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Boron-Doped Silicon Surfaces From B_2H_6 Passivated by ALD Al_2O_3 for Solar Cells

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Abstract—A p^+ -doping method for silicon solar cells is presented whereby boron atoms from a pure boron (PureB) layer deposited by chemical vapor deposition using B_2H_6 as precursor were thermally diffused into silicon. The applicability of this doping process for the doped surfaces of silicon solar cells was evaluated in terms of surface morphology after thermal diffusion, the boron dopant profiles, and sheet resistances, as well as the recombination parameter J_{0p+} , when the doped layers were passivated by Al_2O_3 films prepared by atomic layer deposition. Adequate surface passivation could be achieved with a surface recombination contribution to J_{0p+} of <20 fA/cm² for most samples. However, when a boron-rich layer (BRL) was present at the Si surface, a much higher recombination current density was observed, proving that a BRL was detrimental to the high-quality surface passivation of boron-diffused surfaces. It was found that sufficient O_2 in the furnace during the thermal diffusion process could eliminate any potential residual BRL, while excessive O_2 concentration results in boron depletion and a higher sheet resistance. Therefore, in addition to optimizing the initial PureB layer thickness and thermal budget to control the dopant profiles, the O_2 concentration during the diffusion must also be well controlled.

Index Terms—Atomic layer deposition (ALD), emitter, photovoltaic cells, semiconductor device doping, silicon, surface passivation, surfaces.

I. INTRODUCTION

THE majority of industrially produced silicon solar cells have a p-type base in combination with an n^+ highly doped region. However, due to superior electronic properties of n-type Si wafers, which include a high bulk lifetime, no light-induced degradation [1]–[3], and a higher tolerance to metallic impurities [4], there is an increasing focus on n-type cells both in research as well as in industrial production [5], [6].

There are several methods used to manufacture p^+ -regions for n-type silicon solar cells. Methods include diffusion from boron

glass formed by gaseous BBr_3 [5]–[9] and BCl_3 [10] precursors, diffusion from spin-on boron source [11], inkjet-printed boron source [12], [13], and atmospheric pressure chemical-vapor-deposited boron silicate glass (BSG) [14], as well as conventional boron ion implantation [15], [16] and plasma ion implantation [17] followed by thermal diffusion. The various doping methods have their unique advantages and disadvantages. Thermal gas-phase diffusion by BBr_3 using a conventional furnace is an established method, with high throughput and low cost of ownership. In fact, industrial n-type solar cells have achieved $>20\%$ efficiency with this method, whereby a BSG layer is first formed before the dopant is driven-in [5], [6]. Generally, this otherwise undesirable layer has to be subsequently removed and replaced by a suitable passivation layer, in order to attain surface passivation.

The spin-on dopant technique offers single-sided diffusion, but it can suffer from contamination by metallic impurities initially present in the spin-on dopant film [11]. The ink-jet printing technique, on the other hand, has the added advantage of creating selective emitters. Compared with the aforementioned methods, ion implantation offers improved control, uniformity, and flexibility over the dopant profile, as well as the elimination of wet processing steps. Moreover, localized one-sided doping can be easily achieved in a single step using a shadow mask. This comparative advantage allows for novel process flows and high-efficiency cell architecture [16]. However, it is well known that ion implantation induces defects that must be completely removed in subsequent annealing and may additionally induce dopant deactivation, especially for boron [18], [19]. Plasma immersion ion implantation has an advantage in terms of being able to quickly implant very high doses at a lower cost. It has a very low implantation energy suited for the fabrication of ultrashallow junctions, which show optimal behavior in the short-wavelength region [17].

For application in standard n-type screen-printed crystalline silicon solar cells, regardless of the dopant source, substantial diffusion is required to achieve the dopant profiles and sheet resistances necessary for a low series resistance through the p-type region and associated contacts. More critically, a well-passivated surface is required to ensure a low surface recombination rate of charge carriers. Traditionally, thermally grown SiO_2 has been used as high-quality surface passivation for fabricating high-efficiency solar cells due to its low interface defect density. More recently, it was demonstrated that Al_2O_3 is an excellent material to passivate p-type crystalline silicon [20]. It offers a relatively high negative fixed charge density in the range of 10^{12} – 10^{13} cm⁻², as well as a low interface defect density [21].

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The high negative charge density effectively reduces the electron concentration at the surface and, consequently, reduces the recombination rate. This way, Al₂O₃ provides an effective field-effect passivation. In contrast, thermal SiO₂ has a positive fixed charge density in the range of 10¹⁰–10¹¹ cm⁻² [22].

The compatibility of p^+ doping with high-quality Al₂O₃ surface passivation is important for achieving a low recombination parameter, J_{0p+} . However, it is known that in some cases, the boron diffusion process can induce a boron-rich layer (BRL), which prevents the passivation of the surface. This way, the J_{0p+} of the highly doped region becomes comparable with an unpassivated doped surface [9]. In other work, it is shown that BRLs thicker than 10 nm lead to a degradation of bulk lifetime [8]. The BRL is formed during the diffusion process due to very high concentration of boron at the surface of the wafer, which is effectively transformed into a silicon boride layer. The BRL is hydrophilic and insoluble in HF. Under certain process conditions for BBr₃-based diffusion, a BRL can be formed and is clearly observable from cross-sectional scanning electron microscopy (SEM) [8], [9] extending up to tens of nanometers. A BRL has also been identified as dark agglomerations seen in transmission electron microscopy (TEM) images when using inkjet-printed paste as a source for boron diffusion [13]. Due to its detrimental effects to cell efficiency, BRLs are usually avoided or if formed, removed by oxidation [7], [8], which converts the BRL into BSG that is easily etched away by diluted HF.

In this study, with solar cell application as objective, a further development is presented of a recently demonstrated p^+ doping method by chemical vapor deposition (CVD) of boron layers (PureB) using B₂H₆ precursors [23], [24]. Up until now, the application of PureB deposition has primarily been for the fabrication of photodiodes. Due to the special properties of PureB layers deposited at 700 °C, p^+n photodiode detectors have been realized that already are well established as the devices of choice for detection of low-penetration-depth beams such as vacuum-ultraviolet light (VUV) [25] and low-energy electrons [26], where the photosensitive region must lie in the top few nanometers of the silicon. These applications rely on the PureB-to-Si interface properties to achieve low dark current and on the robustness of the PureB layer for high stability [27]. However, the sheet resistance of as-deposited PureB layers prepared at 700 °C is about 10 kΩ/sq, which can be too high for some specific applications. Extra *in-situ* thermal drive-in has been shown to be an efficient way of lowering the sheet resistance. An additional 850 °C 1-min diffusion reduced the sheet resistance to about 1 kΩ/sq and a 950 °C 20-min diffusion brought it down to about 100 Ω/sq [28]. From studies of the quantum efficiency of VUV photodiodes [25] fabricated with PureB anode regions subjected to various drive-in procedures, it has been found that the high efficiencies are maintained despite the increase in junction depth from a few nanometers to the hundred-nanometer range, particularly if the PureB layer is preserved on the surface [27]. In cases where it was removed, the efficiency dropped but still remained much higher than that of junctions produced by implantations [25]. This was attributed to the defect-free nature of the doping process and the lack of

roll-off of the resulting dopant profiles. These two features have also been shown in our previous work to be potentially attractive for manufacturing p^+ -doped regions in Si solar cells [23], [24].

For solar cell applications, the PureB layer has to be thermally diffused into the silicon to lower the sheet resistance. At the same time, obtaining a low recombination in the resulting doped layer is critical. In this study, processes are investigated that give increased control of the doping and surface conditions. It will be shown that by adjusting the thickness of the initial PureB layer, which acts as dopant source, as well as the subsequent thermal diffusion conditions, the dopant profiles can be well controlled. In particular, the role of gas composition during the diffusion process was investigated. To evaluate the applicability of this doping process in solar cell manufacturing, several aspects were studied. First, the surface morphology of the layers before and after the thermal diffusion step was analyzed. Second, boron profiles and sheet resistances were evaluated. Finally, the recombination parameters of the doped layers passivated by Al₂O₃ were investigated.

II. EXPERIMENTAL METHODS

A. Deposition of PureB Layers

The CVD of the PureB layers was performed in a commercial ASM single-wafer Epsilon 2000 epitaxial reactor. During deposition, B₂H₆ (0.2%) was used as a source gas and H₂ as the carrier gas. Before deposition, the native oxide was removed from the Si surface by 0.55% HF dip etching and Marangoni drying. PureB was deposited at 700 °C and atmospheric pressure with different deposition times. To form symmetrically doped $p^+/n/p^+$ samples for lifetime measurements, PureB was deposited on one side of a bare wafer, 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 gave a very limited drive-in of boron into the Si as set by the corresponding solid solubility of boron of 2×10^{19} cm⁻³ [29]. This effect was negligible since the final dopant profile was entirely determined by the subsequent thermal diffusion step at 950 °C. A customized batch furnace system for the high-volume manufacturing is currently under development for this process. Preliminary results are promising but are beyond the scope of this paper [30].

B. Surface Morphology

The thickness and surface morphology of the deposited and diffused layers was characterized using ellipsometry, high-resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). The Si substrates used were phosphorus-doped Czochralski wafers of (1 0 0) orientation and 1–5 Ω-cm resistivity.

The TEM samples were prepared using *in-situ* focused ion beam (FIB) lift out technique on a FEI Strata Dual Beam FIB/SEM. The samples were coated with platinum prior to FIB milling. The samples were imaged with a FEI Tecnai TF-20 FEG/TEM. In addition, EELS was used to determine the elemental composition of the surface layers. The EELS analyses

were done in scanning TEM mode using a nominal 2-nm electron beam and a Gatan Enfina DigiPEELS Spectrometer. For the line scan, the beam was stepped 4 nm apart and acquired for 1.5 s.

C. Boron Diffusion and Dopant Profiles

For application in various n-type crystalline silicon solar cells, specific requirements are demanded of the p^+ -doped regions in terms of dopant profile, sheet resistance, and homogeneity. As the chemical vapor-deposited PureB layer from B_2H_6 precursors acts as a dopant source, subsequent thermal diffusion was required to drive in the dopants to achieve the desired profile.

Thermal diffusion was performed with different concentrations of O_2 mixed with N_2 in a Tempress furnace TS 3603 oxidation system at 950 °C for 10 min, in order to investigate the effect of the gas composition on the properties of the boron doped region. It should be noted that this thermal diffusion was done without any capping layer, and the PureB layers acted as dopant source. For measurements of the dopant profiles and sheet resistances, n-type monocrystalline Si (1 0 0) wafers were used, which were float zone, 4-in diameter, double-side polished, 1–5-Ωcm resistivity, and 260–300 μm in thickness. The active boron dopant profiles were analyzed by electrochemical capacitance voltage (ECV) measurements using a WEP wafer profiler CVP21 table-top unit and sheet resistances were determined from four-point probe measurements.

D. Surface Passivation by Al_2O_3

An important aspect of using B_2H_6 as boron doping method for silicon solar cells is the compatibility with high-quality surface passivation. After the doping process, samples were etched in 1% HF to remove any undesirable surface layer, followed by plasma-assisted atomic layer deposition (ALD) of Al_2O_3 as a passivation layer in order to evaluate the recombination parameter of the highly doped region. A 30-nm Al_2O_3 layer was deposited on both sides of the lifetime samples by plasma-assisted ALD in an Oxford instruments OpAL reactor at 200 °C, using $Al(CH_3)_3$ (TMA) as precursor and O_2 plasma as reactant. Finally, a postdeposition 400 °C anneal in N_2 was performed for 10 min to activate passivation. The recombination parameter J_{0p+} was evaluated from quasi-steady-state photoconductance decay (QSS-PC) and generalized mode measurements on a Sinton WCT100. It was extracted from the slope of the inverse effective lifetime τ_{eff} at high excess carrier concentrations Δn , (i.e., $(0.7 - 1.3) \times 10^{16} \text{ cm}^{-3}$) using the method of Kane and Swanson [31]:

$$\frac{1}{\tau_{eff}} - \frac{1}{\tau_{Auger}} = \frac{1}{\tau_{SRH}} + J_0 \cdot \frac{(N_d + \Delta n)\Delta n}{qn_i^2 W} \quad (1)$$

with τ_{Auger} being the (bulk) Auger lifetime, τ_{SRH} the Shockley–Read–Hall lifetime, q the elementary charge, W the wafer thickness, N_d the base doping concentration, and n_i the intrinsic carrier concentration (we used $n_i = 9.65 \times 10^9 \text{ cm}^{-3}$, corresponding to a temperature of 300 K [32]). To ensure an accurate extraction of J_{0p+} , we compared the use of QSS-PC mode with generalized mode (see Fig. 1). Interestingly, even though the

Fig. 1. Inverse effective lifetime, corrected for Auger recombination, as obtained from photoconductive lifetime measurements on boron-doped samples with three different sheet resistances and passivated by Al_2O_3 . Straight lines were found for all measured samples in the excess carrier concentrations range $\Delta n(0.7 - 1.3) \times 10^{16} \text{ cm}^{-3}$, indicating that the method of Kane and Swanson to extract J_{0p+} was appropriate.

Fig. 2. HRTEM image of an as-deposited PureB layer formed by a 9-min deposition on a Si (1 0 0) surface.

absolute effective lifetime values changed in the different analysis modes, they did not result in significantly different J_{0p+} values. Furthermore, the use of a short flash, which is typically used for transient measurements, also yielded very similar results to the QSS-PC measurements. To study the influence of surface orientation on the surface passivation quality, some planar Si (1 1 1) wafers were additionally included in the analysis.

III. RESULTS AND DISCUSSION

A. Surface Morphology

The surface morphology of the as-deposited and diffused layer was analyzed with HRTEM. In Fig. 2, an image is shown of the PureB layer deposited with a 9-min deposition time, resulting in an approximately 3-nm-thick PureB layer. The result of diffusing this layer on Si (1 0 0) in a furnace at 950 °C for

Fig. 3. HRTEM image of a BSG layer formed by a 9-min deposition of PureB followed by furnace diffusion at 950 °C for 30 min in N_2 ambient on a Si (1 0 0) surface.

Fig. 4. HRTEM image of a BSG layer formed by a 9-min deposition of PureB followed by furnace diffusion at 950 °C for 30 min in 14% O_2 in N_2 on a Si (1 0 0) surface.

30 min in either N_2 ambient (7 slm) or in 14% O_2 in N_2 (1 slm O_2 , 6 slm N_2) can be seen in Figs. 3 and 4, respectively. Note that on planar Si (1 1 1) surfaces, the results are very similar [23]. During diffusion in N_2 ambient, it should be noted that the furnace is not completely O_2 -free, although the gas flow into the furnace is N_2 only. During diffusion, an amorphous layer was formed on the silicon. Diffusion of the as-deposited 3-nm-thick PureB layer in N_2 ambient resulted in an oxide thickness of about 24 nm (see Fig. 3), while diffusion in 14% O_2 resulted in an even thicker oxide layer, measured to be about 40 nm (see Fig. 4). For comparison, a Si (1 0 0) control sample without PureB layer annealed in N_2 ambient did not result in any layer that is detectable by ellipsometry, while annealing in 14% O_2 concentration formed only 9 nm of silicon oxide. It is well known that the presence of boron significantly increases the rate of oxidation [33].

On the other hand, when an anneal was performed *in situ* in the Epsilon reactor in N_2 ambient instead of the furnace, no

Fig. 5. EELS analysis from a line scan of the surface layer as shown in Fig. 3. The boron peak at the interface of the amorphous layer and Si substrate indicates the presence of a BRL.

Fig. 6. EELS analysis from a line scan of the surface layer as shown in Fig. 4.

oxide layer was detected by ellipsometry. This can be explained by the fact that the carrier gases used in the Epsilon reactor pass through a purifier and have impurity levels below 10 ppb, such that the PureB deposition and *in-situ* thermal diffusions take place under practically O_2 -free conditions. For the determination of the oxide layer thickness by ellipsometry, a pure SiO_2 layer was assumed. As the ellipsometry results were found to be consistent with the layer thicknesses observed in the TEM images, all subsequent layer thicknesses were determined only from ellipsometry measurements.

Based on EELS characterization, the elemental composition of this amorphous layer is predominantly silicon, followed by oxygen, with small amounts of boron. Therefore, this layer can be identified as a BSG layer. The EELS analysis of the diffused samples in N_2/O_2 ambient of Figs. 3 and 4 are shown in Figs. 5 and 6, respectively. The amorphous layer of the diffused sample shown in Fig. 3 was grown in an oxygen-limited ambient, and in contrast with the sample of Fig. 4, a clear peak in boron signal was observed at the amorphous layer and Si interface, indicating the presence of a BRL. There is no significant difference in EELS results for Si (1 0 0) or Si (1 1 1) surfaces.

Fig. 7. Oxide thickness after 950 °C, 10-min thermal diffusion as a function of the O₂ concentration in N₂ gas for samples with different thicknesses of the initially deposited PureB layers.

For the as-deposited layer, no EELS line scan was performed, as the as-deposited layer was thinner than the beam step size of 4 nm. However, EELS spot analysis was able to pick up a strong boron signal in the as-deposited layer. Furthermore, SIMS measurements showed that the peak concentration saturated at the equivalent atom density of pure amorphous boron for long deposition times [34].

Fig. 7 shows the oxide layer thickness as a function of O₂ concentration during 10-min diffusion at 950 °C for various initial PureB thicknesses that were obtained by varying the deposition time in the Epsilon reactor. The PureB layer thickness increases proportionately with B₂H₆ deposition time. From Fig. 7, it can be seen that the resulting oxide thickness after the diffusion process depended strongly on the initial PureB layer thickness. There was an appreciable increase in oxide thickness when the O₂ concentration during diffusion was increased from 0% to 14%. However, a further increase in O₂ concentration had little effect on the final oxide thickness.

The rate of oxide growth depends on the mass transfer (diffusion) rate and the reaction rate. Earlier work showed that the thicknesses of the oxide layers formed during diffusion in N₂ ambient (0% O₂ concentration) were insensitive to the diffusion temperature between 850 °C and 1050 °C and were determined only by the thicknesses of the initial PureB layer [23]. However, in the presence of 14% O₂ concentration, the oxide thickness increased with diffusion temperature. This could be explained by the fact that during furnace diffusion in N₂ ambient (i.e., no O₂ gas admixed), the supply of O₂ to the silicon surface was very limited. Therefore, the reaction was diffusion-limited, which explained the negligible effect of temperature on the final oxide thickness. However, in the presence of a sufficiently high concentration of O₂ in a N₂/O₂ ambient, the reaction was not limited by O₂ concentration but by the speed in which the reaction took place. In this case, the growth is reaction-limited and then temperature becomes a determining factor for the final oxide thickness. Fig. 7 shows that diffusion in 14% O₂ concentration provides sufficient O₂ to the silicon surface and that further increase in O₂ concentration does not significantly increase the resulting oxide thickness.

Fig. 8. Active boron concentration profiles as measured by ECV for various PureB layers after thermal diffusion at 950 °C for 10 min in 14% O₂ in N₂. Sheet resistances of these profiles are given in the legend.

More details of the surface layers were obtained by testing with chemical etchants. It is known that BRLs are hydrophilic and resistant to various acidic solutions like H₂SO₄, HF, and H₃PO₄ due to the low solubility of the layers [35], [36]. As a chemical etch test, various samples were subjected to a 1% HF etch treatment. The samples thermally diffused in N₂ ambient remained hydrophilic after prolonged HF dipping, although ellipsometry measurement showed that the oxide layer was effectively etched away. The hydrophilic nature of the silicon surface indicated the existence of a BRL, which is consistent with TEM and EELS results in Figs. 3 and 5. The BRL can be seen from the TEM images in Fig. 3 of diffused samples as a distinct dark agglomeration at the interface of oxide/Si. Furthermore, the EELS results in Fig. 5 showed a boron peak at the oxide/Si interface. All samples that were diffused with various concentrations of O₂, as shown in Fig. 7, became hydrophobic after a 3–4 min 1% HF etch, which indicates that surface was free of both oxide and BRL after etching.

B. Boron Diffusion and Dopant Profiles

Boron-doped surfaces prepared by CVD using B₂H₆, followed by thermal diffusion, were evaluated on the basis of dopant profiles and sheet resistance, which were controlled by optimizing the initial PureB layer thickness, diffusion temperature and time, as well as the O₂ concentration in the furnace during diffusion.

Fig. 8 shows the ECV-measured active boron profiles for various initial thicknesses of PureB layers, followed by thermal diffusion at 950 °C for 10 min in 14% O₂ in N₂. The corresponding sheet resistances of the various profiles are also indicated in Fig. 8, showing that sheet resistance decreases with increasing initial PureB layer thickness. The initial PureB layer acts as a source of the boron dopants, which diffuse into silicon up to the solid solubility, which is about $1.3 \times 10^{20} \text{ cm}^{-3}$ at 950 °C [29]. For a thinner initial PureB layer, the amount of dopants for diffusion into silicon was limited, leading to higher sheet resistance and lower peak doping concentration. It is worth noting that the

Fig. 9. Active boron concentration profiles as measured by ECV of two different (3.4-nm and 6-nm-thick) initial PureB layers, followed by thermal diffusion at 950 °C for 10 min in 0%, 30%, and 100% O_2 in N_2 . Lines serve as a guide to the eye.

Fig. 10. Recombination parameters J_{0p+} of Al_2O_3 -passivated symmetrical $p^+/n/p^+$ lifetime samples fabricated by thermal diffusion of PureB on Si (1 0 0) and Si (1 1 1) at 950 °C for 10 min with various O_2 concentrations.

diffusion was performed without any capping layer. Therefore, some of the dopants from the initially deposited PureB layer were lost during the diffusion process to the furnace ambient.

A characteristic dip in surface concentration is typically observed at the Si/SiO₂ interface due to the higher solubility of boron in silicon oxide than in silicon [37]. A high surface dopant concentration can be desirable to reduce the minority carrier concentration near the surface, especially in the absence of field-effect passivation. Earlier work showed that the removal of the surface boron-depletion region resulted in a lower recombination parameter J_{0p+} , where the passivating layer did not contain a high density of negative fixed charges, which translated to an absolute efficiency gain of 0.2% on the cell level [6].

The effect of O_2 concentration during diffusion on dopant profiles is shown in Fig. 9. The sheet resistances from the dopant profiles range from about 70 Ω/sq after diffusion in N_2 ambient (0% O_2) to 300 Ω/sq after diffusion of the 6-nm initial PureB layer in O_2 ambient (100% O_2). (The uniformity of the diffused layers as measured by the standard deviation of the sheet resistance over the wafer is shown in Fig. 10 and will be addressed

in Section III-C.) During diffusion in N_2 ambient (0% O_2), both the initial PureB layer thicknesses of 3.4 and 6 nm provided a virtually unlimited source of dopants, as can be observed from the similar dopant profiles and sheet resistances of about 70 Ω/sq in both cases. In the case of such a virtually unlimited dopant source, the thickness and thereby the uniformity of the initial PureB layer is not critical, as the final dopant profile and sheet resistance are only dependent on the diffusion conditions such as temperature and time. On the other hand, increasing the O_2 concentration during diffusion depletes boron, leading to lower peak concentration and higher sheet resistance. For comparison, diffusion in 14% O_2 required an initial PureB layer thickness of about 7.5 nm to achieve a sheet resistance of 70 Ω/sq , as shown in Fig. 8.

When there was an intentional flow of O_2 in the diffusion furnace, the thickness of the initial PureB layer became a factor in determining the final dopant profile and sheet resistance, as can be seen in Figs. 8 and 9. This can be attributed not only to the difference in amount of source boron but to the absence of a BRL as well. As O_2 diffuses through the amorphous surface layers of different thicknesses created through the different initial PureB layers, thermal oxide grows at the amorphous layer-Si interface, depleting boron at the Si surface and thereby eliminating a BRL. As can be seen from Fig. 9, at sufficiently high O_2 concentration (30%), the dopant concentration exhibits the characteristic dip at the Si/SiO₂ interface. Therefore, with the intentional O_2 flow during diffusion, the uniformity of the initial PureB layer becomes a prerequisite for achieving homogeneous diffusion and uniform sheet resistance. A further increase of O_2 concentration to 100% decreased the surface and peak dopant concentrations significantly, although the oxide thicknesses, as shown in Fig. 7 remained relatively unchanged for the same initial PureB layer thickness, despite the increase in O_2 concentration. All in all, the dopant profile and peak concentration are not only determined by the initial PureB layer thickness and diffusion temperature but by the O_2 concentration during diffusion that can be used as a parameter to optimize the performance as well.

C. Surface Passivation by Al_2O_3

One of the important prerequisites for high-efficiency silicon solar cells is a high effective carrier lifetime, which requires well-passivated interfaces and surfaces. Plasma-assisted ALD Al_2O_3 is known to provide excellent passivation for p^+ Si surfaces [20] and is used here in experiments to compare the recombination parameters J_{0p+} obtained for the different dopant profiles. The results are shown in Fig. 10. The uniformity of the diffused layers over the wafer becomes apparent from the standard deviation of sheet resistance and recombination parameter. As expected, the J_{0p+} increases with decreasing sheet resistance due to higher Auger recombination. This is further illustrated by calculating the theoretical Auger recombination limits obtained from the dopant profiles using the freeware program EDNA [38]. In the simulations, the most up-to-date empirical models were used for Auger recombination [39] and bandgap narrowing [40], which are consistent with Fermi-Dirac statistics.

Note that simulations revealed that the contribution from Auger recombination was very sensitive to the choice of band gap narrowing model and the use of Fermi–Dirac statistics rather than Boltzmann statistics. The ECV dopant profiles of the samples were scaled by a factor close to 1, in order to match the sheet resistance obtained by four-point probe measurements and to compensate for systematic measurement errors. It can be seen from Fig. 10 that the results from both planar Si (1 0 0)- and (1 1 1)-oriented wafers were not significantly different and are close to the Auger limit. Acceptable surface passivation could be achieved, with the contribution of surface recombination to the total J_{0p+} of <20 fA/cm² for most samples.

Interestingly, some of the samples with the lowest sheet resistance of ~ 70 Ω /sq exhibited very high J_{0p+} of ~ 260 – 502 fA/cm². This could be explained by the presence of a BRL, as these samples were thermally diffused in N₂ ambient and remained hydrophilic after prolonged HF dipping. By means of etching off the boron-diffused surface layer, it was shown elsewhere that the bulk carrier lifetime degradation was associated with the presence of a BRL and it was even proportional to the thickness of the BRL [8]. Note that the J_{0p+} only describes the recombination in the highly doped region and at its surface. Therefore, it can be concluded that a BRL is detrimental for surface recombination, preventing passivation of the surface. This also supports the results of Phang *et al.* [9], which noted that the J_{0p+} in the presence of BRL was comparable with an unpassivated diffused surface. Before HF dipping and Al₂O₃ passivation, we found J_{0p+} of ~ 602 fA/cm² for the samples containing a BRL. Apparently, the passivation and HF dip only improved the J_{0p+} slightly. Potentially, the samples containing a BRL layer can still be further improved by etching of the BRL prior to passivation [13].

IV. CONCLUSION

In this study, a p⁺-doping method was demonstrated, in which a PureB layer was deposited by CVD using B₂H₆ as precursors, followed by thermal diffusion. The applicability of this method for the formation of highly boron-doped regions for silicon solar cells was evaluated in terms of surface morphology after thermal diffusion, the boron dopant profiles, and sheet resistance. Furthermore, the compatibility of this p⁺-doping method with Al₂O₃ films prepared by plasma-assisted ALD was investigated. With the use of this surface passivation layer, it was found that for most lifetime samples, the J_{0p+} values were found to be close to the fundamental Auger limit, and the results from both planar Si (1 0 0)- and (1 1 1)-oriented wafers are not significantly different. However, the lifetime results also indicate that when a BRL is present after diffusion, a much higher J_{0p+} was observed. For instance, for ~ 70 Ω /sq samples with BRL, J_{0p+} of ~ 260 – 502 fA/cm² were measured. The presence of a BRL clearly impedes the high-quality surface passivation of boron-diffused surfaces, which is essential for high-efficiency n-type solar cells, and a BRL should certainly be avoided or removed. Therefore, in addition to optimizing the initial PureB layer thickness and thermal budget to control the dopant profiles, the ambient during the thermal diffusion process of PureB layers can

be optimized to avoid the formation of a BRL. The experiments demonstrate that with correct tuning of the O₂ concentration during diffusion, no additional processing step is needed to etch away BRLs, and promising parameters for solar cells in terms of J_{0p+} and sheet resistance can be achieved. For the high-volume manufacturing in Si solar cell industry, a customized batch furnace system is currently under development for the B₂H₆ doping process.

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