

# Conductive and Stable Magnesium Oxide Electron-Selective Contacts for Efficient Silicon Solar Cells

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A high Schottky barrier (>0.65 eV) for electrons is typically found on lightly doped n-type crystalline (c-Si) wafers for a variety of contact metals. This behavior is commonly attributed to the Fermi-level pinning effect and has hindered the development of n-type c-Si solar cells, while its p-type counterparts have been commercialized for several decades, typically utilizing aluminium alloys in full-area, and more recently, partial-area rear contact configurations. Here the authors demonstrate a highly conductive and thermally stable electrode composed of a magnesium oxide/aluminium (MgO,/Al) contact, achieving moderately low resistivity Ohmic contacts on lightly doped n-type c-Si. The electrode, functionalized with nanoscale MgO, films, significantly enhances the performance of n-type c-Si solar cells to a power conversion efficiency of 20%, advancing n-type c-Si solar cells with full-area dopant-free rear contacts to a point of competitiveness with the standard p-type architecture. The low thermal budget of the cathode formation, its dopant-free nature, and the simplicity of the device structure enabled by the  $MgO_x/Al$  contact open up new possibilities in designing and fabricating low-cost optoelectronic devices, including solar cells, thin film transistors, or light emitting diodes.

## 1. Introduction

Crystalline silicon (c-Si) has been dominating worldwide photovoltaic (PV) production for decades, with a global market share of around 90%, making it unequivocally the most important PV technology nowadays. The majority of commercialized c-Si PV devices are based on a simple solar cell architecture—a p-type c-Si wafer with a front phosphorus diffusion and a full-area aluminium (Al) alloyed rear back surface region. The success of this architecture is largely due to the simple, low-cost formation of a highly doped p<sup>+</sup> region upon alloying, which leads to a low contact resistance for hole transport and a reasonable

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level of recombination suppression at the rear surface. When Al is directly deposited on n-type c-Si, however, and even if it is not alloyed with the silicon, the contact behaves in a rectifying fashion and is associated with a high contact resistance, despite the small difference (≈0.1–0.2 eV) that exists between the Al work function and the electron affinity of silicon and the consequently low barrier height predicted by the Schottky-Mott rule.<sup>[1,2]</sup> This behavior is widely attributed to the Fermilevel pinning phenomenon, induced by a high density of bandgap states or defects at the metal/semiconductor interfaces, which leads to a relatively high Schottky barrier height ( $\Phi_B$ ) of  $\approx 0.65$  eV that hinders the flow of electrons out of the n-type silicon wafer.<sup>[1,2]</sup>

the approaches for addressing this problem can be inferred by looking into the dependence of contact resistivity  $\rho_c$ , on the Schottky barrier height  $\Phi_B$ , and the surface doping concentration of the semiconductor  $N_d$ ,

which is given by  $\rho_c \propto \exp\left(\frac{\Phi_B}{\sqrt{N_d}}\right)$ . Historically, an Ohmic contact to n-type silicon wafers has been achieved by means of heavy phosphorus doping at the surface of the solar cells (i.e., increasing  $N_d$ ) via thermal diffusion or plasma-assisted deposition. Despite its success in producing record-efficiency silicon solar cells, doping usually creates process complexity and requires a high temperature, in excess of 800 °C for the thermal diffusion of dopants<sup>[3]</sup> or for the recrystallization of deposited silicon layers.<sup>[4]</sup> Noxious gasses are normally used in silicon heterojunction solar cell technology to introduce dopants in hydrogenated amorphous silicon layers deposited by PECVD.<sup>[5]</sup>

Another obvious approach to reducing  $\rho_c$  is to reduce  $\Phi_B$ . One straightforward technique to reduce  $\Phi_B$  for electron transport is the utilization of a metal layer with a very low work function, such as calcium<sup>[6]</sup> and magnesium,<sup>[7–10]</sup> resulting in a relatively low barrier height of  $\approx 0.35$  eV on n-type c-Si.<sup>[2,7]</sup> An alternative, or complementary, technique is the depinning of the Fermi-level by inserting an interfacial layer between the outer metal electrode and the inner silicon absorber. The inter-layer functions as a passivating layer to reduce the density of states/defects at the metal/silicon interface while being conductive enough to allow significant transport of carriers through it. Several properties of the interlayer are desirable for achieving

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a low contact resistivity: (i) low conduction band offset to c-Si, (ii) low tunneling effective mass, (iii) low bulk resistivity, and (iv) possible capability of reducing the work function of the outer metal layer.

Based on abovementioned implications, extensive efforts have been devoted to explore materials to form electron-selective contacts on n-type c-Si wafers without intentional dopants. Materials such as alkali/alkaline earth metal salts and carbonates (e.g., lithium fluoride,<sup>[11–13]</sup> magnesium fluoride,<sup>[14]</sup> and cesium carbonate<sup>[15,16]</sup>) and transition metal oxides (e.g., titanium oxide<sup>[17,18]</sup>) have been reported to enhance significantly the Ohmic contact of Al to n-type c-Si, enabling the power conversion efficiency (PCE) of silicon solar cells to reach about 20%.

Another candidate which has been shown to have promise in light-emitting diodes<sup>[19]</sup> but without much development in solar cells is magnesium oxide (MgOx). Stoichiometric MgO<sub>x</sub> (x = 1) is well-known to be an insulator with a wide energy band gap.<sup>[20]</sup> Recently, MgO<sub>x</sub> has been reported to suppress the recombination loss within a titania compact layer in perovskite solar cells.<sup>[21,22]</sup> To our knowledge, however, the application of those oxides as electron-selective contacts to n-type c-Si has not been explored. In this work, we develop a conductive and thermally stable electron-selective contact on n-type c-Si facilitated by a nanoscale  $MgO_x$  film. We investigate the electronic band structure and conduction properties of the thermally evaporated MgO<sub>x</sub>/Al electron-selective contacts.

The electron contact is then applied to the full rear surface of n-type silicon solar cells, for the first time with this material, achieving a fill factor of 80.5% and a power conversion efficiency of 20%. Finally, the devices featuring the MgO<sub>x</sub>/Al contact are shown to be thermally stable upon annealing at a temperature of up to 400 °C for 40 min.

### 2. Results and Discussion

MgO<sub>x</sub> films were thermally evaporated at a rate of 0.2 Å s<sup>-1</sup> from a 4N-purity MgO<sub>x</sub> powder source, with a base pressure of  $<2 \times 10^{-6}$  mbar. X-ray diffraction measurements showed that the evaporated MgO<sub>x</sub> thin films have an amorphous structure without any observable peaks, in contrast with the MgO<sub>x</sub> powder, which has distinctive diffraction peaks (see Figure S1a in the Supporting Information). The electronic band structure was characterized via X-ray photoelectron spectroscopy (XPS), using monochromatic Al K $\alpha$  X-rays with a photon energy of 1486.7 eV at a pressure in the range of 10<sup>-9</sup> to 10<sup>-10</sup> mbar. Figure 1 shows the XPS measurement results, including (a) core levels of Mg 1s, (b) core levels of O 1s, (c) the valence band region, and (d) secondary electron cut-off work function



**Figure 1.** X-ray photoelectron spectroscopy (XPS) measurements of thermally evaporated  $MgO_x$  films. a,b) The core level spectrum of Mg 1s and O 1s, respectively. The extracted stoichiometry of  $MgO_v$  is also included. c) The valence band spectrum of the  $MgO_x$  film. d) The secondary electron cut-off spectrum measured at the  $MgO_x/Al$  interface with a gold (Au) reference.

measurement of the MgO<sub>x</sub>/Al interface. While the Mg 1s spectra exhibits a typical peak at ~1304 eV, the core level of O 1s can be split into the oxide O<sup>2–</sup> and peroxide O<sub>2</sub><sup>2–</sup> doublet peaked at 529.8 and 531.5 eV, respectively, as ascribed in previous work.<sup>[23]</sup> Extraction of the MgO<sub>x</sub> film stoichiometry based on core level peak areas shows the thermally evaporated MgO<sub>x</sub> to be more metallic, with an O to Mg atomic fraction of 0.75, significantly lower than the stoichiometry of the powder source, found to be 0.95 (see Figure S1d in the Supporting Information). Note that the sample for core level analysis has a bare MgO<sub>x</sub> layer (i.e., it does not have an Al over-layer), and hence the stoichiometry may not be representative of the layer affected by aluminium deposition in the final contacts.

We now turn to the discussion of the valence band spectrum of the MgO<sub>x</sub> films shown in Figure 1c. Comparing to the valence band spectrum of the powder source (see Figure S1b in the Supporting Information), a broad defect band in the band gap centered at a binding energy of 1 eV exists in the as-deposited film. It is interesting to note that there is a very high density of filled states at the Fermi level, indicating electronic behavior similar to a metal. This defect band is probably derived from oxygen vacancies, consistent with the highly substoichiometric MgO<sub>x</sub> film composition (i.e., x = 0.75) determined from the core level XPS



analysis. Further, Hall effect measurements on the as-deposited  $MgO_x$  films show that they behave as an n-type semiconductor, with conductivity of 173 S cm<sup>-1</sup>, electron concentration of  $\approx 2 \times 10^{21}$  cm<sup>-3</sup> and electron mobility of 0.23–0.57 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Interestingly, it has been argued that the enrichment of MgO<sub>x</sub> with metallic Mg, which may act as an electron donor species, caused the layer to become an n-type semiconductor,<sup>[23]</sup> in agreement with our observations. The high conductivity of the film revealed by Hall effect is also consistent with the metal-rich composition and the oxygen deficient defect band observed by XPS. Finally, the XPS secondary electron cut-off analysis of a  $MgO_x/$ Al stack thinned by sputtering (Argon ion gun, 4 keV) illustrated in Figure 1d shows a work function in the vicinity of 4.1 eV, which is comparable to the work function of the Al metal itself  $(\approx 4.2 \text{ eV})^{[24]}$  and to previously measured values of the MgO work function.<sup>[25]</sup> As will be presented in the next section, the high conductivity and high electron concentration of bulk MgO<sub>x</sub> film plays a crucial role in enabling Ohmic contact behavior between the Al electrode and the n-type silicon substrates.

To evaluate the electrical contact behavior of the MgO<sub>x</sub>/Al structure, the contact resistivity  $\rho_c$  was measured using the method devised by Cox and Strack,<sup>[26]</sup> as shown schematically in insets of Figure 2a,b, which show a series of I-V measurements of samples without and with 1 nm MgO<sub>x</sub> interlayer between Al and n-type c-Si, respectively. The resistance versus diameter trend is fitted with a spreading resistance model, allowing accurate extraction of  $\rho_c$ . As we can see in Figure 2a, the sample with Al directly on n-type c-Si (i.e., without  $MgO_x$ ) exhibits somewhat Ohmic contacts for large area pads, but then turns to rectifying behavior when pad areas become smaller. The contact resistance of this particular structure was extracted to be  $2 \pm 0.5 \Omega$  cm<sup>2</sup>. A high contact resistance, or rectifying behavior, between the Al metal and n-type c-Si is attributable to the presence of a large surface potential barrier known to exist at this surface.<sup>[2]</sup> By contrast, the insertion of a nanoscale  $MgO_x$  ( $\approx 1$  nm) film improves dramatically the contact behavior, leading to an Ohmic contact (i.e., linear I-V curve) between the Al electrode and the n-type c-Si substrate. Note that the scale



**Figure 2.** Contact resistivity measurements of MgO<sub>x</sub> based contacts to n-type c-Si. a,b) A series of *I*–*V* measurements of samples without and with 1 nm MgO<sub>x</sub> interlayer between Al and n-type c-Si, respectively. Schematics of the contact resistivity test structure for both samples are included in respective inset. c) The contact resistivity  $\rho_c$  as a function of MgO<sub>x</sub> thickness.

of *x*-axis (i.e., the voltage) for MgO<sub>x</sub>/Al sample is one order magnitude lower than that for samples without MgO<sub>x</sub> interlayer. The extracted contact resistance  $\rho_c$  for the structure with  $\approx 1$  nm MgO<sub>x</sub> is determined to be 17.5 ± 2 m $\Omega$  cm<sup>2</sup>, which is more than two orders of magnitude lower than the contact of Al directly on n-type c-Si. The low resistance for electron transport provided by the MgO<sub>x</sub>/Al contact structure is likely attributed to (i) a high conductivity and high electron concentration in MgO<sub>x</sub> bulk film, as revealed by the Hall effect measurements, and/or (ii) the release, or unpinning, of the Fermi-level by passivating the gap states between Al metal and the silicon substrate. It is not anticipated that the work function of MgO<sub>x</sub>/Al plays a critical role here in reducing the contact resistivity since its work function is comparable to that of Al metal, as presented in Figure 1d.

Figure 2c presents the effect of MgO<sub>x</sub> thickness on contact resistivity. It can be seen that  $\rho_c$  first decreases dramatically as the MgO<sub>x</sub> thickness increases from 0 to 1 nm, and then increases sharply when MgO<sub>x</sub> exceeds 1 nm. The initially decreasing  $\rho_c$  could potentially be a result of partial MgO<sub>x</sub> surface coverage for the ultra-thin films (for example, less than 1 nm), due to commonly reported island growth for thermal evaporation.<sup>[27]</sup> The increase in  $\rho_c$  for thicker films is likely due

to the bulk resistivity of the MgO<sub>x</sub> material. It is interesting to note that the contact is still Ohmic even when the MgO<sub>x</sub> thickness reaches 60 nm, consistent with the high conductivity and high electron concentration presented above. Nevertheless, it is remarkable that the insertion of  $\approx$ 1 nm thick MgO<sub>x</sub> layer results in a contact resistivity of only 17.5 m $\Omega$  cm<sup>2</sup>, promoting an opportunity in fabricating high efficiency silicon solar cells with full-area rear electron contacts. In fact, the contact resistivity stays within tolerable levels for a full area contact up to a MgO<sub>x</sub> layer thickness of  $\approx$ 60 nm.

To demonstrate the MgO<sub>x</sub>/Al electron contact at the device level, we fabricate a proof-of-concept solar cell with full-area MgO<sub>x</sub>/Al stack at the rear surface of an n-type silicon wafer. **Figure 3**a depicts the cell schematic structure and Figure 3b presents a cross-sectional transmission electron micrograph (TEM) of the rear contact layers, respectively. The front (sunward) surface of the cell features (i) a textured surface morphology with an array of random upright pyramids to enhance light trapping,<sup>[28,29]</sup> (ii) a boron diffused p<sup>+</sup> region to form a pn junction and collect holes, and (iii) an alumina/silicon nitride (Al<sub>2</sub>O<sub>3</sub>/ SiN<sub>x</sub>) stack to passivate the dangling bonds at the p<sup>+</sup> silicon surfaces and provide antireflection to enhance light coupling into the silicon absorber. The rear surface of cell is coated with a



**Figure 3.** Device results with full-area rear MgO<sub>x</sub> based electron-selective contacts. a) The schematic of an n-type silicon solar cell featuring full-area rear MgO<sub>x</sub>/Al electron-selective contacts. b) The 10 nm scale cross-sectional transmission electron micrograph (TEM) of the rear layers of the cell. c) Photoluminescence image of the front (sunward) side of a representative solar cell, using a 1025 nm short-pass filter. d) The light J-V behavior and electrical parameters of the cell measured under standard one sun conditions for cells without and with  $\approx$ 1 nm MgO<sub>x</sub> interlayer. e) The external and internal quantum efficiencies accompanied the measured reflectance for the two cells.



full-area 1 nm MgO<sub>x</sub>/300 nm Al stack. Compared to conventional phosphorus diffused contacts, the MgO<sub>x</sub> based contact employed here mitigates the need of (i) the high-temperature phosphorus diffusion; and (ii) the patterning of the rear dielectrics (by photolithography in many labs, and commonly by laser ablation in industry). Figure 3c provides a photoluminescence image of the front side of a representative solar cell, using a 1025 nm short-pass filter. It shows uniform front and rear surface optics and passivation, and a high excess carrier density over the cell area, which are necessary conditions for a high power conversion efficiency.

The J-V photovoltaic characteristic curve under one sun standard illumination is plotted in Figure 3d for cells with and without MgO<sub>x</sub> interlayer. The electrical parameters of both cells are also tabulated in the inset. The insertion of a 1 nm thick MgO<sub>x</sub> layer enhances substantially all cell parameters, leading to a power conversion efficiency of 20%, associated with an open-circuit voltage ( $V_{OC}$ ), short-circuit current ( $J_{SC}$ ), and fill factor (FF) of 628.8 mV, 39.5 mA cm<sup>-2</sup>, and 80.4%, respectively. Compared to the control cell (i.e., without  $MgO_x$  interlayer), an absolute 73.6 mV increase of  $V_{OC}$  was gained, which is likely attributable to (i) a moderate level of passivation of the rear silicon surface, and/or (ii) the elimination of rectifying contact behavior, both of which are provided by the  $MgO_x/Al$  stack. We estimate the recombination current density  $(J_{0c})$  under the MgO<sub>x</sub>/Al electron-selective contact to be  $9.5 \times 10^{-13}$  A cm<sup>-2</sup> after accounting for  $1 \times 10^{-13}$  A cm<sup>-2</sup> recombination parameter of the front  $p^+$  doped region (composed of  $3 \times 10^{-13}$  A cm<sup>-2</sup> for the metal-contact area and  $7 \times 10^{-14}$  A cm<sup>-2</sup> for the passivated noncontact area) and  $5 \times 10^{-14}$  A cm<sup>-2</sup> for recombination in the bulk of silicon wafer.

Another significant gain in cell performance is the enhancement of FF by an absolute 7.1%, which is mainly attributable to the dramatic reduction of the rear contact resistivity, as indicated by  $R_{\text{series}}$  values in inset of Figure 3d, consistent with the significant improvement in Ohmic behavior of the contact enabled by the MgO<sub>x</sub> interlayer, as presented in Figure 2. The reasonable  $V_{\text{OC}}$  and high FF measured on the cell with a MgO<sub>x</sub>/Al contact demonstrate that the latter presents good electron-selective characteristics. Notably, the high *FF* is sustained for a thickness of MgO<sub>x</sub> up to 60 nm (see Figure S2 in the Supporting Information), again consistent with (i) the trend of contact resistivity with thickness, and (ii) the high conductivity and high electron concentration in the film bulk revealed by Hall effect measurements.

The low  $J_{SC}$  of the Al control cell compared to the MgO<sub>x</sub>/Al cell is also consistent with a higher recombination loss at the c-Si/Al rear interface compared to the Si/MgO<sub>x</sub>/Al interface. An accompanying spectral response analysis is presented in Figure 3e for both cells (i.e., with and without MgO<sub>x</sub> interlayer). While the reflectance of the two cells is comparable, the insertion of MgO<sub>x</sub> interlayer enhances significantly the quantum efficiency (QE) response at long wavelengths (i.e., ≈900–1200 nm range). This result indicates again that the MgO<sub>x</sub> interlayer provides some passivation of the rear surface of the silicon wafer, consistent with the improvement in  $V_{OC}$  and with the lower  $J_{0c}$  presented above. Such passivation of interface defects is also consistent with a de-pinning of the Fermi level and a low contact resistivity.

While the  $MgO_x/Al$  electron-selective contacts have been demonstrated to enable high efficiency n-type c-Si solar cells,

the thermal stability of the device remains an important consideration for device longevity and module encapsulation. Cells with 1 nm MgO<sub>x</sub> interlayer were annealed in air ambient for 10 min at different elevated temperatures in a thermal furnace. Note that the cells for annealing have been fabricated and stored in air for more than two months, exhibiting little change in performance. The resultant cell electrical parameters were plotted in **Figure 4** as a function of annealing temperature. As can be seen, the solar cell performance is essentially



**Figure 4.** Thermal stability of the devices. Electrical parameters ( $V_{OC}$ ,  $J_{SC}$ , FF, PCE,  $R_{series}$ , and  $R_{shunt}$ ) as function of annealing temperature in thermal furnace air ambient for 10 min.

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constant up to 400 °C, and starts deteriorating when temperature increases further. Annealing at 500 °C deteriorated substantially the device performance. The degradation is most likely attributable to the degradation of the MgO<sub>x</sub>/Al contact, as evidenced by a significant increase in series resistance, while the shunting resistances exhibit little change. We also conducted Hall effect measurements on the 500 °C annealed  $MgO_x$  sample, which showed that the conductivity of the film decreased to  $2.4 \times 10^{-5}$  S cm<sup>-1</sup>, which is almost seven orders of magnitude lower than that of the as-deposited  $MgO_x$  film. This decrease in conductivity upon annealing is accompanied with a significant increase in film transmittance (see Figure S3 in the Supporting Information). There are several possible causes for the decrease in conductivity: (i) a reduction of excess metallic Mg upon annealing in air, leading to a more stoichiometric, less conductive material, (ii) a change in the crystallographic structure, evidenced by a change in X-ray diffraction (XRD) pattern (see Figure S4 in the Supporting Information), and (iii) the onset of diffusion of Al through the  $MgO_x$  into the n-type c-Si, which has been shown to exhibit a rectifying contact. Finally, we also investigated the effect of annealing duration on cell performance by submitting another cell to air-ambient furnace at 400 °C for various lengths of time. As shown in Figure S5 in the Supporting Information, all cell parameters were stable for annealing times up to 40 min. These results demonstrate a great device longevity and sufficient thermal budget for module encapsulation (typically less than 200 °C).

#### 3. Conclusion

This work has demonstrated a novel dopant-free MgOx/Al electron-selective contact for silicon solar cells. This contact scheme enabled a reduction in contact resistivity by more than two orders of magnitude compared to Al directly deposited on n-type c-Si, which is attributed to a depinning (defect passivation) of the Fermi level, together with a high conductivity and high electron concentration in bulk  $MgO_x$  film. The 20%-efficient n-type c-Si solar cell enabled by these full-area MgO<sub>x</sub>/Al electron-selective contacts is remarkable, given the very early proof-of-concept stage of this contact technology. The power conversion efficiency is already comparable to the counterpart p-type cells with full-area Al alloyed rear surfaces, which has been achieved after decades of extensive development by worldwide industries and laboratories. The low temperature thin film deposition techniques used in this work, together with the simplified proof-of-concept dopant-free rear contact structure, open up new possibilities in designing and fabricating contact cathodes for organic and/or inorganic optoelectronic devices.

#### 4. Experimental Section

The structure of MgO<sub>x</sub> thin film was studied with XRD. For XRD characterization, thin films of MgO<sub>x</sub> were deposited on single side polished c-Si wafers. A PANalytical X'Pert PRO MRD diffractometer with X-ray parabolic mirror and parallel plate collimator (0.27°) was used for the measurements. The diffraction pattern was obtained by using Ni-filtered Cu K $\alpha$  radiation. A software MDI Jade was applied for analysis of XRD data.

For XPS characterization, thin films of MgO<sub>x</sub>/Al were deposited on single-side polished c-Si wafers. A Kratos AXIS Ultra DLD system with a monochromatic Al K $\alpha$  X-ray source and a hemispherical analyzer was used for the measurements. Secondary electron cut-off and valence band measurements were performed using X-ray excitation, with an added bias to extract the cut-off edge. Work function measurements of the MgO<sub>x</sub>/Al interfaces were taken after thinning the Al over-layer thickness to <5 nm via sputtering. Stoichiometry information was extracted based on fits to the presented core level spectra, and Voigt line shapes were used for these fits. An Au reference work function at 5.1 eV was measurement accuracy.

Hall effect and resistivity measurements were performed with the four contact van der Pauw configuration using Lake Shore 7704A analyzer. The contacts constituting of  $\approx$ 50 nm MgO<sub>x</sub> and  $\approx$ 300 nm Al layer were fabricated on microscopy glass slab. Current (10 mA for nonannealed, and 1 nA for annealed sample) reversals were used to remove the unwanted thermal electric effects. The magnetic field was kept between 0.1 and 0.5 T, positive to negative, throughout the measurement to remove the influence of misalignment voltage. All samples were measured in air, under a dark environment, and at room temperature.

The n-Si/MgO<sub>x</sub>/Al electron-selective contacts were fabricated on planar Czochralski (Cz) n-type c-Si wafers with a resistivity of  $\approx 1 \Omega$  cm and a thickness of  $\approx 250 \mu$ m. Samples were subjected to a dilute HF dip prior to evaporation of the contact structures. An array of circular pads with different diameters was evaporated on the front of the test structures via a shadow mask. These pads were deposited as a stack of MgO<sub>x</sub> with a variety of thicknesses capped with  $\approx 300 \text{ nm}$  of Al. A full area Mg ( $\approx 10 \text{ nm}$ )/Al ( $\approx 300 \text{ nm}$ ) metal stack was evaporated on the rear surface of the contact samples. Note that Mg thin layer was used here to enhance the Ohmicity of rear contacts reducing the system error in determination of front contact resistivity. Current–voltage (I–V) measurements were taken at room temperature using a Keithley 2425 source meter.

Proof-of-concept cells were fabricated on Cz n-type c-Si wafers with a resistivity of ~2.0  $\Omega$  cm and a thickness of ~180  $\mu\text{m}.$  The as-cut (100)-oriented silicon wafers were subjected to an alkaline solution of tetrmethylammonium hydroxide (TMAH), deionized water, isopropyl alcohol, and dissolved silicon at a temperature of 85 °C for 60 min, forming textured morphologies with an array of random pyramids.<sup>[30-34]</sup> After cleaning all samples by the Radio Corporation of America (RCA) procedure, full-area boron diffusion with sheet resistance of  $\approx$ 120  $\Omega$ was then performed in a dedicated clean quartz furnace. The front boron diffused textured surfaces were then passivated with a stack of  $\approx$ 20 nm atomic layer deposited alumina (Al<sub>2</sub>O<sub>3</sub>) and  $\approx$ 65 nm plasma enhanced chemical vapor deposited silicon nitride  $(SiN_x)$ . Note that the stack also functions as an antireflection coating. The undiffused rear silicon surfaces were then coated with the novel electron-selective contacts (i.e.,  $\approx$ 1 nm MgO<sub>x</sub>/300 nm Al). The front metal grid contact with 10  $\mu$ m width lines and 1.3 mm pitch was patterned via photolithography, followed by thermal evaporation of a Cr (≈10 nm)/Pd(≈10 nm)/Ag (≈100 nm) stack, and finally thickened by Ag electroplating.

TEM images were acquired from the rear surface of the silicon solar cell that was fabricated per the procedures mentioned above. Cross section of the rear layers was prepared using the focused ion beam (FIB) lift-out technique in a Helios NanoLab 600 DualBeam scanning electron micorscope SEM/FIB system. Final thinning was performed at 5 kV and 16 pA to reduce FIB induced damage. TEM images were obtained using JEOL 2100F system operating at 200 kV.

The photovoltaic *J*–*V* behavior was measured under standard one sun conditions (100 mW cm<sup>-2</sup>, AM1.5 spectrum, 25 °C) with a 2 cm × 2 cm aperture mask using a solar simulator from Sinton Instruments. This simulator was calibrated with a certified Fraunhofer CalLab reference cell. The spectral response measurements were taken using a Protoflex Corporation QE measurement system (QE-1400-03). The reflectance and transmittance were measured using a PerkinElmer Lambda 1050 UV/ VIS/NIR spectrophotometer (with an integrating sphere attachment). Photoluminescence images were taken with a BTimaging LIS-R1 imager using a 1025 nm short-pass filter.

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### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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