The effect of introducing Macroporous Silicon as the Cathode of Bulk Heterojunction Hybrid Solar Cell

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Abstract—This article focuses on the photocurrent enhancement of bulk-heterojunction hybrid solar cell by using macroporous silicon (macro-PSi) as the cathode that provided increased effective contact surface area at the interface of organic-inorganic material. Solar cell was fabricated with poly (3-hexylthiophene) (P3HT) and phenyl-C61-butyric acid methyl ester (PCBM) polymer blend at 1:1 ratio. It was found that the pore-diameter of the porous silicon plays an important role on short-circuit current of the fabricated hybrid solar cell. Huge enhancement of short-circuit current density (about 73 fold) was obtained when the average pore diameter of macro-PSi was comparable to the photogenerated carrier transport length of the photoactive polymer. The annealing of the whole structure further enhanced the overall performance of the fabricated hybrid solar cell.

Index Terms—Hybrid-solar-cell, Macroporous Silicon, Bulk-heterojunction, Solar cell performance parameters.

I. INTRODUCTION

Hybrid solar cells are made of organic and inorganic materials. Hybrid solar cells hold promise for low cost energy production [1], but only if further developments in their design and manufacture make them practical for real-world applications. In the conventional photoactive polymers like P3HT:PCBM the transport length is reported to be 180 nm [2]. Therefore, it is advantageous to form well-ordered nanostructures which will provide large interface with an organic semiconductor to inorganic semiconductor. As a result most of the excitons are expected to reach at the interface between the two semiconductors and all of the charge carriers have a pathway to the appropriate electrode. This will increase the charge collection efficiency of a solar cell [3]. As a result enhancement in the short-circuit current density was observed when Si nanowires (NW) were embedded in the bulk-heterojunction made of P3HT:PCBM solar cells [4]. Similarly a porous matrix, particularly porous silicon (PSi) matrix, appears to be an ideal material for this purpose as its pore-size, morphology and the conductivity of the PS layers [5] can be controlled. PSi has also been investigated as an anti-reflection coating in the hybrid solar cells for extending and enhancing the absorption of hybrid solar cells [6].

In this work macroporous silicon (macro-PSi) has been investigated as the cathode of the P3HT:PCBM-based solar cell. The photocurrent of the fabricated solar cell was found to vary with pore size of PSi and heat-treatment of the whole structure. As was expected when the pore diameter was comparable to the transport length of photo-generated carriers the short-circuit current density enhanced drastically. The highest enhancement was about 73 times compared to conventional cathode (without porous structure) [7]. The experimental investigations indicate lots of promise for porous-cathode in the hybrid solar cells having higher performance.

II. EXPERIMENTAL

A. Macroporous silicon (macro-PSi) preparation

Three types of pores are generally observed in silicon: (a) Nanopores, b) Mesopores c) Macropores [8]. In most cases, the PSi is fabricated by electrochemical etching of Si wafers in electrolytes including hydrofluoric acid (HF) and surfactants (conventionally ethanol) [9]. In this work macro-PSi having two-dimensional periodicity has been fabricated by electrochemical etching of p-type silicon substrate (Resistivity of 1-5 Ω-cm, (100) oriented) having Al back contact, with 1HF:4DMSO (v/v) solution [10]. Three different samples were prepared for three different etching times (10min, 3min, & 1min) with constant etching current density of 30mA/cm². After the etching process, the samples were rinsed in ethanol and blown dry in air. The experimental set-up of electrochemical etching cell is shown in Fig. 1. The Si wafer acts as the anode and the Pt-wire mesh acts as the cathode. The porosity is determined by the anodization condition, composition electrolyte, and the doping density of Si substrate.

Platinum electrode
Silicon wafer
Screws to hold wafer
HF electrolyte

Fig. 1. Electrochemical etching cell used to fabricate PSi.
B. Device fabrication

A schematic of the fabrication process of hybrid solar cells is shown in Fig. 2. The fabrication of hybrid solar cells starts with an indium tin oxide (ITO) film coated on a glass substrate. Very thin layer of ITO (~ 100 nm) was deposited by electron-beam evaporation process with the chamber pressure of $2.5 \times 10^{-5}$ mbar, Beam current of 30 mA and voltage of 2KV. After ITO deposition, the samples were annealed in a furnace (Carbolite CWF 12/13) in air at 600°C for 10 min.

The fabrication process begins with "Process-1" where a thin layer of photo-active material (P3HT:PCBM) was deposited onto the ITO coated glass substrate by spin coating process at 500 RPM for 40 sec. In a separate process (Process-2) a thin layer of P3HT:PCBM was deposited onto macro-PSi by drop casting method. Heat treatment of PSi/P3HT:PCBM at 45°C for 5 min was done to liquefy the P3HT:PCBM for penetration into the pores of PSi. Thus prepared PSi sample containing P3HT:PCBM layer was then pasted with the P3HT:PCBM layer on the ITO by pressing the two substrates (PSi and glass). Finally, the whole structure [ITO/P3HT:PCBM/PSi/Al] was annealed at 120°C for 20 min to establish good contacts between two different P3HT:PCBM layers and also with PSi. Electron-beam evaporated ITO and Aluminum (Al) have been used as anode and back-contact of PSi respectively. The active area of our device was 0.7 cm². 

The value of work-function of macro-PSi is assumed to be around that of bulk silicon as the position of the conduction band of macro-PSi is not expected to be significantly different from the bulk. The 2 eV optical band gap of macro-PSi allows proper bands alignment, carrier separation and transportation to the cathode. Also the dissociation of excitons that are generated under illumination is expected to be enhanced because of the electric field produced due to the different electron affinities and ionization potentials. Therefore according to the energy relationship efficient charge transfer and collection can be expected.

III. RESULTS AND DISCUSSION

The pore-diameter and nature of porosity is important for the enhancement of the performance of organic solar cell fabricated with the macro-PSi as the cathode. Formation of macro-pore in Si wafer was studied by SEM. Fig. 4 shows the SEM image of the top of the PSi sample with anodization current density of 30mA/cm² and anodization time 10 min. The average pore diameter was about 790 nm and the porosity was about 66%. The pore diameter and porosity were calculated using SEM image processing.

The pore diameter was found to vary linearly with the etching time up to 10 min. This gives us the tunability of the average pore diameter, which is shown in Fig. 5.
The pore initiation time as found from Fig. 5 was about 30 sec. This is due to use of DMSO as the electrolyte and high etching current density. DMSO has very good oxidizing property and forms silicon oxide very fast. The similar linear relationship for pore-depth with etching time has been reported [11].

![Fig. 5. SEM image of cross-section for full structure with 150 magnifications.](image)

Fig. 6 shows the cross-sectional view of the fabricated device that shows the various layers of the glass/ITO/P3HT:PCBM/PSi/Al heterostructure. The ITO layer is not clearly visible as the thickness of ITO layer was around 100 nm whereas the other layers (P3HT:PCBM, Al, bulk-Si, etc were in the range of micrometer). Huge influence of pore diameter on the forward and reverse current density (J) in dark as well as under 1.5 AM simulated light was observed. The J-V characteristic in dark is shown in Fig. 7.

![Fig. 7. J-V characteristics (in dark) of fabricated hybrid solar cells.](image)

The dark J-V characteristic of the fabricated hybrid solar cell (Fig. 7) shows a typical rectifying junction behavior with threshold voltage of 0.3V. The dark current was found to increase with the increased pore diameter. The reverse J-V characteristics under simulated light illumination were investigated to find the influence of pore diameter on the performance of fabricated hybrid solar cell. Fig. 8 shows the J-V characteristics under 1.5 AM simulated light illumination for the solar cells fabricated with 1, 3, and 10 min etched porous silicon cathode. The corresponding average pore diameter was 90, 250 and 930 nm respectively.

![Fig. 8. J-V characteristics under 1.5 AM light of hybrid solar cell with macro-PSi cathode having various pore diameters.](image)

The short circuit current density ($J_{SC}$) was very low for larger pore diameter. The $J_{SC}$ was also smaller for lower diameter. When the pore diameter was very high compared to the reported carrier transport length of the acceptor polymer the charge collection was poor. Again for the smaller pores the pore filling cannot provide a sufficiently dense filling of P3HT:PCBM blend to be able to form a “conductive path” for electron transport to the cathode. But when the pore diameter was 250 nm (3 min etching time with current density of 30 mA/cm²) the observed $J_{SC}$ was highest.

The mentioned enhancement in $J_{SC}$ is believed to be due to enhanced charge collection efficiency. Being situated with in the electron transport distance the cathode was able to collect electrons more efficiently. Although we did not measure the depth of the etched pore but with the mentioned etching condition we can assume a shallow depth of couple of 100 nm as reported by Bettotti et al [12].

![Fig. 9. Schematic of bulk heterojunction hybrid solar cell with macro-PSi as the cathode.](image)
Similarly, assuming a partial filling of the pore by the P3HT:PCBM blend, the dissociated holes are also expected to be collected efficiently by the ITO anode. This hypothesis can be viewed schematically from Fig. 9, where the blue region is the P3HT and the yellow region is the PCBM.

The influence of average pore diameter on the J_{SC}, open-circuit voltage (V_{OC}) and fill-factor (FF) has been summarized in Table-1. From the Table-1 it is seen that the V_{OC} is decreasing with the smaller pore diameter. This may be due to the insufficiently dense filling of pores.

**TABLE I. INFLUENCE OF AVERAGE PORE DIAMETER ON THE SOLAR CELL PERFORMANCE.**

<table>
<thead>
<tr>
<th>Average Pore diameter [nm]</th>
<th>J_{SC} [μA/cm²]</th>
<th>V_{OC} [V]</th>
<th>FF [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>930</td>
<td>2.67</td>
<td>0.278</td>
<td>38.5</td>
</tr>
<tr>
<td>250</td>
<td>2.18</td>
<td>0.254</td>
<td>40.1</td>
</tr>
<tr>
<td>90</td>
<td>48</td>
<td>0.175</td>
<td>39.7</td>
</tr>
</tbody>
</table>

Heat treatment of the whole structure had direct influence on the solar cell parameters. Fig. 10 shows the influence of annealing of the whole structure at 120°C for 10 min on the J-V characteristics of the fabricated solar cell. From Fig. 10 it is seen that, by annealing at 120°C for 20 min the open-circuit voltage and short-circuit current density has been increased. The annealing of the fabricated final structure may have established good contacts between P3HT:PCBM and PSi.

**Fig. 10. Comparison the effect of annealing on J-V (Under 1.5AM light) characteristics.**

**IV. CONCLUSIONS**

The performance parameters such as, J_{SC}, V_{OC}, FF and conversion efficiency was low for our fabricated cells. This we believe was due to fabrication process used to fabricate the solar cell, processing environment, quality of the polymer blend etc. The highest improvement in short-circuit current density was approximately 73 times compared to the normal structure (without PSi). As the mentioned processing factors were common during the fabrication of all the solar cells, the enhancement in performance can be attributed to the incorporation of porous cathode with pore-diameter comparable to photogenerated charge transport length. It ensures a highly efficient charge extraction by macro-PSi, as most of generated charges are very close to the electrodes, giving a high probability of being collected before recombining. Furthermore use of macroporous silicon might have also contributed in reduction of light reflection and increase in light trapping [13]. Altogether, it can be concluded that macroporous silicon having optimized pore-diameter and pore-depth that are comparable to the photogenerated charge transport length can be used in the hybrid solar cells for enhanced performance.

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