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Black silicon formation using cryogenic etching and photoresist layer

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Abstract. A series of experiments were conducted to develop the plasma etching of black silicon through a layer of polydimethylglutarimide (PMGI) photoresist. The silicon wafers were previously subjected to wet-chemical treatment. A ~25 nm thick photoresist layer facilitates the process of creating regular black silicon structures on substrates with a diameter of 100 mm. The etching process was varied in terms of the sulfur hexafluoride (SF_6) and oxygen (O_2) gas mixture ratio, RF power applied to the substrate holder (bias power), inductively coupled plasma (ICP) power and chamber pressure. Increasing the bias power from 10 to 30 W under otherwise constant conditions enhances the etching rate. Reducing the pressure in the reactor from 10 to 5 mTorr at a constant gas flow rate leading to a higher etching rate. Increasing the proportion of oxygen in the SF_6/O_2 gas mixture (2:1) enhances passivation, reducing the black silicon structures size.

Keywords: black silicon, PMGI photoresist, cryogenic etching, solar cell

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Формирование черного кремния с использованием криогенного травления и слоя фоторезиста

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Аннотация. Была проведена серия экспериментов по разработке технологии плазменного травления черного кремния через слой фоторезиста полидиметилглутаримида (PMGI). Кремниевые пластины предварительно подвергались жидкой химической обработке. Слой фоторезиста толщиной ~25 нм способствует процессу создания регулярных структур черного кремния на подложках диаметром 100 мм.

Процесс травления проведен с вариаций соотношения газовой смеси гексафторида серы (SF_6) и кислорода (O_2), мощности радиочастотного излучения, подаваемого на держатель подложки (мощность смещения), мощности индуктивно-связанной плазмы (ИСП) и давления в камере. Увеличение мощности смещения с 10 до 30 Вт при прочих равных условиях увеличивает скорость травления. Снижение давления в реакторе с 10 до 5 мТорр при постоянном расходе газа приводит к увеличению скорости травления. Увеличение доли кислорода в газовой смеси SF_6/O_2 (2:1) усиливает пассивацию, уменьшая размер структур черного кремния.

Ключевые слова: черный кремний, резист PMGI, криогенное травление, солнечный элемент

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Introduction

Solar photovoltaic power is among the most dynamically advancing fields in renewable energy. Around 95% of the global photovoltaic market consists of silicon solar cells [1]. Nanostructured black silicon (*b*-Si) is a promising solution for reducing optical reflectance in solar cells. This material exhibits excellent optical characteristics across a wide wavelengths range and angles of light incidence [2].

Black silicon can be obtained by various methods, including metal assistant chemical etching (MACE) [3], laser texturing [4] and plasma etching [5]. MACE and laser texturing methods are inferior to plasma etching in terms of precision, structure control, safety and scalability. Thus, plasma etching demonstrates the best balance between structural quality and process flexibility. The cryogenic etching [6] makes it possible to create highly aspect structures on a silicon substrate using plasma etching techniques.

During cryogenic etching of substrates that had wet-chemical treatment, we encountered an issue with the non-uniform formation of areas with *b*-Si structures. Therefore, a series of experiments were conducted to develop and optimize the etching process for nanostructured silicon using a photoresist layer. The influence of key parameters such as bias power, ICP power, gas composition and pressure on the morphology and optical properties of black silicon is investigated.

Experimental section

The etching was carried out using *c*-Si (100) wafers (*n*-type doped, $2–3 \cdot 10^{15}$ cm^{-3}) through a PMGI photoresist layer. The substrates were previously subjected to wet-chemical treatment. It were boiled in carbon tetrachloride and then in isopropyl alcohol for 5 minutes. Then the substrates were dipped in a hydrofluoric acid solution for 1 minute to remove the natural oxide. The substrates were washed with deionized water after each stage.

To obtain a thin and uniform coating, PMGI was diluted with the solvent T-Thinner (by Micro Chem). Before applying PMGI, it was heated to room temperature to ensure optimal adhesion of the photoresist to the substrate surface and to reproduce the layer thickness. The PMGI photoresist was applied via spin coating at 4000 rpm for 4 minutes across the entire surface of silicon substrate with a diameter of 100 mm. Followed by baking on a hotplate of 5 minutes at 180 °C. A thin (~25 nm) photoresist layer acts as the organic layer that initiates the formation of ordered black silicon structures.

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Then we used cryogenic etching (–150 °C) in an SF_6/O_2 gas mixture to obtain *b*-Si structures. The etching process time was 10 min. A series of experiments was conducted with variations in SF_6/O_2 process gas flow ratio, RF power, ICP power and pressure. The different technological parameters of cryogenic etching summarized in Table.

Table

Investigation of different cryogenic etching parameters

<table>
<tr><th>№</th><th>RF power, W</th><th>SF_6/O_2</th><th>Pressure, mTorr</th><th>ICP power, W</th><th>h, µm</th></tr>
<tr><td>1.1</td><td>10</td><td rowspan="4">3/1</td><td rowspan="6">5</td><td rowspan="8">1000</td><td>~4.1</td></tr>
<tr><td>1.2</td><td>20</td><td>~6.3</td></tr>
<tr><td>1.3</td><td>30</td><td>–</td></tr>
<tr><td>1.4</td><td>5</td><td>~1.1</td></tr>
<tr><td>2.2</td><td rowspan="6">10</td><td>2/1</td><td>~1.4</td></tr>
<tr><td>2.3</td><td>5/1</td><td>–</td></tr>
<tr><td>3.2</td><td rowspan="4">3/1</td><td>7</td><td>~2.8</td></tr>
<tr><td>3.3</td><td>10</td><td>–</td></tr>
<tr><td>4.2</td><td rowspan="2">5</td><td>1200</td><td>~6.3</td></tr>
<tr><td>4.3</td><td>700</td><td>–</td></tr>
</table>

The *b*-Si morphology was examined by SEM (Carl Zeiss Supra 25). The total reflectance spectra were measured using an integrating sphere and an AvaSpec SensLine spectrometer.

Results and Discussion

The key challenge is to optimize the nanostructure geometry (height, shape, and periodicity) to achieve low reflectivity through surface texturing while maintaining effective passivation properties for recombination suppression.

The etched silicon wafers consist of high density of *b*-Si structures. Figure 1 shows a SEM images of nanostructures at different bias power (*a*–*c*), pressure (*d*) and ICP power (*e*).

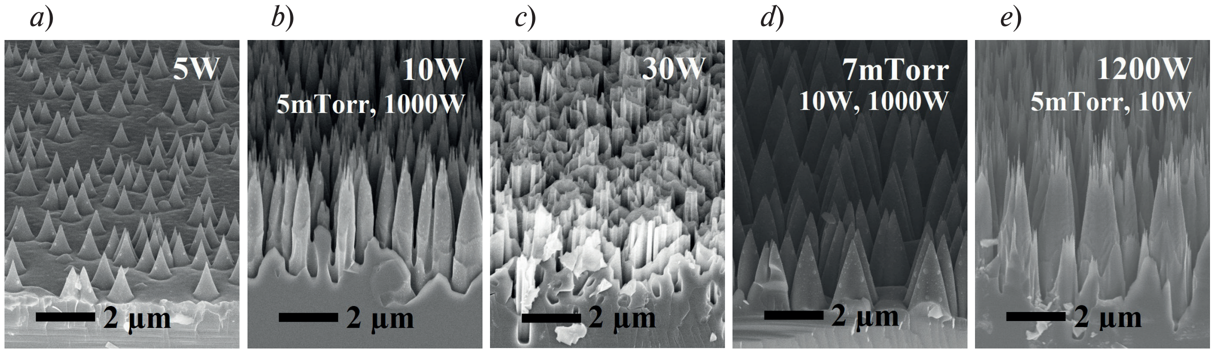

Fig. 1. A SEM image of the *b*-Si at different RF power (*a*–*c*), pressure (*d*) and ICP power (*e*)

Increasing the RF power from 10 to 30 W under otherwise constant conditions (SF_6/O_2 of 3/1, pressure of 5 mTorr, ICP power of 1000 W) enhances the etching rate due to the growing contribution of the ion-induced (physical) component of the etching process. However, at 30 W, the process becomes destructive to the *b*-Si structure formation.

To investigate the effect of the oxygen ratio in the SF_6/O_2 gas mixture, the gas proportion was varied while keeping the other parameters constant (RF power of 10 W, pressure of 5 mTorr, ICP power of 1000 W). Increasing the proportion of oxygen in the SF_6/O_2 gas mixture (2:1) enhances passivation, reducing the structures size. With an SF_6/O_2 ratio of 5:1, the oxygen proportion may be too low for passivation, and black silicon structures do not form.

Reducing the pressure in the reactor from 10 to 5 mTorr at a constant gas flow rate increases the mean free path and energy of ions, leading to a higher etching rate.

Raising the ICP power to 1200 W causes excessive etching of the nanostructures tips, making subsequent surface passivation more challenging. Constant process parameters include RF power of 10 W, SF_6/O_2 of 3/1, pressure of 5 mTorr.

Figure 2 compares the total reflectance spectra of the non-cryogenically etching *c*-Si wafer and substrates with black silicon structures.

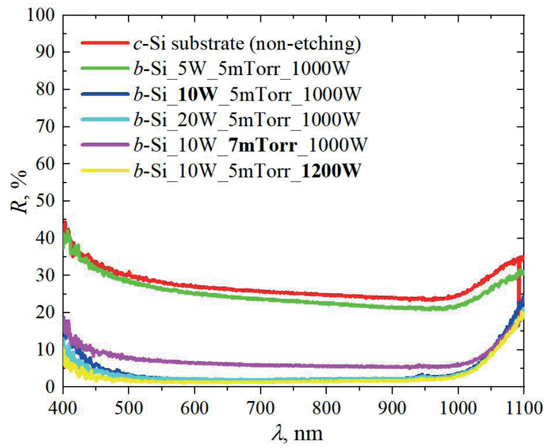

Fig. 2. Total reflectance spectrum of *b*-Si structures fabricated under different etching parameters

The Si substrate exhibits the total reflectance of more than 24% from 400 to 1000 nm. The nanostructure obtained at a RF power of 5 W consists of sparse cone-shaped formations approximately 1.1 µm in height. Its reflectance is similar to that of an non-etched substrate.

The *b*-Si structures obtained at a pressure of 7 mTorr exhibit a conical shape with a height of ~2.8 µm. It demonstrate a total reflectance below 10% across a broad spectral range and are likely to achieve even lower reflectivity after the emitter layer deposition.

Conclusion

The technology for plasma etching of black silicon on substrates subjected to wet-chemical treatment has been developed. A ~25 nm thick PMGI resist layer, formed via spin-coating, facilitates the process of creating black silicon structures on substrate with diameter of 100 mm. The etching process was carried out by varying parameters such as the SF_6/O_2 gas mixture ratio, bias power, ICP power and chamber pressure.

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