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High efficiency silicon nanohole/organic heterojunction hybrid solar cell

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High efficiency hybrid solar cells are fabricated based on silicon with a nanohole (SiNH) structure and poly (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS). The SiNH structure is fabricated using electroless chemical etching with silver catalyst, and the heterojunction is formed by spin coating of PEDOT on the SiNH. The hybrid cells are optimized by varying the hole depth, and a maximum power conversion efficiency of 8.3% is achieved with a hole depth of 1 μm . The SiNH hybrid solar cell exhibits a strong antireflection and light trapping property attributed to the sub-wavelength dimension of the SiNH structure. © 2014 AIP Publishing LLC.

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Recently, low cost Si nanowires (SiNWs)/polymer hybrid solar cells have been actively researched as they can potentially lower the cost of solar cells.^{1–5} The hybrid solar cells incorporating both Si and organic semiconductor enjoy the benefits of both materials.⁶ Furthermore, due to the use of the nanowire structure, the cells have excellent antireflective and light trapping properties, and exhibit significantly enhanced light absorption. In addition, the metal induced electroless chemical etching method used to achieve the nanowire structure is simple, low cost, and applicable to large area wafers. Such hybrid cells, however, suffer from the drawbacks that the stand alone SiNWs tend to break easily, and agglomerate when the wire length increases. Recently, Si nanohole (SiNH) structure has been developed to overcome these shortcomings of the SiNW structure.⁷ The interconnecting SiNH structure is mechanically more robust, facilitates carrier transport, and eases electrode formation compared to the SiNW structure. Moreover, it has also been reported that the SiNH structure has much higher light absorption than the SiNW structure due to its better light trapping ability.⁸ SiNH solar cell device based on just Si material has been recently fabricated by Peng *et al.* with a short circuit current of 32.2 mA/cm² and an efficiency of 9.51%.⁷

In this paper, we present a low cost maskless approach to fabricate large scale SiNH arrays. SiNH solar cell is then fabricated by spin coating poly (3,4-ethylenedioxythiophene) (PEDOT) onto the SiNH structure to form a heterojunction device. The SiNH/PEDOT hybrid solar cells fabricated exhibit a power conversion efficiency (PCE) of 8.3%. The process developed in this work can be easily transferred to Si thin film and thus, paves a way for the development of thin film Si/polymer hybrid solar cells with high efficiency.

The starting 625 μm thick N-type Si (100) wafers were cleaned sequentially in piranha solution at 90 °C and RCA solution at 75 °C for 10 min each. A thin layer of Ag of 25 nm was then deposited on top of the Si wafer via

electron-beam evaporation. After that, KrF excimer laser with wavelength of 248 nm and pulse duration of 20 ns was used to anneal the Ag film to result in the formation of a monolayer of Ag nanospheres. The excimer laser has a beam dimension of 3 mm $\times$ 3 mm square. The laser power density used was 300 mJ/cm², and the sample was placed on a moveable computer-controlled X-Y stage. During the laser annealing, the laser beam position was fixed, and the stage moved in the X direction. After a complete scan over the sample in the X direction, the stage was shifted in the Y direction by 2.8 mm, and the scan along the X direction was repeated. The laser beam only illuminated each spot of the sample once.⁹ After the formation of the Ag nanospheres, the sample was next immersed in a mixture solution of hydrogen dioxide (H₂O₂) and hydrofluoric acid (HF), where etching of Si occurred to form a SiNH structure, with the Ag nanospheres acting as catalyst. The wet etching process was governed by the mechanism as proposed by Li and Bohn based on the local coupling of redox reaction.¹⁰ The remaining Ag nanospheres inside the SiNHs were then removed using a HNO₃ solution. After that, conductive (3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) mixed with 5 wt. % dimethyl sulfoxide (DMSO) was spin coated on the SiNH structure to form a p-n junction. Finally, a layer of Ag grid and Ti/Pd/Ag were evaporated on the PEDOT layer and the back side of Si, respectively, to complete the solar cell device. In the experiments, cells with four different NH depths (D) of 0.5 μm , 1 μm , 2 μm , and 4 μm were fabricated by controlling the etching time. Scanning electron microscopy (SEM, LEO 1550 Gemini) was used to analyze the surface morphology of the SiNH structure. The light reflection of the SiNH structure was investigated using a Lambda 950 UV/VIS/NIR spectrometer with an integrating sphere. The current density voltage characteristic (J-V) of the cells was analyzed using a solar simulator (San-EI Electric). The incident photon-electron conversion efficiency (IPCE) was measured using a spectral response/IPCE measurement system.

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Figure 1(a) shows the SEM image of the sample after the laser annealing of the Ag layer. It is clearly observed that a layer of Ag nanospheres is formed on the surface of the Si substrate. Most of the Ag nanospheres have diameters that range from ~ 200 nm to ~ 400 nm, and the separations between neighboring Ag nanospheres vary from ~ 300 nm to ~ 1000 nm. The planar Ag film initially deposited using the e-beam evaporation experienced internal stress. Upon the laser pulse irradiation, it gained enough energy to break up and reshape to form nanospheres, so as to reach a low energy state.^{11,12} Fig. 1(b) shows the top view image of the Si substrate after wet etching to form SiNHs with $D = 1 \mu\text{m}$. The chemicals only etched the parts of the Si wafer where Ag nanospheres exist, and the diameters of the SiNHs and their separations follow those of the starting Ag nanospheres. Figs. 1(c)–1(f) show the cross-sectional view of the SiNH structure with a hole depth of $\sim 0.5 \mu\text{m}$, $\sim 1 \mu\text{m}$, $\sim 2 \mu\text{m}$, and $\sim 4 \mu\text{m}$, respectively, which were achieved with corresponding etching times of ~ 15 s, 30 s, 60 s, and 120 s. It can be seen that the SiNHs fabricated are vertically aligned. Figure

1(g) shows the tilted view of the $1 \mu\text{m}$ SiNH structure coated with PEDOT polymer of ~ 120 nm thick. Note that PEDOT is found mainly on the top surface of the SiNH structure and does not penetrate into the holes. This is similar to the case of PEDOT coated on SiNWs, where PEDOT does not penetrate into the gaps between the SiNWs.³

Figure 2 shows the reflectance spectra of the SiNH structure with different D . For comparison, the reflection of a planar Si wafer was measured and shown in the inset of Fig. 2. The reflectance of planar Si is generally high and over 30%, due to the large difference between the refractive indices of the silicon substrate and air. In contrast, the reflectance is significantly reduced for the SiNH structures with different depths over the solar spectrum of interest from $\lambda = 300$ nm to 1100 nm. At D of $0.5 \mu\text{m}$, the reflectance is relatively high with an average value of 12.6%. At such a small D , the light harvesting ability of the nanostructure is relatively weak. It is found that the reflectance reduces with increasing D from 0.5 to $2 \mu\text{m}$, mainly due to the stronger light trapping ability at greater hole depth.^{13,14} As the

FIG. 1. (a) Ag nanosphere formed upon laser annealing, (b) top view SEM of the nanohole structure with D of $1 \mu\text{m}$, (c)–(f) cross-sectional views SEM of the nanohole structure with hole depth of $0.5 \mu\text{m}$, $1 \mu\text{m}$, $2 \mu\text{m}$, and $4 \mu\text{m}$, respectively, and (g) tilted view SEM of the SiNH structure coated the PEDOT:PSS on top.

FIG. 2. Reflectance spectra of the SiNH structures with different hole depths.

dimension of the SiNH structure is comparable with the wavelength of main spectrum of sunlight, there is strong scattering within the SiNH structure which prolongs the effective optical path length and traps light.¹⁵ When D increases further to $4\text{ }\mu\text{m}$, the average reflectance does not decrease, but increases slightly instead, attributed to the rougher surface formed. This can be seen from the SEM image of the surface with $D = 4\text{ }\mu\text{m}$, as shown in Fig. 3, compared to the surface of the structure with a smaller $D = 1\text{ }\mu\text{m}$, as shown in Fig. 1(b). With longer etching time, the surface where there is no Ag nanoparticle reacted with the solution resulting in a rougher surface.

Figure 4 shows the IPCE of the SiNH hybrid solar cell with different D . Among them, the cell with $D = 2\text{ }\mu\text{m}$ has the highest IPCE, and it peaks at 68.1% at $\lambda = 590\text{ nm}$. The high IPCE results from the lowest reflectance observed for this structure. At $D = 0.5\text{ }\mu\text{m}$, the IPCE is low which is consistent with the high reflectance as seen in Fig. 2. It is observed that for $D = 4\text{ }\mu\text{m}$, the IPCE drops even below that for D of $0.5\text{ }\mu\text{m}$, which is not in accordance with their reflectance results shown in Fig. 2. This lower IPCE at shorter wavelength is attributed to a higher recombination rate for the photo-excited minority carriers,³ arising from the rougher and more defective surface. Such surface also contributes to a higher series resistance because of the poorer contacts formed between Si and PEDOT:PSS and results in lower

FIG. 3. Top view SEM of the nanohole structure with D of $4\text{ }\mu\text{m}$.

FIG. 4. IPCE of the SiNH hybrid solar cells with different hole depths.

IPCE. It is noted that the IPCE at $\lambda > 800\text{ nm}$ is generally lower and comparable for all the cells with different D . This is because the wavelength is larger than the dimensions of the SiNHs, and hence, the scattering of light is weaker. The absorption thus occurs deeper in the Si substrate and is less dependent on the SiNH depth. Besides, there is increased absorption of light in the PEDOT:PSS film in this wavelength range.¹⁶

Figure 5 shows the current-density-voltage (J - V) curves of the SiNH hybrid solar cells with different D , under the illumination of the standard AM 1.5 G irradiation with a total energy density of 100 mW/cm^2 . Table I summarizes the PCE, short circuit current (J_{SC}), open circuit voltage (V_{OC}), and fill factor (FF) of the cells. Four samples were studied and characterized for each cell, and the results presented represent the average values of the samples. The PCE increases with D and reaches a maximum of 8.3% for the cell with $D = 1\text{ }\mu\text{m}$. It then decreases as D is further increased and exhibits a value of 5.6% at $D = 4\text{ }\mu\text{m}$. As for V_{OC} , it is relatively stable and varies between 0.52 V and 0.55 V. The J_{SC} increases initially and reaches a maximum of 25.7 mA/cm^2 at $D = 2\text{ }\mu\text{m}$, before it decreases with increasing hole depth,

FIG. 5. Current-density-voltage (J - V) curves of the SiNH hybrid solar cells with different hole depths under the illumination of the standard AM 1.5 G irradiation.

TABLE I. Summary of the photovoltaic parameters.

SiNH depth (μm)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF (%)	PCE (%)
0.5	24.0	0.52	46.1	5.7
1	25.0	0.55	60.4	8.3
2	25.7	0.54	46.0	6.3
4	23.7	0.52	45.1	5.6

which is consistent with the IPCE results. On the other hand, the FF increases from 46.1% to 60.4% as D increases from 0.5 μm to 1 μm . This is because as the hole depth increases, the light absorption ability is enhanced due to a strong scattering effect. Most of the light will be absorbed at the top of the sample where the SiNH structure exists. Hence, the effective minority carrier diffusion length is reduced which facilitates carriers collection¹⁷ and gives rise to a high FF at D of 1 μm . However, at larger D of 2 and 4 μm , the FF drops to only 46.0% and 45.1%, respectively. With longer etching time, the surface becomes rougher and more defective, leading to increased surface recombination and higher series resistance. This is consistent with the series resistances calculated based on the slopes of the J - V curves ($dJ/dV|_{V=V_{oc}}$) in Fig. 3, which are 9.4, 4.1, 8.5, and 10.4 Ωcm^2 , respectively, for the cells with D = 0.5, 1, 2, and 4 μm .

In conclusion, a simple and low cost approach for fabricating hybrid SiNH solar cells has been proposed. The SiNH structure, which is produced with laser thermal annealing and electroless chemical etching process, demonstrates strong light absorption ability. Hybrid cell devices with different hole depths have been fabricated. The optimized structure is identified with a hole depth of 1 μm , which reveals the highest power conversion efficiency of 8.3%. Cells with longer hole depth lead to poorer performance because of the rougher surface and higher series resistance arising from the poor contact. It is believed that the cell performance can be

further improved through optimizing the SiNH structural dimensions such as the hole diameter and spacing, and the spin coating speed which controls the thickness of the PEDOT:PSS layer. Note that the fabrication technique can also be easily adapted to Si thin film solar cell to improve its cell efficiency.

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