Black Silicon Layer Formation using Radio-Frequency Multi-Hollow Cathode Plasma System and Its Application in Solar Cell

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A low-cost, large area, random, maskless texturing scheme independent of crystal orientation is expected to have significant impact on terrestrial photovoltaic technology. We investigated silicon surface microstructures formed by reactive ion etching (R IE) in Multi-Hollow cathode system. Desirable texturing effect has been achieved when radio -frequency (rf) power of about 20 Watt per one hollow cathode glow is applied for our RF Multi -Hollow cathode system. The black silicon etched surface shows almost z ero reflectance in the visible region as well as in near IR region. The etched silicon surface is covered by columnar microstructures with diameters from 50 to 100 nm and depth of about 500 nm. We have successfully achieved 11.7 % efficiency of mono-crystalline silicon solar cell and 10.2 % for multi-crystalline silicon solar cell.

Keywords : Reactive ion Etching, Hollow cathode, Reflectance, Solar cell

1. INTRODUCTION

Surface texturization is usually promoted to enhance the light absorption in silicon solar cells[1]. Wet anisotropic chemical etching technique used to form random pyramidal structure on <100> silicon wafers usually is not effective in texturing of low-cost multi-crystalline silicon wafers because of random orientation nature. The quality of lower cost multi-crystalline silicon (mc-Si) solar cell performance is close to that of mono-crystalline (c-Si) solar cell, with the major difference resulting from the inability to texture mc-Si surface. Expensive anti-reflection layers like silicon nitride and magnesium fluoride have been applied to mc-Si solar cell's front surface to reduce light reflection. Recently, various forms of surface texturing approach have been applied to mc-Si surface including laser structuring[2], mechanical diamond saw cutting[3], porous-Si etching [4-7], photo-lithographically defined etching[8], and Reactive Ion Etching (RIE) method[9].

Historical review for RIE texturing of silicon can be found in Sandia report (S.H. Zaidi, SAND2000-0919, Sandia contract #BE-8229, April 2000). From the review, it is evident that different gas mixture can be used for fabrication of black silicon surfaces. Jansen et al.,[10] reported on a black silicon method in planar parallel plate (Plasmafab 340, Plasmatherm 500) and hexode (AME-8100) reactors for $SF_6/CHF_3/O_2$ plasma. Only SF_6/O_2 plasma chemistry was sufficient to have black silicon surfaces. In the SF_6/O_2 plasma, SF_6 is the source of active fluorine that etches silicon and O_2 supply oxygen radicals that passivate the surface of the etched silicon structures. The microstructures consist of a silicon body with a thin passivating silicon oxyfluoride skin. The origin of micro masks on the top of the etched silicon structures is caused by the silicon surface contaminations. An extensive study of SF_6/O_2 RIE in parallel plate reactors was done by Sandia group [11] for silicon solar cell application.

Different shapes of etched microstructures were observed. When a certain balance between the etching and the passivation was found, nearly vertical walls of the structures were obtained. Special technique received a patent support for sputtering metal contaminations on the surface so-called metal-catalyst approach[12]. Possibility of other types of reactors to produce the black silicon surfaces is very important. We are probably the first to report about the possibility to obtain black silicon surface in a RF multi-hollow cathode discharge. Due to the low-voltage operating characteristics, RIE in rf multi-hollow cathode system produce lower plasma induced damage to silicon than that of the conventional RF diode plasma systems. Multi-electrode embodiment makes our RF Multi-Hollow cathode system adapt to a high production environment.

In this paper, we have reported the formation of uniform black silicon surface on both c-Si and mc-Si wafer in RF Multi-Hollow cathode system. We have also reported the fabrication of black c-Si and mc-Si solar cells using conventional $POCl_3$ diffusion.

2. EXPERIMELTAL

2.1 RF Multi-Hollow cathode reactor

The RF Multi-Hollow cathode reactor proposed in our experiment for black silicon etching of both c-Si and mc-Si are shown in the Fig. 1. Our proposed hollow cathode reactor consists of a Pyrex tube defining the vacuum chamber, with a grounded metal cylindrical electrode, outside acting as a counter electrode for powered aluminum electrodes assembly which are in electrical contact with silicon wafers. The last plate electrodes have diameter of 150 mm. The electrodes are electrically and structurally connected by metal supports close to their outer rim to have separation of the electrodes which equals to 25 mm. The Pyrex tube has inside diameter of 190 mm. Applied RF power create electrical field at each powered electrode surface causing excitation of reactive gases in spaces preferably between the silicon wafers to produce a high level of ionization of the gas and dense plasma therein. These dense plasma regions are obtained by the means of repelling movement of entrapped electrons between powered electrodes, so called hollow cathode effect. Uniform micro-masks disposition on the silicon surface is a necessary condition for uniform texturing. The origin of micro-masks in our case may be the result of re-sputtering of both the aluminum electrodes and the Pyrex tube.

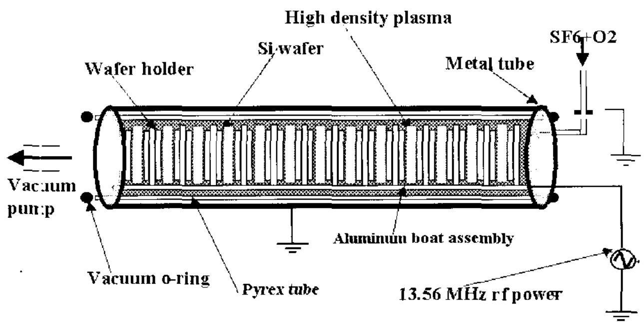


Fig. 1. Schematic diagram of proposed Radio Frequency Multi-Hollow Cathode system.

2.2 Black silicon etching

Initially, we took 1-5 Ωcm, <100>, p-type 350 μm thick as-cut c-Si wafers and 1-5 Ωcm, p–type, 275 μm as-cut mc-Si wafers respectively. Before black silicon surface etching, we textured c-Si wafer by conventional wet texturing technique and chemically polished mc-Si wafer by 21HNO_3 : 7HF : 16CH_3COOH mixture respectively.

In our black silicon etching experiment, 103mm ×103mm textured c-Si and 100mm×100mm polished mc-Si samples were mounted on aluminum electrodes inside the Multi-Hollow cathode plasma reactor. The plasma etching process was developed which uses SF_6/O_2 mixtures to produce a randomly textured silicon surface that looks black because of near zero surface reflection. The silicon surface is covered by a lot of columnar micro-structures to have this property. Desirable texturing result was achieved when RF power of about 20 Watt per one hollow cathode glow is applied for our Multi-Hollow cathode reactor. RF power frequency was 13.56 MHz. The SF_6/O_2 partial pressure ratio was 2.5 and the etching pressure was 50 mTorr for plasma glowing conditions. The texturing time was 20 min. We investigated a new method of mc-Si texturing. Black silicon surface reflection was characterized from visible to IR spectral regions by UV-VIS Spectrophotometer (model no. SCINCO S-2100).

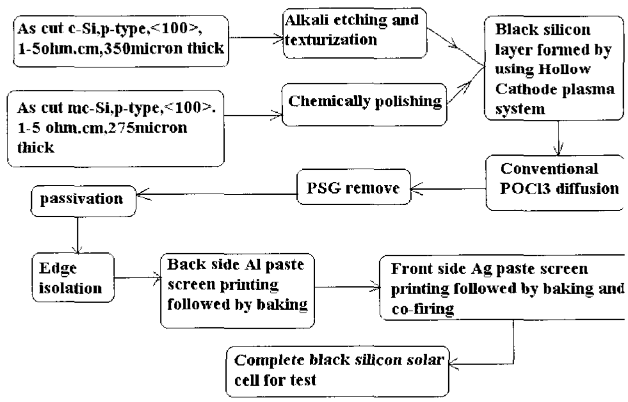


Fig. 2. Block diagram of detail of the procedure of fabrication of black c-Si and mc-Si solar cells.

2.3 Black silicon solar cell fabrication

In this experiment, we have used conventional $POCl_3$ diffusion and screen printed metallization for black silicon solar cell fabrication. The block diagram for fabrication of black silicon solar cells is shown in Fig. 2. Black silicon wafers were diffused by n-type impurity in open-tube furnace using conventional $POCl_3$ diffusion source at 860 °C, 20 min pre-deposition followed by 40 min drive-in. Phosphosilicate Glass (PSG) removed $POCl_3$ diffused silicon wafers were thin oxide passivated (≤10nm) at temperature 750 °C.

After edge isolation, the front and back metallization of the diffused black silicon wafers were carried out using standard Al-paste (product no. FX 53-038, Ferro Electronic Materials) and Ag-paste (product no. 3349, Ferro Electronic Materials) screen printed metallization technique followed by baking and co-firing at the temperature of 740 ^{o}C in a conveyer belt furnace.

3. RESULTS AND DISCUSSION

Figure 3 shows a typical normal incidence spectral reflectance of black mc-Si surface. The reflectance of polished silicon is also plotted for comparison. The black silicon etched surface shows almost zero reflection in the visible region as well as in the near-IR region. We have carried out scanning electron microscope (SEM) investigation of these randomly black silicon etched surfaces. The SEM photographs of black silicon surface on c-Si and mc-Si substrates are shown in Fig. 4 (a) and (b) respectively. From these photographs, we have found that the black silicon surface is a silicon surface covered by a lot of columnar microstructures. The columnar microstructures have diameters ranging from 50 to 100 nm and depth of about 500 nm. The region of technological conditions was very narrow to have good uniformity for large area black silicon surface. The sidewall passivation of etched columns with silicon oxyfluoride film is very sensitive to oxygen content at the silicon surface. Any deficiency of oxygen was the main cause of changing from black surface to polished one.

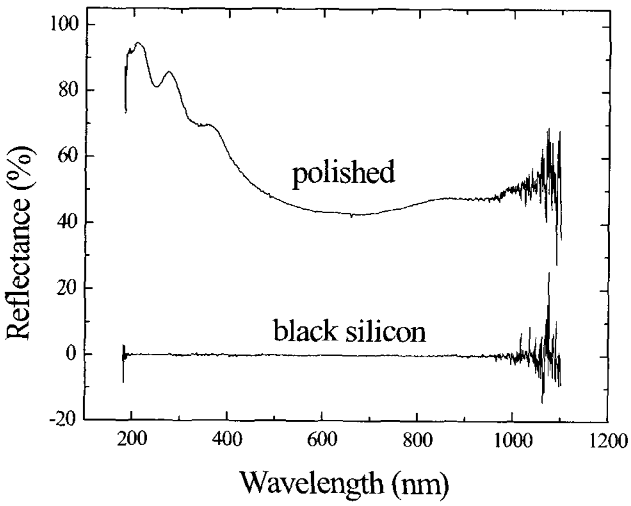
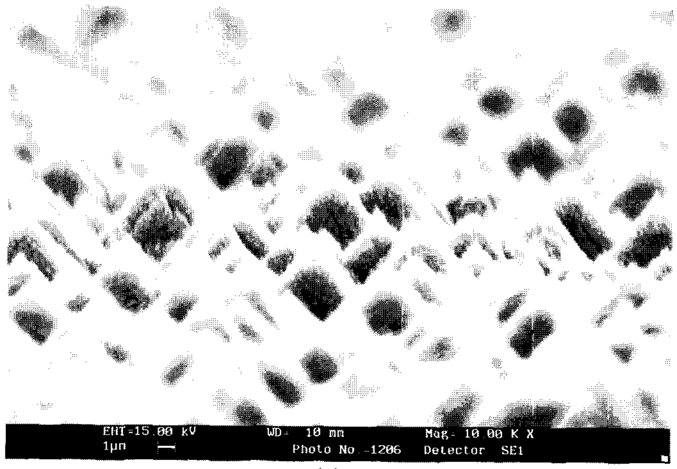
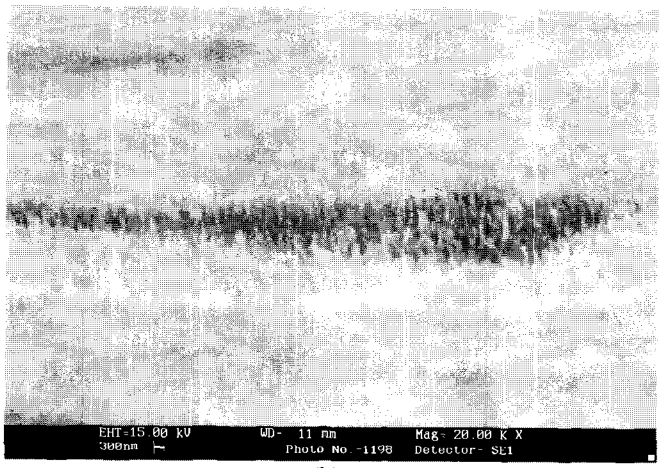


Fig. 3. Normal incidence spectral reflectance from multi-crystalline black silicon surface and polished silicon surface.

Moreover in our proposed hollow cathode system, RF hollow cathode discharge allows an improvement of plasma density by an order of magnitude in comparison to a standard r.f. parallel plate discharge. The increase in



(a)



(b)

Fig. 4. SEM photographs of top view of (a) black c-Si and (b) black mc-Si surfaces. Hollow cathode RIE parameters: SF_6/O_2 partial pressure ratio 2.5; texturing time 20 min; pressure 50 mTorr for plasma glowing condition; RF power 20 Watt per one Hollow cathode glow.

the plasma density has been achieved with the hollow cathode configuration, and it is attributed to the so called "electron mirror" effect in which a negative self-developed bias voltage on the two opposing RF powered electrodes both help to increase the density of the high energy electrons (responsible for ionization) and to reduce their recombination rate. Moreover, the hollow cathode effect can be enhanced by an appropriate discharge confinement that results in raising plasma density, an increase in the ion flow to the electrodes (substrates), and a decrease in the average ion energy. The electrons have much higher mobility than the ions, and they are very easily collected on an electrode whenever it becomes positive with respect to the glow space. This fact in turn, causes depletion of electrons

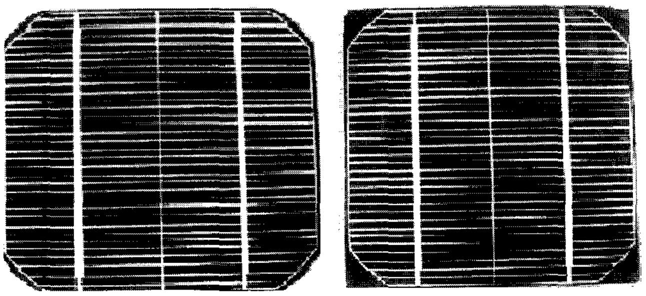


Fig. 5. Photographs of (a) 103mm×103mm black c-Si solar cell and (b) 100mm×100mm Black mc-Si solar cell.

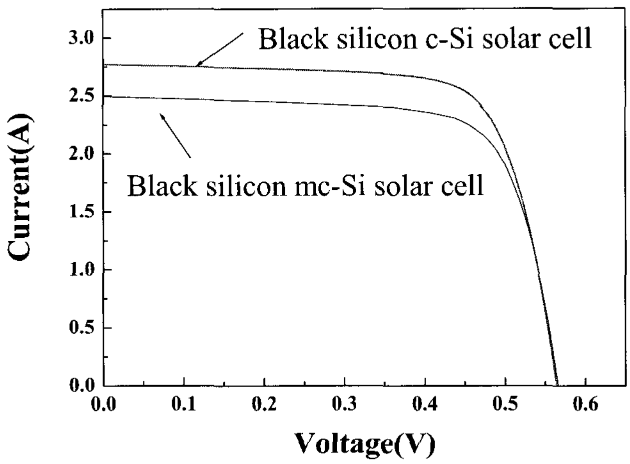


Fig. 6. Illuminated I-V characteristics of black silicon solar cells.

from the dark space with consequent rise in potential of the glow space with respect to the electrodes.

The surface of the r.f. powered hollow cathode electrode has acquired a self-bias which will have a value equal to nearly half of the applied RF peak to peak voltage. The r.f. electrode surface voltage is positive for a very short fraction of each cycle, so ion bombardment is almost continuous. The energy of the majority of the ions centers about the bias voltage across the dark space at the substrate because the ions will undergo several oscillations on its way across the sheath at high frequency (>4MHz). The electrons originated at the hollow cathode surface traverse the inter-electrode space to the opposite surface of the hollow cathode. The surface electrical field serves as a mirror for electrons so that the electrons are forced to move towards the glow space plasma region from both sides. This electrode configuration leads to the oscillation of electrons; it also leads to an increase in the number of ionization events per electron when compared with a conventional parallel plate r.f. plasma discharge. For rf hollow cathode discharge characterized by the low voltage, high current density regimes. The lower voltage means more ion flux

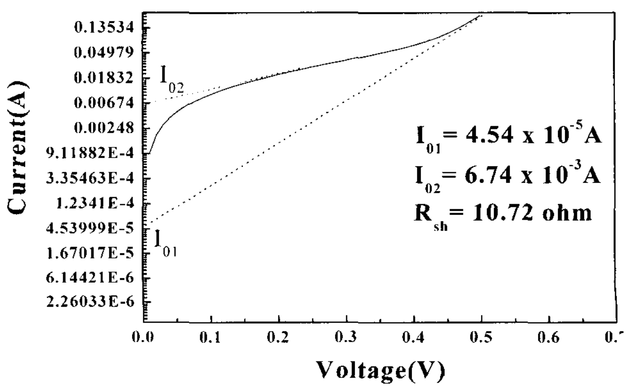
Table 1. The performance of different black silicon solar cells fabricated in our laboratory.

Type of solar cell	c-Si	mc-Si
Area of solar cell (cm^2)	98	100
Method of doping	$POCl^3$	$POCl_3$
V_{OC} (V)	0.564	0.566
I_{SC} (A)	2.80	2.50
F.F.	0.73	0.72
Eff. (%)	11.7	10.2

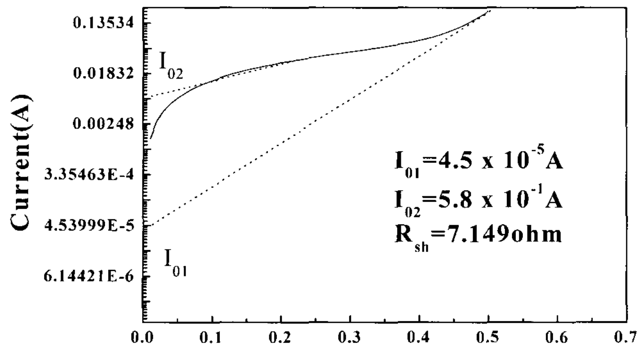
(current) leading to higher etch rate in comparison to the conventional RF discharge at the same power.

Figure 5 demonstrates the photographs of large area black c-Si and mc-Si solar cells fabricated in our laboratory. The dimensions of c-Si and mc-Si are 103 × 103 mm and 100×100 mm respectively. The performances of the black silicon solar cells were measured under the standard 100 mW/cm^2 AM1.5 (air mass) global spectrum at 25 °C. Table 1 lists the performance of the black silicon solar cells fabricated in our laboratory.

The Light illuminated current-voltage (LIV) characteristics of black silicon solar cells are shown in Fig. 6. From the performance of the black silicon solar cells fabricated in our laboratory as shown in Fig. 6 and table-1, we have observed the low open circuit voltage of both black c-Si as well as mc-Si solar cells. Moreover, from dark current-voltage characteristics as shown in Fig. 7(a) and Fig. 7(b), we have observed that the recombination current components (I_{02}) of dark current (consist of injection current components I_{01} and recombination current component I_{02}) for both c-Si and mc-Si solar cells are very small indicating the shunt path across the junction of fabricated solar cells. The low values of shunt resistance as shown in Fig. 7(a) & (b) have also proven the information of leakage across the junction which leads to the low values of open circuit voltages of the fabricated black silicon solar cells. So our novel RF Multi-Hollow cathode plasma system has capability to produce uniform black silicon etched surface which has the compatibility with the rest of the solar cell fabrication process.



(a)



(b)

Fig. 7. Dark I-V characteristic of (a) $98cm^2$ pseudo square black mono-crystalline silicon solar cell,(b) $100cm^2$ black multi-crystalline silicon solar cell.

4. CONCLUSION

We probably are the first in reporting the success of black silicon RIE of both c-Si and mc-Si samples using RF Multi-Hollow cathode plasma system. Plasma texturing has been shown to produce almost zero reflectance of black silicon etched surfaces. The silicon surface was covered by the columnar microstructures with the diameters of 50 to 100 nm and the depth of about 500 nm. We have also shown that our novel RF Multi-Hollow cathode plasma system has capability to produce uniform black silicon etched surface which has the compatibility with the rest of the solar cell fabrication process. We have successfully achieved 11.7% efficiency of black c-Si solar cell and 10.2% of black mc-Si solar cell by using the industrial mass production line system. Further improvement in black silicon solar cell performance can be expected using proper optimization of solar cell fabrication process parameters.

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