Low-Cost Plasma Immersion Ion Implantation Doping for Interdigitated Back Passivated Contact (IBPC) Solar Cells

David L. Young, William Nemeth, Vincenzo LaSalvia, Matthew R. Page, San Theingi, Jeffery Aguiar, Benjamin G. Lee and Paul Stradins

ABSTRACT — We present progress to develop low-cost interdigitated back contact solar cells with pc-Si/SiO₂/c-Si passivated contacts formed by plasma immersion ion implantation (PIII). PIII is a lower-cost implantation technique than traditional beam line implantation due to its simpler design, lower operating costs, and ability to run high doses ($1\text{E}14 - 1\text{E}18\text{ cm}^{-2}$) at low ion energies (20 eV – 10 keV). These benefits make PIII ideal for high throughput production of patterned passivated contacts, where high-dose, low-energy implantations are made into thin (20 – 200 nm) a-Si layers instead of into the wafer itself. For this work symmetric passivated contact test structures (~100 nm thick) grown on n-Cz wafers with PH₃ PIII doping gave implied open circuit voltage (iV_{oc}) values of 730 mV with J_0 values of 2 fA/cm². Samples doped with B₂H₆ gave iV_{oc} values of 690 mV and J_0 values of 24 fA/cm², outperforming BF₃ doping, which gave iV_{oc} values in the 660 - 680 mV range. Samples were further characterized by SIMS, photoluminescence, TEM, EELS, and post-metallization TLM to reveal micro- and macro-scopic structural, chemical and electrical information.

Keywords: plasma immersion ion implantation; passivated contacts; silicon; solar cells.

1 Introduction

The U.S. Department of Energy's SunShot goals for photovoltaics (PV) are for the utility scale levelized-cost-of-electricity (LCOE) to be ~ \$0.06/kWh by 2020.[1] Using recent SunShot balance-of-systems cost targets, this LCOE goal demands that PV modules be at least 20% efficient and cost ~\$0.40/W (2016 dollars).[2] Higher efficiency modules obviously reduce the cost burdens on all components of the balance-of-system costs. An interdigitated back contact (IBC) cell is known for its ability to reach these high efficiencies, but costs have limited its widespread commercialization. One of the main cost drivers for IBC cells is the need to pattern dopants on a length scale of tens of micrometers. Masked ion implantation can provide this level of dopant fidelity while also providing highly reproducible dopant profiles leading to high cell yield and narrow efficiency distributions during manufacturing.

While ion implantation has been, and continues to be, used in the production of microelectronics, recent advances in tool design have allowed it to be utilized in solar cell manufacturing where \$/cm² costs dominate. Non-mass analyzed beam line implanters have been shown to have throughputs and costs-of-ownership that meet the PV industry needs and have provided similar emitter results to traditional dopant diffusion processes.[3] However, in some IBC cell designs, an even simpler plasma immersion ion implanter (PIII) can be utilized for significant capEx and production cost savings.[4]

Recently an interdigitated back contact cell was introduced using c-Si/SiO₂/poly-Si

passivated contacts formed by ion implantation[5-9] with a record 23.9% efficiency achieved by Rienäcker et al.[10] In this cell configuration, the ions are implanted into a-Si or polycrystalline-Si (pc-Si) layers separated from the c-Si wafer by a thin oxide layer, instead of directly into the c-Si wafer. This eliminates the end-of-range damage such as dislocation loops[11] to the wafer, which in turn, lowers the post implantation thermal budget needed to activate and diffuse dopants in the pc-Si layer, rather than anneal out induced defects in the c-Si. These contacts have excellent passivation, $J_0 < 10 \text{ fA/cm}^2$, in both the p-type emitter and the n-type contact regions, and low enough specific contact resistivities to not limit the device. Additionally, the interdigitated back passivated contact (IBPC) device[5] has several advantages over traditional ion implanted IBC cell designs such as the ability to passivate all surfaces of the cell by a single process step and metallized contacts that are effectively area independent – the latter being ideal for high current IBC cells.

This paper explores the use of a simple, non-beam line, **plasma immersion ion implanter (PIII)** to form IBPC solar cells. PIII technology has long been used in semiconductor device production[12] where high-dose and low-energy implants are necessary, but, to our knowledge, has not been used to form passivated contacts to c-Si solar cells. This work shows that PIII can form well-passivated n-type and p-type pc-Si/SiO₂/c-Si contacts suitable for high efficiency IBPC cells.

2. PIII Technology

Traditional mass-analyzed beam line implanters contain a series of complex parts to generate, extract, select, accelerate and deposit ions into a target.[13] These tools implant precise charge-to-mass ratio ion species at exact energies routinely in the electronics industry. For the PV industry, less precise control over species and energy may be needed for some device designs. Much simpler implant tools can be designed without mass analysis to increase throughput and lower capital equipment costs. One tool design approach is to extract beam current from an ion source (i.e. a plasma of desired ions) and allow the beam to expand toward a target wafer under the application of an accelerating voltage. This type of tool generates an expanding beam of ions with a spectrum of species and energies according to the species (and their ionization state) in the plasma. Tools such as these have been shown to meet the PV industry cost goals[14] and provide good cell results.[3]

Another route to an even simpler ion implanter is to place the target wafers directly into the plasma chamber and accelerate the plasma ion species into the wafer by application of a negative voltage to the wafer platen. This voltage expands the plasma sheath such that the target wafer is engulfed and ions are accelerated into the wafer. This type of tool is known as a plasma immersion ion implanter, or PIII, and is commonly used in the electronics industry where high-dose, low-energy implants are needed. Additionally, because electric field lines are always perpendicular to equipotential lines (and the wafer is at a common potential) the ions are implanted everywhere perpendicular to any surface exposed to the plasma, even rough or three-dimensional structures (i.e. FinFETS). The latter benefit allows very uniform depositions over pyramid-textured wafers for PV applications, and is also why implant shadow mask features translate with high fidelity to the target wafer.

Because the ion current is not extracted from the ion source chamber through a collimation slit, as is the case for beam line implanter designs, PIII can provide very high ion flux (as high as $10^{20} \text{ m}^{-2} \text{ s}^{-1}$) [15] at low energies (20 eV – 10 keV). What is lost in inhomogeneous energy and species distribution of the implant dose, is gained in terms of low capital investment, ease of operation and maintenance, and uniformity across rough surfaces. The high-dose, low-energy implantation parameters make PIII ideal for low-

cost patterned IBPC solar cells where high dose (10^{16} cm^{-2}) and low energy ($< 5 \text{ keV}$) implants are necessary to achieve heavily doped (10^{20} cm^{-3}) thin pc-Si layers without high-energy implant damage to the underlying passivating SiO_2 layer. High dose at low energy (or low ion penetration depth) is difficult to achieve for a beam line implanter where ion current is governed by extraction voltage and beam optics for the final desired beam profile. This voltage may be so high that a deceleration voltage may need to be added to the beam path to lower the energy of the ions before implantation – increasing the complexity of the tool.[13]

One characteristic of PIII implanters is that samples experience the reactive chemistry of the ion source plasma that can etch, deposit and/or implant. This is used to advantage in some applications, but has not been tested in the formation of pc-Si/ SiO_2 passivated contacts for solar cells until now.

3. Experiment

Intrinsic a-Si/ SiO_2 /c-Si/ SiO_2 /a-Si symmetric test samples were grown on rough, saw-damage-removed (KOH etch), 4 ohm-cm, n-Cz wafers with initial lifetimes $> 1 \text{ ms}$. Wafers were RCA cleaned before thin (1.5 nm) SiO_2 layers were grown by thermal oxidation at 700°C , followed by growth of 100 nm thick intrinsic a-Si films by plasma enhanced chemical vapor deposition (PECVD) of silane. Samples were then ion implanted by PIII with PH_3 , B_2H_6 , or BF_3 plasma species over a dose range of 1×10^{15} to $5 \times 10^{15} \text{ atoms/cm}^2$ using an accelerating voltage of 4 kV at room temperature. All of the implants were done at Ion Beam Services in Peynier, France using either a traditional mass-analyzed beam line implanter, or a PULSION PIII implanter. Samples were sent back and forth between laboratories in double-bagged, cleanroom prepared, wafer carriers to minimize contamination. Identical witness samples were implanted with B or P using mass-analyzed beam line implantation at 5 keV over dose ranges of $4\text{--}7 \times 10^{15} \text{ atoms/cm}^2$, and $5\text{--}8 \times 10^{15} \text{ atoms/cm}^2$, respectively. Both sides of the samples were implanted to maintain the symmetric geometry. Next, after an RCA clean, the samples were annealed at 850°C for 30 min to crystallize the a-Si to pc-Si, and to diffuse and activate dopants. The $^\circ\text{C/min}$ ramp rate from loading temperature ($\sim 300^\circ\text{C}$) to crystallization temperature (850°C) was adjusted to eliminate blistering in the samples due to H-effusion. Finally, the samples were passivated with a 20 nm Al_2O_3 layer deposited by thermal atomic layer deposition (ALD) over all surfaces of the sample and annealed at 400°C in N_2 for 20 mins to provide H to the whole structure.[16] Secondary ion mass spectroscopy (SIMS) depth profiles were performed to measure the carrier concentration of dopants and H after implantation and after certain process steps. Low primary beam ion bombardment energies (1.5 keV, O_2^+ atoms) were used to minimize collisional mixing as discussed in an earlier publication.[5]

Contact resistivity values, ρ_c , were determined by the transmission-line-method (TLM) using metal contact pads. Photoluminescence (PL), transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) were used to image the samples. Photoconductive decay (PCD) measurements were made using a Sinton WCT-120 instrument in either generalized or transient mode to extract an implied open circuit voltage (iV_{oc}), an emitter saturation current density, J_0 , and a bulk lifetime, τ_{bulk} . We used Sinton's Auger correction model and an optical constant of 0.75. The top graph of Fig. 1 shows typical lifetime as a function of excess minority carrier density (MCD) data over several orders of magnitude. To extract the J_0 contribution, we identify a high-injection region ($> 5 \times 10^{15} \text{ cm}^{-3}$) with a slope of one, consistent with the theory of Kane and Swanson.[17] We then use the corresponding MCD region to fit a line to the $1/\tau_{Auger}$ corrected vs MCD data in the lower graph of Fig. 1 to extract the bulk lifetime and $\bar{J}_0$. This process ensures that we are using the appropriate region of the PCD data to extract contact and bulk parameters. The uncertainty associated with the fit for J_0

(shown in Figure 6) was estimated based on the change in J_0 depending on the choice of MCD used for the fit.

4 Structural Analysis

Figure 2 shows a cross-sectioned, post annealed, P implanted sample imaged with high angle annular bright and dark field (scanning) transmission electron microscopy (STEM) coupled with point-resolved energy-dispersive x-ray (EDX) and electron energy loss spectroscopy (EELS) to analyze the layer structures, interfaces, and chemistry. Figures 2A)_a-f show increasing magnification of the interface in bright and dark field. The images show the undamaged, perfect c-Si lattice, the abrupt c-Si/SiO₂ interface, the continuous thin SiO₂ layer, and the fine-grain (~5 - 10 nm grain size) polycrystalline character of the pc-Si layer. Note the lack of defects in the c-Si indicative of the implant ions stopping mainly in the pc-Si layer and not in the c-Si wafer. Figures 2B and 2C show STEM HAADF (a), EELS images of the oxygen K line (b), and an oxygen integration map across the SiO₂ layer (c). The oxide interface for a P implanted sample (2_B) appears to be more uniform compared with the B implanted sample (2_C) over the limited length imaged. The images show that oxygen remains confined to the SiO₂ layer, but does show varying, symmetric densities throughout the entire layer. We note that the images of Figure 2 are highly representative of the films we have imaged by TEM and the character of the SiO₂ interface with the pc-Si and the c-Si wafer. Continuous cross-sectional TEM images over 30 μm in length have only revealed an apparently uniform SiO₂ layer without noticeable oxide ball-up or pin-hole structures.

5 Results

5.1 SIMS

Figure 3a shows as-implanted SIMS depth profiles of B, P and H for samples ion implanted by PIII. Source gases, dose levels and accelerating voltages are given in the legend. Typical of PIII implant profiles, there is a large concentration of dopants near the surface which decrease steeply with depth to background levels around 70 nm. The variation in B dose is only slightly detected in these data. The H concentration is very high for the B implanted sample shown, but this is also the case for the P implanted sample. Both precursor gases (B₂H₆, and PH₃) have plenty of H that gets implanted along with the dopant atoms. The very shallow P profile is indicative of the larger P atom not penetrating into the surface of the a-Si for the same accelerating voltage as B. However, Figure 3b shows that after crystallization doping concentration uniformly distributes itself within the pc-Si layer. The samples in Fig 3b still have the 30 nm Al₂O₃ layer on the surface, thus the dopant and H profiles are affected by this layer and interface. The doping concentration for B in Figure 3b is about $1.5\text{E}20\text{ cm}^{-3}$, whereas the P doping is about $3\text{E}19\text{ cm}^{-3}$. The B doping level is close to our target value, but the P doping is about 10x lower than we had anticipated. Further experiments are on-going to raise this doping level by increasing the dose and accelerating voltage. Finally, because the PIII implant profile is so shallow, there is concern that many dopants will be removed before crystallization if a cleaning step is performed that could remove material. This would be more pronounced for the P profiles compared with the B profiles and may be the reason for the reduced carrier concentration seen in the P implanted samples. Figure 3c shows the influence of cleaning the samples before the crystallization anneal with and without using an oxide-removing HF solution. For this case, there is no

affect on the final dopant profile with removing the native oxide. However, the RCA cleaning step itself can remove material by forming oxide layers. We note that integrating the as-implanted SIMS profiles matches the integrated annealed SIMS profiles only if we assume about 8 nm of material was removed from the surface of the as-implanted samples. This may indicate that our cleaning protocol does indeed remove dopants from the surface. More research is needed in this area to fully understand the consequences of cleaning or not cleaning the surface before crystallizing the implanted layers.

5.2 Passivation

Fig. 4 shows the iV_{oc} values from PCD data taken on the symmetric samples after each process step. Post implantation, all of the samples have very low iV_{oc} values presumably due to non-activated dopants in the a-Si. Following the 850 °C crystallization anneal most of the samples either remain poorly passivated or decrease in their iV_{oc} values. Beneficial in-situ H remaining in the films would be expected to effuse at these high temperatures. However, after the Al_2O_3 deposition and anneal, all of the samples significantly improve in iV_{oc} . In other work we have shown that the passivation essentially remains even after the removal of the Al_2O_3 layer, implying that the dielectric layer is acting more as a H reservoir than a field-effect layer,[16] but ongoing experiments will hopefully elucidate the chemical and physical changes to the pc-Si contacts with this process. The data of Fig. 4 show the tremendous benefit of adding H back to the contacts after the crystallization anneal. We note that if our samples are crystallized above 920 °C the iV_{oc} values are much less than 650 mV, and that adding the H-rich Al_2O_3 layer and anneal does not enhance the passivation quality. This has been seen by others working with similar PECVD material and passivation techniques[6, 18] and is commonly thought to be associated with a degradation of the SiO_2/c -Si interface.

The passivation of the doped pc-Si contacts using a Al_2O_3 layer has the added benefit of passivating intrinsic pc-Si as well. In an IBC cell configuration, intrinsic pc-Si would separate n-type and p-type contact regions (the gap) providing high shunt resistance. We have shown that Al_2O_3 can passivate these intrinsic regions to a level of $J_0 = 14$ -29 fA/cm^2 depending on process conditions. Additionally, we have shown that the front, undoped surface of the n-type IBC cell, can be passivated with an $Al_2O_3/SiNx$ dielectric stack to a level of $J_0 = 5$ - 21 fA/cm^2 . The ability to well passivate the gap and front surface region of an IBC cell using Al_2O_3 is a great benefit for reducing costs for high efficiency devices in that all regions of the device can be passivated with a single anneal.

The addition of H to a structure to passivate dangling bonds always raises concerns about long-term stability. To this end we have subjected encapsulated (Tedlar/EVA/sample/EVA/glass) symmetric passivated contact structures to a standard 85°C/85% humidity damp-heat test for over 1000 hours. The encapsulate materials allow direct Sinton lifetime testing to be done without removing the sample. No observed degradation in the passivation quality was observed in this preliminary test, but much more verification is needed in the area of long-term stability for these contacts.

Figure 5 shows the iV_{oc} data for all samples studied after passivation as a function of implantation dose. The witness beam line implanted samples (open squares) show that traditional beam line implantation gives iV_{oc} values on par with *in-situ* grown samples for both n-type and p-type contacts. The n-type contacts give iV_{oc} values between 720 – 730 mV, while the p-type contacts give iV_{oc} values between 690 and 700 mV. The samples implanted by PIII with PH_3 plasma species (PH_x , H_2^+ , P_2H_y) gave remarkably high iV_{oc} values near 730 mV, bettering the beam line doped n-type contacts, but not quite as good as the *in situ* doped samples. We note that the implant doses are different between the beam line and the PIII techniques, but neither process shows much of a

dependence on dose for the range studied with the P doping. The results for the P doping of the 100 nm poly-Si passivated contact structure give state-of-the-art passivation, regardless of the implant technology. However, at 5 keV implant energies, the beam line implanter is nearing its lower limit for energies still able to give reasonably high dose levels, whereas the PIII technology has another order of magnitude energy range for high dose levels. This lower range may allow thinning of the a-Si layer without fear of damaging the c-Si wafer or the delicate SiO₂/c-Si interface by using PIII with much lower implant energies than are practically possible with beam line technologies.

For the p-type contacts implanted by the PIII technique, we implanted B species using either BF₃ or B₂H₆ process gases. These gases give plasma implant species of BF_x⁺, B⁺, and F⁺ for BF₃, and B₂H_x⁺, B⁺, BH_x⁺ for B₂H₆. [4] For the B₂H₆ implants, we find that the iVoc values are only slightly lower than those implanted with pure B using the beam line technique. iVoc ~ 700 mV is nearly state-of-the-art for PECVD grown c-Si/SiO₂/poly-Si contacts annealed below the oxide breakup temperature, so the PIII technique using B₂H₆ neither hampers nor improves upon this value. However, this is not the case for BF₃ process gas. Here Figure 4 shows that the p-type contacts formed with BF₃ plasmas give iVoc values between 680 – 660 mV as the implant dose increases. This process gas is the only one tested that showed a distinct correlation between iVoc and implant dose. Previous studies by Reichel *et al.* [6] using beam line implanted BF₂ into a-Si passivated contacts (TOPCon structures) showed that p-type contacts could reach iVoc values of 690 mV using similar dose levels. [6] Interestingly, their iVoc vs dose correlation is opposite to what Fig. 4 shows for the PIII implanted material. They reported an increasing iV_{oc} (from 660 to 690 mV) with increasing dose (from 0.5 - 5e15 cm⁻²). It is possible that due to the shallow implant depth typically seen for PIII, that the actual dopant carrier density in the pc-Si film does not match the implant dose as mentioned in the SIMS section above.. This can be especially true for samples that have been etched with an HF-based solution (such as an RCA clean) that removes dopant-containing oxide layers prior to crystallization anneals. Previous depth profile SIMS measurements on our samples (not shown) reveal that the B diffusion is apparently impeded by the presence of F compared with non-F implant samples, as also observed by Reichel *et al.* [6] and explained by Lopez *et al.* [19] It should be noted that others have found implantation of BF_x species to give good emitter properties for solar cells, [20] so our results should not be considered universal.

To better understand the influence of implanted dose on iVoc values we plotted the sheet resistance of the samples, as measured by the PCD method, in the lower part of Figure 5. This R_{sheet} value is a weighted average of carriers and mobilities for both the pc-Si layer and the near surface diffused region in the c-Si (see SIMS data). Comparing similar dopants we see that for P the R_{sheet} values overlap between the PIII and beam line implanted samples. Curiously, the higher beam line dose shows a higher R_{sheet}, with more scatter, than the lower P doses of the PIII samples. The beam line B samples give about the same R_{sheet} regardless of doping level, and share about the same magnitude with the B₂H₆ implanted samples. The BF₃ implanted samples show a slight trend in R_{sheet}, showing a lower R_{sheet} with increasing dose, as would be expected for increasing carrier density.

Figure 6 shows the J_o values for each sample tested. Consistent with the excellent iVoc values for the P doped samples, the J_o values are < 4 fA/cm² for both the beam line and PIII implanted samples. These low J_o values show the distinct advantage of implanting into the pc-Si/SiO₂/c-Si contact structure rather than into the wafer itself, where J_o values one order of magnitude higher are typically achieved. [4, 21] For the B implanted samples the J_o values are between 15 -35 fA/cm². The B₂H₆ implanted species show a decreasing J_o value for increasing dose, while the other samples do not show much of a trend with implant dose. All of these J_o values would be considered excellent for p-type PECVD passivated contacts, but still about a factor of 10 higher than is seen in oxide-breakup passivated contacts. [22, 23] Nevertheless, we conclude that PIII implantation is

capable of providing patterned doping to pc-Si passivated contacts equally as well as either in-situ grown, or beam line implanted samples.

Finally, Figure 7 shows bulk lifetime values extracted from PCD measurements for all post passivation samples. All of the samples, except those implanted with BF_3 , have bulk lifetimes greater than ~ 2 ms, with the B implanted samples showing remarkably higher bulk lifetimes. The high bulk lifetimes may be attributed to several process conditions: (1) The n-Cz wafers used for these experiments were purchased with specifications for bulk lifetimes greater than 1 ms. The processing steps did not alter already high bulk lifetimes. The implanted ion energies were not high enough to damage the bulk c-Si wafers (the SIMS profiles indicate this); or (2) the processing steps and thermal budget *improved* the bulk wafer lifetimes. All of the wafers underwent a thermal pretreatment known as Tabula Rasa (TR).[24, 25] This treatment is a high temperature anneal (>1000 °C, ~ 15 mins) that dissolves large oxygen precipitates that can getter metal impurities and form deep level recombination centers - reducing bulk lifetimes. The TR treatment possibly allows metal impurities to be gettered to the highly defective pc-Si layers - improving bulk lifetimes during processing. Ongoing experiments to determine the effectiveness of this TR treatment for pc-Si/ SiO_2 passivated contact processing as a function of growth conditions of the wafer will be presented in a different paper.[26]

Returning to the bulk lifetime values for the samples implanted with BF_3 we note that their lifetime values are much lower ($300 - 700$ μs) than the starting wafer lifetimes (>1 ms). This dramatic decrease in bulk lifetime with fluorine-containing implanted species has been seen by others when the implantation was done directly into the wafer.[4] However, this appears to be the first report of lower bulk lifetimes caused by F implantation for passivated contacts. F is well known to cause several different positive and negative phenomena associated with the passivation of pc-Si/ SiO_2 contacts including higher surface defect levels, reduced B diffusion and oxide thickening.[6] For our samples we observe not only a decrease in passivation quality (iVoc), but also a distinct drop in bulk lifetime that is not fully understood. Ongoing experiments will hopefully discover the cause and solution of this lifetime killing phenomena to allow the less toxic BF_3 gas to be used for passivated contacts.

Finally, we observe a common drop in lifetime with decreasing injection level in most of our samples in this study, as indicated in Figure 1a. This behavior is currently under investigation, but is beyond the scope of this paper.

5.3 Contact Resistivity

Contact resistivity measurements, ρ_c , were made on samples using e-beam deposited Al and evaporated Ag TLM contact pads following a 400 °C forming gas anneal. The metal depositions were made through a photolithographic polymer mask followed by a liftoff technique. A dilute HF etch was performed prior to metallization until the surfaces went hydrophobic indicating complete removal of a surface oxide layer. In addition, quantitative PL measurements were made on metal and non-metallized areas to assess deposition damage from each technique that might affect passivation. Preliminary results show that low resistivity ohmic contacts can be made to the B-doped pc-Si material, regardless of implant technique, using Al (< 2 $\text{m}\Omega\text{-cm}^2$) and Ag (< 40 $\text{m}\Omega\text{-cm}^2$). However, non-ohmic, or very high resistivity contacts are made to P-doped pc-Si material independent of implant technique, or metal deposition. The latter result is counter to our previous experience with beam line P implanted samples[5] where ohmic contacts were made to passivated contacts using an e-beam deposited Ti/Pd/Ag metal stack. This anomaly is currently under investigation, but again may be tied to a lower dopant concentration at the surface of the P-doped samples (See SIMS measurements) and/or due to dopant-containing oxide removal prior to the crystallization anneal, as discussed earlier. The SIMS data show that the smaller B atoms penetrate deeper into the surface

than the larger P ions and thus may not be affected by the oxide removal. If this is the reason for the poor contact resistivity to the P-doped contacts, then both the PIII and beam line implant dose levels and/or implant energies need to be increased. The fact that both PIII and beam line P-doped samples were not able to be contacted decreases the chance that a chemical reaction at the surface of the samples, brought on the reactive PIII plasma environment, is to blame.

The Al e-beam deposition caused a significant decrease in the iV_{oc} , as observed by PL, for all samples tested. This decrease was partially restored after the FGA anneal, but never back to the pre-metallization state. This degradation has been observed by other groups and was shown to be caused by surface damage, and pc-Si/SiO₂ interface damage.[27, 28] The e-beam damage can be annealed out, but only at temperatures that might cause the Al to spike through the pc-Si/SiO₂ interface.[27, 28] Our 400 °C post-metallization anneal may be too high for Al-based contacts to our PECVD-grown pc-Si/SiO₂ contacts.

The evaporated Ag deposition did not produce the large iV_{oc} drop in the B-implanted samples presumably due to the more gentle evaporation technique compared with e-beam deposition. Curiously, we observe no drop in iV_{oc} after Ag evaporation for samples that were shadow masked instead of masked by photolithography. We are investigating the effect of the photolithographic chemicals on our pc-Si/SiO₂ contacts that might cause this passivation degradation.

One of the great potential selling points of pc-Si/SiO₂ passivated contacts for IBC cells is their ability to not be area constrained for metallization. In other words, their passivation quality does not decline with metallization area coverage. This appears to be the case for evaporated Ag,[29] and possibly Al on thicker LPCVD grown pc-Si layers,[10] but other techniques and metals appear to degrade the contacts. This is an area needing further attention.

6. Summary

This work shows that pc-Si/SiO₂ passivated contacts can be doped with B (B₂H₆ plasma gas) and P (PH₃ plasma gas) using the plasma immersion ion implantation (PIII) technique. The potential etching and/or deposition environment enabled by the sample being immersed in the plasma during implantation does not seem to affect the final passivation quality of the pc-Si contacts. Symmetric contact structures formed by PIII exhibited equal or better passivation than beam line implanted samples giving B-doped iV_{oc} values of ~690 mV and P-doped values of ~730 mV. J_0 values are < 4 fA/cm² for P-doped samples and between 15 – 35 fA/cm² for B-doped samples. Bulk lifetimes greater than ~ 2 ms were preserved or enhanced during the contact formation process that may be linked to a pre-process anneal of the wafer known as Tabula Rasa. However, for BF₃ doped passivated contact samples, degradation of bulk lifetimes to between 300 and 700 μs were observed, consistent with literature, but not yet explained. Finally, metallization of the passivated contacts produced acceptable resistivity values for all B-doped samples, but not for P-doped samples. E-beam passivation damage was also observed for both B-and P-doped samples, but evaporated Ag did not produce passivation damage.

Acknowledgements: This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308 with the National Renewable Energy Laboratory.

References:

- [1] DOE. "SunShot Initiative's Mission". 2015; Available from: <http://energy.gov/eere/sunshot/mission>.
- [2] Jones-Albertus, R., D. Feldman, R. Fu, K. Horowitz, and M. Woodhouse, "Technology Advances Needed for Photovoltaics to Achieve Widespread Grid Price Parity". *Progress in Photovoltaics: Research and Applications*, **24**(6) 2016.
- [3] Bhosle, V., T. Miller, J. Graff, and N. Bateman, Annealing temperature reduction for non-mass analyzed boron Implantation, in *31st European Photovoltaic Solar Energy Conference and Exhibition*. 2015: Hamburg, Germany. p. 425-428.
- [4] Lanterne, A., J.L. Perchec, M. Coig, F. Milesi, J. Boucher, and Y. Veschetti, "Solar-grade boron emitters by BF₃ plasma doping and role of the co-implanted fluorine". *Progress in Photovoltaics: Research and Applications*, 2015.
- [5] Young, D.L., W. Nemeth, V. LaSalvia, R. Reedy, S. Essig, N. Bateman, and P. Stradins, "Interdigitated Back Passivated Contact (IBPC) Solar Cells formed by Ion Implantation ". *Journal of Photovoltaics*, **6**(1) p. 41, 2016.
- [6] Reichel, C., F. Feldmann, R. Müller, R.C. Reedy, B.G. Lee, D.L. Young, P. Stradins, M. Hermle, and S.W. Glunz, "Tunnel oxide passivated contacts formed by ion implantation for applications in silicon solar cells". *Journal of Applied Physics*, **118** 2015.
- [7] Muller, R., C. Reichel, J. Benick, and M. Hermle, "Ion implantation for all-alumina IBC solar cells with floating emitter". *Energy Procedia*, **55** p. 265, 2014.
- [8] Romer, U., R. Peibst, T. Ohrdes, B. Lim, J. Krugener, T. Wietler, and R. Brendel, "Ion implantation for Poly-Si Passivated Back-Junction Back-contacted solar cells". *IEEE Journal of Photovoltaics*, **5**(2) p. 507, 2015.
- [9] Yang, G., A. Ingenito, N.v. Hameren, O. Isabella, and M. Zeman, "Design and application of ion-implanted polySi passivating contacts for interdigitated back contact c-Si solar cells". *Applied Physics Letters*, **108** p. 033903, 2016.
- [10] Rienacker, M., A. Merkle, U. Romer, H. Kohlenberg, J. Krugener, R. Brendel, and R. Peibst, Recombination Behavior of photolithographic-free back junction back contact solar cells with carrier-selective polysilicon junctions for both polarities, in *SiliconPV 2016*. 2016: Chambery, France.
- [11] Chang, R., C. Lin, and L. Ho, "Diffusion of boron near projected ranges of B and BF₂ ions implanted in silicon". *Japanese Journal of Applied Physics*, **47** 2008.
- [12] Chu, P.K., "Semiconductor applications of plasma immersion ion implantation". *Plasma Phys. Control. Fusion*, **45** p. 555, 2003.
- [13] Felch, S.B., M.I. Current, and M.C. Taylor. "Ion implantation for semiconductor devices: The largest use of industrial accelerators". in *PAC 2013*. Pasadena, CA, 2013, p. 740.
- [14] Materials, A., Solion® XP Ion Implanter For Cost-Effective Advanced PV Cell Manufacturing press briefing. 2013, Applied Materials: <http://www.appliedmaterials.com/products/applied-solion-xp-ion-implanter>. p. 10.

- [15] Gupta, D., "Plasma Immersion Ion Implantation (PIII) Process-Physics and Technology". International Journal of Advancements in Technology, **2**(4) p. 471-490, 2011.
- [16] Nemeth, W., D.L. Young, M.R. Page, V. LaSalvia, S. Johnston, R. Reedy, and P. Stradins, "Polycrystalline Silicon Passivated Tunneling Contacts For High Efficiency Silicon Solar Cells". Journal of Materials Research, **31**(6) p. 671, 2016.
- [17] Kane, D.E. and R.M. Swanson, Measurement of the emitter saturation current by a contactless photoconductivity decay method, in *IEEE PVSC*. 1985. p. 578.
- [18] Feldmann, F., R. Muller, C. Reichel, and M. Hermle, "Ion implantation into amorphous Si layers to form carrier-selective contacts for Si solar cells". Phys. Status Solidi RRL, **8**(9) p. 767, 2014.
- [19] Lopez, G.M., V. Fiorentini, G. Impellizzeri, S. Mirabella, and E. Napolitani, Phys. Rev., **72**(1) p. 045219, 2005.
- [20] Krugener, J., R. Peibst, E. Bugiel, D. Tetzlaff, F. Kiefer, M. Jestremski, R. Brendel, and H.J. Osten, "Ion implantation of boric molecules for silicon solar cells". Solar Energy Materials & Solar Cells, **142** p. 12, 2015.
- [21] Bateman, N., P. Sullivan, C. Reichelb, J. Benick, and M. Hermle, "High quality ion implanted boron emitters in an interdigitated back contact solar cell with 20% efficiency". Energy Procedia, **8** p. 509, 2011.
- [22] Peibst, R., U. Romer, Y. Larionova, H. Schulte-Huxel, T. Ohrdes, M. Haberle, B. Lim, J. Krugener, K. Stichtenoth, T. Wutherich, C. Schollhorn, J. Graft, and R. Brendel. "Building blocks for back-junction back-contacted cells and modules with ion-implanted poly-Si junctions". in *40th IEEE PVSC*. Denver, 2014, p.
- [23] Romer, U., R. Peibst, T. Ohrdes, B. Lim, J. Krugener, T. Wietler, and R. Brendel, "Ion Implantation for Poly-Si Passivated Back-Junction Back-Contacted Solar Cells". IEEE Journal of Photovoltaics, **5**(2) p. 507, 2015.
- [24] Kelton, K.F., R. Falster, D. Gambaro, M. Olmo, M. Cornara, and P.F. Wei, "Oxygen precipitation in silicon: Experimental studies and theoretical investigations within the classical theory of nucleation". Journal of Applied Physics, **85** p. 8097, 1999.
- [25] Falster, R., M. Cornara, D. Gambaro, M. Olmo, and M. Pagani, "Effect of high temperature pre-anneal of oxygen precipitates nucleation kinetics in Si". Solid State Phenomena, **57-58** p. 123, 1997.
- [26] LaSalvia, V., M.A. Jensen, A. Youssef, W. Nemeth, M. Page, T. Buonassisi, and P. Stradins, Utilization of Tabula Rasa to Stabilize Bulk Lifetimes in n-Cz Silicon for High-Performance Solar Cell Processing, in *IEEE PVSC*. 2016, IEEE: Portland, OR.
- [27] Kopp, J., W. Warta, A. Aberle, S. Glunz, and J. Knobloch. "Impact of metallization techniques on 20% efficient silicon solar cells". in *IEEE PVSC 1991*, 1991, p.
- [28] Blakers, A.W., M.A. Green, and T. Szpitalak, "surface damage caused by electron-beam metallization of high open-circuit voltage solar cells". IEEE Electron Device Letters, **EDL-5**(7) p. 246, 1984.
- [29] Feldmann, F., M. Bivour, C. Reichel, M. Hermle, and S.W. Glunz, "Passivated rear contacts for high-efficiency n-type Si solar cells providing high interface passivation quality and excellent transport characteristics". Solar Energy Materials and Solar Cells, **120** p. 270, 2014.

Figure captions for SolMat paper:

Figure 1. a) Photoconductance lifetime as a function of minority carrier density (MCD) data. The arrow shows where a slope = 1 in the data (arrow). b) Auger corrected, one over lifetime data as a function of MCD. The arrow shows the MCD (from Fig. 1a) where the data should be analyzed to fit the Kane and Swanson theory.

Figure 2. a) High resolution bright and dark field STEM images of the passivated contact structure ion implanted with P. b) High resolution STEM and EELS data from the same sample as in 2A). c) High resolution STEM and EELS data from a passivated contact structure ion implanted with B.

Figure 3. a) SIMS depth profiles for as-implanted samples showing H, P, and B profiles. The ion plasma source gas, dose (cm^{-2}) and accelerating voltage are given in the legend. B) SIMS depth profiles for post crystallization and passivation anneal samples implanted with B, P and H. The Al_2O_3 dielectric layer on the surface of the implanted pc-Si film was not removed before the measurements were taken. C) SIMS depth profiles for an as-implanted, post crystallization and passivation annealed sample implanted with B, and H. The red data are for a sample that was cleaned prior to annealing without HF. The blue data are for the same sample that was cleaned prior to annealing with HF.

Figure 4. Implied Voc (iVoc) data for all samples studied post implantation (blue squares), post crystallization anneal (red triangles), and post Al_2O_3 deposition and activation anneal (green circles).

Figure 5. Implied Voc (iVoc) versus implantation dose for all samples implanted by beam line and PIII techniques. Arrows on the right show typical iVoc values for in-situ grown passivated contact samples. The bottom graph shows R_{sheet} values calculated from the PCD data.

Figure 6. Recombination parameter, J_0 , as a function of implant dose for all samples implanted by beam line and PIII techniques.

Figure 7. Bulk lifetimes as a function of implant dose for all samples implanted by beam line and PIII techniques.

Fig 1

Fig 3

Fig 4

Fig. 5

Fig. 6

Fig. 7