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

James Bullock[†], *Peiting Zheng*[†], *Quentin Jeangros, Mahmut Tosun, Mark Hettick, Carolin M. Sutter-Fella, Yimao Wan, Thomas Allen, Di Yan, Daniel Macdonald, Stefaan De Wolf, Aïcha Hessler-Wyser, Andres Cuevas*, Ali Javey**

[†] These authors contributed equally to this work.

James Bullock, Mahmut Tosun, Mark Hettick, Carolin M. Sutter-Fella, Ali Javey

[1] Department of Electrical Engineering and Computer Sciences, University of California, Berkeley, California 94720, USA.

[2] Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA.

(Email: ajavey@berkeley.edu)

James Bullock, Peiting Zheng, Yimao Wan, Thomas Allen, Di Yan, Daniel Macdonald, Andres Cuevas

[3] Research School of Engineering, The Australian National University (ANU), Canberra, ACT 0200, Australia

(Email: andres.cuevas@anu.edu.au)

Quentin Jeangros, Stefaan De Wolf, Aïcha Hessler-Wyser

[4] École Polytechnique Fédérale de Lausanne (EPFL), Institute of Micro Engineering (IMT), Photovoltaics and Thin-Film Electronic Laboratory (PVLab), Maladière 71b, CH-200 Neuchatel, Switzerland

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Abstract. 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 we demonstrate a simple and robust process for achieving mΩcm^2 scale contact resistivities on lightly doped n-type c-Si via a lithium fluoride / aluminium contact. The realization of this low-resistance contact enables the fabrication of a first-of-its-kind high-efficiency 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 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 on-going 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.

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 electro-chemical energy for 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 behaviour is seldom seen, owing to the persistent 'Fermi level pinning' (FLP) 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, amongst 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 photovoltaics 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 minimised by confining the rear contact to a small percentage of the surface area (commonly less than 1%). However, such an approach is only effective if low contact resistivities are realised. 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 (6 orders of magnitude in this case), fixed by the phosphorus doping concentration, decreases the width of the Schottky barrier at the contact allowing carrier tunnelling (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^{o}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 vapour form, it is composed primarily of monomers, dimers and trimers,[16] and produces slightly sub stoichiometric (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 localised 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 ~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 sub-oxide 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 behaviour 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_D ~5×10^{15}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 ρ_c of ~2 mΩcm^2 is obtained.[15] It should be noted that despite the increase in ρ_c at lower temperatures, no departure from Ohmic behaviour (linear *IV*) was seen for individual *IV* measurements. The inset of Figure 2b shows a high correlation between measured and modelled 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 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 (linear *I*-*V*) behaviour – a contrast to analogous samples made to wafers without the LiF$_x$ interlayer (See supporting information S1). 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/Al contact. Firstly, as is evident from the micrographs 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 bandgap of bulk LiF, electron transport through this layer to the Al electrode could occur via quantum mechanical tunnelling. 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 with thickness above 1.5nm, likely due to the exponential increase in tunnelling 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 is unlikely to be a significant contributor towards the low ρ_c (Li forms a shallow donor level in silicon[29]). If chemical doping of the c-Si was 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 modelled $\rho_c(N_D)$ behaviour 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 realised by the addition of the LiF_x interlayer for a wide range of wafer doping layers, 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 supporting information S2). To concurrently consider these effects a two-dimensional idealised 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 idealised efficiency (colour contours) is obtained. For further details on these simulations see supporting information S2. 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. 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 2×2 cm^2 solar cells were fabricated on n-type (N_D ~$5\times10^{15} cm^{-3}$), float-zone grown wafers with ~0.9 % area LiF_x / Al partial rear electron contact (for further design and fabrication details see experimental section and supporting information 2). Figure 3a provides a schematic representation of the cell structure, showing cross sectional scanning electron micrographs (SEM) of the cell's front and rear surfaces. The cells feature a random pyramid textured front surface with a boron diffusion layer c-Si(p$^+$), 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 micrographs 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 *J*-*V* behaviour 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 optimised 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 realised. In addition, a fill factor of 78.3%, despite a contact fraction of less than 1% confirms the low 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 analyse the stability of the contact system, light *J*-*V* characteristics are remeasured after a period of 3 months storage in air with no significant change in performance (for details see supporting information S3). The voltage of the cells is also confirmed by SunsV_{oc} measurements, shown in Figure 4b, which include a measured 1 sun V_{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 V_{oc} values of which (indicated by the coloured data points) agree well 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_{sc} values obtained from light *J-V* measurements above. An estimation of the surface recombination velocity (SRV) at the LiF_x / 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 supporting information S4, suggests that the SRV is significantly reduced with a value of ~5,000 cm/s compared to the directly metallised c-Si surface (~10^6 cm/s).

3 Conclusion

This work demonstrates the general applicability of LiF_x / Al based electron contacts for silicon solar cells. Micrographs and elemental mapping of the *c*-Si(n) / LiF_x / Al interface indicate that a ~1.5nm 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 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, FZ wafers. A LiF_x (~1.5 nm) and Al (~200 nm) stack was thermally evaporated from high purity sources (> 99.99%) at a base pressure < 2×10^{-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 micrographs 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/channel. The convergence semi-angle 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 ~3×10^{20} cm^{-3}) was achieved by diffusing phosphorus into the surface from a $POCl_3$ source in a dedicated clean quartz furnace. TLM pads composed of a LiF_x (~1.5 nm) / Al (~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 (~$5\times10^{15}$$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 approximately 120 Ω/□ was performed in a dedicated clean quartz furnace. This boron diffusion was passivated using a ~18 nm plasma assisted atomic layer deposited (PAALD, Beneq TFS 200) AlO_x and ~75 nm plasma enhanced chemical vapour deposited (PECVD, Roth & Rau AK400) SiN_y antireflection stack. The undiffused rear surface was passivated using a single PEVCD SiN_y film. The front (10 µm width lines, 1.3mm pitch) and rear (30 µm diameter dots, hexagonal pitch of 300 µm) contact areas were defined photolithographically using a buffered 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 (~1.5 nm) / Al (~200 nm) stack under the same vacuum (MBraun MB-PROVAP). The light *J-V* behaviour was measured under standard 1 sun conditions (100 mW/cm^2, AM 1.5 spectrum, 25^{o}C) with a 2×2 cm^2 aperture mask using an inhouse system (the cell's bus bar is included within the measured cell area). This system is calibrated with a certified Fraunhofer CalLab reference cell and we estimate the accuracy to be ± 1%. The EQE 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. SunsV_{oc} and PL measurements were taken using a Sinton SunsV_{oc} tester and a BTImaging luminescence imager, respectively. Cross sectional scanning electron micrographs 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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Figure 1: (a) STEM HAADF micrograph of the *c*-Si(n) / LiF_x / polycrystalline Al interface. (b) EDX mapping of Al, F and Si signals of the region highlighted in 1a. (c) STEM HAADF micrograph with an overlying EDX F signal alongside EDX line scan of the Al, F, Si, and O signals (K edges). (d) STEM HAADF micrograph 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 artefact of sample preparation.

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 – 360 K. The inset of this plot shows measured and modelled 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. Shown in the same plot is the modelled 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 tunnelling effective mass of 0.3 – both of which are typical for directly metalized n-type silicon surfaces. Error bars in 2b and c reflect the estimated error in measurement. (d) Idealised n-type PRC cell simulations showing optimum contact fraction (dark lines) and idealised efficiency (coloured contours) as a function of the wafer and contact resistivity.

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 non-contacted region (bottom left) and front random pyramid texturing on a 1 um (top middle)

and 100nm (top right) scale. (b) Optical and photoluminescence (PL) images of the front surface of representative LiF_x / Al PRC cells.

Figure 4: (a) Light *J-V* behaviour under 1 sun conditions of the LiF_x / Al PRC cell (blue squares) with inset cell characteristics alongside a pseudo *J-V* curve (obtained from SunsV_{oc} measurements) reflecting the cells performance in the absence of series resistance. (b) SunsV_{oc} behaviour 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).

Exceptionally low contact resistivity is demonstrated on lightly doped (~5 × 10^{15} cm^{-3}) n-type silicon via a nanometer thin LiF_x interlayer. This advancement enables the fabrication of a first-of-its-kind n-type silicon solar cell with a LiF_x/Al partial rear contact made to less than 1% of the cell's area. An efficiency of over 20% is achieved at the proof-of-concept stage.