Nanocrystalline CIS/Conjugated Polymer based Hybrid Solar Cells

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Abstract

1. Introduction

Plastic Solar Cells [1] provide the possibility of easy and cheap production of large area photovoltaic devices on low cost polymer substrates. Based on interconnected networks of p-type polymers with percolating electron conducting C_{60} derivatives, our group recently achieved more than 2.5 % solar efficiency in devices of less than 100 nm thickness of the absorber layer, in which only a portion of the solar light is absorbed [2].

The key for improving organic solar cell efficiencies was the fabrication of an interconnected network structure of p- and n-type materials to form a so-called bulk heterojunction. In such devices the flat interface of classical organic solar cells [3a] is replaced by an extremely rough network such as also used in modern sensitization solar cells [3b]. However, C_{60} derivatives exhibit relatively low absorption coefficients in the order of only some 10^4 cm^{-1}. In order to overcome this problem we decided to replace the electron transporting fullerene derivative by classical semiconductor nanoparticles. A first example of these new devices will be discussed in this paper. We investigated blends of our classical plastic solar cell polymer poly (2-methoxy-5-(3´,7´- dimethyloctyloxy)-1,4-phenylene vinylene) (MDMO-PPV) , regioregular poly (3-hexylthiophene) (P3HT) and of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) with copper indium diselenide (CISe) and copper indium disulfide (CIS) nanocrystals, one of the best solar absorbers for photovoltaic applications.

2. Experimental

$CuInSe_2$ (CISe) was synthesized by a solvothermal route described by Y. Qian et al [4]. The particles formed are usually crystalline and don't need post-treatment at high temperatures. Also, no organometallic precursor, which can complicate the system, and no organic stabilizers are used in this route. In solvothermal process, the solvent plays an important role in the formation of the chalcopyrite CISe controlling the form of the particles. We used anhydrous ethylendiamine to form elongated particles, because it is an excellent template for the formation of one-dimensional materials [5]. Because of the bidentate N-chelation capability of ethylendiamine, it can effectively form a stable complex of $[Cu(en)_2]^+$ and thereby prevent the formation of binary copper chalcogenides.

Synthesis of $CuInS_2$ (CIS) particles was performed by a colloidal route [6]. In order to prevent the aggregation of the particles for long time storage the particles were capped with triphenyl phosphite (TPP). The capping layer weakly bounded on the particles can be removed by washing with organic solvents like pyridine.

Composite films were prepared by spin coating a chlorobenzene solution of commercially available P3HT, or MDMO-PPV, kindly provided by Covion, Frankfurt, with semiconductor particles suspended therein without any high temperature treatment. PEDOT/PSS is commercially aviable by Bayer (Baytron).

3. X-Ray studies

The crystallographic structure of the particles was determined by powder X-ray diffraction using Cu K_α radiation of 1.5418 Å. Figure 1 shows the X-ray diffraction pattern of CISe and CIS. An intense peak at $2\theta = 26.6°$ oriented along the (112) direction and other prominent peaks observed at 44.3° ((220) / (204)) and 52.3° ((312)/ (116)) indicate the chalcopyrite structure of CISe. These pattern are in a good agreement with JCPDS data [7].

In contrast, the upper plot shows the results of X-ray diffraction investigations performed on the sulfide CIS. The three now broad reflections at 2θ values of 27.9 (112) ,46,5 (220)/(204) and 55.0 (312)/(116) are those of the chalcopyrite structure of CIS. However, in the range between 15 and 35° a broad halo appears, probably due to an amorphous contribution. This may indicate that still TPP is present, which may not have been removed completely.
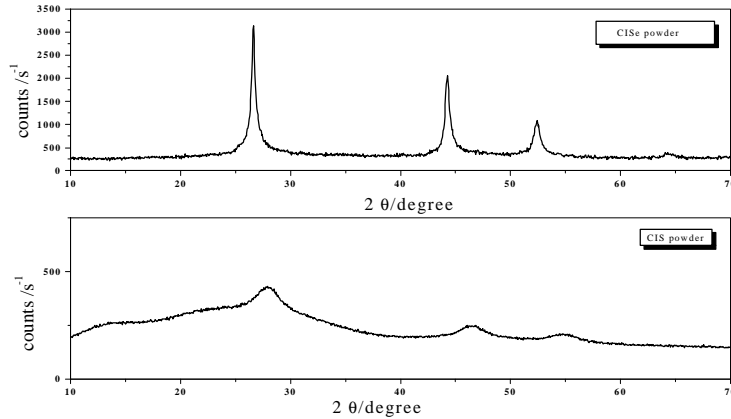

Fig. 1: X-ray diffractogramms of CISe and CIS

Apart from this, a comparison of the diffraction pattern clearly shows a pronounced broadening of the CIS diffraction patterns, which can be evaluated to determine the approximate dimensions of the particles using the Scherrer Formula:

$$L = \frac{l}{\Delta'(2\Theta) \cdot \cos\Theta_0}$$

λ: Wavelength of röntgen beam (1,5418 Å)
Θ_0:   Location of diffraction pattern
$\Delta'(2\Theta)$:   FHWM of the peak

An average size of the CIS particles of ca. 3 nm can be estimated from this analysis. The sharp diffraction pattern of CISe indicates the excistence of rather large particles.

4.   Optical properties and photovoltaic activity

In P3HT und MDMO-PPV matrices , we observed no onset of the CIS or CISe absorption in the spectral range between 350 and 900 nm as it would be expected for quantisized particles. Using PEDOT/PSS as amatrix, which does not absorb in the visible range, the absorbance of CIS nanoparticles with an absorbance edge at ca 600 nm is detected. AFM images of the films show more homogenous films in the case of PEDOT/PSS comparing to P3HT or MDMO-PPV. The morphology of the MDMO-PPV and P3HT films containing large amounts of CIS is not yet favourable for charge generation in solar cells due to pronounced clustering of the materials. The investigations on PEDOT/PSS-CIS blends give promising hints for a bulk heterojuction formation. Systems based on PEDOT/PSS- CIS blends will be the topic we want to discuss in more detail in this meeting.

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