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A magnesiam/amorphous silicon passivating contact for n-type crystalline silicon solar cells

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Among the metals, magnesium has one of the lowest work functions, with a value of 3.7 eV. This makes it very suitable to form an electron-conductive cathode contact for silicon solar cells. We present here the experimental demonstration of an amorphous silicon/magnesium/aluminium (a-Si:H/Mg/Al) passivating contact for silicon solar cells. The conduction properties of a thermally evaporated Mg/Al contact structure on n-type crystalline silicon (c-Si) are investigated, achieving a low resistivity Ohmic contact to moderately doped n-type c-Si (≈5 × 10^{15} cm^{-3}) of ≈0.31 Ω cm² and ≈0.22 Ω cm² for samples with and without an amorphous silicon passivating interlayer, respectively. Application of the passivating cathode to the whole rear surface of n-type front junction c-Si solar cells leads to a power conversion efficiency of 19% in a proof-of-concept device. The low thermal budget of the cathode formation, its dopant-less nature, and the simplicity of the device structure enabled by the Mg/Al contact open up possibilities in designing and fabricating low-cost silicon solar cells. Published by AIP Publishing. [http://dx.doi.org/10.1063/1.4962960]

P-type silicon solar cells are still the workhorse for industrial crystalline silicon (c-Si) solar cell manufacturing. However, as the silicon photovoltaic (PV) industry moves to introduce advanced high-efficiency solar cell concepts, the quality of the base material is becoming more and more important.¹ The high oxygen content in the standard quality of the base material is becoming more and more important. As the silicon photovoltaic (PV) industry moves to industrial crystalline silicon (c-Si) solar cell manufacturing.

However, as the silicon photovoltaic (PV) industry moves to introduce advanced high-efficiency solar cell concepts, the quality of the base material is becoming more and more important.¹ The high oxygen content in the standard quality of the base material is becoming more and more important.
In this work, we explore the possibility of using Mg to form electron-selective contacts on n-type c-Si wafers and solar cells. Note that a capping Al layer is added to suppress the oxidation of Mg in air or during possible final sintering processes. We investigate the conduction properties of a thermally evaporated Mg/Al contact structure on n-type c-Si, showing a low contact resistivity $\rho_c$ of $\sim 0.31 \Omega \text{cm}^2$ and $\sim 0.22 \Omega \text{cm}^2$ to moderately doped n-Si ($\sim 5 \times 10^{15} \text{ cm}^{-3}$) for samples with and without an a-Si:H passivating interlayer, respectively. We then apply this passivating electron contact structure to the full rear surface of n-type silicon solar cells, achieving a power conversion efficiency of 19%.

Mg layers were thermally evaporated at a rate of 5 Å/s from a 3 N-purity Mg ingot source, with a base pressure of $< 2 \times 10^{-6}$Torr. The a-Si:H interlayers located between the Mg film and the n-Si substrate, which were inserted in some cases to suppress the recombination at the c-Si surface, were deposited using a direct plasma enhanced chemical vapour deposition (PECVD) reactor (Oxford PlasmaLab 100) at a temperature set-point of 400°C, a base pressure of 1.9 Torr, a plasma power of 10 W, a frequency of 13.56 MHz, and a gas flow of 20 sccm. Note that no annealing is required to activate the passivation by a-Si:H used in this work. While the thickness of the metal layer ($\sim 10$ nm) was determined by the quartz crystal thickness monitor, the thickness of a-Si:H layers was determined by fitting polarized reflectance using the Tauc–Lorentz model, as measured by spectroscopic ellipsometry (J.A. Woolam M2000 ellipsometer) on the single-side polished c-Si substrate.

The thicknesses of both Mg and a-Si:H layers were also confirmed by the transmission electron micrograph (TEM), as shown in Figure 1. TEM images were acquired from the rear surface of the silicon solar cell that was fabricated as per the procedures to be described later. The cross section of the rear layers was prepared using the focused ion beam (FIB) lift-out technique in a Helios NanoLab 600 DualBeam SEM/FIB system. Final thinning was performed at 5 kV and 16 pA to reduce FIB induced damage. TEM images were obtained using a JEOL 2100F system operating at 200 kV. Also included in Figure 1 is an energy-dispersive X-ray spectroscopy (EDX) line scan of the local Si, Al, Mg, and O elemental distributions across the interface. Figure 1 seems to indicate some overlap between the Mg and a-Si:H layers, but we ascribe that to an artefact of the TEM/EDX measurement due to a poor TEM/EDX spatial resolution (i.e., $\sim 3$ nm). In addition, the possible formation of a sub-oxide species seems to be negligible at the c-Si surface.

A highly selective contact is achieved through a simultaneous reduction in two measurable parameters. The positive selectivity towards majority carriers, that is, the efficient transport of electrons of the Mg/Al contact structure, can be evaluated via its contact resistivity $\rho_c$. The contact test structures were fabricated on planar Czochralski (Cz) n-Si wafers with a resistivity of $\sim 1 \Omega \text{ cm}$ and a thickness of $\sim 250 \mu\text{m}$. 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. A full area Al metal of $\sim 300 \text{ nm}$ was evaporated on the rear surface of the contact samples. Current–voltage ($I$–$V$) measurements were taken at room temperature using a Keithley 2425 source-meter.

Figure 2 shows a series of representative $I$–$V$ measurements of samples with (i) Al metal directly on a-Si:H ($\sim 6$ nm) passivated n-Si (Al/a-Si:H/n-Si), (ii) Mg interlayer between Al and a-Si:H passivated n-Si (Al/Mg/a-Si:H/n-Si), and (iii) Al/Mg directly on n-Si (Al/Mg/n-Si). Note that the $I$–$V$ measurements of the three groups of samples were performed on the same pad area ($\sim 1.96 \text{ cm}^2$) for direct comparison. As we can see in Figure 2, the sample with Al directly on a-Si:H/n-Si (i.e., without Mg) exhibits rectifying behavior, similar to the behavior of Al/n-Si, preventing an accurate extraction of contact resistivity. In contrast, the insertion of a thin Mg ($\sim 10$ nm) layer improves dramatically the conductivity of the contact.
contacts, leading to an Ohmic contact (i.e., linear \( I-V \) curve) between the Al electrode and the \( n\)-Si substrate. The extracted contact resistance \( \rho_c \) for the structure with Mg is determined to be \( \sim 0.22 \Omega \text{cm}^2 \), which is more than one order of magnitude lower than that without the Mg layer. The higher electron conductivity provided by the Mg/Al contact structure is mainly attributable to the lower work function of Mg, compared to that of Al. It is worth noting that (i) a low work function might only serve as a general guideline for the formation of a good contact by reducing the Schottky barrier height for electron transport and that (ii) surface states still can play a key role in the final height of the metal-semiconductor barrier (Fermi level pinning).

Furthermore, also included in Figure 2 is the \( \rho_c \) of the samples with \( \sim 6 \text{ nm} \) a-Si:H, exhibiting only a slightly higher \( \rho_c \) of \( \sim 0.31 \Omega \text{cm}^2 \), as shown in Figure 2 inset-(a). One of the drawbacks of inserting an intrinsic a-Si:H interlayer is that it can introduce additional resistance to current transport through the contact structure. Figure 2 inset-(b) presents the dependence of the measured \( \rho_c \) on a-Si:H thickness. It can be seen that \( \rho_c \) increases as the a-Si:H thickness increases, exhibiting approximately a factor of 4 increase as the a-Si:H layer increases from 0 to 10 nm. The increase in \( \rho_c \) for thicker a-Si:H films is likely due to the bulk resistivity of the a-Si:H, as also revealed in Ref. 13. Preliminary studies indicate that the thickness of the Mg layer has a negligible impact on contact resistivity when it is greater than 2 nm, both for samples with and without an a-Si:H layer. Mg films thinner than 2 nm were difficult to deposit controllably, due to very low melting point of the Mg metal, which caused a fluctuating evaporation rate.

Given that the surface passivation quality by a-Si:H has been shown to saturate when a-Si:H reaches \( \sim 6 \text{ nm} \) (see Ref. 13) and that a reasonably low \( \rho_c \) (\( \sim 0.31 \Omega \text{cm}^2 \)) can still be maintained at this thickness, a 6 nm a-Si:H/10 nm Mg/300 nm Al stack was employed for the proof-of-concept cell design. Figure 3(a) depicts the schematic structure of such an \( n \)-type front-junction silicon solar cell with a full-area rear a-Si:H/Mg/Al contact. Compared to conventional high-temperature diffused \( n^+ \) contacts, an advantage of the full area electron contacts is the removal 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).

Solar cells were fabricated on Cz \( n \)-type c-Si wafers with a resistivity of \( \sim 1.0 \Omega \text{cm} \) and a thickness of \( \sim 200 \mu \text{m} \). The as-cut (100)-oriented silicon wafers were subjected to an alkaline solution of TMAH, deionized water, isopropyl alcohol (IPA), and dissolved silicon at a temperature of 85°C for 60 min, forming textured morphologies with an array of random pyramids. The resultant final wafer thickness is \( \sim 175 \mu \text{m} \). After cleaning all samples by the Radio Corporation of America procedure, full-area boron diffusion with a sheet resistance of \( \sim 120 \Omega \square \) was then performed in a dedicated clean quartz furnace. The front boron diffused textured surfaces were then passivated with a stack of \( \sim 20 \text{ nm} \) atomic layer deposited (ALD) alumina (\( \text{Al}_2\text{O}_3 \)) and \( \sim 65 \text{ nm} \) PECVD silicon nitride (\( \text{Si}_3\text{N}_4 \)). The undiffused rear silicon surfaces were then fully coated with the a-Si:H/Mg/Al layers. The front metal grid contact with 10 \( \mu \text{m} \) width lines and 1.3 mm pitch was patterned via photolithography, followed by thermal evaporation of a Cr (\( \sim 10 \text{ nm} \))/Pd (\( \sim 10 \text{ nm} \))/Ag (\( \sim 100 \text{ nm} \)) stack, and finally thickened by Ag electroplating.

The photovoltaic \( J-V \) behavior was measured under standard one sun conditions (100 mW/cm\(^2\), AM1.5 spectrum, 25°C) with a 2 \times 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 and reflectance measurements were taken using a Protoflex Corporation QE measurement system (QE-1400-03) and a PerkinElmer Lambda 1050 UV/VIS/NIR spectrophotometer (with an integrating sphere attachment), respectively.

The \( J-V \) photovoltaic characteristic curve under one sun standard illumination is plotted in Figure 3(b) for cells with
and without Mg interlayers. As can be seen, Al directly on the a-Si:H passivated n-Si (i.e., without Mg) rear side behaves as a severe Schottky diode, which opposes the photovoltaic effect of the front pn junction, leads to a typical S-shape \(J-V\) curve, and results in a power conversion efficiency of only 2.2%. Such cell behavior is consistent with the rectifying contact of Al/a-Si:H/n-Si presented above. By contrast, the insertion of a Mg layer enhances substantially the cell performance, leading to a conversion efficiency of 19%.

The electrical parameters of the two cells are also summarized in Table I. The reasonable \(FF\) of the cell with a Mg layer demonstrates a good transport of electrons across the contact structure. Figure 3(c) presents the accompanying spectral response analysis for the two cells. Interestingly, the two cells (i.e., with and without Mg layers) have similar performance in quantum efficiency, despite a significant discrepancy in electrical parameters (i.e., the \(J–V\) curves). The results imply that, although the cell without Mg layer has similar carrier generation and recombination and slightly higher rear reflectance, it has a very poor electron transport to the electrode due to the rectifying contact at the rear surface. It should be noted that the loss in \(V_{OC}\) to the electrode due to the rectifying contact at the rear surface has enabled a power conversion efficiency of 19%. The low thermal budget of the cathode formation, its dopant-less nature, and the simplicity of the device structure enabled by the Mg/Al contact open up possibilities in designing and fabricating low-cost silicon solar cells.

In conclusion, we have developed a dopant-free a-Si:H/Mg/Al electron-selective contact deposited at low-temperature. We have investigated the conduction properties of a thermally evaporated Mg/Al contact structure on n-type c-Si, demonstrating a sufficiently low contact resistivity of \(\rho_c \sim 0.31 \Omega \text{cm}^2\) and \(\sim 0.22 \Omega \text{cm}^2\) on moderately doped n-Si for samples with and without an amorphous silicon (a-Si:H) passivating interlayer, respectively. Application to the full-area rear surface has enabled a power conversion efficiency of 19%. The low thermal budget of the cathode formation, its dopant-less nature, and the simplicity of the device structure enabled by the Mg/Al contact warrants further investigations.

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### Table I. Photovoltaic performance of cells without and with Mg metal layers.

<table>
<thead>
<tr>
<th></th>
<th>(V_{OC}) (mV)</th>
<th>(J_{SC}) (mA/cm²)</th>
<th>(FF) (%)</th>
<th>(\eta) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Without Mg</td>
<td>405.0</td>
<td>29.5</td>
<td>18.2</td>
<td>2.2</td>
</tr>
<tr>
<td>With Mg</td>
<td>636.6</td>
<td>38.0</td>
<td>78.4</td>
<td>19.0</td>
</tr>
</tbody>
</table>

![Fig. 4. Photoluminescence (PL) images of a-Si:H passivated samples (a) before and (b) after Mg/Al evaporation using a 1025 nm short-pass filter. Note that the PL imaging was performed in an uncalibrated mode and therefore, under the same illumination and exposure condition, the PL mean counts presented here only give an indication in the relative change in recombination at the silicon surfaces.](image)


