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Passivating electron-selective contacts for silicon solar cells based on an a-Si:H/TiO_x stack and a low work function metal

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Abstract

In this work, the ATOM (intrinsic a-Si:H/TiO_x/low work function metal) structure is investigated to realize high-performance passivating electron-selective contacts for crystalline silicon solar cells. The absence of a highly doped Si region in this contact structure is meant to reduce the optoelectrical losses. We show that a low contact resistivity (ρ_c) can be obtained by the combined effect of a low work function metal, such as calcium (Φ 2.9 eV), and Fermi-level depinning in the metal-insulator-semiconductor contact structure (where in our case TiO_x acts as the insulator on the intrinsic a-Si:H passivating layer). TiO_x grown by ALD is effective to achieve not only a low ρ_c but also good passivation properties. As an electron contact in silicon heterojunction solar cells, inserting interfacial TiO_x at the i-a-Si:H/Ca interface significantly enhances the solar cell conversion efficiency. Consequently, the champion solar cell with the ATOM contact achieves a V_{OC} of 711 mV, FF of 72.9%, J_{SC} of 35.1 mA/cm², and an efficiency of 18.2%. The achievement of a high V_{OC} and reasonable FF without the need for a highly doped Si layer serves as a valuable proof of concept for future developments on passivating electron-selective contacts using this structure.

KEYWORDS

carrier-selective, electron-selective, heterojunction, passivating contact, TiO_x, calcium, low work function metal

1 | INTRODUCTION

Industrial crystalline silicon solar cells (eg, passivated emitter rear totally diffused (PERT) cells, passivated emitter and rear contact (PERC) cells, or silicon heterojunction solar (SHJ) cells) use highly doped silicon layers.^{1–4} The high doping concentration of these n⁺ or p⁺ silicon layers is very effective to lower the contact resistivity (ρ_c). However, heavy doping can induce parasitic absorption, Auger recombination, and Shockley-Read-Hall recombination.^{5,6} Carrier-selective contacts without the use of highly doped silicon layers are getting attention to avoid these disadvantages.^{7,8} However, a lowly doped silicon surface typically results in a high ρ_c .

Based on the Schottky-Mott rule,^{9,10} when a metal work function is lower than the work function of a semiconductor, the band

of the semiconductor near the metal-semiconductor (MS) interface should move downwards (forming an accumulation contact for electrons). Accordingly, many groups have aimed to reach a low ρ_c for electron-selective contacts on n-type-based c-Si solar cells using low work function metals either individually^{11,12} or in combination with other materials such as alkaline earth metal fluorides.^{13,14} However, the main challenge of these approaches is that the penetration of the metal wave function into the semiconductor overlaps with surface states in the semiconductor energy band gap¹⁵ resulting in metal Fermi-level ($E_{F,metal}$) pinning.¹⁶ Therefore, the promised gain of the low work function is not fully realized, and a non-negligible Schottky energy barrier can still be formed at the interfaces with c-Si or a-Si:H.^{17–19}

As an alternative, a metal-insulator-semiconductor (MIS) contact can mitigate the $E_{F,metal}$ pinning due to the reduction of surface states or dipoles at the interfaces of the contact.²⁰⁻²³ In addition, when using low doping concentrations, it has been shown that an MIS contact can outperform the contact resistivity of an MS contact.^{24,25} In the MIS structure, the thickness of the insulator is a critical parameter to obtain low ρ_c : the thicker the insulator layer is, the larger the reduction in the $E_{F,metal}$ pinning but also the larger the resistance for the carrier transport through the insulator itself. The position of the energy bands of the dielectric also plays an important role in this resistance. In this respect, TiO_x stands out as a good candidate because it has a suitable band structure for electron-selective contacts: a small E_C offset and a large E_V offset relative to c-Si.²⁶

For the aforementioned reasons, MIS contacts including TiO_x layers with a typical thickness below 2 nm have been intensively studied in the field of CMOS^{24,25,27-29} to achieve the lowest possible ρ_c by mitigating $E_{F,metal}$ pinning. In silicon solar cells, solar cell efficiencies of above 20% have been successfully shown based on a slightly thicker TiO_x layer of 3.5 nm which was subjected to a forming gas annealing treatment at 350°C.³⁰⁻³² When it is aimed to realize silicon solar cells that do not include highly doped silicon regions, a low-temperature process at or below 200°C is still required to be compatible with the fabrication of hole-selective contacts based on high work function transition metal oxides.³³⁻³⁹ Therefore, electron-selective contacts with an intrinsic a-Si:H/ TiO_x stack have been researched because of good chemical passivation of i-a-Si:H, but a high contact resistivity for i-a-Si:H/ TiO_x likely limited the reported cell efficiencies.^{40,41} In our previous work,⁴² we demonstrated the ATOM (intrinsic a-Si:H/ TiO_x /low work function metal) contact which achieves a reduction of 2 orders of magnitudes in ρ_c by combining merits of a MIS contact and a low work function metal. Furthermore, the process temperature was below 200°C for the layers in the contact structure. However, the experiments performed to quantify the recombination losses clearly showed a higher dark saturation current density at the metalized area ($J_{0,metal}$) for the ATOM contacts adopting e-beam evaporated TiO_x when compared to the contacts without TiO_x . It is believed that the a-Si:H passivation quality was degraded by e-beam radiation damages during the evaporation.^{43,44}

In this work, ATOM contacts involving TiO_x layers fabricated by atomic layer deposition (ALD) are evaluated in ρ_c and J_0 to assess their potential in a passivating electron-selective contact. Finally, the ATOM contact structure with TiO_x is integrated in heterojunction solar cells and compared to a classical SHJ solar cell.

2 | CHARACTERIZATION OF ATOM TEST STRUCTURES

2.1 | Preparation of test structures

Mirror polished n-type FZ-Si wafers (3 Ω cm, 200- μ m thickness) were used to evaluate ρ_c and the contact passivation quality. After HF:HCl cleaning, 8-nm-thick intrinsic a-Si:H (i-a-Si:H) layers were deposited on both sides of the substrate by plasma-enhanced chemical vapor deposition (PECVD) at temperatures below 200°C in an AK1000 Inline

system of MicroSystems. Wafers were diced into squares of 54 $\times$ 54 mm² (for the determination of J_0) and 30 $\times$ 30 mm² (for the determination of ρ_c). After HF dip, on top of the i-a-Si:H layers, TiO_x layers of 2 nm were deposited on both sides of the substrate by ALD (Oxford Instruments FlexAL, UK). For the ALD- TiO_x process, titanium tetra-isopropoxide (TTIP) and H_2O were used as Ti precursor and oxidant, respectively, and the substrate temperature was set to 200°C.

For the measurement of J_0 , thin blanket layers of 4-nm-thick Ca and 6-nm-thick Al were deposited by thermal evaporation (Angstrom Engineering, USA) on the rear side of the substrate (see Figure 1A, B). The metal layer thickness was monitored using a quartz sensor in the evaporation tool. These metal layers were kept thin and were deposited only on the rear side to allow a quasi-steady-state photoconductance (QSSPC) measurement⁴⁵ with illumination from the front. The metal layer needs to be thin enough to achieve sufficiently low conductivities for the QSSPC measurement while thick enough to show metal-induced effects on the passivation. The metal thickness of a few Angstroms is sufficient to allow for a metal-induced effect to the band structure at the contact region.⁴⁶ Moreover, to avoid the nonconformal coating of metals and complete oxidation of Al, a few nanometers can be adequate.^{47,48} A similar methodology to extract $J_{0,metal}$ have been previously reported in the literature.⁴⁹⁻⁵¹

The QSSPC measurement was carried out before and after the thermal evaporation of the Ca/Al stack (see Figure 1A, B). This allowed us to calculate the J_0 of the complete ATOM stack based on implied V_{OC} with a J_{SC} of 36 mA/cm² (typical J_{SC} of our SHJ solar cells), $kT/q = 25.9$ mV, and $J_{0,bulk} = 0$ fA/cm² (high-quality FZ-Si wafers).

Before Ca/Al evaporation, $J_{0,front}$ is calculated based on the symmetry of the structures. After Ca/Al deposition (see Figure 1B), $J_{0,rear}$ Ca/Al is determined by subtracting $J_{0,front}$, which was already measured before Ca/Al evaporation, from $J_{0,total}$, after Ca/Al. Assuming the same $J_{0,front}$ before and after Ca/Al evaporation is an acceptable approximation for these contact structures, as during Ca/Al thermal evaporation, the wafer temperature does not exceed 40°C and no process damage is generated because no plasma or e-beam is used.

For the measurement of ρ_c , 100 nm Ca and 200 nm Al were thermally evaporated through a shadow mask, yielding circular contacts with different diameters (200-600 μ m) (see Figure 1C). The values of ρ_c were extracted using the 2-contact 2-terminal method.^{42,52} Consequently, the measured ρ_c includes the ρ_c contribution of all contact layers, as well as the resistive contributions of the bulk of these layers (i-a-Si:H/ TiO_x /Ca/Al).

Samples for additional analysis were prepared using the same process as the ρ_c samples based on double side chemically polished n-type Cz-Si wafers (3.7 Ω cm, 180- μ m thickness). The nanoscale layer structure and the chemical distribution were further investigated by means of transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX) measurements.

2.2 | Results of test structures

As shown in Table 1, no process damage of a-Si:H is observed after ALD- TiO_x deposition, in contrast to the e-beam evaporated TiO_x in our previous study⁴² (note that all TiO_x layer in this study were deposited using ALD). J_0 and $J_{0,metal}$ of the i-a-Si:H/ TiO_x structure exhibit

FIGURE 1 Schematic of the sample structures to determine: (A) J_0 , (B) $J_{0,\text{metal}}$, and (C) ρ_c [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 1 J_0 and contact resistivity comparison between contacts with/without TiO_x layer

Contact Structure	J_0 (fA/cm ²)	ρ_c (average $\pm$ standard deviation) (Ω cm ²)
i-a-Si:H	12.6	
i-a-Si:H/Ca/Al	17.4	8.2 ± 1.9
i-a-Si:H/ALD- TiO_x	12.6	
i-a-Si:H/ALD- TiO_x /Ca/Al (ATOM)	13.4	$1.5 \pm 0.4 \times 10^{-2}$

values similar to the structure without ALD- TiO_x , which means that neither the deposition of the TiO_x layer nor the subsequent metallization results in significant damage to the passivation quality that is provided by the a-Si:H layer. A significant reduction of about 2 orders of magnitude in ρ_c was achieved by the interfacial TiO_x , which illustrates that the presence of a TiO_x layer induces Fermi-level depinning on the a-Si:H surface. As can be seen in Figure 2, the contact type is also changed from a Schottky contact to an Ohmic contact.

The features of the ATOM contact structures with TiO_x were characterized by TEM and EDX and are shown in Figure 3. The rough c-Si/a-Si:H interface is because of a phase transition region of a few

nanometers from crystalline to fully amorphous.^{53,54} The TiO_x layer, of which the thickness is around 2 nm, was deposited uniformly on the i-a-Si:H surface, showing no isolated islands. A closed TiO_x layer is important to achieve $E_{F,\text{metal}}$ depinning, and a uniform TiO_x layer thickness with an amorphous phase is required for homogeneous surface passivation.⁵⁵ Furthermore, an interfacial amorphous SiO_x layer can be found in the EDX image between the i-a-Si:H and the TiO_x layers (see Figure 3A). This interfacial SiO_x may have a potentially positive impact on the passivation properties of the ATOM contact structure. According to Kita et al.,⁵⁶ a dipole can be generated by oxygen movement resulting from a charge imbalance at the $\text{SiO}_x/\text{TiO}_x$ interface, which produces a downward band bending at the contact (see Figure 4B) which is beneficial in passivating electron-selective contacts.

After Ca/Al evaporation, the a-Si:H passivation layer preserves the original amorphous phase in both cases with and without TiO_x in Figure 3C and in Supporting Information Figure S1. Moreover, Al on Ca formed a stack with a clear interface between Ca and Al (see Figure 3D).

Based on previous work,^{42,57} it can be speculated that Ca diffused into the TiO_x layer without any additional annealing. This in-diffusion of Ca within the TiO_x layer may work as a dopant in the TiO_x , which results in lowering the conduction band of TiO_x .⁵⁸ Alternatively, it can be imagined that Ca also induces the formation of defects in the TiO_x layer, especially when Ca is not active as a dopant. This could lead to enhanced trap-assisted transport that also lowers ρ_c . Furthermore, oxygen vacancies can be generated by oxygen extraction from the TiO_x layer by Ca or Al metal.^{31,57,59} It implies that the oxygen vacancies of TiO_x , interfacial SiO_x , and likely Ca in-diffusion possibly have a positive impact on increasing the major carrier conductivity and thus a reduction in ρ_c .

The energy band structures of the i-a-Si:H/Ca/Al and ATOM contact are illustrated in Figure 4. It is based on an effective Schottky energy barrier height ($\Phi_{B,\text{eff}}$), the layer stacks depicted in Figure 3, and the energy band of amorphous SiO_x .⁶⁰ Additionally, the movement of oxygen at the a-SiO_x/TiO_x interface induces a dipole (negatively charged at SiO_x side and positively charged at TiO_x side from the interface).⁵⁶

Allen et al calculated the $\Phi_{B,\text{eff}}$ based on ρ_c using Equation (1) in thermionic emission condition.^{11,61}

$$\rho_c = \left(\frac{k}{qA^{**}T} \right) \exp(\Phi_{B,\text{eff}}/kT) \quad (1)$$

FIGURE 2 Dark IV curve comparison between i-a-Si:H/Ca/Al and ATOM contact [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 3 TEM cross-sectional images for ATOM contact structures using TiO_x deposited by ALD. In particular, EDX images of Ti, Si, and O are shown in (A), TEM images before Ca/Al evaporation in (B), and TEM images after Ca/Al evaporation with high magnification (C) and with low magnification (D) [Colour figure can be viewed at wileyonlinelibrary.com]

FIGURE 4 Schematic band diagram of i-a-Si:H/Ca/Al and the ATOM contact structures based on effective Schottky energy barrier height, metal Fermi-level pinning, and a dipole at the $\text{SiO}_x/\text{TiO}_x$ interface. A, Ca layer induces upward band bending because of $E_{F,\text{metal}}$ pinning on the a-Si:H layer. B, The ATOM contact band structure includes an additional TiO_x layer that induces Fermi-level depinning and hence enables a lower Schottky energy barrier [Colour figure can be viewed at wileyonlinelibrary.com]

where A^{**} is the reduced effective Richardson constant ($110 \text{ A/cm}^2/\text{K}^{262}$), k is the Boltzmann constant, and $\Phi_{B,\text{eff}}$ is the effective Schottky energy barrier at the contact. When this methodology is applied, the extracted $\Phi_{B,\text{eff}}$ on the i-a-Si:H layer is 0.6 eV for Ca and 0.4 eV for the ATOM contact. A significant change of the electron conductivity at the contact is resulting from this difference in barrier height, and $\Phi_{B,\text{eff}}$ of the ATOM contact is comparable to that of a n-Si/Ca/Al contact.¹¹ Temperature-dependent ρ_c measurements could provide more detailed information about the barrier height, although they were not part of this study.

3 | SOLAR CELLS

3.1 | Solar cell preparation

Our ATOM contact was applied to 2-side contacted SHJ cells. The schematic cell structures are shown in Figure 5. All the cell structures investigated had the same hole-selective contact approach featuring the stack i/p-a-Si:H/ITO/Ag on the front side. On the rear side, different stacks were applied: i-a-Si:H/Ca/Al and i-a-Si:H/ALD- TiO_x /Ca/Al as highly doped Si layer free electron-selective passivating contact

FIGURE 5 Schematic cross-sectional structures for the different solar cells with candidate electron-selective contacts [Colour figure can be viewed at wileyonlinelibrary.com]

structures. As a reference contact, i/n-a-Si:H/ITO/Ag, which is commonly used in a classical SHJ cell, was applied.

To fabricate these solar cells, n-type Cz-Si wafers ($3.2 \Omega \text{ cm}$, $165\text{-}\mu\text{m}$ thickness) with a textured front side and a chemically polished rear side were used. After HF:HCl:O₃ and HF:HCl cleaning,⁶³ the i/p-

a-Si:H stack was deposited on the textured front side. Subsequently, after a short HF cleaning, i-a-Si:H and n-a-Si:H layers with thicknesses of 4 and of 8 nm, respectively, were deposited by plasma-enhanced chemical vapor deposition (PECVD) for the reference sample, while 8 nm of i-a-Si:H was deposited on the other samples. For the SHJ cell,

FIGURE 6 Effect of candidate electron-selective contact structures on the light IV parameters. A, J_{sc} . B, V_{oc} . C, FF. D, Efficiency. The numbers in the box plot are the average external parameters of the solar cells in that group, while the sample quantity of each group is indicated in (A) with braces ({}). [Colour figure can be viewed at wileyonlinelibrary.com]

a 4-nm-thick i-a-Si:H layer leads to the best cell results. For the other cells, 8-nm-thick i-a-Si:H was applied as this resulted in the best passivation quality without n-a-Si:H, as has been demonstrated previously.⁴² After HF dip, the TiO_x layer was deposited by ALD to obtain a layer thickness of 2 nm for the samples with the i-a-Si:H/TiO_x/Ca/Al structure. After ITO sputtering, Ag fingers (100 μ m wide, 17 μ m high) and full area Ag (thickness of 17 μ m) were printed on the front and rear sides of the reference cells, while this was only done on the front side of the other samples. Next, a belt furnace annealing at 175°C was performed to sinter the Ag contacts. In all samples but the reference SHJ cells, the rear metallization was completed with Al evaporation which was directly performed after Ca evaporation without breaking the vacuum. As the final step, the wafers were diced into solar cells of 5 $\times$ 5 cm².

Light IV characterization was conducted with an aperture opening of the same size as the active cell area of 4 $\times$ 4 cm² under calibrated illumination (AM 1.5, 1000 W/m² at 25°C). External quantum efficiency (EQE) and reflectance were measured in the same tool (PV-Tools LOANA, Germany) using a large beam size of 1.5 $\times$ 1.5 cm². Therefore, the EQE and reflectance results include the shading and reflecting effects of the metal grid.

3.2 | Solar cell results

The light IV parameters of the silicon solar cells with the different candidates for electron-selective contacts are shown in Figure 6 and Table 2. The IV curves of champion cells are found in Supporting Information Figure S2. The J_{SC} values of all solar cells appear to be rather low, most likely caused by parasitic absorption in the ITO and the i/p-a-Si:H stack on the front side of the cells. More specifically, the average J_{SC} of the solar cells with and the cells without TiO_x are similar (see Figure 6A) while the reference cell shows a somewhat higher J_{SC} . V_{OC} and FF are strongly dependent on the applied rear contact structure. ATOM contact which includes TiO_x, an average V_{OC} enhancement of 36 mV, and an average FF improvement of 2.3%_{abs} are achieved with respect to i-a-Si:H/Ca/Al contacted solar cells. The champion cell is a device with a TiO_x layer showing a V_{OC} of 711 mV. However, all cell parameters are still higher for the reference SHJ solar cells compared to the other cell structures, which will be discussed further at the end of this section.

To improve the understanding of the differences in J_{SC} , the EQE and reflectance curves were measured. As can be seen in Figure 7, much parasitic absorption in the front stack is inferred by low EQE response in short wavelengths. Moreover, the solar cell with the ATOM contact shows a similar EQE at longer wavelengths compared to the other candidate electron-selective contacts except for the

FIGURE 7 EQE and reflectance for the best cells of the various candidate electron-selective contact structures [Colour figure can be viewed at wileyonlinelibrary.com]

reference SHJ contact. In comparison to the i-a-Si:H/Ca/Al contacted solar cell, the lower J_{SC} of the solar cell with the ATOM contact structure is caused by a lower EQE at short wavelengths. An unintentional variation in front ITO thickness seems to play a role, which can be recognized by the peak shift of the reflectance at shorter wavelengths.

At long wavelengths, there is virtually no difference between the cell with the i-a-Si:H/Ca/Al contact and the cell with the i-a-Si:H/TiO_x/Ca/Al (ATOM) contact. This indicates that the amount of parasitic absorption occurring in substoichiometric TiO_x⁶⁴ is negligible. The differences with the other cells at long wavelengths can be explained by the impact of the specific metal layout on the rear reflectance (see Figure 7). According to Allen et al.,¹¹ the reflectance of the Ca/Al stack is lower than that for both Al and Ag. Furthermore, as shown in Supporting Information Figure S3 and Table S1, changing the metal from Ag to Ca/Al on i/n-a-Si:H/ITO reduces EQE and reflectance in the long wavelength range, similar to the result of the i-a-Si:H/Ca/Al contacted solar cell, while it does not change V_{OC} and FF. Although the high EQE at longer wavelengths for the reference cell is partially because of the superior rear surface passivation quality, most of the J_{SC} improvement is caused by the higher reflectance of Ag. For these reasons, strontium (Sr) and ytterbium (Yb) can be good alternatives to calcium (Ca) because of their superior reflectance properties, although still lower than Al.⁶⁵⁻⁶⁷

To further assess the contact performance and the V_{OC} values of the solar cells, Suns V_{OC} measurements have been conducted (see Figure 8). For the solar cells with i-a-Si:H/Ca/Al rear contacts, a bend (dashed circle areas in Figure 8) can be observed in the Suns V_{OC} curve above 1 sun illumination intensity. This phenomenon occurs when ρ_c is high (typically $>0.1 \Omega \text{ cm}^2$) based on the modified Ebers-Moll equivalent circuit analysis (see the circuit diagram in Figure 8).^{68,69} The measured ρ_c of Ca/Al was about $8 \Omega \text{ cm}^2$ (see, Table 1). In case of a high ρ_c value corresponding to the Ca/Al contacts, therefore, the overall cell output voltage is decreased because the voltage increase at the rear contact (oppositely directed Schottky diode) is larger than the voltage increase at the normal pn junction.

TABLE 2 Light IV parameters of the champion cells within the different contact groups

Candidate Electron-Selective Contact Structure	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)
i-a-Si:H/Ca/Al	35.2	666.3	70.9	16.6
i-a-Si:H/TiO _x /Ca/Al (ATOM)	35.1	710.8	72.9	18.2
i/n-a-Si:H/ITO/Ag	36.0	734.0	76.4	20.2

The active area and the aperture opening area: 16 cm².

FIGURE 8 Suns V_{OC} measurements of the best solar cell in each group. The corresponding circuit diagram is the modified Ebers-Moll equivalent circuit including a Schottky diode in the rear contact.⁶⁸ The bend in the curves measured for both Al and Ca/Al contact is marked using a dashed circle [Colour figure can be viewed at wileyonlinelibrary.com]

Different a-Si:H properties after annealing a-Si:H with and without TiO_x on the rear side might induce a large difference in V_{OC} between the i-a-Si:H/Ca/Al contacted and the ATOM contacted solar cells. However, similar hydrogen contents of i-a-Si:H after belt furnace annealing at 175°C could be expected because of the very low effusion rate of an i-a-Si:H layer at annealing temperatures below 300°C.⁷⁰⁻⁷³ Furthermore, the similar J_0 value in Table 1, the comparable EQE edge at the long wavelength range in Figure 7, and the overlapping Suns V_{OC} curves at the low injection level in Figure 8 support a similar contact passivation quality of both the i-a-Si:H/Ca/Al and the ATOM contacts.

Therefore, it can be seen that the low ρ_c of the ATOM contact leads to high external V_{OC} .

On the other hand, the reference contact shows the highest V_{OC} among the test groups because of the lower $J_{0,metal}$, typically below 10 fA/cm², and a strong field effect passivation. More downward band bending with a low ρ_c should be aimed for to improve the electron-selective contact performance, which will be discussed after the FF analysis.

Because the performance of the various contact structures investigated in this work is very different in their J_0 and ρ_c values, it is interesting to consider the FF losses in more detail as shown in Figure 9A. The series resistance of the solar cells is characterized using the Bowden method,⁷⁴ and the FF loss is outlined using the Khana method.⁷⁵ Generally, the FF can be expressed as:

$$FF = FF_{J01} - \Delta FF_{Rs} - \Delta FF_{Rsh} - \Delta FF_{J02} \quad (5)$$

where FF_{J01} is the maximum attainable FF for the particular cell considering only J_{01} recombination, ΔFF_{Rs} is the FF loss related to the series resistance of the solar cells as depicted in Figure 9B (including a ρ_c), ΔFF_{J02} is the FF loss resulting from J_{02} recombination (the recombination in the space charge region), and ΔFF_{Rsh} is the FF loss associated with the shunt resistance of the solar cells. In all these cells, ΔFF_{Rsh} was only a very minor loss factor (0.01%-0.02%), so it is not considered in further detail here.

In the solar cells with i-a-Si:H/Ca/Al contacts, the sum of FF_{Rs} and FF is already slightly higher (1%-2%) than FF_{J01} because of the lower accuracy of the analysis in case of these solar cells because of the low FF value. Therefore, the FF_{J02} values for the solar cells with i-a-Si:H/Ca/Al contacts are not mentioned in Figure 9A.

The very large ΔFF_{Rs} of 15% in the solar cell with an i-a-Si:H/Ca/Al rear contact can be significantly reduced by inserting the interfacial TiO_x layer. The resulting performance of the ATOM contacts incorporating TiO_x already yields a ΔFF_{Rs} below 10% and a R_s close to 2 $\Omega \text{ cm}^2$, which approaches the values measured for the reference SHJ contact (i/n-a-Si:H/ITO/Ag). This FF analysis underlines that an

FIGURE 9 FF, FF_{J01} , ΔFF_{Rs} , and ΔFF_{J02} comparison (A) and dependence of the total series resistance of solar cells (B) on the type of metal rear contact. The FF_{Rs} and FF_{J02} losses are indicated in (A) [Colour figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Benchmarking the solar cell results for different passivating electron-selective contact structures

Electron Contact Structure	Hole Contact Structure	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)
i-a-Si:H/TiO _x /Al ⁴⁰	i/p-a-Si:H/ITO/Ag	-	677	54.0	-
i-a-Si:H/TiO _x /ITO/Ag ⁴⁰	i/p-a-Si:H/ITO/Ag	-	492	29.2	-
i-a-Si:H/TiO _x /Al ⁷⁸	Boron diffused emitter/Cr/Pd/Ag	40.5	570	57	13.2
i-a-Si:H/TiO _x /Al/ITO/Ag ⁴¹	i/p-a-Si:H/ITO/Ag	35.5	612	71.3	15.5
i-a-Si:H/TiO _x /Ca/Al (ATOM, this work)	i/p-a-Si:H/ITO/Ag	35.1	711	72.9	18.2

added TiO_x layer is strongly beneficial when aiming to make a passivating electron-selective contact based on a low work function metal to finally obtain acceptably low values for both J_0 and ρ_c .

However, the ATOM contact could not yet achieve higher performance than the conventional SHJ contact (i/n-a-Si:H/ITO/Ag). As can be seen in Figure 9A, the lower FF of the cells with the ATOM contact when compared to the reference can be mainly attributed to the higher R_s and the larger recombination (ΔFF_{J02}). Taking into account that all cells have the same front structure, the R_s difference is caused by the rear contacts. The higher R_s of the ATOM contacted cells compared to the reference cell might come from a higher ρ_c resulting from the absence of an n-a-Si:H layer, or be induced by the much thinner rear metal than the printed Ag of the reference. In addition, without n-a-Si:H, and even with the TiO_x and the Ca, the band bending seems to be reduced. Next to that, the thicker i-a-Si:H layer in the ATOM contact (8 nm instead of 4 nm in the reference contact) increases the probability of carrier recombination through the defect states in this layer.

Overall, to improve the ATOM contact performance, it is required to achieve a lower series resistance maintaining similar or lower $J_{0,metal}$ by forming more downward band bending at the electron contacts. The work of Matsui et al⁷⁶ demonstrated that the band bending could be tunable by the ALD TiO_x growth conditions, likely because of the presence of fixed charge. Therefore, TiO_x material development to control the fixed charge can be another alternative to enhance the band bending. Additionally, replacing the Ca with a lower work function metal could help to bend the bands further down to repel minority carriers more effectively. Possible materials here are again Sr or Yb ($\Phi = 2.4$ – 2.5 eV instead of 2.9 eV for Ca⁷⁷). These results are first cells demonstrating the ATOM contact, and there is room for further improvement.

In Table 3, the IV parameters for the best ATOM contact cells fabricated in this work are compared with previously reported results.^{40,41,78} Especially, Ali et al⁷⁸ tested a-Si:H/TiO_x/Al contact in a boron diffused junction solar cell because of good contact passivation of a-Si:H/TiO_x with respect to SiO_x/TiO_x. However, the cell performance was likely limited by a high contact resistivity and high anneal temperature of 350°C. In the work of Sacchetto et al,⁴¹ a thin Al layer between TiO_x and ITO was applied to form additional oxygen vacancies in the TiO_x layer. However, it seems difficult to attain a good

carrier selectivity⁷⁹ (a low ρ_c and a low $J_{0,metal}$) by using TiO_x with not sufficiently low work function metals on an i-a-Si:H passivation layer. As illustrated in this work, combining TiO_x with a low work function metal such as Ca is an efficient route to decrease the ρ_c and preserve a low $J_{0,metal}$, such that the V_{OC} and FF values of the solar cells can be increased. Additionally, the low-temperature processing of the ATOM contact structure is compatible with the fabrication of hole-selective contacts based on high work function transition metal oxides.^{33–39}

Finally, it has been reported that the quality of the Ca/Al electrode can be reduced because of the penetration of water through the pinholes in the capping layers.^{80,81} Therefore, the stability improvement of ATOM contacts should also be a point of interest for future work.

4 | CONCLUSION

The ATOM contact structure including a TiO_x layer and a low work function metal on an a-Si:H passivation layer was evaluated as a candidate for a passivating electron-selective contact for c-Si solar cells. Applying ALD-TiO_x in the ATOM contact is an effective way to obtain a contact structure that combines good passivation properties with a low ρ_c . The integration of the ATOM contact into SHJ solar cells was successfully demonstrated and the best cell with an ATOM contact achieved a high V_{OC} of 711 mV, a FF of 72.9%, J_{SC} of 35.1 mA/cm², and an efficiency of 18.2%. However, the absence of a n-a-Si:H layer in the ATOM contact leads to losses in V_{OC} and FF possibly caused by a weaker field effect passivation. These challenges may be overcome by applying a metal with a lower work function and possibly a higher reflectance than Ca, double side randomly textured substrates, improved i-a-Si:H passivation with thinner thickness, and the use of positively charged TiO_x or extrinsically doped TiO_x.^{82–87} Although the maximum efficiency of the ATOM contacted solar cell was lower than the more optimized conventional SHJ solar cell, the presented results indicate that the ATOM contact can pave the way toward highly efficient silicon solar cells without heavily doped Si layer.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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