Surface Passivation of Boron-Diffused Junctions by a Borosilicate Glass and In Situ Grown Silicon Dioxide Interface Layer

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Abstract—An in situ oxidation during the boron tribromide diffusion process to form $p^+$-doped junctions on crystalline Si solar cells leads to the formation of a layer stack system consisting of a borosilicate glass (BSG) (a binary $B_2O_3–SiO_2$ system) and a SiO$_2$ layer at the Si interface. We present a method to passivate the $p^+$-doped regions by using this in situ grown SiO$_2$ in combination with a plasma-enhanced-chemical-vapor-deposited SiN$_x$ layer. We show that the etching rate of the BSG layer, in a hydrofluoric acid solution, varies over the wafer. The etching rate depends on its local $B_2O_3$ content in the BSG and is markedly higher than that of the SiO$_2$ layer. This difference in the etching rates can be used to controllably etch back the BSG layer in order to obtain a thin and uniform passivating oxide layer for solar cell application. Using this oxide/SiN$_x$ stack, we obtained implied $V_{oc}$ of 705 mV and $J_{sc}$ as low as 14 mA/cm$^2$ on symmetrically diffused boron emitters on n-type Czochralski wafers. These passivation results are comparable, on similar structure and boron emitters, with state-of-the-art Al$_2$O$_3$-based passivation methods. Moreover, we have successfully implemented this passivation method in the fabrication of n-type passivated emitter and rear totally diffused back contact solar cells, avoiding the need of adopting additional process steps and costs for boron emitter passivation.

Index Terms—Boron diffusion, borosilicate glass (BSG), solar cells, $n$-type, surface passivation.

I. INTRODUCTION

Boron tribromide (BBR$_3$) tube diffusion is today the most common used method to form the $p^+$-diffused regions on wafer-based crystalline silicon solar cells [1]. However, a high-throughput industrial BBR$_3$ diffusion process and the passivation of the resulting $p^+$-doped surfaces are often considered to be challenging. The optimization of doping profile and the passivation and metallization thereof are essential for further increasing the conversion efficiency of crystalline Si solar cells. The current industrial used methods for the passivation of boron-doped surfaces involve additional process steps and surface treatments, such as thermal or chemical oxidation [2], [3], atomic layer deposition (ALD) of Al$_2$O$_3$ [2], [4], or plasma-enhanced chemical vapor deposition (PECVD) of AlO$_x$ [5]. More recently, excellent surface passivation on heavily doped $p^+$ emitters was reported by ALD of TiO$_2$ [6], [7] or by using PECVD SiO$_2$/SiN$_x$ stacks [8]. Most of these methods, however, increase process complexity and potentially increase the cost of solar cells.

A typical BBR$_3$ diffusion process consists of a deposition phase, where BBR$_3$ vapor is mixed with oxygen to form B$_2$O$_3$ and bromine:

$$4BBR_3 + 3O_2 \rightarrow 2B_2O_3 + 6Br_2$$

During the subsequent drive-in phase, the deposited B$_2$O$_3$ reacts at the Si interface to form elemental boron and SiO$_2$:

$$2B_2O_3 + 3Si \rightarrow 4B + 3SiO_2$$

Since the vapor pressure of the B$_2$O$_3$ at typical deposition temperatures (900–1000 °C) is rather low, liquid B$_2$O$_3$ condenses on the silicon wafers as well as on furnace walls [9], [10]. If the diffusion parameters are carefully chosen, the formation of the undesirable boron-rich layer (BRL), which is responsible for lifetime degradation in the Si bulk [11], can be avoided. Then, a boron-rich borosilicate glass (BSG), i.e., a mixed B$_2$O$_3$–SiO$_2$ system, is formed during the diffusion process. Furthermore, if the drive-in phase occurs partially or totally under an oxygen-containing atmosphere, the silicon surface under the BSG is further oxidized by the following reaction:

$$Si + O_2 \rightarrow SiO_2$$

This process leads to an additional in situ grown SiO$_2$ layer at the Si/BSG interface. The formation of the BSG layer during the deposition phase results inevitably in a relatively thick and nonuniform layer over the silicon wafer and along the diffusion boat. Therefore, the utilization of this in situ grown BSG layer in combination with a SiN$_x$ layer, as a passivation and antireflection coating (ARC) stack, would lead to solar cells with nonuniform optical appearance and lower photocurrent due to the increase in the surface reflection. That is why the BSG layer is typically stripped off in a hydrofluoric (HF) acid solution, and an additional passivation layer (such as AlO$_x$) is deposited on the $p^+$-doped surface prior to PECVD of the SiN$_x$ ARC layer.

This work describes the properties of the oxide layers formed in situ during BBR$_3$ diffusion in crystalline Si. We present a method that yields a thin and uniform in situ grown SiO$_2$ layer...
with a surface passivation quality comparable with the state-of-the-art Al₂O₃-based passivation methods [2], [4], [5] but with a process simplification potential. This method can easily be implemented in cost-effective production processes for n-type passivated emitter and rear totally diffused (nPERT) [12] and interdigitated back contact (IBC) cells [13], avoiding additional process steps and costs.

II. EXPERIMENTAL PROCEDURE

For our experiments, we used 6-in semisquare n-type Czochralski (Cz) wafers with a base doping of 10 Ω-cm and an as-cut thickness of 200 μm. All wafers were etched in an alkaline solution followed by a piranha cleaning step and subsequently underwent a boron diffusion process in a tube furnace (c.DIFF, Centrotherm AG) using BBr₃ as the boron source. For this study, we choose a typical industrial BBr₃ diffusion recipe, which yields a uniform sheet resistance ($R_{sh}$) distribution over the wafer as well as along the entire diffusion boat. Such a recipe consists of a deposition phase during a temperature ramp up from 830 to 900 °C and a subsequent drive-in phase at a temperature plateau with a peak temperature of 1020 °C.

The diffusion parameters, namely the gas flows and duration, were selected according to the best-known method in our lab in order to obtain an emitter with an $R_{sh} \approx 135$ Ω/sq. ±5% without formation of the BRL layer. The drive-in phase was done partially in a 100% oxygen-containing atmosphere in order to grow an additional in situ SiO₂ at the BSG/Si interface and to reduce the surface concentration of the diffused boron. In order to estimate the effect of this additional in situ grown SiO₂ layer, a thermal SiO₂ layer was grown on undiffused wafers in a separate oxidation tube, using an identical recipe as for the boron diffusion (i.e., temperature profile, gas flows, and duration) but without the BBr₃ flux. A schematic diagram of the diffusion recipe together with a typical layer structure expected directly after deposition and after the drive-in phase is shown in Fig. 1.

All wafers were separated in three groups. The first group was loaded in the diffusion tube, but received only the BBr₃ deposition, i.e., the wafers were unloaded under N₂ atmosphere directly after the deposition phase. The second group received the complete BBr₃ diffusion process, and the third group was processed in the separate oxidation furnace, as described above. The thickness of the BSG and SiO₂ layers was measured on 25 points equally distributed over the wafer using a Sentech SE800-PV ellipsometer assuming a refractive index of $n = 1.46$ for BSG and SiO₂ layers [14]. Some of the wafers with boron diffusion were selected for lifetime measurements using the quasi-steady-state photocurrent (Sinton, WCT-120) method and received an additional 80 nm ($n = 2.03$) PECVD SiNₓ deposition (c.PLASMA, Centrotherm AG) on both sides. Subsequently, the lifetime samples underwent a firing process at a peak temperature of 850 °C in order to activate the passivation. In order to study the etching rate of the BSG and SiO₂ layers, the wafers were etched by immersion in a 2-vol% HF acid solution at room temperature for a defined period of time followed by thickness measurements. This process was repeated until the oxide layers were completely etched off.

III. RESULTS AND DISCUSSION

A. Effect of Deposition and Drive-in on Borosilicate Glass Properties

The carrier concentration profiles, as measured by the electrochemical capacitance–voltage (ECV) technique, at the end of the deposition phase and after the drive-in phase are shown in Fig. 2. The measurements show a significant boron doping occurring already during the deposition phase, with an $R_{sh} \approx 200$ Ω/sq., despite of the fact that the temperature is relatively low (<900 °C) and the deposition time is short (<20 min). During deposition, liquid B₂O₃ is continuously produced [see reaction (1)] and condensed on the Si wafers. At the same time, B₂O₃ reacts at the Si interface to produce elemental boron and solid SiO₂ [see reaction (2)]. At this stage of the diffusion process, the B₂O₃ rapidly dissolves or melts through the underlying SiO₂ and forms the binary BSG [15], [16], i.e., a low viscosity glass layer. Brown and Kennicott estimated that, in this molten
phase, the diffusion coefficients of B$_2$O$_3$ in SiO$_2$ are $\approx$1000 times higher than the corresponding solid-state diffusion coefficients [16], bringing boron dopant to the Si interface with a very little time delay. Hence, the concentration of boron in Si during the deposition phase is expected to be limited by its solid solubility, which is $\approx 7 \times 10^{-10}$ cm$^{-3}$ at 900 °C [17]. This seems to be confirmed by the experimental data shown in Fig. 2. A prolonged process under this diffusion condition is expected to lead to the formation of the BRL at the Si interface [10], [11]. Brown et al. showed that attaining the boron solid solubility limit in Si would require a B$_2$O$_3$ concentration in the BSG of more than 18 mol% [15], [16]. A BSG layer whose composition exceeds this B$_2$O$_3$ concentration has a glass transition temperature ($T_G$) below the deposition temperature (850–900 °C) chosen in our diffusion, and it is, therefore, characterized by low viscosity [16]. This seems to be the case for our diffusion recipe at the end of the deposition phase, where the structure of the glass layer is expected to be as shown in Fig. 1(a) and leading to a surface concentration of B in Si of no more than $\approx 7 \times 10^{-10}$ cm$^{-3}$.

During the drive-in phase of the diffusion, no additional B$_2$O$_3$ is produced or deposited on the wafer surface, and the low-viscosity BSG layer is being diluted by additions of SiO$_2$ produced by the ongoing reaction (2) at the Si interface. The dilution of the B$_2$O$_3$ content in the glass increases its melting point, as well as its viscosity. This process is significantly enhanced with the addition of an in situ oxidation [see reaction (3)]. When the concentration of B$_2$O$_3$ in the BSG drops below that required to maintain a low-viscosity phase at the given process temperature, the dissolution of underlying SiO$_2$ stops, and a thermal SiO$_2$ grows beneath the BSG layer at the Si interface during the remaining oxidation phase [as shown schematically in Fig. 1(b)] [15], [16]. In this region, the migration of the boron dopant from the BSG layer to the Si interface is governed by the solid-state diffusivity of B-carrying species in SiO$_2$, which is orders of magnitude lower than in a molten glass phase [16], [18]. Hence, this in situ grown SiO$_2$ layer functions as a blocking layer for further boron doping of Si as soon as a critical thickness is reached. Furthermore, as the solubility of boron is higher in SiO$_2$ than in Si, the oxidation process lowers the surface concentration of the boron emitter (as shown in Fig. 2), and the SiO$_2$ becomes boron doped. This in situ oxidation can effectively be used to prevent the formation of the BRL [10].

**B. Etching Rate of Silicon Dioxide/Borosilicate Glass Stack Layers**

In order to be used as an ARC, the thickness uniformity of the BSG layer must be very good across the wafer as well as along the entire diffusion boat. In practice, however, for a diffusion process of relevant throughput with tightly packed wafers in a long boat, this is not the case; the fast decomposition of BBr$_3$ under the oxidizing atmosphere [see reaction (1)] results in an uneven condensation of B$_2$O$_3$ over the silicon surface and along the boat [10], [11], [19]. The resulting BSG layer is often much thicker at the wafer edges and at the boat ends [11], [19]. Therefore, partially etching back of the in situ grown BSG and SiO$_2$ layers could be a viable and simple process solution for industrial application.

Fig. 3 shows the thickness $d$ of the oxide layers studied in this work as a function of etching time in the HF solution for different processes (see legend). For the boron-diffused samples, the area with minimum and maximum BSG thickness is plotted after both the deposition phase and the drive-in phase. The thermal SiO$_2$ layer was grown in a separate oxidation tube set with an identical recipe to the boron diffusion (i.e., temperature profile, gas flows, and duration) but without the BBr$_3$ flux.

For the boron-diffused samples, the in situ grown SiO$_2$ during the drive-in phase is expected to be similar in thickness and even, despite of the presence of an uneven BSG layer. This is because the diffusion coefficient of oxygen in the BSG is higher than in pure SiO$_2$, and hence, the presence of the BSG layer presents very little resistance for the diffusion of oxygen to the Si surface [20]. Thus, the growth rate of SiO$_2$ is not hindered by a BSG layer of varying thicknesses, and therefore, the grown SiO$_2$ layer has a uniform thickness. In fact, this is also confirmed by the experimental data shown in Fig. 3. One can see that, within the experimental uncertainty, at $t_{etch} = 0$ s, the total thickness $d_{total}$ is the sum of the BSG thickness $d_{BSG}$ and the oxide thickness $d_{SiO_2}$ for both the thickest and the thinnest BSG layer. One should note here that the wafers that received only the deposition phase were loaded in the same boat position as those that received the complete diffusion process.

The etching rate for each process conditions was determined from the linear fit to the thickness measurements after sequential etching and is indicated by the arrows in Fig. 3. The largest contribution to the etching rate measurement errors comes from our inaccuracy to estimate the actual etching time. The wafers were immersed in the HF solution followed by the immersion in deionized water, in order to stop the etching process. During the
transport between the two baths, the surface is hydrophilic and the etching process continues, but probably at a slightly lower rate. Overall, the relative measurement error of the etching rate due to the inaccuracy in $t_{\text{etch}}$ is approximately 15%, whereas the relative error in the thickness measurement is $\leq$ 1.5%. For the thermally grown SiO$_2$, the measured etching rate of 0.16 nm/s (green solid line in Fig. 3) is in agreement with literature values for comparable etching conditions [21]. For the diffused samples with the BSG layer, the etching rate is significant higher. Previous studies showed that the etching rate of the BSG layer in HF etchants exponentially increases with the increasing B$_2$O$_3$ content in the glass [22], [23]. This is because, in HF etchants, the breakage rate of the B–O bond is higher compared with that of the Si–O bond [21]. This is also observed in Fig. 3, where the BSG layer on the samples with only the deposition process show markedly higher etching rate than that of pure SiO$_2$.

Moreover, the results in Fig. 3 clearly show that the etching rate is higher for areas on the wafer with a thicker BSG layer as compared with areas with a thinner BSG layer. The areas with a thicker BSG layer arose as a result of a thicker B$_2$O$_3$ film condensed during the BB$_3$ deposition and, therefore, a higher B$_2$O$_3$ content in the glass. The same observations are made on the samples that received the complete boron diffusion process (including the drive-in phase); thicker areas are etched faster than thinner areas, but with overall lower etching rates than for the as-deposited layer. The etching rate of the BSG is a characteristic function of the B$_2$O$_3$ content in the glass, and therefore, it can be used to estimate the glass composition [23]. For instance, by comparing the ratios of etching rates of BSG layers to SiO$_2$ in Fig. 3 with those reported by Kern and Heim [23], and assuming a linear increase in the etching rate with HF etchant concentration [21], one could roughly estimate the B$_2$O$_3$ content in the BSG. This gives approximately 17–22 mol% B$_2$O$_3$ after the deposition phase and about 8–11 mol% after the drive-in phase, with higher values corresponding to the thicker BSG areas.

For boron diffused samples with in situ thermal oxidation during the drive-in phase, a second important observation is made: The etching rate decreases significantly after a certain time and reaches a value equal to thermal SiO$_2$ (green dashed line in Fig. 3). Obviously, the high etching rates of the first phase correspond to etching of the BSG film with different B$_2$O$_3$ content and different initial thicknesses, while the lower etching rates of the second phase correspond to etching of the uniform SiO$_2$ film grown beneath the BSG. The transition to this second phase corresponds roughly to the initial thickness of the thermal SiO$_2$ film, indicating that the BSG layer and the in situ grown SiO$_2$ layer do not substantially intermix. As shown above, this is the case when B$_2$O$_3$ concentration in the BSG drops below the values that is required to maintain a low-viscosity condition. This increase in the etching rate of BSG layers depending on its B$_2$O$_3$ content in comparison with pure SiO$_2$ can be used to advantage. For instance, the in situ grown SiO$_2$ during the drive-in step of a BB$_3$ diffusion process could readily be used as a buffer layer for the etch back of the BSG. In this way, a very uniform passivation films of a desired thickness can be obtained easily over an entire diffusion boat. This is demonstrated in Fig. 4, which shows the mean and the standard deviation of the thickness values over the wafer as a function of boat position, directly after the diffusion process and after $\approx$130-s HF etching, respectively. One can see that, before HF thinning, the BSG layer uniformity is obviously not suited in combination with SiN$_x$ as an ARC. The photocurrent generation over the cell and boat would vary $\geq$ 1.0 mA/cm$^2$ in this case. In contrast, after HF thinning, the BSG layer is completely etched, and a 13.9 ± 1.3-nm-thin in situ SiO$_2$ layer remains on the Si surface, which serves as an interface passivation layer.

A similar diffusion process with the in situ oxidation and HF thinning principle described here for boron can also be applied for phosphorous diffusion. The etching rate of a binary phosphosilicate glass (PSG) system shows a similar behavior as for BSG, i.e., the etching rate increases with the increasing P$_2$O$_5$ content in the PSG and is distinctly higher than that of SiO$_2$ [21], [24]. At high P$_2$O$_5$ concentrations in the PSG, a melt-through process of the underlying SiO$_2$ layer, as described for boron, is expected from the P$_2$O$_5$–SiO$_2$ phase diagram [24]. Such an observation has been made recently by Werner et al., who showed that the in situ grown SiO$_2$ layer thickness is reduced by an additional POCl$_3$ deposition phase introduced in situ after the drive-in phase [25]. One should note that the same glass/SiO$_2$ layer stack system could also be obtained during annealing of chemical-vapor-deposited BSG (or PSG) layer in an oxygen-containing atmosphere, providing that the B$_2$O$_3$ (or P$_2$O$_5$) content in the glass drops below the melt-through condition.

C. Influence of Oxide Thickness on Surface Passivation

In order to investigate the passivation quality of the in situ SiO$_2$/BSG layer stacks, we fabricated lifetime samples, in the same batch, on symmetrically diffused n-type Cz wafers. Fig. 5 shows the implied $V_{oc}$ and $J_{sc}$ values as a function of the SiO$_2$/BSG total stack thickness for various etching back levels. The $J_{sc}$ values were extracted from the slope of the inverse lifetime at an injection level of $1 \times 10^{16}$ cm$^{-3}$, using the method.
proposed by Kane and Swanston [26]. The Auger recombination limit of the B-diffused emitter was estimated using EDNA [27] to be about 5 fA/cm². It can be seen from the experimental data that a good surface passivation is obtained, even without HF thinning. With increasing etching time, the BSG layer thickness decreases until it is completely removed after ≈50 s (as shown in Fig. 3), and ≈32 nm of in situ SiO₂ layer remains on the Si surface. Nevertheless, the data in Fig. 5 show that this SiO₂ layer can be further etched back down to 10–15 nm without sacrificing the passivation quality. This, combined with the results shown in Fig. 4, demonstrates that the in situ grown SiO₂ layer can readily be used as an interface passivation and ARC layer when capped with SiNₓ.

Fig. 6 compares the Jₜₒ results obtained in this work with several literature-reported values by SiO₂- and AlOₓ-based passivation methods commonly used in industry for the passivation of boron emitters. Only the experimental data reported for a polished Si surface are plotted in Fig. 6. Although there are certainly differences in sample preparation and emitter doping profiles (e.g., surface concentration), the in situ grown SiO₂ passivation method shows a similar passivation quality as AlOₓ-based passivation method, but with the merit of no additional process steps or costs.

IV. CONCLUSION

In this paper, we discuss the formation and properties of in situ grown oxide layers during the BBr₃ diffusion process used to form p⁺-doped regions in crystalline Si solar cells. We showed that an in situ thermal oxidation during the diffusion process leads to the formation of a two-layer stack system consisting of a BSG (a binary B₂O₃–SiO₂ system) layer and a SiO₂ layer at the Si interface. The thickness of this BSG layer grows unevenly over the wafer and diffusion boat, and it would be unsuitable as an ARC for solar cell fabrication. However, we demonstrated that, due to much higher etching rates of the BSG layer in diluted HF acid solutions, this in situ grown SiO₂ can readily be used as a buffer layer for partially or totally etching back of the nonuniform BSG layer. Then, the remaining thin and uniformly grown SiO₂ layer at the Si interface can be used, in combination with a PECVD SiNₓ layer, as a passivation and ARC stack that reaches a passivation quality comparable with those of state-of-the-art Al₂O₃-based passivation methods.

This passivation method using the in situ grown SiO₂ during a BBr₃ diffusion process was integrated successfully in the process sequence of n-PERT and IBC Si solar cells [12], [13]. Recently, we have demonstrated that this passivation method is viable in mass production of n-PERT bifacial solar cells using a low-pressure BBr₃ furnace with a batch size of 1000 wafers per run [12].

REFERENCES


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