Chemical-vapor-deposited pure boron (PureB) layers can be used as a source of p-type boron dopants for thermal diffusion into silicon during a drive-in anneal. In this work, the effect of thermally annealing PureB layers is investigated in terms of surface morphology and electrical properties. The presence of a few nanometer-thick PureB layer on the Si surface was found to increase the silicon oxide growth rate by several factors during annealing in an oxygen-containing atmosphere. The oxide thickness was dependent on the initial PureB layer thickness and oxygen concentration during anneal. In an oxygen-limited ambient, the final thickness is insensitive to the anneal temperature as the reaction is diffusion-limited and, after oxide removal, a hydrophilic boron rich layer remains on the Si surface. With a high oxygen concentration, the boron is depleted by an oxidation of the boron-doped silicon resulting in a lower surface concentration and higher sheet resistance. A reaction mechanism involving the oxidation of Si-B compounds to form $\text{B}_2\text{O}_3$ is proposed to explain the experimental observations. With solar cell and other photodiode applications in mind, the sheet resistance and carrier lifetime measurements were performed and show that a one-step oxidation process can simultaneously drive-in the dopants and form an oxide passivation layer.

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**Experimental**

For the surface morphology analysis and sheet resistance measurements, phosphorus-doped Czochralski wafers of (100) orientation and 1–5 $\Omega \cdot \text{cm}$ resistivity were used in this work. The PureB layers were deposited in an ASM single-wafer Epsilon 2000 reactor. During deposition, diborane was used as a source gas and hydrogen as the carrier gas. Since PureB selectively deposits on silicon and not on silicon oxide, it is essential for the silicon surface to be native oxide free. Therefore, the native oxide is first removed from the silicon surface by HF dip-etching and Marangoni drying before deposition.

In this study, PureB was deposited at 700 °C and atmospheric pressure with different deposition times of 4, 9 and 20 min. The subsequent drive-in diffusion was done at 850, 950 and 1050 °C for 30 min in nitrogen ambient in a Tempresp furnace system. In order to investigate the effect of oxygen concentration, annealing was performed either in-situ in the Epsilon reactor in nitrogen ambient, or during dry oxidation in the furnace system with 14% oxygen concentration (1 slm $\text{O}_2$, 6 slm $\text{N}_2$).

Ellipsometry was used to characterize the thickness of as-deposited PureB layers and silicon oxide layers after anneal. Surface morphology of the deposited, annealed and oxidized layers was analyzed with high-resolution transmission electron microscopy (HRTEM). Electron energy loss spectroscopy (EELS) was used to determine the elemental composition of the surface layers.

The samples prepared for HRTEM were partially textured with inverted pyramids. This was done by first growing a 300-nm-thick thermal oxide layer on bare silicon wafers. Squares 10-micrometer wide were then plasma-etched to expose the silicon. The samples were dipped in a 0.55% HF solution for 4 minutes to remove native oxide and the exposed silicon was subsequently chemically etched by 2% tetramethylammonium hydroxide (TMAH), 10% isopropyl alcohol (IPA) in deionized water at 80 °C. The silicon oxide acts as a mask while the TMAH solution preferentially etches silicon along the (100) and (110) crystallographic planes, resulting in (111) surfaces being exposed on the textured surface.

For lifetime measurements, phosphorus-doped monocrystalline float zone (FZ), double-side polished wafers of (100) orientation, 1–5 $\Omega \cdot \text{cm}$ resistivity and 260–300 μm thickness were used. To form symmetrical $p^+/n/p^+$ samples, PureB was deposited on one side, and then the wafer was manually flipped ex-situ and immediately processed with the same recipe on the other side. The second exposure of the first side to 700 °C gives a very limited drive-in of boron into the Si as set by the solid solubility of $2 \times 10^{19}$ cm$^{-3}$. This effect is negligible compared to the effect of the subsequent anneal/oxidation. The bulk effective carrier lifetimes were measured using the transient photo-conductance method.
Results and Discussion

The surface morphology of the as-deposited, annealed and oxidized layer was analyzed with High-Resolution Transmission Electron Microscopy (HRTEM). Figure 1 shows an image of the PureB layer deposited with a 9-min deposition time, resulting in a ∼3-nm-thick PureB layer. On the (111) surfaces resulting from texturing by TMAH, the PureB layer is conformal but has a slightly lower thickness than the non-textured (100) surface.

Figure 2 shows an image following a furnace anneal at 950°C for 30 min in nitrogen ambient, whilst Figure 3 shows an image following a dry oxidation at 950°C for 30 min in 14% oxygen concentration. On the Si, an amorphous layer can be seen to have been formed in both cases. Based on Electron Energy Loss Spectroscopy (EELS) characterization, the elemental composition of this layer is predominantly silicon, followed by oxygen, with trace amounts of boron. Apparently, a silicon oxide layer is grown in both cases. For the annealed sample of Figure 2, this layer grows in an oxygen limited atmosphere and, in contrast to the sample of Figure 3, a clear peak in boron signal is observed at the SiO₂-Si interface.

For the anneal in nitrogen ambient the furnace is known to not be completely oxygen-free but the resulting oxide thickness of ∼24 nm is impressive since it would otherwise be barely significant. During the dry oxidation with 14% oxygen concentration, the oxide layer was even thicker, ∼40 nm, as compared to ∼9 nm on a control sample of bare (100) silicon. Moreover, it is generally understood that, as compared to (100) surfaces, the (111) silicon surface has a higher oxide growth rate due to the higher silicon atomic density.
Figure 3. HRTEM image of a PureB layer formed by a 9-min deposition followed by dry oxidation at 950°C for 30 min in 14% oxygen concentration on a (100) surface (a) and on a (111) surface formed after TMAH texturing (b).

Figure 4. Oxide thickness resulting from a 30-min anneal in nitrogen ambient at different temperatures as a function of the original PureB thickness.

In the in-situ anneal case, boron atoms can react with silicon atoms at the surface of the silicon upon high-temperature annealing. Based on work done on molecular layer doping, Saitoh et al. analyzed the composition of a pure boron layer after annealing at 900°C using Rutherford backscattering (RBS) analysis and they estimated the Si-B compound to be SiB₆. The composition of Si-B compound has been widely investigated and different compositions have been suggested. As a result, it is generally referred to as the boron-rich layer. This boron-rich layer acts as a source of dopants from which boron atoms thermally diffuse into the silicon bulk as governed by the concentration gradient and the solid solubility.

The same reactions of B with the Si surface occur in the furnace system. However, in the presence of oxygen, the following additional reactions of B with the Si surface may occur:
reactions take place:12–13

\[
4 \text{B} + 3 \text{O}_2 \rightarrow 2 \text{B}_2\text{O}_3 \quad [1]
\]

\[
\text{Si} + \text{O}_2 \rightarrow \text{SiO}_2 \quad [2]
\]

\[
2\text{SiB}_6 + 11\text{O}_2 \rightarrow 6\text{B}_2\text{O}_3 + 2\text{SiO}_2 \quad [3]
\]

\[
2\text{B}_2\text{O}_3 + 3\text{Si} \rightarrow 4\text{B} + 3\text{SiO}_2 \quad [4]
\]

Initially, B or SiB6 in the boron-rich layer reacts with oxygen to form B2O3. Silicon from the bulk then diffuses to the surface to react with B2O3 to form silicon oxide and the resulting boron can diffuse into the bulk silicon. This reaction mechanism explains why the initial PureB layer thickness determines the final silicon oxide thickness as seen in Fig. 4. In addition, during furnace annealing in a nitrogen ambient whereby the supply of oxygen to the silicon surface is limited, Si-B compounds or a boron-rich layer may remain at the Si-SiO2 interface. This appears to happen in our case since such a residual B-layer is consistent with EELS results and the chemical etch tests. Furthermore, as the source of oxygen is very limited, the reaction becomes diffusion-limited, which explains the negligible effect of temperature on the final oxide thickness.

At sufficiently high oxygen concentration, the Si-B compound is completely oxidized preventing the formation of a hydrophilic boron-rich layer.12–14 Moreover, the reaction can be expected to become reaction-limited, whereby the annealing temperature becomes a factor in the final oxide thickness. This type of behavior can be deduced from Figure 5 where a plot is shown of the oxide thickness resulting from a 20-min PureB deposition followed by a 30-min anneal in nitrogen ambient or 10-min dry oxidation in 14% oxygen as a function of furnace temperatures. On the one hand, the oxide thickness resulting from the 30-min furnace anneal in nitrogen ambient is constant even up to 1050 °C, and on the other, in the presence of 14% oxygen concentration, the oxide thickness increases with temperature. It should be noted the oxide thickness resulting from annealing in nitrogen ambient is not influenced by the loading and unloading temperature of the wafers. Both 800 °C and a lower temperature of 600 °C show the same trends, implying that the loading and unloading conditions are unimportant for achieving an oxide thickness that is unrelated to the annealing temperature.

The diffusion of silicon from the bulk substrate into the boron-rich layer has previously been observed to result in large spike formation at the edges and corners of SiO2-isolation windows to the Si substrate when a PureB layer was deposited and exposed to thermal drive-in at 1100 °C for 195 min.15 It has been proposed that the large spikes were formed because, at such elevated temperatures, the Si reacts with SiO2 at the window edges to form volatile SiO.16 This results in both spiking and a lateral widening of the windows. These detrimental effects become more severe in the presence of boron. This can be understood from the reaction mechanism, whereby the boron-rich layer in the windows reacts with small amounts of oxygen in the furnace during the drive-in to form B2O3. Subsequently, silicon from the window perimeter diffuses to react with B2O3, leaving behind large cavities or spike formation at the window edges and particularly in the corners.

An important criterion for high-efficiency Si solar cells is a high effective carrier lifetime. It has previously been reported that boron-rich interface layers of more than 10-nm thick should be avoided to prevent degradation of carrier lifetime in the bulk of the silicon wafer.16 In order to test the suitability of this process for solar cell applications a few symmetrical samples were prepared as shown in Table I to evaluate the passivation quality of the surface layer. All three samples were exposed to a maximum temperature of 950 °C. For the sample 1 that first was annealed at this temperature, it was important to avoid any detrimental impact of the boron-rich layer on the effective carrier lifetimes. Therefore, the sample underwent chemical etch treatment involving boiling HNO3, followed by HF to remove both the oxide and boron-rich layers. Successful removal was indicated by the eventual hydrophobicity of the surface. Subsequently, a 800 °C 10-min dry-oxidization process was performed for passivation. The low thermal budget of this oxidation step compared to the diffusion step was not expected to produce any further boron diffusion of significance. As a final step, a forming gas anneal was also performed on all the samples. The lifetime values shown in Table I were measured immediately after processing and forming gas anneal to avoid inconsistent comparisons due to degradation with time, as recombination in oxide-passivated boron-diffused samples has in the past been found to increase severely with time.17 The lifetimes were obtained by the transient photoconductance method and the sheet resistances were measured on separate test wafers by 4-point probing.

From Table I, it can be seen that the lowest sheet resistance is achieved for sample 1 that was annealed in nitrogen ambient for 30 min. Despite exposure of sample 2 to a similar thermal budget during an oxidizing step in 14% oxygen, the sheet resistance of this sample is much higher. As can be seen from Figures 2 and 3, the oxide layer resulting from this comparable treatment was 24 nm for sample 1 and ~40 nm for sample 2. This indicates that boron depletion has taken place in sample 2 as boron-doped silicon was oxidized leading to a lower surface concentration of boron and higher sheet resistance. By reducing the oxidation time to 10 min, sample 3 has a lower sheet resistance due to a higher surface concentration. More importantly, the maximum bulk effective lifetime was obtained with sample 3, showing that the surface layer resulting from a one-step B-driven anneal/oxidation has passivating properties at least comparable to an oxide layer grown separately on a clean Si-surface as in sample 1.

In addition to optimizing the initial PureB layer thickness and thermal budget needed to reach the required boron activation, sheet resistance and junction depth, it can be concluded that the oxygen concentration during the drive-in anneal is also critical. Sufficient oxygen

### Table I. Sheet resistance and lifetimes (measured at minority carrier concentration of 10^{15} \text{ cm}^{-2} \text{ eV}^{-1}) for samples processed with various anneal and oxidation conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Process Condition</th>
<th>Sheet Resistance [Ω/sq]</th>
<th>Lifetime [μs]</th>
</tr>
</thead>
</table>
| 1      | PureB 9 min Deposition  
Anneal (N2) 950°C 30 min | 61.2 | 257 |
| 2      | PureB 9 min Deposition  
Oxidation 800°C 10 min | 205 | 251 |
| 3      | PureB 9 min Deposition  
Oxidation 950°C 10 min | 136 | 353 |

Figure 5. Oxide thickness as a function of the anneal temperature resulting from a 20-min PureB deposition followed by a 30-min furnace anneal in nitrogen ambient or a 10-min dry oxidation in 14% oxygen. The oxide thickness formed by the latter thermal process on a bare Si wafer is also included.
can eradicate any potential residual boron-rich layers that may otherwise degrade the bulk lifetime while excessive oxygen results in boron depletion due to oxidation of the boron-doped silicon. Therefore, a process condition in terms of oxygen concentration has to be optimized to find an optimal balance. In this respect, it should be noted that the optical properties of the surface layer will be influenced by the oxide thickness, an effect that is not considered here. However, it may also be an important factor for optimization of the solar cell efficiency.

Conclusion

In this work, it has been demonstrated that for the annealing of chemical-vapor-deposited PureB layers on Si, the oxygen concentration during the anneal plays a critical role in determining the surface morphology and electrical properties. It was found that nanometer-thick PureB layers, upon annealing in the presence of oxygen function as a catalyst for silicon oxide growth. The resulting silicon oxide thickness was shown to be strongly dependent on the original PureB layer thickness as well as the oxygen concentration during the thermal anneal. In an oxygen-limited atmosphere, the silicon oxide thickness becomes insensitive to the process temperature since the reaction is diffusion-limited. In this case, a boron-rich layer remains at the SiO2-Si interface after annealing. This layer proved to be hydrophilic when exposed to air by selective wet etching. On the other hand, an ample supply of oxygen during annealing results in boron depletion of the boron-doped Si surface due to an enhanced oxidization and this results in a lower surface concentration and higher sheet resistance. In terms of solar cell and other photodiode applications, the sheet resistance and lifetime results show that a one-step process can be used to simultaneously drive-in the dopants and form a good oxide passivation layer.

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