Electron-Selective Lithium Contacts for Crystalline Silicon Solar Cells

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Abstract: Separating photo-generated charge carriers by carrier-selective hetero-structure contacts, rather than by doped homo-junctions, is a promising pathway to approach the theoretical power conversion efficiency (PCE) limit of crystalline silicon (c-Si) solar cells. This work presents an electron-selective, hole-blocking lithium contact for c-Si solar cells by simple thermal evaporation of air-stable Li$_3$N powder. We find that this lithium contact introduces only a minimal Schottky barrier height for electron transport at its interface with lightly-doped n-type c-Si surfaces, resulting in a contact resistivity of 12.8 mΩ·cm$^2$. By implementing a full-area electron-selective lithium contact, an n-type c-Si solar cell with a PCE of 19% is achieved, representing a 4% absolute PCE improvement over reference devices with an aluminum contact. This work extends the choices of electron-selective contact materials for photovoltaic devices, using simple, scalable fabrication methods.

Effectively separating and collecting photo-generated charge carriers is essential for high-efficiency crystalline silicon (c-Si) solar cells. [1], [2] In conventional homojunction c-Si solar cells, charge-carrier separation is realized by high-temperature diffused p-n junctions. Despite their widespread use, such heavily doped homojunctions induce significant limitations on device performance due to Auger recombination, band gap narrowing, and parasitic optical absorption by free charge carriers [3], [4]. Carrier-selective heterojunction contacts can overcome the optical and recombination limitations of homojunction contacts and have attracted significant attention in the photovoltaic (PV) community in recent years [1]. High quality carrier-selective contacts combine a low contact resistivity with a low recombination velocity at the contact interface. To date, the best performing c-Si cells use passivating, charge-selective contacts based on thin films of doped silicon, such as the silicon heterojunction (SHJ) and poly-Si passivating contact
technologies [5]–[9]. However, the silicon layer deposition processes involve flammable and toxic gases (e.g., SiH₄, PH₃, B₂H₆, etc.) with mandatory safety control and may require significant capital expenditure. Thanks to a simpler deposition process at a low temperature, such as sputtering, thermal evaporation, atomic layer deposition (ALD), and solution processing (including spin, spray, or slot-die coating), various so-called ‘dopant-free’ carrier-selective heterocontact materials have emerged as a promising alternative approach to contact formation to c-Si. Low-workfunction metal oxides, nitrides, and 2D materials, such as TiO₂, TaOₓ, ZnO, TaNₓ, TiN, and MXenes have been reported as electron-selective layers (ESLs), and high-workfunction MoOₓ and VOₓ have been developed as hole-selective layers (HSLs) for c-Si solar cells [5], [10]–[22]. The band energetics of these thin films play a crucial role in achieving carrier selectivity of the contacts. Generally, the work function of the ESL in an electron-selective contact is required to be close to or lower than the conduction band minimum (CBM) of c-Si (~4.05 eV, relative to the vacuum level). Similarly, the work function of the HSL in a hole-selective contact has to be close to or higher than the c-Si valence band maximum (VBM, ~5.17 eV). In case of the absence of significant Fermi-level pinning (FLP) at the device interface, which can be resolved by interface passivation, these energetic differences lead to electron (hole) extraction at the electron (hole) selective contacts, combined with a depletion of the opposite type of charge carrier, forming asymmetrical conductivities for electrons and holes in the vicinity of the contacts [2]. Often, such dopant-free passivating contacts, especially when located at the sun-facing front side of the device, may also minimize parasitic optical absorption issues associated with their doped-silicon layer counterparts [10]. Despite their opacity, direct deposition of metals as contact materials may also be of interest, as they offer simplicity of fabrication and may feature sufficiently extreme work functions to achieve low contact resistivities to the c-Si surface. However, commonly used metals, such as Ag and Al, show a non–ohmic contact behavior when directly deposited on lightly doped n-type c-Si surfaces, due to FLP caused by surface-defect induced gap states (i.e. silicon dangling bond (DB)) as well as metal-induced gap states (DIGS and MIGS), resulting in a large energetic barrier for charge-carrier transport [1], [23]–[26]. Very low workfunction metals overcome such limitations and obtain excellent electron-selective contacts on n-Si wafers without the need for heavy sub-surface doping. For instance, magnesium (Mg) and calcium (Ca), have been applied to silicon-based solar cells and proven to show a low contact resistivity on n-type c-Si wafers [27]–[29]. In terms of Mg contacts, Mg layers were evaporated from a Mg source, and an Al capping layer was added in-situ to protect Mg from oxidation. A thin amorphous-silicon passivation interlayer between the c-Si and the Mg has also been demonstrated to enhance the passivation of the device. A power conversion efficiency (PCE) of 19% and ~0.22 Ω·cm² contact resistivity were obtained on n-type c-Si solar cells[27]. Compared with Mg, the c-Si/Ca contact showed a lower energy barrier, and a PCE of 20.3% was achieved, and 21.8%, when combined with a thin
passivating layer of TiO$_2$, with a partial rear contact cell design [28], [29]. However, the Ca contacts were prepared by thermal evaporation using highly reactive metallic calcium, which limits its widespread application. The present work investigates the potential of low-workfunction lithium as an ESL for c-Si solar cells. The lithium film was deposited by thermal evaporation of air-stable Li$_3$N powder. We find that lithium is an excellent ESL on c-Si, yielding a low contact resistivity of ~12 mΩ/cm$^2$ on a lightly doped n-type c-Si substrate. By implementation of a full-area electron-selective lithium contact, n-type c-Si solar cells with a PCE of 19% were achieved.

The lithium films were prepared by thermal evaporation in a high vacuum environment (between 1×10$^{-7}$ and 3×10$^{-6}$ Torr) using Li$_3$N powder. X-ray photoelectron spectroscopy (XPS, Kratos Axis from Kratos Analytical Ltd.) equipped with a monochromatic Al Kα x-ray source (1486.6 eV) and Raman spectroscopy was used to characterize the composition of the deposited film. Lithium films (15 nm) were deposited on a mirror-polished c-Si substrate, and then an Al capping layer (30 nm) was deposited, without breaking vacuum to protect the lithium films from possible oxidation. The Al capping layer was etched in-situ by an argon plasma in a high vacuum chamber (<1×10$^{-7}$ Torr) before the XPS measurements. For Raman spectroscopy, Li films (30 nm) capped with Al (200 nm) were thermally evaporated on a CaF$_2$ substrate, as sketched in Fig.2(a). Raman measurements were performed at a laser power of 0.47 mW from the CaF$_2$ side by micro-Raman spectroscopy (WiTec) using a 532 nm laser and ×100 magnification. After the Al protection layer was scratched in order to allow the interfacial lithium layer to interact with air, characterization by Raman spectroscopy was carried out again. The contact resistivity of the lithium contact on a moderately doped (0.3 Ω·cm; $N_D$≈1.5×10$^{16}$ cm$^{-3}$) n-type c-Si surface was measured by the Cox and Strack method [30]. For this, circular Li/Al contacts with different diameters (0.2-0.8 mm) were evaporated through a shadow mask. A full-area aluminum contact (300 nm) was then evaporated on the rear side of
the c-Si wafer. Contact resistance measurements were performed using a probe station and the contact resistivity was calculated from the dark $J-V$ curve using a spreading resistance model [30]. Finally, we evaluated the lithium film on the rear side of an n-type c-Si solar cells as the ESL. Starting from as-cut wafers, after surface texturing and RCA cleaning, the front $p^+$ region was formed by boron diffusion in a tube furnace. The boron diffused surface was then passivated by 20 nm of Al$_2$O$_3$, which was deposited by plasma-assisted ALD at 175 °C, and then capped with a SiN$_x$ antireflection coating (50 nm) deposited by plasma-enhanced chemical vapor deposition (PECVD). The front contact regions were defined by photolithography using a buffered HF dip to selectively remove the underlying dielectric SiN$_x$/Al$_2$O$_3$ bilayer. The front metal fingers were formed by thermal evaporation of a Cr/Pd/Ag stack, subsequently thickened using Ag electroplating. Finally, a full-area Li/Al stack (4/300 nm) was thermally evaporated on the rear side for electron collection. The light $I-V$ performance of the devices was characterized by an LED-based solar simulator under standard 1-Sun condition (AM1.5G spectrum, 25 °C), and cross-sectional images of the c-Si/Li/Al stacks were acquired by high-resolution transmission electron microscopy (HRTEM, FEI Titan 80-300ST). Numerical device simulations were also carried out to calculate the band alignments of Al/c-Si(n) and Li/c-Si(n) by AFORS-HET v2.5 [31].

![Image](image1.png)

**Figure 2:** (a) Sample structure for Raman spectroscopy characterization. (b) Image of the lithium layer before air exposure (perspective from the CaF$_2$ substrate). (c) Image of lithium layer after reacting with air (perspective from the CaF$_2$ substrate). (d) Raman spectra of lithium samples before and after air exposure.

Fig.1 shows the XPS core-level spectrum of Li 1$s$ in the thermally evaporated film using Li$_3$N as the source material. The binding-energy peak of Li 1$s$ is determined at 55.03 eV, which is consistent with the reported 54.97 ± 0.06 eV binding-energy core level and indicates that metallic lithium film is obtained [32]. Equation (1) illustrates how Li$_3$N is decomposed into metallic lithium and nitrogen gas during the evaporation process [33], which is consistent with our experimental results.

$$2\text{Li}_3\text{N} \rightarrow 6\text{Li} + \text{N}_2$$ (1)
Raman spectroscopy further confirms that the interfacial layer evaporated from Li$_3$N powder is metallic lithium. The Raman spectrum of the pristine film in Fig. 2(d) shows no feature from 400 cm$^{-1}$ to 3600 cm$^{-1}$, which suggests that the film does not contain components with corresponding vibrational frequencies in that wavenumber range. However, the absence of such vibrational signals is not sufficient evidence to prove the presence of metallic lithium. Hence, we also characterized the interfacial layer after reacting with air. We observed a fast reaction process upon air exposure. Fig.2(b) and Fig.2(c) show the surface morphologies of the interfacial layer before and after air exposure characterized by a microscope viewed through the CaF$_2$ substrate. Upon air exposure, Li may react with O$_2$, CO$_2$ and H$_2$O, forming Li$_2$O, Li$_2$O$_2$, LiOH, LiOH-H$_2$O, Li$_2$CO$_3$, Li$_2$C$_2$, H$_2$, among other products [34]--[36], resulting in a rough surface with voids (Fig.2c). With peak fitting, we find that the Raman spectrum of the film after air exposure to exhibit four Gaussian peaks with wavenumbers centered at 783 cm$^{-1}$, 864 cm$^{-1}$, 1875 cm$^{-1}$, and 2985 cm$^{-1}$; the 864 cm$^{-1}$, 1875 cm$^{-1}$, and 2985 cm$^{-1}$ corresponds to Li$_2$CO$_3$, Li$_2$C$_2$ and LiOH-H$_2$O, respectively [31], [34]. Therefore, reactions of Li with CO$_2$ as well as with H$_2$O can be confirmed, but the vibrational frequencies of Li$_2$O and Li$_2$O$_2$, located at 523cm$^{-1}$ and 741cm$^{-1}$, can not be observed directly from Raman spectroscopy. This might be attributed to the relatively low characterization sensitivity and the amorphous nature of the lithium film, which broadens the vibrational spectrum. It is therefore difficult to obtain fitted Gaussian peaks at 523cm$^{-1}$ and 741cm$^{-1}$. Despite the lack of direct evidence of LiO, from Raman spectroscopy, the reactions of Li with CO$_2$ and H$_2$O are sufficient to demonstrate that the interfacial layer is likely metallic lithium.

In terms of carrier-selective contact formation, the combination of a low contact resistivity for charge-carrier transport from the c-Si wafer to the outer electrodes, with low recombination losses is required for effective carrier selectivity. Fig.3(a) shows the dark J-V curves of Cox and Strack structures (Fig.3(a) inset) with 1 mm contact diameter of Al/Li(4nm)/c-Si(n) contacts and Al/c-Si(n) direct contact structures, measured at room temperature. Fig.3(b) shows the Al/Li(4nm)/c-Si(n) bilayer contacts feature a linear J-V behavior under different contact diameters. Meanwhile, the measured resistances decrease with increasing contact diameters, from 2 mm to 10 mm. In contrast, the Al/c-Si(n) direct contact exhibits a clear non-ohmic contact character in the same voltage range, due to the presence of a high Schottky barrier for electron transport [38]. In a nitrogen-filled glove box, a low contact resistivity of 12.8 m$\Omega$·cm$^2$ is achieved with a 4 nm lithium interlayer. Assuming thermionic emission of carriers over an interfacial Schottky barrier is the main electron transport path across the Li/c-Si(n) interface, owing to the moderate doping concentration of the c-Si substrate (~1.5×10$^{16}$ cm$^{-3}$), the energy barrier at the Li/c-Si(n) interface is calculated to be 0.39 eV [39]. Generally, the magnitude of an electrostatic barrier between a metal and semiconductor depends on the work function of the contact metal but also on the interfacial density of states (DOS) within the c-Si bandgap [23]. The mismatched work functions between metallic aluminum and c-Si(n), combined with the presence of interfacial states (DIGS and MIGS), contribute to a significant electron transport barrier (> 0.6
However, insertion of the low work function (~2.9 eV) metallic lithium film [41] results in a reduction in barrier height for electron transport.

Furthermore, the Li/c-Si(n) contact interfaces are investigated by considering the effects of lithium diffusion on electron transport, because the metallic lithium diffusion into c-Si could be activated at room temperature [42]. The silicon dangling bond density of a clean, cleaved c-Si surface is about ~ 5×10¹⁴ cm⁻² [43]. Assuming these defect states are energetically distributed as a Gaussian centered about the mid-gap of c-Si [44], [45] and by fixing the phosphorous doping concentration of the c-Si wafer bulk to 1.5×10¹⁶ cm⁻³, we simulate the band alignment of Li/c-Si(n) contacts with and without interfacial Li at the c-Si surface, located at ~ E-Eᵥ = 1.086 eV [46] within the c-Si bandgap. Fig.4 (a), (b) shows the band alignments of Al/c-Si(n) and Li/c-Si(n) respectively. Due to the donor-like character of Li, its energetic level is close to the CBM of c-Si, and the electrons associated with the Li⁺ at c-Si surface can be captured by acceptor-like DB states. Consequently, the positive defects centers [47] become neutral, reducing the energy barrier for electron transport created by c-Si surface dangling bonds. From the simulation, the energy barrier is found to reduce from 0.45 eV to ~0.34 eV with a surface Li doping density up to 1×10¹⁴ cm⁻². This corresponds well with the energy barrier obtained from experiments of about 0.39 eV, suggesting that a shallow Li doped region may be formed, which further decreases the barrier height at the Li/c-Si contact. In contrast, a high barrier of ~0.51 eV for electron transport is observed at the Al/c-Si interface, which are reasonable values compared with the reported barrier heights of pre-cleaned silicon surface [38][48]. The simulated band alignment of the Li/c-Si(n) interface is represented in Figure 4b). Here, the work function of lithium (W_Li) is lower than the work function of silicon (W_Si). After contacting, electrons flow from lithium to silicon, the CBM and VBM of c-Si(n) bend slightly upwards, the energy level of the c-Si(n)
CBM, and the Fermi level of lithium forms a small energy offset around the contact interface, yielding effective electron collection. In contrast, the simulated band structure of the Al contact is represented in 4a), showing a larger barrier for electron transport.

Figure 4: AFORS-HET v2.5 simulated band bending at (a) Al/c-Si(n) and (b) Li/c-Si(n) interfaces with and without 4×10^{14} cm^{-2} interfacial Li doping. All the simulation regards c-Si surface DB density as 5×10^{14} cm^{-2}, and the states distributions also indicated.

Next, we applied Li as ESL on the rear side of c-Si(n) solar cells, as sketched in Fig.5(a). The device features a single-side textured front surface with boron-diffused p^+ emitter for hole collection. Fig.6 presents the statistical data of devices with and without metallic Li layer, and Fig.5(b) shows the light J-V curve of the best device with a Li/Al contact, and the J-V curve of a control device with a thermally evaporated Al rear contact is shown for comparison. The photovoltaic parameters are shown in the inset table. A high contact resistivity and a high carrier recombination rate at the Al/c-Si interface limits the FF (66%) and V_{oc} (598 mV) of the control device, resulting in a low PCE of 15%. By inserting only 4 nm of evaporated Li between the Al/c-Si structure, both the FF (81.1%) and V_{oc} (619 mV) are significantly improved, boosting the device PCE to 19%, representing a 4.0% absolute efficiency enhancement over the control device. The FF improvement can be attributed to the reduced contact resistivity at the Li/c-Si interface, which is consistent with Fig.6(a), showing that the devices series resistivity decreased from >2Ω·cm^2 to ~0.33 Ω·cm^2 after inserting the 4 nm Li layer. In addition to improved FF, a ~27 mV V_{oc} increase is shown in Fig.6d. Compared with the c-Si/Al contact, the c-Si/Li contact features a lower energy barrier for electron transport and consequently a reduced hole concentration at the contact interface at thermal equilibrium, and so a relative suppression of charge carrier recombination. The reduced recombination at the rear Li/c-Si interface improves the V_{oc}. According to the high-resolution cross-sectional TEM image of the Al/Li/c-Si (n) interface (Fig.5c), we did not observe an alloy between Al and Li, and no interlayer at the Li/c-Si (n) interface as well, which indicates the integrity of the Li contact. In terms of the stability of Al/Li/c-Si contacts, we find these to be vulnerable to physical scratches which could destroy the thin Al layer and
expose the reactive lithium layer into the air. Therefore, further capsulation is required to promote the device stability.

Figure 5. (a) Device structure with the rear-lithium (4nm)/c-Si(n) contact. (b) J-V curves of devices with and without a 4nm metallic interlayer (c) High-resolution TEM cross-section image of the Al/Li/c-Si contact.
Conclusion

We have developed an electron-selective lithium contact for c-Si solar cells. This lithium contact is deposited by thermal evaporation using stable Li$_3$N powder and is demonstrated to exhibit a low contact resistivity on c-Si, due to its low work function. By implementing this electron-selective Li contact, n-type c-Si solar cells with an efficiency of 19% is achieved, representing a 4% absolute efficiency improvement over an Al contact. This work presents a new electron-selective, hole-blocking Li contact, using a stable Li$_3$N powder, which may also be used for other electronic devices, such as light emitter diodes or other PV technologies.

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