Poly(3,4-ethyllenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS), a P-type organic polymer is frequently employed in the fabrication of heterojunction p-n solar cell devices due to its proper HOMO-LUMO band gap as well as its tunable conductivity. Addition of small volume percentage of organic additives such as dimethyl sulfoxide (DMSO) has a positive effect on the conductivity of this polymer. In this report we describe the incorporation of gold (Au) nanocluster in the PEDOT: PSS and the effect of this blend on the power-conversion efficiency (PCE) on planer silicon (Si) hybrid heterojunction solar cell devices. Specifically, the reference sample Au nanocluster and PEDOT: PSS blend in the electricalPerformance of Hybrid silicon solar cell.

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Organic-Inorganic Hybrid Solar Cell Efficiency Improvement by Employing Au Nanocluster

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Abstract — Poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), a P-type organic polymer is frequently employed in the fabrication of heterojunction p–n solar cell devices due to its proper HOMO-LUMO band gap as well as its tunable conductivity. Addition of small volume percentage of organic additives such as dimethyl sulfoxide (DMSO) has a positive effect on the conductivity of this polymer. In this report we describe the incorporation of gold (Au) nanocluster in the PEDOT: PSS and the effect of this blend on the power-conversion efficiency (PCE) on planer silicon (Si) hybrid heterojunction solar cell devices. Specifically, the reference sample without the aforementioned nanocluster were measured to exhibit a 6.10 % PCE value that increase to 7.55% upon the addition of the Au nanocluster. The observed increase in the PCE is attributed to the enhanced electrical conductivity of the PEDOT: PSS film due to the incorporation of the nanocluster, which is directly reflected in their improved fill factor. It is further theorized that presence of Au nanocluster in the insulating PSS layer in the PEDOT: PSS blend have a positive influence in the charge collection effectiveness of the devices produced. Considering that the Au nanoparticles involved in this research exercise had an average size of only 4nm, it is consider that plasmonic effect did not play a relevant role in the observed PCE improvement.

Index Terms — hybrid solar cell, tunable conductivity, organic polymer, heterojunction, nanocluster

I. INTRODUCTION

Recently, organic/inorganic hybrid heterojunction solar cells have been extensively studied because the organic material spin cast on a wafer surface forms a Schottky junction with silicon (Si), that replaces the conventional Si p–n junction. These heterojunction devices are intended to exploit the advantageous properties of both organic and inorganic materials in terms of low temperature and attractive fabrication cost of the devices involved. Frequently, the produced structures are based on poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), i.e., PEDOT:PSS, on silicon. This particular selection is based on the reported relatively high power conversion efficiency and high stability of the devices produce. Additionally, several schemes including three dimensional (3D) nanowires structures, the addition of guest materials, surface and interface passivation, among others, have been employed in an attempt to improve the efficiency of the described devices. Nonetheless, the power conversion efficiency (PCE) of the produced structures remains below the values of their purely inorganic counterparts. Some major hurdles, such as excessive recombination of carriers, decay of excitons within their diffusion length (≤10 nm) and ineffective carrier transport inside the PEDOT:PSS layer, represent serious limitations to the efficiency of the fabricated devices. In order to address some of these issues, different groups have also incorporated Si nanostructures such as silicon nanowires (SiNWs), silicon nanocones (SiNCs), silicon nanoholes (SiNHS), silicon nanopillars (SiNPs), etc., in their respective active polymer layers. The commercially available PEDOT:PSS solution does not wet easily a highly hydrophobic SiNW array textured surface and the spacing between the nanowires is normally too small to be filled with the conductive polymer to form a core–shell heterojunction. Therefore, other organic compounds are frequently added to ensure a complete coverage on the dense vertical SiNW array. Furthermore, the performance of a SiNW/organic polymer hybrid solar cell depends on the surface/interface preparation. Carrier recombination at the surface/interface of the SiNWs. Here, we describe hybrid heterojunction solar cells based on Au nanoclusters embedded in PEDOT:PSS films spin cast on planar silicon surfaces. The 4-mercaptopbenzoic acid protected Au nanoclusters of size 3-5 nm were synthesized by wet chemical methods and were incorporated to pristine PEDOT:PSS films. The charge collection efficiency of the described devices was noticeably improved by the incorporation of the aforementioned nanoclusters due to the improved electrical conductivity, additionally, AFM inspection indicated a decreased surface roughness of the Au nanoclustered embedded PEDOT:PSS films. The observed plasmonic effects of the Au nanoclusters employed were considered to have a marginal influence on device performance.

II. EXPERIMENTAL DETAILS

The nanoclusters were synthesized by slightly modifying reaction times in some of the steps and scale of the reaction of the procedure reported by Wong et al [1]. Four inch, single side polished, n-type silicon (100) wafers with a resistivity of 1–10 Ω-cm, were cleaned using a piranha solution for device fabrication. Subsequently, the samples were subjected to a standard RCA cleaning procedure. The samples were then exposed to ambient air for approximately one hour to increase
the hydrophilicity of the surface. 10 nm Ni and 400 nm Ag films were sputtered on the unpolished side of the wafer as a rear electrode. Then, highly conductive poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) in 5 wt% dimethyl sulfoxide (DMSO) was mixed with the previously prepared Au nanocluster solution in the volume ratio of 1:1. Two series of samples were fabricated and tested, which are henceforth referred to as samples A and samples B, respectively. The former samples were prepared by spin casting the organic polymer PEDOT:PSS (DMSO included) without Au nanoclusters, on the rigorously cleaned silicon samples at different spin coating speeds. Samples B were prepared by spin casting the aforementioned organic polymer with Au nanoclusters, on similarly cleaned silicon substrates also at different spin casting speeds. All the samples were then annealed at 140°C on a hot plate for 30 min. Finally, 200 nm thick Ag finger electrodes were fabricated as a front side contact of the devices employing a shadow mask. The devices were then diced creating an active area of 1cm × 1cm for testing. Figure 1 depicts the schematics of the fabricated hybrid heterojunction devices with and without Au nanoclusters.

III. RESULTS AND DISCUSSION

Figure 2a depicts the TEM image of the highly monodisperse Au nanoclusters. The p-MBA is employed to preclude the synthesized nanoclusters from coalescing. Figure 2b shows the particle size distribution of the Au nanoclusters that had an average size of 4 nm. Once the nanoclusters had been synthesized, they were mixed with the PEDOT: PSS. The performance of the fabricated devices was anticipated to depend on several parameters associated with the polymer films, including conductivity, thickness, and surface roughness, to name a few.

Figures 3a-b depict the measured values of $V_{OC}$ and $J_{SC}$ for both samples A and B, as a function of the spin coating rate of the PEDOT:PSS blend. Ostensibly, the values of both the $V_{OC}$ and $J_{SC}$ initially improve with the increase in spin coating rate of the polymer blend PEDOT:PSS for all the samples. However, the values for samples A deteriorate as the spin coating rate increases beyond 3500 rpm, while the values for samples B decrease when the spin coating rate exceeds 3000 rpm. The maximum values of $V_{OC}$ and $J_{SC}$ of 538 mV and 21.6 mA/cm² measured for samples B (with Au nanocluster in the PEDOT:PSS blend), compare favorably to the corresponding measured values of 529 mV and 18.1 mA/cm² of samples without the nanoclusters. Figures 4a-b depict the measured values of the fill factors and power conversion efficiencies for all samples as a function of the spin coating rate of the PEDOT:PSS blends. The influence of nanoclusters on the collected $V_{OC}$ and $J_{SC}$ was reflected on higher fill factor and power conversion efficiency (PCE) values measured on the samples with Au nanoclusters. Specifically, the measured PCE reached 7.55% when the nanoclusters were employed while the PCE was observed to be 6.10% when the nanoclusters were absent. Figure 5 depicts the J-V characteristics of the curves for the optimized devices for both the samples A and B respectively, while the Table 1 shows the photovoltaic performance parameters of the corresponding devices.
Table 1: Solar cell performance parameters including $J_{SC}$, $V_{OC}$ and PCE of devices without (Samples A) and with (Samples B) Au nanoclusters embedded in the PEDOT:PSS layer.

<table>
<thead>
<tr>
<th>Cell type</th>
<th>$V_{OC}$ (mV)</th>
<th>$J_{SC}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>$Rs$ (ohm-cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>529</td>
<td>18.1</td>
<td>63.0</td>
<td>6.10</td>
<td>10.1</td>
</tr>
<tr>
<td>Sample B</td>
<td>538</td>
<td>21.6</td>
<td>65.1</td>
<td>7.55</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Furthermore, the electrical performance of samples with Au nanoclusters embedded in the PEDOT:PSS blend was observed to be better than on samples without nanoclusters. This is attributed to the increased electrical conductivity of the PEDOT:PSS films with the incorporation of the aforementioned nanoclusters. Specifically, the average measured sheet resistivity with a four-point-probe tool of a nanoparticle-free, polymeric blend was 195 Ω/sq, whereas this value was reduced to an average of 116 Ω/sq upon dispersing the Au nanoclusters in the corresponding films.

Figure 5 J-V characteristics curves of devices with (in red) and without (in blue) Au nanoclusters incorporated in the PEDOT:PSS blend.

This damping in the plasmon peak can be associated to particle size where ohmic losses are reported to be prevalent[2].

Figure 6 a.) Measured UV-VIS spectra of the synthesized Au nanoclusters as a function of wavelength for three different nanocluster concentrations of 3mL (black), 4mL (blue) and 6mL (red) in the original solution prior to centrifugation, (b.) measured Raman spectra of R6G dye molecules on an aluminum substrate without (in red) and with Au nanoclusters (in blue), respectively.

in solar cell performance was mostly due to the increased electrical conductivity of the PEDOT:PSS blend due to the incorporation of Au nanoclusters, rather than their plasmonic effects

IV. CONCLUSIONS

We report the enhancement in the power conversion efficiency of a heterojunction hybrid solar cell based on p-type organic polymer PEDOT:PSS and n-type planar silicon by the incorporation of Au nanoclusters in the polymer layer. The synthesized p-MBA protected nanoclusters manifested a relatively weak plasmonic peak in the collected UV-VIS absorption spectrum. However, the presence of Au nanoclusters in the PEDOT:PSS blend increased the electrical conductivity of the films employed. A power conversion efficiency in excess of 7.5% has been measured for the described devices with Au nanoclusters in the PEDOT:PSS blend, which is almost ~23.77% higher than the values observed in devices without the aforementioned nanoclusters. The observed increase in the PCE of the device is mainly due to an improved charge collection efficiency which is also reflected in the collected values of $J_{SC}$ and FF that increased due to the improved electrical conductivity of the PEDOT:PSS blend.

REFERENCES