Passivating Polysilicon Recombination Junctions for Crystalline Silicon Solar Cells

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Polysilicon recombination junctions whose n-type bottom layers double as a passivating contact to the silicon surface are investigated. Such recombination junctions are a key element in the interconnection of tandem devices with a silicon bottom cell, and they could be used to simplify the processing sequence of single-junction cells with interdigitated back contacts (IBCs). Polysilicon tunneling junctions require high processing temperatures to crystallize the layers; however, this also facilitates interdiffusion of dopants, whereas tunnelling relies on degenerate doping concentrations in the constituent layers and sharp interfaces between them. Using secondary-ion mass spectrometry (SIMS) in dynamic mode, it is found that dopants diffuse readily across the interface, thus compromising the junction. The undesired diffusion is suppressed by modifying the interface with C, O, or a combination of these. Moreover, it is found that the modification does not interfere with diffusion of H, an essential element to passivate defects at the surface of the silicon wafer. Thus, implied open-circuit voltages \( (V_{oc}) \) of up to 740 mV are demonstrated for contact resistivities less than 40 m\( \Omega \) cm\(^2\).

1. Introduction

Over the last decades, photovoltaic modules have seen a spectacular cost reduction accompanied by an enormous expansion of their production capacity.\(^\text{[1]}\) More than 90% of the global market is based on crystalline silicon and it is unlikely that this will change in the foreseeable future. Nevertheless, the balance of system (BOS) creates an immense pressure on the cost, requiring improved efficiency of modules and cells. Currently, the highest efficiencies for single-junction cells are achieved with interdigitated back contacts (IBCs), using passivating contacts based on either amorphous silicon\(^\text{[8]}\) or an approach using an interfacial oxide and doped polysilicon.\(^\text{[9]}\) The latter approach is attractive as it is compatible with high processing temperatures such as those used in dopant diffusion or sintering of printed metallization pastes.

For both IBC approaches, the use of a recombination junction for one of the two contact polarities promises a substantial simplification of the process flow as the number of masking and alignment steps can be reduced.\(^\text{[4,5]}\) The high conductivities of sintered contacts are advantageous for IBC cells as large photocurrents around 40 mA cm\(^{-2}\) or above have to be extracted, whereas their areas cannot exceed half of the rear surface.

In addition to its use in single-junction solar cells, silicon is also used as the bottom cell in monolithically connected tandem devices whose efficiencies approach 30\%\(^\text{[6]}\) with a perovskite top cell.\(^\text{[7]}\) The recombination junction between the two component cells assumes a pivotal role in this approach. Here, the required conductivity is more moderate as the contact extends over the full area and the current in a tandem cell is around 20 mA cm\(^{-2}\), but it has to comply with other requirements as it should ideally have a low lateral conductivity to isolate shunts and it should be highly transparent to IR light. Moreover, the front surface of the bottom cell should be textured to provide light scattering in the bottom cell and to reduce the reflection of the top cell by a double rebound at the texture.\(^\text{[8]}\) As the passivation of textured surfaces with p-type layers is difficult,\(^\text{[9]}\) the tandem cell would preferably use a p-type wafer with an n layer on the interfacial oxide that forms the junction,\(^\text{[10]}\) followed by a recombination junction.
that terminates with a p-layer. Thus, it would connect easily to the hole transport layer (HTL) at the rear of the top cell,[11–13] which is also the preferred configuration for perovskite cells because of reduced parasitic absorption.[14]

As the orientation of the recombination junction is opposed to the current flow, its constituent layers should be doped degenerately to make it a tunneling junction.[15] To avoid compensation of dopants by interdiffusion, either the whole junction[10] or at least its second layer[13] should be manufactured at low temperature. Alternatively, diffusion barriers such as SiO, SiC, or SiNx may be incorporated,[5,16] provided they do not interfere with current transport.

We investigate recombination junctions based on an interfacial oxide at the surface of the wafer and a stack of n-type and p-type SiCx. Even though we use a rapid thermal annealing process to crystallize the p-layer and to activate its dopants, we observe severe interdiffusion of dopants across the interface, thus compromising the band-to-band tunneling of the recombination junction due to dopant compensation. We demonstrate that the insertion of additional layers between the two SiCx layers suppresses the interdiffusion, resulting in combined contact resistivities of the full stack as low as 7 mΩ cm. We find that diffusion of hydrogen is only marginally impeded by these additional layers; thus, we are able to passivate defects at the surface of the wafer, resulting in implied Voc (iVoc) as high as 740 mV.

2. Experimental Section

In this investigation, P-doped float zone wafers that were 200 μm thick and had a resistivity of 2 Ω cm and <100> orientation were used. After cleaning, an interfacial oxide was grown by immersion in hot HNO3. After that, plasma-enhanced chemical vapor deposition (PECVD) was used to grow an amorphous bilayer stack to and intended thickness of 35 nm. It started with an intrinsic Si buffer layer using silane (SiH4) and hydrogen (H2) as precursor gases to protect the interfacial oxide, similar to the design of p-type passivating contacts.[17] On top of the buffer, a n-doped SiCx layer was grown, adding phosphine (PH3) and methane (CH4) to obtain a C content between 3 and 5 at%.[18] At this stage, the sample set was split in half. One half of the deposition was finished with reduced SiH4 flux with the intention to obtain a carbon-rich surface. Subsequently, all layers were annealed in a tube furnace for 30 min at 850 °C. The samples were then etched in a 5% HF solution for 1 min. Subsequently, the sample set was split again and half of the samples were exposed to UV light (Jelight, UVO cleaner 42) to grow a thin SiCx layer intended to act as a diffusion barrier for dopants. Next, the sample set was split once more to grow p-layers with thicknesses of 20 and 40 nm, respectively, using silane, methane, hydrogen, and trimethylboron (B(CH3)3) (TMB).[19] All samples were fired for 24 s at 800 °C to crystallize the p-layer (Jetfirst 200, Jipelec). Finally, the samples were hydrogenated. To this end, a layer of SiNx:H was deposited, hydrogen was released by a short anneal in a firing furnace at a set temperature of 800 °C (Camini, Meyer-Burger), and the SiNx:H layer was stripped by immersion for 10 min in diluted HF (5%). To avoid issues with the H background during the secondary-ion mass spectrometry (SIMS) measurements, deuterium (D2) was added during the deposition of the SiNx:H layer.

The design of the eight different sample configurations is shown in Figure 1.

The samples were cleaved for characterization and elemental depth profiles were recorded by dynamic SIMS (CAMECA SC-Ultra) using Cs+ primary ions with an impact energy of 1 keV and a primary current of 2 nA scanned over an area of 300 × 300 μm2. The secondary ions were collected from a central region of 60 μm diameter. Note that matrix effects, i.e., a dependence of the ionization yield on the composition of the sputtered material, can be dismissed as the intensities of the elements were obtained from MCs clusters, where M represents the element to be analyzed. The conversion of sputtering time into depth was conducted using reference images taken by transmission electron microscopy (TEM). The transfer length method (TLM) was used to measure the contact resistivities, using contact pads of indium tin oxide (ITO)/Ag sputtered through a shadow mask. After sputtering, the samples were cleaved along the TLM pattern to avoid lateral current spreading; the spreading within the wafer was corrected according to Eidelloth and Brendel.[20] The layer stack between the pads was not etched as an earlier investigation showed that its contribution to the current transport is minor.[21] Charge carrier lifetimes and implied open-circuit voltages were assessed by quasi-steady-state photocurrent (QSSPC) (WCT-120, Sinton Instruments) on symmetrical samples.

3. Results and Discussion

3.1. SIMS Depth Profiling

Figure 2 shows dynamic SIMS profiles normalized to the O peak of the interfacial oxide at the surface of the wafer, which is nominally the same in all samples. Different from that, the O peak at
the interface between the two doped layers shows clear differences; samples (a), (b), and (c) have similar O peaks, which is unexpected as no oxide was intended in sample (b). Only sample (d) shows a less pronounced O peak in agreement with its design. The locations of the O peaks suggest a uniform p-layer thickness of ≈45 nm in all samples, whereas the n-layer thicknesses are 35 nm in sample (a) and closer to 30 nm in samples (b), (c), and (d).

The H profiles appear to correlate with those of O. At the interface between the wafer and the n-layer they are very similar in extent and shape with a steep decay into the wafer and a gentle decay toward the doped layers. The bilayer structure of the n-layer is clearly visible with a high H content in the buffer and a lower H content in the doped part. Only sample (a) appears to have a higher H content in the doped region.

At the interface between the doped layers, samples (a) and (c) have high H peaks, apparently correlating with the intentional oxides in these samples. The C-rich interface of sample (b) contains less H, reflecting the unintentional native oxide in this sample. In sample (d), there is only a small H peak, but still more than expected for an interface without intentional oxide.[22] Finally, in the p-layer, the H content is similar to the doped part of the n-layer.

The profiles of the two dopant species, B and P, are shown in Figure 3. All p-layers show a uniform B content across the full layer, whereas the n-layer shows a small undulation of the P content in its doped part, followed by a clear drop in the region of its undoped buffer and another peak toward the wafer. A comparison with the O and H profiles in Figure 2 suggests that P accumulates just before the interface between the undoped buffer layer and the interfacial oxide.

Sample (d) with its direct contact between the doped layers shows a strong interdiffusion of dopants across the interface of the recombination junction. As this observation is reproduced in the set of samples with a thinner p-layer, we can rule out an artifact. The two overlaid cerf(x) characteristics illustrate diffusion from an infinite reservoir, i.e., a tail of B extending into the n-layer and a tail of P extending into the p-layer. For simplicity, we assumed that the time of diffusion is equal to the dwell time of the firing process. This would suggest a diffusivity of ≈2 × 10^{-13} \text{ cm}^{2} \text{s}^{-1} for P in the p-layer at the firing temperature of 800 °C. As the doped part of the n-layer is thinner, we are less confident with overlaying a cerf(x) characteristic to the B profile in the n-layer. Nevertheless, the diffusivity appears to assume a similar value and we note that these are three orders of magnitude higher than those of boron and phosphorus in crystalline Si at 800 °C.[23]

Apart from sample (d), which stands out because of its strong interdiffusion, sample (b) differs from the other samples in terms of its B profile, and also in this case the observation is reproduced in the second set of samples. A zoom into the region around the recombination junction is shown in Figure 4. Whereas the initial decay of the B-profile at 42 nm is very similar to the other samples, it suddenly increases at 45 nm and assumes the interface between the two doped layers shows clear differences; samples (a), (b), and (c) have similar O peaks, which is unexpected as no oxide was intended in sample (b). Only sample (d) shows a less pronounced O peak in agreement with its design. The locations of the O peaks suggest a uniform p-layer thickness of ≈45 nm in all samples, whereas the n-layer thicknesses are 35 nm in sample (a) and closer to 30 nm in samples (b), (c), and (d).

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a pronounced peak at ≈48 nm. The B peak appears earlier than the O peak at 50 nm, which denotes the unintentional native oxide between the doped layers. We conclude that the design of this sample can effectively stop B diffusion, possibly by accumulating it together with carbon.

The O peak of the unintentional oxide appears to coincide with the C peak, even though the processing sequence would suggest that the native oxide should be on top of the C-rich interface. Likewise, H appears throughout the oxide layer. This may be related to the resolution of the measurement as in case of thicker oxide layers H tends to accumulate at the inner and outer interfaces.[22] Interestingly, sample (a) does not show a peak in its C profile, nor does Figure 3 show any B accumulation. We suspect that the oxidation in highly reactive ozone removes C from the surface by reacting it to volatile CO2, whereas sample (b) is exposed to a less reactive environment of ambient air that grows an unintentional oxide but appears to conserve the C-rich surface.

3.2. TEM Analysis

Figure 5 compares TEM images of the n-layer for samples (a) and (c). The undoped buffer is clearly distinguished from the doped region by its darker contrast. Despite the long thermal annealing for 30 min at 850 °C, the buffer as well as the n-layer develops only very few and very small crystalline domains. Different from that, grains with diameter of several nanometers are observed in the p-layer despite its much shorter annealing of 24 s at a lower temperature of 800 °C. We attribute this observation to an impeded crystallization due to the higher carbon content in the n-layer compared to the p-layer.[18] Figure 5 also corroborates the observation of Figure 2 and 3, where the n-layer in sample (a) is thicker than the n-layers of the other samples.

Figure 6 compares concentration profiles obtained by energy-dispersive X-ray spectroscopy (EDS) in scanning TEM mode. The position of the interface can be easily placed at the location where the minimum of the Si profile and the maximum of the O peak coincide. In this case, the P profiles overlap almost exactly, whereas the C profile of sample (a) extends slightly further into the p-layer. We note that the extent is marginal, suggesting that the C-rich conditions are essentially a surface treatment, but they do not deposit a specific material with traceable layer thickness.

3.3. Contact Resistivity

The specific contact resistivity $\rho_c$ of the samples was investigated by TLM. As the layer stack between the TLM pads was not etched, we briefly assess its contribution to the current transport. For the p-layer, IR transmission on reference samples showed free carrier densities between 4 and $6 \times 10^{19}$ cm$^{-3}$ and corresponding optical mobilities between 13 and 15 cm$^2$V$^{-1}$s$^{-1}$ after firing at 800 °C.[24] As the transport mobility is likely less than the optical mobility, we estimate a lower limit for $R_{sh} = 2100 \, \Omega_{sq}$ for a 30 nm thick film. Applying the same method to annealed n-layers, we found a free electron density of $4 \times 10^{19}$ cm$^{-3}$ and an optical mobility of 25 cm$^2$V$^{-1}$s$^{-1}$, suggesting a similar value of $R_{sh}$. Compared to $R_{sh} = 110 \, \Omega_{sq}$ of the wafer, we may neglect lateral transport in the layers. Thus, the resulting value of $\rho_c$ contains three transverse contributions: the first is the transport across the interfacial oxide between the n-type wafer and the n-layer; the second is the recombination junction between the doped layers; and the third is the Schottky junction formed between the p-layer and the ITO–Ag stack.

Assuming a pure tunneling process[25] and a barrier height of 3.2 eV,[26] we estimate 3.5 mΩ cm$^2$ for the current transport between the wafer and an n-layer with the electron density quoted previously. For the Schottky contact between the p-layer and the ITO–Ag stack of the TLM pad, we estimate 1.6 mΩ cm$^2$.[24] As these two contributions are identical for all of the samples, we find a lower limit of 5 mΩ cm$^2$ for $\rho_c$.

We measure the lowest $\rho_c$ on sample (b) with its C-rich interface. The upper panel of Figure 7 shows values between 7 and 40 mΩ cm$^2$ for the stacks with thin and thick p-layers, respectively. For the configuration of sample (a), we find somewhat higher values between 40 and 80 mΩ cm$^2$, even though SIMS does not show any accumulation of C at the interface. On sample (c) with its intentional oxide we measure between 200 and 300 mΩ cm$^2$, similar to values between 300 and 500 mΩ cm$^2$.

![Figure 5. HR-TEM images of the n-layer region in samples (a) and (c) (left and right, respectively).](image-url)
through the effect of trap-assisted during the deposition of the SiN for the 4.8 $10^5/C_25$ $+$ $w$ shows dynamic SIMS profile. Comparison of EDS linescans across the interface between the 40% of the B content in the p-region extends into the 2 $V$ (d). Finally, we reported for similarly designed recombination junctions with intentional growth of an oxide between the doped layers.\cite{5,16} Finally, we find very high values up to 40 $\Omega$ cm$^2$ in sample (d), where the doped layers are in direct contact.

Starting at a depth of $\approx$40 nm, Figure 3 shows that the B profiles of all samples show an initial decrease by one order of magnitude over 10 nm. For the P profiles the final increase appears steeper, changing by an order of magnitude over only 5 nm. In sample (d), both dopants quickly flatten out into broad diffusion tails whose impact on the formation of the recombination junction is likely the reason why this sample shows by far the highest $\rho_c$.

To achieve band-to-band tunneling, the doping concentration should reach degeneracy in both bands, and the junction should be narrow. Taking the free carrier concentrations of $6 \times 10^19$ and $3.9 \times 10^{19}$ cm$^{-3}$ as representative for the p-layer and the n-layer, respectively, the condition of degeneracy would be fulfilled for samples (a), (b), and (c). Applying the depletion approximation with abrupt interfaces for the sake of simplicity, we can roughly estimate the width of the space charge region to be $w_{SCR} = w_p + w_n = (3.1 + 4.8)$ nm for samples (a), (b), and (c).

Instead of an abrupt junction, Figure 3 suggests that a linear grading over 10 nm might be a better description. In this case, the widths of the depletion regions add up to $w_{SCR} = 2 \times 4.9$ nm, i.e., just within the graded region. For sample (d), Figure 3 shows that the P content extending into the p-region directly adjacent to the junction is $\approx$20% of the content in the n-layer. Thus, we estimate that this part of the p-layer is partially compensated, resulting in an effective hole density between 3.2 and $5.2 \times 10^{19}$ cm$^{-3}$. Likewise, $\approx$40% of the B content in the p-region extends into the adjacent n-region, compensating it to an effective electron density between 1.5 and $2.3 \times 10^{19}$ cm$^{-3}$. Thus, the condition of degeneracy may no longer hold. Assuming an abrupt junction, the width of the space charge region extends to (3.3 + 6.7) nm, whereas in case of a linearly graded junction it would extend significantly beyond the graded zone, likely preventing effective band-to-band tunneling and thus leading to high $\rho_c$.

Finally, it is surprising that the unusual doping profile of sample (b) should yield such a low resistivity. However, if we assume that B is the dominant dopant up to the second peak at 48 nm, it would form a much more abrupt junction because thereafter its B profile decays steeply by an order of magnitude over only 5 nm. Moreover, the slightly elevated C content at the interface of this sample could further reduce $\rho_c$ through the effect of trap-assisted tunneling.

### 3.4. Passivation

The lower panel of Figure 7 shows the implied open circuit voltage ($iV_{oc}$) for all samples. With one exception, the values scatter between 735 and 745 mV without any clear dependence on the properties of the junction. Generally the passivation of the wafer surface relies on a reduction of the minority carrier density by means of a shallow indiffused region, and on chemical passivation by saturating dangling bonds with an interfacial oxide whose passivation is substantially enhanced during the thermal release of H from the SiN$_2$:H layer.

Figure 2 did not show any striking differences of the O peak in the interfacial oxide. On the other hand, there seem to be minor differences in the associated H peak, but their full extent could be hidden by the H background despite a vacuum of $\approx5 \times 10^{-9}$ mbar in the SIMS analysis chamber, and they might not be expressed clearly in the normalized data. To avoid the H background, we added D$_2$ during the deposition of the SiN$_2$:H layer. Figure 8 shows dynamic SIMS profiles of D, both for the standard p-layer thickness and for the samples with a thinner p-layer. For the samples (a) and (b), the former configuration appears to incorporate less D in the interfacial oxide, whereas the configuration with the thin p-layer does not show this deficiency. It would be a considerable coincidence if the diffusion through the thinner p-layer would exactly compensate the factor of $\sqrt{2}$ by which the diffusivity of D is reduced with respect to the one of H. Thus, the SIMS data do not make clear whether the C-rich interface between the doped layers interferes with
hydrogenation. Based on the $iV_{oc}$ data in Figure 7, we are led to conclude that this is not the case.

4. Conclusion

We used dynamic SIMS to investigate the interdiffusion of dopants in polysilicon recombination junctions fabricated by PECVD. We found that the interdiffusion of dopants is effectively reduced when the interface between the doped layers is modified by oxidation with $O_3$ (ex situ) or a surface treatment with CH$_4$ (in situ). Thus, we obtain specific resistivities as low as 7 m$\Omega$ cm$^{-2}$. Neither of the interfacial modifications interferes with the diffusion of H. Thus, the defect states at the interfacial oxide between the wafer and the doped layer stack can still be effectively passivated with the thermal release of H from a SiN$_x$:H layer, and we were able to demonstrate $iV_{oc}$ up to 740 mV.

Acknowledgements

This work was funded by the Swiss National Science Foundation (SNF) and the Luxembourg National Research fund (FNR) through the project CHESS (SIS01253-01) and by the European Union within the H2020 project HighLite (857793). The authors thank Dr. Juan Diaz and Dr. Christophe Allebé (CSEM) for annealing and hydrogenation, and Brahime El Adib (LIST—Advanced Characterisation Platform) for support during dynamic SIMS measurements.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in the Zenodo repository at http://doi.org/10.5281/zenodo.4771634.
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