



# Passivated Tunneling Contacts to N-Type Wafer Silicon and Their Implementation into High Performance Solar Cells

## Preprint

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# PASSIVATED TUNNELING CONTACTS TO N-TYPE WAFER SILICON AND THEIR IMPLEMENTATION INTO HIGH PERFORMANCE SOLAR CELLS

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## ABSTRACT

We present a case that passivated contacts based on a thin tunneling oxide layer, combined with a transport layer with properly selected workfunction and band offsets, can lead to high efficiency c-Si solar cells. Passivated contacts contribute to cell efficiency as well as design flexibility, process robustness, and a simplified process flow. Material choices for the transport layer are examined, including transparent n-type oxides and n<sup>+</sup>-doped poly-Si. SiO<sub>2</sub>/n<sup>+</sup>-poly-Si full-area, induced-junction back surface field contacts to n-FZ and n-Cz Si are incorporated into high efficiency cells with deep, passivated boron emitters.

## 1. INTRODUCTION

Minimizing carrier recombination at cell contacts becomes increasingly important for reaching high and ultrahigh cell efficiencies, as bulk and surface passivation quality enables photocarrier lifetimes well above 1 ms. When directly in contact with Si wafer, metals introduce very large densities of electronic states near the interface energetically within the bandgap of Si resulting in >50% recombination losses in high efficiency cells [1]. The contact recombination can be minimized either by 1) small contact areas and local doping (PERL structure) or by 2) a thin-film structure that simultaneously separates metal from Si wafer, passivates the Si wafer interface, and still serves as a conductive contact to the cell. This second approach to “passivated contacts” eliminates (i) the need for diffusion or implantation doping of the wafer and (ii) complicated patterning of selective emitter/BSF. It also simplifies the cell’s process flow and leads to very low recombination at the contact.

While a-Si:H based heterojunction passivated contacts have demonstrated spectacular performance in Panasonic’s current record 25.6% HIT® IBC cell, the passivated contact approach can be extended beyond a-Si:H to other thin-film contact structures, most notably, a stack of tunneling SiO<sub>2</sub> oxide layer and a heavily doped poly-Si (pc-Si) layer [2]. The latter structure is less sensitive to details of surface preparation, can tolerate a higher thermal budget, and has a lower contact

resistance than the a-Si:H bilayer/TCO heterojunction contact stack. In this work, we demonstrate the excellent potential for a full-area passivated BSF contact to n-type Si cells.

## 2. PASSIVATED CONTACTS

As an alternative to <1% metal contact area and the associated complicated dopant patterning, the full-area passivated contacts discussed here combine excellent chemical passivation of dielectric surfaces using the Si/SiO<sub>2</sub> interface with field effect passivation induced by a material with the appropriate work function on the other side of the dielectric layer. As demonstrated below, this combination enables a lower surface recombination current prefactor ( $J_0$ ) than is typically seen for standard thick dielectric stacks (e.g. SiO<sub>2</sub> + SiN<sub>x</sub>) on doped Si surfaces. Moreover, the passivated contact structure also serves a current-carrying contact: the dielectric layer is thin to allow carrier collection into the “transport” layer and from there into the metal contact.

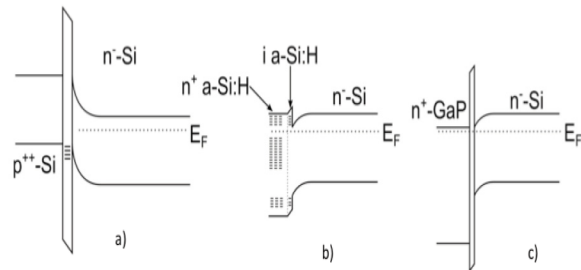


Fig. 1. Band diagram schematics of full-area passivated contacts forming induced junctions to Si: a) p-n junction formed by p<sup>++</sup> poly-Si to n-Si wafer, separated by a thin SiO<sub>2</sub> tunneling/buffer layer; b) n<sup>+</sup> a-Si:H/i-a-Si:H heterojunction to n-Si wafer; c) passivated, electron-selective contact to n-Si wafer, formed by a semiconductor (such as GaP) with large valence band offset to Si for hole rejection, separated from the Si by a wide gap tunneling buffer layer.

Three types of the contacts are shown in Fig.1: (a) poly-Si/c-Si homojunction with poly-Si as a transport layer, and two heterojunctions, with transport layers of doped

a-Si:H (b), and (c) a wide-band-gap semiconductor with a large valence band (VB) offset with Si. In all three cases, an important feature is a thin buffer/tunneling layer between the highly doped, defective transport layer and high lifetime Si wafer. Importantly, direct metal contact to Si with strong recombination due to interface states within Si gap is avoided, because the metal (not shown in Fig.1) only contacts the highly doped, defective transport layer, which is separated from the Si wafer by the buffer (tunneling) layer. In some cases, there is another interlayer such as a TCO in a-Si:H heterojunction cell. Secondly, these passivated contacts don't require dopant diffusions and thus minimize surface and Auger recombination. Finally, no complicated contact patterning is involved.

Figure 2 shows band edge positions for a group of potential passivated contact materials. Some of them have very wide gap (e.g.  $\text{SiO}_2$ ) and are suitable for buffer layers, due to their excellent interface passivation to Si.

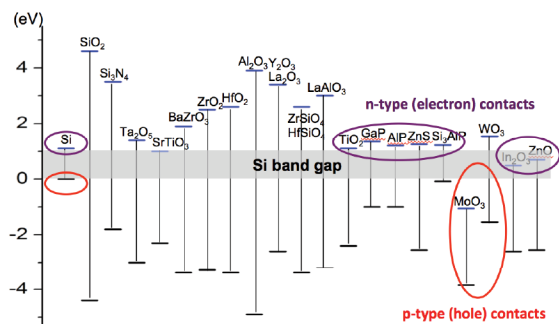


Fig. 2. Dielectric and semiconductor materials as candidates for passivated contacts to Si. Their valence band maxima (VBM) and conduction band minima (CBM) energies are shown with respect to Si VBM. Data are compiled from J. Robertson, Eur. Phys. J. Appl. Phys. 28, 265-291 (2004) and simulations at NREL.

Several candidates for transport layer in n-type BSF contact to n-Si wafer can be identified from Fig. 2 (purple circles). They have energy gaps close to or wider than Si and CBM and workfunctions near the CBM of Si. P-type contact choice (red circles) is more difficult, as most metal oxides have energetically very deep valence band maxima (VBM) and cannot be p-type. Here, the choices are either n-type TCOs with very high WF ( $\text{MoO}_3$ ), or p-type TCOs with gap enclosing that of Si ( $\text{WO}_3$ ). TCOs have advantages for front contacts to the cell, and impressive  $V_{oc}$  was demonstrated with  $\text{MO}_x/\text{a-Si:H}$  contact structure to n-Si [3], despite high layer resistance. Nevertheless, the best transport layer candidate so far is n+ and p+ polycrystalline Si. Their carrier selectivity is primarily based on the induced field effect by doping of poly-Si. Slight differences in

apparent tunneling barrier height of  $\text{SiO}_2$  for electrons and holes, as well as nearly equal e- and h+ effective masses in  $\text{SiO}_2$  unlikely account for observed carrier selectivity. Excellent passivation properties were observed in an early Stanford group's work on SIPOS contact on Si, reaching cell's  $V_{oc}$  of 720 mV [4]. The exact mechanisms of carrier transport in poly-Si/ $\text{SiO}_2$ /Si homojunction contacts are not fully clear, possibilities ranging from trap-assisted tunneling to nano-pinhole transport through the  $\text{SiO}_2$  layer. Most likely reason for high poly-Si/ $\text{SiO}_2$ /Si contact quality is the excellent chemical passivation that  $\text{SiO}_2$  layer provides to interfaces with Si wafer and poly-Si, due to amorphous nature of  $\text{SiO}_2$ , bridging O bonds to Si atoms, and efficient passivation of interface Si dangling bonds by  $\text{H}_2$  forming gas anneal (FGA). Here, we concentrate on poly-Si/ $\text{SiO}_2$ /Si contacts for highest cell efficiencies, but also explore TCO layers for transparent front contacts.

### 3. EXPERIMENTAL DETAILS

Passivated contacts were fabricated on both n-FZ and n-CZ wafers with resistivity of  $\sim 2\text{--}7\ \Omega\text{-cm}$  on either symmetric test structures, or on the  $2\times 2\text{ cm}^2$  solar cells with deep-driven in, B-emitter passivated by  $\text{Al}_2\text{O}_3/\text{SiN}_x$  layer stack. The experimental details on cell process at FhISE can be found elsewhere [1,2]. At NREL, a diffused boron emitter is formed in the furnace in 3 steps: 1) deposition of a  $\text{B}_2\text{O}_3$  layer at  $850^\circ\text{C}$ ; b) Diffusion of B from the  $\text{B}_2\text{O}_3$  layer at  $950^\circ\text{C}$ ; and c) additional high temperature oxidation at  $980^\circ\text{C}$  for 4.5 h to deep-drive in boron for a  $>1$  micron deep doping profile with a B-emitter sheet resistance  $\sim 110\ \Omega/\text{sq}$  and surface [B] of  $\sim 10^{19}\text{cm}^{-3}$ . A concentrated KOH etch defines the mesa-isolated cells on the front and simultaneously planarizes the backside. The mesas get passivated along with the front emitter. Next, a  $\sim 1.5$  nm thick tunneling  $\text{SiO}_2$  is grown either thermally at  $700^\circ\text{C}$  or chemically in  $\text{HNO}_3$ . Then a few 10 nm thick n+ a-Si:H layer is deposited onto the tunneling back-oxide by PECVD. A subsequent anneal at  $\sim 850^\circ\text{C}$  crystallizes a-Si:H into n+ poly-Si. FGA at  $450^\circ\text{C}$  or other hydrogenation further improves the contact passivation. The back poly-Si contact is metallized over its whole area. The TCO transport layers are sputter-deposited. The passivated contact properties are measured on symmetric test structures with Sinton lifetime for  $iV_{oc}$  and  $J_0$ , and with mesa-etched Transmission Line Method (TLM) for contact resistivity  $\rho_c$ .

### 4. RESULTS AND DISCUSSION

Tuning the tunneling  $\text{SiO}_2$  layer properties by fabrication and subsequent treatments strongly affect contact performance. In early NREL experiments, these  $\text{SiO}_2$  layers were prepared by thermal oxidation to 70 nm, then chemically thinning the  $\text{SiO}_2$ . As expected, the  $iV_{oc}$  of test structures drop from  $\sim 700$  mV to below 600

mV as the oxide is thinned to 1 nm [7]. This is likely due to oxide surface contamination, causing tunneling recombination as the oxide is thinned to our target thickness range of 1 – 2 nm. The  $iV_{oc}$  improves dramatically by the deposition of doped a-Si:H, providing field effect and likely passivating defects on the SiO<sub>2</sub> surface (Fig. 3, diamond). Thermal treatment is needed to crystallize the a-Si:H into poly-Si and improve the oxide interfaces. Experimentally, annealing at 850°C results in the best contact passivation. Crystallization of poly-Si happens in just a few seconds at 850°C, so the observed improvement after 30 min of annealing shown in Fig. 3 is likely due to oxide/Si interface restructuring subsequent FGA.

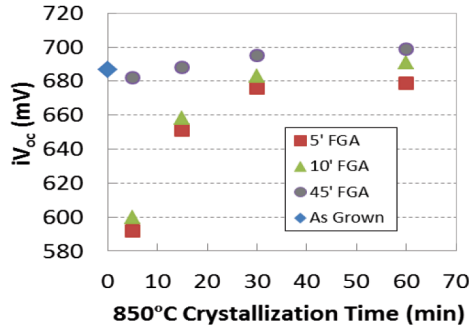


Fig. 3. Implied  $V_{oc}$  as function of annealing time at 850°C of poly-Si/SiO<sub>2</sub> passivated contact on n-CZ wafer, followed by FGA at 450 °C for times indicated (squares, circles, triangles)[5].

Implied  $V_{oc}$  well above 700 mV,  $J_0$  below 10 fA/cm<sup>2</sup>, and contact resistivities  $\sim 20$  m $\Omega$ -cm<sup>2</sup> were achieved with our optimized passivated contact processes. Annealing at 850°C compensates for large differences in initial oxide quality and preparation conditions (excluding contaminants). We observe similar contact passivation and charge transport quality in oxides created thermally at 700°C in furnaces and chemically in HNO<sub>3</sub>. It is important to avoid surface contamination that could degrade the contact and the bulk at 850°C. With proper contamination control, chemical oxides produced at as low as  $\sim 20^\circ\text{C}$  still provide excellent passivated contacts (see Fig. 4).

Notably, this BSF passivated contact outperforms NREL's best *dielectric* surface passivation ( $J_0 = 17$  fA/cm<sup>2</sup>) of the diffused BSF by an oxide/nitride stack, while also serving as a contact. This emphasizes the importance of an engineered combination of chemical and field effect passivation using a multilayer structure. Implementation of these full-area, induced BSF junction passivated contacts into the front passivated B-emitter solar cells obviates doped BSF formation, contact patterning, and should give lower  $J_0$  and higher  $V_{oc}$  of the cell.

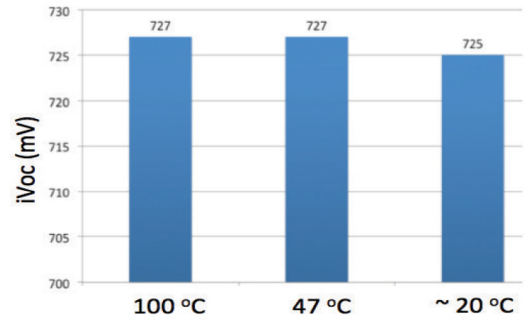
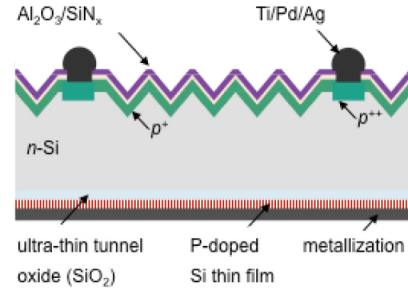


Fig. 4. Implied  $V_{oc}$  of symmetric n+ poly-Si/SiO<sub>2</sub> contact test structure with a chemical oxide layer produced by HNO<sub>3</sub> at different bath temperatures (GIT).

This is confirmed by the high cell efficiency on n-type FZ of 24.4% from FhISE [2]. In that cell, the selective emitter structure is used in addition to low  $\sim 150$   $\Omega$ /sq uniform, deep B emitter, to further suppress front recombination and thus take full advantage of the BSF passivated contact with  $J_{0, \text{back}} = 7$  fA/cm<sup>2</sup>. FhISE's passivated B-emitter surface recombination  $J_{0, \text{surf}}$  is 11 fA/cm<sup>2</sup>. Excess p+ doping under the front grid reduces the front metal  $J_0$  from 1000 fA/cm<sup>2</sup> to 200 fA/cm<sup>2</sup>, thus increasing the cell's  $V_{oc}$  by 12 mV to 715 mV (Fig. 5).



| FhISE cell [2]               | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF (%) | $\eta$ (%) |
|------------------------------|---------------|--------------------------------|--------|------------|
| TOPCon w/o selective doping  | 703           | 41.4                           | 82.5   | 24.0       |
| TOPCon with selective doping | 715           | 41.5                           | 82.1   | 24.4       |

Fig. 5. FhISE passivated contact cells [2].

At NREL, we have fabricated a 21.48% cell with the structure similar to Fig. 5. The cell uses the n-FZ diffused uniform emitter from FhISE. The back metallization of the poly-Si/SiO<sub>2</sub> is challenging due to the interface damage by e-beam deposition. We mitigated this by increasing the thickness of the poly-Si

Table 1. Passivated contact BSF cell by NREL.

| $iV_{oc}$ (mV) | Total $J_0$ (fA/cm <sup>2</sup> ) | $V_{oc}$ (mV) | $J_{sc}$ (mA/cm <sup>2</sup> ) | FF (%) | $\eta$ (%) |
|----------------|-----------------------------------|---------------|--------------------------------|--------|------------|
| 698            | 55                                | 693           | 39.55                          | 78.37  | 21.48      |

layer to 40 nm, introducing an a-Si:H interlayer between metal and poly-Si, and using non-damaging metallization techniques such as thermal evaporation [5].

For industrial applications, replacing dopant diffusions with clean oxidation and thin-film deposition steps not only simplifies the cell process flow, but also allows for easy dopant patterning on intrinsic poly-Si by dopant deposition or ion-implantation, followed by dopant drive-in. Since poly-Si is already defective and separated from the Si wafer by the tunneling SiO<sub>2</sub>, it is more tolerant to defects and high doping. However, because of the high (1kΩ/sq) sheet resistance of the contact, implementation on the front requires a TCO layer as a transport layer or instead of poly-Si. Passivated contacts perform best in an IBC configuration, as demonstrated by the current  $\geq 25\%$  record cells from SunPower, Sharp, and Panasonic. ISFH team has achieved excellent results on ion-implanted, both p- and n-type poly-Si/SiO<sub>2</sub> contacts designed for IBC cell, with 10 fA/cm<sup>2</sup> for p-type and 1.3 fA/cm<sup>2</sup> for n-type contacts [6]. This IBC structure with n- and p-type poly Si back contacts could avoid bulk lifetime degradation in n-Cz during high quality emitter formation, if the contact annealing steps were short. However, good poly-Si/SiO<sub>2</sub> passivated p-type contacts are difficult to achieve, partly due to B segregation.

At NREL,  $\sim 120 \Omega/\text{sq}$ ,  $1 \times 10^{19} \text{ cm}^{-2}$  deep B emitter formation was tuned to minimize bulk lifetime degradation in n-Cz Si. Poly-Si/SiO<sub>2</sub> BSF cell results for the device structure in Fig. 5, but on an n-Cz Si wafer, are summarized in Table 2.

Table 2. NREL poly-Si/SiO<sub>2</sub> BSF cell on n-CZ Si wafer.

| IVoc (mV) | $\tau_{\text{bulk}}$ (μs) | J <sub>0,total</sub> (fA/cm <sup>2</sup> ) | Suns-V <sub>oc</sub> (mV) | Pseudo FF(%) | Pseudo η (%) | V <sub>oc</sub> (mV) | J <sub>sc</sub> (mA/cm <sup>2</sup> ) | FF (%) | η (%) |
|-----------|---------------------------|--------------------------------------------|---------------------------|--------------|--------------|----------------------|---------------------------------------|--------|-------|
| 717       | 3731                      | 17.1                                       | 689                       | 81.8         | 21.4         | 676                  | 38                                    | 79     | 20.3  |

These results, especially 717 mV and 17 fA/cm<sup>2</sup> before metallization, suggest high industrial potential for passivated B-emitter, full-area poly-Si/SiO<sub>2</sub> BSF cells on n-Cz Si. The higher bulk lifetime ( $>3 \text{ ms}$ ) in the cell than that of a symmetric B-emitter (typically  $\sim 1.5 \text{ ms}$ ) suggests impurity gettering by n+poly-Si/SiO<sub>2</sub> layers.

As alternatives to poly-Si transport layers for the front of the cell, we have explored doped n-type ZnO, ITO, and SnO<sub>2</sub> on the tunneling SiO<sub>2</sub> layer. The best J<sub>0</sub> = 55 fA/cm<sup>2</sup> was obtained after FGA on the ITO [7]. Generally, our TCO contacts have lower  $\rho_c$  but higher J<sub>0</sub> than poly-Si/SiO<sub>2</sub>. Their CBM being below CBM of Si and therefore having states inside the Si gap (Fig. 2) might contribute to this effect. Surprisingly, the ITO-based contact had low  $\rho_c = 11.5 \text{ m}\Omega\text{-cm}^2$  despite being paired with  $\sim 5 \text{ nm}$  thick SiO<sub>2</sub> that would block tunneling [7]. Possibly, In or Sn diffuses into the tunneling SiO<sub>2</sub>, as suggested by the TEM micrographs (Fig. 6). The ITO/SiO<sub>2</sub> structures show relatively uniform,  $\sim 5 \text{ nm}$  thick SiO<sub>2</sub> layer after FGA. After few minutes exposure to the TEM electron beam one can see changes in the SiO<sub>2</sub> layer from the ITO side, likely due

to In or Sn diffusion at elevated temperatures. Possibly, this diffusion already starts during FGA.

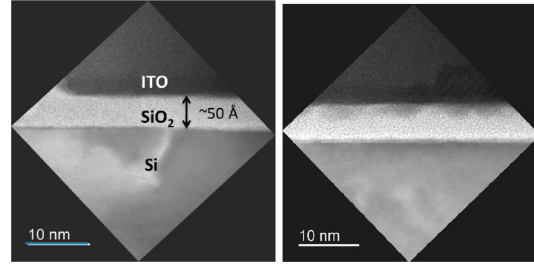


Fig. 6. ITO/SiO<sub>2</sub> contact structures. Left: after FGA. Right: after exposure to the TEM electron beam.

## CONCLUSIONS

Passivated contacts eliminate 1) the need for dopant diffusions into the high quality Si wafer; 2) complicated contact patterning, selective emitter and local doping for reduced contact area; 3) direct Si/metal contact as major cause of recombination losses in the cell. The resulting combination of field effect and chemical passivation with excellent current transport makes these contacts attractive for high efficiency, low cost Si PV.

## ACKNOWLEDGEMENTS

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