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Photovoltaic cells based on cadmium sulphide– phthalocyanine heterojunction

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ABSTRACT

Hybrid photovoltaic (PV) cells based on cadmium sulphide (CdS) single crystal and phthalocyanine (Pc) films have been developed and their PV performance was measured. Five different Pcs have been selected as candidates for the PV cell, PcCu, PcMn, PcZn, PcMg, and PcVO. It was found that all the chosen Pcs are capable of forming a hybrid heterojunction with the CdS surface, and that illumination results in charge separation at the interface. However, the performance of the In/CdS/Pc/Au device was dependent on the Pc used. PV cells with PcMg and PcZn showed the best results. An unoptimized cell with the PcZn film showed an open-circuit voltage $V_{oc} = 0.595$ V, a short-circuit current density $J_{sc} = 1.88 \mu A/cm^2$, a fill factor FF = 0.265, and a power conversion efficiency PCE = 3.0×10^{-4}% under the AM1.5 conditions.

1. Introduction

In the past decade, photovoltaic (PV) devices based on organic materials have attracted great interest due to some advantages of these materials over traditional inorganic semiconductors. This interest was documented by a number of recent review papers (see for example, Refs. [1–9]) that show that both organic polymers [4–6] and small molecules [7–9] can be used in PV devices to produce electricity from solar light energy. At the same time, hybrid organic–inorganic structures have been shown to also possess a potential for application in PV devices. The first examples of fabrication of hybrid organic–inorganic structures for PV applications included bilayer structures based on polyacetylene and inorganic crystals [10,11]. Recently, it has been shown that inorganic nanocrystals can be successfully used in hybrid PV cells [12,13]. The hybrid structures can combine in one assembly the advantages of inorganic compounds, such as a broad range of light absorption, effective transport of charge carriers, firmness, hardness, thermostability, and advantages of organic polymer materials, such as cheapness, plasticity, flexibility, easy chemical modification, and solution processibility. There are additional criteria that should be satisfied and that can strengthen the advantages of the hybrid heterostructures, namely,

(i) the energy levels of the organic and inorganic materials should be adjusted, for example, one can choose a combination of a donor organic material and a n-type inorganic semiconductor, where LUMO level of the organic material lies slightly above the conductance band of the inorganic semiconductor, or a combination of an acceptor organic material and a p-type inorganic semiconductor, where HOMO level of the organic material lies slightly below the valence band of the inorganic semiconductor;
(ii) the absorption spectra of the components complement each other to cover a wider spectral range;
(iii) both of the components are photoconductive and play active role in creation of photocurrents;
(iv) the layers should be stable against oxidation and photo-chemical reactions.

Cadmium sulphide (CdS) and phthalocyanine (Pc) have been selected in this work as candidate materials for the hybrid PV cell. These materials as well as their combination are well suited to satisfy the above criteria. Pcs are normally donor materials [14,15] and their films behave as p-type semiconductors [16], while CdS is a n-type semiconductor. The energy levels of these materials are adjusted to be used in photovoltaics (Fig. 1). Both of the materials are photoconductive and are used in PV devices as organic/organic combinations, for example, in ITO/PcCu/perylene tetracarboxylic bis-benzimidazole/metal (Al or Ag) [17,18], ITO/PcCu/perylene tetracarboxylic acid/In [19], ITO/PEDOT:PSS/PcCu/C_{60}/BCP/Al [20] structures, and in inorganic/inorganic combinations, for example, in CdS/CdTe structures [21]. CdS was also used in hybrid organic–inorganic PV devices in the form of sprayed films [22] or nanocrystals [23]. Both CdS and Pc are known to be stable in air.
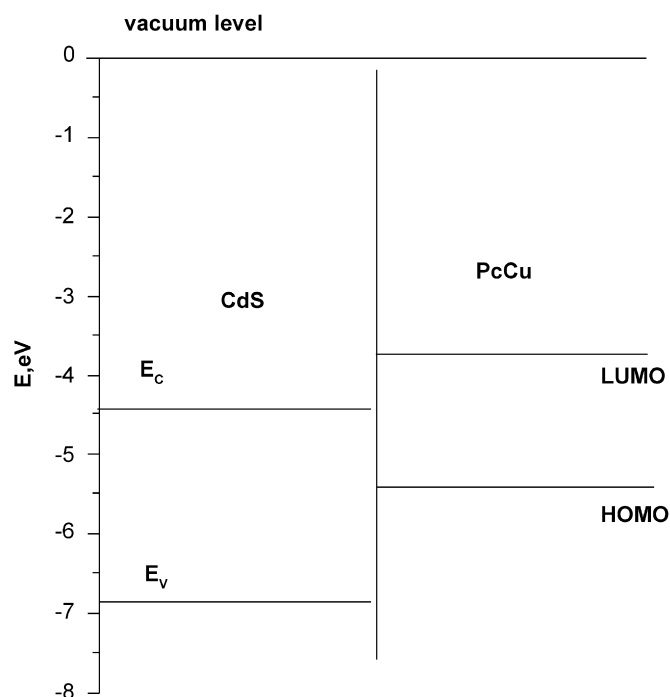
Fig. 1. Energy level diagram of CdS and PcCu materials.

Thus, the good compatibility of the above materials and their potential for application in solar cells encouraged us to design PV structures based on these materials and to study their PV performance.

2. Experimental

2.1. Sample preparation

The technology for the growth of structurally perfect large single crystals of CdS is described in Ref. [24]. The main feature of this technology is that the crystals are grown from the vapour phase as a free growth (i.e., the growing crystal does not contact with the vessel walls inside which it grows), and superfluous cadmium, which negatively influences the crystal parameters, is removed by a specially selected compound that does not affect the crystal growth. As a result, single crystals of cadmium sulphide of volume up to $5\,cm^3$, crystallographic orientation of $(0\,0\,0\,1)$ in the growth direction, specific resistance in the dark of $10^8\,\Omega\,cm$, dislocation density less than $5 \times 10^2\,cm^{-2}$, and impurity density less than $10^{-2}\,cm^{-2}$ were grown. Large crystals were cut or split off into wafers of area up to $1\,cm^2$ and thickness of $1–2\,mm$ for further experiments.

Powders of unsubstituted Pcs were obtained from Aldrich and used as received. Pc films were deposited onto the CdS single crystal surface by thermal vacuum evaporation technique under a pressure of $10^{-3}\,Pa$. Thickness of the Pc films was evaluated through the quartz microbalance technique and was in the range of 10–40 nm. Different Pc films, i.e., PcCu, PcZn, PcMg, PcMn, and PcVO have been deposited with approximately same thickness to compare their properties accordingly. The CdS surface was etched by a hot etching solution before the film deposition. Ohmic contact to CdS was provided by burning into indium electrode, while gold film has been thermally evaporated in vacuum onto the Pc film as a top electrode.

To characterize the CdS material, a Schottky barrier diode was fabricated by evaporating gold contacts on a freshly cleaved surface. Routine checks showed that currents induced by exposure of the CdS crystal to light are one order of magnitude lower in the In/CdS/Au structure as compared to that of In/CdS/PcZn/Au (at the same voltage bias), and no clear charge separation at the CdS/Au interface has been observed.

2.2. Measurements

Quasi-DC measurements were performed by a standard automated tester 14 TKS-100. Voltage sweep was applied to the heterostructure step by step with 250 ms duration of each step and 90 ms measurement time. A halogen lamp of 0.03 sun equivalent power irradiation or a solar simulator has been used to obtain current–voltage characteristics under the light conditions. Spectra of photocurrent were measured in the short-circuit regime and also under a small applied bias in the spectral range 350–1050 nm using a halogen lamp and a prism monochromator. Illumination of the heterojunction was performed through the CdS single crystal, which is transparent in long-wavelength range of the solar spectrum (above ~500 nm). The spectra were reduced to the lamp spectrum according to the standard procedure to calculate the incident photon-to-charge carrier efficiency (IPCE). A silicon photodiode with known spectral efficiency was used as a reference.

3. Results and discussion

3.1. Absorption spectra

CdS single crystal and Pc films demonstrate good complementarity of their electronic absorption spectra (Fig. 2). Absorption of CdS crystal rapidly increases below 500 nm, i.e., at energies higher than the bandgap of CdS (~2.4 eV), whereas absorption of Pc films covers the remaining part of the visible range due to the Q-band. The absorption maximum of the Q-band for the monomer form of Pcs in the solution is about 668 nm for PcMg, 678 nm for PcCu, 701 nm for PcZn, 727 nm for PcMn, and 810 nm for PcVO [25]. The absorption shape of this band changes in solid films of Pcs due to formation of molecular aggregates (Fig. 2). One can observe a clear splitting of the Q-band into two components in films of PcZn, PcCu, PcMg, an additional formation of a long-wavelength absorption component in the PcVO film due to intermolecular
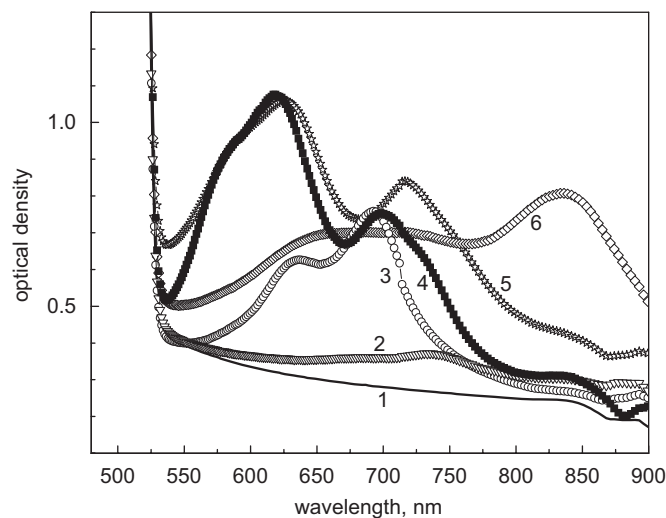

Fig. 2. Electronic absorption spectra of: (1) CdS single crystal and heterostructures of CdS with (2) PcMn, (3) PcMg, (4) PcCu, (5) PcZn, and (6) PcVO films.