

Original Research

# The use of electro-deoxidation in molten salts to reduce the energy consumption of solar grade silicon and increase the output of PV solar cells

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## Abstract

Solar photovoltaics, based upon silicon, are the most popular form of solar cell with efficiencies around 20%. These efficiencies can be further increased by employing light trapping schemes to minimise optical losses through scattering and reflection which enhances the amount of light absorbed and number of photo-carriers generated. Typical approaches employ antireflection coatings (ARCs) or texturise the surface of the silicon disks, so that the structure consists of an array of needles which can absorb most of the light. Usually, these structures are created by leaching the silicon with hydrofluoric-based acids or by reactive ion etching (RIE) methods. This paper reviews some of the methods for improving the energy efficiency of silicon production, and describes the use of electro-deoxidation of SiO<sub>2</sub> layers, on silicon, in molten calcium chloride to form nanoporous black silicon (b-Si) structures. By coating b-Si surface with TiO<sub>2</sub>, a common ARC, extremely black surfaces with negligible reflectance of about 0.1%, are produced, which can have applications for low-cost high efficiency solar cells.

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**Keywords:** Black silicon; Solar cell photovoltaics; Silicon molten salt; Electrochemistry

## 1. Introduction

Silicon solar photovoltaics (PV) are the most widely employed solar technology in today's world. Generally, PV cells have low maintenance costs, no moving parts, operate at near ambient temperature, and enable generation at any scale. As an example, a 10-square-metre (m<sup>2</sup>) PV array is, in theory, no less efficient per unit area than a 10-square kilometre (km<sup>2</sup>) array. During operation, the front surface of the PV module is illuminated by light. Solar photons are transmitted into each cell, and those photons with sufficiently high energy are absorbed. An absorbed photon transfers its energy to an electron and its positively charged counterpart (a hole) creating a "pool" of free charge carriers within the material. An internal

electric field drives electrons toward one electrode and holes toward the other, creating a flow of current.

Solar PV technologies can be classified according to their primary light-absorbing material, either wafer-based or thin film. Wafer-based cells are fabricated on semiconducting wafers and can be freely handled without an additional substrate, although modules are typically covered with glass for mechanical stability and environmental protection. Thin-film cells consist of layers of semiconducting material casting onto insulating layers, such as glass.

For technical and historical reasons the vast majority of commercial PV module production has been, and remains, silicon based. Currently (2015) over 90% of worldwide PV energy production is based upon silicon solar technologies [1]. Silicon can be manufactured into non-toxic, efficient, and extremely robust solar cells, making use of the cumulative knowledge of more than 60 years of semiconductor processing and manufacturing technologies. Crystalline silicon (c-Si) solar

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cells are divided into two categories: single-crystalline (sc-Si) and multicrystalline (mc-Si). The sc-Si affords higher crystal quality and so improves charge generation and power conversion efficiencies, but requires more expensive wafers. Efforts are also underway to improve the energy efficiency of thin film silicon solar cells, thin film panels are not as efficient as crystalline cells and therefore more thin film panels are required to generate the same amount of electricity. A thin film installation can take up to 35% more space (i.e. land) to achieve the same total power output as a premium crystalline installation. Despite small advances in new PV materials, crystalline silicon utterly dominates today's PV landscape, and will continue to be the leading deployed solar PV technology over the next two decades.

The price of solar power continues to fall, and is now on a par or cheaper than grid electricity in many areas of the world. Unsubsidised rooftop solar electricity costs between \$0.08–\$0.13/kWh, which is around 30–40% below the retail price of electricity in many global markets [2]. It is widely predicted that solar systems will be at grid parity in up to 80% of the global market within two years [2]. Despite the massive growth in solar capacity worldwide (40 GW capacity was added in 2014 and 57 GW is expected to be added in 2015, largely in China [3,4] the cost of silicon solar cells PV, makes up less than 1% of the electricity market today but could be the world's cheapest energy source by 2030 [5], and the world's biggest single source by 2050 [1].

There are two ways in which the cost of energy from silicon solar cells can be reduced and these are to reduce cost of the silicon and, secondly, to improve the efficiency of the solar cell. The use of molten salts can make a contribution to both areas.

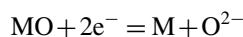
Silicon is one of the world's most abundant elements but comprehensive reduction and refining techniques must be applied before it can be used in the electronic or PV industries. The first step in the production of PV silicon is the melting and reduction of quartzite gravel by carbon in a submerged-electrode arc furnace at around 1800 °C [6]. The product is metallurgical grade silicon, which is about 98–99% pure, with the major impurities being aluminium and iron, as well as boron which is a dopant in silicon. The energy consumed (20 kWhkg<sup>-1</sup>Si) and the CO<sub>2</sub> produced (10 kgCO<sub>2</sub>kg<sup>-1</sup>Si) is substantial. For solar and electronic grade silicon, metallurgical grade silicon is usually refined using the Siemens chlorosilane process in which metallurgical grade silicon is heated with hydrogen chloride to form chlorosilane which is then decomposed to chemically vapour deposit silicon [6]. Again, this is a very energy consuming process (75–130 kWhkg<sup>-1</sup>Si) with a concomitant generation of carbon dioxide (43 kgCO<sub>2</sub>kg<sup>-1</sup>Si).

Solar cell efficiencies can be improved based on the following aspects [7]: (i) absorbing more incident photons to create more photocarriers and (ii) efficiently collecting more photocarriers to generate higher flow of current. The employment of surface nanostructures provides economic potential for capturing more light owing to their unique architectures, large surface-area-to-volume ratio, and quantum confinement effects, which

substantially differ from those of bulk materials. From an optical viewpoint, nanostructures show significant photon capturing and photon confinement abilities to enhance light absorption. Light management is crucial to solar cell design as it increases the path length of light in the absorber layer, thereby enhancing the probability of electron-hole pair generation. By engineering the reflective and refractive properties of the solar cell surfaces, light can be trapped within the active region more efficiently. Better photon trapping allows for physically thin, but optically thick active layers in the solar cells to not only reduce the processing costs and amount of material used, but also to decrease electrical losses during the photocarrier transport.

One way of improving the situation is to use nanotexturised black silicon (b-Si), as a low reflectance optical coating as this offers a simple route towards increased solar cell efficiency by minimising surface reflectance and channels more photons through the photovoltaic medium, leading to increased charge-carrier generation and higher cell currents. The motivation for this work is to produce a low-cost, ultra-black silicon solar absorber. We have developed a simple method to produce a porous layer which, when serving as the substrate for conventional ARC materials such as TiO<sub>2</sub>, can offer enhanced light absorbance and further reduce reflectance losses.

In 2000, it was reported that oxygen could be removed from metal oxides by making the oxide the cathode in a bath of a molten salt of a very electropositive cation such as calcium [8].



This method, termed as electro-deoxidation, has been shown to be applicable to a vast range of metal oxides and, surprisingly, if a mixture of oxides is used as the cathode, an alloy [9] is formed rather than mixtures of individual pure metal particles and has now been successfully commercialised for tantalum. Some work has been done on the reduction of silica [10–13] which is slightly more challenging as the starting oxide is an insulator whereas, although TiO<sub>2</sub> is an insulator, it quickly changes to an electronic conductor on the application of the cathodic potential. Results from several authors show that it is possible to reduce silica to silicon by the electro-deoxidation method. One of the disadvantages of this approach is that only the anionic component of the oxide is removed whilst the elements that form cations will remain in the deoxidised product. As a result it is likely that the purity obtainable by the electro-deoxidation method is unlikely to be greater than 99.99% and an electro-refining step is required which, again, has been demonstrated to be successful. The combination of these two steps will save 100 kWhkg<sup>-1</sup>Si and 50 kgCO<sub>2</sub>kg<sup>-1</sup>Si. A comparison of the two methods is shown in Fig. 1.

Black silicon can be produced via a variety of methods including, reactive ion etching, laser ablation and electrochemical etching [14,15]. Most of these techniques, however, are not cost effective and also include hazardous reactants, such as hydrofluoric acid with the associated environmental concerns. This paper describes the creation of thin silicon films with

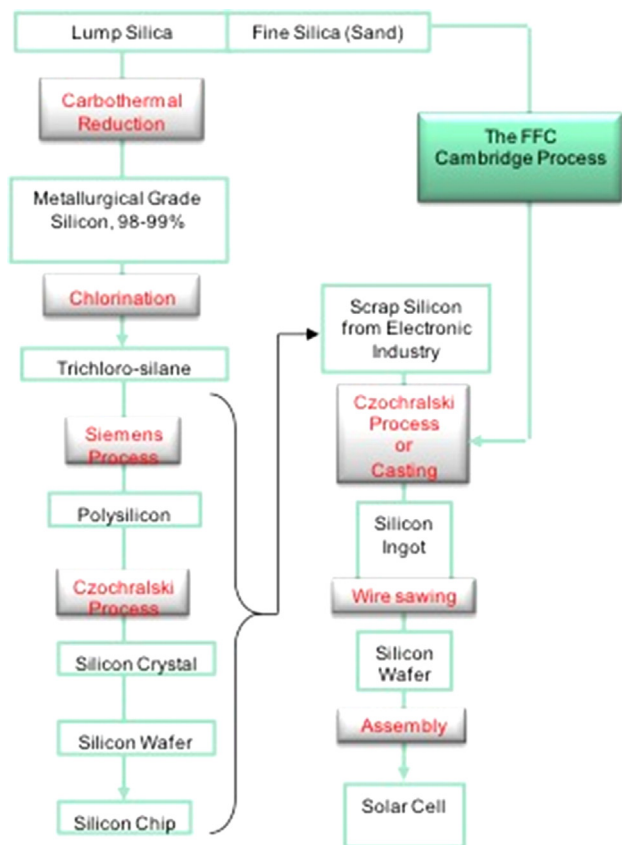


Fig. 1. Comparison of existing processes for silicon with FFC Cambridge Process.

effective light absorbance in molten salts by electro-deoxidation of thin (300 nm) oxide layers. The surface structure comprises micro-nanopores, pits and nanoscale pillars, but antireflection coatings are still necessary in order to get high conversion efficiency. Silicon nanopillared architectures are important as alternatives to a planar design of solar cells. Silicon nanopillars mean the direction of light absorption is orthogonal to the direction of charge-carrier collection. In such architectures, light is absorbed along the axial dimension of the rod while the charge carriers diffuse much shorter distances radially to a p–n junction [16]. The concept opens the route for cheaper solar cells through application of less pure silicon thus, again, reducing processing costs.

Owing to severely reduced surface reflection, it appears extremely matte black. By introducing a random array of micro-nano structures into the facing layer of a solar cell, the surface light collection area is significantly increased. Furthermore, the range of collection angles over which light can be captured is significantly enhanced. Light incident at low angles to a black silicon solar cell surface can still capture photons and create charge-hole pairs, i.e. to produce electrical current flow. Practically, this means black silicon solar cells can exhibit “higher” efficiencies when compared to photovoltaic cells with equivalent efficiencies owing to their greater ability to harvest light.

Recently two record-breaking black silicon solar cell efficiencies have been announced [17,18]. First the Barron group

at Rice University announced a black silicon cell efficiency 8.9% using a modified electrochemical etch to create the nanoscale textured porous layer. The novelty in this method is that the top (gold) electrical contact in the cell is deposited on the wafer prior to etching which then itself serves as the catalyst to drive the electrochemical reaction. Under normal crystalline silicon solar cell manufacturing methods, the top contacts must be added later after surface texturing and the back contacts have been formed, so this method offers a chance to omit 2–3 steps from the production process.

Following this, the Savin group [17] in Aalbo, Finland announced the highest black silicon cell efficiency yet of 22.1%, very close to the PV crystalline silicon theoretical limit of 25% by engineering the top surface to control how the charges created within the nanoporous layer travel through the crystal wafer. Here, the black silicon porous layer was made by plasma ion implantation. Ordinarily, when light is absorbed by a nanoporous silicon solar cell, electron-hole charge pairs are created which, owing to the large surface area of the nanostructured layer, recombine before being collected at the contacts, reducing the efficiency. By coating the top surface with a layer of aluminium oxide, this unwanted recombination was much reduced.

Some caution must be taken with these results. In both cases, hazardous hydrofluoric (HF) acid washes is used either pre or post-synthesis. Although a relatively weak acid, HF is extremely corrosive and requiring considerable safety procedures in handling and disposal. These methods may be difficult to scale up to meet industrial-scale production without significant modification to existing PV manufacturing lines. Plasma ion implantation is an inexpensive method, but any cost savings will be negated by the necessary upgrades to PV wafer handling supply lines. Nonetheless, these efficiency results have provided new knowledge of surface coatings and cell designs to incorporate into our inexpensive b-Si wafers produced by molten salt.

Recent data show incorporating black silicon into a solar cell can result in a 3% increase in daily energy production when compared with a reference cell with the same efficiency [17]. This means power can still be delivered on cloudy days and/or when the sun is low in the sky. A greater ability to capture light increases the number of sites where black silicon solar cells can be sited, thus bringing the cost benefits of solar power generation to a greater number of markets. These can range from small scale arrays, making use of crowded/partially covered urban locations, to vast scale solar farms sited in previously supposed unlikely northern or southern latitudes.

Although nanostructured black silicon offers superior optical performance, the efficiency of b-Si solar cells is lower compared to conventional crystalline silicon solar cells. The difficulties to achieve high-efficiency b-Si solar cells are mainly attributed to the enlarged surface area and the associated surface defects created by the fabrication process of producing the black silicon layer. To date surface coatings have been explored in order to further optimise high optical absorption within the porous b-Si layer and to passivate the

surface to inhibit charge recombination. Initial studies presented have been performed on wafers coated with titanium dioxide, a common solar antireflection coating used in the PV manufacturing industry.

## 2. Experimental

Early work on producing black silicon by electrolysis in molten salt focused on the novelty of the process and the morphology of the textured surface structures formed [19,20]. The processing technique has been changed to improve the degree of control of the porous layer, and have scaled up manufacture to produce full 10 cm diameter wafers for PV testing at lower costs and in shorter timescales. The experimental arrangement is shown in Fig. 2. Briefly, 500  $\mu\text{m}$  thick, p-type, and boron-doped  $\langle 100 \rangle$  silicon wafers with a 300 nm wet thermal oxide layer were obtained from a commercial supplier (Virginia Semiconductor, USA). After thorough degreasing with acetone and isopropanol, the wafers were immersed in an alumina crucible (Almath Crucibles, UK) containing molten calcium chloride salt (Sigma Aldrich, UK) at 850  $^{\circ}\text{C}$ . All molten salt experiments were performed in a sealed Inconel retort that was continuously purged with argon gas. The lid is removable and sealed with a Viton O-ring, and the entire assembly is fitted within a vertical furnace (Instron, UK). Prior to melting the calcium chloride salt, several pre-melt steps were followed. Owing to the hygroscopic nature of the salt, drying is necessary to remove any traces of water. The salt is dried for 3 h at 60  $^{\circ}\text{C}$ , 3 h at 120  $^{\circ}\text{C}$ , then 18 h at 180  $^{\circ}\text{C}$ . The salt is stored in sealed vessels in a glovebox prior to use. Further removal of moisture and trace impurities was carried out by melting the salt and undertaking pre-electrolysis between a pair of graphite electrodes at  $-2$  V for 4 h. After this pre-electrolysis step, the graphite cathode was removed and replaced with the working electrode which held the silicon.

The silicon disks were held in cradles made from molybdenum and 316 stainless steel. The cradles can hold pairs of parallel standard 10 cm diameter wafers back-to-back, thus doubling the rate of textured wafer fabrication, and can be adapted to hold non-standard shapes and sizes of wafer — thus making them ideal for small test samples for rapid PV characterisation (Fig. 3). 6 cm diameter to 10 cm diameter wafers are shown in Fig. 4 and these could be scaled further to satisfy industrial demands of 30 cm diameter wafers with the introduction of a higher capacity furnace and crucibles to hold the molten salt. All electrolysis experiments were performed with a Solartron SII287 potentiostat controlled via Corware electrochemical interface software. A pre-determined voltage ( $-0.6$  V or  $-0.9$  V) was applied for 20 minutes to the wafers within the molten salt. After this, the wafers were raised from the salt and the furnace was allowed to cool. When at ambient temperature, the wafers were removed, washed in 1:10M0.1 45% HCl:ultrapure water and allowed to dry. The energy consumption was about 15 kWh/kg of reduced silicon.

The reduced black silicon wafers are shown Fig. 5 and titanium oxide layers were applied to the b-Si wafers by sputter (PVD) deposition (Plasmapro 400, Oxford Instruments, UK),

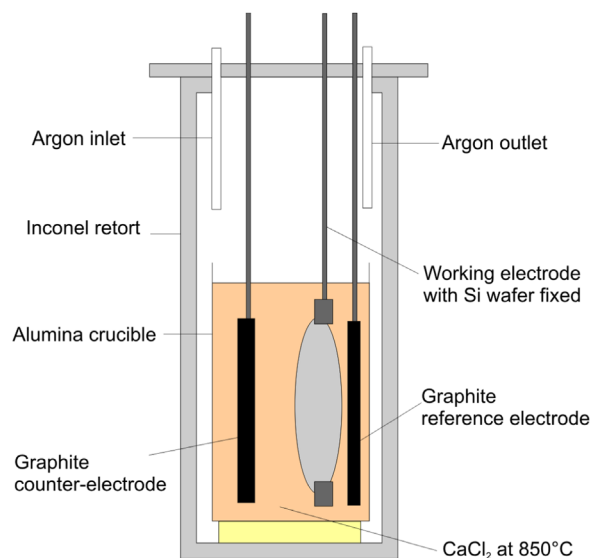


Fig. 2. Schematic of the FFC electro-reduction setup for preparing nanotextured black silicon. The exterior of the upper part of the retort employs water-cooling to preserve the condition of the electrical feedthroughs.

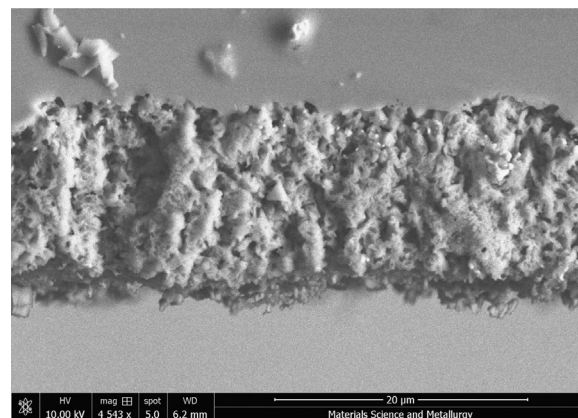


Fig. 3. SEM cross-section image of b-Si formed on p-type silicon substrate (bottom edge) with 100 nm thick oxide layer by polarisation in molten  $\text{CaCl}_2$  at  $E = -0.9$  V vs graphite for 3 h. The pitting propagates into the bulk of the silicon layer forming a dense network layer of wires, pits and nodules. The high density and random orientation aid trapping of light. Light incident on the bottom surface is scattered within the network and absorbed by the bulk crystal.

at a rate of 10 nm per minute using ceramic  $\text{TiO}_2$  target (Kurt Lesker Co, USA). The layer thickness was checked by in-situ profilometry against a polished silicon standard. Considerable effort was taken to ensure a uniform thickness profile across the wafer surfaces. Because of the high aspect ratio of the b-Si surface, after a series of extended trials, a multiple-pulse scheme was adopted to improve the penetration of  $\text{TiO}_2$  into the deep porous cavity structure.

## 3. Results

### 3.1. XPS characterisation on $\text{TiO}_2$ coated wafers

Measurements were performed with a Kratos ES300 electron spectrometer with an energy resolution (E/dE) of

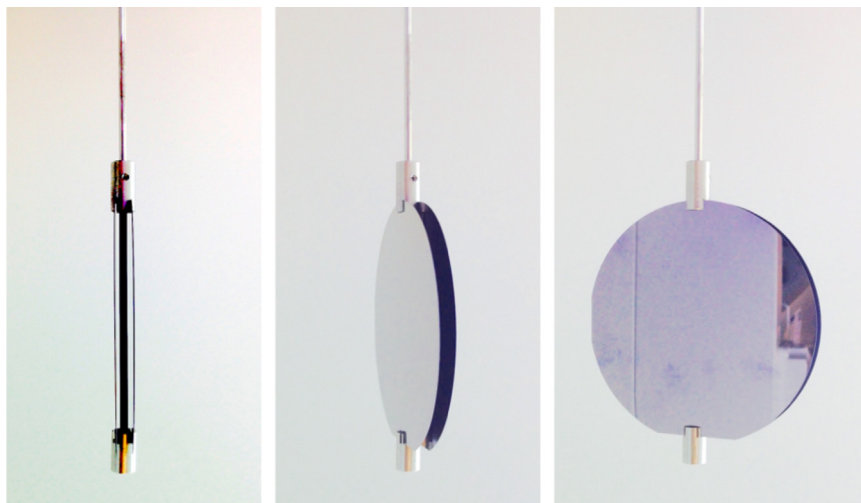


Fig. 4. Loaded cradle with two  $< 100 >$   $p$ -type Si, thermal-grown oxide wafers prior to electroreduction in molten salt bath.

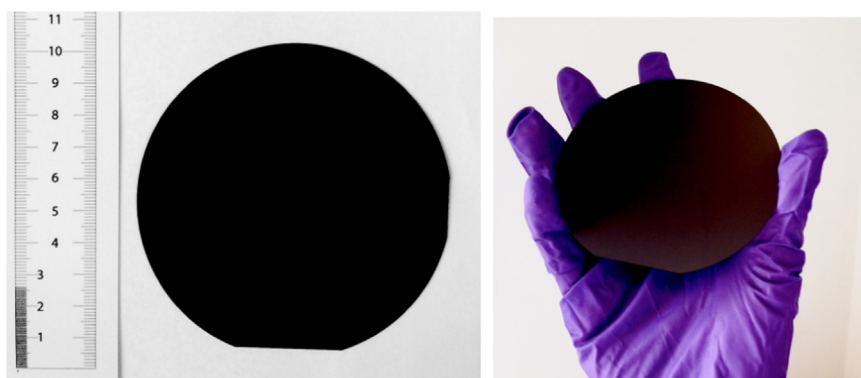


Fig. 5. Reduced black silicon wafers from cradle in Fig. 3, electrolysis conditions  $-0.9$  V for 20 min. Photographed under ambient lighting conditions, with no image post-processing applied.

300 meV and analyser pass energy of 20 eV. The X-ray source is a monochromatic Mg  $K\alpha$  (1253 eV). Fig. 6 shows the survey spectrum for a b-Si wafer prepared by reducing the 300 nm thick native oxide layer on  $p$ -type boron doped silicon, in molten  $\text{CaCl}_2$  at  $-0.9$  V for 20 min coated with 50 nm (upper panel) and 100 nm (lower panel) coating of  $\text{TiO}_2$ . Since XPS only probes the topmost 10 nm of a surface the oxygen O1s peak is particularly strong owing to the highly surface-specific nature of the technique. Surface roughness leading to differential charging effects ( $\sim 2$ – $3$  eV) is also present which is typical in semiconducting samples.

Fig. 6 shows the survey spectrum for reduced oxide b-Si wafers prepared at  $-0.9$  V for 20 min, coated with a layer of  $\text{TiO}_2$ . Fig. 6a shows the survey for b-Si coated with 50 nm and Fig. 6b shows 100 nm  $\text{TiO}_2$  coating.

A close inspection of the survey shows the presence of  $\text{TiO}_2$  within the top layer; this is, as would be expected, clearer in the 100 nm spectrum, although the signal from oxygen (O1s level) at 534 eV dominates owing to the oxygen species in Si–O, Si=O and Ti–O<sub>2</sub>. Fig. 7 shows a

wide scan collection of the Si2p region, to help identify the coordination environment of the silicon species in the top layer. The spectrum shows the XPS profile of the Si2p region. Peaks were fitted with CasaXPS using a convoluted Gaussian (66%) and Lorentzian (33%) profile upon a standard Shirley background function. These results demonstrate the presence of some surface oxygen. The spectrum is decomposed into three components at 99.05 eV (Si–Si bonds); 102.72 eV (Si–O) and 104.09 eV (Si=O) from within the surface silicon oxide layer. Si=O bonds commonly form and stabilise the interface, since it requires neither a large deformation energy nor an excess element present. This also serves to passivate the top layer against degradation caused by ageing.

### 3.2. Reflectance results

Optical absorptivity is a key factor to be considered before evaluating the photoelectrical conversion performance of solar cells. Reflectance measurements were taken with an Ocean

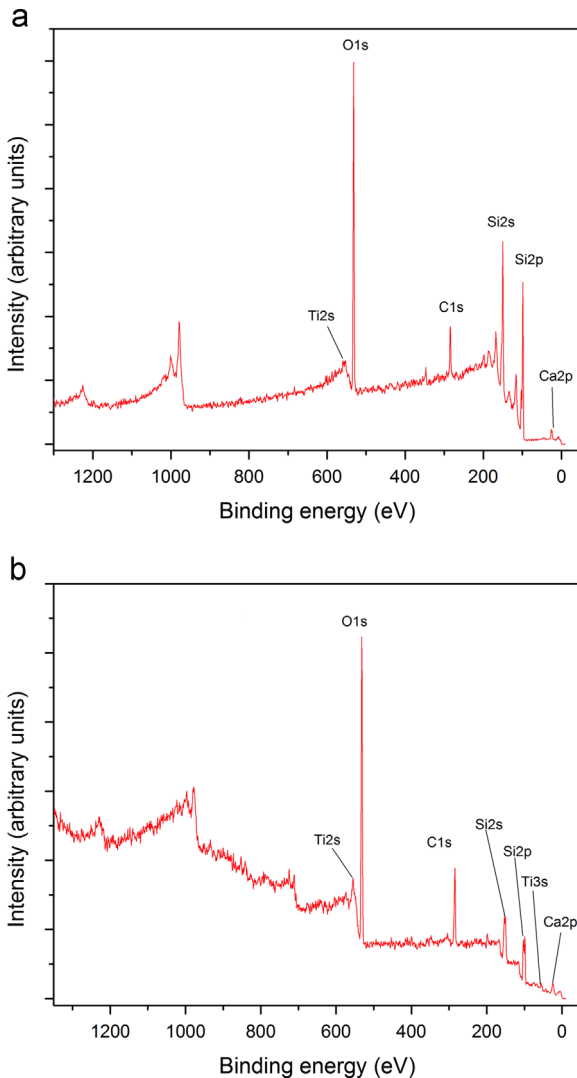


Fig. 6. XPS survey spectrum for 50 nm (a) and 100 nm (b)  $\text{TiO}_2$  coated b-Si wafers after electrolysis for 20 min at  $-0.9$  V.

Optics USB2000+ spectrophotometer with a white LED source and a 150 mm integrating sphere.

Wafers were prepared using an optimised set of electrolysis conditions to maximise the surface porosity and achieve lowest optical reflectance, as determined from prior experiments. Sample batches were coated in 50 nm or 100 nm thick layers of titanium dioxide ( $\text{TiO}_2$ ) to further reduce reflectance. Fig. 8 shows samples of the black silicon prepared under 20 min of electrolysis at  $-0.6$  V, with 0 nm, 50 nm and 100 nm  $\text{TiO}_2$  coating. The samples are irregular in shape since the deposition chamber cannot hold full 10 cm diameter wafers and can only hold samples  $3 \times 4$  cm<sup>2</sup> in area. Since molten salt electrolysis reduces the wafer thickness by up to 25% fracture during wafer slicing occurs.

The average weighted reflectances for the tested black silicon wafers coated by 50 nm and 100 nm layers of  $\text{TiO}_2$  are shown in Figs. 9 and 10, and in Table 1. The average reflectance values are weighted with respect to the standard solar atmospheric AM1.5 spectrum according to the method in

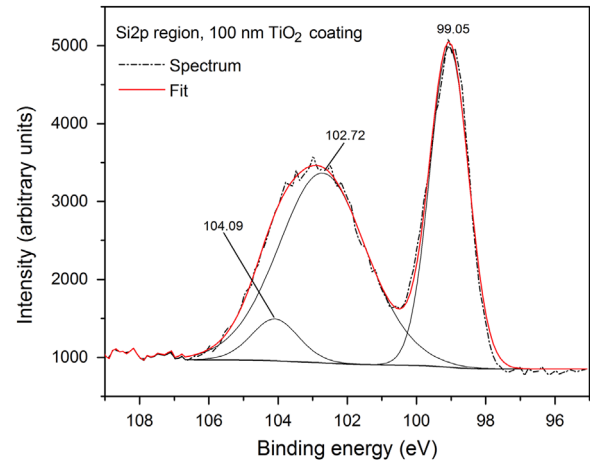


Fig. 7. Si2p XPS spectrum for 100 nm  $\text{TiO}_2$  coated b-Si wafer showing the photoemission decomposition.

[21]. The values 0.1% are remarkable compared to other studies, and the results from sample D and G are especially striking. One of the world's blackest materials, VANTAbblack, produced by SurreyNanosystems reflects only 0.035% of visible light [22] comprises a vertical array of carbon nanotubes grown upon aluminium foil. After five years of development it is now being scaled in production for aerospace and defence applications.

#### 4. Conclusions

To date, by focussing on depositing  $\text{TiO}_2$  coatings we have succeeded in obtaining extremely low (sub 1%,  $\sim 0.1\%$  reflectance) layers of black silicon. This is among the lowest reflectance ever achieved for black silicon including that produced by more expensive/labour intensive techniques such as electrochemical etching and, the lowest ever achieved for black silicon produced by molten salt electrolysis to date, representing a  $\sim 3$  to 4% improvement upon previous results. This places our material firmly in the family of low reflectance optical surfaces and potentially opens up further applications where low-reflective materials are desired. There is potential for optimisation to improve this result even further by incorporating a dual layer of aluminium oxide on top of the  $\text{TiO}_2$ .

To reduce the material cost and improve the efficiency further, designs of solar cells based on crystalline (c-Si) film of several microns thick have also been explored. Two typical models are silicon nanowire array and nanohole array in silicon [23,24], but it is difficult to get high efficiency from such purely nano-structured c-Si films, due to the increased recombination loss and contact resistance arising from surface nano-structures. Our material has nano and microporous structures with a smaller surface area than an equivalent porous layer comprising only nanoscale pores. This is important since the enhancement in optical absorption through light trapping should overwhelm the increase in surface recombination loss. The present microporous b-Si

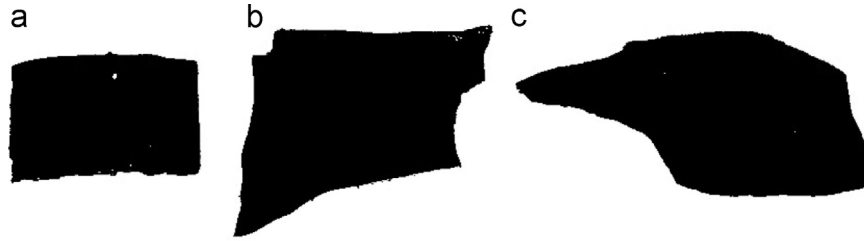


Fig. 8. Approx 1 cm<sup>2</sup> black silicon samples coated with 0 nm, 50 nm, and 100 nm TiO<sub>2</sub> (a), (b), and (c) respectively. Image taken under ambient lighting conditions with no post-processing or image filtering applied.

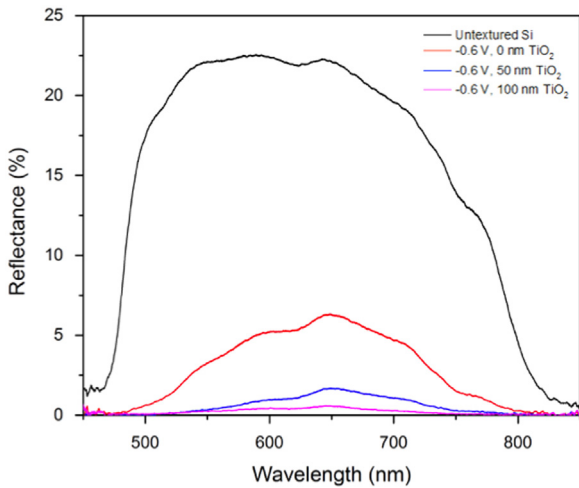


Fig. 9. Reflectance of b-Si at  $-0.6$  V electrolysis for 20 min, coated with 0 nm, 50 nm and 100 nm TiO<sub>2</sub> layer.

film is thus promising as a thin active layer for a high efficiency silicon solar cell.

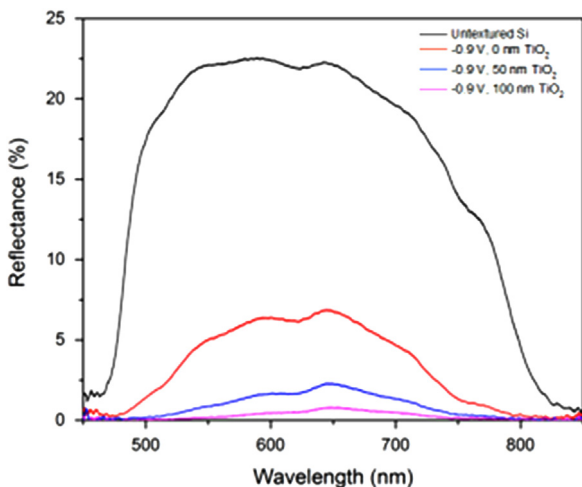


Fig. 10. Reflectance of b-Si at  $-0.9$  V electrolysis for 20 min, coated with 0 nm, 50 nm and 100 nm TiO<sub>2</sub> layer.

Table 1

Weighted average reflectance spectra for coated and uncoated b-Si samples.

| Sample | Applied potential (V) | TiO <sub>2</sub> thickness (nm) | Weighted average reflectance (%) |
|--------|-----------------------|---------------------------------|----------------------------------|
| A      | 0                     | 0                               | 21.490                           |
| B      | $-0.6$                | 0                               | 4.045                            |
| C      | $-0.6$                | 50                              | <b>0.339</b>                     |
| D      | $-0.6$                | 100                             | <b>0.109</b>                     |
| E      | $-0.9$                | 0                               | 2.401                            |
| F      | $-0.9$                | 50                              | <b>0.376</b>                     |
| G      | $-0.9$                | 100                             | <b>0.107</b>                     |

### Acknowledgements

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