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Performance and Thermal Stability of an a-Si:H/TiO_x/Yb Stack as an Electron-Selective Contact in Silicon Heterojunction Solar Cells

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Supporting Information

ABSTRACT: Low contact resistivity (ρ_c) and low recombination current density at the metallized area ($J_{0,\text{metal}}$) are the key parameters for an electron-selective contact in solar cells, and an i-a-Si:H/TiO_x/low work function metal (ATOM) structure could satisfy these criteria. In this work, to achieve strong downward band bending, an Yb ($\Phi = 2.5\text{--}2.6$ eV)/Ag stack is used. Moreover, the impact of (1) substrate topography (flat or textured), (2) TiO_x thickness, and (3) Ti precursor (TTIP vs TDMAT) on the ATOM contact performance is investigated. The results show that the ATOM contact is relatively insensitive to the surface topography and to the Ti precursors (TTIP or TDMAT) used for the atomic layer deposition (ALD) of TiO_x. However, the TiO_x thickness has a significant impact on the ρ_c and marginally on the $J_{0,\text{metal}}$ of the ATOM contact. For all topography cases and Ti precursors, 1 nm thick TiO_x results in the lowest ρ_c value, most likely due to $E_{F,\text{metal}}$ depinning. In the silicon heterojunction solar cell, this ATOM contact (i-a-Si:H/TiO_x/Yb/Ag) yields a solar cell efficiency of 19.2% with a high V_{OC} of 723 mV without the need of a doped n-a-Si:H layer. Concerning the thermal stability of these contacts, TEM images confirm that Yb does not diffuse into the i-a-Si:H layer after an annealing at 180 °C for 30 min thanks to the TiO_x layer behaving as a diffusion barrier. 98% of the initial solar cell efficiency is preserved even after successive annealing treatments at 150 and 175 °C, which are values in the same temperature range used in the module lamination and the sintering of the printed Ag. These results in combination with the demonstrated efficiency underline that the ATOM contact is a promising route to realize high-efficiency solar cells.

KEYWORDS: low work function metal, Yb, MIS contact, electron-selective contact, passivating contact

1. INTRODUCTION

Two-side-contacted silicon heterojunction (SHJ) solar cells are very attractive because of the high-efficiency potential and the relatively simple process flow for fabrication.¹ Intrinsic hydrogenated amorphous silicon (i-a-Si:H) layers in SHJ solar cells provide excellent chemical surface passivation, while n-type or p-type hydrogenated amorphous silicon (n-a-Si:H or p-a-Si:H) layers, added on top of the i-a-Si:H, induce band bending at the surface region of the c-Si substrate, which results in field-effect passivation. The band offsets between the c-Si and a-Si:H stacks give rise to the electron and hole

selectivity at the a-Si:H (i/n) and a-Si:H (i/p) contacts. In spite of the good chemical and field-effect passivation of the a-Si:H stack (i/n or i/p), there are significant optoelectrical losses associated with a-Si:H, in particular when it is doped.² For this reason, fine-tuning the deposition conditions and the layer thickness of doped a-Si:H is required to minimize those losses. In another approach, carrier-selective contacts can also

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be realized without such doped layers, by using transition metal oxides (TMOs) instead. TMOs have been recently getting more attention because of their high band gap, typically above 3 eV, and their asymmetric band structure with respect to c-Si.^{3–5}

Typically, contacts that do not include a doped layer have relatively high contact resistivity (ρ_c) and low contact passivation quality,⁶ characterized by a high recombination current density (J_0), because of a weak or undesired band bending. By introducing metal oxide layers in solar cell contacts, advantageous band bending and contact passivation have been achieved. Depending on the work function and band offsets, TMOs can be used as either electron- or hole-selective contacts to replace heavily doped regions and doped a-Si:H layers. Regarding electron-selective contacts, several research groups have demonstrated low ρ_c and low J_0 using different metal oxides/nitrides in combination with different metals, such as TiO_x/Al ,^{7–9} MgO_x/Al ,¹⁰ NbO_x/Al ,^{11,12} $\text{TaO}_x/\text{Mg}/\text{Ag}$,¹³ and TaN_x/Al .¹⁴ Moreover, to further reduce ρ_c , lower work function metals have been investigated either individually, e.g., Ca/Al ,¹⁵ or in combination with other materials such as alkaline earth metal fluorides, e.g., LiF/Al ⁴ and MgF/Al ^{16,16} and/or metal oxides, e.g., $\text{TiO}_x/\text{LiF}/\text{Al}$ ³ and $\text{TiO}_x/\text{Ca}/\text{Al}$.^{6,17–19}

On the other hand, as hole-selective contacts, TMOs with a high work function, i.e., MoO_x , WO_x , and VO_x have also been intensively studied by many groups to replace p-a-Si:H in SHJ solar cells because these TMOs induce upward band bending at the hole contact region with reduced parasitic absorption.^{20–26} When TMO-based hole- and electron-selective contacts are integrated into the same device, doping processes or doped layers can be completely eliminated. However, the deposition of TMO layers enforces a more constrained processing window where the temperature should be kept below approximately 180 °C to avoid severe performance degradation of TMOs.^{27,28}

To satisfy these requirements, the ATOM (i-a-Si:H/ TiO_x /low work function metal) contact has been developed as a high-quality electron-selective contact structure without an n-type a-Si:H layer,^{6,17} having a metal–insulator–semiconductor (MIS) structure where i-a-Si:H and TiO_x act as the semiconductor and the insulator, respectively. The i-a-Si:H layer is the main contact passivation layer, but placing a metal directly in contact with i-a-Si:H would result in the pinning of its Fermi level.^{29,30} For a simple test structure resembling a classical SHJ solar cell with i-a-Si:H/metal as the electron contact,³⁰ the pinning factor (S) for this contact structure is estimated to be around 0.3,³⁰ which indicates that strong pinning occurs on the a-Si:H/metal interface. To mitigate this problem in the ATOM contact, a thin TiO_x layer is used. Inserting the TiO_x layer between i-a-Si:H and the metal reduces the ρ_c thanks to the metal Fermi level depinning effect.^{6,17}

Atomic layer deposition (ALD) has been demonstrated as a promising fabrication method to grow TiO_x such that the passivation quality provided by the underlying a-Si:H passivation layer is preserved.^{17,31} Using the i-a-Si:H/ TiO_x /Ca ($\Phi = 2.9$ eV) stack with an Al capping layer,¹⁷ where Ca is the low work function metal of the ATOM contact, a low ρ_c of 15 $\text{m}\Omega\cdot\text{cm}^2$ and a low $J_{0,\text{metal}}$ (recombination current density at the metallized areas) of about 13 fA/cm^2 could be achieved, which represents an excellent electron-selective contact. In our previous work, this electron-selective ATOM contact was

studied using titanium isopropoxide ($\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$, TTIP) as the ALD Ti precursor and a fixed TiO_x thickness of 2 nm on a flat surface.¹⁷ However, a detailed parameter study of the ATOM contact was not performed in previous work.¹⁷

In this work, the influence of the substrate topography and the TiO_x thickness on the ATOM contact performance was studied in detail. Furthermore, a new Ti precursor (tetrakis-(dimethylamido)titanium ($\text{Ti}[\text{N}(\text{CH}_3)_2]_4$, TDMAT, 0.43 Å/cycle at 225 °C) was also investigated as an alternative ALD Ti precursor to TTIP because of its potential to overcome the lower growth rate per cycle (0.18 Å/cycle at 200 °C) when using TTIP. As a low work function metal, Yb ($\Phi = 2.5$ –2.6 eV) was applied instead of Ca ($\Phi = 2.9$ eV) in the ATOM contact structure^{32,33} to enhance the downward band bending at the contact region because of its lower work function. Then, SHJ solar cells were fabricated using the optimized ATOM contact based on i-a-Si:H/ TiO_x /Yb/Ag. As a reference, SHJ solar cells with an i-a-Si:H/Yb/Ag (no TiO_x or n-a-Si:H) contact and a classical i/n-a-Si:H/ITO/Ag contact were also fabricated. Finally, the thermal stability of the developed ATOM contact was also studied using annealing treatments at various temperatures.

2. EXPERIMENTAL METHODS

2.1. Sample Preparation. **2.1.1. Test Structures for J_0 , $J_{0,\text{metal}}$ and ρ_c Evaluation.** Double-side textured (3.3 $\Omega\cdot\text{cm}$, 180 μm thickness) and double-side chemically polished (3.7 $\Omega\cdot\text{cm}$, 180 μm thickness) n-type Cz-Si wafers were used to measure ρ_c and $J_{0,\text{metal}}$ to assess the contact performance. After wafer cleaning using $\text{O}_3/\text{HCl}/\text{DI H}_2\text{O}$ and HF/HCl solutions, an 8 nm thick intrinsic a-Si:H layer was deposited on the front and rear of the substrates by plasma-enhanced chemical vapor deposition (PECVD). After a short HF dip, a TiO_x layer was deposited using a spatial thermal atomic layer deposition (ALD) tool on the front and rear side of the substrates to make a symmetrical sample structure while varying the film thickness from 1 to 4 nm. Either TDMAT (0.43 Å/cycle at 225 °C) or TTIP (0.18 Å/cycle at 200 °C) was used as the Ti precursor and H_2O as the oxidant species.

For the $J_{0,\text{metal}}$ characterization, a very thin Yb (4 nm)/Ag (5 nm) stack was sequentially thermally evaporated on top of the i-a-Si:H/ TiO_x layers at the rear side without breaking the vacuum (see Figure 1a,b). The J_0 value was determined using quasi-steady-state

Figure 1. Schematic sample structure to determine: (a) J_0 , (b) $J_{0,\text{metal}}$ and (c) ρ_c .

photoconductance (QSSPC) measurements. The $J_{0,\text{total}}$ was calculated assuming a typical J_{SC} value of 36 mA/cm^2 in our SHJ cells. The values of $J_{0,\text{total}}$ for all the samples before and after metallization were compared. The $J_{0,\text{bulk}}$ of the Cz wafer was determined to be approximately 3 fA/cm^2 , by comparing the $J_{0,\text{total}}$ of a symmetrical i-a-Si:H-passivated Cz wafer with that of a high-quality float zone wafer (n-type, 200 μm , 3.3 $\Omega\cdot\text{cm}$).

For ρ_c characterization, an Yb (40 nm)/Ag (150 nm) stack was sequentially thermally evaporated on the front side with a shadow mask with a contact pattern and on the rear side without any mask.

Figure 2. (a–c) Schematic cross-sectional solar cell structures with the following electron-selective contact structures: (a) i-a-Si:H/Yb/Ag (Yb-contacted cell), (b) i-a-Si:H/TiO_x/Yb/Ag (ATOM-contacted cell), and (c) i/n-a-Si:H/ITO/Ag (classical SHJ cell). (d) Process flowchart for the cell fabrication.

Figure 3. Comparison of the ATOM contact performance as a function of TTIP- and TDMAT-TiO_x thickness in terms of ρ_c on flat (a) and on textured (b) surfaces and $J_{0,\text{metal}}$ on flat (c) and on textured (d) surfaces.

(see Figure 1c), resulting in contact pads with varying diameters (250–2000 μm) on the front side. The ρ_c value of the electron contact was determined using the two-contact–two-terminal method in order to include all resistive components of the contact in the measured ρ_c .^{6,34} More details on the sample preparation and the methods used to measure and calculate the ρ_c and J_0 are described in the Supporting Information (Figure S1 and eqs S1–S4) and elsewhere.^{6,17}

The layers of this ATOM contact and their interfaces, as well as the elemental distribution, were analyzed by transmission electron microscopy (TEM), high-angle annular dark-field imaging in scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive X-ray spectroscopy (EDX). The procedure for TEM sample preparation is explained in the Supporting Information.

2.1.2. Solar Cells. The ATOM contact structure was applied in two-side-contacted SHJ cells. The schematic structures of the three cell types fabricated in this work are shown in Figure 2a–c. All of the cell structures investigated had the same hole-selective contact featuring the i/p-a-Si:H/ITO/Ag stack on the front side. On the rear side different electron-selective contacts were applied: i-a-Si:H/Yb/Ag (Yb-contacted cell) and i-a-Si:H/TDMAT-TiO_x/Yb/Ag (ATOM-contacted cell) as dopant-free electron-selective contact candidates, and the reference electron-selective contact, i/n-a-Si:H/ITO/Ag, which is commonly used in a classical SHJ cell. These contact structures will be simply referred to as Yb-contacted, ATOM-contacted, and classical SHJ cell, respectively.

To fabricate these solar cells as summarized in Figure 2d and also described in ref 17, n-type Cz–Si wafers (4.8 $\Omega\cdot\text{cm}$, 180 μm thickness) with double-side textured surfaces were used. After HF:HCl:O₃ and HF:HCl cleaning,³⁵ the 8 nm thick i-a-Si:H and 8 nm thick p-a-Si:H layers were 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 8 nm, respectively, were deposited at 175 $^{\circ}\text{C}$ by PECVD for the classical SHJ sample, while only an i-a-Si:H layer with a thickness of 8 nm was deposited on the other samples. The reason for the different i-a-Si:H thickness is that, for the classical SHJ cell, a 4 nm thick i-a-Si:H layer is sufficient to achieve the best cell results. On the other hand, for cells incorporating an ATOM contact, an 8 nm thick i-a-Si:H layer is needed⁶ to achieve high-quality passivation in the absence of n-a-Si:H. The rear side of the three cell types were prepared differently. For the ATOM-contacted cell, after a short HF dip, a 1 nm thick TDMAT-based TiO_x layer was deposited by ALD. ITO on the front side was deposited by sputtering for the three cell types, while ITO on the rear side was deposited only for the classical SHJ cells. Subsequently, a Ag front grid (with fingers 80 μm wide and 17 μm high) was realized for all of the cells using screen-printing, and full-area Ag (17 μm thick) at the rear side of the classical SHJ cells was also performed by screen-printing. All the cells were then annealed using a belt furnace at 160 $^{\circ}\text{C}$ for about 25 min in N₂ atmosphere to sinter the printed Ag contacts. For the Yb-contacted and ATOM-contacted cells, a 40 nm thick Yb and a 150 nm thick Ag stack was thermally evaporated (sequentially without vacuum break) on the rear side of the cells. As the final step, the wafers were diced into solar cells of 5 $\times$ 5 cm² with an active cell area of 4 $\times$ 4 cm².

The illuminated IV parameters were measured with an aperture opening of the same size as the active cell area of 4 $\times$ 4 cm² under calibrated illumination (AM 1.5G, 1000 W/m² at 25 $^{\circ}\text{C}$). External quantum efficiency (EQE) and reflectance were measured using an illumination spot size of 1.5 $\times$ 1.5 cm². Therefore, the EQE and reflectance results include the shading and reflection effects of the front metal grid.

2.2. Annealing Experiments. **2.2.1. Test Structures.** To investigate the thermal stability of the contact structures investigated in this work, another set of samples, with the structure given in Figure 1c, was prepared for contact resistivity measurements using textured wafers, with and without the TiO_x layer, in a manner similar to that described in section 2.1. These samples were annealed at 150 or 180 $^{\circ}\text{C}$ in N₂ atmosphere using a rapid thermal annealing system. After every 10 min of annealing, the ρ_c was measured. These particular annealing temperatures were chosen because the temperature range of

150–180 $^{\circ}\text{C}$ is used during the sintering of printed Ag for SHJ solar cells and during the lamination process for module fabrication.

2.2.2. Solar Cells. After cell fabrication, the ATOM-contacted solar cell was annealed in a rapid thermal annealing system to evaluate its thermal stability, using a method described elsewhere.³ The illuminated IV characteristics were measured after successive anneals in N₂ atmosphere for 10 min each, and at incrementally increasing temperatures between 150 and 225 $^{\circ}\text{C}$ with a temperature step of 25 $^{\circ}\text{C}$. Therefore, the last measured point corresponds to a cumulative annealing time of 40 min.

3. RESULTS AND DISCUSSION

3.1. Contact Performance Evaluation. To get a better understanding of the ATOM contact, the performance parameters of this contact, such as ρ_c and $J_{0,\text{metal}}$, were investigated as a function of (1) Ti precursor for TiO_x growth, (2) TiO_x thickness, and (3) topography of the c-Si substrate.

As shown in Figure 3a,b, when the Yb/Ag metal stack is in direct contact with i-a-Si:H in the absence of TiO_x, the ρ_c value is very high on both flat and textured surfaces likely due to the formation of a Schottky energy barrier as a result of metal Fermi level pinning. The corresponding ρ_c values are all above 0.1 $\Omega\cdot\text{cm}^2$, which is typically considered as the upper limit for the integration of any contact into silicon solar cells.^{5,36} For the ATOM contact, the TiO_x thickness has a strong impact on ρ_c . The ρ_c values in a MIS (metal–insulator–semiconductor) contact depend strongly on the thickness of the insulator,³⁷ which is TiO_x in this study and which is positioned between the i-a-Si:H and the Yb layers. An ohmic contact is achieved when the TTIP-TiO_x thickness is 1 or 2 nm and when the TDMAT-TiO_x thickness is 1 nm in the ATOM-contact structure. All the other contacts are Schottky contacts. An overview of the IV curves and the method used to determine ρ_c of the Schottky contacts in this study is described in the Supporting Information. Note that the five ρ_c values of each condition are included in the box graphs of Figure 3a,b. The optimum thickness of the TiO_x layer is the one for which the $E_{\text{F,metal}}$ pinning is effectively reduced while the tunneling resistance through the layer is still as low as possible. This explains why the lowest ρ_c was achieved for a TiO_x thickness of 1 nm for both Ti precursor cases: for TDMAT-TiO_x, this corresponds to 1.7 m $\Omega\cdot\text{cm}^2$ on a flat surface and 1.0 m $\Omega\cdot\text{cm}^2$ on a textured surface, while for TTIP-TiO_x, this is 11 m $\Omega\cdot\text{cm}^2$ on a flat surface and 23 m $\Omega\cdot\text{cm}^2$ on a textured surface. Whereas TDMAT-TiO_x exhibits lower ρ_c at 1 nm thickness compared to TTIP-TiO_x, the opposite is true for higher TiO_x thicknesses. This faster increase in ρ_c for TDMAT-TiO_x is typically resulting from different tunneling resistance of the layer³⁸ which might be induced by slight variations in thickness (i.e., slightly thicker TDMAT-TiO_x) or/and by differences in density of oxygen vacancies in TiO_x, which affects electron density and band bending.³⁹

Furthermore, the ρ_c values of i-a-Si:H/2 nm-TTIP-TiO_x/Ca/Al (on a flat surface)¹⁷ and i-a-Si:H/2 nm-TTIP-TiO_x/Yb/Ag (this work, on a flat surface) are in the similar range of several tens of m $\Omega\cdot\text{cm}^2$. This means that the difference of 0.3–0.4 eV in work function between Ca (Φ = 2.9 eV) and Yb (Φ = 2.5–2.6 eV) might not significantly affect the ρ_c , or that this difference might have been screened out due to the nonoptimal TiO_x thickness of 2 nm in the MIS contact.⁴⁰

As to the $J_{0,\text{metal}}$ of the ATOM contacts, the flat and textured surfaces are comparable for each TiO_x thickness, and a weak decreasing trend is observed with respect to the TiO_x thickness (see Figure 3c,d). However, since there is no direct contact

Figure 4. TEM cross-sectional images for ATOM contact structures (a, b) and chemical component distribution images measured by EDX measurement with high-angle annular dark-field imaging (HAADF), (c, d), before metallization: (a, c) TTIP-TiO_x and (b, d) TDMAT-TiO_x.

Figure 5. TEM cross-sectional image of ATOM contact structures (a, b) and chemical component distribution images measured by EDX measurement (c, d) after metallization of Yb/Ag: (a, c) TTIP-TiO_x and (b, d) TDMAT-TiO_x.

between the absorber and the TiO_x layer, it is not very surprising that the $J_{0,\text{metal}}$ does not strongly depend on the TiO_x thickness, as the passivation quality is largely determined by the i-a-Si:H layer. Taken together, a TiO_x thickness of 1 nm with both Ti precursors appears to be the optimal condition for solar cells because of the resulting lowest ρ_c on textured surfaces (see Figure 3b) in combination with a low $J_{0,\text{metal}}$ below 25 fA/cm² (see Figure 3d).

To investigate the contact structure in more detail, a TEM analysis was carried out on a textured sample with 1 nm TiO_x before and after metallization (see Figures 4 and 5). As can be seen in Figure 4a,b, epitaxially grown crystallized a-Si:H at the c-Si/a-Si:H interface is shown because of a phase transition from crystalline to amorphous, which has been reported elsewhere.^{41,42} This phenomenon could be mitigated by applying a porous a-Si:H layer on c-Si.^{43,44} As for the TiO_x, the thickness of the deposited TiO_x layer corresponds to the nominal thickness of 1 nm, and the TiO_x layer is closed while it conformally covers the i-a-Si:H surface. As shown in Figure 4c,d, the interfacial SiO_x formed as a result of the ALD TiO_x process, can be found underneath both TTIP- and TDMAT-TiO_x, although the thickness of this SiO_x layer is slightly different in both cases. The SiO_x thickness increases after metal

evaporation as shown in Figure 5, but the thickness increase is more pronounced for TTIP-TiO_x. Such interfacial SiO_x formation has already been shown in the literature¹⁷ and it is probably the result of oxygen migration from the TiO_x toward the substrate during the TiO_x deposition,⁴⁵ as there was no additional thermal treatment. The thicker SiO_x layer formed underneath the TTIP-TiO_x layer might be due to the longer processing time that is needed for TTIP-TiO_x when compared to the TDMAT-TiO_x process. Also, a different oxygen concentration of the TiO_x layers might contribute to the effect. Nevertheless, a relatively lower ρ_c value of the contact stack with 1 nm of TDMAT-TiO_x compared to that with 1 nm of TTIP-TiO_x is probably due not only to the slightly thinner i-a-Si:H layer but also to the significantly thinner SiO_x layer when compared to TTIP-TiO_x.

Even without an additional postdeposition thermal annealing treatment, the Yb layer is partially mixed with Ag. According to the literature,⁴⁶ temperatures above 446 °C are required to form an Yb–Ag alloy. Nevertheless, the driving force to alloy both metals may be different when combining very thin layers of Yb and Ag and may be influenced by the presence of any other impurities in the contact stack. This mixing might result in the negligible difference observed above

Figure 6. Light IV results of the solar cells with different electron contacts: (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) efficiency. The numbers of samples are 4, 4, and 8 for Yb-contacted, ATOM-contacted, and classical SHJ cells, respectively.

Table 1. Champion Solar Cells for Each of the Different Rear Contact Structures (Cell Area, 16 cm²)

structure	rear surface	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)	R_s (Ω ·cm ²)
i-a-Si:H/Yb/Ag	textured	33.5	607	75.9	15.4	1.8
i-a-Si:H/TDMAT-TiO _x /Yb/Ag(ATOM)	textured	33.8	723	78.6	19.2	0.97
i/n-a-Si:H/ITO/Ag	textured	35.4	732	79.5	20.6	1.1

between Yb and Ca as the low work function metal in terms of ρ_c .

Moreover, both TTIP- and TDMAT-TiO_x layers have been in-diffused with Yb, which might make for more favorable condition for downward band bending. When Yb acts as a dopant in TiO_x, the Fermi level of TiO_x could be shifted up because Yb reduces the density of deep traps in the TiO_x layer.⁴⁷ Yb nevertheless forms a closed layer on top of the TiO_x layer (see Figure 5c,d), such that the low work function of Yb can still induce downward band bending in the contact region. According to the literature, a few angstroms of metal is already sufficient to bring metal-induced band bending to the underlayer,⁴⁸ and even when part of the Yb layer oxidizes to YbO₃, the low work function associated with the desired downward band bending is preserved.⁴⁹ Although the metal layers were mixed during the process, Yb and Ag do not pass through the TiO_x layer and thus there is no diffusion of metal into the i-a-Si:H, which would have led to a dramatic increase in J_0 . Yb confinement by TiO_x will be discussed further in the section on thermal stability of the ATOM contacts.

3.2. Integration of ATOM Contacts into SHJ Solar Cells. Since the lowest ρ_c value is obtained for a 1 nm thick TDMAT-TiO_x layer, with a corresponding $J_{0,metal}$ of 24 fA/cm² on a textured surface (see Figure 3b,d), TDMAT-TiO_x with a thickness of 1 nm in combination with Yb was tested further in solar cells. The schematic cell structures with the different candidates for the electron-selective contacts are shown in Figure 2.

The illuminated IV parameters for the three cell types are shown in Figure 6, and the parameters of the champion cell of

each group are listed in Table 1. The Yb-contacted (no TiO_x and no n-a-Si:H) solar cells perform the worst, particularly in terms of V_{oc} and FF. As reported in the literature,^{17,36,50} the high ρ_c values obtained for this contact structure due to the existence of a Schottky barrier result not only in a FF loss but also in a V_{oc} loss. For the case of Al^{51,52} or Ni⁵³ on a-Si:H, metal-induced crystallization of a-Si:H led to severe passivation degradation resulting in a low V_{oc} . However, Yb seems not to crystallize i-a-Si:H, as indicated by the low $J_{0,metal}$ value of 25 fA/cm² which is similar to the ATOM contact which contained noncrystallized a-Si:H (see Figure 3c,d). The TiO_x layer in the ATOM contact significantly increases the FF and the V_{oc} of the solar cells with respect to Yb-contacted solar cells. This also correlates well with the much lower ρ_c value for this contact, which is the result of the expected metal Fermi depinning effect of the TiO_x layer. As such, the FF and the V_{oc} of the ATOM-contacted cells are at a level similar to those of the classical SHJ cells, which suggests that a strong band bending could be achieved by Yb in combination with a 1 nm thick TiO_x layer, even without the use of any doped layers (e.g., n-a-Si:H).

Both the Yb-contacted and the ATOM-contacted solar cells showed a lower average J_{sc} compared to the classical SHJ devices. In a previous study, an i-a-Si:H/TTIP-TiO_x/Ca/Al contact structure was applied to achieve a solar cell efficiency of 18.2% with a V_{oc} of 711 mV and FF of 72.9%. In comparison, the champion ATOM-contacted cell in this work yielded a higher V_{oc} of 723 mV and a higher FF of 78.6% resulting in an efficiency of 19.2% (see Table 1).

Figure 7. (a) Series resistance of the solar cells in this work implementing different electron contacts. (b) Fill factor loss analysis of the champion cells in each group.

Figure 8. Results of the optical loss analysis for the champion solar cell of each group: (a) i-a-Si:H/Yb/Ag contact, (b) i-a-Si:H/TiO_x/Yb/Ag contact, and (c) i/n-a-Si:H/ITO/Ag contact. (d) Comparison of the absolute J_{sc} loss associated with each loss component in the solar cells.

A detailed FF loss analysis was done on the cells of this work presented in Table 1. The R_s value for the solar cells in this

work is quantified by using the Bowden method⁵⁴ and is plotted in Figure 7a, while the FF loss analysis is carried out

Table 2. Benchmarking Results of SHJ Solar Cells Using i-a-Si:H/TiO_x Stack in Electron Contacts

electron contact structure	TiO _x thickness (nm)	metal work function (eV)	<i>J</i> _{SC} (mA/cm ²)	<i>V</i> _{OC} (mV)	FF (%)	η (%)	size (cm ²)
i-a-Si:H/TiO _x /Al ⁶¹	3.5	4.3		677	54.0		4 or 1
i-a-Si:H/TiO _x /ITO/Ag ⁶¹	3.5	4.4–4.5		492	29.2		4 or 1
i-a-Si:H/TiO _x /Al/ITO/Ag ⁶²		4.3	35.5	612	71.3	15.5	4
i-a-Si:H/TiO _x /Ca/Al ¹⁷ (ATOM)	2	2.9	35.1	711	72.9	18.2	16
i-a-Si:H/TiO _x /LiF/Al ³	1.5	2.9	37.5	713	78.1	20.9	4
i-a-Si:H/TiO _x /Yb/Ag (ATOM, this work)	1	2.5–2.6	33.8	<u>723</u>	<u>78.6</u>	19.2	<u>16</u>

following the approach of Khanna et al.⁵⁵ and is plotted in Figure 7b. The FF loss related to the shunt resistance is not mentioned due to its negligible contribution. Moreover, for the i-a-Si:H/Yb/Ag-contacted solar cells, the sum of FF and FF_{R_s} already exceeds FF_{J₀₁}, which is the maximum available FF considering only J₀₁ recombination and therefore FF_{J₀₂} is not depicted. When R_s of cells is too high, such as in the case of the Yb-contacted cell, the accuracy of the loss analysis is reduced and some mismatch in values of loss factors could occur.¹⁷ As shown in Figure 7a and Table 1, the R_s value of the Yb-contacted cells is significantly higher than that of the ATOM-contacted cells. The contribution of the thin Ag and Yb layers to the R_s of the solar cells is likely marginal due to the very low sheet resistance of the metal stack of about 0.15 Ω/□ when considering ρ_{Ag} and ρ_{Yb} values of 2.3 μΩ·cm^{56,57} and 45 μΩ·cm,⁵⁸ respectively. In addition, a full-area metal chuck in the illuminated IV measurements could further reduce the resistance loss resulting from R_{sheet} of the metal at the rear side of the cells. This is reflected in the fact that the main FF loss component for Yb-contacted cells, in Figure 7b, is the series resistance, FF_{R_s}. Inserting a 1 nm thick TiO_x layer between i-a-Si:H and Yb significantly reduces the FF_{R_s} loss from 6.7%_{abs} to 4%_{abs}, which corresponds to a 40%_{rel} reduction due to the presence of TiO_x that likely induces E_{F,metal} depinning. In fact, the FF_{R_s} loss of the ATOM-contacted cell is even lower than that for the classical SHJ cells and the ATOM contact enables a lower contact resistivity of only a few mΩ·cm² (see Figure 3) compared to 100–200 mΩ·cm² that is known for the traditional i/n-a-Si:H/ITO/Ag contacts. The higher FF_{J₀₂} loss in the ATOM-contacted solar cells could be attributed to the thicker i-a-Si:H layer and weaker band bending at the electron contact compared to the classical SHJ contact. This challenge should be adequately addressed to close the gap in performance between the ATOM-contacted and the classical SHJ solar cells.

To understand the optical losses, a detailed J_{SC} loss analysis was done following the method described in ref 59, which is based on EQE and wavelength-dependent reflectance. In this study, light transmission through the cells was assumed to be zero because of the full-area metallization on the rear side of the cells.

Panels a–c of Figure 8 depict the different spectral losses leading to the eventual EQE, namely, (1) front shading, (2) front reflection, (3) front escape, and (4) parasitic and/or recombination losses (at three wavelength ranges), in the three solar cell types investigated in this work. These losses are quantified in terms of their noncontribution to the J_{SC} of the cell in Figure 8d. The losses associated with the front shading and the front reflection are approximately the same for all of the devices because those contributions are defined by the front side structure (metal grid, textured surface, and so on),

which is common to all devices investigated here. The front escape refers to the reflected light at the rear side, especially middle and long wavelength light, which can escape back out of the front side without being fully absorbed by the silicon. The parasitic absorption losses come from optically unwanted absorption in a-Si:H, ITO, TiO_x, and/or metal layers, which eventually do not contribute to the device current. The recombination losses are due to an imperfect collection of generated carriers. A solid red line in the figures denotes the ideal EQE for a cell where the c-Si wafer thickness is 180 μm.

In all three cell structures, there is a similar significant amount of parasitic absorption on the front side of the solar cell due to the presence of ITO and i/p-a-Si:H layers. However, at long wavelengths (1000–1200 nm), the parasitic absorption/recombination losses are different for the three contact structures, which is the reason for the lower J_{SC} in the ATOM- or Yb-contacted solar cells compared to the reference SHJ devices. Low EQE at long wavelength might occur because of the close proximity of the metal to the c-Si absorber on the rear side, leading to the penetration of the evanescent waves to the rear metal and surface plasmons at the metal reflector.⁶⁰ These parasitic losses are prevented in the SHJ cells by having an ITO layer which acts as an optical buffer. Those parasitic absorption losses could be reduced by applying a highly reflective metal, such as Al or Ag. However, those metals yield a high contact resistivity due to insufficiently low work functions and other side effects (e.g., p-doping effect of Al). As discussed in the Introduction, Al can be used when it is combined with alkaline rare-earth metal fluoride LiF or MgF, which do have a low work function of 2.9 eV⁴ and 3.5 eV¹⁶, respectively. For these cases, precise thickness control for layers thinner than 1 nm has to be carefully considered. Therefore, highly reflective low work function metals would be very interesting for solar cell application.

As shown in Table 2, when an electron contact was formed using thick TiO_x with relatively high work function metals, simultaneously achieving FF above 70% with V_{OC} above 700 mV is very challenging. However, i-a-Si:H and a TiO_x layer thinner than 2 nm, combined with a low work function metal, was very effective in attaining high V_{OC} and FF. The ATOM-contacted cell of this work achieved superior V_{OC} and FF in relatively larger cells thanks to the a-Si:H passivation, the likely Fermi level depinning effect induced by the TiO_x layer, and the low work function metal, Yb.

4. THERMAL STABILITY OF THE ATOM CONTACTS

4.1. Influence of Annealing on ρ_c. A good reliability of the metal contacts in a solar cell is obviously an essential criterion. Furthermore, the layers that are present in a solar cell need to be able to withstand the lamination process that is required to fabricate modules. Therefore, an additional thermal budget has to be applied after the cell manufacturing process. Recently, Bullock et al. have demonstrated acceptable thermal

Figure 9. (a) Contact resistivity dependence on annealing temperature and time (five data points per group). (b) TEM cross-sectional images for ATOM contact and (c) chemical component distribution images measured by EDX, after annealing at 180 °C for 30 min.

stability in solar cells that included a TiO_x layer between a-Si:H and LiF/Al, which passed the damp-heat test (1000 h, 85 °C, 85% humidity).³

To evaluate the thermal stability, postannealing treatments were done on the ATOM-contact structure at two different temperatures and the ρ_c was intermittently measured. Figure 9, which plots ρ_c as a function of cumulative annealing time, shows that as the annealing time increases, the ρ_c value of the ATOM contact increases. At a higher annealing temperature, the escalation in ρ_c is faster. After annealing at 150 °C for 30 min, the average ρ_c of the ATOM contact is $0.15 \Omega \cdot \text{cm}^2$, which is slightly above the earlier mentioned limit of $0.1 \Omega \cdot \text{cm}^2$ for device integration. The annealing-induced change in ρ_c could be linked to the transformation of the interface at the contact region. To investigate this, TEM and EDX analyses were conducted using the samples annealed at 180 °C for 30 min. As shown in Figure 9b, the i-a-Si:H passivation layer is clearly distinguished from the blurred TiO_x/Yb/Ag stack. Moreover, no Yb is found in the i-a-Si:H layer of the ATOM contact (see Figure 9c). TiO_x seems to work as a barrier layer against Yb diffusion; therefore, the presence of the TiO_x layer may be beneficial to preserve the passivation quality even after the annealing process. The increase in ρ_c after annealing for the ATOM contacts (see Figure 9a) might be related to oxygen diffusion from the TiO_x layer into the metal stack of Yb/Ag such as that observed in the cases of TiO_x/Ti⁶³ and TiO_x/Ca/Al.¹⁹ This could be inferred from the EDX map shown in Figure 9c, where O is detected throughout the thickness between and including the TiO_x and Yb layers. The oxygen movement from TiO_x to the metal might be preferred due to the already existing SiO_x layer between TiO_x and i-a-Si:H (Figure 4c and Figure 5c). Similar to the results of Yu et al.,⁶³ as fabricated, the ATOM contact is a metal–insulator–semiconductor contact on i-a-Si:H. However, as the total thermal budget on the contact is increased, the ATOM contact structure seems to gradually change from a MIS contact to a semi-MS (metal–semiconductor) contact by losing oxygen in the TiO_x layer,⁶³ which may finally become a semi-metallic TiO.⁶⁴ Accordingly, the $E_{F,\text{metal}}$ depinning properties of the as-fabricated ATOM contact may progressively disappear, which may lead to an increase in ρ_c . The large scatter on the ρ_c value

for the sample annealed at 180 °C is not very clear (see Figure 9a). It might come from nonuniformity of the sample. Some interaction between a-Si:H and metal might have occurred through pinholes or cracks formed in the metal layer once exceeding a certain annealing temperature. Nonetheless, an increasing trend in ρ_c is seen after annealing at higher temperature. In addition, studies on annealing times below 10 min could be very interesting because there is a big jump in the result after annealing for 10 min.

4.2. Solar Cells. In order to quantify the impact of the annealing on the IV parameters of the solar cells fabricated in this work, the cells were successively annealed for 10 min at incrementally increasing temperatures. Figure 10 shows the IV results for the cells after those successive anneals.

Figure 10. Normalized IV results after successive annealing for 10 min at each temperature between 150 and 225 °C. Initial cell parameters before annealing are written in the figure. The Bowden method⁵⁴ was used for R_s characterization.

J_{sc} and FF were maintained in successive cumulative anneals until an annealing temperature of 225 °C; however, the V_{oc} value starts to significantly decrease from the annealing at 200 °C onward, which also results in a reduction in the efficiency. As the annealing temperature increases, the cell efficiency gradually decreases from the initial efficiency of 19.1% for as-

fabricated solar cells, to 18.8% and 18.7% after consecutively annealing at 150 and 175 °C, respectively, which means that 98.2% of the initial efficiency is preserved at this point. Although the ρ_c value of the ATOM contact structure probably already increases by about a factor of 10 after annealing at 150 °C for 10 min (see Figure 9a), a rise in the ρ_c of the ATOM contact structure only marginally contributes to the total R_s until the annealing at 200 °C. The earlier mentioned limit of 0.1 $\Omega\cdot\text{cm}^2$ in ρ_c for the solar cells might be too stringent or the separately extracted ρ_c could be higher than the actual values in the complete solar cell. After annealing at 225 °C, the R_s of the cell increases significantly and a dominant reduction in the efficiency is due to the reduction in V_{OC} of the cell. It is believed that modified interface properties reduce the downward band bending and passivation quality at the contact region.

These annealing test results imply that a temperature below 175 °C is preferred for the subsequent processes of the ATOM-contacted cells to maintain the cell performance. Fortunately, the ATOM contact structure is compatible with module encapsulation process temperatures of around 150 °C.⁶⁵ Furthermore, an increased ρ_c after annealing at 175 °C does not induce a detrimental effect on the FF or the efficiency of the ATOM-contacted solar cells.

In addition, increasing the thermal stability further is one of the important topics for further research to ensure the stability of these solar cells. Preserving the MIS contact structure of the ATOM contact through interfacial engineering could be one of the pathways for improving thermal stability of these solar cells. On the other hand, a stability test at module level after encapsulation, i.e., damp-heat test or thermal cycling test, could also be very interesting to understand the current state for long-term stability.

5. CONCLUSION

An electron-selective contact, termed ATOM contact, is fabricated using an i-a-Si:H/TiO_x/Yb contact structure with Ag as the capping metal layer. The contact performance is investigated in terms of ρ_c and $J_{0,\text{metal}}$. It appears that both Ti precursors used in this work for TiO_x deposition, TTIP and TDMAT, show comparable contact characteristics. In addition, the surface topography of the c-Si substrate, flat or textured, did not influence the contact properties. Concerning the TiO_x layer thickness in the i-a-Si:H/TiO_x/Yb/Ag (ATOM) contact, 1 nm seems optimal to achieve depinning of $E_{F,\text{metal}}$ in a MIS contact configuration. ATOM contacts with Yb as a low work function metal have been successfully integrated into SHJ cells, enabling a champion cell efficiency of 19.2% with a V_{OC} of 723 mV.

The annealing temperature and time strongly affect the ρ_c so the thermal stability of the contact has to be carefully considered. It was found that when annealing the ATOM contact at temperatures not exceeding 175 °C, it is possible to preserve 98.2% of the initial efficiency thanks to the barrier function of the TiO_x layer in this contact, which blocks metal diffusion.

This study could be a stepping stone for achieving highly efficient and more reliable solar cells without the need for doping processes or doped layers.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsam.8b01969.

Contact resistivity characterization method and TEM sample preparation method (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Adachi, D.; Hernández, J. L.; Yamamoto, K. Impact of Carrier Recombination on Fill Factor for Large Area Heterojunction Crystalline Silicon Solar Cell with 25.1% Efficiency. *Appl. Phys. Lett.* **2015**, *107*, 233506.
- (2) Holman, Z. C.; Descoeudres, A.; Barraud, L.; Fernandez, F. Z.; Seif, J. P.; De Wolf, S.; Ballif, C. Current Losses at the Front of Silicon Heterojunction Solar Cells. *IEEE J. Photovoltaics* **2012**, *2*, 7–15.
- (3) Bullock, J.; Wan, Y.; Xu, Z.; Essig, S.; Hettick, M.; Wang, H.; Ji, W.; Boccard, M.; Cuevas, A.; Ballif, C.; et al. Stable Dopant-Free Asymmetric Heterocontact Silicon Solar Cells with Efficiencies above 20%. *ACS Energy Lett.* **2018**, *3*, 508–513.
- (4) Bullock, J.; Hettick, M.; Geissbühler, J.; Ong, A. J.; Allen, T.; Sutter-Fella, C. M.; Chen, T.; Ota, H.; Schaler, E. W.; De Wolf, S.; et al. Efficient Silicon Solar Cells with Dopant-Free Asymmetric Heterocontacts. *Nat. Energy* **2016**, *1*, 15031.
- (5) Melskens, J.; van de Loo, B. W. H.; Maccò, B.; Black, L. E.; Smit, S.; Kessels, W. M. M. Passivating Contacts for Crystalline Silicon Solar Cells: From Concepts and Materials to Prospects. *IEEE J. Photovoltaics* **2018**, *8*, 373–388.
- (6) Cho, J.; Debucquoy, M.; Recaman Payo, M.; Malik, S.; Filipič, M.; Radhakrishnan, H. S.; Bearda, T.; Gordon, I.; Szlufcik, J.; Poortmans, J. Contact Resistivity Reduction on Lowly-Doped n-Type Si Using a Low Work Function Metal and a Thin TiO_x Interfacial Layer for Doping-Free Si Solar Cells. *Energy Procedia* **2017**, *124*, 842–850 (7th International Conference on Silicon Photovoltaics, Silicon PV 2017).
- (7) Yang, X.; Zheng, P.; Bi, Q.; Weber, K. Silicon Heterojunction Solar Cells with Electron Selective TiO_x Contact. *Sol. Energy Mater. Sol. Cells* **2016**, *150*, 32–38.
- (8) Yang, X.; Bi, Q.; Ali, H.; Davis, K.; Schoenfeld, W. V.; Weber, K. High-Performance TiO₂-Based Electron-Selective Contacts for Crystalline Silicon Solar Cells. *Adv. Mater.* **2016**, *28*, 5891.
- (9) Yang, X.; Weber, K.; Hameiri, Z.; De Wolf, S. Industrially Feasible, Dopant-Free, Carrier-Selective Contacts for High-Efficiency Silicon Solar Cells. *Prog. Photovoltaics* **2017**, *25*, 896–904.
- (10) Yu, J.; Fu, Y.; Zhu, L.; Yang, Z.; Yang, X.; Ding, L.; Zeng, Y.; Yan, B.; Tang, J.; Gao, P.; et al. Heterojunction Solar Cells with

Asymmetrically Carrier-Selective Contact Structure of Molybdenum-Oxide/Silicon/Magnesium-Oxide. *Sol. Energy* **2018**, *159*, 704–709.

(11) Macco, B.; Black, L. E.; Melskens, J.; van de Loo, B. W. H.; Berghuis, W. H.; Verheijen, M. A.; Kessels, W. M. M. Atomic-Layer Deposited Nb₂O₅ as Transparent Passivating Electron Contact for c-Si Solar Cells. *Sol. Energy Mater. Sol. Cells* **2018**, *184*, 98–104.

(12) Macco, B.; Bivour, M.; Deijkers, J. H.; Basuvalingam, S. B.; Black, L. E.; Melskens, J.; van de Loo, B. W. H.; Berghuis, W. J. H.; Hermle, M.; Kessels, W. M. M. Effective Passivation of Silicon Surfaces by Ultrathin Atomic-Layer Deposited Niobium Oxide. *Appl. Phys. Lett.* **2018**, *112*, 242105.

(13) Wan, Y.; Karuturi, S. K.; Samundsett, C.; Bullock, J.; Hettick, M.; Yan, D.; Peng, J.; Narangari, P. R.; Mokkapati, S.; Tan, H. H.; et al. Tantalum Oxide Electron-Selective Heterocontacts for Silicon Photovoltaics and Photoelectrochemical Water Reduction. *ACS Energy Lett.* **2018**, *3*, 125–131.

(14) Yang, X.; Aydin, E.; Xu, H.; Kang, J.; Hedhili, M.; Liu, W.; Wan, Y.; Peng, J.; Samundsett, C.; Cuevas, A.; et al. Tantalum Nitride Electron-Selective Contact for Crystalline Silicon Solar Cells. *Adv. Energy Mater.* **2018**, *8*, 1800608.

(15) Allen, T. G.; Bullock, J.; Zheng, P.; Vaughan, B.; Barr, M.; Wan, Y.; Samundsett, C.; Walter, D.; Javey, A.; Cuevas, A. Calcium Contacts to N-Type Crystalline Silicon Solar Cells. *Prog. Photovoltaics* **2017**, *25*, 636–644.

(16) Wan, Y.; Samundsett, C.; Bullock, J.; Allen, T.; Hettick, M.; Yan, D.; Zheng, P.; Zhang, X.; Cui, J.; McKeon, J.; et al. Magnesium Fluoride Electron-Selective Contacts for Crystalline Silicon Solar Cells. *ACS Appl. Mater. Interfaces* **2016**, *8*, 14671–14677.

(17) Cho, J.; Melskens, J.; Debucquoy, M.; Recamán Payo, M.; Jambaldinni, S.; Bearda, T.; Gordon, I.; Szlufcik, J.; Kessels, W. M. M.; Poortmans, J. Passivating Electron-Selective Contacts for Silicon Solar Cells Based on an a-Si:H/TiO_x Stack and a Low Work Function Metal. *Prog. Photovoltaics* **2018**, *26*, 835–845.

(18) Cho, J.; Debucquoy, M.; Payo, M. R.; Schapmans, E.; Gordon, I.; Szlufcik, J.; Poortmans, J. Evidence of TiO_x Reduction at the SiO_x/TiO_x Interface of Passivating Electron-Selective Contacts. *AIP Conf. Proc.* **2018**, *1999*, 040005 (SiliconPV Conference 2018).

(19) Allen, T. G.; Bullock, J.; Jeangros, Q.; Samundsett, C.; Wan, Y.; Cui, J.; Hessler-Wyser, A.; De Wolf, S.; Javey, A.; Cuevas, A. A Low Resistance Calcium/Reduced Titania Passivated Contact for High Efficiency Crystalline Silicon Solar Cells. *Adv. Energy Mater.* **2017**, *7*, 1602606.

(20) Macco, B.; Vos, M. F. J.; Thissen, N. F. W.; Bol, A. A.; Kessels, W. M. M. Low-Temperature Atomic Layer Deposition of MoO_x for Silicon Heterojunction Solar Cells. *Phys. Status Solidi RRL* **2015**, *9*, 393–396.

(21) Bivour, M.; Macco, B.; Temmler, J.; Kessels, W. M. M. E.; Hermle, M. Atomic Layer Deposited Molybdenum Oxide for the Hole-Selective Contact of Silicon Solar Cells. *Energy Procedia* **2016**, *92*, 443–449 (Proceedings of the 6th International Conference of Crystalline Silicon Photovoltaics (Silicon PV 2016)).

(22) Sacchetto, D.; Jeangros, Q.; Christmann, G.; Barraud, L.; Descoeudres, A.; Geissbühler, J.; Despeisse, M.; Hessler-Wyser, A.; Nicolay, S.; Ballif, C. ITO/MoO_x/a-Si:H(i) Hole-Selective Contacts for Silicon Heterojunction Solar Cells: Degradation Mechanisms and Cell Integration. *IEEE J. Photovoltaics* **2017**, *7*, 1584–1590.

(23) Mews, M.; Korte, L.; Rech, B. Oxygen Vacancies in Tungsten Oxide and Their Influence on Tungsten Oxide/Silicon Heterojunction Solar Cells. *Sol. Energy Mater. Sol. Cells* **2016**, *158*, 77–83.

(24) Bivour, M.; Zähringer, F.; Ndione, P.; Hermle, M. Sputter-Deposited WO_x and MoO_x for Hole Selective Contacts. *Energy Procedia* **2017**, *124*, 400–405 (7th International Conference on Silicon Photovoltaics, SiliconPV 2017).

(25) Gerling, L. G.; Mahato, S.; Morales-Vilches, A.; Masmitjà, G.; Ortega, P.; Voz, C.; Alcubilla, R.; Puigdollers, J. Transition Metal Oxides as Hole-Selective Contacts in Silicon Heterojunctions Solar Cells. *Sol. Energy Mater. Sol. Cells* **2016**, *145*, 109–115.

(26) Masmitjà, G.; Gerling, L. G.; Ortega, P.; Puigdollers, J.; Martín, I.; Voz, C.; Alcubilla, R. V₂O₅-Based Hole-Selective Contacts for c-

Si Interdigitated Back-Contacted Solar Cells. *J. Mater. Chem. A* **2017**, *5*, 9182–9189.

(27) Neusel, L.; Bivour, M.; Hermle, M. Selectivity Issues of MoO_x Based Hole Contacts. *Energy Procedia* **2017**, *124*, 425–434 (7th International Conference on Silicon Photovoltaics, SiliconPV 2017).

(28) Geissbühler, J.; Werner, J.; Martin De Nicolas, S.; Barraud, L.; Hessler-Wyser, A.; Despeisse, M.; Nicolay, S.; Tomasi, A.; Niesen, B.; De Wolf, S.; et al. 22.5% Efficient Silicon Heterojunction Solar Cell with Molybdenum Oxide Hole Collector. *Appl. Phys. Lett.* **2015**, *107*, 081601.

(29) Wronski, C. R.; Carlson, D. E. Surface States and Barrier Heights of Metal-Amorphous Silicon Schottky Barriers. *Solid State Commun.* **1977**, *23*, 421–424.

(30) Bivour, M. Silicon Heterojunction Solar Cells: Analysis and Basic Understanding. Ph.D. Dissertation, Fraunhofer Verlag: Stuttgart, Germany, 2017.

(31) Matsui, T.; Bivour, M.; Ndione, P.; Hettich, P.; Hermle, M. Investigation of Atomic-Layer-Deposited TiO_x as Selective Electron and Hole Contacts to Crystalline Silicon. *Energy Procedia* **2017**, *124*, 628–634 (7th International Conference on Silicon Photovoltaics, SiliconPV 2017).

(32) Skriver, H. L.; Rosengaard, N. M. Surface Energy and Work Function of Elemental Metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1992**, *46*, 7157–7168.

(33) Michaelson, H. B. The Work Function of the Elements and Its Periodicity. *J. Appl. Phys.* **1977**, *48*, 4729–4733.

(34) Schroder, D. K. *Semiconductor Material and Device Characterization*, 3rd ed.; John Wiley & Sons: Hoboken, NJ, USA, 2005; Vol. 44. DOI: 10.1002/0471749095.

(35) Haslinger, M.; Soha, M.; Jambaldinni, S.; Hajjiah, A.; Szlufcik, J.; Poortmans, J.; John, J. Novel Wet Chemical Cleaning Concepts for High Efficiency Silicon Solar Cells. *33rd European Photovoltaic Solar Energy Conference and Exhibition*; WIP Renewable Energies: Munich, Germany, 2017; pp 628–630.

(36) Green, M. A.; Blakers, A. W.; Zhao, J.; Milne, A. M.; Wang, A.; Dai, X. Characterization of 23-Percent Efficient Silicon Solar Cells. *IEEE Trans. Electron Devices* **1990**, *37*, 331–336.

(37) Agrawal, A.; Lin, J.; Barth, M.; White, R.; Zheng, B.; Chopra, S.; Gupta, S.; Wang, K.; Gelatos, J.; Mohny, S. E.; et al. Fermi Level Depinning and Contact Resistivity Reduction Using a Reduced Titania Interlayer in N-Silicon Metal-Insulator-Semiconductor Ohmic Contacts. *Appl. Phys. Lett.* **2014**, *104*, 112101.

(38) Agrawal, A.; Shukla, N.; Ahmed, K.; Datta, S. A Unified Model for Insulator Selection to Form Ultra-Low Resistivity Metal-Insulator-Semiconductor Contacts to n-Si, n-Ge, and n-InGaAs. *Appl. Phys. Lett.* **2012**, *101*, 042108.

(39) Wahlström, E.; Vestergaard, E. K.; Schaub, R.; Rønnau, A.; Vestergaard, M.; Lægsgaard, E.; Stensgaard, I.; Besenbacher, F. Electron Transfer-Induced Dynamics of Oxygen Molecules on the TiO₂(110) Surface. *Science (Washington, DC, U. S.)* **2004**, *303*, 511–513.

(40) Agrawal, A.; Lin, J.; Zheng, B.; Sharma, S.; Chopra, S.; Wang, K.; Gelatos, A.; Mohny, S.; Datta, S. Barrier Height Reduction to 0.15 eV and Contact Resistivity Reduction to $9.1 \times 10^{-9} \Omega\text{-cm}^2$ Using Ultrathin TiO_{2-x} Interlayer between Metal and Silicon. *2013 Symposium on VLSI Technology (VLSIT)*; IEEE, 2013; pp T200–T201.

(41) Abdulraheem, Y.; Gordon, I.; Bearda, T.; Meddeb, H.; Poortmans, J. Optical Bandgap of Ultra-Thin Amorphous Silicon Films Deposited on Crystalline Silicon by PECVD. *AIP Adv.* **2014**, *4*, 057122.

(42) Meddeb, H.; Bearda, T.; Abdulraheem, Y.; Ezzaouia, H.; Gordon, I.; Szlufcik, J.; Poortmans, J. Structural, Hydrogen Bonding and In Situ Studies of the Effect of Hydrogen Dilution on the Passivation by Amorphous Silicon of n-Type Crystalline (1 0 0) Silicon Surfaces. *J. Phys. D: Appl. Phys.* **2015**, *48*, 415301.

(43) Sai, H.; Chen, P.; Hsu, H.; Matsui, T. Impact of Intrinsic Amorphous Silicon Bilayers in Silicon Heterojunction Solar Cells. *J. Appl. Phys.* **2018**, *124*, 103102.

- (44) Macco, B.; Melskens, J.; Podraza, N. J.; Arts, K.; Pugh, C.; Thomas, O.; Kessels, W. M. M. Correlating the Silicon Surface Passivation to the Nanostructure of Low-Temperature a-Si:H after Rapid Thermal Annealing. *J. Appl. Phys.* **2017**, *122*, 035302.
- (45) Kita, K.; Toriumi, A. Origin of Electric Dipoles Formed at High-k/SiO₂ Interface. *Appl. Phys. Lett.* **2009**, *94*, 132902.
- (46) Gschneidner, K. A.; Calderwood, F. W. The Ag-Yb (Silver-Ytterbium) System. *Bull. Alloy Phase Diagrams* **1985**, *6*, 147–149.
- (47) Roose, B.; Pathak, S.; Steiner, U. Doping of TiO₂ for Sensitized Solar Cells. *Chem. Soc. Rev.* **2015**, *44*, 8326–8349.
- (48) Street, R. A. *Hydrogenated Amorphous Silicon*; Cambridge University Press: Cambridge, U.K., 1991. DOI: 10.1017/CBO9780511525247.
- (49) Bertel, E.; Strasser, G.; Netzer, F. P.; Matthew, J. A. D. Surface Oxidation of Ytterbium. *Surf. Sci.* **1982**, *118*, 387–400.
- (50) Glunz, S. W.; Nekarda, J.; Mäkel, H.; Cuevas, A. Analyzing Back Contacts of Silicon Solar Cells by Suns-Voc-Measurements at High Illumination Densities. *Proceedings of the 22nd European Photovoltaic Solar Energy Conference*, Sep. 3–7, 2007, Milan, Italy; EU PVSEC, 2007; pp 849–853.
- (51) Schaper, M.; Schmidt, J.; Plagwitz, H.; Brendel, R. 20.1%-Efficient Crystalline Silicon Solar Cell With Amorphous Silicon Rear-Surface Passivation. *Prog. Photovoltaics* **2005**, *13*, 381–386.
- (52) Plagwitz, H.; Nerdling, M.; Ott, N.; Strunk, H. P.; Brendel, R. Low-Temperature Formation of Local Al Contacts to a-Si:H-Passivated Si Wafers. *Prog. Photovoltaics* **2004**, *12*, 47–54.
- (53) Kawazu, Y.; Kudo, H.; Onari, S.; Arai, T. Low-Temperature Crystallization of Hydrogenated Amorphous Silicon Induced by Nickel Silicide Formation. *Jpn. J. Appl. Phys.* **1990**, *29*, 2698–2704.
- (54) Bowden, S.; Rohatgi, A. Rapid and Accurate Determination of Series Resistance and Fill Factor Losses in Industrial Silicon Solar Cells. *17th European Photovoltaic Solar Energy Conference and Exhibition*, Munich, Germany; EU PVSEC, 2001.
- (55) Khanna, A.; Mueller, T.; Stangl, R. A.; Hoex, B.; Basu, P. K.; Aberle, A. G. A Fill Factor Loss Analysis Method for Silicon Wafer Solar Cells. *IEEE J. Photovoltaics* **2013**, *3*, 1170–1177.
- (56) Zhang, W.; Brongersma, S. H.; Richard, O.; Brijs, B.; Palmans, R.; Froyen, L.; Maex, K. Influence of the Electron Mean Free Path on the Resistivity of Thin Metal Films. *Microelectron. Eng.* **2004**, *76*, 146–152.
- (57) Kim, H. C.; Alford, T. L.; Allee, D. R. Thickness Dependence on the Thermal Stability of Silver Thin Films. *Appl. Phys. Lett.* **2002**, *81*, 4287–4289.
- (58) Bist, B. M. S.; Srivastava, O. N. Electrical Resistivity of Ytterbium Thin Films. *Thin Solid Films* **1973**, *18*, 71–75.
- (59) Paviet-Salomon, B.; Tomasi, A.; Descoeudres, A.; Barraud, L.; Nicolay, S.; Despeisse, M.; Wolf, S. D.; Ballif, C. Back-Contacted Silicon Heterojunction Solar Cells: Optical-Loss Analysis and Mitigation. *IEEE J. Photovoltaics* **2015**, *5*, 1293–1303.
- (60) Holman, Z. C.; Filipič, M.; Descoeudres, A.; De Wolf, S.; Smole, F.; Topič, M.; Ballif, C. Infrared Light Management in High-Efficiency Silicon Heterojunction and Rear-Passivated Solar Cells. *J. Appl. Phys.* **2013**, *113*, 013107.
- (61) Boccard, M.; Yang, X.; Weber, K.; Holman, Z. C. Passivation and Carrier Selectivity of TiO₂ Contacts Combined with Different Passivation Layers and Electrodes for Silicon Solar Cells. In *2016 IEEE 43rd Photovoltaic Specialists Conference (PVSC)*; IEEE, 2016; pp 2403–2407. DOI: 10.1109/PVSC.2016.7750072.
- (62) Sacchetto, D.; Jeangros, Q.; Christmann, G.; Barraud, L.; Descoeudres, A.; Geissbühler, J.; Despeisse, M.; Hessler-Wyser, A.; Nicolay, S.; Ballif, C. MoO_x and TiO₂ Carrier Selective Contacts for Dopant-Free SHJs. *7th International Conference on Crystalline Silicon Photovoltaics 2017*, Freiburg, Germany, Apr. 3–5, 2017.
- (63) Yu, H.; Schaekers, M.; Schram, T.; Demuyne, S.; Horiguchi, N.; Barla, K.; Collaert, N.; Thean, A. V.-Y.; De Meyer, K. Thermal Stability Concern of Metal-Insulator-Semiconductor Contact: A Case Study of Ti/TiO₂/n-Si Contact. *IEEE Trans. Electron Devices* **2016**, *63*, 2671–2676.
- (64) Valeeva, A. A.; Rempel', A. A.; Gusev, A. I. Electrical Conductivity and Magnetic Susceptibility of Titanium Monoxide. *JETP Lett.* **2001**, *73*, 621–625.
- (65) Li, H.-Y.; Perret-Aebi, L.-E.; Chapuis, V.; Ballif, C.; Luo, Y. The Effect of Cooling Press on the Encapsulation Properties of Crystalline Photovoltaic Modules: Residual Stress and Adhesion. *Prog. Photovoltaics* **2015**, *23*, 160–169.