

Schottky diodes on nanowires of copper phthalocyanine

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ABSTRACT

Vertically aligned nanowire arrays of copper phthalocyanine (CuPc) of 30 nm diameter and 500 nm length were fabricated by cathodic electrodeposition of CuPc into anodized alumina (AAO) templates. Schottky diodes were formed between CuPc nanowires and aluminum electrode; ITO served as the ohmic contact. Insertion of a thin layer of PEDOT:PSS between CuPc nanowires and the ITO electrode improved the contact and reduced the series resistance by an order of magnitude. Effective diode ideality factors in the dark and under illumination were 30.5 and 12.3, respectively; corresponding values for the effective reverse saturation currents, J_0 , were 23 and 13 $\mu\text{A}/\text{cm}^2$.

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1. Introduction

Organic semiconductors like copper phthalocyanine (CuPc) are finding applications in a wide variety of optoelectronic devices including light-emitting diodes [1,2] and solar cells [3–14]. CuPc-based solar cells are of interest because of their potentials as flexible, lightweight and inexpensive devices for generating electrical power. High open circuit voltage (V_{oc}) values in CuPc-based solar cells have already been demonstrated [4,5,11]. However, short circuit current densities (J_{sc}) in these cells, as in organic semiconductor solar cells (OSSCs), in general, are low.

The major reason for low J_{sc} in OSSCs is the rather small exciton diffusion length of a few nanometer in these semiconductors. Nanowire cell designs and use of ordered structures offer a way out of this serious limitation and thus a path to high-efficiency OSSCs [12,13]. These device designs can be fabricated by first depositing a semiconductor like CuPc in the vertical pores of an anodized aluminum oxide (AAO) template, etching off the alumina walls and filling the gaps thus created with another suitable semiconductor like C_{60} [12,13]. We have taken a step forward in the development of this technology by forming CuPc–Al Schottky diodes in a nanowire mode and studying their characteristics.

Tong et al. [15,16] reported earlier on the synthesis of metal phthalocyanine nanoribbons and nanowires by organic vapour phase deposition. However, these were not formed inside a

template and therefore do not have the advantage of a tight control on the diameter, spacing and length of nanowires. Xu et al. [17] fabricated CuPc nanowire arrays in porous AAO templates and used a double-layer photoreceptor to demonstrate enhanced photosensitivity. We are the first group to take this further by employing ITO and aluminium electrodes to form Schottky diodes and study their characteristics. These results are presented and discussed in this article. Experimental procedures are given in Section 2. In Section 3, material characteristics of electrodeposited CuPc films in the pores of alumina are described and compared with the characteristics of electrodeposited CuPc films on planar ITO-coated glass. Electrical characteristics of Al/CuPc nanowire Schottky diodes and Al/planar CuPc Schottky diodes are presented and compared in Section 4.

2. Experimental procedures

Device structure (Fig. 1) showing CuPc nanowires on an aluminum substrate was fabricated by first preparing a short-length (~ 500 nm) anodized aluminum oxide template and subsequently filling it with CuPc by electrodeposition.

2.1. Fabrication of nanoporous alumina templates

AAO templates were prepared by anodizing aluminum tape at room temperature, in a vertical two-electrode cell with platinum as a counter electrode. The electrolyte was a solution containing 0.3 M oxalic acid dissolved in de-ionized water; one side of the tape was protected by glue and paper. The 2-step anodization

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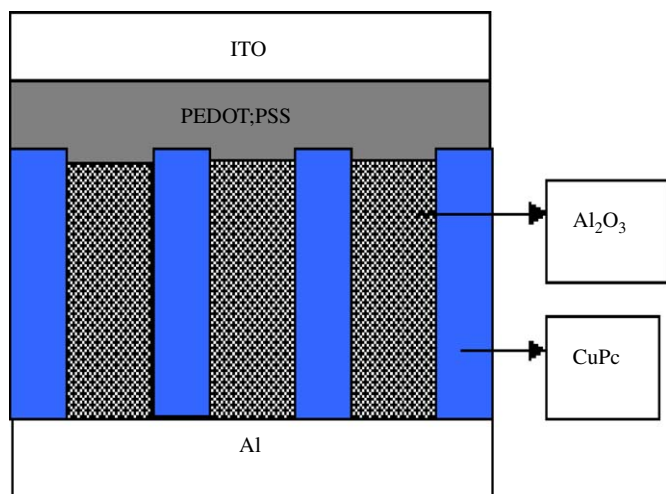


Fig. 1. Schematic device configuration of Schottky diodes between aluminum and CuPc Nanowires embedded in a porous alumina template.

process that we reported previously [18] was used to obtain highly ordered patterned pores. Removal of the barrier layer is critical for the formation of a suitable Al–CuPc interface. In an attempt to remove the barrier layer, ramp-down voltage was employed [18].

2.2. Electrodeposition of CuPc in AAO template

CuPc was electrodeposited inside the pores of alumina template supported by the underlying aluminum substrate [17–19]. Pores were, typically, 500 nm in length and 25 nm in width. The electrolyte was a chloroform (CHCl_3) solution containing 0.005 g CuPc with 1 ml Trifluoroacetic acid (CF_3COOH); CF_3COOH acted as a protonating reagent [17]. A $1'' \times 1''$ platinum electrode was used as anode and the AAO template served as cathode. Electrodeposition was carried out with an applied DC voltage of 15–30 V (ramped at the rate of 1 V/min). In the electrolyte solution, CuPc is thought to form complex structures of the form $\text{CuPc}(n\text{H})^{n+}$ (n varying from 1 to 4) in the presence of excess CF_3COOH [17]. These complexes, having a net positive charge, migrate towards the cathodic alumina substrate.

During the electrodeposition process, a thin layer of CuPc (10–50 nm) also got deposited over the surface of aluminum oxide; *N,N*-dimethylformamide solution was used for removing this top layer of CuPc. This process was repeated, typically two or three times, until the pores were completely filled with CuPc. The AAO template with CuPc nanowires was then annealed at 300 °C in vacuum for 5 h. Later, circular dots (0.07 cm^2 in area) of a thin layer of ITO (80 nm thick) were sputtered for making a conducting contact to CuPc nanowires. In some cases, to improve the contact between CuPc and ITO, a thin interlayer of PEDOT:PSS was spin-coated on top of CuPc. Aluminum at the bottom-end of the pores served as the Schottky contact to the CuPc nanowires. Next, current–voltage characteristics of these Schottky diodes were measured and analyzed.

For the electrodeposition of CuPc on planar substrates, for comparison, ITO-coated glass sheets with a sheet resistance of 4–8 Ω/Square from Delta Technologies were used as the starting substrates. CuPc film was next electrodeposited and aluminum contact was formed by vacuum evaporation [14]. Material characterization of these nanowires and films was performed with the techniques of X-ray diffraction (Bruker-AXS D8 DISCOVER Diffractometer), optical absorption spectroscopy and scanning electron microscopy (Hitachi S-900 field emission

SEM). Electrical characterization was performed with an automated system, which included an *I*–*V* tester, a solar simulator and an HP 4192A LF impedance analyzer.

3. CuPc characteristics

3.1. Electron microscopy

Fig. 2 shows the scanning electron micrographs of a typical starting alumina template used for electrodeposition of CuPc. The top view of the template (Fig. 2a) reveals hexagonal packed pores with pore diameter in the 20–30 nm range and pore spacing in the 30–40 nm range, for a template anodized at 40 V at room temperature. The cross-sectional view of this 500-nm-long AAO/Al template is shown in Fig. 2b. It can be seen that the pores get narrower along the bottom with branching as a result of ramp-down voltage. The pore diameters at the bottom of the anodized AAO/Al template ranged from 15 to 20 nm [18].

Cross-sectional view of the AAO sample after electrodeposition of CuPc is seen in Fig. 3a. The left side of the image includes the top surface of the AAO template with the pore openings. Fig. 3b shows the cross section at another location near the bottom (Al–CuPc interface) of the AAO pores. The unfilled portions of AAO pores seen in Fig. 3b are thought to have lost their CuPc nanowires due to the stress produced during the process of breaking the device and mounting it on the stub for electron microscopy.

3.2. Optical absorption

Measurement of the optical absorption spectrum of CuPc nanowires grown on aluminum was complicated by the presence of the opaque aluminum substrate. Therefore, for this measurement, AAO templates on ITO-coated glass were fabricated by first depositing an aluminum film through electron beam evaporation and subsequently anodizing it. Next, CuPc was electrodeposited in the pores using either a D.C. voltage or a pulsed voltage. Results are shown in Fig. 4. Two absorption bands were observed in the 300–450 and 550–750 nm regions. The intense band at 300–450 nm is related to direct electronic transition from $d-\pi^*$ orbitals and is called the Sorret band (S-band). On the other hand, strong absorption band in the red region of the spectrum is called the Q-band (550–750 nm). For the top curve, the electrolyte was 150 ml chloroform (CHCl_3) solution containing 0.004 g CuPc and 5 ml trifluoroacetic acid (CF_3COOH). Electrodeposition was conducted for 4 min, with voltage pulses of 125 V amplitude, 2 s pulse width and 6 s time period. The top CuPc layer was not removed intentionally. For the bottom curve, the electrolyte was a 50 ml chloroform solution containing 0.005 g CuPc with 1 ml trifluoroacetic acid. Electrodeposition was conducted with a D.C. voltage ramped from 15 to 30 V at a rate of 1 V/min with the top layer removed. Both were annealed at 200 °C. The SEM micrograph of the pulse-deposited CuPc showed a thick CuPc film over the top (~ 700 nm) but no deposition inside the pores (Fig. 5a), while with D.C. voltage CuPc filled the pores forming nanowires (~ 500 nm) (Fig. 5b). Thus, we note that a ramp voltage is preferable for getting the CuPc into the pores of AAO on ITO. The absorption curves for both conditions show peaks at 620 and 691 nm in conformity with the two peaks seen earlier for planar electrodeposited films [14]. CuPc has two absorption bands in the visible region: Sorret band (S-band) and Q-band. The absorption peaks in the visible region are generally interpreted in terms of $\pi-\pi^*$ excitation between bonding and anti-bonding molecular orbitals [20].

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