

Enhanced Stability of Exposed PECVD Grown Thin n^+ Poly-Si/SiO_x Passivating Contacts with Al₂O₃ Capping Layer During High Temperature Firing

Keeya Madani, Ajeet Rohatgi, Brian Rounsaville, Min-Gu Kang, Hee-Eun Song, Young-Woo Ok

Abstract— Carrier selective poly-Si/SiO_x contacts have become a very strong contender for next generation high efficiency Si solar cells as well as Si-based tandem cells. A thin un-metallized poly-Si/SiO_x passivated contact on the top surface of the bottom Si cell provides an excellent opportunity for higher efficiency two-terminal Si-based tandem cells. However, this paper shows when the manufacturable low-cost screen-printed contacts are applied on the rear side of the Si cell, then the exposed poly-Si/SiO_x contact on the front undergoes appreciable degradation in J_0 during high temperature contact firing without a capping layer on the front poly-Si. In this study, un-metallized n-TOPCon structures with ~10 nm poly-Si showed significant degradation after a typical simulated firing process (~750°C), resulting in decreased implied V_{oc} from 728 to 708 mV and increased J_0 from 5 to 15 fA/cm². We found that a ~7 nm Al₂O₃ capping layer on poly-Si provides excellent protection with no degradation and can also be easily removed after firing for subsequent processing. For comparison, PECVD grown ~20 nm SiN_x and SiO_x layers were also investigated for firing stability. The SiN_x capping layer was also found to be effective in preserving stability, but the SiO_x failed due to lack of hydrogen supply. Large area n-type front junction Si solar cells were fabricated with a B diffused screen-printed emitter on the front and Ag evaporated thin n-TOPCon on the rear to demonstrate ~0.3% higher absolute efficiency when the rear n-TOPCon is capped with Al₂O₃ during the firing of the front screen-printed contacts.

Index Terms - Carrier selective passivated contact, TOPCon, PECVD poly-Si, Thermal stability, 2T tandem

I. INTRODUCTION

THE commercial Si solar cell efficiency in most state-of-the-art manufacturing lines today is limited by recombination caused by heavily doped regions and metal contacts to the silicon absorber [1, 2]. In order to overcome these fundamental bottlenecks, carrier selective passivated contacts are considered an ideal candidate for next generation solar cells because doped regions and metal contacts are physically decoupled from the Si

absorber. Heterojunction with intrinsic thin layer (HIT) cells and tunnel oxide passivated contact (TOPCon) cells are great examples of carrier selective passivated contacts where a thin intrinsic a-Si interlayer or thin tunnel oxide is used to decouple the doped layer and metal contact regions from the Si substrate [3-9]. Several groups have reported very high cell efficiency (> 25%) and outstanding V_{oc} (> 700 mV) from these cell structures [10-15]. However, HIT cell technology is complicated and expensive due to high CapEx as well as processing and materials costs due to indium tin oxide (ITO) and low temperature cured Ag paste [16]. On the other hand, TOPCon technology can be easily transferred into current Si passivated emitter rear contact (PERC) and full Al back surface field (BSF) cell production lines by adding few poly-Si deposition tools due to process simplicity and excellent thermal stability, which enables the continued use of traditional low-cost screen-printed contacts.

TOPCon structures are composed of a very thin tunnel oxide (< 1.5 nm) and a heavily doped poly-Si layer. It is well known that tunnel oxide can be grown by wet chemistry, UV treatment, or thermal annealing, which results in excellent passivation quality after deposition of a doped poly-Si capping layer [17, 18]. Several tools have been investigated to deposit phosphorus- or boron-doped poly-Si, such as low pressure chemical vapor deposition (LPCVD) and plasma enhanced chemical vapor deposition (PECVD) [19-21]. The LPCVD process can deposit thick doped poly-Si layers on both surfaces with high throughput, but it requires masking and etching steps to remove the same polarity poly-Si from one side. On the other hand, the PECVD process can deposit a doped Si layer on a single side with better thickness uniformity but often with a slower deposition rate. Meyer Burger recently announced the development of a new PECVD tool with very high deposition rate, and SERIS demonstrated a very high efficiency (> 23%) large area (244 cm²) bifacial n-type cell with n-TOPCon on the rear grown by the aforementioned tool [22]. Generally, poly-Si

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should be thick (> 100 nm) and capped with a SiN_x layer for the screen-printed fire-through contact process to avoid degradation in passivation and contact quality [23, 24]. However thick poly-Si absorbs more light, resulting in J_{sc} loss. Due to this reason, several groups are investigating various metallization schemes on thin poly-Si using transparent conductive oxide (TCO), plating, and full metal evaporation as well as screen printing technology [25, 26]. In addition, the TOPCon structure with a thin poly-Si layer can be used for new and exciting photovoltaic structures such as double side TOPCon or Si-based tandem solar cells [27-31]. The combination of inexpensive manufacturable processing and potential for very high efficiency makes TOPCon the most suitable choice for next generation solar cells, but its implementation in next generation double side TOPCon or tandem cell configurations is not without challenges. For example, a thin un-metallized TOPCon layer on the top surface of the bottom Si cell provides an excellent opportunity for $\sim 30\%$ efficient two-terminal Si-based tandem cells because of its very low saturation current density ($J_0 = 1\text{-}5 \text{ fA/cm}^2$) in conjunction with minimal absorption loss due to very thin poly-Si thickness (~ 10 nm) enabled by no front metal contacts and absence of high energy photons in the filtered spectrum through the top cell. However, if low-cost screen-printed contacts are used on the rear side of the Si cell, then the exposed TOPCon layer on the front could degrade during high temperature contact firing without a capping layer. Likewise, if double side TOPCon cells are to be produced someday with screen-printed contacts, the very thin front side TOPCon will have to withstand a contact firing cycle.

In this work, we report on the passivation instability of exposed PECVD grown very thin (~ 10 nm) phosphorus-doped poly-Si on top of chemically grown SiO_x after a high temperature firing process. In addition, we compare the effect of ALD grown Al_2O_3 and PECVD grown SiN_x and SiO_x capping layers on top of the thin poly-Si in an effort to preserve its excellent passivation quality after high temperature firing and subsequent processing. Finally, large area single side rear TOPCon cells are fabricated with screen-printed diffused B emitter on the front and evaporated Ag contact on the rear to demonstrate and quantify the benefit of an Al_2O_3 capping layer during firing of the front screen-printed contacts.

II. EXPERIMENTAL DETAILS

In order to explore the thermal stability of the TOPCon structure during high temperature firing, symmetric n^+ poly-Si/ SiO_x /n/ SiO_x /n $^+$ poly-Si structures were prepared on planar high resistivity Cz Si wafers. After saw damage etching and a planarization process using KOH solution, a very thin ~ 15 Å chemical oxide was grown by immersing the samples in 68 wt% HNO_3 at $\sim 100^\circ\text{C}$ for 10 min. A ~ 10 nm thick n^+ (phosphorus) doped amorphous Si (a-Si) layer was grown on top of chemical oxide on both sides followed by 875°C furnace annealing in N_2 ambient for the dopant activation and crystallization. In order to investigate the effect of the Al_2O_3 capping layer, some samples received a ~ 7 nm Al_2O_3 coating on both sides using a

plasma assisted atomic layer deposition (ALD) tool. For comparison, samples were also prepared with ~ 20 nm PECVD SiN_x and SiO_x . After that, all TOPCon symmetric structures, with and without a capping layer, were subjected to a simulated firing process in a belt furnace at 750°C without metallization. Implied V_{oc} (iV_{oc}) and saturation current density (J_0) were determined from quasi-steady-state photoconductance (QSSPC) technique using a Sinton WCT-120 lifetime tester before and after firing [32]. A cross-sectional image of the TOPCon structure was obtained by transmission electron microscopy (TEM) measurement and chemical compositions were analyzed by secondary ion mass spectroscopy (SIMS). After firing, all samples were immersed in HF for different durations to investigate passivation stability after Al_2O_3 removal and HF treatment. For the purpose of investigating the beneficial effect of the Al_2O_3 capping layer on the cell efficiency, we fabricated large area n-type Si solar cells with screen-printed contacts on an implanted B emitter on the front and n-TOPCon on the rear with evaporated Ag contacts. Cell fabrication involved saw damage etching and texturing, then B implantation with a dose of $2 \times 10^{15} \text{ cm}^{-2}$ at 10 keV on the front followed by an annealing and oxidation step at 1050°C , which resulted in a $\sim 120 \Omega/\square$ emitter. After rear side planarization, an n-TOPCon layer was grown on the rear side using the process described before [1]. Following an 875°C annealing and crystallization of PECVD poly-Si, ALD Al_2O_3 (~ 7 nm) and PECVD SiN_x (65 nm) films were deposited on the B emitter for passivation and AR coating and a ~ 7 nm ALD Al_2O_3 capping layer was deposited on the rear poly-Si. Some samples were kept aside without rear Al_2O_3 deposition to serve as a reference to assess the impact of the Al_2O_3 capping layer. For the front contacts, Ag/Al paste was screen printed using 100 grid lines followed by a $\sim 750^\circ\text{C}$ contact firing process, during which the rear poly-Si layer was exposed to firing ambient for reference samples without an Al_2O_3 capping layer. Finally, Ag metal was evaporated on the rear side after a short HF dip to remove the Al_2O_3 layer and native oxide. All cells were measured by a light I - V tool using a reference cell measured at Fraunhofer ISE.

III. RESULTS AND DISCUSSION

A. PECVD poly-Si composition and comparison of contact firing stability of three different capping layers on poly-Si

Fig. 1 shows measured chemical composition of the TOPCon region by SIMS and cross-sectional high resolution TEM images of the n^+ poly-Si/ SiO_x /n/ SiO_x /n $^+$ poly-Si symmetric structure after 875°C annealing used for crystallization and dopant activation in poly-Si. The TEM image shows a very thin (~ 1.5 nm) SiO_2 capped with ~ 9 nm n^+ doped poly-Si. The SIMS result shows high oxygen peak in the tunnel oxide between the Si substrate and poly-Si layer and a pile up of phosphorus dopants near the top surface of tunnel oxide due to segregation [33]. In addition, it shows high hydrogen concentration near the top surface of poly-Si.

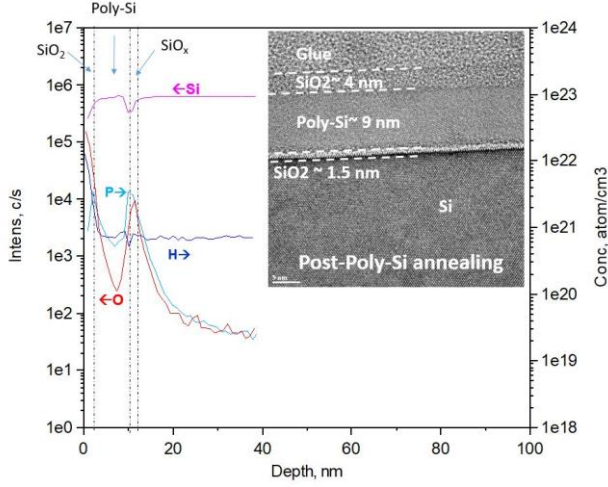


Fig. 1. Measured SIMS profile and TEM images from n-TOPCon structure after crystallization anneal

Fig. 2 shows the measured iV_{oc} and J_0 values for a symmetric n-TOPCon structure without a capping layer before simulated contact firing as a function of immersion time in 5% HF solution. Starting values of 717 mV iV_{oc} and 9 fA/cm² J_0 were essentially unchanged for about 20 s. Beyond that, the passivation quality declined rapidly, with iV_{oc} and J_0 reaching 690 mV and 20 fA/cm², respectively, in 60 s. This is attributed to the inhomogeneity of the very thin poly-Si, which enables HF to attack the underlying tunnel oxide layer and degrade passivation [34].

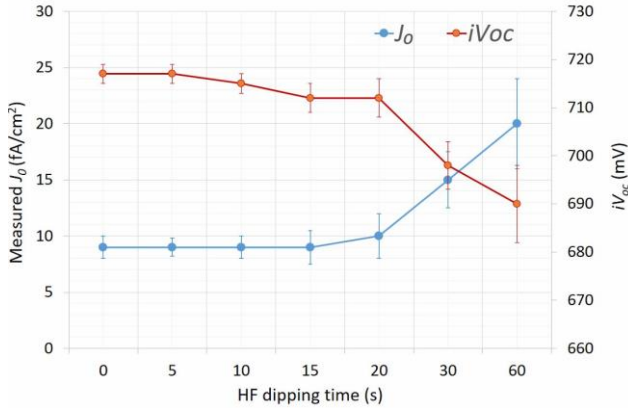


Fig. 2. Measured iV_{oc} and J_0 of PECVD poly-Si as a function of time in 5% HF after annealing

After determining that the very thin PECVD poly-Si lacks stability in HF, annealed large area symmetric samples were dipped in 5% HF for ~10 s to remove a very thin SiO₂ layer grown during the anneal step. Then, the samples were cut into quarters and protected with three different capping layers (Al₂O₃, SiN_x, and SiO_x) and subjected to a standard 750°C for a few secs contact firing cycle. The QSSPC measurements before and after firing are shown in Table 1. For the samples with an Al₂O₃ or PECVD SiN_x capping layer, the iV_{oc} and J_0 actually showed a slight improvement after firing. However, PECVD grown SiO_x showed degradation with iV_{oc} decreasing 6 mV and J_0 increasing 8 fA/cm². The observed enhanced stability from hydrogen containing Al₂O₃ and SiN_x capping layers in our

study is attributed to the supply of hydrogen to the poly-Si/SiO₂ interface during firing [35, 36], which is limited or absent in the case of the SiO_x film. Therefore, we conclude that Al₂O₃ and SiN_x are both effective candidates for a capping layer during firing of planar TOPCon, with Al₂O₃ having a slight edge. These results are in general agreement with van de Loo et al. [36], who showed a significant increase in hydrogen concentration at the poly-Si/SiO_x interface after firing with the Al₂O₃ capping layer. They also demonstrated the passivation stability after firing of ex-situ doped 200 nm LPCVD poly-Si with Al₂O₃ and SiN_x capping layers and achieved the best result with an Al₂O₃/SiN_x stack, but not on very thin (10 nm) in-situ doped PECVD n^+ poly-Si investigated in this study. Hollemann et al. [37] also recently showed that AlO_x film is very effective in maintaining firing stability of thick (220 nm) in-situ doped LPCVD poly-Si on planar and textured surfaces with ~1.5 nm wet chemical tunnel oxide, but that for poly-Si layers on thick thermal oxide (~10 nm instead of 1.5 nm tunnel oxide), only AlO_x capping layers lead to improved firing stability while the SiN_y cap or no capping layer showed significant degradation.

TABLE I
MEASURED iV_{oc} , J_0 , AND iFF BEFORE AND AFTER HIGH TEMPERATURE SIMULATED FIRING WITH SiN_x, SiO_x, AND Al₂O₃ CAPPING LAYERS

Capping layer	Process	iV_{oc} (mV)	J_0 (fA/cm ²)	iFF (%)
ALD Al ₂ O ₃ (~7 nm)	pre-firing	703	15	85.2
	post-firing	707	13	85.1
PECVD SiN _x (~20 nm)	pre-firing	697	21	84.5
	post-firing	698	20	84.5
PECVD SiO _x (~20 nm)	pre-firing	701	17	85.0
	post-firing	695	25	84.5

Besides the stability requirement of thin passivated contacts during the firing process, one should be able to remove the capping layer easily for subsequent processing for use in tandem or double side TOPCon cells. It is well known that Al₂O₃ etches much more quickly than SiN_x in diluted or buffered HF based solutions [38]. We found that to be true for capping layers deposited and fired in this study (Table 2) with Al₂O₃ exhibiting > 20 times faster etching rate compared to the fired SiN_x in 5% HF. Therefore, Al₂O₃ is the more desirable candidate for preserving passivation and ease of removal.

TABLE II
ETCHING RATE OF AL₂O₃, SiN_x, AND SiO_x IN 5% HF

Capping layer	Etching rate in 5% HF (nm/min)
SiN _x	~ 3
SiO _x	~100
Al ₂ O ₃	~70

B. Further investigation of Al₂O₃ capping layer on poly-Si

Fig. 3 shows the measured iV_{oc} and J_0 values from a

symmetric n-TOPCon structure through the entire process. After further optimization of TOPCon process, we achieved a low J_0 of ~ 5 fA/cm² (one side) after 875°C annealing of symmetric n-TOPCon. However, it increased to 15 fA/cm² after a subsequent simulated firing process at $\sim 750^\circ\text{C}$ without the capping layer. The J_0 increase indicates that passivation quality of n-TOPCon degrades during the high temperature contact firing cycle, which also resulted in iV_{oc} decrease from 728 to 708 mV. It has been recently suggested by Hollemann et al. [37] that such degradation can be attributed to stress induced defects at the poly-Si/SiO_x interface due to rapid thermal gradient during the contact firing cycle.



Fig. 3. Measured iV_{oc} and J_0 from the samples with and without Al₂O₃ capping layer after simulated high temperature firing process

However, the symmetric n-TOPCon sample capped with an Al₂O₃ layer maintained very high iV_{oc} of ~ 724 mV and low J_0 of ~ 6 fA/cm², which is very similar to the values achieved directly after annealing. Additionally, measured effective lifetime in Fig. 4 showed a very clear difference in the lifetime as a function of injection level for the three samples. After simulated firing, the effective lifetime of the n-TOPCon structure without a capping layer decreased over the entire injection level range (5×10^{14} – 2×10^{16} cm⁻³), but the samples fired with an Al₂O₃ capping layer did not show any decrease in effective lifetime. It is noteworthy that fired samples with a capping layer show very similar or even slightly better effective lifetime compared with the annealed sample before firing, endorsing the effectiveness of a thin Al₂O₃ capping layer.

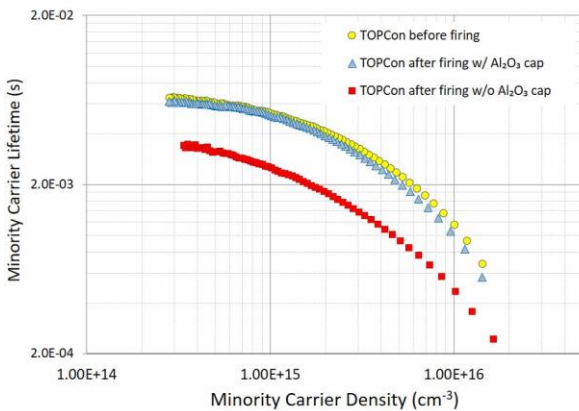


Fig. 4. Effective lifetime from the samples with and without Al₂O₃ capping layer after simulated high temperature firing process

After firing, we investigated the stability of the n-TOPCon layer subjected to HF treatment because we may need to remove the Al₂O₃ capping layer in order to deposit the top cell for tandem devices or to make metal contacts for a standalone TOPCon Si cell. Fig. 5 shows the measured iV_{oc} and J_0 as a function of HF (1% in DI H₂O) etching time. The samples fired with an Al₂O₃ capping layer showed very stable iV_{oc} and J_0 before and after the removal of Al₂O₃. The Al₂O₃ capping layer was easily removed after 30 s in HF as evidenced by a hydrophobic surface. However, the SiN_x capping layer took much longer to remove after the firing process.

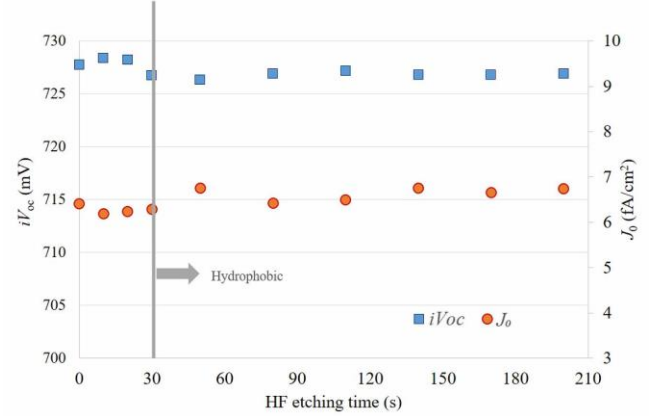


Fig. 5. Measured iV_{oc} and J_0 from the simulated fired samples with Al₂O₃ capping layer as a function of immersion time in 1% HF

Finally, in order to validate the positive effect of an Al₂O₃ capping layer on cell performance, we fabricated large area n-TOPCon test cells with an ion implanted B emitter and screen-printed Ag/Al contacts on the front and a very thin (~ 10 nm) n-TOPCon on the rear with an evaporated Ag contact, as shown in Fig. 6. Note that the B emitter was screen printed and fired first, followed by Ag evaporation. Samples with and without an Al₂O₃ capping layer on n-TOPCon were prepared prior to screen printing and firing the B emitter. After that, Ag was evaporated on the rear TOPCon after a short HF treatment to remove the Al₂O₃ capping layer as well as the native oxide grown on all samples during firing. The cell fired with the Al₂O₃ capping layer gave $\sim 20.8\%$ efficiency with V_{oc} of 671 mV, but the cells fired without capping layers measured $\sim 20.5\%$ with V_{oc} of 665 mV. Thus, the presence of Al₂O₃ resulted in 6 mV increase in V_{oc} and $\sim 0.3\%$ higher absolute efficiency.

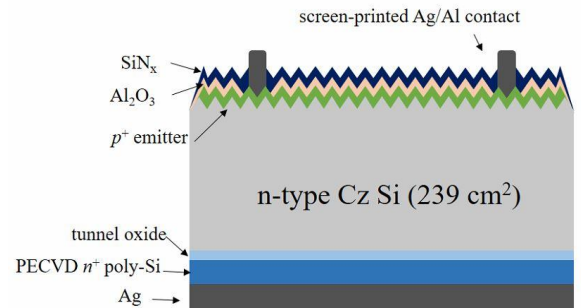


Fig. 6. Schematic of fabricated large area n-type Cz Si solar cell with B emitter on the front and P-doped TOPCon and Ag evaporation on the rear

IV. CONCLUSIONS

We reported on the study of thermal stability of n-TOPCon with 15 Å chemically grown tunnel oxide and very thin (~10 nm) PECVD grown poly-Si during a high temperature (750°C) contact firing process. Passivation properties of the TOPCon structure showed an appreciable decrease in implied V_{oc} and increase in J_0 after simulated firing. However, TOPCon structures capped with an Al_2O_3 layer showed no degradation after the same firing process while maintaining excellent iV_{oc} , J_0 , iFF , and effective lifetime at low level injection. A PECVD SiN_x capping layer also demonstrated similar efficacy, but the speed and ease with which Al_2O_3 can be removed makes it more desirable for advanced cell structures such as double side TOPCon and tandem solar cells. A cell efficiency of ~20.8% was achieved on the TOPCon cell with the Al_2O_3 capping layer with ~6 mV higher V_{oc} and ~0.3% higher absolute efficiency compared to the cell without the Al_2O_3 capping layer.

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