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# Laser doping through anodic aluminium oxide silicon solar cell



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#### ABSTRACT

This paper reports on the use of AAO layers as a source of p-type dopants for laser doping processes that forms localised p + regions on Si surfaces. Sheet resistances as low as 2  $\Omega$ /sq were demonstrated when a laser was used to scribe through a region of AAO using a speed of 500 mm/s and power of 9 W. Unlike laser-doping through spin-coated polyboron sources, it was shown that laser doping through AAO layers can be performed without introducing any voids into the Si and form a local BSF  $\sim$ 5  $\mu$ m into Si which is advantageous for PERL cell structure. This co-doping process was used to fabricate rear-passivated cells with efficiencies of up to 19.9%. However, although the heavily-doped local p<sup>+</sup> regions could reduce  $R_s$  to values as low as 0.54  $\Omega$  cm<sup>2</sup>, there was a penalty in terms of a high ideality factor in the  $V_{mp}$  – $V_{oc}$  voltage range which limited *FF*s to  $\sim$ 76%.

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## 1. Introduction

Goodrich et al. [1,2] suggests the market share for passivated emitter rear locally-diffused (PERL) silicon cell variants will significantly increase in next 4 years, because this design can be easily adapted to use n-type, p-type and multi-crystalline wafers. Introduction of p-type dopants by laser doping of silicon can be used to form p<sup>+</sup> silicon (Si) surface regions which can act as local emitter regions for n-type solar cells or reduce both the contact resistance at the metal/Si interface and the dark saturation current density of p-type solar cells by shielding minority carriers from the high surface recombination velocity at the Si interface [3,4]. An approach that has been reported by many is to form Al-alloyed local back surface field (BSF) regions by firing screen-printed aluminium (Al) paste through openings formed by either laser ablation or laser doping in a rear dielectric layer [5-10]. This process can therefore potentially eliminate the multiple steps required in performing masked solid state diffusion processes for the fabrication of Si solar cells. Dielectric layers have also been previously investigated as dopant sources for a subsequent laser doping process, with the advantage of this process being that the dielectric layer can passivate the surface outside of the laser-doped regions [11-14]. The use of an anodic aluminium oxide (AAO) layer, which acts both as a dopant source and a passivation layer, can be used for different cell structures, with examples including PERL cell variants and various bifacial cells.

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This paper introduces the use of AAO layers as sources of ptype dopants for a laser doping process used to create p+ regions on a Si surface. First, the relationship between sheet resistance and laser damage for different laser doping conditions where the intrinsic dopant, Al, was introduced from the AAO into the Si during laser doping. Later experiments explored the potential of incorporating additional (extrinsic) impurities into the AAO layer by anodising Al in electrolytes containing the impurities in ionic form. Second, electrochemical capacitance voltage dopant profiles and photoconductance measurements were used to assess the success of incorporating both the intrinsic and extrinsic dopants into the Si and the effect of the laser doping process on the effective minority carrier lifetime in the wafer. Finally, the developed AAO laser doping process was trialled in the fabrication of small-area PERL cells which employed a rear screen-printed Al electrode and a laser-doped and metal-plated front contact grid. The fabricated cells, which were laser-doped through an AAO layer, were compared to reference cells which employed Al<sub>2</sub>O<sub>3</sub>/ SiN<sub>x</sub> rear dielectric layers which were laser-doped through a B spin-on source. Both groups of cells were metallised by screenprinting Al paste over the entire rear surface and fired to form alloyed Al contact regions. Although this Al alloying process appears to negate the advantages of forming locally heavily-doped regions on the rear surface, previous studies have shown that higher  $V_{oc}$  values and efficiencies result if Al alloying is used to form contact to laser-doped regions rather than sintering of evaporated Al [4]. Laser doping through the boron-doped AAO layer resulted in a junction depth of 12 µm with the electrically-active p-type dopant concentration in excess of 10<sup>20</sup> cm<sup>-3</sup> over the first  $4 \,\mu m$ . Given that a good localised contact needs to be at least  $2 \,\mu m$ thickness of the localised BSF [15], a 12 µm junction should assist

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formation of a localised BSF on cell performance. The correlation between junction depth and cell performance is not well explained. One theory that has been proposed is that the laserdoped Si regions are more easily dissolved in the Al. Provided the contact regions are not spaced too far apart, increased dissolution of Si in the Al can result in thicker and more uniform local BSF formation [10,16–18]. Anodising a layer of aluminium on top of intervening dielectric layer can further improve the effective lifetime time. Part of the reason for this improvement is the stored positive charges [19]. This paper demonstrates cell results on a ptype PERL cell structure with rear passivating layers of  $AlO_{x}/SiN_{x}/$ AAO stack. Without AlO<sub>x</sub> layer the inversion layer created by  $SiN_x/$ AAO stack limited the cell efficiency to below 19%. However, based on the results presented in this paper, 19.9% efficiency on PERL cell structure was achieved using laser doping through AlO<sub>x</sub>/SiN<sub>x</sub>/AAO. These results suggest that  $SiN_x$ /AAO could be a good candidate for N-type cell.

#### 2. Experimental

Commercial-grade 156 mm  $1-3 \Omega$  cm B-doped, alkalinetextured Cz Si wafers were lightly-diffused with phosphorus to an emitter sheet resistance of  $\sim$  120  $\Omega$ /sq. The residual phosphorus at the rear surface was removed by rear-side etching and  $\sim\!10~\text{nm}$ SiO<sub>2</sub> layers were thermally-grown on both surfaces. Wafers were separated into groups for sheet resistance, laser induced damage and cell fabrication studies as shown in Fig. 1. For sheet resistance and laser induced damage studies, a 75 nm thick SiN<sub>x</sub> layer was deposited using remote plasma enhanced chemical vapour deposition (PECVD) at the front surface and 200 nm SiN<sub>x</sub> deposited at the rear surface. The refractive index of both layers was  $\sim$ 2.0. For cell fabrication, a 65 nm thick  $SiN_x$  layer was deposited onto the front surface and  $\sim 10 \text{ nm}$  of AlO<sub>x</sub> and 200 nm SiN<sub>y</sub> were deposited onto the rear surface using remote PECVD (Roth & Rau, MAiA). The wafers were then cleaved into fragments of  $\sim$ 4 cm  $\times$  4 cm for the experiments.

The anodisation process used the electrochemical cell apparatus shown in [19]. Wafers were processed one at a time, with each wafer being immersed in the electrolyte and connected to the positive terminal of a power supply by a clip (which was not immersed so as to prevent anodisation). A nickel (Ni) electrode, connected to the negative terminal of the power supply, was used as the counter electrode and a magnetic stirrer was employed to ensure a good mixing of the electrolyte at all times during the anodisation process in order to achieve a uniform AAO layer. A constant voltage was applied to the Al surface of the wafer during anodisation. The Al layer on the wafer for anodisation process was formed by thermal evaporation of 5 N purity Al wire in Tungsten boats. Anodisation commenced as soon as the external voltage was applied to the Si wafer. During anodisation, H is evolved at the Ni electrode (cathode) due to the reduction of H ions in the acidic electrolyte. At the anode (i.e. rear Al surface of the solar cell), Al is oxidised to Al<sup>3+</sup>. The oxidation commences at initial sites on the surface, the spacing depends on the type of electrolyte and the nature of the prepared surface (e.g. presence of surface defects). At oxidation sites, oxygen in the electrolyte can accept some of the generated electrons to form OH<sup>-</sup> which can then combine with the  $Al^{3+}$  ions to form  $Al(OH)_3$ , which can then subsequently dehydrate to Al<sub>2</sub>O<sub>3</sub>. The anodisation current was used as an indicator of anodisation progress, with a minimum value indicating when the layer of evaporated Al was fully anodised. For all experiments, the anodisation time was approximately 10 min unless otherwise specified. After the anodisation process, samples were rinsed for 2 min in deionised (DI) water and the dried using a N<sub>2</sub> gun.



Fig. 1. Schematic diagram of process flow.

Laser doping was then performed using a high-powered 532 nm wavelength laser with a Gaussian beam distribution and scanning optics. The laser beam diameter  $(1/e^2)$  was 20  $\mu$ m. The average power of laser reaching the stage is approximately 13 W for a laser power setting of 15 W. The peak average intensity,  $I_0$ , of the laser is approximately 8.2 MW/cm<sup>2</sup>, with a corresponding intensity at the focus size radius [3].

## 2.1. Sheet resistance and morphology studies

Wafers were then cleaned by Piranha etch (3:1 in volume of H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>) followed by 1 min immersion in 1% (w/v) HF. Finally, an Al layer of thickness ~650 nm was thermally-evaporated on the rear SiN<sub>x</sub> surface and anodised to form an AAO layer. Wafers were anodised one at a time in 0.5 M H<sub>2</sub>SO<sub>4</sub> and connected to the positive terminal of a power supply unit at a set voltage of 25 V.

A 532 nm laser with scanning optics was used to scribe (and dope) a rectangular box (1.5 cm  $\times$  0.6 cm) through the formed AAO, by scribing a number of lines 20  $\mu$ m apart. A separate line was scribed to monitor the morphology of the laser-doped region. The laser speed was varied from 500 to 8000 mm/s and the laser power was varied between 9 and 15 W. A four-point probe was used to measure the sheet resistance of the laser-doped rectangular box for the different laser doping conditions.

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