Hybrid solar cells based on porous Si and copper phthalocyanine derivatives

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We demonstrate a solar cell based on n-type nanoporous Si (PSi) filled with copper phthalocyanine (CuPC) and its derivatives (including a discotic liquid crystal form). The CuPC device shows conversion efficiency up to 2% under white light illumination (20–30 mW/cm^2), distinct from cells filled with CuPC derivatives with alkyl chains attached to the core. It is concluded that a critical issue for efficient photocarrier generation is the distance between the CuPC core and the PSi surface. Both organic and inorganic components contribute to photoinduced charge transfer and transport processes. The influence of the PSi structure and pore filling on the solar cell performance is discussed. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1839280]

The study and development of organic and hybrid thin film photovoltaics (PVs) (third generation solar cells) has attracted attention due to the opportunity to reach 10% conversion efficiency. Substantial improvement has been made in device design and choice of new organic and inorganic materials. For purely organic solar cells, the use of donor–acceptor molecules,[1–3] polymers,[4,5] liquid crystals,[6] and carbon nanotubes[7,8] in combination with various heterojunctions (blended, flat, laminated) resulted in new device concepts and improved understanding of energy conversion processes. Organic–inorganic hybrid cells also demonstrated enhanced performance due to nanoscale fabrication of inorganic components (nanodots,[9] nanorods[10]), the use of Si and III–V type semiconductors,[11,12] and novel types of dyes and hole transport materials for solid dye synthesized solid cells (DSSCs).[13] DSSCs based on mesoporous TiO$_2$ have been an attractive alternative to the purely organic devices because of their huge interfacial area and high electron mobility in mesoporous titania.[13,14] The main efforts in this area have been directed toward synthesis of dyes with an absorption spectrum in the near-infrared (NIR) range (better matching the solar spectrum) and improving the hole-transport properties of the p-type semiconductors. Meanwhile, employment of other nanoporous inorganic matrices filled with organic materials could lead to fabrication of hybrid photovoltaics systems with efficient photoinduced charge transfer (PCT) and fast charge transport.

In this letter we demonstrate a solar cell based on n-type nanoporous Si (PSi) filled with copper phthalocyanine (CuPC) and its derivatives (including a discotic liquid crystal form). The distinctive feature of such a cell is the contribution of the semiconductor matrix to light absorption and energy conversion, which is impossible for TiO$_2$ based DSSCs. Also, the PSi structure provides a large interfacial area between the organics and the semiconductor, in contrast to a flat heterojunction,[11,12] and reduces reflection as compared with bulk Si.

PV cells were prepared as follows. The back side of a Si wafer was treated with HF/ethanol solution to remove SiO$_2$ followed by evaporation by Al (20 nm) or Cr/Au (20 nm/150 nm) to form an ohmic contact. We used n-type Si (100 orientation, resistivity=0.025 Ω cm) because PCT from CuPC to Si has been observed for n-type Si but not p-type Si.[15] Nanoporous Si layers (300–2000 nm) were prepared by Si anodization in HF/ethanol solution (15%) followed by plasma etching to ensure that all pores were opened [Fig. 1(a)]. Some samples were processed without plasma etching to provide references. CuPC (Aldrich) and its derivatives CuPC1 (Aldrich) and CuPC2 (discotic liquid crystal, Polymer Source, Inc.) were chosen as organic fillers
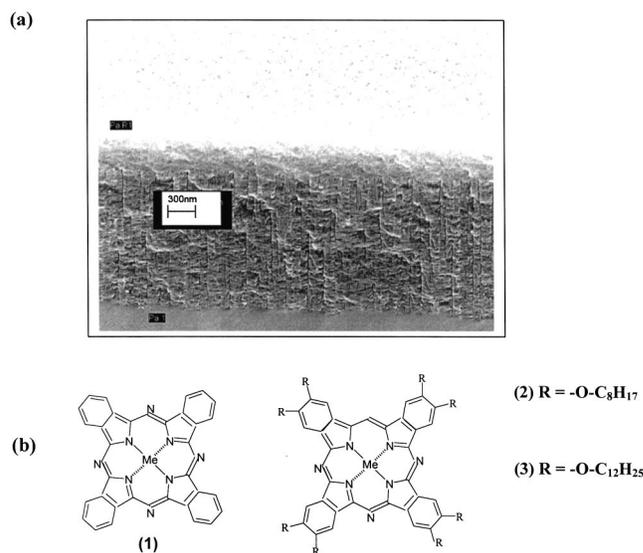

FIG. 1. (a) SEM image of Si surface and cross section after electrochemical etching: 15% HF/ethanol solution, 20 s, 50 mA/cm^2, 300 nm scale; (b) chemical structure of CuPC (1), CuPC1 (2), and liquid crystal CuPC2 (3).

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[Fig. 1(b)]. The choice of CuPC2 was motivated by the possibility of increasing the hole mobility along the quasi-one-dimensional columns similar to the LC coronene derivatives.[6] A DSC measurement of CuPC2 showed the LC mesophase in the range of 67–250 °C, consistent with previously reported data.[16] CuPC1 was used as an intermediate form between CuPC and CuPC2. It is important that LC phthalocyanines can preserve their columnar structure in the solid phase after cooling.[17]

PSi was filled by dropping a solution ($\sim 10^{-2}$ M) of CuPC (concentrated H_2SO_4), CuPCl ($CHCl_3$), or CuPC2 ($CHCl_3$) onto the surface followed by the mechanical pressing (~ 7 kg/cm^2) for 30 s and rinsing with water (CuPC) or chloroform (CuPC1, CuPC2). LC CuPC2 was also spin-cast onto a PSi substrate followed by heating to 80 °C (above the solid–LC transition) and left to cool slowly to ambient temperature. The top electrode (anode) was deposited onto the organic/PSi surface by sputtering gold (~ 20 nm) or ITO (80–100 nm) through a shadow mask. The active area of the cell was about 0.05 cm^2.

The devices were tested under dark and illuminated conditions using a 250 W halogen–tungsten lamp (QTH 6334, Oriel) equipped with a KG4 heat absorbing filter. Proximity to the standard solar simulator (class B) was estimated by the value of conversion efficiency of the calibrated silicon photodiode, which was less than 25% of NREL data. The light intensity was measured by an Oriel 70260 broadband power meter and was varied by circular neutral filters. I–V characteristics were detected by a Keithley 236 source-measure unit connected to a PC. A Perkin-Elmer Lambda 900 spectrophotometer was used to record vis–NIR absorption spectra.

The physical picture of the PCT and charge transport to the external electrodes is complex even without an organic filler: such a cell has one heterojunction between PSi ($E_g \sim 2$ eV, $\chi = 3.6$ eV) and bulk Si ($E_g \sim 1.1$ eV, $\chi = 4.0$ eV) and probably a Schottky barrier between PSi and gold or ITO (top electrode), which could be a source of a PV effect. Therefore, references samples without organic fillers were tested. It was found that the conversion efficiency (η) for these samples is small ($\eta < 0.01\%$) under white light illumination (30 mW/cm^2). I–V characteristics of these samples demonstrate a diode behavior and can be fitted well by the diode equation[18] in the range of 0–0.07 V.

PV response of the Au/PSi–CuPC1/Al cell was low, but higher than that for reference cells without organics. The best conversion efficiency was $\sim 0.02\%$ (30 mW/cm^2) and could be slightly improved after 15 h annealing at 100 °C. No significant change was observed for an ITO electrode. Although we expected to find a strong PV response in the PSi filled with the LC CuPC2, the device conversion efficiency was comparable to that of references cells ($< 0.01\%$) for different kinds of PSi and top electrodes.

Relatively high conversion efficiency (up to 2%) was observed for PSi filled with CuPC. Figure 2 shows the series of I–V characteristics, conversion efficiency, and fill factor for an ITO/PSi–CuPC/Al cell at variable light power. The η value reaches a maximum at ~ 20–30 mW/cm^2 and then decreases at higher intensity due to the effect of series resistance ($R_s = 24$ Ω cm^{-2}). It was found that I–V curves of PSi samples that were not treated by plasma etching to open all pores exhibited a "kink" behavior [Fig. 2(a), inset] leading to a decrease of the V_{oc} and I_{sc} values. A similar "kink" was
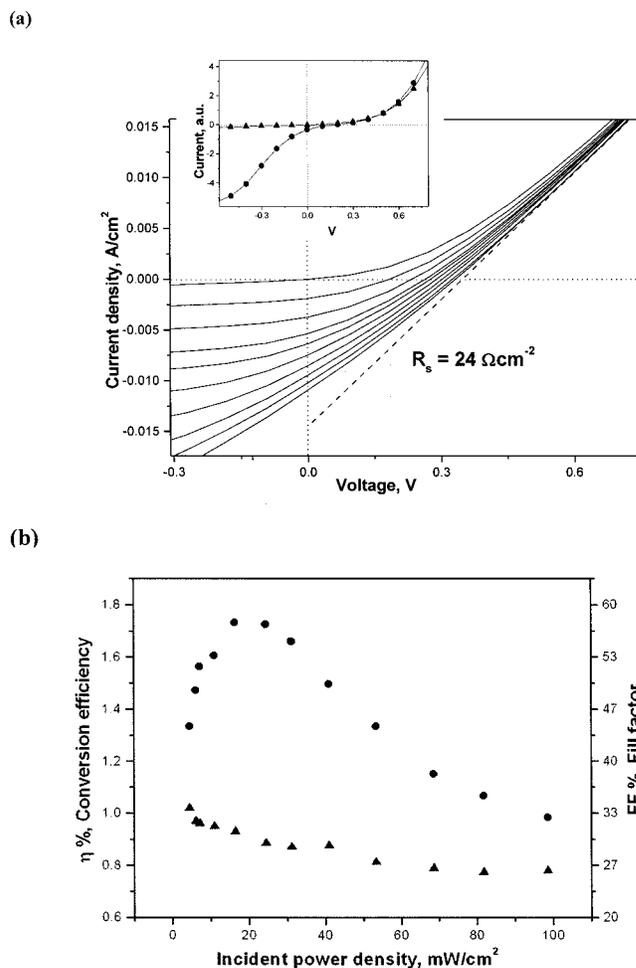
(a)

(b)

FIG. 2. (a) I–V characteristics of the ITO/PSi–CuPC/Si/Al cell at variable light power. From top to bottom: dark, 7, 16, 24, 30, 40, 52, 68, 80, 100 mW/cm^2; (b) power conversion efficiency (circles) and fill factor (triangles) of this cell. Some samples demonstrate $\eta \sim 2$–2.2% at 20–30 mW/cm^2. Inset shows the I–V characteristic for cell without plasma treatment (triangle-dark, circle-light, 30 mW/cm^2).

observed in other reports[2,19,20] and was explained recently in a theoretical study.[21] We can suggest that samples with a poorly developed pore structure or with partially opened pores cannot provide a sufficiently dense filling of CuPC molecules to form a "conductive wire" for hole transport to the anode. This is consistent with the theoretical model,[21] which indicates that the I–V curve degradation ("kink" feature) occurs as a result of a decrease of the hopping coefficient: poor pore filling leads to isolation of the CuPC aggregates making them insulated from each other.

The striking difference between low (CuPC1, CuPC2) and high (CuPC) conversion efficiency of hybrid devices can be understood in terms of the interfacial area between organic and inorganic components. Likely, the electron transfer from CuPC1 to Si is slow or nonexistent due to relatively long alkyl chains [Fig. 1(b)], which can prevent close contact of the CuPC1 molecular core with PSi. This is supported by the fact that the LC CuPC2 based cell has the lowest η value, comparable to that of the references. Thus, the critical issue becomes an average distance between a CuPC core to the PSi surface and LC organization cannot compensate for the low PCT caused by the long alkyl chains.

Contribution of the CuPC to the PV effect can be seen in the spectral dependence of external conversion efficiency,
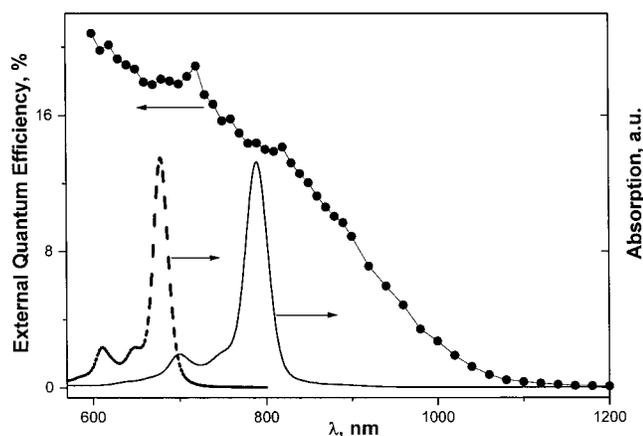
FIG. 3. External quantum efficiency of the Au/PSi–CuPC/Si/Al cell. Absorption spectra of CuPC in concentrated H_2SO_4 solution (solid line) and CuPC1 in chloroform solution (dashed line). Concentration is 10^{-5} M. Shift of CuPC spectrum with respect to CuPC1 spectrum is the result of CuPC protonation in H_2SO_4 solution.

which exhibits two peaks (720 and 820 nm), matching the absorption bands of the protonated CuPC form in H_2SO_4 solution (Fig. 3). A small shift to longer wavelengths ($\sim$20 nm) can be associated with aggregate formation of the protonated CuPC inside the nanopores. The long wavelength edge of the spectrum corresponds to the band gap of Si (1.1 eV) but not PSi ($\sim$2 eV). Hence, the absorbance of the porous layer is low or the porosity in the *n*-type Si is not sufficient to change the band gap. Replacement of the ITO anode by Au does not change the V_{oc} value ($\sim$0.3 V, 30 mW/cm^2), but decreases the backward dark current. Independence of V_{oc} on electrode work function (ITO, 4.5–4.7 eV and Au, 5.1 eV) can be associated with the fact that organic and hybrid PV cells do not require a built-in electrostatic potential for charge separation, unlike inorganic devices.[21,22]

In summary, we demonstrate that the heterojunction between nanoporous Si and copper phthalocyanine can provide an efficient PV effect with conversion efficiency up to 2% under white illumination (20–30 mW/cm^2). Our preliminary x-ray photoelectron spectroscopy data for CuPC based cells demonstrates that the characteristic depth for pore filling is about 150–200 nm. Both CuPC and PSi contribute to the photocarrier generation. Further improvements in the device performance are expected with pore diameter/depth/structure optimization, increasing of the filling pressure, and fabrication of thin, free-standing PSi membranes.

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