \%$), while the hydrogen dilution, H$_2$/SiH$_4$, is varied between 500 and 1000. Test structures consisting of a double layer of (i)a-Si:H/(p)nc-SiO$_x$:H (50 nm/50 nm) are also fabricated and analyzed by Raman spectroscopy to verify the effect of CO$_2$ plasma treatment on the nc-SiO$_x$:H growth.

Devices with p-doped nc-SiO$_x$:H emitters are fabricated on n-type monocrystalline float zone-grown silicon wafers with resistivity of 3 $\Omega$cm, thickness of 270 $\mu$m, and <100> crystal orientation. Both surfaces are texturized to create a random pyramids on the surface (average height of 5 $\mu$m). Subsequently, wafers are cleaned by the RCA procedure. Prior the PECVD depositions, the substrates are etched in 1% HF to remove the native oxide layer. The emitter surface is passivated by 6 nm of intrinsic a-Si:H and a stack of (i)a-Si:H/(n)a-Si:H is deposited as passivation and BSF layers on the back side. Afterwards, the emitter layer is deposited with the following process variations:

- bulk emitter deposition: variation of refractive index n and F$_c$
- i-layer surface treatments: with and without CO$_2$ plasma treatment
- non-oxidic (p)nc-Si:H contact layer: nominal thickness from 0 to 10 nm

To complete the device, a stack of 80 nm ZnO:Al and 200 nm Ag is deposited on the non-illuminated side by DC sputtering and the front is covered with 80 nm of TCO (In$_2$O$_3$:Sn, ITO) and a metallic grid (10 nm Ti and 1500 nm Ag). Finally, 12 cells with area of 1x1 cm$^2$ are defined on each wafer by photolithography.

The devices are characterized using a class AAA+ solar simulator with dual-source illumination under standard test conditions (25°C), illumination dependent open-circuit voltage (Suns-V$_{oc}$), external quantum efficiency (EQE) and absorptance measurements (1-total reflection).

Quasi-Steady-State Photoconductance (QSSPC) lifetime measurements were performed on simplified cell structures (emitter/(i)layer/(n) type c-Si wafer substrate/(i)layer/BSF) on <111> oriented both sides polished c-Si wafers to assess the effect of CO$_2$ plasma treatments and emitter deposition parameters on the passivation (i)a-Si:H layer quality.

3. Results and discussion

Fig. 1 (a-b) shows the material properties of (p)nc-SiO$_x$:H films deposited on glass substrates as function of gas pressure and RF power. We find that F$_c$ and n can be varied in a wide range by independently changing pressure and power, as previously discussed for n-type nc-SiO$_x$:H material in Ref. [15]. In Fig. 1 (b), when decreasing the gas pressure and/or increasing the power, n linearly changes from 3.3 (at 330 W/9 Torr) to 2.8 (at 600 W/5 Torr). In Fig. 1 (a) two parameters regions can be identified. Region I is characterized by no dependence of F$_c$ on P and p, while at higher power and pressure – region II – the material presents a stronger amorphous phase fraction due to increased oxygen incorporation, confirmed also by a lower refractive index.

With the aim to further decrease the refractive index without affecting the crystallinity or even improving it, the hydrogen dilution is varied for selected layers as reported in Fig. 1 (d-e). We find a significant reduction in refractive indexes (from ~ 2.95 to ~ 2.65) with a crystallinity above 40 %. The EQE spectra measured on cells with selected emitter layers are depicted in Fig. 1 (c). The emitter thickness is fixed at about 30 nm and a thin recombination layer (2.5 nm) is also added for reasons that will be discussed below. For emitter layers deposited at higher hydrogen dilutions, short circuited currents of 40 mA/cm$^2$ are measured mainly due to the lower refractive indexes of these films. The cell parameters (not shown here) suggest us that further work has to be done to optimize the emitter deposition using these harsher PECVD conditions that mainly affect the open circuit voltage V$_{oc}$, i.e. probably degrade the a-Si/c-Si interface passivation.

To check the effect of a (soft) CO$_2$ plasma on the crystalline volumes fraction simple test structures are deposited on glass substrates: an (i)a-Si:H layer is deposited prior to the emitter to simulate the same substrate as in the cell configuration. In Fig. 2 (b) the Raman spectra of these glass/a-Si/nc-SiO$_x$ samples are dominated by the amorphous phase, but a clear 520 cm$^{-1}$ peak from the crystalline volume fraction arises for the sample with CO$_2$ plasma treatment.
Fig. 2 (c) shows the effect on cell level of varying plasma conditions, while all the other layers are nominally the same and similarly processed. We can summarize that a soft plasma treatment helps to reduce (ohmic) series resistance effects that we suspect to be correlated to thicker incubation layer thickness and lower crystallinity within the bulk emitter layer.

Fig. 1. (a) Raman crystallinity ($F_c$) and (b) refractive index ($n$) as function of gas pressure and RF power variations in PECVD depositions ($r_{CO_2}=40\%$, $r_{TMB}=0.5\%$ and $H_2/SiH_4=500$). Symbols represent experimental measurements. (c) Absorptance 1-R and EQE as a function of wavelength for the best cells on textured wafers with three different ($p$)nc-SiO$_x$:H emitters (30 nm). (d-e) Refractive index and Raman crystallinity as function of $H_2/SiH_4$ ratio.
In Fig. 2 (a) we analyze the impact of CO$_2$ plasma treatment (30 W/10 s) and two different emitters on the intrinsic layer passivation quality on simplified cell structures (emitter/(i)layer/(n)type c-Si wafer substrate/(i)layer/BSF) characterized by QSSPC measurements. The implied open circuit voltage, impl-V$_{oc}$, is measured for varying (i)a-Si:H layer thickness and emitter material. For standard (p)a-Si:H emitters, we find that the CO$_2$ plasma treatments does not affect the passivation quality also with different intrinsic layer thicknesses ($\tau_{\text{eff}} \sim 1.5$ ms and impl-V$_{oc}$ ~ 700 mV); this also prove that the plasma treatments does not etch away the (i)a-Si:H layer. In case of (p)nc-SiO$_x$:H emitters much higher impl-V$_{oc}$ are measured ($\tau_{\text{eff}} > 2.5$ ms and impl-V$_{oc}$ ~ 720 mV) however with a thicker (i)a-Si:H layer underneath (deposition time 30 s). We believe that this is mainly due to a much higher H$_2$ dilution which further passivates dangling bonds within the intrinsic layer.

The devices fabricated with nc-SiO$_x$:H emitters show higher V$_{oc}$s but suffer from a lower FF as compared to the standard cell configuration with (p)a-Si:H emitter (FF=77 %, not shown here). This can be attributed to transport losses at the (p)emitter/(n)TCO interface and in the emitter bulk material. The TCO/(p) emitter contact is known to be critical for cell performance [16]. In our (p)nc-SiO$_x$:H emitter (300 W/5 Torr/H$_2$-dilution = 500) the crystalline volume fraction seems to be too low to assure high doping density within the layer and at the (n)TCO interface, therefore the resulting tunnel junction is inefficient. To support our hypothesis, a highly doped and highly crystalline layer (“contact layer”) with variable thickness was introduced between the oxide emitter (~ 30 nm thick) and the front TCO as shown in Fig. 3 (a-b). The nominal thickness of such contact layer was varied in the range 0-10 nm. The FF and the p-FF, respectively calculated from the light IV curve and from Suns-V$_{oc}$, are compared to the series resistance, $R_{s,\text{light}}$, calculated as described in Ref. [17]. In Fig. 3 (a), the cell with only 30 nm thick nc-SiO$_x$:H emitter shows a FF below 63 % with a high p-FF (~ 81 %). With introducing the contact layer and progressively increasing the layer thickness, the FF increases with a simultaneous reduction in contact resistance losses. Both parameters saturate at a thickness of 10 nm (FF=77 %, $R_{s,\text{light}}=1 \Omega \text{cm}^2$). The p-FF remains constant in the entire range investigated (0-10 nm) and it is likely that the residual difference in FF is caused by losses in the emitter bulk material, ITO and front metal grid. On the other hands, the addition of a thicker nc-Si:H layer (10 nm) penalizes the current density, because the emitter stack is not a graded index series from c-Si to air anymore. This leads to a reduction in $J_{sc}$ of 1.5 mA/cm$^2$. Further work has to be done to reduce as much as possible the thickness of such a contact layer by adjusting carefully the trade-off between photocurrent and series resistance.

Fig. 2. (a) Implied-V$_{oc}$ measured by QSSPC on cell structures with standard (p)a-Si:H emitter (10 nm) and (p)nc-SiO$_x$:H (20 nm) with and without CO$_2$ plasma treatment as function of intrinsic layer thickness. (b) Raman measurements on test structures (see inset) with and without CO$_2$ plasma treatments. (c) Fill factor, FF, and series resistance ($R_{s,\text{light}}$) for solar cells with different CO$_2$ plasma treatments on the (i)a-Si:H.
4. Conclusion

In this work, we investigated the variation of refractive index $n$ and crystallinity $F_c$ of (p)nc-SiO$_x$:H by means of varying PECVD deposition conditions (gas pressure and plasma power) in a wide range. The refractive index of such layers progressively changed from 3.3 to 2.8 by decreasing the pressure and increasing the power. However, the most interesting parameter set from the optical point of view (Region II in Fig. 1 (a)), results in a lower crystalline fraction $F_c$ mainly due to oxygen incorporation and consequent increasing in the amorphous fraction. By increasing the $H_2$-dilution we were able to independently change $n$ and $F_c$, and the most promising layers were tested on devices, as discussed in Fig. 1 (c-e). A short circuit current density ($J_{sc-EQE}$) of 40 mA/cm$^2$ was measured, i.e. an improvement of 2% if compared to nc-SiO$_x$:H emitters with higher $n$ and up to 4% with respect to standard emitters (10 nm of (p)a-Si:H). Regarding the incubation layer, we have shown that bulk emitter properties can be strongly changed by modifying the (i)a-Si:H interface with CO$_2$ plasma treatments. It was also proven that the passivation quality is not deteriorated by the optimized plasma treatments. Finally, by inserting a progressively thicker nc-Si:H layers embedded between the emitter and the TCO the fill factor was significantly improved from 62.1% (0 nm) and 76.8% (10 nm contact layer nominal thickness).

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References


