# Screen-Printable Conductor Metallizations for Industrial n-TOPCon Crystalline Silicon Solar Cells

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Abstract—Optimally prepared industrial n-type TOPCon c-Si bifacial solar cells (156 mm × 156 mm) fabricated with costeffective screen-printable front-side and rear-side metallization pastes had a median solar cell efficiency of 22.19 ±0.10% and bifaciality Eff factor of 82.3%. A front-side paste comprising silver, metallic aluminum, and inorganic frit was designed to contact p+ boron-diffused Si emitter surfaces with SiN<sub>x</sub>:H-Al<sub>2</sub>O<sub>3</sub> antireflection-passivation layers. A rear-side paste comprising silver and inorganic frit was designed to contact n+ phosphorousdiffused Si surfaces with tunnel-SiO<sub>x</sub>/n<sup>+</sup>poly-Si/SiN<sub>x</sub>:H layers. Solar cell electrical data suggests efficiency is being limited primarily by the front-side metallization paste. The final front-side metallization microstructure shows isolated metallic aluminum particles surrounded by solidified glass within the bulk sintered silver conductor line. The front-side conductor metal-p+ borondiffused Si emitter contact region shows continuous interfacial films decorated with silver colloids located between the bulk conductor metal and Si emitter surface. A microstructural model suggests electrical contact for the front-side contact region occurs by a tunneling mechanism though the residual interfacial films.

Key Words—bifacial, metallization, n-type, paste, photovoltaic cells, screen print, silicon, solar cells, thick-film, TOPCon

## I. INTRODUCTION

Tunnel oxide passivated contacts (TOPCon) cell technology has become the leading next-generation choice after mono PERC. Compared to technologies such as HJT and IBC, TOPCon architectures can be achieved by upgrading current industrial PERC or PERT manufacturing lines which means a lower capital expenditure is needed for existing PERC or PERT manufacturers who want to upgrade their existing production lines. We investigated n-type TOPCon since n-type silicon wafers have inherent advantages over p-type silicon such as higher minority carrier diffusion length and less sensitivity to metal impurities, and n-type cells don't have boron-oxygen (BO) related light induced degradation (LID) [1-3]. A TOPCon structure offers a gain in cell efficiently of ~1% absolute compared to previous generation technologies [4,5].

Industrial solar cell manufactures utilize screen-printable metallization pastes as a cost-effective metallization solution because of their low cost, high throughput, and relatively high performance. Among the challenges for introducing a TOPCon architecture to industrial solar cell manufacturing is utilizing cost-effective screen-printable metallizations that effectively contact both the front-side (FS) and rear-side (RS) surfaces of the solar cell in a single metallization firing step while maintaining the benefits of the TOPCon architecture [6].

We explore both FS and RS state of the art screen-printable metallization pastes on an industrial n-type TOPCon bifacial structure shown in Fig. 1. It has a FS  $p^+$  boron diffused emitter and a RS  $n^+$  phosphorus diffused passivating contact, with screen-printed conductor finger lines on both the front and rear sides to obtain bifaciality.

The challenge for screen-printable pastes is to etch-through the  $SiN_x$ :H and passivation layers on both the front and rear sides at the same time during the metallization firing process to make electrical contact with the underlaying semiconductor surfaces without damaging the contact regions under the metallization lines, which can increase the  $J_0$  recombination current density and reduce the final solar cell  $V_{\rm OC}$ . Electrical contact is further made complicated by oxide passivation layers on the FS ( $Al_2O_3$ ) and RS ( $SiO_x$ ) which are more difficult to etch-through to establish contact.

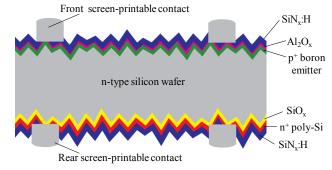


Fig. 1. Industrial n-TOPCon c-Si bifacial solar cell with front-side and rear-side screen-printable metallizations.

### II. EXPERIMENTAL

Screen-printable pastes were prepared by mixing metal powder (~90 wt%), inorganic frit powder (~2 wt%) and organic media (~8 wt%) in a planetary mixer followed by 3-roll milling

and viscosity adjustment (measured by a Brookfield DV2T-HB). Pastes were roll milled to a fineness of grind (FOG) of  $\sim$ 5  $\mu$ m in accordance with ASTM Test Method D 1210-05. Pastes were adjusted to a final viscosity between 200 and 450 Pa-s. at 10 rpm.

Paste solar cell performance was evaluated on commercially available industrial processed bifacial n-type TOPCon mono c-Si pseudo-square (156 mm × 156 mm) random pyramid solar cells. The cell fabrication process included alkali texturing, p<sup>+</sup> boron diffusion (BBr<sub>3</sub>), rear p<sup>+</sup> removal (single side HF/HNO3 etching), thermally deposited SiO<sub>x</sub> and intrinsic poly-Si films (LPCVD), n<sup>+</sup> phosphorus diffusion (POCl<sub>3</sub>), front n<sup>+</sup> removal (single side etching), and double sided SiN<sub>x</sub>:H (PECVD) deposition. For the metallization, an industrial Baccini screen printer was used to print front and rear surface five busbar H-patterned conductor lines. The fired FS conductor line mean width was ~30 µm and height was ~15 μm. The fired RS line mean width was ~50 μm and height was ~12 μm. An industrial 9-zone Despatch furnace was used to fire the screen-printed wafers. The final screenprinted TOPCon cell configuration is shown in Fig. 1.

An industrial Berger I-V tester was used to measure solar cell efficiency (Eff), fill factor (FF), open circuit voltage ( $V_{\rm OC}$ ), short circuit current ( $I_{\rm SC}$ ) and series resistance ( $R_{\rm S}$ ). Electrical data values are median and standard deviation values for about ten cells. Specific contact resistivity ( $\rho_c$ ) was measure using the transfer length method (TLM) [7] on 1.0 cm wide strips cut from fired cells.  $\rho_c$  values are median and standard deviation values for fifty TLM measurements.  $\Delta G$  values were determine using FactSage<sup>TM</sup>. Microstructure sample preparation and characterization was performed on a Auriga 60 CrossBeam (FIB/FE-SEM).

# III. RESULTS AND DISCUSSION

A critical challenge for the introduction of a TOPCon architecture to industrial scale solar cell manufacturing is the implementation of cost-effective screen-printable metallizations on both the front and rear sides of the TOPCon solar cell. Each surface presents unique paste development challenges. The front surface requires a paste optimized for contact to a p<sup>+</sup> doped Si surface, the rear surface requires a paste optimized for contact to a n<sup>+</sup> doped Si surface. Electrical contact must occur with minimal damage to the semiconductor surface under the metallization lines.

A thick-film, screen-printable paste typically consists of an organic phase, metallic silver particles, and an inorganic solid-state frit. The paste is printed on the wafer surface and rapidly fired at relatively high temperature (~780°C). During the firing process the frit forms a liquid phase flux that helps sinter the silver particles to high bulk density and etches-through the SiN<sub>x</sub>:H antireflective coating (ARC) and passivation layers to allow the sintered conductor line to make electrical contact to the underlaying semiconductor surface, ideally without damaging the surface. Sintering the silver particles to high density reduces conductor line resistance which reduces solar cell R<sub>S</sub>. Effective contact to the semiconductor surface minimizes the metal-semiconductor contact resistance which

again reduces  $R_S$ . Contact to the underlaying semiconductor surface without damage to the surface reduces  $J_0$  in the contact region which increases  $V_{\rm OC}$ .

Screen-printable pastes designed to contact n<sup>+</sup> surfaces currently contain telluride-based frits [8]. These pastes are relatively well established as FS pastes for p<sup>+</sup> base wafers with n<sup>+</sup> emitters. Pastes designed to contact p<sup>+</sup> surfaces are less well established and contain aluminum metal particle additions to accomplish contact, but which suffer high emitter damage and relatively high contact resistance and conductor line resistance compared to pastes for n<sup>+</sup> surfaces. Oxide surface passivation layers (on both front and rear sides) further complicate the ability for a paste to make effective contact to the underlaying semiconductor surface.

In this work the RS paste, designed to make electrical contact to phosphorous doped  $n^{\scriptscriptstyle +}$  Si surfaces, contained silver metal and a telluride-based frit. Telluride-based frits form a liquid phase flux during the firing process that oxidizes and etches-through the SiN $_x$ :H ARC layer which allows the silver conductor line to make electrical contact with the underlaying  $n^{\scriptscriptstyle +}$  surface [9].

The FS paste, designed to contact boron doped  $p^+$  Si surfaces, contained silver metal, a lead-silicate based frit, and aluminum (Al) metal particles. Metallic Al is required to contact  $p^+$  surfaces. The Al metal is thought to promote electrical contact by reacting with and penetrating into the  $p^+$  doped Si surface during the firing process [10]. The paste must contain both frit and Al metal for good contact. Paste comprising frit sans Al metal or comprising Al metal sans frit were both tested and resulted in solar cells with high  $\rho_C$  and poor JV characteristics (Eff <1%).

TABLE I
SCREEN-PRINTED N-TOPCON CELL JV DATA

	Eff (%)	FF (%)	V <sub>oc</sub> (mV)	J <sub>SC</sub> (mA/cm <sup>2</sup> )	$R_s$ (m $\Omega$ )
FS Median	22.19 ±0.10	79.47 ±0.42	673.2 ±1.7	41.49 ±0.08	3.01 ±0.17
FS Best Cell	22.27	79.73	675.7	41.58	2.87
RS Median	18.27 ±0.18	79.27 ±0.50	667.9±1.4	34.77±0.21	3.52 ±0.35
RS Best Cell	18.53	79.71	660.0	34.84	3.07

Table I lists JV data for n-TOPCon bifacial cells printed with front and rear-side metallization pastes showing median and "Best Cell" values for the FS and RS of the cells. The bifacial cells had a FS median Eff of 22.19 ±0.10% and a maximum Best Cell Eff of 22.27%, and a RS median Eff of 18.27 ±0.18% and maximum Best Cell Eff of 18.54%. The median bifaciality Eff factor is 82.3% according to the ratio of the RS illumination efficiency to the FS illumination efficiency (Eff<sub>-rear</sub>/Eff<sub>-front</sub>). Since the front and rear sides have similar V<sub>OC</sub> and FF, the bifaciality Eff factor is comparable to the bifaciality  $J_{SC}$  factor ( $J_{SC\text{-rear}}/J_{SC\text{-front}} = 83.8\%$ ). The FS had a median specific contact resistivity ( $\rho_C$ ) of 2.72  $\pm 0.38$  m $\Omega$ -cm<sup>2</sup>. This value is  $\sim 3x$  higher than is typically achieved by state-of-theart screen-printable pastes for contact to phosphorous doped surfaces [9] indicating a need to improve FS  $\rho_C$ . In addition to a need to improve FS  $\rho_C$ , Al metal in the FS paste increases conductor line resistance and exacerbates emitter damage under the metallization. The electrical data suggests solar cell

performance is being limited primarily by the FS paste. Future paste development is focused on improving FS pastes. Improvements in the base wafer quality can also improve cell performance.

Fig. 2 is an SEM micrograph of the FS contact region. The FS has a boron doped p<sup>+</sup> emitter coated with an Al<sub>2</sub>O<sub>x</sub> layer and PECVD SiN<sub>x</sub>:H ARC. The light contrast area (top portion) is the sintered bulk silver conductor metal and the dark area (bottom portion) is the bulk silicon emitter. An interfacial (IF) film is observed at the interface between the bulk silver metal and silicon emitter. During the paste firing process, the inorganic frit in the paste forms a low viscosity liquid phase which migrates to the silver-silicon interface region where it enables the oxidation, dissolution and removal of the SiN<sub>x</sub>:H layer. The final IF film is decorated with silver colloids from precipitation of silver ions dissolved in the IF liquid phase according to the following reaction:

$$\begin{array}{l} Si_{3}N_{(4\text{-}x)}H_{x\,(solid)} + 6Ag_{2}O_{\,(IF\,\,liquid)} = 3SiO_{2\,(IF\,\,liquid)} + 12Ag_{\,(solid)} + \\ (2\,\text{-}\,0.5x)N_{2\,\,(gas)} + (0.5x)H_{2\,\,(gas)}, \end{array}$$

$$\Delta G = -477 \text{ kcal}$$

It is not surprising to observe silver colloids along the interface considering the large negative  $\Delta G$  for this reaction.

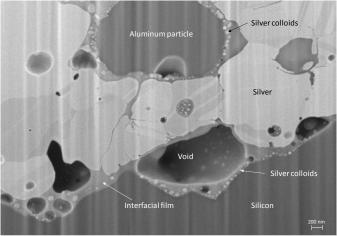


Fig. 2. SEM cross section micrograph of the final front-side fire-through metallization interface region.

A microstructural model suggests the silver colloids along the interface participate in electrical contact between the emitter and bulk silver by a tunneling mechanism through the IF film during cell operation [11]. The microscopy observation shows the IF film to be continuous along the interface and relatively thick with no directed contact between the bulk silver and emitter layer. If direct contact does occur, it is intermittent and spotty, and not within the observed area. The  $SiN_x$ :H and  $Al_2O_3$  layers appear to be dissolved/removed along the interface.

Voids, pockets of solidified liquid, and an isolated metallic Al particle are observed in the bulk silver. The aluminum particle is surround by solidified liquid phase decorated with silver colloids that form during firing according to the following reaction from silver dissolved in the liquid phase frit.

$$4Al_{(solid)} + 6Ag_2O_{(liquid)} = 2Al_2O_{3 (solid)} + 12Ag_{(solid)}$$
  
 $AG = -695 \text{ kcal}$ 

It is not surprising to observe silver colloids surrounding the metallic Al particle considering the large negative  $\Delta G$ . The isolated Al metal particle is not in contact with the surrounding bulk silver; therefore, it does not contribute to electrical conduction and increases conductor line resistance since it is inherently less conductive than Ag. Metallic Al particles and/or Si-Al eutectic reaction products are not observed directly along the interface or in direct contact with the emitter surface. If these do occur, they are sporadic and outside the cross-sectional viewing area, or they may occur at firing temperatures different from this study. Silver crystallites are not observed along the interface.

### IV. CONCLUSIONS

In the development of an industrial n-type Topcon solar cell, cost-effective front and rear-side screen-printable metallization pastes were investigated resulting in a median bifacial cell efficiency of 22.19 ±0.10% and a maximum efficiency of 22.27%. The bifacial electrical data indicates efficiency is being limited primarily by the FS metallization paste. The final FS metallization microstructure shows isolated metallic aluminum particles surrounded by solidified glass within the bulk sintered silver conductor line. The front-side conductor metal-p<sup>+</sup> borondiffused Si emitter contact region shows continuous interfacial films decorated with silver colloids located between the bulk silver conductor metal and silicon emitter surface. A microstructural model suggests electrical contact for the frontside contact region occurs by a tunneling mechanism though the residual interfacial films. Future work will include a detailed examination of the RS contact region microstructure and an analysis of the front and rear-side J<sub>0</sub> parameters in the contact regions. Future paste development is focused on improving FS metallization pastes.

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