

# HYBRID SOLAR CELLS USING GAAS NANOPILLARS

R. B. Laghumavarapu<sup>1</sup>, G. Mariani<sup>1</sup>, B. Tremolet de Villers<sup>2</sup>, J. Shapiro<sup>1</sup>, P. Senanayake<sup>1</sup>, A. Lin<sup>1</sup>, B. J. Schwartz<sup>2,3</sup> and D. L. Huffaker<sup>1,3</sup>

<sup>1</sup>Electrical Engineering Department, University of California at Los Angeles, Los Angeles, CA-90094, USA

<sup>2</sup>Department of Chemistry and Biochemistry, University of California Los Angeles, Los Angeles, CA-90094, USA

<sup>3</sup>California NanoSystems Institute, University of California Los Angeles, Los Angeles, CA-90094, USA

## ABSTRACT

Light conversion and carrier transport in hybrid solar cells fabricated by spin coating poly(3-hexylthiophene) (P3HT) on ordered *n*-GaAs nanopillars are studied via electrical and optical characterization. The performance of hybrid nanopillar/P3HT solar cells is compared to control cells having either only P3HT or only GaAs nanopillars. The hybrid devices show better performance, with a  $V_{oc}$ ,  $J_{sc}$  and FF of 0.2 V, 8.7 mA/cm<sup>2</sup> and 32% respectively. Efficient exciton dissociation at the P3HT/GaAs interface was confirmed by PL quenching measurements.

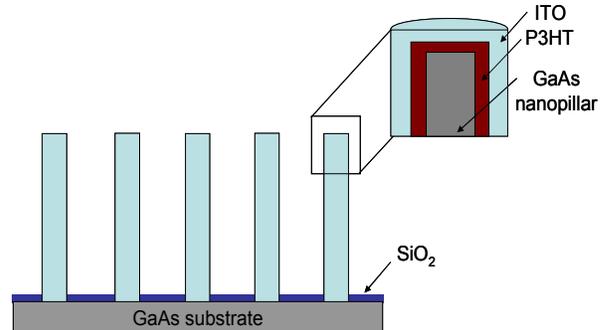
## INTRODUCTION

Recently, semiconducting conjugated polymers have been used in low-cost and flexible photovoltaic (PV) applications. Though significant improvements have been made, polymer-based solar cells still suffer from low energy conversion efficiencies ( $\leq 8\%$ ). This is largely because of the low charge-carrier mobilities ( $\sim 10^{-4}$  cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>) and short exciton diffusion lengths ( $\sim 10$  nm) that are intrinsic to disordered organic materials. Hybrid solar cells that combine conjugated polymers with inorganic materials offer the potential for improved power conversion efficiency by utilizing the strong light absorption of conjugated polymers and the high charge mobilities of inorganic semiconductors. To this end, there have been many marginally-successful attempts to use various nanostructures such as nanospheres [1-2], nanorods [3-6], and carbon nanotubes [7] in polymer-based solar. In this work, we use an ordered array of GaAs nanopillars engineered onto a GaAs substrate that is coated with poly(3-hexylthiophene) (P3HT) to increase exciton dissociation and to create higher mobility pathways for the charge carriers. These nanostructured hybrid solar cells thus have several benefits: the hybrid structures have low reflective losses and the nanopillar architecture helps to trap the absorbed solar radiation [8]; the P3HT excitons created by the absorbed light readily undergo dissociation, as verified by photoluminescence (PL) measurements; and carrier extraction from the devices is efficient, as seen in the high short-circuit current densities.

## DEVICE FABRICATION

To understand the operation of our hybrid solar cells, we worked to make a comparative study between GaAs nanopillar devices with and without P3HT as well as P3HT/GaAs planar devices without nanopillars. Figure 1

shows a schematic of GaAs nanopillars/P3HT hybrid solar cells used in this work. Nanopillars were grown using metal organic chemical vapor deposition (MOCVD) on *n*-GaAs (111)B substrates. Prior to the pillar growth, SiO<sub>2</sub> was deposited onto the substrate and 500  $\mu\text{m} \times 500 \mu\text{m}$  patterns were made using e-beam lithography. The nanopillars have an *n*-doping level of  $5 \times 10^{17}$  cm<sup>-3</sup>. Before



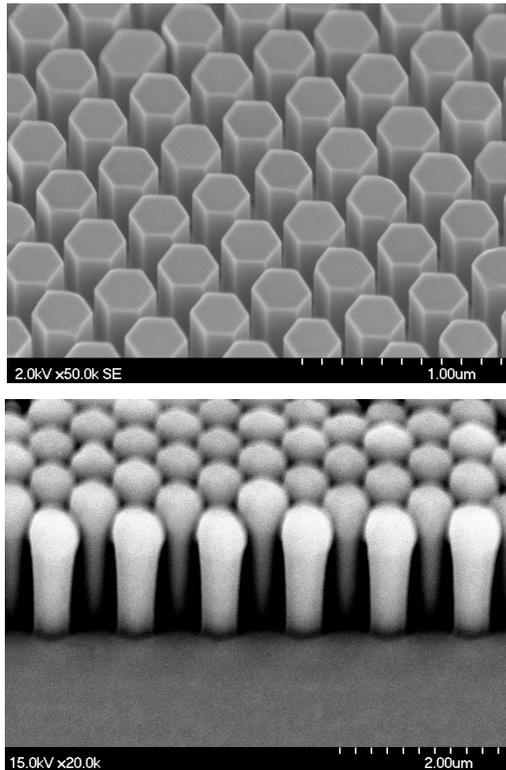
**Figure 1 Schematic diagram of P3HT/GaAs nanopillars hybrid solar cells.**

spincoating P3HT onto the nanopillars, the native oxide was removed using an HCl:H<sub>2</sub>O mixture for 30 s. Ohmic bottom contacts were prepared using AuGe/Ni/Au and annealing the substrate at 400 °C for 45 seconds. The hybrid solar cells were then prepared by spincoating P3HT (90-93% regioregular, Rieke Metals) from a 1,2-dichlorobenzene solution onto the nanopillar samples to produce a polymer film ( $\leq 100$  nm thick). To complete the devices, transparent indium tin oxide (SnO<sub>2</sub>/In<sub>2</sub>O<sub>3</sub> 10:90 wt%) (ITO) was RF sputtered at room temperature; the ITO was sputtered immediately after spincoating the P3HT to avoid photo-oxidation of the polymer. The ITO was not thermally annealed due to thermal destruction of P3HT at the necessary  $\sim 400$  °C temperature. Figure 2 shows an SEM image of both the as-grown *n*-GaAs nanopillars and the final hybrid solar cells. The average nanopillar height is about 1.5  $\mu\text{m}$  with a center-to-center pitch of 600 nm. Fig. 2 shows that ITO did not planarize the sample but instead conformally coated the surface of the pillars, a fortuitous consequence that leads to both trapping and guiding of the incident light during device operation.

## EXPERIMENTAL

The current density versus voltage (J-V) characteristics of the hybrid solar cells, measured under AM 1.5G, 1000

$W/m^2$  illumination conditions using a 300 W Oriel solar simulator and a Keithley 2602 source meter, are shown on linear and semi-logarithmic scales in Figs. 3 (a) and (b), respectively. The P3HT/GaAs nanopillar hybrid device exhibited an open circuit voltage ( $V_{oc}$ ), short circuit current density ( $J_{sc}$ ), and a fill factor of 0.2 V, 8.7  $mA/cm^2$ , and 32%, respectively, demonstrating a power conversion efficiency of 0.6%. The control sample with only GaAs nanopillars showed no photovoltaic response, as expected given the lack of a  $p-n$  junction for dissociating the

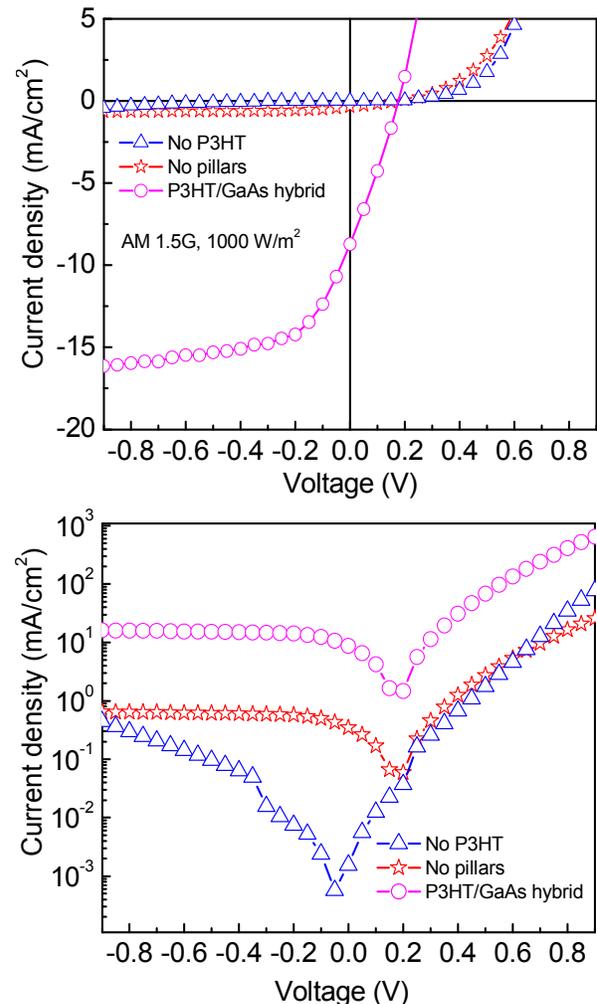


**Figure 2** SEM image of as grown n-GaAs nanopillars (top) and final hybrid solar cells after P3HT and ITO deposition (bottom).

excitons in this sample. The control sample with no pillars showed a weak photoresponse, demonstrating that the small amount of planar P3HT/GaAs contact through the patterned  $SiO_2$  layer does allow for some degree of exciton dissociation and subsequent transport of the charges to the electrodes. Clearly, the presence of both P3HT and GaAs nanopillars is critical to the successful operation of the hybrid devices.

We believe that the hybrid nanopillar devices lead to improved performance over single-material planar devices in two important ways. First, the SEM image in the bottom panel of Fig. 2 suggests that the P3HT layer spin-cast onto the pillars is thinner compared to the P3HT films used in planar cells. This allows excitons to easily diffuse to the donor/acceptor heterojunction within their lifetime, improving exciton harvesting. Second, the pillar architecture creates significantly more interfacial area in

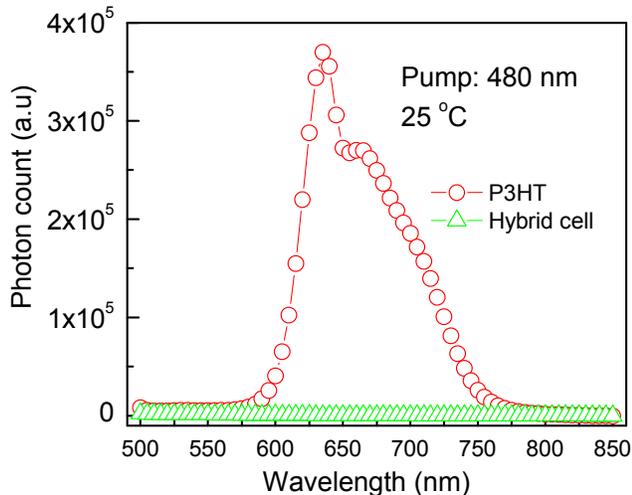
contact with P3HT, therefore improving the number of excitons that are split and hence increasing the photocurrent.



**Figure 3** (a) J-V (b)  $\ln(J)$ -V characteristics of a P3HT / GaAs hybrid solar cell and cells without P3HT and without nanopillars.

In previous work, we have shown that the photocurrent in hybrid P3HT/GaAs nanopillar solar cells can be increased further if the pillar surface is passivated with ammonium sulfide ( $(NH_4)_2S$ ) for 60 minutes [9]. This is because passivation helps reduce the presence of surface states on the pillars that can act recombination sites and traps for charge carriers. The fact that the cells with the passivated GaAs pillars still show only  $\sim 1.44\%$  power conversion efficiency [9] means that the performance of these solar cells remain limited by several other factors, including: 1) the non-ideal energy band offsets of the organic and inorganic components, which leads to low  $V_{oc}$ ; 2) the misbalanced charge mobilities of the two components (the hole mobility in P3HT is much lower than the electron mobility in GaAs), which leads to poor carrier extraction and thus a poor device fill factor [10,11].

To better understand the separation of the photo-generated charge carriers in our hybrid devices, we performed PL quenching measurements, which are shown in Fig 4. These measurements were carried out with a Horiba-Jobin Yvon Fluorolog-3 fluorimeter, with the samples excited at 480 nm and P3HT emission collected between 500 and 850 nm. In the absence of the GaAs



**Figure 4 Photoluminescence spectra from the GaAs nanopillars/P3HT hybrid solar cell (squares) and hybrid cell without nanopillars (circles).**

nanopillars, the P3HT displayed the strong emission that is typical of conjugated polymers. But in the presence of the nanopillars, the P3HT emission is highly quenched, confirming that photo-generated excitons in the polymer are efficiently split at the P3HT/GaAs nanopillar interface.

### CONCLUSIONS

We have demonstrated that hybrid solar cells using GaAs nanopillars and P3HT polymer present a promising strategy for simultaneously exploiting the large absorption of conjugated polymers and the efficient charge conduction of inorganic semiconductors. Our results show that a significant photovoltaic effect takes place only when both the GaAs nanostructures and P3HT are present. Our PL experiments confirm that efficient exciton dissociation takes place at the P3HT/GaAs nanopillar interface. For future improvements, we are working towards obtaining a detailed understanding of carrier transport at the organic/inorganic heterojunction as well as the requirements for optimal band alignment of the polymer and inorganic semiconductor materials.

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Authors R.B. Laghumavarapu, G. Mariani and B. Tremolet de Villers contributed equally to this work.

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