Boron doped SiO$_x$ dielectrics for bifacial n-type and p-type silicon solar cells

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Abstract

Bifaciality offers a high potential to increase the efficiency of industrial silicon solar cells and their integration to sustainable building design. However, not enough work has been presented on doped dielectrics for bifacial solar cells. In this work we show a study on $p$-doped SiO$_x$ layers for bifacial solar cells. We use a non-conventional gas precursor, hexamethyldisiloxane (HMDSO) for the silicon-oxygen source, mixed with diborane as the $p$-type dopant and carbon-dioxide as the additional oxygen source. Our analysis reveals that layers deposited with HMDSO are thermally stable compared to the case when silane is used. Electrochemical capacitance voltage and secondary ion mass spectrometry measurements confirm the formation of a uniform boron doped layer inside the silicon bulk. Furthermore, we found that the depth of $p^+-n$ and $p^-p$ junction can be controlled by the deposition parameters and the time of thermal diffusion. Chemical analysis shows that carbon is accumulated at the dielectric/wafer interface due to a barrier formation inside the carbon rich silicon. The $p$-SiO$_x$ layers can be applied on $n$-c-Si and $p$-c-Si base material as an emitter and back surface field respectively, demonstrating a feasible bifacial solar cell device.

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1. Introduction

Bifacial solar cells are gaining interest in the photovoltaic (PV) industry due to their bifacial spectral response and increased power generation at the module level. Solar cells fabricated in one diffusion step [1,2] offer a great

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potential in the PV industry as they reduce the processing steps and thus lower the production cost. In these structures, generally the $p$-type layer and the $n$-type layer is deposited on a bulk $c$-Si substrate by plasma deposition processes like Radio Frequency-Plasma Enhanced Chemical Vapor Deposition (RF-PECVD) [1,3], Microwave Plasma Chemical Vapor Deposition (MW-PECVD) [4] or Atmospheric Plasma Vapor Deposition (APCVD) [5]. Conventionally, borosilicate glass (BSG) and phosphorous silicate glass (PSG) is deposited with Si-(O)$_n$ precursors such as silane (SiH$_4$) [1], tetraethylorthosilicate (TEOS) [6], with an additional oxygen (O) source such as oxygen (O$_2$) [6], nitrous oxide (N$_2$O) [1] or carbon dioxide (CO$_2$) [7]. From a practical point, these chemistries are toxic and from a performance perspective these precursors may not provide the full range of optical and electrical properties in the layers. Hexamethyldisiloxane (HMDSO) is a precursor which is used to deposit thermally stable SiO$_2$ layers [8].

In this work we explore the use of boron doped SiO$_{x}$ layers deposited by HMDSO as the Si-O source, diborane as the $p$-type dopant and carbon-dioxide as the additional oxygen source. Figure 1 shows the structure of $n$-type and $p$-type bifacial silicon solar cells.

Fig. 1. Bifacial solar cells shown in this work: (left) $p$-doped SiOx used as emitter; (right) $p$-doped SiOx used as back surface field (BSF).

2. Experimental method

The $p$-type SiO$_x$ layers were deposited on float zone (FZ) $n$-$c$-Si wafers. The base resistivity of the wafers is 4 $\Omega$-cm. The depositions were performed in a RF-PECVD reactor operated at a fixed frequency of 13.56 MHz. The PECVD reactor is a Plassys CVD 300. The distance between the electrodes is chosen to be 25 mm for an optimal plasma ignition. Helium (He) was used as a carrier gas and the flow rate was fixed at 1000 sccm. HMDSO flow rate was 3.5 sccm, CO$_2$ flow rate was 5.1 sccm and B$_2$H$_6$ flow rate was varied in the range of 0 to 0.8 sccm (maximum). The power was fixed at 10W and pressure at 0.5 Torr, allowing low deposition rate (~ 1 Å/s) and high quality of the layers. The samples were thermally diffused in a quartz tube at 1050ºC under nitrogen flush.

The refractive index of the layers was estimated by Spectroscopic Ellipsometry. The bond configuration in the layers was studied with Fourier Transform Infrared (FT-IR) Spectroscopy. The concentration of active carriers diffused inside the silicon wafers after the thermal diffusion was measured by Electrochemical Capacitance-Voltage (ECV) method. The elemental composition of the $p$-SiO$_x$ layer before and after thermal diffusion was checked by Secondary Ion Mass Spectrometry (SIMS). SIMS is also used to check the diffusion of elements such as boron and carbon in the silicon bulk and this SIMS data was compared with the ECV measurements.

An optimised $p$-type SiO$_x$ layer can be applied to a $n$-$c$-Si base material as an emitter or to a $p$-$c$-Si base material as a back surface field (BSF). Figure 2 shows the process steps of fabricating a bifacial solar cell in emitter configuration and BSF configuration. The bifacial or PERT (passivated emitter and rear totally diffused) solar cell devices were processed as follows: firstly, the Czochralski (Cz) silicon wafer was alkaline textured to form random pyramids on the front side for higher light trapping; next, the rear side was single side polished in an industrial inline wet bench. The rear side passivation and dielectric deposition in general works better when the rear side is perfectly polished. The silicon wafer was then $n$'-doped in an industrial Centrotom therm furnace using POCl$_3$ gas for diffusion. On the $n$-type material the $n'$-layer formed serves as a front surface field, while on the $p$-type material the $n'$-layer is the emitter. Afterwards, the rear side is isolated chemically in an inline process to eliminate the rear side parasitic dopants by removing around 1μm of silicon material. Then the PSG is removed and the substrates are ready for $p$-SiO$_x$ layer deposition. The samples undergo thermal diffusion under N$_2$ atmosphere. The doping profile is measured by ECV. Next, the SiO$_x$ remaining layer is removed by HF and the sheet resistance ($R_{sh}$) is measured. The samples are cleaned using HF to remove native oxide and thereafter PECVD SiN$_x$ passivation is performed on both sides.
Finally, the samples are screen printed using H pattern for high bifaciality. At the front a standard Ag paste is used. The rear side is screen printed using an Ag/Al paste.

3. Results and discussion

3.1 Optical properties

Figure 3 shows the refractive index of the $p$-$\text{SiO}_x$ layers as a function of diborane flow rate. It also compares the $p$-$\text{SiO}_x$ layers deposited with silane/CO$_2$ gas mixture to the layers with HMDSO/CO$_2$ gas mixture and diborane is used as the $p$-type dopant.
Figure 3 shows that for SiH₄/CO₂ gas mixture, refractive index increases significantly from 2.7 to 2.92 as diborane flow rate increases from 0 to 0.8 sccm. In the case of HMDSO/CO₂ gas mixture, refractive index increases slightly from 1.45 to 1.5 as diborane flow rate increases from 0 to 0.8 sccm. This is because the introduction of more dopants makes the layer denser and thus refractive index increases.

Symmetric samples were prepared for lifetime measurements in order to check the passivation properties of the layer. We found that the layers deposited with SiH₄/CO₂ gas mixture have an average lifetime (τₑff) ~ 100 μs while the layers deposited with HMDSO/CO₂ gas mixture have an average lifetime (τₑff) ~ 10 μs. When the dielectric layers were subjected to thermal diffusion (1050°C for 30 min), it was observed that p-SiOₓ layers deposited with SiH₄/CO₂ peeled off, while the ones deposited with HMDSO/CO₂ remained intact on the c-Si surface. The layers deposited with SiH₄/CO₂ peel off as they are rich in hydrogen and hydrogen effuses out of the layers during the thermal diffusion. In our case, we use p-SiOₓ layers as a boron source and thermal diffusion is necessary in order to diffuse boron inside the c-Si bulk. The passivation by this layer is not good for either chemical or field effect passivation of silicon solar cells (τₑff~ 10 μs). However, the primary goal of this layer is the boron source. As explained in the solar cell structure, the dielectric will be etched off after diffusion. Furthermore, silicon nitride (SiₙNₓ) will be applied as surface passivation layer.

At the atomic level, the concentration of boron in a p⁺-emitter is around 2-5 × 10¹⁹ at/cm³ for a depth of 0.4μm [1] (Rsh~85 Ohm/sq) and around 1-2 × 10²⁰ at/cm³ to work as a back surface field (BSF). We choose the maximum flow rate of B₂H₆ (0.8 sccm) and check the concentration of boron diffused in c-Si.

3.2 Fourier transform infrared spectroscopy

A 200 nm thick p-SiOₓ layer (HMDSO/CO₂ gas mixture) was deposited on an intrinsic Czochralski (Cz) for FT-IR measurements. The layer was then subjected to thermal diffusion (1050°C for 30 min) under a nitrogen flush. The thickness of the p-SiOₓ layer was estimated by ellipsometry before and after the thermal diffusion. We find that the layer thickness is 100 nm after the thermal diffusion step. The FT-IR spectrum of the p-SiOₓ layer was taken before and after thermal diffusion. Figure 4 compares the two FT-IR spectra.
Figure 4 shows that there is an upward shift in absorption spectrum of the $p$-$\text{SiO}_x$ layer after thermal diffusion, indicating higher absorption or a denser layer. This suggests that the $p$-$\text{SiO}_x$ layer densifies during the thermal diffusion and this is what we observed from the spectroscopic ellipsometry measurement. We also expect that there is structural change in the layer after thermal diffusion step. The region 1020-1100 cm$^{-1}$ is attributed to asymmetric stretching of Si-O-Si bonds and the sharp peak at 1080 cm$^{-1}$ confirms that the concentration of O in the layer is higher [9]. This could be possible because of thermal oxidation of the $p$-$\text{SiO}_x$ layer after the thermal diffusion. Further, the peak at 1260 cm$^{-1}$ (Si-CH$_3$) disappears after thermal diffusion. This confirms that initially C is present in the layer in a bonded state and this Si-CH$_3$ bond dissociates during the thermal diffusion.

### 3.3 Electro-chemical capacitance voltage measurements

To measure the concentration of the active carriers, $p$-$\text{SiO}_x$ layers were deposited on 250 $\mu$m thick FZ $n$-c-Si wafer (base resistivity~ 4 $\Omega$-cm) and then subjected to thermal diffusion To investigate the depth of $p^+\text{-}n$ junction in the solar cell (emitter configuration), we chose the thickness of $p$-$\text{SiO}_x$ layer and the time of thermal diffusion as the parameter. Figure 5 (left) shows the concentration of diffused carriers as a function of $p$-$\text{SiO}_x$ layer thickness. Figure 5 (right) shows the effect of time of thermal diffusion on the doping profile.

![Fig. 5. Concentration of diffused carriers in c-Si bulk measured by ECV: (left) as a function of p-SiOx thickness; (right) as a function of time of thermal diffusion](image-url)
Figure 5 (left) shows that as the \( p\)-SiO\(_x\) layer thickness increases from 100 nm to 250 nm, the concentration of B at the surface increases from \(5 \times 10^{18}\) at/cm\(^3\) to \(2.1 \times 10^{19}\) at/cm\(^3\). This is possible because higher concentration of B in the layers helps in-diffusion of more B in \( n\)-\( c\)-Si bulk. The \( p^-n\) junction depth remains constant at around 300 nm (0.3\( \mu\)m junction depth). This is equivalent to a sheet resistance of around 350 Ohm/sq.

Figure 5 (right) shows that as the time of thermal diffusion increases from 30 min to 60 min, the depth of \( p^-n\) junction increases from 300 nm to 600 nm, as expected since B diffusivity in Si is high. This is equivalent to a sheet resistance of around 230 Ohm/sq. In the emitter configuration, generally 250 nm \( p^-n\) junction depth with a carrier concentration of \(10^{20}\) at/cm\(^3\) is sufficient for a standard sheet resistance of around 65 Ohm/sq. This suggests that a 30 min diffusion time is optimum for a junction depth of around 0.3\( \mu\)m but a thicker \( p\)-SiO\(_x\) layer is needed for higher B concentration in order to reach \(10^{20}\) at/cm\(^3\).

### 3.4 Secondary ion mass spectrometry

The diffusion of elements such as C, O and B inside the \( n\)-\( c\)-Si wafer was also checked after the thermal diffusion by SIMS measurements. Figure 6(left) shows the concentration of elements as a function of depth inside \( n\)-\( c\)-Si wafer; and Figure 6(right) shows the elemental composition of the \( p\)-SiO\(_x\) layer after diffusion.

![Fig.6 (left) Concentration of B, C and O in the c-Si bulk after thermal diffusion; (right) elemental composition of the p-SiO\(_x\) layer after thermal diffusion](image)

Figure 6(left) shows that there is O present inside \( n\)-\( c\)-Si wafer upto 50 nm (\( \sim 10^{18}\) cm\(^3\)). We expect that this O is seen in the SIMS measurement because of the native surface oxidation of the \( n\)-\( c\)-Si wafer after HF dip. We also see the diffusion of C upto 100 nm (\( \sim 10^{18}\) cm\(^3\)) in \( n\)-\( c\)-Si wafer. Rucker et al. reported that there is suppression of carbon diffusion in carbon rich silicon [10,11]. Thus, we expect that this carbon in the first 100 nm region of the \( n\)-\( c\)-Si wafer acts as a barrier for further diffusion of carbon in the wafers. However, boron diffuses deeper upto 300 nm (\( \sim 10^{18}\) cm\(^3\)) into \( n\)-\( c\)-Si wafer and is still useful as emitter in the solar cell. This is due to the higher solubility of B in Si compared to O and C in Si. Vick et al [12] found an important improvement from \(1.6 \times 10^{19}\) at/cm\(^3\) to \(2.4 \times 10^{20}\) at/cm\(^3\) of solid solubility of B into Si, while increasing diffusion temperature above 1000°C. However, the solubility of O and C in Si is much lower and remains constant at around \(3 \times 10^{18}\) at/cm\(^3\) above 1000°C. The initial concentration of O in the Si bulk is low and around \(10^{18}\) at/cm\(^3\) [13]. In the same manner, it has been shown that C is highly soluble in growing Si during melting, which can explains the higher content of C (even higher than O) within the Si bulk.

To investigate deeper, we check the elemental composition of a 200 nm \( p\)-SiO\(_x\) layer deposited on \( n\)-\( c\)-Si wafer before and after thermal diffusion. The concentration of elements in the \( p\)-SiO\(_x\) layer is B (2.5%), O (18%), C(16%), H(20%) and Si (44%) before thermal diffusion, which remains uniform throughout the layer. Figure 6(right) shows...
the concentration of different elements as a function of $p$-SiO$_x$ layer after thermal diffusion. It shows that the thickness of $p$-SiO$_x$ layer reduces to 120 nm after the thermal diffusion (indicated by silicon percentage ~100%) due to a densification of dielectrics during diffusion. This confirms the thickness estimation from ellipsometry measurement discussed in section 3.1.

Also we find that C concentration increases linearly from 0 to 10% upto 100 nm in the layer. This linear trend indicates that C diffuses and gets closer to $n$-c-Si wafer. However, there is a sharp peak at 110 nm (~25% concentration) indicating the accumulation of C at the interface of $p$-SiO$_x$ and c-Si. We expect that this happens because C present inside $n$-c-Si wafer acts a barrier and stops further C diffusion inside the wafers from the $p$-SiO$_x$ layer. The concentration of B follows a similar trend indicating the boron peak (10%) at 100 nm. The concentration of O increases from 18% initial to 60% in the layer after thermal diffusion. Also there is no H present (< 1%) in the $p$-SiO$_x$ layer after thermal diffusion step. This suggests that H has effused out while O has diffused in the $p$-SiO$_x$ layer because of thermal oxidation.

To check if the B diffusion in the wafer is functioning as active carriers, we compare one ECV and SIMS measurements. Figure 7 shows this ECV and SIMS comparison. It shows that the boron (carrier) concentration measured by ECV and SIMS is same and within the measurement errors. This confirms that all the B diffusing in $n$-c-Si wafer is active.

![Fig. 7. Comparison of ECV and SIMS profile in c-Si bulk](image)

4. Conclusion

In this work, we demonstrate the use of $p$-SiO$_x$ layers deposited by PECVD process in $n$-type and $p$-type bifacial solar cells. These $p$-SiO$_x$ layers were deposited with HMDSO/CO$_2$ plasma chemistry and diborane is used as the $p$-type dopant. Optical properties reveal that these layers are thermally stable and can thus act as dopant sources for diffusion in bulk silicon wafers. Also, ellipsometry and FT-IR measurements confirm the densification of $p$-SiO$_x$ layer after thermal diffusion (1050°C for 30 min). ECV measurements reveal that there is diffusion of B in the bulk silicon and it is possible to control the depth of $p^+ - n$ junction with time of thermal diffusion. Thicker $p$-SiO$_x$ layer reduce the sheet resistance and carrier concentration on the surface increases. SIMS measurements confirm that there is small C diffusion inside bulk silicon upto 100 nm but it acts as a barrier for further diffusion of C inside the wafers. However, boron diffusion is not affected significantly because of the presence of C in the silicon wafer. These $p$-SiO$_x$ layers can be used in a $n$-type bifacial solar cell in emitter configuration and in a $p$-type solar cell in a back surface field (BSF) configuration.

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