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## LIFETIME OF NANO-STRUCTURED BLACK SILICON FOR PHOTOVOLTAIC APPLICATIONS

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**ABSTRACT:** In this work, we present recent results of lifetime optimization for nano-structured black silicon and its photovoltaic applications. Black silicon nano-structures provide significant reduction of silicon surface reflection due to highly corrugated nanostructures with excellent light trapping properties. We applied reactive ion etching technology at  $-20^{\circ}\text{C}$  to create nano-structures on silicon samples and obtained an average reflectance below 0.5%. For passivation purposes, we used 37 nm ALD  $\text{Al}_2\text{O}_3$  films. Lifetime measurements resulted in 1220  $\mu\text{s}$  and to 4170  $\mu\text{s}$  for p- and n-type CZ silicon wafers, respectively. This is promising for use of black silicon RIE nano-structuring in a solar cell process flow.

**Keywords:** c-Si, black silicon, ALD  $\text{Al}_2\text{O}_3$ , passivation, lifetime, light trapping, nano-structured silicon

## 1 INTRODUCTION

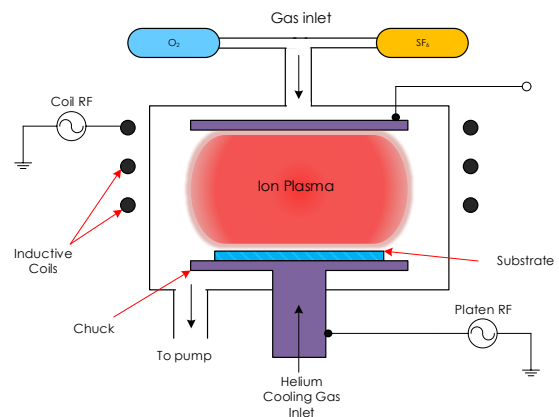
Nano-textured silicon, known as black silicon, is currently a subject of great interest in photovoltaics [1–4, 5]. It has extremely low surface reflectance, in some cases below 1%, in a broad range of wavelengths and incident angles even with a simple antireflective coating [6, 7]. Reactive plasma etching is a most promising alternative to any other silicon texturing method like wet etching [8–11], plasma immersion ion implantation etching, metal nanoparticles assisted etching and laser induced etching [12–15]. Key advantages of dry plasma silicon structuring are no usage of toxic chemicals, easy morphology control of structure size and shape, less silicon waste and mask-less processing. Solar cells with improved light trapping nano-structures show improved characteristics, such as high open circuit voltage and large short circuit current. However, surface-texturing methods like RIE also induce surface damage and potentially contamination, and therefore increased surface recombination velocity resulting in poor performance of nano-structured solar cells [3, 5, 16, 17]. Thus, effective surface passivation of nano-textured surfaces and optimization of the texturing process towards reduction of surface defect damage is required for further black silicon application in photovoltaics [18–22]. Atomic layer deposition (ALD) of  $\text{Al}_2\text{O}_3$  is one of the best methods for black silicon passivation, since it has conformal coverage of plane and corrugated surfaces. Thermal ALD of  $\text{Al}_2\text{O}_3$  leads to high chemical interface quality on crystalline silicon, low density of defect states, and the strongest known field effect due to fixed negative charges [18, 20, 21, 23–32].

## 2 EXPERIMENT

### 2.1 Sample Details and Black Silicon Etching

Black silicon nanostructuring was realized on Czochralski (CZ) mono-crystalline Si 4" (100) n- and p-type (1-20  $\Omega\text{cm}$ ) wafers with thickness 350  $\mu\text{m}$  by mask-less reactive ion etching (RIE) in  $\text{SF}_6$  and  $\text{O}_2$  inductively coupled plasma at  $-20^{\circ}\text{C}$  in DRIE SPTS Pegasus (Fig.1). Prior to final sample preparation, the RIE process was optimized: platen power was reduced from 50 to 10 W to reduce kinetic energy of ions, directed towards the substrate surface; coil power was increased from 2500 to

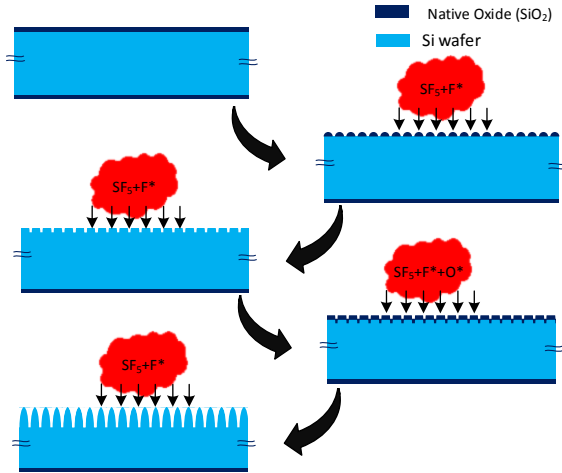
3000 W to increase homogenous ion plasma density and maintain a stable etch rate; aspect ratio of nanostructures was controlled via the low gas pressure (38 mTorr) which determined the directionality of the ions and the physical etching components by reducing the mean free path of the plasma species; average flow of  $\text{SF}_6$  gas (70 sccm) allowed to a stable Si etch rate and high  $\text{O}_2$  flow (100 sccm) allowed to passivate Si surface and reduce etch rate. The first samples had shown low lifetime after ALD  $\text{Al}_2\text{O}_3$  passivation and are not referred in this report. For conducting the experiment we used six silicon wafers of n- and p-type: two wafers had single side RIE processing for 16 min, another two wafers had double sided RIE processing for 16 min on each side and the last two wafers were kept as plain polished references.



**Figure 1:** Schematic of inductive coupled plasma system used for RIE

The black silicon nano-structuring process was conducted in the following order as shown on Fig. 2. A sample wafer was loaded in to the ICP RIE chamber and cooled to  $-20^{\circ}\text{C}$ .  $\text{SF}_6$  gas was supplied to the chamber and fluorine radicals rapidly attacked the silicon and destroyed native oxide on top of the wafer forming volatile  $\text{SiF}_4$ . In the next step, oxygen was supplied to the chamber. Oxygen radicals form silicon-oxyfluorine  $\text{SiF}_4 + \text{O}^* = \text{SiO}_x\text{F}_y$  at low temperature ( $-20^{\circ}\text{C}$ ).  $\text{SiO}_x\text{F}_y$  acts as an etch stop for  $\text{F}^*$  and passivated sample surface. Horizontal planes were more

intensively bombarded by ions from plasma while on the vertical sidewalls the ion bombardment was weaker due to directionality of the plasma ions and the sidewalls therefore remained protected from chemical etching by fluorine radical [1-2].



**Figure 2:** Schematic view of black silicon nanostructures formation

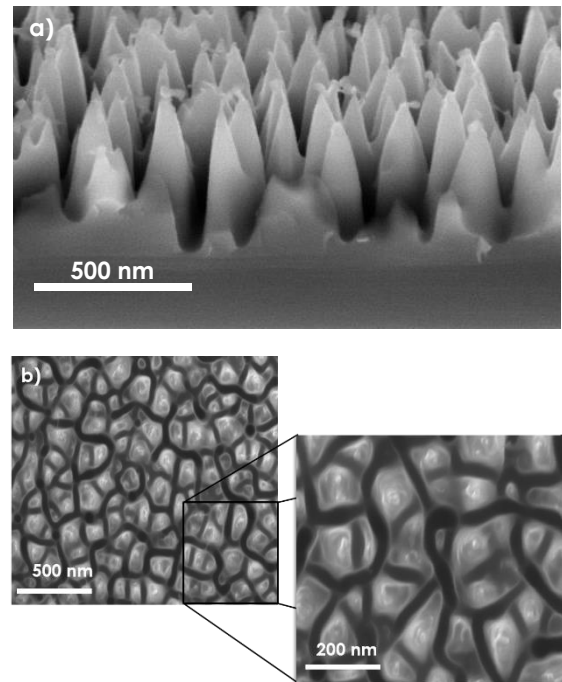
### 2.2 Surface cleaning and ALD Al<sub>2</sub>O<sub>3</sub> passivation

After RIE all samples were cleaned in standard RCA cleaning solutions, RCA1 and RCA2, each with a subsequent HF-dip, rinsed in deionized water and spin dried. Subsequently, wafers were coated with 380 cycles of ALD Al<sub>2</sub>O<sub>3</sub> synthesized from trimethylaluminium (TMA) and H<sub>2</sub>O. For reference purposes two polished wafers (p- and n-type) were also included in ALD Al<sub>2</sub>O<sub>3</sub> passivation procedure. The passivation layers were activated by post-deposition in-situ annealing in N<sub>2</sub> ambient at 375-390 °C for 30 min. The resulting Al<sub>2</sub>O<sub>3</sub> thickness of 37 nm was measured from polished reference samples using ellipsometry. Charge carrier lifetime was measured after annealing with the microwave detected photoconductivity (MDP) method in transient as well as in injection dependent single point modes, and lifetime mapping mode using a MDPmap setup from Freiburg Instruments.

## 3 RESULTS AND DISCUSSIONS

### 3.1 Black Silicon SEM Morphology Study

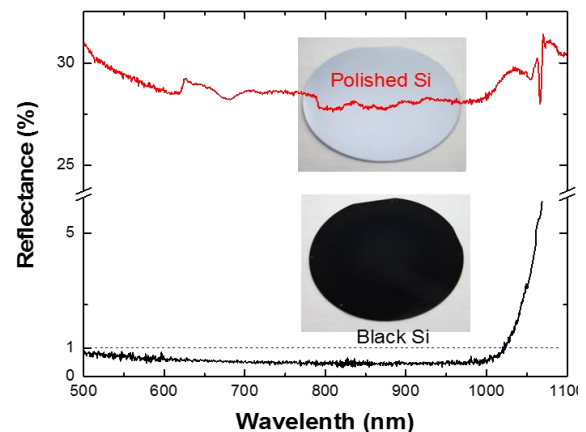
In Fig. 3 scanning electron microscope (SEM) images of the resulting black silicon nano-structures are shown without Al<sub>2</sub>O<sub>3</sub> coating. The nanostructure topology consists of slightly rounded conical-like hillocks with average height of 500 nm and average spacing of 250 nm. There is a slight variation in the dimensions of the surface structures. The height of the nanostructures was controlled by etching time with an average etch rate of 30 nm/min.



**Figure 3:** SEM image of the black silicon nano-structure topology processed with plasma assisted mask-less reactive ion etching: a) side view with scale 500 nm, b) top views with scale 500 nm and 200 nm

### 3.2 Reflectance

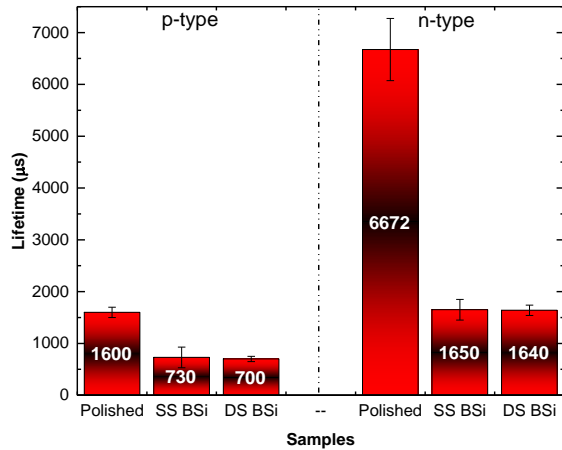
The main purpose of nanostructuring is to reduce reflectance and improve light trapping properties of the Si surface [3, 33]. The spectral reflectance of black silicon and polished samples were measured in the wavelength range from 500 to 1100 nm. Fig. 4 shows the reflectance of the samples as a function of wavelength. Photographic images are inserted in the reflectance figure to illustrate the difference between polished and nanostructured samples. It can be seen that polished silicon wafer in average has reflectance of 30%, while the black silicon sample has reflectance below 1% up to 1000 nm. Above 1000 nm the reflectance still remains low but shows a slight increase up to 5% which is still much lower than that of the polished wafer, and this long wavelength reflectance may partly be due to reflectance of the chuck below the silicon sample.



**Figure 4:** Experimental reflectance spectra of polished and black silicon without Al<sub>2</sub>O<sub>3</sub> coating

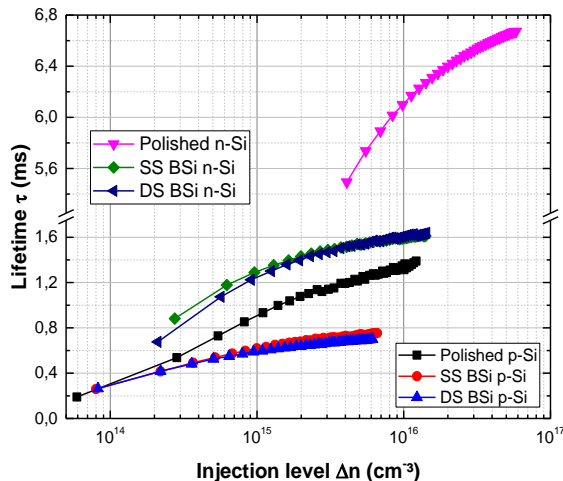
### 3.3 Minority Carrier Lifetime

Fig. 5 shows measured effective minority carrier lifetime for p- and n-type wafers for polished as well as for nano-textured samples. MDP measurements were conducted with a MDPmap setup from Freiberg Instruments to determine the effective carrier lifetimes as a function of injection level. The effective minority carrier lifetime is a figure of merit to estimate surface recombination and surface damage [18, 21, 25, 34, 35].



**Figure 5:** Comparative graph of average lifetime wafer mapping values with standard deviation for p- and n-type silicon samples with polished, single side nanostructured and double side nanostructured black silicon, passivated with ALD Al<sub>2</sub>O<sub>3</sub> 37 nm film. Legend: SS BSi - single side nanostructured black silicon, DS BSi - double side nanostructured black silicon

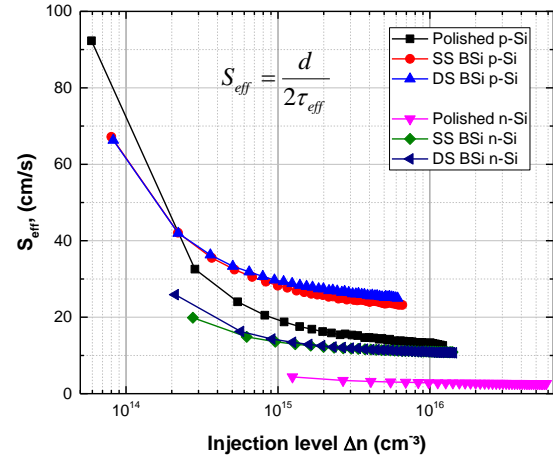
For p-type Si wafers, the lifetime difference between polished and textured samples is a factor of two. For some samples we have recorded a lifetime approaching 1 ms and higher, however to report these results additional testing is required. Injection dependent lifetime for p-type samples shown in Fig. 6 confirms stability of above results. A similar tendency is present for n-type samples, however lifetime difference between polished and nanostructured samples is in that case a factor of four.



**Figure 6:** Lifetime dependency on injection level

The surface recombination velocity was calculated from

effective minority carrier lifetime from the equation shown in Fig. 6 [25].



**Figure 7:** Surface recombination velocity dependencies on injection level

where  $d$  is the wafer thickness,  $\tau_{eff}$  is the measured effective lifetime. Fig. 7 shows the calculated surface recombination velocity as a function of injection level.

## 4 CONCLUSION

We have presented recent results of effect of reactive ion process optimization for improvement of minority carrier lifetime. The optimized RIE recipe with reduced ion damage of the surface allows us to achieve comparatively high effective lifetime for n- and p-type wafers and for single and double side nano-textured samples. For further investigation of electro-optical properties all samples were passivated with Al<sub>2</sub>O<sub>3</sub> and annealed at 375-390°C for 30 min. The surface morphology of textured samples was studied using SEM, and the optical reflectance was measured with an integrated sphere in the range of 500-1100 nm. Reflectance measurements allow us to evaluate the antireflective properties of nanostructures. With the plasma-assisted mask-less etching method we achieved broad spectral reflectance below 0.5%. Finally, the effective lifetime was measured on all textured and reference polished samples to evaluate the passivation effect and to estimate surface recombination velocity. Our overall results are promising for black silicon fabrication and lifetime improvement to facilitate incorporation in solar cell fabrication.

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