Metal-assisted chemically etched black silicon for crystalline silicon solar cells

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Abstract
Nanoscale textured silicon has the potential to overcome the optical challenges faced in the photovoltaic (PV) industry that remain in maximisation of photo-generation. However, due to the high aspect ratio of these structures, the electrical losses remain a huge challenge for this type of architecture. In this work, we use a Metal Assisted Chemical Etch (MACE) process to fabricate black silicon and analyse the influence on morphology of etch time and silver nitrate concentration. Furthermore, we show good surface passivation of the nanostructures using atomic layer deposition of AlOx, and study the optical influence of dual-passivation stacks using ultra-thin oxides.

Introduction
Minimising top surface reflectance and enhancing light trapping is vital in the design of high efficiency solar cells. For crystalline silicon cells, this has traditionally been addressed through micron-scale texturing and thin film coatings. Recently, nanoscale texturing, namely ‘black silicon’ has emerged as a more effective approach to achieving exceptionally low broadband reflection[1]. A ‘top-down’ approach to fabricate black silicon is through Metal-Assisted Chemical Etching (MACE), which has the potential to be a cheap, fast and scalable wet-etching process. This chemical etching method works by reducing Ag+ ions to elemental Ag which are deposited on top of the silicon substrate[2]. The initial oxidation of Si atoms from the surface leaves pits that are immediately filled by Ag particles. This is followed by an injection of holes into the silicon valence band at the Ag/Si interface, which begins oxidizing the silicon. The SiO2 is subsequently etched by the presence of hydrofluoric acid (HF). The silicon covered with Ag particles is etched due to the preferential charge transfer occurring and the agglomeration of holes below the Ag particles [2].

Despite the optical benefits from these structures, as shown in previous work [3][4], an increase in exposure of the top surface area can diminish the electrical quality of the structure due to surface recombination. Hence, passivation techniques using dielectrics such as AlOx and SiO2 have been used in the quest to reduce such losses [5]. In this work, we study the influence of etching conditions on anti-reflective properties of the silicon nanowire array (NWA), including etch time and AgNO3 solution concentration. We then present our latest results using Atomic Layer Deposition (ALD) AlOx for surface passivation of these structures. Finally, Finite-Difference Time-Domain (FDTD) optical simulations of SiO2/AlOx stacks on nanowires are presented to analyse the optical benefits of such passivating stacks.

Methods
The one-step MACE presented in this work consists of an aqueous AgNO3 solution and a diluted HF solution of 14 M. 4 cm x 4 cm silicon wafer samples are first cleaned using a standard 3:1 Piranha solution to remove organic particles, followed by a thorough de-ionised (DI) water rinse and finally dipped into a 7:1 HF bath for native oxide removal. The samples are then submerged into the MACE solution for the desired etch time (1-10 minutes), then thoroughly rinsed with DI water. A fuming Nitric Acid (FNA) solution is used to remove the silver dendrites residue on the samples after the etching process. Reflection measurements are carried out using an integrating sphere and a white diffuse 99% reflective standard, whilst morphology studies are undertaken using a JEOL field emission gun scanning electron microscope (FEGSEM).

AlOx deposition on these nanostructures was carried out via thermal Atomic Layer Deposition (ALD) with a Savannah Cambridge tool and trimethylaluminium (TMA) and water as precursors. High quality and uniform thin films are achieved by alternating exposure of the precursors to the surface of the substrate. For this study, the thickness of the alumina layer is 17 nm, as it exhibits the best conformal coverage on our nanostructures. Annealing is
required to activate the charges in the alumina layer, with optimal conditions for thermal ALD on n-type substrates at 400°C in N₂ atmosphere for 30 minutes[5][6][7].

Minority carrier lifetimes were measured using a calibrated Sinton photoconductance decay Lifetime Tester (WCT-120), both in transient and quasi-steady state modes [3]. For this, the etching process was carried out both on the front and on the back of the silicon wafers, for symmetry.

Optical simulations in this work are performed using FDTD methods, implemented with Lumerical software [8]. This enables rapid identification and optimization of various thin film stacks that can be placed on top of the nanowires to help further reduce surface reflection. The unit cell model and the full simulation conditions used are shown in previous work [9].

Results

MACE process optimization is carried out on single-side polished <100>, 1-30 Ωcm, p-type CZ wafers, to provide in-depth understanding of the etching mechanisms. Firstly, the etching time was varied, while keeping the silver nitrate solution fixed to 60 mM and the HF solution fixed to 14 M. Fig. 1 a) shows the resulting nanostructure height and the average reflectance as a function of process time. Longer nanostructures were formed with an increase in etch time, and consequently lower reflectivity, as the silver particles can further oxidise the substrate [2]. Moreover, a constant etch rate of approximately 500 nm/min for the etch durations of interest was determined based on the linear relationship found in Fig. 1 a).

Similarly, the effect of the molarity of the AgNO₃ solution was evaluated by keeping the etching time fixed to 6 minutes and the HF molarity fixed to 14 M. As seen in Fig. 1 b), higher concentrations lead to taller nanowires and consequently reduced reflectivity. This can be attributed to an increase in the hole injection rate into the substrate, which in turn directly influences the oxidation rate of silicon [2]. Another factor contributing to the reduced reflectance is the increased density of silver particles nucleating the silicon surface, forming denser nanostructures with smaller diameters.

The unusually large average reflectance corresponding to the 20 mM silver nitrate solution is attributed to the formation of porous-silicon, rather than well-defined vertically-aligned nanowires [10]. The resulting trends can be used to accurately predict the length of the nanowires and choose the desired parameters for various applications.

![Fig. 1: Nanowires length and their average reflectance as a function of a) MACE process time, b) AgNO₃ concentration](image-url)

It is evident that longer nanowires yield lower surface reflectance, as seen in both Fig. 1 a) and b). Whilst reducing reflectivity, the resulting large surface area strongly relates to increased surface recombination causing electrical losses. Thin dielectric films, such as silicon dioxide and silicon nitride, have been traditionally used to provide silicon surface passivation, by employing two mechanisms. Firstly, the dangling bonds can be saturated chemically to remove surface states[3]. Secondly, a charge can be activated in the thin dielectric film to repel minority carriers from the silicon-passivating film interface, and thus, limit recombination at the surface[5]. Table 1 shows the measured effective minority carrier lifetimes (τ_eff) for various samples, specified at a minority carrier density (MCD) of 10¹⁵ cm⁻³. This shows a significant boost in lifetime when
passivating with AlOx. The variance in lifetime for the NWA samples is attributed to the different morphologies of the structures, indicated in the table.

<table>
<thead>
<tr>
<th>Sample description</th>
<th>$\tau_{\text{eff}}$ @ MCD = $10^{15}$ cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare flat silicon</td>
<td>4 $\mu$s</td>
</tr>
<tr>
<td>Flat silicon with 17 nm annealed AlOx</td>
<td>1 ms</td>
</tr>
<tr>
<td>Bare silicon NWA</td>
<td>2.3 $\mu$s</td>
</tr>
<tr>
<td>Silicon NWA with 17 nm annealed AlOx layer</td>
<td>790 $\mu$s (1 $\mu$m NWs)</td>
</tr>
<tr>
<td></td>
<td>230 $\mu$s (3 $\mu$m NWs)</td>
</tr>
</tbody>
</table>

Table 1: Measured $\tau_{\text{eff}}$ at MCD of $10^{15}$ cm$^{-3}$ for various samples in the study.

Fig. 2 a) shows an SEM cross-section of the bare silicon nanowire array (NWA). In Fig. 2 b), the bright thin layer on top of and in-between the structures is the 17 nm alumina film, which exhibits good conformal coverage.

FDTD simulations are performed to further assess the applicability of the thin passivating alumina layer from an optical perspective. Fig. 3 shows the reflectance as a function of wavelength for both the uncoated and the coated (with AlOx) nanowire. In this case, the nanowire was simulated as a periodic structure and does not exhibit the broadband reduced surface reflection of the heterogeneous black silicon surface [9]. However, the reduction in reflectance is evident and is confirmed by measurements performed on the fabricated samples.

Fig. 2: SEM cross-section image of a) the bare NWA of 3 $\mu$m height and b) the NWA of 1 $\mu$m height coated with a 17 nm of alumina.

We have calculated the weighted average reflectance (WAR) as a figure of merit, indicated in the legend, using equation (1), where $F(\lambda)$ is the incident photon flux and $R(\lambda)$ is the reflectance, both as functions of wavelength. The 2.72% decrease in WAR shows that a 17 nm AlOx does not only provide good surface passivation, but it is also optically beneficial.

$$\text{WAR} = \frac{\int_{400}^{1000} F(\lambda)R(\lambda) d\lambda}{\int_{400}^{1000} F(\lambda) d\lambda}$$

Wavelength-dependent reflectance measurements were performed on the fabricated samples and averaged across multiple batches to avoid anomalies. Fig. 4 below presents the reflectance in the 400-1000 nm wavelength range of interest for flat bare Silicon, bare NWA on silicon and passivated NWA on silicon, where the wires length was approximately 1.5 $\mu$m.

The resulted weighted average reflectances are 3.33% and 3.08% for the coated NWs and the as-fabricated NWs, respectively, in good agreement with the trends derived from the simulation results.
To further improve the quality of passivation, a very thin silicon dioxide layer can be deposited on top of the nanowires before the deposition of the alumina layer. This thin layer will provide good chemical passivation, in addition to the strong field-effect component of the alumina film [5]. The influence of these dual stacks can be analysed optically using FDTD simulations. Fig. 5 shows the WAR for various thin oxide layers (1-10 nm) stacked in-between the nanowire and the AlOx film. This shows that even such a thin layer can have a great optical impact on the overall structure, with thicker silicon dioxide layers yielding even lower reflectance values.

**Conclusion**

This work has presented a wet-etching ‘top-down’ method of creating black silicon using MACE. This consists of an aqueous AgNO₃ solution and a concentrated HF solution of 14 M. Results show an increase in nanowire height (and consequently reduced reflectivity) with increasing etch time and silver nitrate solution molarity. The latter also reduced reflectivity due to an increase in density of NWs. Good quality passivation using ALD alumina has been demonstrated, achieving minority carrier lifetimes in excess of 700 μs for nanostructured silicon on CZ wafers. FDTD simulations, as well as measured reflectivity, show also an optical benefit of the passivating alumina layer, with reduced WAR compared to bare NWs. The FDTD simulation have also shown that an additional ultra-thin silicon dioxide layer placed in-between the AlOx and nanostructures can further reduce reflectivity. In order to fabricate such dual stacks, which has superior capability to that of a single film, with good conformity of the nanowire surface, we aim to look at nitric acid oxidation of silicon (NAOS), as well as the use of ALD SiO₂ in future work.

**References**


