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Electronic properties of Al $p^+$ surfaces formed by laser doping from aluminium oxide precursors: implications for PERC cell design and performance

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Abstract

Aluminium oxide ($\text{Al}_2\text{O}_3$) functions doubly as a high-quality surface passivation material for crystalline silicon and as an aluminium ($\text{Al}$) $p$-type precursor for laser doping. Thus, $p^+$ doping based on laser ablation of $\text{Al}_2\text{O}_3$ thin-films deposited on a silicon substrate is an attractively simplified process for concurrent local contact definition and aligned surface doping. A number of studies have demonstrated this process, but a careful examination of the influence of laser parameters on the electronic properties of the Al laser doped $p^+$ surface itself, including the influence of post-doping annealing, has yet to be presented. Such information is valuable for establishing process windows and for providing parameters by which the contact geometry can be optimized and the performance of locally $\text{Al}_2\text{O}_3$ laser doped solar cells predicted. In this work, we present accurate characterization of the electronic properties of primary importance to solar cell performance: effective surface recombination and contact resistivity. Recombination at the $\text{Al}_2\text{O}_3$ laser doped $p^+$ surface is found to exceed that of equivalently-doped $p^+$ silicon from furnace diffused boron, while contact resistivity to vacuum evaporated Al is up to two orders of magnitude less than screen-printed, fired Al. Based on this characterization, computer simulations demonstrate that with optimized rear contact geometries, an industrially relevant PERC cell can approach 21% efficiency, and the high-performance UNSW PERL structure can exceed 24%.

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1. Introduction

Focused laser irradiation is a well-established tool for locally doping the near-surface region of silicon substrates and solar cells [1,2]. The laser energy simultaneously ablates surfaces films, forming a vapour, and locally melts the near-surface region of the silicon substrate, into which the vaporised elements can diffuse. In this fashion, surface films containing silicon dopant elements can act as precursors for n- and p-type doping. Concurrent ablation and doping is ideally suited for aligned local contact openings and back-surface field (BSF) or emitter formation, and in recent years several studies have demonstrated locally laser doped contact openings in high efficiency cell structures [3–6].

A major limitation of laser doping, however, is the requirement for customised or additional surface layers to provide the dopant element. Examples include the doping of conventional passivating dielectric films such as silicon nitride [7,8], or the deposition of dopant-specific films, such as phosphoric acid [9]. These approaches complicate processing by requiring an additional or customised deposition and/or the subsequent removal of the precursor residual.

Aluminium oxide (Al$_2$O$_3$) potentially avoids such complications by functioning both as a high quality surface passivation material for p-type silicon [10] and a rich source of aluminium (Al), a p-type dopant in silicon [11]. Laser doping from Al$_2$O$_3$ thus requires no customisation of the dielectric, and avoids post-doping removal. Previous work has described p-type doping of silicon from Al$_2$O$_3$ dielectrics using a range a laser wavelengths, from the ultraviolet [12] to the infrared [4,11,13], and pulse lengths from pico [14] to microseconds [4]. Al$_2$O$_3$ and typical SiN capping layers are both transparent throughout the near UV, optical and infrared wavelengths, and we can therefore expect the laser wavelength to have a minimal influence on the doping process. However, the laser pulse length may influence laser damage by changing the instantaneous pulse energy, the duration of the melt cycle and the corresponding recrystallization velocity.

Where recombination has been measured directly, the general consensus is that Al$_2$O$_3$ laser doped (Al$_2$O$_3$-LD) silicon is more recombination active than would be expected from the equivalent doping density of boron or fired aluminium*. Values ranging from approximately 4,500 fA cm$^{-2}$ [11] to 30,000 fA cm$^{-2}$ [13] have been quoted for Al-LD silicon from a range of Al$_2$O$_3$ dielectric configurations†. The wide range of values may be the influence of dielectric capping layers and/or the variable temporal laser pulse lengths. Laser damage itself has been attributed to crystalline defects formed during melt re-solidification, which may accumulate with the number of melt cycles, or to thermal stresses between the substrate and dielectric films [21,22]. These factors may not be specific to laser doping from Al$_2$O$_3$ itself, and it is also possible that there is a contribution to recombination from Al-O complexes, which have been implicated in increased recombination in Al doped silicon formed by non-laser doping [23–25]. Al$_2$O$_3$ is of course rich in aluminium and oxygen, both of which are incorporated into the laser-induced silicon melt at high concentrations.

Two approaches have been presented to reduce recombination in Al$_2$O$_3$-LD silicon using pulsed laser irradiation. The first involves doping from a dielectric stack of an intermediate Al$_2$O$_3$ layer and a boron-rich silicon carbide capping layer, thereby over-doping Al with boron [4]. This approach has demonstrated a marginal reduction in recombination ($j_0 \approx 4,000$ fA cm$^{-2}$), and was implemented for rear contact openings on small-area PERC cells with efficiencies of 21.4 %. It also indirectly demonstrates a dilemma of laser processing Al$_2$O$_3$ passivated surfaces: a potentially unavoidable increase in recombination as a result of the indiscriminate inclusion of the elements present in the dielectric. The second approach proposes annealing the laser doped silicon in the presence of hydrogen, which may be sourced either from the surface dielectrics or the ambient atmosphere (e.g. forming gas) to passivate the laser induced defects [26]. In this case, post-annealing increases in implied $V_{oc}$ on laser doped test structures were

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* The exception is the work of Harder et al [15], who use the slope of the high-injection inverse lifetime curve described by Kane & Swanson [16] to measure recombination at Al$_2$O$_3$-LD silicon equivalent to that of furnace-diffused boron. However, this characterisation method is prone to understatement at high values of $j_0$ where the surface carrier concentration strongly deviates from the average value, as observed by several studies [17–19] and the original authors themselves [16].

† In the literature recombination is often extracted using the Fischer method [20] and reported as an effective surface recombination velocity, $S_{eff}$. For comparison to the data presented in this study, $S_{eff}$ was converted to $j_0$ using the relationship $j_0 = S_{eff} \sqrt{q} \tau (N + dn)$. 
reported, but quantification of the recombination properties themselves were not. This recovery is also general to laser processed silicon, as demonstrated for other laser-doped silicon [27].

In the context of previous work, the outstanding question is to what extent laser doping from Al₂O₃ dielectric layers, which results in relatively high contact recombination, is compatible with high efficiency solar cells. Accurate quantification of the key electronic parameters of Al₂O₃-LD – minority carrier recombination and contact resistivity – would facilitate cell simulations and optimisation and define process windows. Thus, this work presents a careful characterisation of recombination and contact resistivity of Al₂O₃-LD silicon across a range of laser parameters for a 532 nm, nanosecond pulse length laser. We perform doping from single layer Al₂O₃ and from an industrially relevant Al₂O₃/SiN dielectric stack in order to expose the influence of the SiN capping layer, which has been correlated with increased recombination at laser-doped silicon [21]. We measured the response of recombination to post-doping annealing in ambient and forming gas atmospheres. Contact resistivity was measured to vacuum evaporated aluminium. With this information, three-dimensional numerical computer simulations are used to predict the efficiency potential of an industrially typical PERC cell and the record-efficiency UNSW PERL cell [28] when these structures are modified to incorporate rear-surface Al₂O₃ passivation and Al₂O₃ laser doping. In doing so, we provide an indication of efficiency potential in current industrial cell technologies, in addition to a device in which the Al₂O₃-LD contacts will be a primary source of recombination.

2. Experimental details

Laser doping was performed using an Innolas 532 nm, nanosecond pulse-length laser system. The laser repetition rate was 100 kHz, for which the full-width half maximum pulse length was approximately 48 ns. The laser scan speed was varied to produce spatial pulse overlaps of 30, 50 and 90 %, which increases the number of melt cycles in the near-surface region of the silicon substrate. Pulse energy was varied from the threshold of ablation of the dielectric film, through to the threshold of ablation of the silicon substrate. These thresholds were determined using light microscope images of the laser-processed substrate, and determined from the first visual evidence of dielectric removal through to clear ablation of the silicon substrate. As a result, the thresholds are only approximate and some silicon ablation is possible at the intermediate pulse energies. Across this energy range, the pulse diameter ranged from approximately 13 – 22 μm, as determined by optical microscopy.

The Al₂O₃ films were deposited as both a single layer and as the intermediate layer in an Al₂O₃/SiN stack on p-type, (100), 200 Ω-cm, chemically-polished float-zone, 300 μm-thick silicon substrates. The Al₂O₃ films were deposited with an Oxford Instruments Flex-Al system with a thickness of approximately 20 nm. Capping layers of SiN were deposited using a Roth & Rau SiNA inline PECVD system. The Al₂O₃ passivation was activated with a 15 minute anneal at 425 °C in ambient conditions on a hotplate. The SiN thickness was approximately 80 nm, with a refractive index of 2.05 at 632 nm. These dielectrics are of course highly transparent in the optical wavelengths, and will therefore be ablated indirectly by the 532 nm laser, via thermal transfer from the silicon substrate and at higher energies by the ablation of the silicon itself.

For both dielectric configurations, two sets of each laser parameter were processed. Each set of parameters then received different post-doping thermal treatments. One was annealed on a hotplate in ambient conditions at increasing temperatures of 250, 350 and 450 °C, each for 30 minutes. The other sample received a single anneal at 450 °C in forming gas (2 % H₂ in N₂) for 30 minutes. For the hotplate anneal, a source of hydrogen was available in the dielectric films themselves. The Al₂O₃ film has a hydrogen concentration of approximately 1 – 2 % (atomic percentage) [10], and the SiN film has a concentration of 15 – 20 % [29]. Once doped and ablated, no further depositions were performed and the measured recombination is for doped, un-metalised and un-passivated silicon.

Recombination at the Al₂O₃-LD surface was measured via luminescence-coupled numerical device simulations in Quokka [30], which is described in detail in [31]. This technique uses electronic and luminescence models of test structures to numerically fit recombination at Al₂O₃-LD lines to measured luminescence signals of the test structures. Uncertainty in the extracted recombination was determined by the standard deviation of the output of 100 Monte Carlo simulations for three input parameters. The laser line width, luminescence signal and luminescence calibration factor were treated as normally distributed variables with a standard deviation reflecting the approximate measurement uncertainty. The steady-state photoluminescence signal of the test structures was measured via
photoluminescence imaging before and after annealing. A reference region was left unprocessed on each sample to ensure that the annealing step did not alter recombination at the undoped, Al2O3-passivated surfaces.

In this work, recombination is parameterised by $j_0$, the recombination current prefactor, in units of fA cm$^{-2}$. The use of this term follows the recent prescription of Cuevas et al [32]. It is also referred to in the literature variously as the reverse saturation current density and the dark current density, among other terms.

Contact resistivity was measured with the transfer length method [33]. The Al2O3-LD process was extended to continuously dope areas measuring $22 \times 5$ mm$^2$, with consistent pulse overlap in the x and y directions. Two sets of parameters were again processed, with one set receiving a brief, 30 s etch in 1 % (by volume) aqueous hydrofluoric (HF) acid solution. The samples were then metallised by vacuum evaporated aluminium in an Applied Materials ATON 500 inline evaporator. The aluminium thickness was approximately 2 μm. The un-etched samples were then sintered on a hotplate for 30 minutes at both 250 and 350 °C.

Sheet resistance was measured using four-point probe on continuously doped square features measuring 10 x 10 mm$^2$ on high resistivity p-type substrates.

3. Results and discussion

3.1. Recombination

Prior to annealing, recombination at the Al2O3-LD surface for both dielectric configurations and all laser parameters exceeded 10,000 fA cm$^{-2}$ (figure 1, top). Recombination decreases with increasing pulse energy, correlated with decreasing sheet resistance. However, increased pulse overlap measurably increases recombination. This observation is consistent with an accumulation of crystalline defects with an increasing number of melt cycles. The additional thermal cycles did not reduce sheet resistance, which is an indication that the Al2O3 film is exhausted as a dopant source as a result of it being ablated from the wafer surface after the initial thermal cycles.

However, independent of the pulse overlap or pulse energy, annealing in either forming gas, or on a hotplate, reduced recombination to equal levels for all but one parameter set. For the Al2O3/SiN stack, 90 % pulse overlap (the maximum number of melt cycles) resulted in $j_0 > 100,000$ fA cm$^{-2}$ for all pulse energies, which could not be recovered by annealing. For the Al2O3 single layer, the optimal hot plate annealing temperature was 250 °C, while the lowest recombination for the Al2O3/SiN stack was measured following hot plate annealing at 350 °C. From the Al2O3 single layer post-annealing recombination was approximately 5,000 – 7,000 fA cm$^{-2}$ across all pulse energies and overlaps, and 8,000 – 10,000 fA cm$^{-2}$ for doping from the Al2O3/SiN stack. The increase in recombination in the presence of the SiN capping layer is consistent with the model of thermal mismatch between the SiN film and the silicon substrate enhancing recombination [21], or from the incorporation of additional impurity elements (e.g. N) that enhance recombination.

Annealing in forming gas provided no advantage over the optimal hot-plate annealing conditions (figure 1, bottom). If hydrogen is indeed key to the recovery of laser damage, a hydrogen-rich atmosphere thus provides no measurable advantage over annealing in ambient conditions where hydrogen is present in the Al2O3 and/or SiN films.

For both dielectric configurations, recombination is approximately independent of pulse energy and pulse overlap after annealing. This indicates that the damage that accumulates with an increasing number of melt cycles can be restored to roughly equivalent levels by annealing. The exception is the 90 % pulse overlap with Al2O3/SiN, which implies a threshold level of damage that is unrecoverable by annealing. This is evidence that recombination at the annealed Al2O3-LD surface may not be dominated by laser-induced damage, instead being the result of the aforementioned Al-O complexes. Nonetheless, it is conclusive that annealing is necessary to minimize recombination at Al2O3-LD silicon, but this process is likely to reflect a recovery of dopant-independent laser damage. This is in agreement with previous work that has demonstrated lifetime recovery following annealing of laser damage with or with Al [26,27].

For reference, recombination at metallised, furnace boron-doped p$^+$ silicon in the range of 100 – 200 Ω$\square$ rises weakly with sheet resistance from approximately 1,000 – 1,200 fA cm$^{-2}$ [34]. In addition, industrially typical fired aluminum emitters are approximately 800 fA cm$^{-2}$ at 60 Ω$\square$, although it must be acknowledge that there is a lack of reliable data for this process [35].
3.2. Contact resistivity

When the as-doped surface was contacted with vacuum evaporated Al, contact resistivity exhibited a great deal of scatter, with values ranging between $10^{-2} - 10^{1}$ Ω cm$^2$ (figure 2, left). A local minimum was measured at 22 μJ for the 30 % pulse overlap, but no clear relationship between energy, overlap and contact resistivity is observed. The resistivity exceeds that of the reference screen-printed and fired Al, which is approximately $3 \times 10^{-3}$ Ω cm$^2$. However, sintering at 350 °C for 30 minutes reduced contact resistivity, revealing a strong dependence on pulse energy with minimum values of approximately $2 - 5 \times 10^{-4}$ Ω cm$^2$ at the highest pulse energies.

The largest reduction in resistivity was measured following a dilute, aqueous, 1 % (by volume) hydrofluoric (HF) acid etch after laser doping but prior to metallisation. This reduction was measured for all laser energies and overlaps, with non-sintered contact resistivity falling into the range of $10^{-4} - 10^{-5}$ Ω cm$^2$. Similar to recombination, contact resistivity to the etched surface is broadly independent of pulse energy and pulse overlap. It is uncertain why we observe such a large reduction in contact resistivity after etching, but scanning electron microscope images of an Al$_2$O$_3$-LD surface revealed an extremely thin surface film that was present following Al$_2$O$_3$-LD, but was removed by an HF etch. The necessity of a wet-chemical etch to achieve minimum contact resistivity is an unfortunate complication of the Al$_2$O$_3$-LD process. However the energy independence of the contact quality is positive from the perspective of process control, revealing that for the two most critical electronic properties of the Al$_2$O$_3$-LD silicon – contact resistivity and recombination – there exists an extremely broad process window that spans the visible energy thresholds of dielectric and substrate ablation. As we will see from the
simulations of section 4, low contact resistivity is crucial to maximise the efficiency of solar cells incorporating rear-surface Al₂O₃-LD silicon.

Fig 2. Contact resistivity for an evaporated Al/Al₂O₃ p⁺ laser doped silicon interface. Recombination was measured without HF etching, following sintering (left), and after HF etching, but without sintering (right). Following a short HF etch, contact resistivity is approximately uniform across the entire energy range. Note that for legibility the range of the contact resistivity differs between plots.

4. Efficiency potential of PERC-type solar cells incorporating Al₂O₃ laser doping

We have measured recombination at Al₂O₃-LD surfaces, with or without annealing, that exceed that of p⁺ silicon of equivalent concentration formed by furnace-doped boron. It is reasonable, therefore, to expect a performance penalty in solar cells incorporating p⁺ pulsed laser doping from Al₂O₃. However, we have also measured low contact resistivity to evaporated Al – two orders of magnitude lower than fired Al, for example – that allows the rear contact fraction to be reduced to a small area without compromising the internal resistance of the cell. There will exist an optimal contact geometry that is a compromise between series resistance and effective rear surface recombination. In fabricating the local contact openings with this process, computer controlled laser systems are readily programmed to precisely define arbitrary geometries.

To predict the potential conversion efficiency of PERC cell structures that implement Al₂O₃-LD with an optimized rear surface contact geometry, simulations of two cell structures were performed in Quokka. The first device is a PERC cell, which has a uniform, full-area front surface emitter, and screen-printed front and rear contacts. The optical and electronic parameters are industrially typical values, and the reference efficiency is 20.7 %. The UNSW PERL simulation replicates the best device parameters available in the literature for this cell, simulating a reference one-sun efficiency of 24.8 %. Simulations based on these two cell structures provide an indication of the efficiency potential of an industrially relevant cell, in addition to a device with highly optimized optical and electronic properties for which the Al₂O₃-LD contact openings will be a dominant source of recombination. The parameters for both cells have been taken from the forthcoming “Solar Cell Library” [35], available shortly at the PV Lighthouse website [36]. This resource provides Quokka simulation definitions for a range of crystalline silicon cell types using the most up-to-date values available in the literature.

Both simulations were modified to account for rear-surface passivation with a 20 nm Al₂O₃ / 80 nm SiN dielectric stack. Recombination at the non-contacted, undoped rear surface was set to 5 cm/s, which is a conservative value of recombination for this dielectric configuration on p-type silicon [37]. The generation profiles
were modified to account for the rear surface reflection of the Al₂O₃/SiN/pure-Al stack. Changing the rear surface recombination resulted in an initial increase (all other parameters held constant) in device efficiency for both cells, as neither structure originally incorporated such effective rear surface passivation\(^\dagger\). Therefore, these simulations capture both the advantage of reduced non-contacted rear surface recombination provided by Al₂O₃/SiN passivation, and the disadvantage of increased recombination at the Al₂O₃ p\(^+\) doped contacts.

The contact openings were defined as circular, with a diameter of 20 \(\mu\)m and a contact resistivity equal to \(\rho_c = 10^{-4} \text{ \Omega cm}^2\), a conservative upper limit on the resistivity measured for the HF etched Al₂O₃-LD surfaces. Initial simulations demonstrated that point-contacts, arranged in an equidistant square matrix, reached higher efficiencies than line contacts, and the results presented here are restricted to a point contact geometry. The rear surface contact fraction was varied by dependently sweeping the contact pitch in the x and y axis, while the recombination current factor, \(j_0\), was independently varied. The output of these simulations demonstrate the efficiency potential for each combination of contact fraction and recombination (figure 3).

The simulations demonstrate that with low contact resistivity, the rear surface contact fraction can be reduced to less than 1 %, which mitigates the total level of rear surface recombination. For contact recombination at \(j_0 = 10,000\) fA cm\(^-2\), the industrial PERC cell has a simulated efficiency of 20.9 %, while the PERL cell can exceed 24 % with an optimised rear contact geometry. It is notable that the combination of laser doping and metal evaporation facilitates a point contact, small feature geometry that allows the PERC cell to exceed the reference level of performance where the rear contacts are line-shaped with fired Al. This despite an increase in contact recombination of approximately 1 order of magnitude relative to screen printed and fired Al.

5. Conclusions

In this work we have characterised recombination and contact resistivity of Al₂O₃ laser doped p\(^+\) silicon formed by a range of laser energies and number of melt cycles using a nanosecond pulse length, 532 nm laser. We observe that recombination, before and after annealing, exceeds that of furnace diffused p\(^+\) boron doped silicon of equivalent sheet resistance. Increasing thermal cycles correlates with increasing laser damage, but this damage is equally recovered by low temperature annealing. Following annealing, recombination is between 8,000 – 10,000 fA cm\(^-2\) when doping from an Al₂O₃/SiN dielectric stack, and between 5,000 – 7,000 fA cm\(^-2\) when using a single layer Al₂O₃ precursor. Low resistivity contact requires a short dilute HF etch, following which contact resistance is in the range of \(10^{-4} – 10^{-5} \text{ \Omega cm}^2\) when contacted with evaporated aluminium. Therefore, following annealing and a dilute HF etch, both pulse energy and pulse overlap have a negligible influence on recombination and contact resistivity, which reveals a broad process window.

For PERC cells with local Al₂O₃ laser doped rear contacts, an optimal geometry can be found that minimises effective rear surface recombination while avoiding excessive series resistance. So configured, we see that cell efficiencies can approach 21 % for an industrially typical PERC cell, while the efficiency can exceed 24 % when implemented into a high efficiency locally doped and contacted PERC cell, in this case represented by the UNSW PERL cell.

The primary conclusion is that the reduction in cell efficiency is less than may be initially expected given values of contact \(j_0\) of up to 10,000 fA cm\(^-2\). In particular, efficiencies in excess of 24 % can be theoretically achieved by an otherwise highly optimised cell structure. These structures are readily achieved, as computer controlled laser systems can process arbitrary contact geometries at high speed. Al₂O₃ laser doping is therefore compatible with high efficiency PERC-type solar cells.

\(^\dagger\) For example, the surface recombination velocity of the passivated, undoped rear surface of the UNSW PERL cell is estimated at approximately 15 cm s\(^-1\) at \(\Delta n = 1 \times 10^{15} \text{ cm}^2\) using the parameterisation in [35].
Fig 3. Simulated one-sun efficiency for point contacted industrial PERC (left) and UNSW PERL cell (right) incorporating rear surface passivation with Al₂O₃/SiN and Al₂O₃-LD rear contact openings. Rear contact resistivity is 10⁴ Ω cm². The pentagrams locate the peak efficiency for rear contact recombination, \( j_0 \), of (1) \( j_0 = 10,000 \) fA cm⁻², the post-anneal recombination for Al₂O₃/SiN doping; (2) \( j_0 = 5,000 \) fA cm⁻², the post-anneal recombination for Al₂O₃ doping; and for the PERL cell (3) the original (non-laser doped) contact recombination where \( j_0,\text{PERL} = 130 \) fA cm⁻². Note different efficiency scales for each plot.

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