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PHOTOVOLTAIC PROPERTIES OF NANOCRYSTALLINE CuInS_2 /METHANOFULLERENE SOLAR CELLS

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First attempts were made to use nanocrystalline CuInS_2 with the fullerene derivatives to form flat interface donor-acceptor heterojunction solar cells. We synthesized nanocrystalline CuInS_2 in a colloidal route, the particle surfaces were shielded by an organic surfactant. We present photovoltaic data of nanocrystalline CuInS_2 Schottky diodes in comparison with heterojunctions of CuInS_2 and methanofullerene derivatives. Flat interface heterojunction solar cells show significant better photovoltaic response than solar cells consist of nanocrystalline CuInS_2 single-layers. In comparison to the single-layers, an increase of cell efficiency about factor 25 is received.

Keywords: composite solar Cell-1; CuInS_2 -2; methanofullerene-3

1. INTRODUCTION

A large number of conjugated polymers and oligomers investigated for their photovoltaic activities, show an efficient electron transfer from the excited state of the conjugated polymer to electron acceptors. Presently, the highest efficiencies of plastic solar cells are obtained for fullerenes as acceptors in combinations with poly phenylene vinylene as a donor [1]. However, the power conversion efficiency of conjugated polymer/fullerene photovoltaic devices is limited by the light absorption in the films, since its maximum thickness is limited by the mobility of the holes in the conjugated polymer [2]. Replacing the fullerene derivatives by a better absorbing

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electron acceptor may therefore be a way to improve the efficiency of such solar cells.

An interesting feature of nanoparticles, and one of the main reasons for intensive investigations of them is the high surface to volume ratio as well as the tunability of their optical and electrical properties by utilizing size quantization effects [3]. Unique activities as solar cell materials may be expected if the particles can be prepared as rough nanostructured layers. Typical structures of these devices consist of two materials with donor and acceptor properties either as a single-layer of the mixture or bilayers of the pure components, sandwiched between two electrodes.

Photo induced electron transfer as well as photocurrent generation in the more or less rough interface of these two types of materials had been demonstrated already in composites of conjugated polymer/CdS and CdSe nanocrystals [3] as well as in conjugated polymer/TiO₂ [4,5] structures.

Here we report a more extensive investigation of flat interfaces formed in bilayer structures of the materials chosen, CuInS₂ (CIS) and the nicely soluble methanofullerene, 1-(3-methoxy carbonyl)-propyl-1-1-phenyl-(6,6) C₆₁ (PCBM). CIS, besides its as yet more important sister material CuInSe₂ (CISE) is a classical material for photovoltaic applications, with a high absorbance coefficient ($\alpha = 10^5 \text{ cm}^{-1}$) and photoconductivity [6]. First investigations mainly had been published before [7,8].

The CIS clusters we synthesized are smaller than the bulk exciton diameter and exhibit typical size-quantization effects. The absorption range of the particle can be tuned depending on the particle size. In the past decade quantized semiconductor particles with diameters of a few nanometers have attracted growing interest because of their new opto-electronical [9,10,11], magnetic [13] and chemical [15] properties. Although the opto-electronical behavior of II–VI quantum dots have been characterized extensively [16,17], there are to our knowledge as yet no investigations on quantized CIS. Preparation of nanocrystalline CIS films that are uniform in composition, size and surface chemistry was a first goal of our investigations. Bilayer devices consisting of CIS and PCBM were fabricated and characterized by current-voltage (I-V) measurements under AM 1.5 conditions and by wavelength dependent short circuit photocurrent measurements. These data were compared with single-layer CIS devices.

2. EXPERIMENTAL

2.1. Materials

Synthesis of CIS particles was performed by a colloidal route [12]. In this synthesis the CIS particle are shielded by an organic surfactant against

environmental influences and fusion: the surface of the CIS particles is covered by triphenyl phosphite (TPP), to prevent further growth up of the nanoparticle and to reduce the oxidative degradation.

The electron transporting and hole blocking "gate"-material in our devices was 1-(3-methoxy carbonyl)-propyl-1-1-phenyl-(6,6) C₆₁ (PCBM) synthesized in the group of K. Hummelen in Groningen [14]. One advantage of PCBM is its solubility in toluene. The TPP-capped CIS particles are only slightly soluble in toluene. However, when PCBM [18] (HOMO = -6.0 eV, LUMO = -4.0 eV) is deposited onto a previously prepared CIS film, some swelling of the CIS layer may occur due to the solubility of the organic surfactant. The consequence is probably the formation of a rougher interface between these two layers.

2.2. Cell Preparation and Experimental Methods

Nanocrystalline films of CIS were prepared from a 0.06 M solution by spin coating onto indium tin oxide (ITO) glass (supplied by BALZER). Film thicknesses in the order of 200 (+/-50) nm were obtained this way. The films were annealed at 120°C in vacuum for 48 hours. It should be noted that the CIS dispersion retains good film forming capabilities. Absorption studies were carried out using a HP 8453 spectrometer.

Current-voltage (I-V) measurements were performed at room temperature in argon using a Keithley 617 source-monitor unit. In order to improve the quality of the ITO electrode, we coated the ITO surface with films of poly (3,4-ethylene-dioxythiophene)/poly (styrene-sulfonate) (PEDOT/PSS) of about 100 nm thickness.

PEDOT:PSS (Baytron from Bayer, Leverkusen) is widely used in organic electronics in order to smoothen the ITO surface and to improve the hole injection at the ITO anode. PCBM was spin coated onto the CIS layer from a 0.002 M toluene solution. Lithium fluoride (0.6 nm) and aluminum (300 nm) were evaporated onto the films as counter electrodes. The two layer deposition of LiF/Al has been shown to enhance the charge injection at the interface between the active layer and the cathode [19].

For electrical characterization the cells were illuminated with 80 mW/cm² power intensity of white light using a Steuernagel solar simulator (active area limited to about 5–6 mm²) by the size of the back electrode. The filling factor FF was calculated by $FF = V_p \cdot I_p / (V_{oc} \cdot I_{sc})$ with V_p and I_p being the voltage and current of the maximum power point and V_{oc} and I_{sc} being the open circuit voltage and the short circuit photocurrent, respectively.

The spectral photocurrent was detected using a lock-in amplifier while the sample was illuminated with monochromatic light of $\sim 200 \mu\text{W}/\text{cm}^2$ and a FWHM of \sim about 4 nm. The spectrum of the light source was measured with a calibrated mono crystalline silicon diode. The illumination of the

sample was always from the side of ITO electrode. IPCE η_c (%) was calculated according to the formula $\eta_c(\%) = V_{oc}(V) \cdot I_{sc}(A/cm^2) \cdot FF/P_{inc}(W/cm^2)$, where P_{inc} is the incident light power.

3. RESULTS AND DISCUSSION

Figure 1 shows the shape of the absorbance spectra of a CIS film prepared from a 0,06 M dispersion in acetonitrile and PCBM prepared from a 0.002 M toluene solution. The absorption spectrum of CIS exhibits a high shoulder at 700 nm and a weak absorbance at longer wavelengths. Freshly synthesized CIS exhibits a significant hypsochromic shift of the absorption relative to the bulk material absorption at 825 nm (12), indicating the size quantization. Most of the particles are smaller than the exciton radius of ca. 8 nm. It is obvious from these results that the surfactant TPP can prevent the particle growth to bulk-material even in films if the right spin coating parameters are chosen. Due to the weak bond of the surfactant, the size-distribution of the particles in the film is very sensitive to the preparation

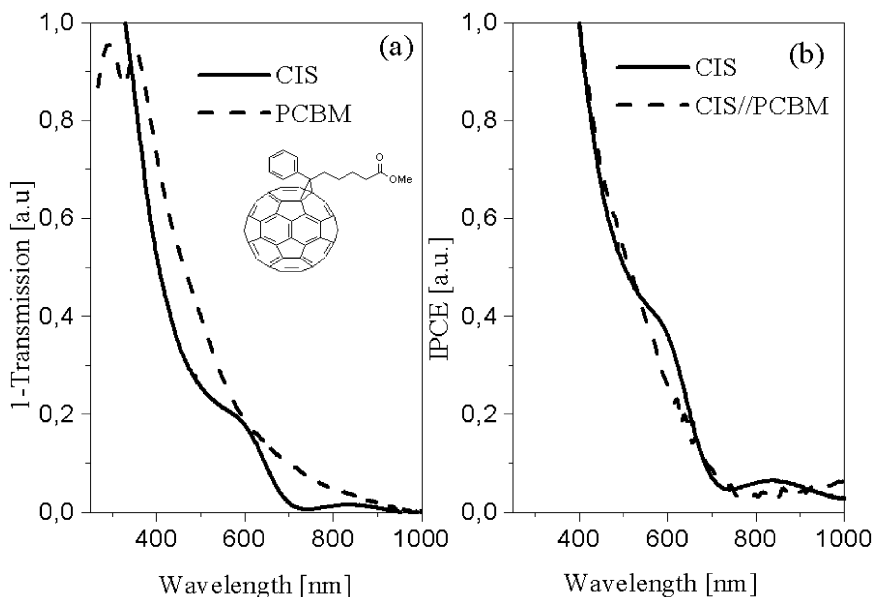


FIGURE 1 (a) Optical transmission spectra of CIS and PCBM films on glass substrates. (b) IPCE spectra (normalized) for photovoltaic devices using CIS single-layers and CIS/PCBM bilayers as the photoactive films. The inset shows the molecular structure of PCBM.

parameters. Figure 1 shows also the shape of the PCBM absorbance with two maxima, at 293 and at 352 nm. The absorbance spectra here are not normalized with respect to the film thickness.

Figure 1 shows also the normalized short circuit photocurrent spectra of ITO/CIS/LiF/Al in comparison to the ITO/CIS/PCBM/LiF/Al diodes illuminated through the ITO electrode.

The IPCE on-sets are more or less identical with the on-sets of the corresponding absorbance spectra. The shoulder at 700 nm for the CIS single-layer structure is more pronounced than in double layers, with contacts to PCBM. The shape of the short circuit photocurrent spectra in double layers is given by the superposition of absorptions of both components.

The most significant differences between the different cell types investigated can be seen from the not normalized IPCE spectra.

For the sake of comparison the IPCE curves were integrated in the range between 400 and 900 nm (Fig. 2). The obtained photocurrent for the CIS single-layer is very poor, the photo-generated electron hole pairs (or excitons) mostly recombine, before reaching the electrodes. However, current generation can be improved significantly by adding PCBM as a strong electron acceptor. The integrated IPCE value increases by a factor of ca. 25.

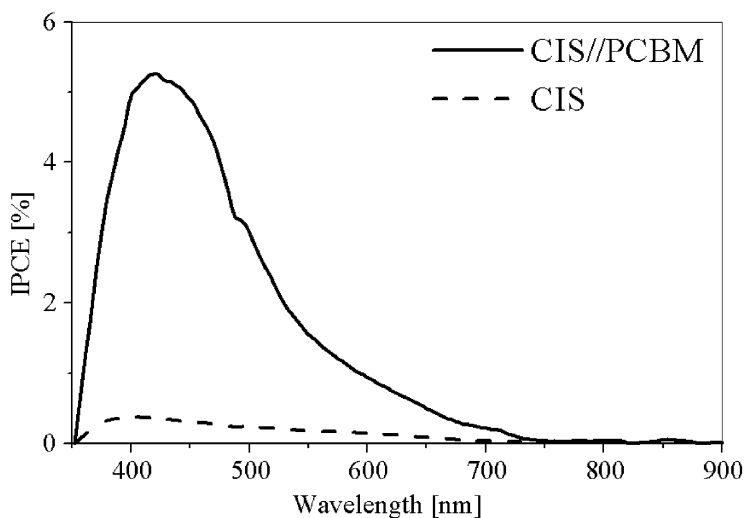


FIGURE 2 IPCE spectra of solar cells investigated using CIS single-layer and CIS//PCBM bilayer configurations.

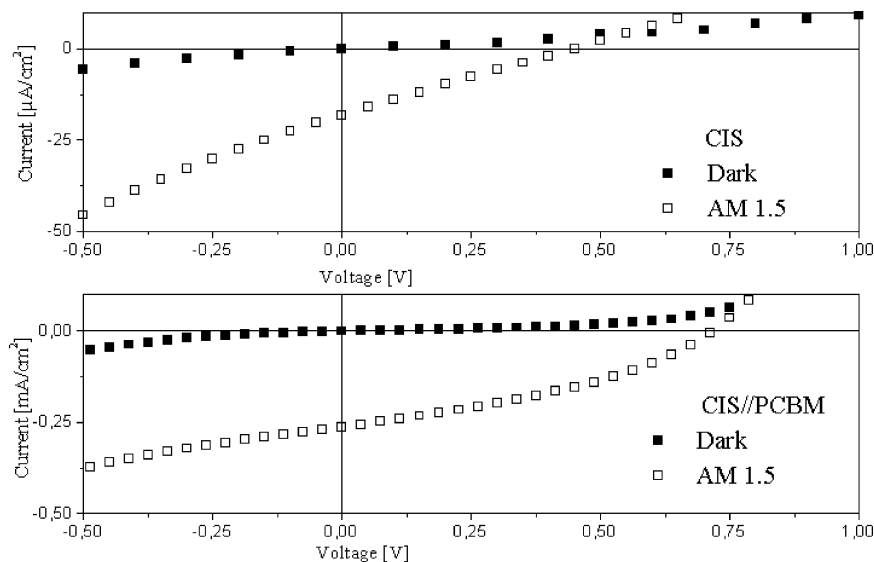


FIGURE 3 I/V characteristics of solar cells in the dark and upon AM 1.5 illuminations.

All solar cells were produced in the sandwich geometry as mentioned above, i.e. between two metal electrodes with different work functions, ITO (~ -4.7 eV)/PEDOT:PSS (~ -5.0 eV) as anode and aluminum (~ -4.3 eV) as cathode.

The I-V characteristics of an ITO/PEDOT/CIS/LiF/Al photovoltaic device in dark and under 80 mW white light illumination is shown in Figure 3. In the case of a negative applied bias, i.e. positive contact to the Al and negative contact to the ITO, the diode produce a short circuit density I_{sc} of $18 \mu\text{A}/\text{cm}^2$ and an open circuit voltage V_{oc} of 450 mV. However, for a larger number of samples the V_{oc} values vary between 265 and 450 mV (I_{sc} of 6 to $20 \mu\text{A}$) depending on the history of the sample. Repeating the measurements and drying the films under argon leads to an improvement of the cell characteristics. A fill factor of about 0.25 indicates that the serial resistance controls the power plot. A rectification ratio RR at + and -2V in dark of only 2.6 and under illumination of 6.5 also indicates a bad rectification of the diode.

In contrast, the CIS//PCBM double layer exhibits a better diode behavior with a typical current versus voltage response as shown in Figure 4. Illuminating cells with $80 \text{ mW}/\text{cm}^2$ white light from a solar simulator produces open circuit voltages of 712 to 792 mV and short circuit current densities of ca. $0.26 \text{ mA}/\text{cm}^2$. The calculated fill factor of the diode is 0.44.

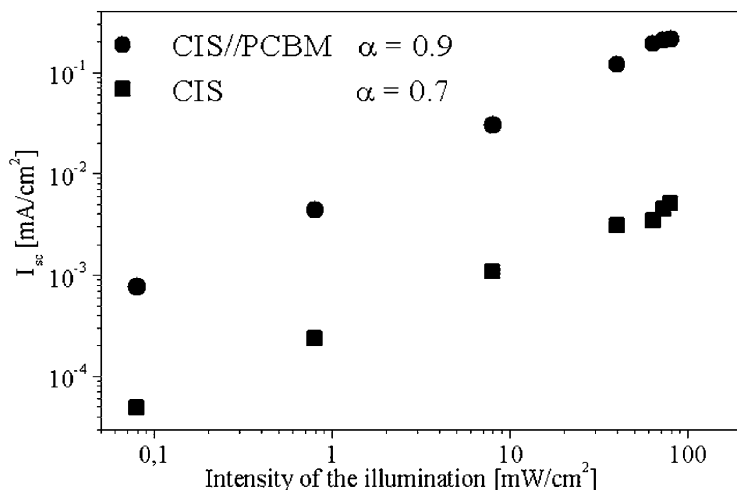


FIGURE 4 Dependence of the short circuit current on the incident light intensity of ITO/PEDOT:PSS/ CIS/ LiF/Al (squares) and ITO/PEDOT:PSS/ CIS/ PCBM/LiF/Al (circles) solar cells. α is the scaling exponent discussed in the text.

A conversion efficiency up to 0.09% is obtained. The rectification ratio at ± 2 V is 2,6 in the dark and 3.4 under illumination.

Figure 4 shows the dependence of the short circuit current on the incident light intensity, which follows a power law $I_{sc} \sim F^\alpha$ with a scaling exponent α fitted of around 0.7 for mono layers of CIS. The sub linear intensity dependence thereby indicates a strong contribution of photo-conductivity for which a bimolecular recombination of free electrons and holes additionally reduces the film conductivity. On the other hand, for the bilayer configurations CIS/ /PCBM the dependence of the I_{sc} follows a power law $I_{sc} \sim F^\alpha$ with $\alpha \sim 0.9$. A scaling exponent α of almost 1 indicates a mainly mono-molecular recombination in these cells.

4. CONCLUSIONS

Preparation and opto-electronical characterization of films consisting of quantized CuInS₂ nanoparticles have been studied. The particle were shielded by an organic surfactant TPP, which prevents the aggregation and partly passivates the particle surface among others also against oxidation. Layers of the quantized CIS/TPP particles were prepared by spin-coating. Probably due to the insufficient charge transport properties or not optimized contacts to the back electrodes the photovoltaic response of these devices are rather poor. On the other hand, the diodes clearly show

photoconductivity. Further work is needed to optimize the photovoltaic parameters. By introduction of a strong electron acceptor layer (PCBM), between the CIS layer and the Al electrode we received an increase of the open circuit voltage up to 780 mV and a short circuit current up to 0.26 mA.

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