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Lithium Fluoride Based Electron Contacts for High Efficiency n-Type Crystalline Silicon Solar Cells

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Low-resistance contact to lightly doped n-type crystalline silicon (c-Si) has long been recognized as technologically challenging due to the pervasive Fermi-level pinning effect. This has hindered the development of certain devices such as n-type c-Si solar cells made with partial rear contacts (PRC) directly to the lowly doped c-Si wafer. Here, a simple and robust process is demonstrated for achieving m Ω cm² scale contact resistivities on lightly doped n-type c-Si via a lithium fluoride/aluminum contact. The realization of this low-resistance contact enables the fabrication of a first-of-its-kind highefficiency n-type PRC solar cell. The electron contact of this cell is made to less than 1% of the rear surface area, reducing the impact of contact recombination and optical losses, permitting a power conversion efficiency of greater than 20% in the initial proof-of-concept stage. The implementation of the LiF_x/Al contact mitigates the need for the costly high-temperature phosphorus diffusion, typically implemented in such a cell design to nullify the issue of Fermi level pinning at the electron contact. The timing of this demonstration is significant, given the ongoing transition from p-type to n-type c-Si solar cell architectures, together with the increased adoption of advanced PRC device structures within the c-Si photovoltaic industry.

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1. Introduction

Schottky-Mott theory states that when two materials with different chemical potentials are placed in contact, a perfectly balancing electrical potential will form, resulting in a flat electrochemical energy for charge carriers (Fermi energy). This implies that metals with different chemical potentials could be used to manipulate surface potentials and carrier concentrations of semiconductors - a ubiquitously desirable tool in semiconductor electronics. Unfortunately, such behavior is seldom seen, owing to the persistent "Fermi level pinning" effect. Resultantly, in most cases a large Schottky barrier to the majority carrier forms at a semiconductor surface when directly contacted by a metal. This effect has been empirically demonstrated to be largely independent of the metal's chemical potential - frequently preventing the formation of Ohmic contacts on lowly doped surfaces.^[1] A commonly cited

example of this, and the one explored in this study, is that of n-type crystalline silicon (c-Si) – which typically exhibits a large Schottky barrier of more than 0.65 eV for electrons at the c-Si interface with a variety of outer contact metals.^[1,2]

This barrier, among other issues, has been problematic for the development of c-Si solar cell architectures which require low contact resistivity to lightly doped n-type c-Si. The use of n-type, rather than p-type c-Si, is desirable because n-type silicon wafers typically exhibit longer and more stable carrier lifetimes. This arises due to a reduced impact of metallic impurities and surface defects in n-type c-Si (both generally having larger electron than hole capture-cross sections^[3]) as well as the absence of light-activated boron-oxygen complexes,^[4] which result in further carrier recombination losses. These factors have motivated an ongoing trend within the photovoltaic industry to switch from p- to n-type c-Si solar cell architectures.^[5] One attractive n-type cell architecture, which requires a low contact resistivity due to a small contact fraction, is the n-type partial rear contact (PRC) cell. In this structure, the effects of high carrier recombination and poor reflectance at the contact interface can be minimized by confining the rear contact to a small percentage of the surface area (commonly less than 1%). However, such an approach is only effective ADVANCED ENERGY MATERIALS ______ www.advenergymat.de

if low contact resistivities are realized. Traditionally, heavy phosphorus doping has been applied underneath the partial contact to circumvent the issue of the Schottky barrier.^[6] The large increase in electron concentration (six orders of magnitude in this case), fixed by the phosphorus doping concentration, decreases the width of the Schottky barrier at the contact allowing carrier tunneling (via thermionic field emission) across the interface, thereby reducing the contact resistivity to acceptably low values. However heavy phosphorus doping, typically achieved by thermal diffusion, also introduces the requirement of processing temperatures greater than 800 $^{\circ}$ C,^[7] and so the stringent need for cleanliness – greatly increasing the complexity of the n-type PRC cell.

An alternative approach, commonly implemented on organic semiconductor devices,[8-12] but with limited exploration on c-Si,^[13-15] is the use of alkali and alkaline earth metal salt interlayers between the outer metal electrode and the absorber material. In particular, lithium fluoride (LiF_x) stands out as a promising candidate due to its fabrication simplicity and stability. LiF_x is a wide band gap (>10 eV) material normally deposited via thermal evaporation. In its vapor form, it is composed primarily of monomers, dimers, and trimers,^[16] and produces slightly substoichiometric (LiF_x, x < 1) films when deposited on c-Si.^[15] Typically, only a very thin film (≈ 1 nm) of LiF_x is required under an Al electrode to dramatically improve electron injection/extraction. A number of different mechanisms have been proposed to explain the low resistance to electrons at this contact found across a number of different semiconductor systems. The three most common explanations include (i) Li chemical doping of the underlying semiconductor;^[10,12,17-19] (ii) protection/separation of the semiconductor layer from the Al layer;^[20,21] and (iii) formation of an exceptionally low work function value localized at the LiF_{x} / Al interface.^[11,22] This paper investigates the interface properties and conduction mechanism of the c-Si(n)/LiF_x/Al contact and demonstrates, for the first time, the simple fabrication of high efficiency (>20%) n-type PRC solar cells without the use of heavy n-type doping.

2. Results and Discussion

To investigate the structure and composition of the LiF_x based electron contact, $c-Si(n)/LiF_x$ (1.5 nm)/Al structures were fabricated and imaged via scanning transmission electron microscopy (STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) and electron energy-loss spectroscopy (EELS). The small atomic weight of Li increases the difficulty of detection by EDX and EELS at the same time as making it susceptible to severe knock-on effects by the electron beam. These issues are less pronounced for F, which was instead used to assess the LiF_x layer. Figure 1a shows a \approx 180 nm width high-angle annular dark-field (HAADF) STEM image of the interface and Figure 1b provides an accompanying mapping of the local Si, Al, and F EDX signals. A uniform F distribution between the Al and Si regions is seen within the measured area, further supported by a higher resolution STEM HAADF image with overlying F EDX data shown in Figure 1c. Also included in Figure 1c is an EDX line scan of the local Si, Al, F, and O elemental distributions



across the interface, which suggests that there is no significant intermixing of the Al and Si layers. In addition, there is evidence for a suboxide species, commonly present at the c-Si surface.^[23,24] Figure 1d provides a high resolution STEM image and accompanying EELS spectrum image of the c-Si(n)/LiF_x/Al interface, confirming again the presence of a continuous F layer confined to a thickness of ≈1.5 nm. The apparently continuous F layer is suggestive of a uniform LiF_x film.

To investigate the electrical behavior of the c-Si (n)/LiF_x/Al contact, transfer length method (TLM) test structures are fabricated as shown in Figure 2a. Figure 2b shows the measured temperature dependence of the LiF_x/Al specific contact resistivity ρ_c made to lightly doped n-type silicon ($N_{\rm D} \approx 5 \times 10^{15} \text{ cm}^{-3}$). A clear thermionic contribution to conduction can be seen at lower temperatures, with the expected exponential increase in ρ_c indicating that a small surface barrier exists at this interface. Near room temperature there is little temperature dependence and at 297 K a $\rho_{\rm c}$ of $\approx 2 \text{ m}\Omega \text{ cm}^2$ is obtained.^[15] It should be noted that despite the increase in ρ_c at lower temperatures, no departure from Ohmic behavior (linear I-V) was seen for individual I-V measurements. The inset of Figure 2b shows a high correlation between measured and modeled sheet resistance of the c-Si wafer as a function of temperature (resultant from the large decrease in mobility with increasing temperature),^[25] supporting the accuracy of the technique.

To expand this study, the LiF_x/Al contact is applied to a wider range of dopant concentrations, as might be used in various c-Si devices.^[6,7,26] Figure 2c shows the room temperature ρ_c as a function of the phosphorus dopant surface concentration N_D in the 10^{13} – 10^{20} cm⁻³ range (the 10^{20} cm⁻³ surface concentration indicated by the star is achieved via a phosphorus surface diffusion). LiF_x based contacts made to all surface concentrations within this range exhibit Ohmic behavior – a contrast to analogous samples made to wafers without the LiF_x interlayer (see Figure S1 in the Supporting Information). The clear dependence of ρ_c on N_D again suggests that a small surface barrier within the c-Si still partially hinders the flow of electrons.

The above information can be used collectively to draw inferences about the mechanism of improved electron transport with the LiF_x interlayer compared to the direct c-Si(n)/Al contact. First, as is evident from the microscopy images of Figure 1, the LiF_x layer appears to provide isolation between the Al and c-Si layers, potentially reducing the Fermi level pinning characteristic at the c-Si surface.^[27] Given the wide band gap of bulk LiF, electron transport through this layer to the Al electrode could occur via quantum mechanical tunneling. These points are supported by our previous measurements of the ρ_c dependence on LiF_x thickness.^[15] This study showed an initial improvement in ρ_{c} , which we attribute to the attainment of full surface coverage at ≈ 1 nm, followed by a large increase in ρ_c for thicknesses above 1.5 nm, likely due to the exponential increase in tunneling resistivity with thickness. It is noted that the increase in ρ_c with LiF_x thickness diminishes for films greater than 2.5 nm suggesting conduction via a different pathway, potentially associated with trap states through the LiF_{x} .^[28]

It is also apparent from the strong ρ_c dependence on N_D shown in Figure 2c that Li chemical doping of the c-Si surface

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Figure 1. a) STEM HAADF microscopy images of the c-Si(n)/LiF_x/polycrystalline Al interface. b) EDX mapping of Al, F, and Si signals of the region highlighted in (a). c) STEM HAADF microscopy images with an overlying EDX F signal alongside EDX line scan of the Al, F, Si, and O signals (K edges). d) STEM HAADF microscopy images and corresponding EELS spectrum image of the Al, F, and Si K edges. The depth dependent F K edge evolution is further highlighted in the series of energy-loss spectra shown in the right hand side. The origin of the darker region situated just below the fluorine layer is the subject of ongoing research and could result from thickness variations due to Li removal or could be an artifact of sample preparation.

is unlikely to be a significant contributor toward the low ρ_c (Li forms a shallow donor level in silicon).^[29] If Li chemical doping of the c-Si was a significant contributor, then ρ_c would be expected to be largely independent of substrate doping. Instead, for the case of c-Si, we believe that the dramatic reduction in work function at the contact, previously measured by our group to be ≈ 2.8 eV in the vicinity of the LiF_x/Al interface,^[15] is the most important parameter for the improved electron extraction. This low work function assists in significantly decreasing the surface barrier height compared to that of the direct Al contact.

As a comparison, the modeled $\rho_c(N_D)$ behavior of a typical c-Si(n) metal interface with a barrier height of ≈ 0.65 eV (a representative value for most metal/c-Si(n) interfaces)^[2] is included in Figure 2c. This comparison shows that, despite the perseverance of a small surface barrier, orders of magnitude improvement in ρ_c can be realized by the addition of the LiF_x interlayer for a wide range of wafer doping concentrations, thereby introducing the possibility of using such contacts in n-type PRC solar cell designs without the need for heavy n-type doping.

The optimal application of LiF_x/Al contacts in a PRC solar cell architecture is not straightforward. In particular, wafer doping must be carefully selected as it simultaneously affects the ρ_c (as seen in Figure 2c), the bulk carrier lifetime, the internal resistance, and the sensitivity to the surface recombination velocity (as discussed in Figure S2 (Supporting Information)). To concurrently consider these effects a 2D idealized PRC cell is simulated with variable bulk and rear contact resistivities, ρ_b and ρ_c . For each combination of ρ_b and ρ_c an optimum contact configuration (% indicated by dotted black lines) is found and the resultant idealized efficiency (color contours) is obtained. For further details on these simulations see Figure S2 (Supporting Information). The data presented in Figure 2c can be superimposed on this simulation plot to find the best configuration in which to apply the LiF_x/Al contact.





Figure 2. a) Representative schematic of the TLM structure. b) Contact resistivity of $c-Si(n)/LiF_x/Al$ contacts at a range of temperatures from 77 to 360 K. The inset of this plot shows measured and modeled sheet resistance values of the c-Si wafer with increasing temperature (also extracted by the TLM procedure). c) Contact resistivity of LiF_x/Al contacts made to c-Si(n) wafers with a range of phosphorus surface concentrations. Shoçwn in the same plot is the modeled contact resistivity as a function of doping concentration using thermionic emission (TE), thermionic field emission (TFE), and field emission (FE) models. These models are constructed with a barrier height of 0.65 V and an electron tunneling effective mass of 0.3 – both of which are typical for directly metalized n-type silicon surfaces. Error bars in (b) and (c) reflect the estimated error in measurement. d) Idealized n-type PRC cell simulations showing optimum contact fraction (dark lines) and idealized efficiency (colored contours) as a function of the wafer and contact resistivity.

These simulations reveal that a wafer base doping of at least 5×10^{15} cm⁻³ is required to make efficient LiF_x/Al PRC cells; lower doping levels produce a prohibitively high ρ_c for these architectures.

Using this information, high efficiency $2 \times 2 \text{ cm}^2$ solar cells were fabricated on n-type ($N_D \approx 5 \times 10^{15} \text{ cm}^{-3}$), float-zone grown wafers with $\approx 0.9\%$ area LiF_x/Al partial rear electron contact (for further design and fabrication details see the Experimental Section and Supporting Information 2). **Figure 3**a provides a schematic representation of the cell structure, showing cross sectional scanning electron microscopy images (SEM) of the cell's front and rear surfaces. The cells feature a random pyramid textured front surface with a boron diffusion layer (labelled c-Si(p⁺) in the figure) used to collect holes, which is passivated by an AlO_x/SiN_y antireflection stack. The boron diffusion is contacted via a Ag plated front metal finger grid with an effective shading fraction of less than 4%. Provided in Figure 3b are optical and photoluminescence (PL) microscopy images of the front (sunward) side of representative LiF_x/Al PRC cells, showing uniform front surface optics and illuminated excess carrier density over the cell area, necessary conditions for a high power conversion efficiency.

The light I-V behavior of a LiF_x/Al PRC cell is provided in Figure 4a, indicating an efficiency of 20.6% has been attained at the proof-of-concept stage for this technology already comparable to alike cells made with a full-area rear phosphorus diffusion which have an optimized efficiency of 21.5%.^[30] The open circuit voltage V_{oc} and short circuit current J_{sc} , measured to be 676 mV and 38.9 mA cm⁻², respectively, demonstrate that the recombination and optical benefits of confining the rear contact to a small area have been realized. In addition, a fill factor of 78.3%, despite a contact fraction of less than 1% confirms the low contact resistivity of the LiF_x/Al interface. Also included in Figure 4a is a pseudo J-V curve without the effects of series resistance R_s obtained from $SunsV_{oc}$ measurements, the comparison between the two curves revealing that the loss due to R_s is only minor. To analyze the stability of the contact system, light J-V



Figure 3. a) Schematic of LiF_x/Al PRC cell and supporting SEM images of the front Ag plated finger (top left), rear stack in a noncontacted region (bottom left) and front random pyramid texturing on a 1 μ m (top middle) and 100 nm (top right) scale. b) Optical and photoluminescence (PL) images of the front surface of representative LiF_x/Al PRC cells.

characteristics are remeasured after a period of three months storage in air with no significant change in performance (for details see Figure S3 in the Supporting Information). The voltage of the cells is also confirmed by SunsV_{oc} measurements, shown in Figure 4b, which include a measured one sun $V_{\rm oc}$ of 678 mV. Provided in the inset of the same plot are a family of J-V curves taken at different illumination intensities, the Voc values of which (indicated by the colored data points) agree well with the $SunsV_{oc}$ trend. To investigate the visible spectrum response, a quantum efficiency analysis included in Figure 4c shows a high internal collection efficiency >90% across the 400–1000 nm range. A J_{sc} of 38.98 mA cm⁻² was extracted from the integrated external quantum efficiency, confirming the accuracy of the $J_{\rm sc}$ values obtained from light *I-V* measurements above. An estimation of the surface recombination velocity (SRV) at the LiF_v/Al contact is made by accounting for recombination in the other areas of the cell via a series of control samples. This analysis, detailed in Figure S4 (Supporting Information), suggests that

the SRV is significantly reduced with a value of \approx 5000 cm s⁻¹ compared to the directly metallized c-Si surface (\approx 10⁶ cm s⁻¹).

3. Conclusion

This work demonstrates the general applicability of LiF_x/ Al based electron contacts for silicon solar cells. Microscopy images and elemental mapping of the c-Si(n)/LiF_x/Al interface indicate that a ~1.5 nm LiF_x layer uniformly separates the Si wafer and the Al layer. This contact system achieves a reduction in ρ_c by several orders of magnitude compared to conventional metal contacts for a range of c-Si phosphorus (n-type) doping levels relevant to solar cell production.^[7] The efficacy of this contact system is tested in an extreme case by integrating it as a <1% area contact in a high efficiency n-type PRC solar cell without the use of phosphorus surface diffusions – an architecture which was not previously possible due to Fermi level pinning. This simplified proof-of-concept cell structure attained



Figure 4. a) Light *J*–V behavior under one sun conditions of the LiF_x/Al PRC cell (blue squares) with inset cell characteristics alongside a pseudo *J*–V curve (obtained from Suns V_{oc} measurements) reflecting the cell's performance in the absence of series resistance. b) Suns V_{oc} behavior of the LiF_x/Al PRC cell with a family of light *J*–V curves measured at 1, 0.5, and 0.25 suns. c) Quantum efficiency analysis of the LiF_x/Al PRC cells showing reflectance (blue squares), external quantum efficiency (purple circles), and internal quantum efficiency (orange triangles).

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a conversion efficiency of greater than 20% - a value which already demonstrates its competitiveness with conventional high efficiency cell structures.

4. Experimental Section

Samples for TEM analysis were fabricated on mechanically polished, n-type, float zone wafers. A LiF_x (\approx 1.5 nm) and Al (\approx 200 nm) stack was thermally evaporated from high purity sources (>99.99%) at a base pressure $< 2 \times 10^{-6}$ mbar (MBraun MB-PROVAP). A cross-section of this stack was prepared for TEM observation using the conventional focused ion beam (FIB) lift-out technique in a Zeiss Nvision 40. Final thinning was performed at 5 kV to reduce FIB induced damage. Scanning TEM microscopy images were then acquired in combination with either EDX or EEL spectra using a probe and image Cs-corrected FEI Titan Themis operated at 300 kV. Dual EEL spectroscopy of the edges Al L_{2,3} and K (73 and 1560 eV), Si L_{2.3} and K (99 and 1839 eV), and F K (685 eV) was performed with a dispersion of 1 eV per channel. The convergence semiangle was set to 20 mrad.

Contact resistivity test structures were fabricated on a range of n-type, float zone, silicon wafers with surface dopant concentrations in the 10^{13} - 10^{20} cm⁻³ range. The heavily doped n⁺ surface $(N_D \approx 3 \times 10^{20} \text{ cm}^{-3})$ was achieved by diffusing phosphorus into the surface from a POCl₃ source in a dedicated clean quartz furnace. TLM pads composed of a LiF_x (\approx 1.5 nm)/Al (\approx 200 nm) evaporated stack were defined either via photolithography or a shadow mask. Each TLM set was isolated along its edges to confine the current flow. Dark current voltage (I-V) measurements between adjacent pad sets were taken in air (for the doping dependent study) or under vacuum (for the temperature dependent study). The specific contact resistivity was extracted as per the description in ref. [31]. The "probe to probe" resistance, was measured and subtracted from each TLM pad set measurement.

Proof-of-concept PRC cell test structures were fabricated on lightly phosphorus doped ($\approx 5 \times 10^{15} \text{ cm}^{-3}$) n-type, float zone, silicon wafers. Following front surface random pyramid texturing and RCA cleaning, a full-area boron diffusion with sheet resistance of \approx 120 Ω \Box^{-1} was performed in a dedicated clean guartz furnace. This boron diffusion was passivated using a ≈18 nm plasma assisted atomic layer deposited (Beneq TFS 200) AlO_x and \approx 75 nm plasma enhanced chemical vapor deposited (PECVD, Roth & Rau AK400) SiN, antireflection stack. The undiffused rear surface was passivated using a single PECVD SiN, film. The front (10 μm width lines, 1.3 mm pitch) and rear (30 μm diameter dots, hexagonal pitch of 300 µm) contact areas were defined photolithographically using a buffered hydrofloric acid (HF) dip to remove the underlying dielectric film. The front contact was formed by thermal evaporation of a Cr (≈10 nm)/Pd (≈10 nm)/Ag (≈100 nm) stack which was subsequently thickened using Ag electroplating. The rear contact was formed by evaporating a LiF_x (\approx 1.5 nm)/Al (\approx 200 nm) stack under the same vacuum (MBraun MB-PROVAP). The light J-V behavior was measured under standard one sun conditions (100 mW cm⁻², AM 1.5 spectrum, 25 °C) with a 2 \times 2 cm² aperture mask using an inhouse system (the cell's bus bar is included within the measured cell area). This system was calibrated with a certified Fraunhofer CalLab reference cell and the accuracy was estimated to be $\pm 1\%$. The external quantum efficiency (EQE) and reflectance measurements were taken using a Protoflex Corporation QE measurement system (QE-1400-03) and a PerkinElmer Lambda 1050 UV-vis-NIR (ultra violet-visable-near infrared) spectrophotometer (with an integrating sphere attachment), respectively. SunsVoc and PL measurements were taken using a Sinton $SunsV_{oc}$ tester and a BTImaging luminescence imager, respectively. Cross sectional scanning electron microscopy images of the cell structure were taken on a Zeiss Gemini Ultra-55.

Supporting Information

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

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- [1] D. K. Schroder, D. L. Meier, IEEE Trans. Electron Devices 1984, 31, 637.
- [2] S. M. Sze, K. K. Ng, Physics of Semiconductor Devices, John Wiley & Sons, Hoboken, NJ, USA, 2006.
- [3] D. Macdonald, L. J. Geerligs, Appl. Phys. Lett. 2004, 85, 4061.
- [4] J. Schmidt, A. Cuevas, J. Appl. Phys. 1999, 86, 3175.
- [5] International Technology Roadmap for Photovoltaic (ITRPV), 2014 Results, Revision 1, July 2015.
- [6] J. Benick, B. Hoex, M. C. M. van de Sanden, W. M. M. Kessels, O. Schultz, S. W. Glunz, Appl. Phys. Lett. 2008, 92, 253504.
- [7] S. W. Glunz, R. Preu, D. Biro, in Comprehensive Renewable Energy (Ed: A. Sayigh), Elsevier, Oxford 2012, pp. 353-387.
- [8] L. S. Hung, C. W. Tang, M. G. Mason, Appl. Phys. Lett. 1997, 70, 152.
- [9] X. J. Wang, J. M. Zhao, Y. C. Zhou, X. Z. Wang, S. T. Zhang, Y. Q. Zhan, Z. Xu, H. J. Ding, G. Y. Zhong, H. Z. Shi, Z. H. Xiong, Y. Liu, Z. J. Wang, E. G. Obbard, X. M. Ding, W. Huang, X. Y. Hou, J. Appl. Phys. 2004, 95, 3828.
- [10] C. Ganzorig, K. Suga, M. Fujihira, Mater. Sci. Eng., B 2001, 85, 140.
- [11] C. J. Brabec, S. E. Shaheen, C. Winder, N. S. Sariciftci, P. Denk, Appl. Phys. Lett. 2002, 80, 1288.
- [12] E. Ahlswede, J. Hanisch, M. Powalla, Appl. Phys. Lett. 2007, 90, 163504.
- [13] S. Kim, J. Lee, V. A. Dao, S. Lee, N. Balaji, S. Ahn, S. Q. Hussain, S. Han, J. Jung, J. Jang, Y. Lee, J. Yi, Mater. Sci. Eng., B 2013, 178, 660
- [14] Y. Zhang, R. Liu, S.-T. Lee, B. Sun, Appl. Phys. Lett. 2014, 104, 83514.
- [15] J. Bullock, M. Hettick, J. Geissbühler, A. J. Ong, T. Allen, C. M. Sutter-Fella, T. Chen, H. Ota, E. W. Schaler, S. De Wolf, C. Ballif, A. Cuevas, A. Javey, Nat. Energy 2016, 1, 15031.
- [16] M. Yamawaki, M. Hirai, M. Yasumoto, M. Kanno, J. Nucl. Sci. Technol. 1982, 19, 563.
- [17] Y. Yuan, D. Grozea, S. Han, Z. H. Lu, Appl. Phys. Lett. 2004, 85, 4959.





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- [18] Q. T. Le, L. Yan, Y. Gao, M. G. Mason, D. J. Giesen, C. W. Tang, J. Appl. Phys. 2000, 87, 375.
- [19] E. D. Głowacki, K. L. Marshall, C. W. Tang, N. S. Sariciftci, Appl. Phys. Lett. 2011, 99, 043305.
- [20] H. Ishii, K. Sugiyama, E. Ito, K. Seki, Adv. Mater. 1999, 11, 605.
- [21] S. E. Shaheen, G. E. Jabbour, M. M. Morrell, Y. Kawabe, B. Kippelen, N. Peyghambarian, M.-F. Nabor, R. Schlaf, E. A. Mash, N. R. Armstrong, J. Appl. Phys. **1998**, 84, 2324.
- [22] R. Schlaf, B. A. Parkinson, P. A. Lee, K. W. Nebesny, G. Jabbour,
 B. Kippelen, N. Peyghambarian, N. R. Armstrong, J. Appl. Phys. 1998, 84, 6729.
- [23] F. Werner, B. Veith, D. Zielke, L. Kühnemund, C. Tegenkamp, M. Seibt, R. Brendel, J. Schmidt, J. Appl. Phys. 2011, 109, 113701.

- [24] R. Hezel, Solid-State Electron. 1981, 24, 863.
- [25] D. B. M. Klaassen, Solid-State Electron. 1992, 35, 953.
- [26] E. Franklin, K. Fong, K. McIntosh, A. Fell, A. Blakers, T. Kho, D. Walter, D. Wang, N. Zin, M. Stocks, E.-C. Wang, N. Grant, Y. Wan, Y. Yang, X. Zhang, Z. Feng, P. J. Verlinden, *Prog. Photovoltaics* **2014**, DOI: 10.1002/pip.2556.
- [27] J. Robertson, J. Vac. Sci. Technol., A 2013, 31, 050821.
- [28] B. F. Bory, H. L. Gomes, R. A. J. Janssen, D. M. de Leeuw, S. C. J. Meskers, *J. Appl. Phys.* **2015**, *117*, 155502.
- [29] J. W. Chen, A. G. Milnes, Annu. Rev. Mater. Sci. 1980, 10, 157.
- [30] J. Bullock, A. Cuevas, C. Samundsett, D. Yan, J. McKeon, Y. Wan, Sol. Energy Mater. Sol. Cells 2015, 138, 22.
- [31] D. K. Schroder, Semiconductor Material and Device Characterization, John Wiley & Sons, Hoboken, New Jersey 2006.

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Supporting Information: Lithium Fluoride Based Electron Contacts for High Efficiency n-type Crystalline Silicon Solar Cells

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Supporting information 1. Contact facilitation

It is known that the fabrication of low resistance contacts on lightly doped n-type c-Si and Al is difficult due to the formation of a surface barrier, resulting in rectifying behaviour.^[1] This was found to be the case for all contacts made to phosphorus dopant concentrations in the $10^{13} - 10^{16}$ cm⁻³ range. The addition of the thin LiF_x interlayer dramatically improved the contact, resulting in Ohmic behaviour even in the extreme cases of low temperature (77 K) and low doping (4 × 10^{13} cm⁻³). An example of the difference between structures made with and without the LiF_x interlayer is provided for a c-Si wafer with a dopant concentration of ~5 × 10^{15} cm⁻³ in Figure S1. The rectifying behaviour of the direct Al contact prevented an accurate extraction of the contact resistivity, but it is estimated to be greater than 5 Ω cm², compared to ~2 m Ω cm² for LiF_x / Al contacts. Ohmic contact was achieved between the heavily doped c-Si(n) surface (N_P ~ 10^{20} cm⁻³) and the direct Al contact due to electron tunnelling through the reduced barrier width.



Figure S1: Simple vertical contact structures, with a top contact diameter of ~3 mm, highlighting the transition from rectifying to Ohmic behaviour as a result of the addition of a thin LiF_x layer on n-type c-Si (N_D = 5×10¹⁵ cm⁻³).

Supporting information 2. Optimisation of LiF_x / Al PRC design

The choice of wafer doping and rear contact configuration for a c-Si PRC cell is not straightforward. This is mainly linked to the heavy dependence that many important parameters have on the wafer doping. Among the most important of these are (i) contact resistivity (as shown in Figure 2c of the main text); (ii) the bulk lifetime (as shown in Figure S2a demonstrated using state-of-the-art SiN_x surface passivation^[2]); (iii) lateral transport and crowding of majority carriers; and (iv) the impact of a given surface recombination velocity (SRV, as shown in Figure S2b). To simultaneously consider all these effects, two dimensional simulations of an idealised n-type PRC cell are run in Quokka.^[3] The input parameters of this cell design are given in Table S2 below, and the results are shown in Figure 2d of the main text. The high efficiency cells detailed in Figures 3 and 4 of the main text utilise a three-dimensional 'dot' PRC structure. It is computationally expensive to simulate such a large $\rho_c - \rho_b$ parameter space and so a two dimensional 'line' contact structure is simulated instead. Whilst the same trends are expected for these two contact systems the optimum fraction for the dot contact will be smaller than that presented in Figure 2d for line contacts, in this case 0.9% is chosen as a suitable contact percentage.



Figure S2: (a) Excess carrier dependent lifetime $\tau_{eff}(\Delta n)$ for c-Si(n) wafers with a range of doping concentrations between 10^{13} – 10^{16} cm⁻³. To assess the bulk lifetime, PECVD SiN_x passivation is applied to both wafer surfaces and the lifetime measured via PCD. (b) Simulated idealised PRC device V_{oc} as a function of wafer resistivity when a high contact SRV of 10^5 cm/s is assumed.

Fable S2: Idealised	l inputs for	n-type PF	RC simulation.
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Parameter	Value
Front recombination	1 fA/cm ²
Bulk lifetime	Variable, intrinsic lifetime based on Richter et. al. parameterisation ^[4]
Wafer doping	Variable, $3 \times 10^{13} - 8 \times 10^{16}$ cm ⁻³ phosphorus concentration
Wafer thickness	160 μm
Rear recombination (non-contact)	1 fA/cm ²
Rear contact recombination	10 ⁵ cm/s
Rear line contacts	Contact width (μ m) = variable (minimum value 2 μ m)
	Contact pitch (μm) = variable

Supporting information 3. Light J-V stability.

Historically the alkali metals have been avoided in silicon processing as they are known to be fast diffusers in c-Si and form energy states within the bandgap. For the case of Li the energy state has been suggested to be a shallow donor.^[5] In order to test the stability of the LiF_x / Al PRC cell, light *J-V* measurements are taken under identical illumination and temperature conditions after a period of ~3 months storage in air. As can be seen in Figure S3, negligible change is seen over this period, suggesting stability of the contacts, for the duration of the time period investigated.



Figure S3: Light *J-V* behaviour measured at 1 sun shortly after fabrication (black) and after an additional 3 months storage in air (blue), showing no change in device efficiency.

Supporting information 4. Estimation of the c-Si(n) / LiF_x / Al contact surface recombination velocity.

To estimate the contribution that the rear LiF_x / Al contact makes to the total recombination, test structures are fabricated to measure the recombination occurring in different areas of the PRC cell. Schematic diagrams of these test structures are detailed in Figures S4a, c, d and e. Recombination factors J_0 are extracted from the excess carrier dependent lifetime $\tau_{\text{eff}}(\Delta n)$ of control test structures measured by photoconductance decay (PCD). J₀ values representing the recombination contribution from the front surface metal and passivated regions as well as the rear passivated regions are included in Figure S4b. In addition, the post-processing bulk τ_{eff} of the silicon wafer, shown in Figure S4c, is found to be ~1.5 ms (at $\Delta n = 10^{15}$ cm⁻³). The AlO_x, SiN_y and Al layers used in these test structures are deposited at thicknesses of 18 nm, 75 nm and ~10 nm using ALD, PECVD and thermal evaporation, respectively. These extracted J_0 and $\tau_{\rm eff}$ values are used in conjunction with those detailed in Table S4 to simulate the performance of the PRC cell as a function of the rear contact surface recombination velocity (SRV). A quasi-analytical, iterative model of the three-dimensional device geometry, ^[6] is used to model the output parameters of the solar cell (V_{oc} , J_{sc} , FF and η) as a function of the SRV at the partial rear contact. Figure S4f shows the V_{oc} as a function of the rear contact SRV. A good match between simulated and measured V_{oc} (676 ± 2 mV) is obtained for an SRV of ~5 x 10³ cm/s. This is more than two orders of magnitude less than that expected from a directly metallised c-Si surface. Figure

S4g shows a comparison of the measured light J-V and that simulated with a SRV of 5 x 10^3 cm/s, both

giving the same maximum output power and an efficiency of 20.6%.

Device property	Parameter	Value
Contact	Front contact fraction	3%
	Rear contact fraction	0.9%
	Rear contact resistivity	2 mΩcm ²
Doping	Base resistivity	1 Ωcm (n-type)
	Boron diffusion sheet resistance	120 Ω/□
	Wafer thickness	160 μm
Recombination	Minority carrier lifetime	1500 μs
	Passivated rear recombination current	3 fA/cm ²
	Front recombination current	72 fA/cm ²
Optics	Front surface shading	3%
	Front antireflection coating on textured surface	~75nm SiN _x
Parasitic resistances	Series resistance	0.75 Ωcm ²
	Shunt resistance	> 10 ⁶ Ωcm ²

Table S4. Parameters utilised in the PRC cell simulation



Figure S4: (a) Test structure used to measure the J_0 of the passivated front region. (b) J_0 measurements of the front passivated and metallised regions and the rear passivated region. (c) The post processing bulk lifetime of the LiF_x /Al PRC cells. (d) and (e) Test structures used to measure the J_0 of the metalized front and passivated rear samples. (f) Simulated V_{oc} of n-type LiF_x / Al PRC cell ($N_D = 5 \times 10^{15}$ cm⁻³) as a function of rear contact SRV showing that a SRV value of ~5000 cm/s agrees well with the measured cell results in Figure 4 of the main text. (g) Comparison between measured and simulated light *J-V* behaviour of n-type PRC cells. A rear contact SRV of ~5000 cm/s is assumed in the model.

References

- [1] D. K. Schroder, D. L. Meier, *IEEE Trans. Electron Devices* **1984**, *31*, 637.
- [2] Y. Wan, K. R. McIntosh, A. F. Thomson, A. Cuevas, IEEE J. Photovolt. 2013, 3, 554.
- [3] A. Fell, Electron Devices IEEE Trans. On **2013**, 60, 733.
- [4] A. Richter, S. W. Glunz, F. Werner, J. Schmidt, A. Cuevas, *Phys. Rev. B* 2012, *86*, 165202.
- [5] J. W. Chen, A. G. Milnes, Annu. Rev. Mater. Sci. 1980, 10, 157.
- [6] A. Cuevas, Prog. Photovolt. Res. Appl. 2014, 22, 764.