Microtextured Hybrid PEDOT:PSS-Silicon Solar Cells Employing Kirigami Graphene<br>Zih-Yang Chen ${ }^{1}$, Yi-Chun Lai ${ }^{1}$, Chi-Hsien Huang ${ }^{2 *}$, and Peichen $\mathrm{Yu}^{1 *}$<br>${ }^{1}$ Department of Photonics, National Chiao-Tung University, Hsinchu 30010, Taiwan<br>${ }^{2}$ Department of Materials Engineering, Ming Chi University of Technology, New Taipei City 24301, Taiwan<br>(*E-mail: chhuang@mail.mcut.edu.tw, yup@faculty.nctu.edu.tw)


#### Abstract

Among developed two-dimensional (2D) materials, graphene holds the highest figure of merit for transparent electrode. However, its applications to optoelectronic devices with textured surface may be limited by the planar atomic nature. In this work, we demonstrate the conformal coverage of patterned kirigami graphene on micro-textured hybrid organic-silicon solar cells to enhance collection of charge carriers. As a result, the photovoltaic characteristics of hybrid solar cells are largely improved, showing notable enhancement of fill factor and power conversion efficiency by $16.1 \%$ and $20.9 \%$, respectively.


## 1. Introduction

It is well known that graphene is a very promising candidate for transparent electrode in solar cell due to its extremely high conductivity and high transparency [1]. On the other hand, surface texturing is a key process in silicon solar cell because it can reduce the optical reflection due to the increase of optical path length leading to enhancement of light absorption [2]. However, graphene is a planar 2D atomic material that limits its transparent electrode application to 3D surface texture due to poor coverage resulting into low carrier extraction. Recently, it is reported that single layer graphene with kirigami pattern can endure high strain without changing its electrical property [3]. The results motivated us to use kirigami graphene to convert the planar 2D material to 3D one. This conversion allows graphene to cover the textured surface conformally. In this study, we transferred kirigami graphene onto hybrid organic/Si solar cell with inverted pyramid array as surface texture and measured the photovoltaic characteristics.

## 2. Experiment

As shown in Fig. 1, the hybrid solar cell fabrication started with N-type $\operatorname{Si}(100)$ substrate with resistivity of $1 \sim 5 \Omega-\mathrm{cm}$ and thickness of $180 \mu \mathrm{~m}$. The Si wafers were cut into $2.8 \times 2.8 \mathrm{~cm}^{2}$ and cleaned following RCA process. For creating inverted pyramid array, $100 \mathrm{~nm} \mathrm{SiO}_{2}$ was firstly deposited on Si wafer as hard mask by PECVD (Plasma-enhanced chemical vapor deposition). Secondly, square hole array were patterned by photo-lithography and wet etching. The square hole size and space between holes are $20 \times 20 \mu \mathrm{~m}^{2}$ and $5 \mu \mathrm{~m}$, respectively. Then, the photoresist was removed by acetone. Thirdly, the sample was etched by $5 \mathrm{wt} \% \mathrm{TMAH}$ (tetramethylammonium hydroxide) at $70^{\circ} \mathrm{C}$. Finally, the $\mathrm{SiO}_{2}$ hard mask was removed by BOE to obtain inverted
pyramid array on substrate surface. After that, PEDOT:PSS was coated onto the sample and then metal contact and back contact were prepared by thermal evaporator to complete the hybrid organic/Si solar cell fabrication.

As shown in Fig. 2, the kirigami graphene transfer started with graphene growth using CVD (chemical vapor deposition). The CVD process details were described in ref. [4]. Secondly, kirigami graphene with cross array on Cu foil was obtained by photolithography followed by Ar RIE (reactive ion etch). The width and length of each cross were $3 \mu \mathrm{~m}$ and $28 \mu \mathrm{~m}$, respectively. It is expected that part of graphene may be able to fold and cover the surface of the inverted pyramid by creating such pattern after transferring kirigami graphene onto textured surface. Fig. 3(a) shows the OM image. Thirdly, after removing photoresist by acetone, PET film (polyethylene terephthalate) with adhesive layer was used to stick onto kirigami graphene/Cu-foil. Fourthly, the Cu -foil was etched away by $\mathrm{Fe}\left(\mathrm{NO}_{3}\right)_{3} \cdot 9 \mathrm{H}_{2} \mathrm{O}$ to obtain kirigami graphene/PET. Fig. 3(b) shows the OM images. After that, kirigami graphene/PET was put onto textured hybrid organic/Si solar cell. Please note that each cross pattern should align each inverted pyramid unit. It was done


Fig.1. Flowchart of the device fabrication


Fig.2. Flowchart of transferring graphene


Fig. 3 (a) cross array of graphene on copper foil;(b) kirigami graphene on PET film (c) kirigami graphene on Si substrate
under microscope. Finally, PET film was slowly peeled off and only kirigami graphene left on the device. Fig. 3(c) shows the OM image. The photovoltaic (PV) characterization of the fabricated hybrid solar cell with and without kirigami graphene was conducted under simulated AM1.5G (Air Mass 1.5, Glob) illumination conductions.

## 3. Result and discussion

Fig. 4 shows the reflectance of Si substrate with inverted pyramid array for various etching times. We can see that the Si wafer after TMAH etching time of 25 min exhibited the lowest reflectance. For solar cell fabrication, the TMAH etching of 25 min for fabricating hybrid solar cell was determined. Figure 5(a) shows the SEM images of inverted pyramid array on Si wafer after TMAH etching time of 25 min. After deciding the TMAH etching time, PEDOT:PSS was coated onto the textured Si wafer followed by metal contact and back contact. In order to confirm the sidewall of inverted pyramid covered by folded graphene, the position of sidewall (red point in Fig. 5(b)) was measured using Raman spectroscopy. As shown in Fig. 6, the Raman spectrum shows clear $G$ and 2D bands with only tiny $D$ band. The result indicates that the graphene exists on the sidewall of the inverted pyramid.


Fig. 4 Reflection of different TMAH etching times


Fig. 5 Scanning electron microscope (SEM) images of (a) inverted pyramid textures and (b) inverted pyramid array covered by kirigami graphene.


Fig. 6 Raman spectrum on the sidewall of the inverted pyramid (red point in Fig. 5(b)).


Fig. 7 Current density-voltage curves of textured hybrid solar cell with and without kirigami graphene

Table1 Photovoltaic parameters of inverted pyramid textured with different process

|  | $\mathrm{V}_{\mathrm{oc}}$ <br> $(\mathrm{V})$ | $\mathrm{J}_{\mathrm{sc}}$ <br> $\left(\mathrm{mA} / \mathrm{cm}^{2}\right)$ | FF | Efficiency <br> $(\%)$ |
| :---: | :---: | :---: | :---: | :---: |
| Reference | 0.469 | 23.19 | 52.8 | 5.75 |
| Remove PET film | 0.471 | 24.03 | 61.3 | 6.95 |

Fig. 7 shows the current density- voltage curves of textured hybrid solar cell with and without kirigami graphene. The PV characteristics including $\mathrm{V}_{\mathrm{oc}}$, $\mathrm{J}_{\mathrm{sc}}$, filling factor (FF) and conversion efficiency were summarized in Table 1. We can notice that FF increased from 52.8 to 61.3. FF was enhanced by up to $16.1 \%$. The power conversion efficiency increased from $5.75 \%$ to $6.95 \%$. It was enhanced by up to $20.9 \%$.

## 3. Conclusions

We successfully fabricated microtextured hybrid organic/Si solar cell employing kirigami graphene. By Raman spectrum, we confirmed that patterned graphene folded onto the sidewall of inverted pyramid The photovoltaic characteristics of hybrid solar cells were largely improved, showing notable enhancement of fill factor and power conversion efficiency by $16.1 \%$ and $20.9 \%$, respectively.

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