A PROPOSAL FOR HOW TO OPTIMIZE B-SI TO BALANCE ABSORPTION AND PASSIVATION

ES173 Final Project

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Abstract

Black silicon (b-Si), a nanotextured semiconductor material, yields unique benefits and challenges for the future of solar cell design. Its high absorbance of both visible and infrared light makes it an excellent material for photovoltaic applications. However, black silicon's high surface area leads to greater surface recombination of electron hole pairs. As such, determining ideal levels of passivation for specific nano-structure geometry is a valuable next step in improving the optical performance of b-Si.

In the following proposal, we advocate for the use of Direct Reactive Ion Etching (DRIE) to manufacture five different pillar heights of black silicon nanostructures and pair them with five different thicknesses of passivation layers. For the twenty-five experiments, we will measure the absorbance and efficiency before and after passivation. We anticipate finding a favorable combination of pillar length and passivation layer thickness. In addition, we will analyze if conventional passivation techniques used on crystalline silicon are also sufficient for b-Si.

Introduction

Background
The fabrication of Black silicon (b-Si) is a valuable development in solar cell technology. Its structure dramatically reduces surface reflectance and thus increases the absorption of light, both attributes being beneficial for solar cell efficiency metrics. These characteristics are created by etching an array of nanostructures on the surface of silicon wafers. These fine geometries lend b-Si its black appearance, different from the silver color of conventional planar silicon wafers.

Many fabrication methods for b-Si have been developed to make the process cheaper and more easily reproduced. However, different fabrication methods result in different nano-structure geometry at the surface of the material. Direct Reactive Ion Etching (DRIE), a cyclic etching technique, can be used to make grass-like nano pillars on the surface of silicon [5]. These are particularly effective at capturing light, lending b-Si properties that are beneficial for metrics of solar cell efficiency.

DRIE alternates between two steps to build the nanostructures. First, a fluorocarbon, in this case, octafluorocyclobutane (C_4H_8), is deposited onto the silicon surface. Second, sulfur hexafluoride (SF_6) and fluorine radicals are deposited to etch the material. These two steps are repeated until the desired nanostructures are formed on the surface [5]. The etchant and deposition time are parameters that can be changed in order to alter the aspect ratio of the nanostructures.

Passivation
Given the presence of nano-structures and subsequently high surface area of b-Si, black silicon is particularly susceptible to high surface recombination rates. The dangling bonds and impurities at the material's surface leads to electron recombination within these traps. As such, effective passivation of black silicon is critical for ensuring reduced recombination and higher efficiency rates [8].

Al_2O_3 has been a common passivation material for semiconductor materials, including b-Si. Passivation using Al_2O_3 has both chemical and electrostatic benefits. The chemical benefits are a result of the material's ability to chemically plug dangling bonds at the surface of the material, thus decreasing the opportunity for electrons to recombine [4]. The electrostatic benefits are the result of an anneal performed after the deposition on alumina films. The anneal induces an electric field that repels charged carriers, further discouraging recombination at the surface.

Proposal Details
This proposal looks to determine if standard crystalline silicon (c-Si) passivation techniques apply to DRIE b-Si, or if new passivation techniques need to be developed. Additionally, we will investigate the optimal level of passivation layer thickness. Although passivation reduces recombination time, it can also reduce the absorption of the silicon surface [2]. Thus, these two properties, absorption and recombination, must be balanced to find the optimal conditions for DRIE b-Si.

Within the experiment, the pillar height of the b-Si as well as the thickness of the passivation layer will be varied by DRIE and passivation with atomic layer deposition (ALD) respectively. An increase in pillar height increases absorption but increases surface recombination rates. As well, an increase in thickness of the passivation layer decreases absorption but decreases recombination rates [2]. The combination of these values will determine the optimal b-Si efficiency conditions, and will be plotted in a table similar to the following.

Table 1: Mock efficiency results for proposed pillar height and passivation layer thickness combinations. Note: Each value other than (0.8 um / 90 nm) is an estimate.

	Passivation Thickness 10 nm	Passivation Thickness 30 nm	Passivation Thickness 50 nm	Passivation Thickness 70 nm	Passivation Thickness 90 nm
Pillar Height 1 0.4 um	18.2%	19.4%	20.8%	20.9%	21.2%
Pillar Height 2 0.8 um	19.1%	19.6%	20.9%	22.3%	22.1% [5]
Pillar Height 3 1.2 um	19.7%	21.1%	21.3%	22.9%	22.7%
Pillar Height 4 1.6 um	18.9%	20.3%	20.9%	22.4%	22.5%
Pillar Height 5 2.0 um	18.8%	19.4%	20.6%	22.3%	22.4%

Determining the proper passivation levels and methods for b-Si will allow for further research around b-Si utility in commercial products. Specifically, by maximizing the efficiency of b-Si, more applications may arise for the material – thus allowing for greater b-Si utilization.

Methods and Measurements

Manufacturing Methods
We propose to build interdigitated back-contact solar cells with varying b-Si nano-pillar heights and passivating thin film thicknesses. The b-Si manufacturing will employ Deep Reactive-Ion Etching (DRIE), and the passivating film will be Al_2O_3 deposited with atomic layer deposition (ALD). The following sections detail these processes.

Fabrication of B-Si
The process will start with (100) orientation, test grade 4-inch crystalline silicon wafers, supplied from University Wafers.

The wafers will be cleaned with 9:1 mixture of 98% sulfuric acid and 30% hydrogen peroxide for 30 minutes at 120 °C. Then, the silicon oxide layer will be removed with a 10:1 (by volume) 20%

hydrofluoric acid bath for 30 s. Finally, the wafers will be cleaned with deionized water (DI) and a N_2 gun.

Etch processes to produce b-Si will employ Deep Reactive-Ion Etching (DRIE) with the SPTS Rapier DRIE system located in the Harvard Center for Nanoscale Systems (CNS) [3] . DRIE is characterized by cycles of etching (with SF_6 plasma) and polymer deposition (with C_4F_8 plasma). It was demonstrated by Yusuf et. al, that polymer deposition time during the cycle changes the features that are formed by the DRIE process, with a specific time window creating b-Si characteristics (nano-pillar structure, long aspect ratio features, low reflectance) [4].

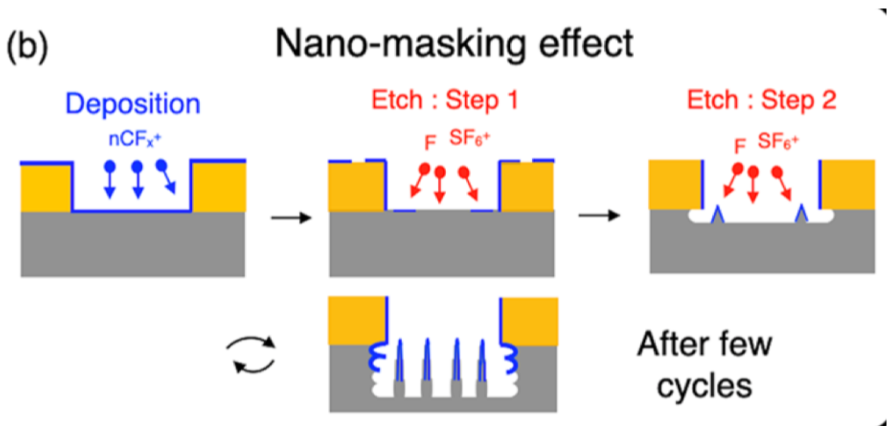

Figure 1: For the given etch process parameters, the etch process is strong enough to remove the deposited polymer at flat surfaces, but not at high aspect ratio structures. The result is a reproducible nano-pillar structure with increasing pillar height and approximately constant pillar thickness, formed without a lithography process. Figure adapted from [4].

Utilizing the documentation provided by Yusuf et al, the following protocol will be used for the etch process.

Table 2: Etch Protocol

Step	**Bias RF Voltage (V)**	**ICP RF Forward Power (W)**	**Ar(sccm)**	**C_4F_8(sccm)**	**SF_6(sccm)**	**Pressure (mTorr)**	**Duration**
Gas Stabilization	-	-	30	75	-	20	10
Plasma Strike	500	1500	30	75	-	20	5
Deposition	10	1500	30	150	-	30	1.9
Etch #1	250	1500	30	-	150	35	1.2
Etch #2	10	1300	30	-	50	25	1.2
Increase Pressure	-	-	-	-	-	100	5
Detach Pump	-	-	-	-	-	-	30

Before each etching process, the chamber will be prepared with a ‘seasoning protocol’ with the following parameters. In this process, a dummy Si wafer will be used.

Table 3: Preparation Protocol

Step	Bias RF Voltage (V)	ICP RF Forward Power (W)	Ar(sccm)	C_4F_8(sccm)	SF_6(sccm)	Pressure (mTorr)	Duration
Gas Stabilization	-	-	30	75	-	20	10
Plasma Strike	500	1500	30	75	-	20	5
Deposition	10	1500	30	150	-	30	1.0
Etch #1	250	1500	30	-	150	35	1.0
Etch #2	10	1300	30	-	50	25	1.0
Increase Pressure	-	-	-	-	-	100	5
Detach Pump	-	-	-	-	-	-	30

Additionally, each etching experiment will begin with a cleaning process to eliminate or minimize variations. In this process, a dummy Si wafer will be used. This process has the following parameters:

Table 4: Cleaning Protocol

Step	Bias RF Voltage (V)	ICP RF Forward Power (W)	O_2 (sccm)	Pressure (mTorr)	Duration
Gas Stabilization	-	-	45	30	10
Plasma Strike	500	1500	45	30	5
Clean	100	1500	45	30	3600
Increase Pressure	-	-	-	-	30
Detach Pump	-	-	-	-	30

With these process parameters, the number of cycles of the etch process will be varied to create nanopillars with increasing heights in the Si wafers. It was demonstrated that pillar thickness increases linearly with the number of etch cycles, and that pillar pitch was relatively constant, leading to linear increase in aspect ratio for nanopillars.

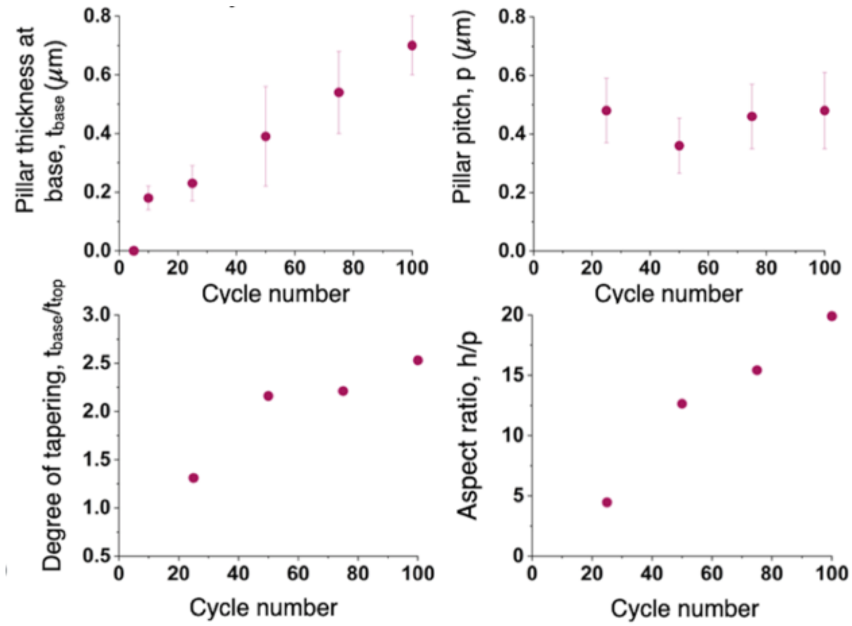

Figure 2: Demonstrates linear increase in aspect ratio and pillar thickness with number of etch cycles. [4]

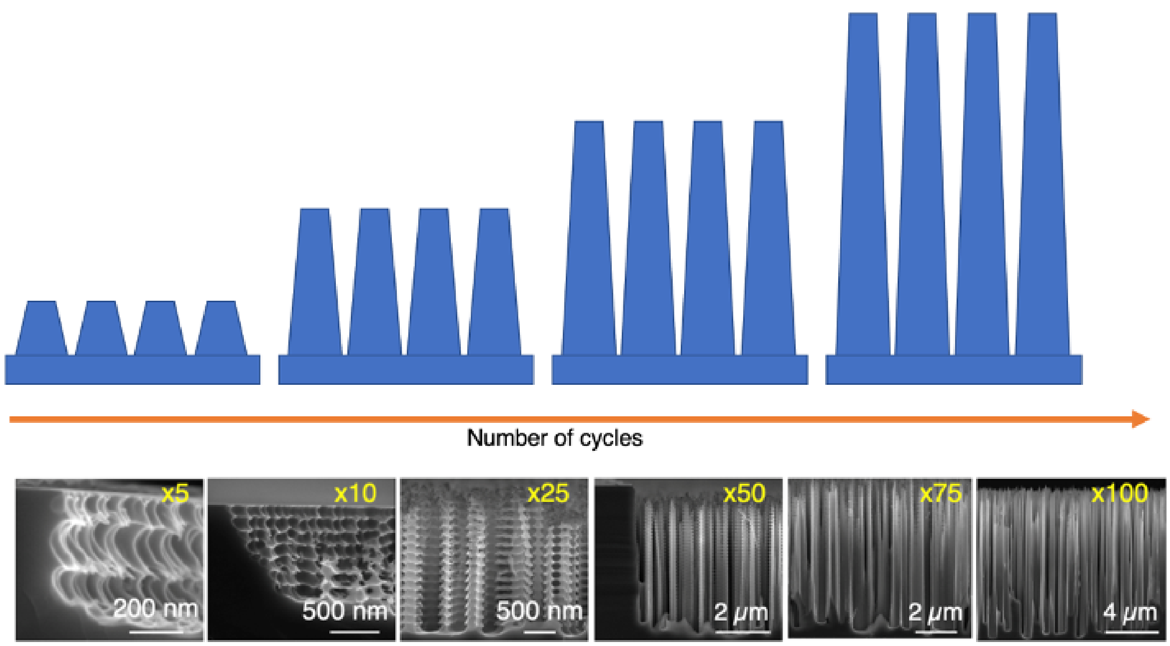

Figure 3: Expected nanopillar structures. SEM images are sourced from [4]. Note that meaningful nanostructures start emerging with >10 cycles.

After the b-Si etching process is complete, the wafers will be cleaned with isopropanol (IPA) and deionized water and dried with a N_2 gun.

Passivation Layer Deposition

In an attempt to combat the increased recombination that comes with the geometry of B-Si, we will passivate the surface with a thin film coating of Al_2O_3. The manufacturing method for the passivation coating of Al_2O_3 is atomic layer deposition (ALD). The process of ALD includes cycles of "half-reactions" and counter-reactant precursor pulses that are repeated until the preferred thickness is achieved. The half-reactions involve alternating pulses of gaseous precursors using TMA as the aluminium source and H_2O as the oxidant. These precursors react with the B-Si surface in a self-limiting process that results in a monolayer of the molecules at the substrates surface. The half-reaction is then followed by a counter-reactant precursor pulse and purge which builds up one layer of material. Once the desired thickness is achieved, the passivation film is activated by a 30-minute annealing process using N_2 at 400°C. This process will be repeated for 5 surfaces for each of the thicknesses outlined previously: 10 nm, 30 nm, 50 nm, 70 nm and 90 nm.

Solar Cell Fabrication

The geometry and manufacturing method of the solar cell can have large implications on its performance. We propose fabricating a thick IBC (interdigitated back contact) solar cell following the manufacturing method as outlined by Savin et. al, that has been shown to achieve 22.1% efficiency with B-Si [5]. In this geometry the junction and contacts are placed at the back of the cell to avoid recombination since most of the photogenerated charge carriers diffuse the distance from the front surface to the back side of the cell. The method of fabrication is as follows: the patterning of diffusions of dopants, deposition of passivation film and then the creation of a back reflector. Using 4-inch high quality p-type silicon (resistivity 2.4 +- 0.2 ohm cm and thickness 280 $\pm$ 20 um), solid dopant sources of boron and phosphorus are patterned on silicon using photolithography. As depicted in Figure 4, the p^+ regions are the base contacts, n^+ regions correspond to low doped emitters and n^{++} region corresponds to a high doped emitter. Following the silicon doping, the passivation deposition will occur, as is described in detail in the above section. Lastly, we will create a back reflector using a stack of thermal SiO_2 and Al. In this case the SiO_2 is 110 nm thick, and the Al is 3 µm. The 3x3 device area is defined by windows in an electron-beam evaporated aluminum metallization layer with thickness 0.4 µm.

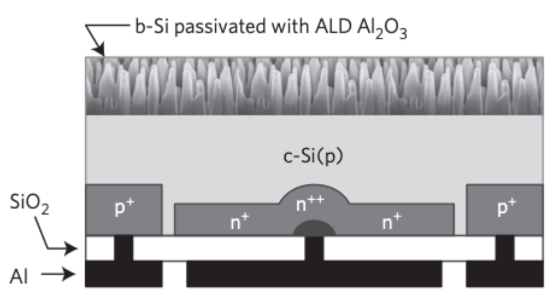

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Figure 4: Example b-Si solar cell

Characterization Methods

Absorption Characterization
In order to quantify the passivation levels effect on absorption of b-Si, the optical properties of b-Si will be measured both before and after passivation. Namely, the reflectance and transmittance of the b-Si can be found using a spectrophotometer (Flinn Scientific) with an integrating sphere. Integrating spheres allow for the measurement of solid surfaces with a UV-VIS spectrophotometer [6]. This allows for the determination of both the reflectance and transmittance of b-Si in the range of 200-1000nm [7].

Considering that all light hitting the surface must either be absorbed, reflected, or transmitted, the absorption can be found from the determined reflectance and transmittance values.

$$\text{Absorption} = 1 - \text{Transmittance} - \text{Reflectance}$$

This setup allows for an entire collection of light scattered by the surface, providing not only the absorption but the absorption fraction of the total light as well [8]. Once the optical properties of non-passivated b-Si are measured, the process will be repeated with the various passivated b-Si samples and the absorption fractions for the various samples will be plotted against each other for different incoming light wavelengths.

Efficiency Characterization
Following solar cell fabrication from each material, the efficiency of each cell will be measured. This efficiency will indicate the most promising materials for commercial production. Since the solar cells will be fabricated with interdigitated back contacts, their efficiency will be measured using the method of Savin et al. [5]. Efficiency will be calculated across the AM1.5G solar spectrum as defined by ASTM G-173-03 (1 kW m^{-2}). The IV curve will be measured using a 4-quadrant power amplifier and a calibration resistor. A SciSun-LP-300 solar simulator will be used to simulate the AM1.5G solar spectrum. The solar cell will be kept at a constant temperature of 25 ℃ throughout testing.

Budget and Budget Justification

We request a budget of $100,000 for the funding period of one academic year starting January 15, 2022 - January 15, 2022. The following table itemizes our expected spending.

Table 5: Proposed budget

Type	Item	Cost ($)	Explanation
Overhead	Undergraduate Student Assistant	35000	Estimated 500 hours of assistance from one or more undergraduate students in cleanroom and tool training, fabrication and characterization. Based on a rate of $25/hour (cost to employer) with 100% overallocation.
Materials and Equipment	Undergraduate Student Assistant	1000	Based on quotations from Harvard's supplier, University Wafers, with 100% over-allocation [9].
	Solar Simulator	9000	Estimated cost of SciSun-LP-300 Solar Simulator for solar cell efficiency evaluation [10].
	Clean room access	30000	The cleanroom at Harvard's Center for Nanoscale Systems will provide access to manufacturing processes such as e-beam lithography, e-beam evaporator, atomic layer deposition, reactive-ion etching, and to characterization tools such as spectrophotometers and ellipsometers. Estimate is based on specific tool usage, general cleanroom access, and training of student assistants. Includes 100% overallocation [11].
Other operating expenses	Publishing costs	10000	Cost of publishing two articles in ACS Applied Nano-materials Journal under the CC-BY license [12].
	Conference travel costs	15000	Based on expected travel costs incurred in attending 2-4 scientific conferences to present work-in-progress and potential manufacturer consultations to tune process parameters for b-Si generation.
Grand Total		$100,000	

Summary

Black silicon is a promising material for solar cells due to its high light absorption, but its high surface recombination time is currently an obstacle to development. Fabrication of b-Si with Direct Reactive Ion Etching creates pillar nanostructures; longer pillars increase light absorption but also increase recombination rates. To counter this, a passivation layer of Al_2O_3 can be applied via atomic layer deposition; a thicker passivation layer decreases recombination rates but can also decrease absorption. We propose to vary pillar length and passivation layer thickness of DRIE b-Si to investigate whether standard crystalline silicon passivation techniques adequately decrease surface recombination rates, and to determine the optimal conditions for fabrication of black silicon. Existing b-Si solar cells have already demonstrated high efficiency, and this research would indicate how nanostructure design and surface passivation could potentially increase commercial viability.

Citations

[1] N. Huang and M. L. Povinelli, "Design of Passivation Layers on Axial Junction GaAs Nanowire Solar Cells," *IEEE J. Photovolt.*, vol. 4, no. 6, pp. 1511–1517, Nov. 2014, doi: 10.1109/JPHOTOV.2014.2351624.

[2] S. Ma *et al.*, "A theoretical study on the optical properties of black silicon," *AIP Adv.*, vol. 8, no. 3, p. 035010, Mar. 2018, doi: 10.1063/1.5018642.

[3] Harvard Center for Nanoscale Systems, "CNS Tool List." 2021. [Online]. Available: https://cns1.rc.fas.harvard.edu/tool-search/

[4] M. Yusuf *et al.*, "Optimized Deep Reactive-Ion Etching of Nanostructured Black Silicon for High-Contrast Optical Alignment Marks," *ACS Appl. Nano Mater.*, vol. 4, no. 7, pp. 7047–7061, Jul. 2021, doi: 10.1021/acsanm.1c01070.

[5] H. Savin *et al.*, "Black silicon solar cells with interdigitated back-contacts achieve 22.1% efficiency," *Nat. Nanotechnol.*, vol. 10, no. 7, pp. 624–628, Jul. 2015, doi: 10.1038/nnano.2015.89.

[6] "Integrating Spheres-Shimadzu." Shimadzu. [Online]. Available: https://www.shimadzu.com/an/service-support/technical-support/analysis-basics/fundamentals-uv/integratingspheres.html#1

[7] "Flinn Scientific Spectrophotometer." Flinn Scientific Inc., 2021. [Online]. Available: https://www.flinnsci.com/uv-vis-spectrophotometer/

[8] Y. Su *et al.*, "Direct and stand-off fabrication of black silicon with enhanced absorbance in the short-wavelength infrared region using femtosecond laser filament," *Appl. Phys. B*, vol. 124, no. 11, p. 223, Nov. 2018, doi: 10.1007/s00340-018-7092-9.

[9] "University Wafers Product Catalogue." UniversityWafers.com, Dec. 2021. [Online]. Available: https://order.universitywafer.com/default.aspx?cat=Silicon

[10] "SciSun LP-300 Solar Simulator Product Page." Science Technology Inc., 2021. [Online]. Available: https://sciencetech-inc.com/shop/product/160-9104-scisun-lp-300-solar-simulator-class-aaa-300w-5050mm-2-suns-eps-power-supply-14468

[11] "CNS Consolidated Rate Data Sheet." Harvard University CNS, Oct. 01, 2021. [Online]. Available: https://cns1.rc.fas.harvard.edu/documents/2018/06/cns-consolidated-rate-sheet.pdf

[12] American Chemical Society, "ACS Open Access Pricing." ACS, 2021. [Online]. Available: https://acsopenscience.org/open-access/pricing/