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SiO_xNy:B Layers for Ex-situ Doping of Hole-Selective Poly Silicon Contacts: A Passivation Study

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Abstract. Passivating the contacts of crystalline silicon (c-Si) solar cells with a polycrystalline silicon layer (poly-Si) on a thin oxide (SiO_x) film allows to decrease the recombination current at the metal/c-Si interface. In this study, an ex-situ doping method of poly-Si is proposed, involving a SiO_xNy:B layer as a dopant source. In this study, we compare the properties (crystallinity of the deposited layer, doping profile and surface passivation properties) of the resulting ex-situ doped poly-Si(B) layer with our in-situ doped reference.

INTRODUCTION

Passivating the contacts of c-Si solar cells with a polycrystalline silicon (poly-Si) layer on top of a thin silicon oxide (SiO_x) is known to reduce carrier recombination at the interface between the metal electrodes and the c-Si substrate¹⁻³. In this study we focused on boron-doped poly-Si (poly-Si(B)) structures which are of prime interest to passivate the rear side of next-generation PERC solar cells. Poly-Si(B) layers are prepared by Plasma-Enhanced Chemical Vapor Deposition (PECVD) of an amorphous silicon (a-Si:H) layer followed by a crystallization annealing step. Poly-Si(B) layers were previously developed in our lab by in-situ doping the a-Si:H layer with the addition of B₂H₆ to the precursor gas mix⁴. However, the use of H-rich precursor gases during the PECVD step is leading to a blistering phenomenon of the layer^{5,6}. Moreover, the addition of B to the deposited layer is impeding the crystallization of the in-situ doped poly-Si(B) layer⁷.

For these reasons we developed an ex-situ doping method which consists in depositing a B-rich dielectric layer (SiO_xNy:B) on top of an intrinsic Si layer deposited by PECVD. In this contribution we compared the ex-situ doped poly-Si(B) layer with our reference in-situ doped poly-Si(B): we first studied the effect of removing the B₂H₆ during the PECVD step on the crystalline nature of the deposited layer. Then, we confront the active doping profiles of poly-Si(B) layers obtained with in-situ and ex-situ doping methods. Finally, we compare the passivation properties of in-situ and ex-situ doped poly-Si(B)/SiO_x structures as function of the annealing temperature.

EXPERIMENTAL

Symmetrical samples were prepared from 180 μm-thick KOH-polished 156 mm n-type Cz wafers (3-6 Ω.cm). First, a thin SiO_x layer (~1.3 nm) was grown on the surface of the wafers by ozonized DI-H₂O rinsing. Reference

in-situ doped poly-Si(B) layers were prepared by PECVD of 25 nm-thick B-doped a-Si:H layers on both sides of the wafer using H₂-diluted diborane (B₂H₆) as doping precursor gas and followed by an annealing step under argon (T_a = 700-900°C) to crystallize the layer and activate dopants. Ex-situ doped poly-Si(B) layers were prepared by PECVD of a SiO_xN_y:B layer on top of a 25 nm-thick intrinsic Si layer deposited by PECVD, followed by the same annealing step to ensure dopant diffusion and activation. A hydrogenation step was carried out on both in-situ and ex-situ poly-Si(B) layers by PECVD of a H-rich silicon nitride (SiN:H) layer, followed by a firing step in a belt furnace (T_{firing} = 800-900°C).

Thicknesses of initial a-Si and final poly-Si layers were measured by spectroscopic ellipsometry (SE) respectively after PECVD and crystallization annealing. The imaginary part of the dielectric function (ϵ_i) obtained as a function of the photon energy (E_p) through SE measurement was used to assess the crystalline nature of the layers. Electrochemical Capacitance-Voltage (ECV) and Hall effect measurements were performed to respectively assess the active doping profile and electrical properties (carrier density, conductivity and mobility) of the final poly-Si(B) layers. Eventually, the photo-conductance decay (PCD) technique was used to evaluate the surface passivation properties (in terms of implied open circuit voltage (iV_{oc}) and recombination current density (J_0)) of in-situ and ex-situ doped poly-Si(B)/SiO_x structures.

RESULTS AND DISCUSSION

Effect of B₂H₆ Removal on the Deposited Layer

In this paragraph, we compare the crystalline nature of the B-doped and intrinsic Si layer after deposition.

In-situ B-doped a-Si:H layer were previously developed in our lab by PECVD. The use of a high deposition temperature (T_{dep} = 300°C) and a high gas ratio (R = H₂/SiH₄ = 50) afforded blister-free passivating poly-Si(B)/SiO_x structures after annealing⁴. The use of a high gas ratio R during PECVD could promote a deposition of microcrystalline Si layers (μc-Si)⁸. However, the addition of B during the process is known to impede its crystallization⁷. Indeed, our B-doped layer was verified to be amorphous after deposition as the curve representing ϵ_i versus E_p featured a broad peak centered around 3.3 eV (for a layer thickness of 25 nm, see Fig. 1)⁹. Therefore we denote the in-situ B-doped layer after deposition as: a-Si:H(B).

In order to use an ex-situ doping method we needed to develop an intrinsic layer by PECVD. For this purpose we used the same PECVD parameters than the ones used for a-Si:H(B) deposition except that we removed B₂H₆ from the precursor gases. This resulted in the crystallization of the deposited layer into a μc-Si intrinsic layer (μc-Si(i)). The μc nature of the layer was evidenced by SE as the ϵ_i versus E_p curve featured a plateau shape due to the apparition of a second peak around 4.1 eV typical of a μc-Si phase⁹ (see Fig. 1).

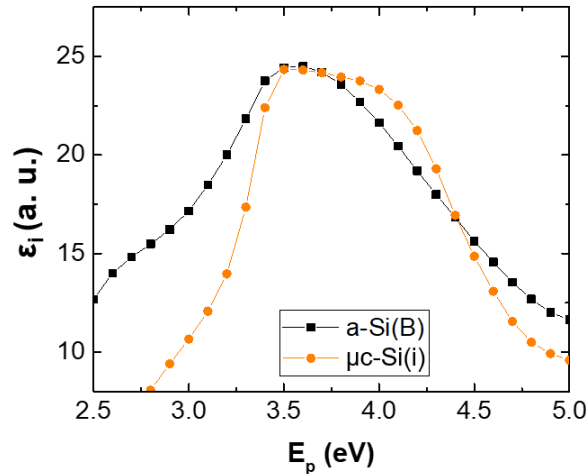


FIGURE 1. Imaginary part of the dielectric function (ϵ_i) vs. photon energy (E_p), from SE measurement performed after deposition of in-situ doped a-Si:H(B) layer and intrinsic μc-Si(i) (both 25 nm-thick). The removal of the doping precursor gas B₂H₆ had the effect of changing the nature of the deposited layer from amorphous to microcrystalline (a-Si to μc-Si).

In-situ and Ex-situ Poly-Si(B) Doping Profiles

In this paragraph we compare the active-doping profiles obtained on reference in-situ doped poly-Si(B) layers and on ex-situ doped poly-Si(B) layers. The active-doping profiles were measured by ECV after annealing in the range $T_a = 700\text{-}800^\circ\text{C}$ (Fig. 2). For $T_a = 700\text{-}750^\circ\text{C}$, a gradually fading doping density was observed for the ex-situ doped layer (from $2 \times 10^{19} \text{ cm}^{-3}$ to $2 \times 10^{18} \text{ cm}^{-3}$). In this T_a range, the in-situ doping profile showed more of a plateau around $1.5 \times 10^{20} \text{ cm}^{-3}$. For $T_a = 800^\circ\text{C}$, although the shape of the in-situ and ex-situ doping profiles were similar, the doping density in the ex-situ layer was found to be ten times lower than the doping density in the in-situ layer. Interestingly, for $T_a = 800^\circ\text{C}$, the B-diffusion length in the c-Si was found to be similar for both in-situ and ex-situ doped layers. For $T_a = 850^\circ\text{C}$ (not shown here), the doping plateau remained similar as for $T_a = 800^\circ\text{C}$ for both in-situ and ex-situ poly-Si layers but the B-diffusion tail into c-Si was deeper (respectively 150 nm and 100 nm-deep for in-situ and ex-situ layers).

Hall effect measurements were performed on in-situ and ex-situ doped layers for $T_a = 700^\circ\text{C}$ to avoid any B-diffusion in the c-Si that could induce current flowing in the c-Si and therefore would not enable an accurate estimation of the poly-Si electrical properties. The ex-situ carrier density measured was lower than the in-situ one ($1.2 \times 10^{19} \text{ cm}^{-3}$ and $1 \times 10^{20} \text{ cm}^{-3}$ respectively), which is consistent with the ECV doping profiles showing a lower doping density for the ex-situ doped layer.

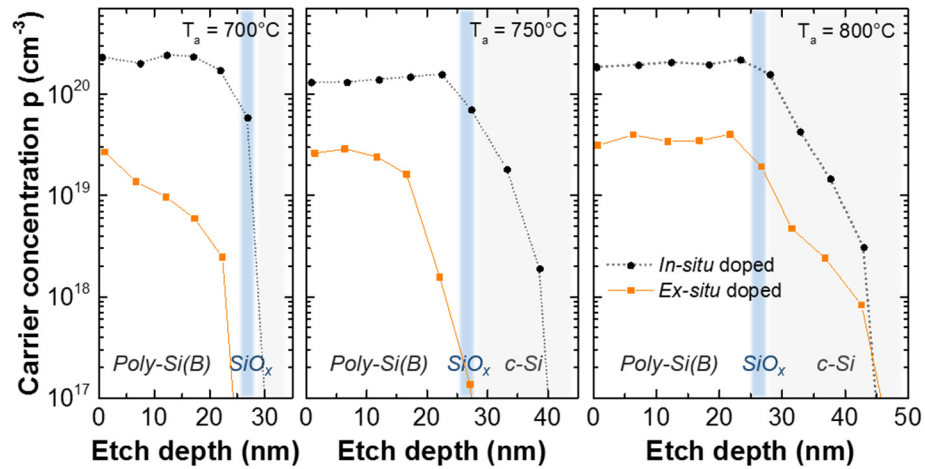


FIGURE 2. ECV active doping profiles of in-situ and ex-situ doped poly-Si(B) layers (25 nm-thick) after annealing at T_a . The SiO_x layer is depicted for reference.

Surface Passivation Properties

The passivation level provided by the ex-situ doped poly-Si(B) structure was then evaluated (in terms of iV_{oc} and J_0) as a function of the annealing temperature (T_a), after annealing and after SiN:H deposition (i.e. before firing). It was compared to the passivation level obtained with in-situ doped poly-Si layer (see Fig. 3). It is to note that the stability of the bulk effective carrier lifetime was verified on the range of T_a investigated.

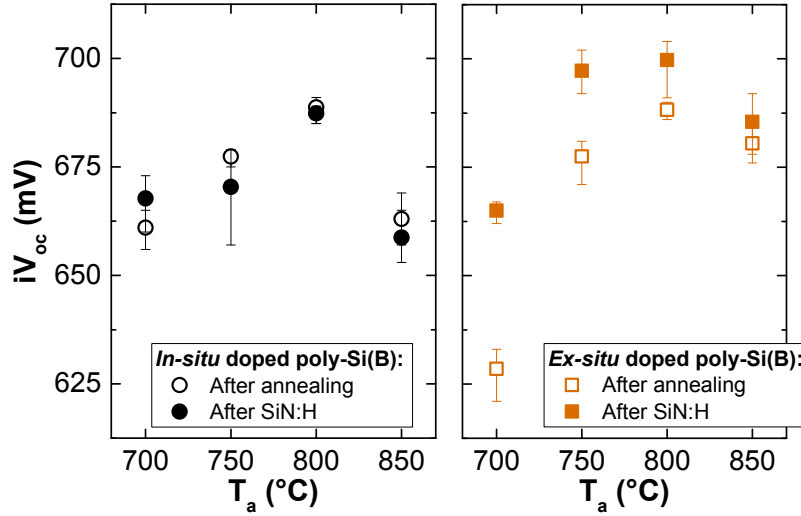


FIGURE 3. iV_{oc} as function of T_a with in-situ and ex-situ doped poly-Si/SiO_x after annealing and right after SiN:H deposition (before firing).

After annealing, the iV_{oc} evaluated on in-situ and ex-situ structures showed a similar trend featuring an increase of the iV_{oc} value from 700°C to 800°C and a decrease of iV_{oc} for $T_a > 800^\circ\text{C}$. For T_a in the range 750°C – 850°C, the iV_{oc} values measured with both structures were equivalent. For $T_a = 700^\circ\text{C}$, the ex-situ doped structure showed lower passivation properties than the in-situ doped structure (iV_{oc} of 628.5 mV and 661 mV respectively). This could be the result of a lower field-effect passivation provided by the ex-situ poly-Si layer that was only partially doped for $T_a = 700^\circ\text{C}$ (see Fig. 2). The subsequent SiN:H deposition involved only slight changes in the iV_{oc} measured on in-situ doped structures whereas it enabled an iV_{oc} gain for ex-situ doped structures on all the T_a range investigated (up to 30 mV for $T_a = 700^\circ\text{C}$). This resulted in slightly higher passivation level provided by the ex-situ doped poly-Si/SiO_x structure after SiN:H deposition, with a maximum iV_{oc} of 702 mV. For both in-situ and ex-situ layers, the drop of iV_{oc} for $T_a > 800^\circ\text{C}$ was attributed to the degradation of the SiO_x layer¹⁰ and/or excessive B-diffusion in the c-Si¹¹.

After subsequent firing at $T_f \sim 860^\circ\text{C}$, an important gain in surface passivation was observed for both in-situ and ex-situ doped poly-Si/SiO_x structures on all the T_a range investigated. Best iV_{oc} values of 736 mV for in-situ structures and 733 mV for ex-situ structures were obtained after annealing at $T_a = 750^\circ\text{C}$ (both corresponding to $J_0 = 6 \text{ fA}\cdot\text{cm}^{-2}$). In conclusion, despite the lower doping density of the ex-situ poly-Si layer, the final passivation properties offered by in-situ and ex-situ poly-Si/SiO_x structures were found to be equivalent.

CONCLUSION

We proposed an ex-situ doping method for poly-Si passivating structures using a boron-rich dielectric layer as a dopant source and we compared the properties of the resulting ex-situ doped poly-Si layer to our reference in-situ doped layer. First, we observed that the removal of the B-rich doping gas during PECVD resulted in crystallization of the deposited layer. Then, the active doping profiles of in-situ and ex-situ poly-Si layers were compared. The doping density of the ex-situ poly-Si layer was observed to be ten times lower than the in-situ layer. Finally, we evaluated the surface passivation provided by in-situ and ex-situ doped poly-Si/SiO_x structures after different step of the process. After annealing both structures showed equivalent surface passivation properties. After SiN:H deposition and subsequent firing, both in-situ and ex-situ structures showed excellent surface passivation. Best $\{iV_{oc}; J_0\}$ couple were of $\{736 \text{ mV}; 6 \text{ fA}\cdot\text{cm}^{-2}\}$ and $\{733 \text{ mV}; 6 \text{ fA}\cdot\text{cm}^{-2}\}$ for in-situ and ex-situ structures respectively.

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