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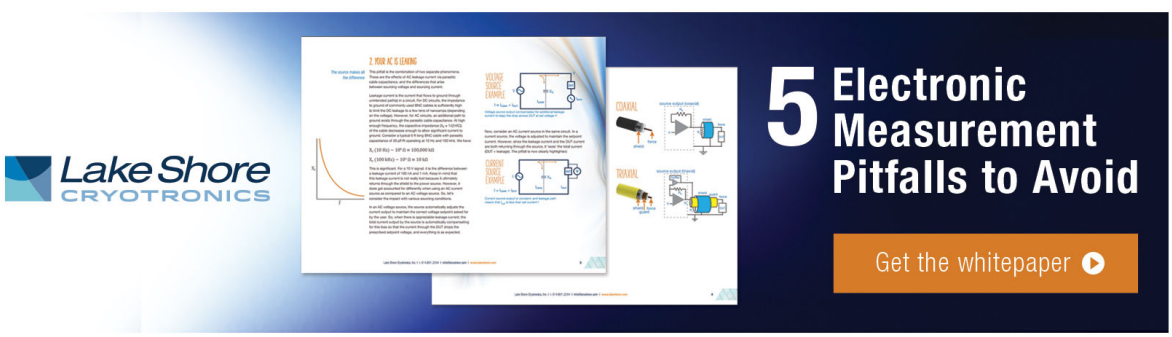

Two-layer organic photovoltaic cell

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A thin-film, two-layer organic photovoltaic cell has been fabricated from copper phthalocyanine and a perylene tetracarboxylic derivative. A power conversion efficiency of about 1% has been achieved under simulated AM2 illumination. A novel feature of the device is that the charge-generation efficiency is relatively independent of the bias voltage, resulting in cells with fill factor values as high as 0.65. The interface between the two organic materials, rather than the electrode/organic contacts, is crucial in determining the photovoltaic properties of the cell.

This letter reports a novel photovoltaic cell based on a two-layer structure of organic thin films. The structure is novel[1] in the sense that its photovoltaic properties are significantly different from those of conventional organic photovoltaic cells[2] in which a single layer of organic material is sandwiched between two dissimilar electrodes. In these single-layer cells, the built-in potential is derived either from the difference in work function of the electrodes or from a Schottky-type potential barrier at one of the metal/organic contacts.[3–9] In both cases, the photovoltaic properties are strongly dependent on the nature of the electrodes. Another characteristic commonly observed in single-layer cells is their poor fill factor (ff), which is usually attributed either to a large series resistance associated with the insulating nature of the organic layer or to the field-dependent generation of charges generally found in organic photoconductors.

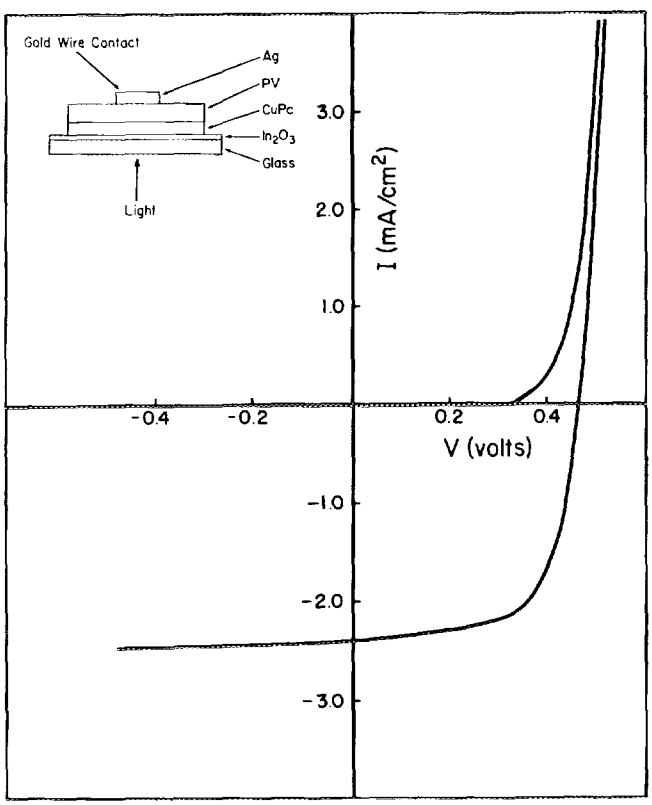
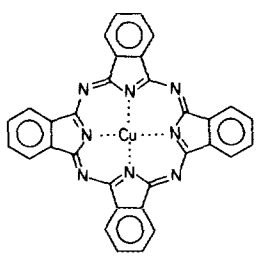


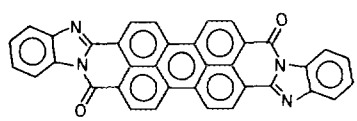
FIG. 1. Configuration and current-voltage characteristics of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell.

The present two-layer organic photovoltaic cell differs from conventional single-layer cells in that the interface between two thin organic layers is crucial in determining its photovoltaic properties. In particular, the interface region is primarily responsible for the photogeneration of charges. This generation efficiency is only weakly dependent on the bias field, thus overcoming the serious limitation of single-layer cells and providing the two-layer cell with a significantly higher fill factor. Furthermore, the magnitude and polarity of the open-circuit voltage (V_{oc}) in this two-layer system show a stronger dependence on the nature of the organic-organic interface than on that of the electrode-organic interfaces. It appears that the electrodes simply provide ohmic contacts to the organic layers.

Figure 1 shows the configuration of a typical two-layer organic cell. The indium tin oxide (ITO) coated glass (Nesatron by PPG) provided the transparent conducting substrate on which a layer of copper phthalocyanine (CuPc), about 300 Å thick, was deposited by conventional vacuum evaporation. A second layer of organic material, a perylene tetracarboxylic derivative (PV),[10] about 500 Å thick, was deposited on top of the CuPc layer by vacuum evaporation, and finally an opaque Ag layer was evaporated on top of the PV layer.



CuPc



PV

The area of the Ag electrode, 0.1 cm^2, defined the active area of the cell. Both CuPc and PV are thermally very stable, thus allowing their deposition by vacuum evaporation requiring source temperatures of about 500 and 600 °C, respectively. The substrate was maintained nominally at room temperature during deposition.

The current-voltage (I-V) characteristics of the cell in the dark and under simulated AM2 illumination (75 mW/cm^2) are shown in Fig. 1. The forward bias direction corresponds to a positive voltage on the ITO electrode. The dark

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I-V curve in the forward bias can be described by the Shockley equation

$$I = I_0[\exp(qV/nkT) - 1],$$

over a voltage range of 150–550 mV. The values of I_0 and n are $\sim 5\text{–}10 \times 10^{-9}$ A/cm^2 and 1.5–1.7, respectively.

Typical cell parameters, under simulated AM2 illumination (75 mW/cm^2), are the following. $V_{oc} = 450 \pm 20$ mV, $I_{sc} = 2.3 \pm 0.1$ mA/cm^2, and ff $= 0.65 \pm 0.03$. The best power conversion efficiency obtained under such illumination, and without correcting for reflection or electrode absorption losses, was 0.95%, which represents one of the highest efficiencies reported for organic solar cells. Likewise, a fill factor of 0.65 represents a substantial improvement over values previously obtained for organic cells. The I-V characteristics illustrated in Fig. 1 also show that the photogenerated current has only a weak dependence on the reverse bias voltage. The short-circuit photocurrent and the photocurrent at 0.5 V reverse bias differ by only about 5%. In the forward direction, the dynamic resistance is about 100 Ω, which represents an upper limit of the series resistance of the two-layer cell.

Figure 2 shows the photovoltaic spectral response of the ITO/CuPc (~ 300 Å)/PV(~ 500 Å)/Ag cell, as well as the absorption spectrum of the CuPc/PV layers. Although the absorption spectra of CuPc and PV films overlap to a large extent (the absorption maxima of CuPc and PV films are centered at 615 and 540 nm, respectively), both the CuPc and PV layers contribute to the photogeneration of carriers. The region of maximum photosensitivity is at the CuPc/PV interface. This can be inferred from the dependence of the spectral response on the thickness of the CuPc film, since for a thicker CuPc film an inverse spectral response behavior and a corresponding decrease in efficiency are observed. The absolute collection efficiency of this cell has a maximum value of about 15% at $\lambda = 620$ nm.

The V_{oc} of the CuPc/PV two-layer cell was relatively independent of the electrode materials. A series of cells were prepared with ITO as the transparent electrode adjacent to the CuPc layer and with different metals in contact with the PV layer as the top electrode. Use of several metals of diverse

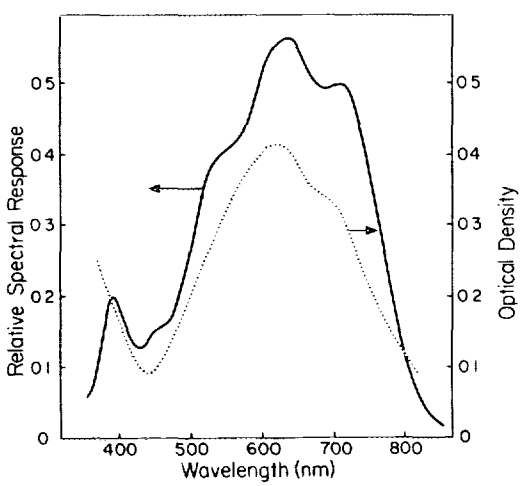

FIG. 2. Spectral response of an ITO/CuPc (250 Å)/PV(450 Å)/Ag cell and absorption spectrum of the CuPc/PV two-layer film.

work functions, such as In, Al, Cu, and Ag, produced cells with V_{oc} differing by 50 mV or less. In contrast, the V_{oc} and other photovoltaic parameters are strongly dependent on the choice of the particular pair of organic layers. Reversal of the order of the CuPc/Pv layers with respect to the electrodes (cell configuration: ITO/PV/CuPc/Ag) reverses the polarity of the photovoltage and somewhat reduces the V_{oc} as well.

The characteristics of the present two-layer organic cell closely resemble those of the more efficient inorganic p-n junction solar cells. However, it would be unwarranted to interpret the results of the present two-layer organic cell simply in terms of p-n junction behavior. It is well known that CuPc, single crystal or thin film, behaves like a p-type semiconductor at room temperature,[11,12] but this behavior does not necessarily imply that the carrier concentration can be influenced by intrinsic or extrinsic shallow dopants. Indeed, the room-temperature resistivity of CuPc, thin film or single crystal, is $\sim 10^{10}$ Ω cm and is fairly independent of sample preparation.[13] Thus CuPc solid in general can very well be regarded as an organic insulator with the p-type conduction being determined by the relative distribution of electron and hole traps. The conduction type of the PV layer is not known, but it is likely that it would also be trap controlled.

A qualitative model for the operation of the ITO/CuPc/PV/Ag two-layer cell is proposed as follows. It is assumed that the absorption of light by both CuPc and PV layers creates excitons, which can diffuse in the bulk of the films. The interface or junction between the CuPc and the PV layer is taken as the location of active sites for the dissociation of the excitons. Thus, upon dissociation of the light-generated excitons at the interface, the holes are preferentially transported in the CuPc layer and are collected by the ITO electrode, while the electrons are transported in the PV layer towards the Ag electrode. The effectiveness of the exciton dissociation at the CuPc/Pv interface may be associated with a high built-in field of unknown origin, perhaps a dipole field or a field due to trapped charges at the interface. If the strength of this built-in field is sufficiently high ($\sim 10^6$ V/cm), the carrier generation efficiency would be virtually saturated and is determined primarily by the diffusion of excitons into this interface region. Superposition of a small external voltage would then moderately affect the carrier collection, thus leading to a weak bias dependence of the collection efficiency.

The observed polarity of the photovoltage, i.e., the CuPc layer is always positive with respect to the PV layer regardless of the electrode materials, is strongly indicative of the conduction types in the two layers. It requires that the CuPc layer be hole transporting, which is consistent with what is commonly observed for CuPc, and that the PV layer be electron transporting. In a separate experiment[14] we determined that the photoionization potential of CuPc is lower than that of the PV layer by about 0.4 eV. Together with the optical absorption data, the relative energetics of the CuPc and PV films have been established and favor the photoinjection of electrons into the PV layer and holes into the CuPc layer. This is also consistent with the direction of the observed photovoltage.

The ITO/CuPc/PV/Ag cell has been subjected to a preliminary stability test. The cell was tested in ambient atmosphere, under continuous illumination from a tungsten light source (75 mW/cm^2) and at short-circuit condition (I_{sc} = 2 mA/cm^2). Both V_{oc} and I_{sc} showed little degradation ($<2\%$) after five days, but the ff had decreased by about 30% at the end of this period of illumination. This degradation can be attributed, at least in part, to the degradation of the Ag electrode, giving rise to an increase in the series resistance of the cell.

In summary, the two-layer, thin-film configuration offers a different approach to the construction of photovoltaic cells based on organic materials. The distinct advantage of the present system over the more conventional single-layer organic cells is that it does not suffer from the usual dependence of charge generation on the electric field. The consequence of this independence is a large enhancement in both the fill factor and the photovoltaic efficiency, as found in the CuPc/PV two-layer system.

I am grateful to Dr. E. A. Perez-Albuerne and Dr. D. J. Trevoy for their critical reading of the manuscript and to Mrs. A. K. Seidel for the synthesis of perylene derivative PV.

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