Magnesium Fluoride Electron-Selective Contacts for Crystalline Silicon Solar Cells

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Supporting Information

ABSTRACT: In this study, we present a novel application of thin magnesium fluoride films to form electron-selective contacts to *n*-type crystalline silicon (c-Si). This allows the demonstration of a 20.1%-efficient c-Si solar cell. The electronselective contact is composed of deposited layers of amorphous silicon (~ 6.5 nm), magnesium fluoride (~ 1 nm), and aluminum (~300 nm). X-ray photoelectron spectroscopy reveals a work function of 3.5 eV at the MgF₂/Al interface, significantly lower than that of aluminum itself (~4.2 eV),



enabling an Ohmic contact between the aluminum electrode and *n*-type c-Si. The optimized contact structure exhibits a contact resistivity of \sim 76 m Ω ·cm², sufficiently low for a full-area contact to solar cells, together with a very low contact recombination current density of ~ 10 fA/cm². We demonstrate that electrodes functionalized with thin magnesium fluoride films significantly improve the performance of silicon solar cells. The novel contacts can potentially be implemented also in organic optoelectronic devices, including photovoltaics, thin film transistors, or light emitting diodes.

KEYWORDS: silicon solar cell, magnesium fluoride, electron-selective contact, Ohmic contact, surface passivation

INTRODUCTION

The vast majority of industrial solar cells are currently fabricated with crystalline silicon (c-Si) wafers, on which two highly doped regions are formed in order to extract electrons and holes, respectively. Highly efficient crystalline silicon solar cells also rely on doped layers of deposited amorphous^{1,2} or polycrystalline silicon.³ Nevertheless, these doping techniques require high temperatures or plasma excitation and involve toxic gases, increasing the fabrication complexity and cost. Moreover, the doped regions exhibit high recombination and/ or parasitic absorption losses, posing a fundamental limit to device performance. In moving toward higher efficiencies, it has long been recognized that major architectural or materialsbased modifications are required. This has fueled a rapidly expanding field of research focused on the search for carrierselective materials that can reduce the losses at the c-Si solar cell contacts, including transition metal oxides,^{4–9} organic polymers,^{10–13} and alkali metal salts.^{14,15}

Magnesium fluoride (MgF_2) , an alkaline earth metal salt, has a long history of being utilized in optical devices, including c-Si solar cells. Its high transparency and low refractive index ($n \approx$ 1.36) have proven useful on the front surface of such devices as an inexpensive second-layer antireflection coating.¹⁶ In fact, several world-record crystalline silicon solar cells used such a layer in addition to zinc sulfide ($n \approx 2.34$), a combination of optical layers that can minimize reflection losses.¹⁷⁻¹⁹ In addition, due to its relatively high threshold to laser-induced

damage, high hardness, and excellent stability in hostile environments, such films have also been utilized for optical components in high power lasers.^{20,21} However, the use of this material to enhance electron transport at the contacts of electronic devices has not been reported, despite the fact that alkali and/or alkaline earth metal salts, for example, lithium fluoride, have been explored intensively as a low work function electrode in photovoltaic and light emitting diodes.^{14,15,22-30}

In this work, we explore the behavior of thin MgF₂ films to form electron-selective contacts on c-Si solar cells. We investigate the conduction and recombination properties of a thermally evaporated MgF_2/Al electron-selective contact on *n*type c-Si (n-Si), both with and without an amorphous silicon (a-Si:H) passivating interlayer. We measure the work function of the contact by X-ray photoelectron spectroscopy (XPS), and find a significantly lower work function than that of pure aluminum. Finally, we apply the novel electron contact to the full rear surface of *n*-type silicon solar cells, for the first time with this material, achieving a power conversion efficiency above 20%.

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Figure 1. X-ray photoelectron spectroscopy (XPS) measurements of MgF₂ based contacts. Parts (a) and (b) present the core level spectrum of Mg 1s and F 1s, respectively. The extracted stoichiometry of MgF₂ is also included. Part (c) shows the valence band spectrum of the MgF₂ film. Part (d) shows the secondary electron cutoff spectrum measured at the MgF₂/Al interface following argon ion sputtering, showing a work function value of 3.5 eV. A gold (Au) reference work function at 5.1 eV was measured in the same measurement to confirm the accuracy of the measurements.

RESULTS AND DISCUSSION

MgF₂ films were thermally evaporated at a rate of 0.25 Å/s from a 3N-purity MgF₂ powder source, with a base pressure of $<3 \times 10^{-6}$ Torr. The electronic band structure was characterized via XPS using monochromatic Al K_a X-rays with a photon energy of 1486.7 eV at a pressure in the low 10^{-9} to mid 10^{-10} mbar range. Figure 1 shows the XPS measurement results, including (i) core levels of Mg 1s and F 1s, (ii) the valence band region, and (iii) the work function of the $MgF_2/$ Al interface. Extraction of the MgF₂ film stoichiometry based on core level peak areas shows the thermally evaporated MgF₂ to be approximately stoichiometric, with a F to Mg atomic fraction of 2. Note that the sample for core level analysis has a bare MgF₂ layer (i.e., it does not have an Al over-layer), and hence the stoichiometry may not be representative of the final contact. The valence band of the MgF₂ film is determined to be \sim 6.1 eV from the Fermi energy level, which is close to that of LiF.¹⁵ No obvious sub-band features were observed, consistent with the stoichiometric film composition determined from the core level XPS analyses. Finally, the XPS secondary electron

cutoff analysis of a MgF₂/Al stack thinned by sputtering (Argon ion gun, 4 keV) illustrated in Figure 1(d) shows a work function of the MgF₂/Al stack in the vicinity of 3.5 eV, which is significantly lower than the work function of the Al metal itself (~4.2 eV).³¹ As will be presented in the next section, the reduction of the work function plays a crucial role in enabling Ohmic contact behavior between the Al electrode and the *n*type silicon substrate.

In general, the MgF₂/Al contact selectivity toward electrons can be evaluated via its contact resistivity ρ_{c} . Conversely, the equally important "blocking action" of the contact structure toward holes can be evaluated via its interface recombination parameter J_{0c} . The contact resistivity ρ_c was measured using the method devised by Cox and Strack,³² as depicted schematically in Figure 2(a). Figure 2(c) shows a series of I-V measurements of a sample with a ~1 nm MgF₂ film, and one representative I-Vmeasurement of a sample with Al directly on *n*-Si. The resistance versus diameter trend is fitted with a spreading resistance model, allowing accurate extraction of ρ_c (see Supporting Information Figure S1).



Figure 2. Contact resistivity measurements of MgF₂ based contacts to *n*-Si. Part (a) depicts a schematic of the contact resistivity test structure. Part (b) presents schematics of energy band diagrams for contacts of Al metal, MgF₂/Al, and a-Si:H/MgF₂/Al on *n*-Si. Part (c) shows a serial of I-V measurements of sample with ~1 nm MgF₂ film, and one representative I-V measurement of sample with Al directly on *n*-Si. The extracted contact resistance ρ_c for the structure with ~1 nm MgF₂ is determined to be ~35 m $\Omega \cdot \text{cm}^2$. Part (d) shows the ρ_c as a function of MgF₂ thickness, with and without a-Si:H interlayer.



Figure 3. Recombination measurements of MgF_2 based contacts to *n*-Si. Part (a) shows the measured effective carrier lifetime as a function of excess carrier density for *n*-Si wafers symmetrically coated with MgF_2/Al , with and without 6.5 nm a-Si:H interlayer. Insets show the schematic of the lifetime measurements using a Sinton Instruments WCT-120 photo-conductance tool and lifetime test structure. Part (b) shows the implied VOC behavior for *n*-Si lifetime samples. The dotted horizontal line highlights the implied open circuit voltages at 1 sun.

As we can see in Figure 2(c), the sample with Al directly on n-Si (i.e., without MgF₂) exhibits rectifying behavior, preventing an accurate extraction of contact resistivity. A high contact

resistance, or a rectifying behavior, between the Al metal and n-Si is attributable to the presence of a large surface potential barrier known to exist at this surface.³³ The insertion of a thin



Figure 4. Device results with full-area rear MgF₂ based electron-selective contacts. Part (a) illustrates the schematic of an *n*-type silicon solar cell featuring full-area rear a-Si:H/MgF₂/Al electron-selective contacts. Parts (b) and (c) present the 50 nm scale and 10 nm scale cross-sectional scanning transmission electron micrographs (STEM) and transmission electron micrographs (TEM) of the rear layers of the cell. Part (d) presents the light J-V behavior and electrical parameters of the cell measured under standard one sun conditions. Part (e) shows the external and internal quantum efficiencies accompanied the measured reflectance for the cell.

MgF₂ (~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*-Si substrate. The extracted contact resistance ρ_c for the structure with ~1 nm MgF₂ is determined to be ~35 m Ω ·cm². The high electron conductivity provided by the MgF₂/Al contact structure can be attributed to (i) a reduction in the work function, compared to that of Al, as revealed by the above-mentioned XPS measurements, and/or (ii) electron tunneling through a reduced barrier width, which is likely similar to the mechanism of the Ohmic contact between the heavily phosphorus doped n^+ c-Si and the direct Al metal.

Figure 2(d) presents the dependence of the measured ρ_c on MgF₂ thickness, with and without a ~6.5 nm a-Si:H interlayer. It can be seen that ρ_c first decreases dramatically as the MgF₂ thickness increases from 0 to 1 nm, and then increases sharply when MgF₂ exceeds 1 nm. When the MgF₂ thickness exceeds 5 nm, the contact behaves in a rectifying fashion instead of a linear one. The initially decreasing ρ_c could potentially be a result of partial MgF₂ surface coverage for the ultrathin films (less than 1 nm), due to commonly reported island growth for thermal evaporation.³⁴ The increase in ρ_c for thicker MgF₂ films

is likely due to the bulk resistivity of the MgF₂ material. Moreover, Figure 2(d) also includes the ρ_c of the samples with ~6.5 nm a-Si:H (which is employed to enhance the passivation of the c-Si surface, as will be presented later) for a range of MgF₂ thicknesses, showing a generally higher ρ_c than those of samples without a-Si:H, and exhibiting a lowest ρ_c value of 76 m Ω ·cm² for 1 nm of MgF₂. The higher ρ_c for samples with a-Si:H could again be related to the bulk resistivity of the a-Si:H interlayer, introducing an additional hindrance to current transport. Nevertheless, it is remarkable that the insertion of the ~6.5 nm thick a-Si:H layer increases the contact resistivity only moderately.

The recombination at the interface between c-Si and the deposited films was evaluated via effective carrier lifetime measurements on symmetrically film-coated samples (see a schematic of the test structure in the inset of Figure 3(a)). The effective carrier lifetime τ as a function of excess carrier density Δn was measured using a Sinton Instruments WCT-120 photo-conductance tool,³⁵ as illustrated in the inset of Figure 3(a). This is one of the most straightforward techniques to probe the recombination properties of c-Si surfaces. It is simple, contactless, and extremely sensitive to bulk and surface

defects.³⁵ The contact recombination parameter, J_{0c} and the implied open-circuit voltage $(V_{\rm OC})$ at one sun can be extracted from the injection-dependent carrier lifetime $\tau(\Delta n)$, as shown in Figure 3(b).

While the MgF₂/Al stack provides excellent Ohmic contact to *n*-Si (that is a low ρ_c), it provides little passivation to the silicon surface, as evidenced by a low effective carrier lifetime of 15 μ s, corresponding to an implied V_{OC} of 534 mV. This motivated us to explore an insertion of a thin a-Si:H film between MgF2 and n-Si-a strategy that has already been proven effective for molybdenum oxide based hole-selective and LiF based electron-selective contacts.^{15,36,37} Intrinsic a-Si:H has been demonstrated to provide a high quality passivation of c-Si surfaces.³⁸⁻⁴² This is attributable to a very low defect density at the a-Si:H/c-Si interface, assisted in part by the high concentration (~10-20% atomic) of hydrogen incorporated into the films, which migrates to the interface and passivates remaining c-Si dangling bonds.^{43–45} As shown in Figure 3(a), upon the insertion of a 6.5 nm-thick a-Si:H layer between MgF₂ and *n*-Si, the surface passivation quality is markedly enhanced, yielding more than 2 orders of magnitude improvement in carrier lifetime, from 15 to 4088 μ s. This corresponds to a twoorder of magnitude reduction in J_{0c} from ~1500 fA/cm² to ~10 fA/cm². Figure 3(b) shows that the implied $V_{\rm OC}$ for samples with and without an a-Si:H thin film increases drastically from 534 mV to 710 mV.

While the contact resistance and recombination results presented in Figures 2 and 3 are promising, a more definitive demonstration of the potential of this electron contact is to integrate it into a solar cell design. For a proof-of-concept solar cell design, a 6.5 nm a-Si:H/1 nm MgF₂/300 nm Al stack was applied to the rear surface of an n-type silicon wafer, as it provides a combination of reasonably low $\rho_{\rm c}$ (~76 m Ω ·cm²) and low J_{0c} (~10 fA/cm²). Figure 4(a) depicts the schematic structure of such an *n*-type silicon solar cell with a full-area rear a-Si:H/MgF₂/Al contact. A cross-sectional scanning electron micrograph and a high resolution transmission electron micrograph of the rear contact layers are included in Figure 4(b) and (c), respectively. As indicated in Figure S2, compared to conventional high-temperature diffused n^+ contacts, an advantage of the MgF₂ based contact approach is the removal of (i) the high-temperature phosphorus diffusion; and (ii) the patterning of the rear dielectrics (by photolithography in many laboratories, and commonly by laser ablation in industry).

The J-V photovoltaic characteristic curve under one sun standard illumination is plotted in Figure 4(d), showing a power conversion efficiency of 20.1%, associated with a $V_{\rm OC}$, short-circuit current (I_{SC}) and fill factor (FF) of 687 mV, 37.8 mA/cm², and 77.3%, respectively. The high $V_{\rm OC}$ and reasonably high FF demonstrate that the good electron-selective characteristics of the contact shown in Figures 2 and 3 above (i.e., low recombination and low resistivity) can be effectively translated to solar cells. The high J_{SC} is within expectations, as the cell features a textured surface with an array of random pyramids and an Al₂O₃/SiN_x passivation/antireflection coating, both of which provide light coupling into the semiconductor absorber.^{46,47} An accompanying spectral response analysis is presented in Figure 4(e), showing a high quantum collection efficiency over most of the AM1.5G spectrum. The J_{SC} calculated by integrating the external quantum efficiency curve with an AM 1.5G reference spectrum is 37.9 mA/cm², which is consistent with the measured J_{SC} from the light J-Vmeasurements. Further enhancement in the cell performance

can potentially result from an optimization of the rear surface reflection. As shown in Figure S3, the parasitic absorption by a thick Al electrode layer is significantly higher than that by a Ag metal layer. By reducing the thickness of the Al electrode layer from the currently used 300 to 1 nm (and capping with a more reflective metal such as silver), a gain in J_{SC} of ~0.6 mA/cm² is expected.

CONCLUSIONS

We have developed a novel dopant-free a-Si:H/MgF₂/Al electron-selective contact deposited at low-temperature. Its passivation qualities enable an open-circuit voltage potential of up to 710 mV, and its moderate contact resistivity is suitable for high efficiency silicon solar cells. Application to the full-area rear surface enables one-dimensional electron flow in an *n*-type silicon wafer. Its good prospects are solidly demonstrated by a proof-of-concept device with a power conversion efficiency of 20.1%. The low temperature thin film deposition techniques used in this work, together with the simplicity of the device structures enabled by the MgF₂/Al contact, open up new possibilities in designing and fabricating organic and/or inorganic optoelectronic devices.

METHODS

The film thickness of MgF_2 was determined by fitting polarized reflectance using the Tauc–Lorentz model,⁴⁸ as measured by ex-situ spectroscopic ellipsometry (J.A. Woolam M2000 ellipsometer) on single-side polished c-Si substrate.

For XPS characterization, thin films of MgF₂/Al were deposited on single-side polished c-Si wafers. A Kratos AXIS Ultra DLD system with a monochromatic Al K α X-ray source and a hemispherical analyzer was used for the measurements. Secondary electron cutoff and valence band measurements were performed using X-ray excitation, with an added bias to extract the cutoff edge. Work function measurements of the MgF₂/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.

The *n*-Si/MgF₂/Al electron-selective contacts were fabricated on float-zoned (FZ), planar, *n*-type c-Si wafers with a resistivity of ~0.5 Ω ·cm and a thickness of ~200 μ 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 MgF₂ with a variety of thicknesses capped with ~500 nm of Al. A full area Al metal of ~500 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.

Samples for carrier lifetime measurements were fabricated on FZ, (100)-oriented, undiffused *n*-type c-Si substrates with a resistivity of ~10 Ω -cm and a thickness of ~195 μ m. All wafers were etched in tetramethylammonium hydroxide (TMAH, 25 wt %) at ~85 °C to remove saw damage, and then cleaned by the RCA (Radio Corporation of America) procedure⁴⁹ and dipped in a 1% diluted hydrofluoric acid (HF) acid solution to remove any remaining oxide prior to film depositions.

The a-Si:H interlayers located between MgF₂ film and *n*-Si substrate were deposited using a direct plasma enhanced chemical vapor deposition (PECVD) reactor (Oxford PlasmaLab 100) at a temperature set point of 400 °C and a frequency of 13.56 MHz. The deposition rate of a-Si:H was approximately 2 Å/s. The thickness of a-Si:H was ~6.5 nm. The deposition power and silane gas flow for a-Si:H were optimized to minimize the deposition rate so as to increase the a-Si:H film thickness control in the nm scale. Note the thickness of the Al over-layer for the carrier lifetime samples was controlled to be thin (<10 nm) to mimic a contact, while still transmitting sufficient light for the photo-conductance measurement.

Proof-of-concept cells were fabricated on n-type c-Si wafers with a resistivity of ~0.5 Ω ·cm and a thickness of ~230 μ 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.^{50–54} After cleaning all samples by the RCA procedure, full-area boron diffusion with sheet resistance of ~120 Ω/\Box was then performed in a dedicated clean quartz furnace. The front boron diffused textured surfaces were then passivated with a stack of ~18 nm atomic layer deposited (ALD) alumina (Al₂O₃) and ~75 nm PECVD 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., 6.5 nm a-Si:H/1 nm MgF₂/500 nm Al). The front metal grid contact with 10 μ 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.

STEM and TEM images were acquired from the rear surface of the silicon solar cell that was fabricated per the procedures abovementioned. Cross section of the rear layers was prepared using the focused ion (FIB) beam lift-out technique in a Helios NanoLab 600 DualBeam SEM/FIB system. Final thinning was performed at 5 kV and 16pA to reduce FIB induced damage. Scanning TEM images were then acquired using FEI Verios operated at 30 kV. TEM images were obtained using JEOL 2100F system operating at 200 kV.

The light J-V behavior was measured under standard one sun conditions (100 mW/cm², AM1.5 spectrum, 25 °C) with a 2 × 2 cm² aperture mask using a solar simulator. This system 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.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b03599.

Extraction of contact resistance of MgF₂/Al on *n*-type c-Si wafer via fitting of a series of J-V measurements, device fabrication sequences in comparison to that of a conventional *n*-type c-Si solar cell, simulated parasitic absorption of rear layers of solar cell (PDF)

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Author Contributions

Y.W. conceived the idea. Y.W. and C.S. carried out the material development, device fabrication, electrical characterization and analysis. J.B. and M.H. assisted with materials characterization. D.Y., T.A., P.Z., X.Y., J.C., and J.M. assisted with device fabrication and discussed the results. A.J. and A.C. discussed the results. Y.W. wrote the paper, and all other authors provided feedback.

Notes

The authors declare no competing financial interest.

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