Enhanced Efficiency of Graphene-Silicon Schottky Junction Solar Cell through Pyramid Arrays Texturation

Cheng Li1 · Yichen Ma2 · Xiyao Zhang1 · Xiuhua Chen2 · Fengshuo Xi1 · Shaoyuan Li1,3 · Wenhui Ma1 · Yuanchih Chang3

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Abstract
Graphene/silicon (Gr/Si) Schottky junction solar cells have attracted extensive research interest due to their simple structure and potential low-cost. Surface texturing is an important part of high-efficiency solar cells. In this paper, the effects of TMAH concentration, IPA concentration and etching time on the structure and anti-reflection ability of silicon pyramid array (SiPa) were systematically studied to obtain uniform and reliable pyramid array. Under the optimized conditions, a large scale SiPa with uniform size distribution was obtained and applied to Gr/Si solar cells. The results show that the TMAH etched SiPa has a better Schottky junction contact between graphene and the SiPa surface, and the SiPa can further improves the ability of collecting photogenerated carriers. Compared with Gr/Si solar cells, the power conversion efficiency (PCE) of Gr/SiPa device is 1.66 times higher than that of Gr/Si solar cells. Finally, Gr/SiPa devices with PCE of 5.67% is successfully obtained by HNO3 doping. This work proposes a new strategy for TMAH etching SiPa to improve the performance of Gr/Si solar cells.

Highlights
The effects of TMAH concentration, IPA concentration and etching time on silicon pyramid structure were studied.
The uniform silicon pyramid arrays with low reflectivity were prepared.
The results show that the TMAH etched SiPa has a better Schottky junction contact between graphene and the SiPa surface.
The PCE of Gr/SiPa solar cells could reach up to 5.67%.

Keywords Gr/Si solar cells · TMAH · Surface texturing · Silicon pyramid array

1 Introduction

The mission of carbon emission reduction are pushing the global energy structure toward a cleaner and more sustainable development. For this reason, photovoltaic technology and industries are getting unprecedented attention and development[1, 2]. At present, crystalline silicon solar cell due to its abundant raw materials, mature preparation technology and excellent stability occupy the main commercial solar cells market[3–6]. However, the high cost and high energy consumption of p–n junction is probably contrary to the development goal of green and clean energy saving and emission reduction[7–10]. Therefore, reducing the cost of solar cell preparation, simplifying the preparation process, and developing solar cells that combine abundant silicon materials to produce simple device structures at low temperature have always been the focus of current research.
In recent years, a new type of Schottky junction solar cell developed by combining graphene with silicon has attracted extensive attention[11–13]. Gr/Si solar cells were prepared by a simple room temperature wet transfer process. At the same time, some relevant theories of Schottky junction have been widely studied in biomolecular sensors, photodetectors, metal–oxide–semiconductor field effect transistor (MOSFET) and other devices, which is convenient for us to understand the working mechanism of this kind of cells[14–18]. In this structure, the light can directly penetrate the graphene film to the Schottky junction, and the excited pairs of electron holes in the silicon are separated by a built-in electric field, generating a photocurrent. Gr/Si Schottky junction solar cells avoid the complex process of p-n/p-i-n junction formation in traditional silicon solar cells, and also facilitate light absorption and carrier separation and transport[19–21]. Therefore, Gr/Si solar cells provide a new idea for the preparation of solar cells with simple structure at low temperature.

The light reflection on the surface of solar cells is one of the key factors limiting their performance, because the high reflectivity of silicon wafers affects the efficient generation of electron–hole pairs in the cells[22–24]. It is necessary to reduce the reflectivity of silicon wafers to improve the conversion efficiency of solar cells. Silicon nanostructures have great attraction in the application of solar cells because of their high efficient anti-reflection (AR) effect. Fan et al.[25] prepared silicon nanowires on the surface of silicon wafer by Ag-assisted chemical etching to improve the light absorption of silicon substrate, and the efficiency of Gr/Si solar cell reached 2.86% through chloride doping. The photolithography and inductive couple plasma (ICP) etching were employed to fabricate the silicon pillar array and the efficiency of the cell increased from 1.96% to 3.55% under HNO3 doping[26]. Dong Hee Shin et al.[27] successfully prepared graphene/porous silicon solar cells with an efficiency of 2.32%, and under the doping of silver nanowires(AgNWs), the power conversion efficiency (PCE) was improved to 4.03%. Tetramethyl ammonium hydroxide (TMAH) is widely used in microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) based sensors and actuators because of its non-toxic, easy removal, no metal ion contamination and good anisotropic corrosion characteristics[28, 29]. Currently, many studies were reported about smooth surfaces for MEMS and NEMS obtained by TMAH etching, but only few results were reported about silicon surface texture to improve the light capture in solar cells.

In this study, the effects of TMAH concentration, IPA concentration and etching time on the morphology and reflection spectra of silicon wafers were systematically studied. Then, the graphene/silicon pyramid (Gr/SiPa) Schottky junction solar cells were prepared by using the large-scale uniform silicon pyramid array obtained under the optimal parameters, and the efficiency reached 5.67% under HNO3 doping. In this paper, we propose a new strategy to introduce pyramid arrays prepared by TMAH etching to improve the performances of Gr/Si solar cells.

## 2 Experimental

### 2.1 Preparation and Transfer of Graphene Films

The few-layer graphene film was prepared on the Cu foils by plasma-enhanced chemical vapor deposition (PECVD) [30–32]. The resulting graphene films were transferred to n-type silicon wafers by cycloododecane supported etching at room temperature. First, a mixture of cycloododecane and cyclohexane with a mass ratio of 1:1 was spin-coated on the graphene films surface as supporting layer, and the copper substrate was etched away by etchant of FeCl3:HCl:H2O=20 g:15 ml:185 ml. After that, the graphene was repeatedly rinsed with deionized water to completely remove the residue.

### 2.2 Preparation of Silicon Pyramid Arrays (Sipa) Texturation

N-Type (100) Si wafers (resistivity of 1–10 Ω·cm−1) with 100 nm thick SiO2 oxidation layer were used as substrates in our study. Si wafers were firstly cleaned in acetone, ethanol, and deionized water for 15 min by ultrasound. An opening window of 3 × 3 mm2 defined on the SiO2/Si substrate by an adhesive tape as the effective work area of the graphene/silicon solar cell. The SiO2 insulative layer within the window was removed by the diluted 5% (v/v) HF solution to expose the Si surface, followed by rinsing in deionized (DI) water for 3 – 5 min. Subsequently, these Si wafers were put in the TMAH-IPA alkaline etching solution to prepare Sipa texturation, and the detailed experimental conditions were shown in the Tables 1, 2 and 3. Then was rinsed using deionized water. Finally, the SiO2/Si substrate was dried by nitrogen gas stream and the adhesive tapes on the SiO2/Si substrate were peeled off.

| TMAH(%) | IPA(%) | Time(min) |
|---------|--------|-----------|
| 1%      | 10%    | 30        |
| 2%      | 10%    | 30        |
| 3%      | 10%    | 30        |
| 4%      | 10%    | 30        |

Table 1 Experimental conditions of silicon wafer etching at different TMAH concentrations
2.3 Fabrication of Photovoltaic Devices

The schematic of fabrication flow of Gr/SiPa Schottky junction solar cells were showed in Fig. 1. The SiPa substrates were formed through the process of TMAH-IPA alkaline etching process (as described in Sects. 2.2). Then, the graphene film was transferred onto the SiPa substrate by a cyclododecane-based transfer method at room temperature, followed cyclododecane on the graphene film was then removed by annealing at 400 °C for 20 min, and the graphene was fully contacted with silicon to form a Schottky junction. Finally, Silver paste and Indium-gallium (In-Ga) eutectic alloy were used as front electrode and back electrode of photovoltaic devices respectively.

2.4 Characterizations of Materials and Devices

The morphology of texturing samples surfaces was analyzed by scanning electron microscopy (SEM, Nova NanoSEM 450). The reflectance measurement was carried out on a spectrophotometer (UV- 2550). The characteristics of photovoltaic devices were collected by a Keithley 2420 source meter and a AAA solar simulator under AM 1.5 G with an irradiation intensity of 100 mW/cm².

3 Results and Discussion

3.1 Effect of TMAH Concentration on Sipa Texturation

In order to investigate the effect of TMAH concentration on the pyramid structure of silicon surface, four kinds of samples were prepared at the mass concentration of TMAH of 1%, 2%, 3% and 4% respectively. The IPA concentration and etch time were fixed at 10% and 30 min, respectively. The silicon wafers were placed in etch solution of 80 °C for constant temperature reaction, and the samples were

| Table 2 | Experimental conditions of silicon wafer etching at different IPA concentrations |
|---------|--------------------------------------------------------------------------------|
| TMAH(%) | IPA(%) | Time(min) |
| 2%      | 0%     | 30        |
| 2%      | 5%     | 30        |
| 2%      | 10%    | 30        |
| 2%      | 15%    | 30        |

| Table 3 | Experimental conditions of silicon wafer etching at different etching time |
|---------|--------------------------------------------------------------------------------|
| TMAH(%) | IPA(%) | Time(min) |
| 2%      | 10%    | 10        |
| 2%      | 10%    | 20        |
| 2%      | 10%    | 30        |
| 2%      | 15%    | 40        |

Fig. 1 Schematic illustration for fabrication of Gr/SiPa Schottky junction solar cell.
characterized by SEM. The detailed experimental conditions were shown in the Table 1.

Figure 2 shows that the SEM diagram of SiPa under different TMAH concentrations. It can be seen that with the increase of TMAH concentration, the size of silicon pyramid has obvious changes. When TMAH concentration is 1%, there are still many parts on the silicon surface that are not etched to form silicon pyramid, and the etched silicon pyramid has different sizes. When the TMAH concentration increases to 2%, the pyramid structure on the silicon surface covers the whole silicon chip, and the size of the pyramid is evenly distributed. When the TMAH concentration increases to 3%, a small number of relatively large silicon pyramid structures will appear, which affects the overall uniformity of the silicon pyramid array. When the concentration of TMAH is further increased to 4%, it can be found that some small silicon pyramids are embedded in the large silicon pyramids.

Figure 3 shows the reflectance spectra of the samples at different TMAH concentrations in the wavelength range of 300 ~ 1200 nm. It can be found that the reflectance of the sample decreases with the increase of TMAH concentration. When the TMAH concentration increases to 2%, the reflectance is the lowest, and the average reflectance can reach 12.07%. After increasing the TMAH concentration, the sample reflectivity decreases. This phenomenon can be explained by the etching reaction mechanism of TMAH solution on silicon wafers.

The formula of etching reaction of TMAH solution on silicon wafer is as follows[33]:

(1) TMAH is decomposed into OH⁻ and TMA⁺((CH₃)₄N⁺) ions in solution:

\[
(CH₃)₄NOH \rightarrow (CH₃)₄N⁺ + OH⁻ 
\]  \hspace{1cm} (1)

(2) Redox reaction takes place in the solution, and the silicon wafer is etched by anisotropy, forming the pyramid structure of silicon:

\[
Si + 2OH⁻ + H₂O \rightarrow SiO₃²⁻ + 2H₂ \uparrow 
\]  \hspace{1cm} (2)
The entire etching reaction of silicon wafer in TMAH solution is:

\[ Si + 2(CH_3)_4NOH + H_2O \rightarrow 2(CH_3)_4N^+ + SiO_3^{2-} + 2H_2 \uparrow \]  

(3)

According to Eq. (1) of reaction, when the concentration of TMAH increases, a large amount of \( OH^- \) will be generated, which accelerates the etching rate. When the concentration is higher, TMAH isotropic etching mainly controls the whole reaction process[34]. According to Eq. (2) of the reaction, with the progress of the reaction, the concentration of \( OH^- \) gradually decreases, and the generated \( (CH_3)_4N^+ \) and \( SiO_3^{2-} \) will be adsorbed on the surface of the silicon chip, thus inhibiting the reaction between \( OH^- \) and the silicon chip and slowing down the etching rate. In this process, there will be a chemical reaction mechanism of TMAH to enhance the anisotropic etching of silicon wafer and weaken the isotropic etching[35–37]. Therefore, in the whole reaction mechanism, reasonable control of TMAH concentration can obtain the silicon pyramid structure array with uniform size and full of silicon wafers, and the reflectivity is the lowest at this time.

3.2 Effect of IPA Concentration on Sipa Texturation

In order to explore how the IPA concentration affected the pyramid structures on the silicon surface, four samples were prepared under different IPA concentrations of 0%, 5%, 10% and 15%. The TMAH concentration and etch time were respectively fixed as 2% and 30 min (as shown in Table 2). The silicon wafers were placed in etch solution of 80 °C for constant temperature reaction. After etching, the samples were directly characterized via SEM.

As a common surfactant, IPA does not directly participate in the etching process of silicon wafers[38]. However, when IPA is contained in TMAH etching solution, it can prevent the \( H_2 \) bubbles generated by the reaction from adhering to the surface of the silicon wafer, and reduce the surface tension of the silicon wafer, increase the surface wettability, weaken the etching strength of the etching solution, increase the anisotropy of the etching, which is conducive to the nucleation and growth of the silicon pyramid. Figure 4 shows the SEM of Sipa under different IPA concentrations. With the addition of IPA, it can be seen that the uniformity of Sipa has been significantly improved. As shown in Fig. 4a, when there is no IPA in the etching solution, the size of silicon pyramids varies greatly, and some silicon wafer surfaces do not have pyramids. This is because the etching rate of the reaction is fast at this time, and a large amount of \( H_2 \) is generated to attach to the silicon surface with bubbles of different sizes. Therefore, the region etching reaction rates were different and the size of silicon pyramids were greatly different. With the increase of IPA concentration, the size of the silicon pyramid on the surface becomes consistent, covering the whole silicon wafers were showed in Fig. 4b and c. This is because with the increase of IPA concentration, the wettability of the solution decreases, the \( H_2 \) bubbles attached to the silicon wafer become smaller, and the etching rate decreases. However, too high concentration of IPA will obviously slow down the etching rate[39]. In a certain period of time, the reaction is not sufficient, resulting in part of the pyramid is not formed was showed Fig. 4d.

The reflectivity of silicon etchings at different IPA concentrations was shown in Fig. 5. It can be seen that without IPA, the reflectivity of silicon wafer is the highest, which is caused by the different sizes of silicon pyramids. There are few pyramids with effective reduction on the surface of silicon wafer, which is not conducive to light absorption. When IPA concentration increases, the uniformity of pyramid increases and it covers the whole silicon chip, which can effectively reflect light multiple times, thus reducing the reflectivity. When IPA concentration is 10%, the reflectivity is the lowest. When the concentration of IPA increases to 15%, the high concentration of IPA inhibits the etching rate, resulting in the unformed positive pyramid in some areas and the increase of reflectivity.

3.3 Effect of Etching Time on Sipa Texturation

In order to explore how the etching time affected the pyramid structures on the silicon surface, four samples were prepared under different etching time of 10 min, 20 min, 30 min and 40 min. The TMAH concentration and IPA concentration were respectively fixed as 2% and 10% (as shown in Table 3). The silicon wafers were placed in etch solution of 80 °C for constant temperature reaction. The samples were characterized by SEM.

Compared with SEM images of Sipa at different etching time in Fig. 6. It can be found that the silicon pyramids were nucleated when etched for 10 min. As the etch time increases to 20 min, the silicon pyramids were grown and formed, forming the silicon pyramid with obvious pyramidal structure and different sizes. When the etch time is increased to 30 min, the size of the silicon pyramids were became more uniform and completely covers the entire surface of the silicon chip. However, with the prolongation of etching time (40 min), part of the large silicon pyramids were etched away and became a small pyramid structure, with obvious difference in size, decreased uniformity and pits in some areas.

The reflectance of silicon wafer samples etched at different times was shown in Fig. 7. The reason for the high reflectivity of silicon wafer after etching for 10 min is that the silicon pyramids were nucleated and had not formed a complete pyramid structure. When the etching time is extended to 20 min to 30 min, the morphology and distribution of
silicon pyramids were gradually become more uniform. The reflectivity was decreased to the lowest 12.07% when the etching time is 30 min. At this time, the SiPa has a good anti-reflection effect. When the etching time increases to 40 min, the reflectance increases to 16.85%. The main reason is that with the increase of the etching time, the original intact pyramids were etched and appeared pits, which affected the uniformity and integrity of the SiPa and caused the rise of surface reflectance.

3.4 Study on Photovoltaic Performance of Gr/SiPa Schottky Junction Solar Cells

In order to study the effect of SiPa on the performance of Gr/Si solar cells, the SiPa with excellent anti-reflection performance was prepared by etching with TMAH concentration of 2% and IPA concentration of 10% for 30 min, and the Gr/planar Si solar cells were prepared at the same time. Figure 8a shows the $J-V$ characteristic curves of Gr/planar Si solar cells and Gr/SiPa solar cells under illumination. As expected, the SiPa devices showed better photovoltaic

![Fig. 4 SEM images of SiPa with different IPA concentration (a) 0%, (b) 5%, (c) 10%, (d) 15%](image-url)

![Fig. 5 Reflection spectra of SiPa at different IPA concentrations](image-url)
The PCE of Gr/Planar Si solar cells is 1.09%, $V_{OC}$, $J_{SC}$, and fill factor (FF) are 0.43 V, 13.11 mA/cm$^2$, and 19.16%, respectively. However, the Gr/SiPa solar cells prepared on the silicon surface by the SiPa increased PCE by 1.66 times, $V_{OC}$ is 0.45 V, $J_{SC}$ is 23.38 mA/cm$^2$, and FF is 27.40%. It can be seen that $V_{OC}$, $J_{SC}$ and FF of the device have improved, while $J_{SC}$ has the most significant improvement. The enhancement of $J_{SC}$ is mainly due to the fact that the silicon surface with the pyramid structure can absorb a large amount of incident light. The reflectivity of the SiPa is 12.07% in the entire visible and near infrared region, while the reflectivity of planar silicon is almost over 40%.

Figure 8b and c show the $J$-$V$ characteristics and corresponding ln$J$-$V$ curves of Gr/Planar Si and Gr/SiPa solar cells in the dark. We noticed that the ln$J$-$V$ curves of Gr/SiPa shifted to the left, which had been also observed in other optoelectronic devices. It could be that the transfer of graphene and the preparation of silver electrode during the device preparation involve the thermal annealing process, and the interface thin layers of different thickness were randomly formed at some places on the interface between the SiPa and Gr. At the same time due to the pyramid of silicon surface roughness, interface layer and barrier inhomogeneity and semiconductor surface electric field and the influence of the interface state changes, thus causing the In$J$-$V$ curves of Gr/SiPa shift to the left[40–45]. The $J$-$V$ characteristic curve in the dark shows that the solar cell prepared by the formation of Schottky junction has good rectification characteristics. In order to provide more insights into the effects of SiPa on Gr/Si solar cell performance, we further analyze their $J$-$V$ characteristic curves. According to the thermal emission theory, The $J$-$V$ characteristics of Gr/Si solar cells are mainly determined by the majority of carriers, and most of the (electron) current can be made by

$$J = J_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$

where $n$ is the ideal factor, $k$ is boltzmann constant, $T$ is the thermodynamic absolute temperature, and $q$ is the
elementary charge. $J_o$ is the reverse dark-saturation current density, which is expressed as a function of the Schottky barrier height:

$$J_o = A^* T^2 \exp \left( - \frac{\phi_B}{kT} \right)$$

(5)

where $A^*$ represents the effective Richardson constant ($\approx 112$ A·cm$^{-2}$·K$^{-2}$ for n-Si), $\phi_B$ represents Schottky barrier height.

For series resistance ($R_s$) of Gr/Si solar cells, Eq. (1) needs to be modified as\cite{46–48}:

$$J = J_o \left[ \exp \left( \frac{q(V - R_s J)}{nkT} \right) - 1 \right]$$

(6)

Take the logarithm and differentiate of Eq. (3), we obtain:

$$\frac{dV}{d(\ln J)} = R_s J + \frac{n kT}{q}$$

(7)

$R_s$ can be obtained by linear fitting the slope of the $dV/d(\ln J)$ curve.

Gr/planar Si and Gr/SiPa solar cells Schottky barriers height and ideal factors ($n$) can be extracted in Fig. 8c. It can be found that Schottky barrier heights are almost equal (see Table 4), which indicates that although the SiPa prepared by TMAH etching increases the specific surface area of the silicon surface, it does not cause relatively large defects on the silicon surface, resulting in serious carrier recombination\cite{41, 49, 50}. The $n$ of Gr/planar Si and Gr/SiPa Schottky junctions are 5.51 and 4.16, respectively. It is worth noting that the $n$ of Schottky junction can measure the dominant degree of interface defects in the total recombination. The lower $n$ goes, the closer it gets to 1. It indicates that the device is closer to the ideal junction and the better the cell.
The performance of Gr/SiPa is lower than that of Gr/planar Si, which is mainly attributed to the uniform size of the SiPa prepared by TMAH etching. The contact area between graphene and the SiPa is larger than that of planar silicon, and a good Schottky junction contact is formed. Meanwhile, the SiPa further improves the ability of silicon to collect photogenerated carriers. Better Schottky junction contact between Gr and Si leads to higher $V_{OC}$, which is closely related to $J_{SC}$ according to its $J-V$ relationship of:

$$V_{OC} = \frac{nkT}{q} \ln \left( \frac{J_{SC}}{J_o} + 1 \right) \approx \frac{nkT}{q} \ln \left( \frac{J_{SC}}{J_o} \right)$$

(8)

It can be seen that the value of $V_{OC}$ is tied to $J_{SC}$ in principle, and the increase of $V_{OC}$ of Gr/SiPa solar cells is due to the enhancement of $J_{SC}$.

Although we took a simple method to fabricate the original Gr/SiPa solar cells, there still exists a major problem of low PCE due to the relatively low electrical conductivity of graphene. To further improve device PCE, graphene was chemically doped. After HNO$_3$ doping, PCE of the Gr/SiPa solar cells increased from 2.90% to 5.67%, $FF$ significantly increased from 27.40% to 52.53%, $V_{OC}$ and $J_{SC}$ increased from 0.45 V and 23.38 mA/cm$^2$ to 0.49 V and 31.07 mA/cm$^2$, respectively (as shown in Fig. 9). This is mainly attributed to the p-type graphene doping formed by HNO$_3$, which effectively improves the conductivity of graphene and increases the Schottky barrier. Finally, the PCE of HNO$_3$/Gr/SiPa Schottky junction solar cells is 5.67%, which is higher than other Gr/Si solar cells with silicon nanowires and porous silicon structure. This work provides a new strategy for introducing SiPa prepared by TMAH etching to improve the performance of Gr/Si solar cells.

### Conclusions

In summary, the effects of TMAH concentration, IPA concentration and etching time on the silicon pyramid structure array were systematically studied, and a large scale silicon pyramid array with uniform size distribution was successfully prepared on the surface of silicon wafer, and good anti-reflection ability was obtained. The silicon pyramid array with the lowest average reflectivity (12.07%) was successfully prepared under optimized conditions of 2% TMAH, 10% IPA and etched for 30 min. The Gr/SiPa Schottky junction solar cells were successfully prepared by introducing SiPa into Gr/Si solar cells, and the PCE was 2.66 times higher than that of planar silicon. As a result, the improvement of cell performance is mainly due to the uniform size of the SiPa prepared by TMAH.
etching, which makes the contact area between graphene and the SiPa larger than that of planar silicon, and forms a good Schottky junction contact. Meanwhile, the SiPa further improves the ability of silicon to collect photogenerated carriers. Chemically doped HNO$_3$ on graphene is an effective way to improve cell performance. Finally, the Gr/SiPa Schottky junction solar cells with efficiency of 5.67% were successfully achieved after HNO$_3$ treatment. In this paper, a new strategy is proposed to introduce the SiPa prepared by TMAH etching to improve the performance of Gr/Si solar cells.

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Data Availability The authors declare that the data and materials for this work are available.

Code Availability Not applicable.

Declarations

Ethics Approval The authors declare that the manuscript is not currently being considered for publication in another journal.

Consent to Participate I testify on behalf of all co-authors that our article submitted to Silicon.

Consent for Publication The authors agree that the manuscript should be published in Silicon.

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