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# SiO<sub>x</sub>Ny: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<sub>x</sub>) 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<sub>x</sub>Ny: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<sub>x</sub>) is known to reduce carrier recombination at the interface between the metal electrodes and the c-Si substrate<sup>1-3</sup>. 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 B<sub>2</sub>H<sub>6</sub> to the precursor gas mix<sup>4</sup>. However, the use of H-rich precursor gases during the PECVD step is leading to a blistering phenomenon of the layer<sup>5,6</sup>. Moreover, the addition of B to the deposited layer is impeding the crystallization of the in-situ doped poly-Si(B) layer<sup>7</sup>.

For these reasons we developed an ex-situ doping method which consists in depositing a B-rich dielectric layer (SiO<sub>x</sub>Ny: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 B<sub>2</sub>H<sub>6</sub> 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<sub>x</sub> 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<sub>x</sub> layer (~1.3 nm) was grown on the surface of the wafers by ozonized DI-H<sub>2</sub>O 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 H<sub>2</sub>-diluted diborane (B<sub>2</sub>H<sub>6</sub>) as doping precursor gas and followed by an annealing step under argon (T<sub>a</sub> = 700-900°C) to crystallize the layer and activate dopants. Ex-situ doped poly-Si(B) layers were prepared by PECVD of a SiO<sub>x</sub>N<sub>y</sub>: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<sub>firing</sub> = 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 ( $\epsilon_i$ ) 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<sub>x</sub> structures.

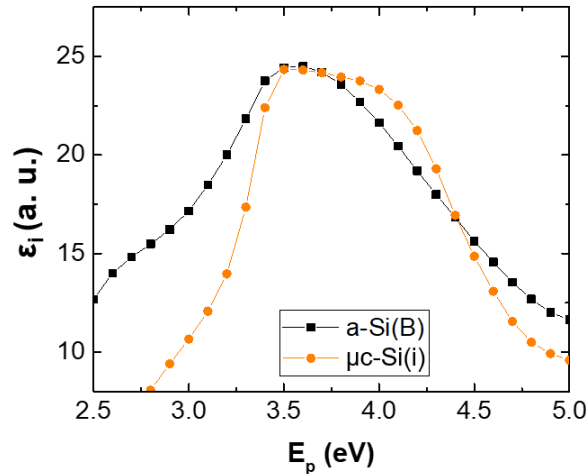
## RESULTS AND DISCUSSION

### Effect of B<sub>2</sub>H<sub>6</sub> 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<sub>dep</sub> = 300°C) and a high gas ratio (R = H<sub>2</sub>/SiH<sub>4</sub> = 50) afforded blister-free passivating poly-Si(B)/SiO<sub>x</sub> structures after annealing<sup>4</sup>. The use of a high gas ratio R during PECVD could promote a deposition of microcrystalline Si layers ( $\mu$ c-Si)<sup>8</sup>. However, the addition of B during the process is known to impede its crystallization<sup>7</sup>. Indeed, our B-doped layer was verified to be amorphous after deposition as the curve representing  $\epsilon_i$  versus  $E_p$  featured a broad peak centered around 3.3 eV (for a layer thickness of 25 nm, see Fig. 1)<sup>9</sup>. 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 B<sub>2</sub>H<sub>6</sub> from the precursor gases. This resulted in the crystallization of the deposited layer into a  $\mu$ c-Si intrinsic layer ( $\mu$ c-Si(i)). The  $\mu$ c nature of the layer was evidenced by SE as the  $\epsilon_i$  versus  $E_p$  curve featured a plateau shape due to the apparition of a second peak around 4.1 eV typical of a  $\mu$ c-Si phase<sup>9</sup> (see Fig. 1).

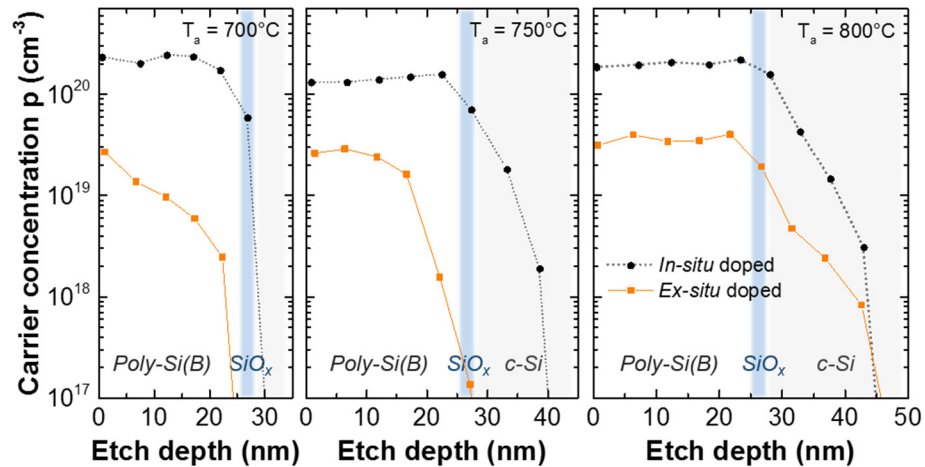


**FIGURE 1.** Imaginary part of the dielectric function ( $\epsilon_i$ ) vs. photon energy ( $E_p$ ), from SE measurement performed after deposition of in-situ doped a-Si:H(B) layer and intrinsic  $\mu$ c-Si(i) (both 25 nm-thick). The removal of the doping precursor gas B<sub>2</sub>H<sub>6</sub> had the effect of changing the nature of the deposited layer from amorphous to microcrystalline (a-Si to  $\mu$ c-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).

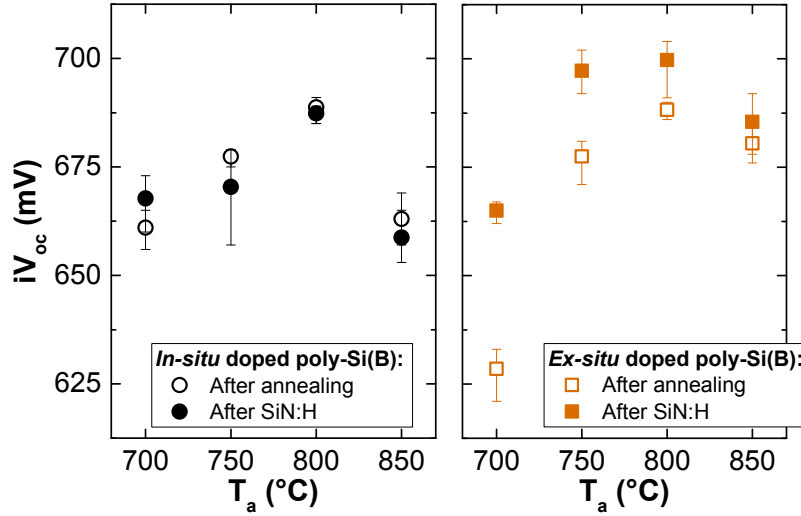
Hall effect measurements were performed on in-situ and ex-situ doped layers for  $T_a = 700^\circ\text{C}$  to avoid any B-diffusion in the c-Si that could induce current flowing in the c-Si and therefore would not enable an accurate estimation of the poly-Si electrical properties. The ex-situ carrier 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  $\text{SiO}_x$  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  $\text{SiN:H}$  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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> layer<sup>10</sup> and/or excessive B-diffusion in the c-Si<sup>11</sup>.

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<sub>x</sub> 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<sub>x</sub> 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<sub>x</sub> 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.

## ACKNOWLEDGMENTS

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