Critical Interface: Poly-Silicon to Tunneling SiO₂ for Passivated Contact Performance

Preprint

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Critical Interface: Poly-Silicon to Tunneling SiO₂ for Passivated Contact Performance

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Abstract. Environmental exposure of our thin tunneling SiO₂ layer on nCz wafer samples prior to poly-Silicon (poly-Si) deposition critically impacts the resulting contact passivation. We present ToF-SIMS evidence of SiO₂ oxide storage-induced degradation, presumably by surface contaminants such as carbon, in symmetric and device poly-Si/SiO₂ lifetime samples as well as in finished cells. We also present methods to resurrect a contaminated SiO₂ layer, including UV-O₃ treatment prior to passivated contact formation to produce >21% TCO-free solar cells.

MOTIVATION AND BACKGROUND

Passivated contact-based silicon (Si) solar cells have shown the highest efficiency potential and are being intensively researched as the most likely next generation Si photovoltaic candidates beyond p-PERC. This approach is based on a thin passivating buffer layer between the silicon wafer and a carrier-selective conductive top layer. This thin insulator can either be amorphous silicon (a-Si:H¹) or SiO₂², and it serves as a leaky dielectric layer that passivates dangling bonds on the wafer surface while still allowing carrier conduction.

The dielectric SiO₂ buffer layer is highly sensitive to post-formation processing leading to structural and compositional changes, while incorporation of impurities changes the nature of the interface. For example, carbon incorporated into SiO₂ may prevent blistering³, the addition of nitrogen hinders B diffusion into SiO₂, while fluorine⁴ promotes B diffusion into SiO₂ and helps to preserve passivation. Ozone applied to the SiO₂ layer can change its stoichiometry, reduces interface states⁵, and removes impurities⁶. On the other hand, environmental contaminants attached to the SiO₂ surface might cause passivation loss. With a deeper understanding of the nature of surface contaminants, specific treatment regimens can be engineered to mitigate their negative effect. This would enable a wider processing window after SiO₂ formation prior to poly-Si deposition and result in: (1) more flexibility in environmental exposure, allowing collaborators to exchange samples with a methodology to maintain SiO₂ passivation and transport properties when incorporated into passivated contacts; and (2) manufacturers a way to mass-produce the SiO₂ based passivated contact cells with less stringent cleanliness or timing considerations.

EXPERIMENTAL PROCEDURE

A schematic of our all poly-Si passivated contact cell is shown in figure 1. The wafer is cleaned in SC-1 and SC-2 solutions, then subjected to a 700°C anneal in a tube furnace with a flowing N₂/O₂ mixture to grow the SiO₂ layer. Samples are then stored in polypropylene containers for one week in a mailing package in a car to simulate a transportation environment, while separate samples are stored in a N₂ box. This is followed by one of the following treatments: 1) SC-1 and SC-2 cleans without HF dips in an attempt to preserve SiO₂; 2) UV-O₃ exposure; (3) a deionized water rinse. Then, doped layers are deposited on the SiO₂ via 13.56 MHz RF plasma enhanced chemical vapor deposition as a-Si:H using SiH₄ and H₂ with PH₃ (for n-type) and B₂H₆ (for p-type) gases at 1 Torr. The resulting
device structures are then annealed in a tube furnace at 850°C to crystallize the a-Si:H into poly-Si. Next, atomic layer deposition (ALD) is used to deposit a sacrificial Al₂O₃ coating, which is annealed at 400°C to hydrogenate the structure. Al₂O₃ is then removed with dilute HF prior to evaporation of aluminum contacts and antireflective SiNx deposition. The process sequence can be seen in figure 2 below. The minority carrier lifetimes are measured using a Sinton WCT-120 lifetime tester. Witness samples on polished wafers are characterized with nanometer resolved ToF-SIMS using 30 keV Bi primary and 1 keV Cs sputtering ions. J-V measurements are taken under 1-sun conditions on an inhouse tester using an official NREL Si reference cell for calibration on a temperature-controlled stage.

FIGURE 1. Schematic of rear emitter all poly-Si passivated contact cell.

FIGURE 2. Process sequence for formation and treatment of passivated contact samples.

RESULTS AND DISCUSSION

As we developed our baseline poly-Si/SiO₂ cell process, we found substantial variations in lifetime and J-V characteristics, which were traced to the storage time between SiO₂ growth and subsequent a-Si:H deposition. This can be seen in figure 3 by the implied Voc (iVoc) extracted from lifetime measurements of several premetallized cells as a function of storage time in an N₂ environment. We find that the shorter duration of time to which the SiO₂ layer is exposed to a controlled N₂ environment prior to n/a-Si:H deposition results in better iVoc values. Environmental contamination from metallic and/or organic sources as well as thickness changes to the SiO₂ layer may explain the differences. Likewise, symmetric p/poly-Si structures on planarized surfaces show similarly reduced lifetimes with longer exposure times for samples stored in an N₂ environment.

After cell metallization, the storage effect becomes more pronounced (figure 4) as the Voc drops to 450 mV (N₂ storage) and to 610 mV (mailing package storage). Post-storage treatment by SC-1 and SC-2 degrades performance by degrading the SiO₂ layer, but not as severely as the storage without any treatment. In contrast, a simple DI H₂O rinse as well as UV-O₃ exposure show a slight increase in iVoc and a modest drop in Voc coupled with an improvement in Fill Factor (FF). It is important to note that an increase in the thickness of the SiO₂ layer will decrease FF substantially due to decreased probability of tunneling, but we do not measure this and infer that the SiO₂ does not thicken. Using these treatments we were able to obtain TCO-free front/back poly-Si passivated contact cells of >20% (DI H₂O) and >21% (UV-O₃) efficiencies. Notably, cells that received no post-storage treatment degraded significantly after metallization (figure 4 labelled N₂ storage and mail storage), while the treated cells did not show such a behavior. It should be noted that since the premetallized iVoc was measured with an intact Al₂O₃ passivation layer, it is likely that this layer masks latent surface recombination centers such as pinholes or blisters in the poly-Si. Once the Al₂O₃ is removed and the structure is metallized, recombination active metal induced gap states are introduced.
We form our p/poly-Si passivated contact by first depositing a blanket i-layer, then a masked p-layer in a rear emitter configuration. Interestingly, the PL image (figure 5b) shows degradation only under the metallized p/poly-Si layer, while the perimeter i-layer retains passivation after removing the Al2O3 layer. Optical microscopic investigation reveals that 30 - 50 µm blisters (figure 5c) do exist in only the p/poly-Si regions, but not in i/ or n/poly-Si areas. This suggests that the boron diffusion may catalyze the aging-related degradation.

FIGURE 3. Pre-metallized cell iVoc decrease with increasing storage time of SiO2 in an N2 environment prior to n/a-Si:H.

FIGURE 4. Device iVoc and Voc and FF after SiO2 storage in an N2 environment with and without post storage treatments.

It is well known that boron increases hydrogen effusion from amorphous silicon7. Additionally, during a-Si:H deposition, a near-surface hydrogenated layer will form on a silicon substrate but not on a glass substrate8. For specific growth conditions, this hydrogen reservoir will also concurrently release hydrogen during the deposition or subsequent thermal treatment, resulting in blistering of the a-Si:H on Si but not on the glass. While this may partially explain the presence of the blisters in our devices, blistering was not observed in the treated samples, so hydrogen effusion and coalescence are not the sole causes for blister induced degradation.
FIGURE 5. Photoluminescence images of UV-O₃ a) treated and b) untreated cells after storage for a week. Blisters (red circles in c) in the p/poly-Si layer.

FIGURE 6. ToF-SIMS tomographic mapping of intact blister though p/poly-Si (top) passivated contact structure on SiO₂ (middle line) capped cSi wafer (bottom).

ToF-SIMS tomographic mapping (figure 6) through an intact ~30 µm blister shows that boron, carbon, fluorine, and C₂H can clearly be seen on the SiO₂/poly-Si interface as well as coalesced in the blister itself, realized by the cylindrical shape in the figures. During the high temperature crystallization anneal, localized weak adhesion points at the interface created conditions favorable for mobile elements to migrate. As they continue to diffuse and collect, the blister gets larger, but the SiO₂ remains intact on the cSi.

When comparing surface spectra (figure 7) of stored-and-treated versus stored-and-untreated tunneling SiO₂, we find polypropylene fragmentations at atomic mass of ~288.3 as a result of the container in which we store our samples. These adhere to the SiO₂ layer to create the localized weak attachment points for the a-Si:H. Environmental conditions such as containment and latent chemistry, even in a cleanroom, are well known to contaminate surfaces. Once the delamination has nucleated, the action of boron enhanced hydrogen effusion as well as contaminant migration produce growing blisters. This results in a final blistered p/poly-Si layer that will allow recombination-active direct metal contact to the cSi absorber.

FIGURE 7. ToF-SIMS Surface spectra with polypropylene fragment signal on untreated SiO₂ surface
CONCLUSIONS

We find that environmental contaminants resulting from storing our tunneling SiO\textsubscript{2} in polypropylene containers in a clean room result in blisters only in the p/poly-Si layer, but not i/ or n/poly-Si of our devices. The mechanism for blister growth occurs by hydrocarbons adhering to the SiO\textsubscript{2} locally creating weak attachment points during a-Si:H deposition. The subsequent anneal into poly-Si reveals the segregation of hydrogen, boron, and carbon to blisters. This leads to eventual recombination active direct metal contact to the underlying cSi absorber. Treatments to the stored SiO\textsubscript{2} layer such as UV-O\textsubscript{3} exposure and even a deionized water dip result in >20% front/back all poly-Si passivated contact cells. The treatments do not cause SiO\textsubscript{2} growth as evidenced by fill factors ~78%.

REFERENCES