

# Comparison of different etching methods on the morphology and semiconductor characters of black silicon

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**Abstract.** Femtosecond laser etching, deep reactive ion etching and metal-catalyzed chemical etching are used to fabricate black silicon. It has been found that the light absorption is significantly enhanced in the wavelength of 400~2200nm, in which the absorption in near infrared band of black silicon etched by femtosecond laser with SF<sub>6</sub> has the highest value. It is observed that, however, the minority carrier lifetime of crystalline silicon is shortened to some extent, which can be adjusted and controlled effectively by depositing SiN<sub>x</sub> film to passivate the surface of black silicon. Finally, a PIN photodetector is manufactured based on black silicon and a higher responsibility of 0.57 A/W at 1060 nm is obtained compared to the PIN silicon photodetector without etching process.

## 1. Introduction

Silicon is the most commonly used semiconductor in microelectronics and optoelectronic devices, but the high reflectivity and low absorption of crystalline silicon (c-Si) restricts the sensitivity and efficiency of silicon-based devices. Moreover, the band gap of c-Si renders it transparent to wavelengths longer than 1100 nm, and makes it useless for near-infrared detecting. Any development that can reduce the reflection and enhance the absorption of silicon from ultraviolet to near-infrared wavelengths will assist in making silicon-based wideband detectors a reality [1-4]. Nano-structured and micro-structured c-Si (with cones, wires, or holes on the wafer surface) [5-8] have received steadily increasing interest as possible architectures for high efficiency and low cost material, because they exhibit very low reflection especially in the visible region. Many approaches such as femtosecond laser etching (FLE), deep reactive ion etching (DRIE) and metal-catalyzed chemical etching (MCE), have been developed to prepare these structures, by which one can increase the light absorption of c-Si effectively. The lifetime of minority carrier in c-Si, however, could be shortened due to the increased recombination loss and contact resistance arising from the nanostructures and micro-structures of black silicon (BS) [9]. Over the past decades, minority carrier lifetime in silicon-based materials have been intensely investigated because it significantly affects the optical and electrical properties of the materials. Wang [10] believes that the defects in the silicon nanowire are related to the dangling bonds of the amorphous silicon itself. Kajjam [11] shows that oxygen increases deep defect densities measured between 0.35 eV and 0.55 eV below the conduction band. It is found that oxygen-induced defects can be reduced and that lifetime can be increased both by compensating with boron. Therefore, how to increase light absorption and adjust minority carrier life are the main thoughts of our research proposal. A passivation layer and a subsequent annealing process should be considered as effective methods to control the minority carrier lifetime of BS.



In this paper, three methods named as FLE, DRIE and MCE to fabricate BS and several anti-reflection/light-trapping structures are simultaneously obtained directly on the c-Si substrates have been carried out. Meanwhile the comparison of morphology, light absorption, minority carrier lifetime with/without  $\text{SiN}_x$  passivation have been made among three different BS materials. And finally a PIN photodetector is manufactured based on BS and the responsibility is compared to the PIN silicon photodetector without etching process.

## 2. Experimental Details

N-type silicon wafers with a thickness of 500  $\mu\text{m}$  and a resistivity of 2500 to 3000  $\Omega\cdot\text{cm}$  were used. MCE was carried out silver-plated nanoparticles and catalytic corrosion on the silicon surface. During the silver-plated nanoparticles process, the cleaned wafers were placed in a mixture solution of  $\text{HF}:\text{AgNO}_3$  (0.009mol/ L) =1:4. Two groups were made for comparison by varying the silvering duration to be 30 s and 60 s. During catalytic corrosion process, silicon wafer coated with silver nanoparticles were placed into  $\text{HF}:\text{H}_2\text{O}_2=1:2$  for 10 min. When the etching processes were over, the silicon pieces were dipped into an aqueous solution of  $\text{HNO}_3$  and then rinsed with deionized water to remove any residual Ag.

The same N-type silicon substrates were irradiated by a regeneratively amplified Ti: sapphire femtosecond laser at 800 nm with a laser pulse width less than 100 fs, which was supplied by Spectra-Physics (Solstice). During scanning, the light power was set at 200 mW with 1000 Hz, the scanning speed was 1 mm/s and the scanning interval of each line was 0.1 mm. Three kinds of medium called  $\text{SF}_6$ ,  $\text{N}_2$  and air were chosen as the atmosphere during femtosecond laser irradiation.

In process of DRIE, photoresist was applied as the mask and the same N-type silicon substrates were etched by using  $\text{SF}_6$  and  $\text{C}_4\text{F}_8$ . During the process,  $\text{SF}_6$  was used as etching gas and  $\text{C}_4\text{F}_8$  as preventing gas, respectively, and the flow ratio of them was 4:3. The upper electrode power was set at 1000 W for  $\text{SF}_6$  etching or 1300 W for  $\text{C}_4\text{F}_8$  preventing, and the working time was 3 min for etching or 2 min for preventing, separately. When the processes were over, the silicon pieces were etched with  $\text{O}_2$  to remove any residual photoresist.

The morphologies of BS materials were characterized by a field emission scanning electron microscope (SEM, JSM-7500F). The light absorption was obtained at room temperature using a fiber optic spectrometer (NIR2500) equipped with an integrating sphere (Idea Optics, IS-20-5). The minority carrier lifetime of BS was measured by LT-100C. The responsivity of experimental PIN detector was calculated by using an optical power meter (OPHIR, Vega), an optical chopper (Scitec Instruments, Model-300CD) and a Keithley 2400 apparatus under dark room environment. In order to ensure the accuracy of the measurement, we carried out calibration before test and each of measurements was performed on a few samples (usually 4 to 6).

## 3. Results and Discussion

### 3.1. Morphologies of BS Materials

Figure 1 presents typical morphologies of BS etched by FLE in  $\text{SF}_6$  and air atmosphere. It can be seen from the figure that under the same laser parameters, the morphologies of BS etched in two kinds of atmosphere are different obviously. In figure 1(a), some cones are larger but the others are smaller, presenting flat blanket-like structure. In fact, the same morphologies can also be obtained when etched in  $\text{N}_2$  atmosphere. In figure 1 (b), the radius of each cone is about 40  $\mu\text{m}$ , the cross-sectional area of the substrate is about 60  $\mu\text{m}^2$  and the diameter of the tapered cone is close to 800 nm. It is observed that the BS prepared in  $\text{SF}_6$  have sharp pointed cones on the surface with nearly no difference between pointed cones, and the direction of the cones is consistent with the incident light. In addition, R. Younkin [12] explained that in the process of FLE, the halogen element and Si can produce volatile compounds, whereas air and  $\text{N}_2$  can't. Therefore, the spike surface of BS etched in  $\text{SF}_6$  are much sharper, while the surface etched in air are more blunt.

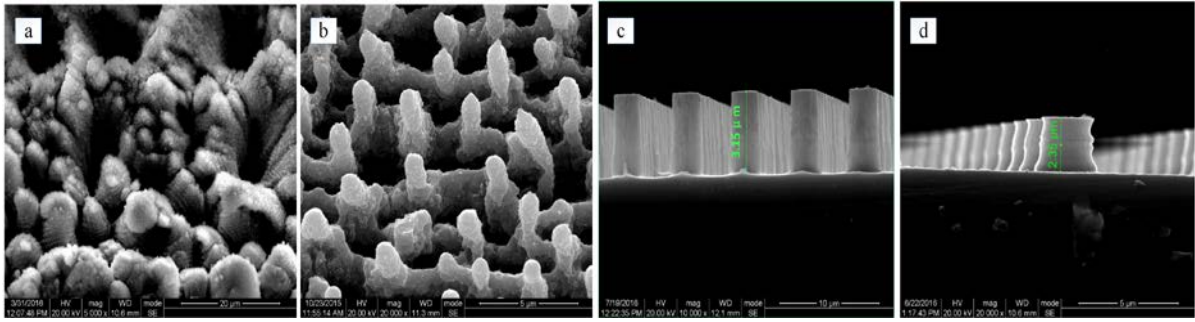


Figure 1. SEM images of BS produced by FLE in air (a), in SF<sub>6</sub> (b), and by DRIE (c, d).

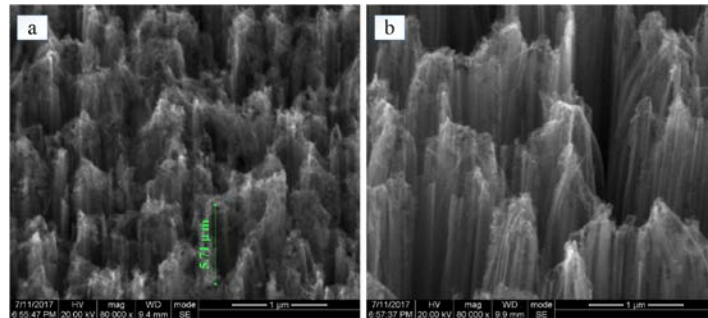


Figure 2. SEM images of BS produced by MCE with silver plated 30s (a) or 60s (b).

Figure 1(c,d) show the BS etched by DRIE. It can be seen from figure 1(c,d) that there are two kinds of cycle as 6 μm or 10 μm, but one same diameter as 4 μm. It can be understood that the BS etched by DRIE is of a cylinder or a round table shape, the diameter is related to the size of the mask plate in lithography step, while the height is depended on repeating times in etching process. The final height is about 3.15 μm after 100 times or 2.35 μm after 70 times.

Figure 2 are SEM graphs of BS etched by MCE, in which silver was plated with 30s(a) or 60s(b), respectively. The diameter of the hole in (a) is obviously larger than that of in (b). It is considered that in the prosesse of our MCE, with the increase of plating time, much more areas are attached on the silicon substrate with silver nanoparticles, resulting in bigger etched areas.

### 3.2. Absorption spectra and minority carrier lifetime of BS materials

Figure 3(a) is the absorption spectra of BS etched by FLE, DRIE and MCE, respectively. It can be seen that the absorption of BS prepared by FLE and MCE both are 70% in the near-infrared, while the absorption of BS could reach as high as 90% by FLE in the SF<sub>6</sub> atmosphere.

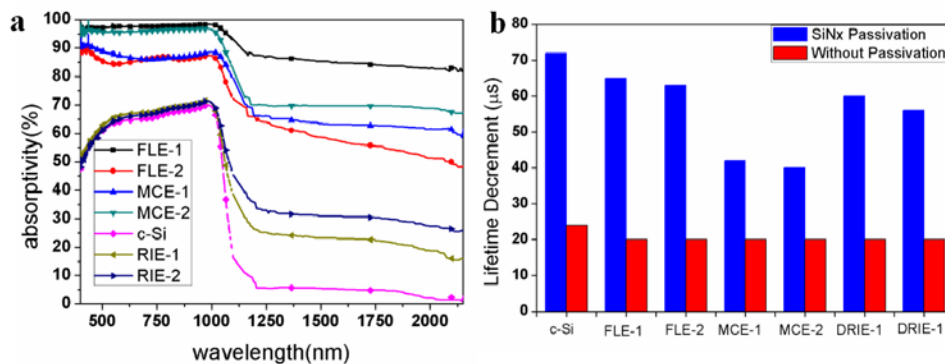


Figure 3. Absorption spectra of different BS (a) and minority carrier lifetime of BS with/without SiN<sub>x</sub> passivation (b).

It is well known that the c-Si has a lower light absorption in the wavelength of 190~1200nm. There are two reasons that can explain above phenomenon: one is that the c-Si surface has a high reflectivity of ultraviolet-infrared light (about 40%), and the other is that the band structure of c-Si limits the photon energy below its band width of the absorption in near infrared, and so it can only absorb incident light with the photon energy larger than the band gap width of 1.12eV. In this experiment, however, the BS materials have excellent optical properties with high spectral absorption, which can be attributed to the following factors. Firstly, the nano- and micro-structures produce multiple reflection to the surface incident light and form the trapping effectiveness. However, no matter what the structure of BS surface is, the absorption of BS in the near infrared is not obviously improved, such as black silicon prepared by DIRE showed in figure 4. It is observed that the BS etched by FLE in the  $\text{SF}_6$  atmosphere can still maintain a high absorption of more than 90% in the wavelengths greater than 1100 nm, which means that there need other explanations. Mazur and his co-workers [13] had used femtosecond laser to fabricate BS with  $\text{H}_2\text{S}$ ,  $\text{SF}_6$  and  $\text{Ar}+\text{SF}_6$ . The surface composition of the sample was analyzed by Rutherford Back Dispersion method, and it was found that BS contains more than 0.6% (atomic percent) of sulfur element. As early as in 1984, Janzen [14] et al. reported that eight kinds of dominate levels could be formed when doping sulfur in silicon. The sulfur element could be doped in two forms of 0.318eV and 0.614eV energy levels. Therefore, the doping of the sulfur group elements can change the silicon band structure, increasing the absorption of the infrared light. In our experiment, the energy of femtosecond laser could exceed the melting point of c-Si, and the decomposed sulfur elements from  $\text{SF}_6$  could be doped to the surface layer of the c-Si sample by means of liquid to solid transformation. Therefore, BS etched by FLE in  $\text{SF}_6$  could still maintain a higher light absorption more than 1100nm.

Figure 3(b) is the minority carrier lifetime of different BS with/without  $\text{SiN}_x$  passivation. As shown in the figure, the minority carrier lifetime of BS prepared by different methods has no obviously change without passivation. It is known that LT100-C is a device-scale instrument based on high frequency photoconductive decay, it is commonly used for testing bulk and stick silicon materials, so it can only give a relatively minority carrier lifetime, not the body lifetime of the carriers, though the surface recombination of carriers is far larger than that of bulk recombination without passivation. Nevertheless, the lifetime of BS can be adjusted by film passivation like  $\text{SiN}_x$ , which has been demonstrated early by Yamazaki et al [15]. Here, by comparing three different etching methods after the same  $\text{SiN}_x$  passivation, we found that the minority carrier lifetime of BS etched by FLE and DRIE are higher than that by MCE, resulting from the fact that the morphologies of BS prepared by FLE and DRIE are rougher than those by MCE. It is also found that passivation with special film like  $\text{SiN}_x$  could decrease the surface recombination and enlarge the difference of minority carriers lifetime among above mentioned three etching methods.

### 3.3. Device Application of Black Silicon

Figure 4 gives the skeleton of a PIN photodetector (a) and the responsibilities of two silicon photodetectors (b). For the photodetector that the surface is etched by FLE with  $\text{SF}_6$ , it can be found that the peak responsivity reaches at 1000nm, and the responsivity at 1060nm can maintain as high as 0.57A/W. For the photodetector that the surface is not etched anymore, however, the peak responsivity reaches at 950nm but the responsivity at 1060nm is only 0.26A/W. It can be concluded that the responsivity of Si-PIN photodetector with BS is higher than that of Si-PIN photodetector without BS in the near infrared band.

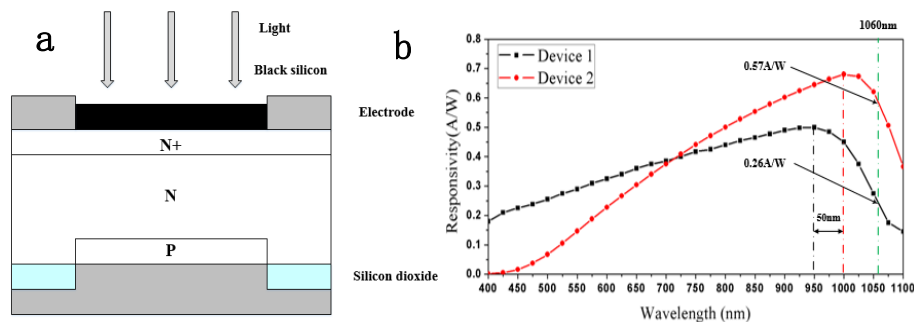


Figure 4. The skeleton of a PIN detector (a) and responsivities of two different devices (b).

#### 4. Conclusions

In summary, black silicon (BS) materials are fabricated by FLE, DIRE and MCE respectively, and the nanocone arrays or holes on the surface of silicon substrate have diameter and length of 100~400nm and 1.5~3 $\mu$ m, differently. Greatly enhanced light absorptance of black silicon has been observed in a wide wavelength range from 400 to 2200 nm, and the maximum absorptance reaches 90%. This enhancement is explained by reduced reflectance, light-trapping effect, and scattering effect caused by the specific nanostructures and/or microstructures on the surface of silicon substrate. However, the minority carrier lifetime of c-Si is shortened due to the increased recombination loss and contact resistance arising from above BS structures. Based on three different etching methods, we have found that the minority carrier lifetime can effectively be adjusted by SiN<sub>x</sub> passivation. A novel Si-PIN photodetector with BS formed on the front surface has been fabricated and the comparison of device responsivities has been made. It is found that the Si-PIN photodetector with BS formed on the front surface has an apparently increase in responsivity particularly in the near-infrared wavelengths.

#### 5. Acknowledgements

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