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CURRENT-VOLTAGE CHARACTERISTICS OF POLYMER-FULLERENE SOLAR CELLS

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ABSTRACT

We have studied the influence of temperature and light intensity on the current-voltage characteristics of polymer-fullerene bulk-heterojunction solar cells. The open-circuit voltage varies linearly with temperature in the range 200K-300K and approaches a value of 930mV at T=80K. Strictly positive temperature coefficients were found for both, the short-circuit current density and the fill factor. These cause the device efficiency to increase steadily with temperature up to T=330K. The short-circuit current density increases almost linearly with light intensity. The fill factor is not significantly influenced by the incident light intensity in the temperature range from 260K to 330K. At lower temperatures, a negative slope of the fill factor is observed. Since the maximum power point varies sublinearly with light intensity, a decrease of the power efficiency is obtained at light intensities higher than 3mW/cm².

1. INTRODUCTION

Semiconducting, conjugated polymers are promising candidates for the realization of cheap, non-toxic photovoltaic (PV) devices. Whilst mechanical flexibility and the option of modifying the optical band gap by chemical engineering are commonly desired for solar cells, the main advantage brought with these compounds is their solubility in organic solvents. This feature does not require any vacuum or high temperature processing steps for the semiconductor deposition, one makes instead use of simple and cost effective deposition techniques, such as spin-coating, screen- or even ink-jet printing [1,2]. Furthermore, these techniques are well suited for large area applications, making conjugated polymers quite attractive for PV applications.

In polymer light absorbers, an efficient charge carrier generation may be realized by blending the polymer, which acts as an electron donor upon photoexcitation, with acceptor type materials. The underlying photophysics may be described by an ultrafast formation of molecularly separated charge carrier species, i.e., a polymer cation and a fullerene anion. This photoinduced electron transfer within donor-acceptor heterojunction takes place on a sub-picosecond time scale and results in a metastable, charge separated state [3].

One of the most promising device concepts makes use of a bulk-heterojunction absorber in which the donor and acceptor moieties form a phase segregated, interpenetrating network, supporting both, efficient charge carrier generation in the whole absorber volume and charge transport within the respective subnetworks [4]. A selective charge carrier collection at the opposite electrodes is provided by the use of contact materials with different work functions. They form ohmic contacts to the appropriate semiconductor and block the minority charge carriers. For organic solar cells with light absorbers based on the sulfanyl-route synthesized conjugated polymer OC₁C₁₀-PPV (3,7-dimethyl-octoxy-methyloxy poly-[phenylene-vinylene]) and the fullerene PCBM ([6,6]-phenyl C₆₁ butyric acid methyl ester), power conversion efficiencies of 3% were demonstrated under AM1.5 white light illumination [5].

We present a study on the influence of temperature T and white light intensity P_{light} on the current-density vs. voltage (J-V) characteristics of such polymer-fullerene bulk-heterojunction solar cells. From the J-V-measurements, we have calculated the main photovoltaic parameters, namely, the open-circuit voltage V_{oc}, the short-circuit current density J_{sc}, the fill factor FF, and the power conversion efficiency, and represented them as function of T and P_{light}.

2. EXPERIMENTAL

2.1 Device preparation and characterization

The devices were built up on thoroughly cleaned glass substrates, coated with a thin, transparent film of indium tin oxide (ITO), which acts as a window electrode. Onto the substrates, a thin layer of poly-[ethylene dioxy thiophene]: poly-[styrene sulfonate] (PEDOT:PSS, BAYTRON P, BAYER AG, Germany) was deposited, in order to form an optional interface layer. The light absorber was spin cast from an o-chlorobenzene solution of OC₁C₁₀-PPV:PCBM (weight ratio 1:4), forming a 100nm thin film. In the case of PEDOT:PSS and the composite material, spin coating was carried out in a dry nitrogen atmosphere. Subsequently the aluminum top electrode was thermally evaporated in a vacuum chamber by shadow masking technique. The corresponding device scheme is shown in Fig. 1.

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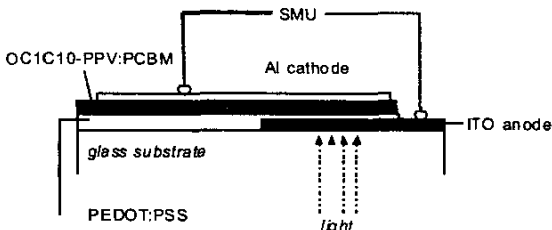


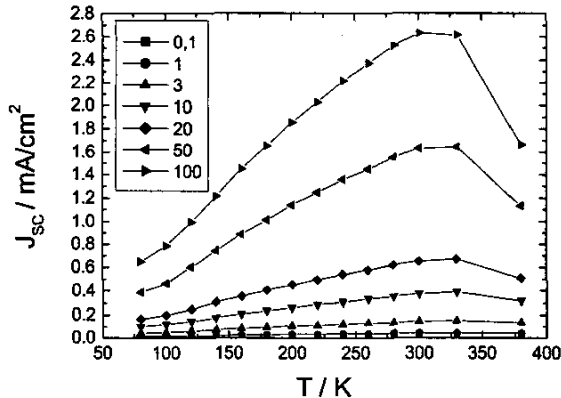
Fig. 1. Typical device configuration for a ITO/PEDOT:PSS/OC₁C₁₀-PPV:PCBM/Al bulk-heterojunction solar cell.

The device characterization was carried out in a variable temperature cryostat with a cooling-heating facility, which allows one to adjust temperatures from 77K to 400K. The samples inside the cryostat were illuminated through a sapphire window by white light of a xenon arc lamp, whose maximum intensity was calibrated to 100mW/cm² by means of a reference photodiode. At a fixed temperature, the incident light intensity was stepwise reduced by a set of neutral density filters, whose transmission coefficients cover three orders of magnitude.

3.2 Temperature Dependences

An interesting feature of polymer-fullerene composite solar cells is found in the temperature dependence of the basic solar cell parameters. Fig. 2 displays J_{sc} as function of temperature T . A monotonic increase ($10\mu\text{Acm}^{-2}\text{K}^{-1}$) of this magnitude was found for all incident light intensities up to 300K. For $T > 300\text{K}$, J_{sc} saturates and breaks down at the point of the glass transition (T_g) for OC₁C₁₀-PPV ($T_g = 330\text{K}$).

Fig. 2. Short-circuit current density as a function of



temperature. The legend indicates the incident light intensity in units of mW/cm².

The strong influence of temperature on J_{sc} is quite unusual, when concerning conventional inorganic solar cells. Instead for disordered media like polymer or fullerene networks, the thermally assisted hopping transport is typical [6] and might contribute to an enhanced conductivity at elevated temperatures.

The transport properties of the composite material are also mirrored in the fill factor, which represents the series and parallel resistance in the equivalent circuit of a solar cell. The fill factor increases monotonically with T and saturates at higher temperatures (See Fig. 4). When

reaching the glass transition at 330K, FF breaks down dramatically. A convergence to FF=42% is observed at higher temperatures close to 300K for different light intensities.

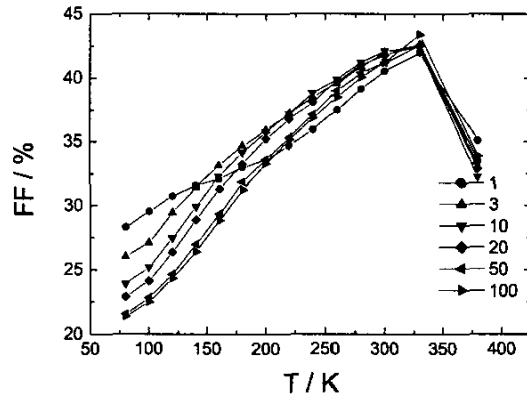


Fig. 3. Fill factor (FF) as a function of temperature for different light intensities in units of mW/cm² (shown in the legend).

The open-circuit voltage decreases approximately linear in the temperature range 200K-330K (see Fig. 4). For $T < 200\text{K}$ a saturation at $V_{oc} = 0.93\text{V}$ becomes visible for intensities between 20mW/cm² and 100mW/cm². This saturation value is close to the value of quasi-Fermi levels splitting of donor and acceptor, i.e., close to the thermodynamic limit, determined by the materials energetics. For OC₁C₁₀-PPV:PCBM composites, this energetic gap is close to 1.2eV. This discrepancy is not clarified at the moment and subject to further investigations.

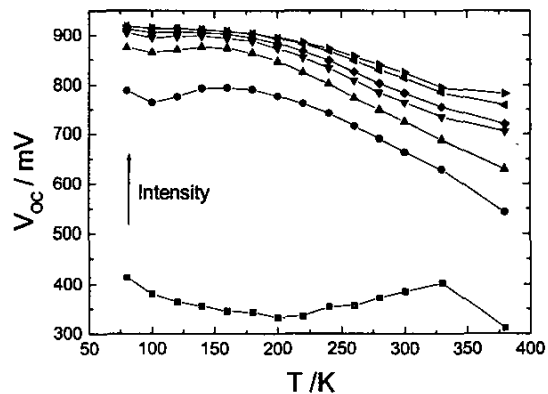


Fig. 4. Temperature dependence of the open-circuit voltage at different light intensities. The arrow indicates the direction of increasing P_{light} from 0.1 to 100mW/cm².

Calculating the device power conversion efficiency, one observes that the decrease of V_{oc} with temperature is overcompensated by the positive temperature coefficients of the short-circuit current density and the fill factor (see Fig. 2 and Fig. 3.). Thus, the device efficiency increases with temperature until the glass transition is reached. The

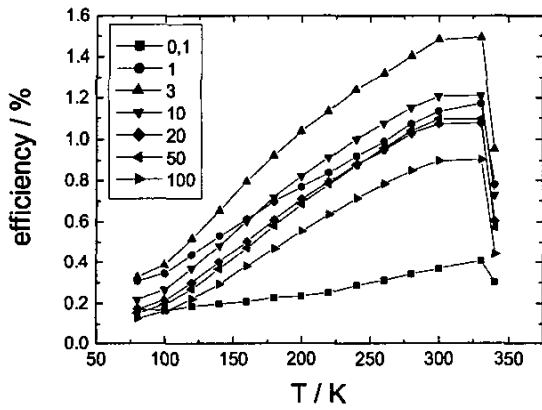


Fig. 5. Power conversion efficiency as function of temperature T at different light intensities.

Power conversion efficiency is shown in Fig. 5. Note that the maximum efficiency is obtained for light intensities around 3mW/cm^2 and a highest temperature of 330K . This finding will be discussed more detailed in the following section.

3.3 Light intensity dependences

A first insight into the complex loss mechanisms in organic semiconductors may be obtained when investigating the relationship between the short-circuit current density and the light intensity. At higher generation rates, a recombination of electrons and holes of bimolecular type is often the case. The latter would lead to a square root dependence for $J_{\text{sc}}(P_{\text{light}})$. However, we do not observe such behavior in the devices studied. Fig. 6 shows the short-circuit current density as a function of light intensity in a double-logarithmic scale.

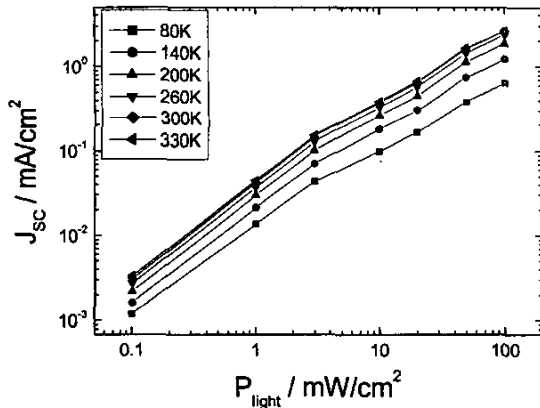


Fig. 6. Intensity dependence of the short-circuit current density for different temperatures, as indicated in the legend.

The slopes are typically between 0.9 and 0.95. Thus, bimolecular recombination does not significantly limit the device operation in this intensity range. However, a slight decrease of the slope can be noticed at intensities between 3mW/cm^2 and 100mW/cm^2 .

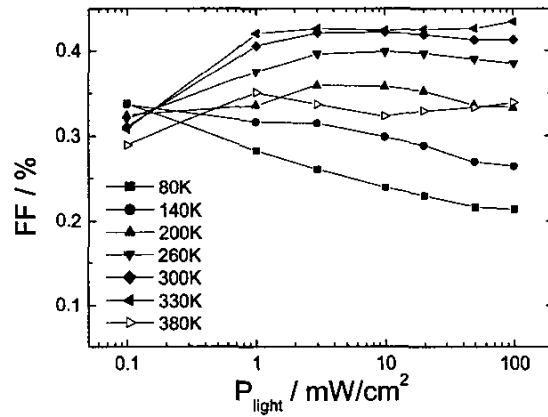


Fig. 7. Variation of the fill factor with incident light intensities for different temperatures, as indicated in the legend.

Fig. 7 proves that the fill factor of the studied polymer-fullerene solar cells depends only weakly on the incident light intensity in the range 260K - 330K . At lower temperatures a decrease of FF with light intensity becomes visible.

For a solar cell, the relationship between the open-circuit voltage and the incident light intensity is given by equation (1).

$$V_{\text{oc}} \propto C \ln \left(\frac{J_{\text{ph}}}{J_0} + 1 \right), \quad (1)$$

where the J_{ph} means the photocurrent density of the solar cell and is often taken equal to the short-circuit current density J_{sc} . J_0 is the saturation current density, which might be dependent on temperature and light intensity. As follows from Fig. 6, $J_{\text{ph}} \approx J_{\text{sc}} \propto P_{\text{light}}$, so that V_{oc} is expected to follow a logarithmic trend. However, this is not seen in Fig. 8, where V_{oc} is plotted against P_{light} in a semi-logarithmic representation. A logarithmic scaling law can be recognized only in the intensity range from 3mW/cm^2 to 100mW/cm^2 , whereas a saturation at lower temperatures is pronounced. Although the discussed magnitudes increase or at least remain constant with increasing light intensity, the device efficiency breaks down at light intensities above moderate values of approximately 3mW/cm^2 .

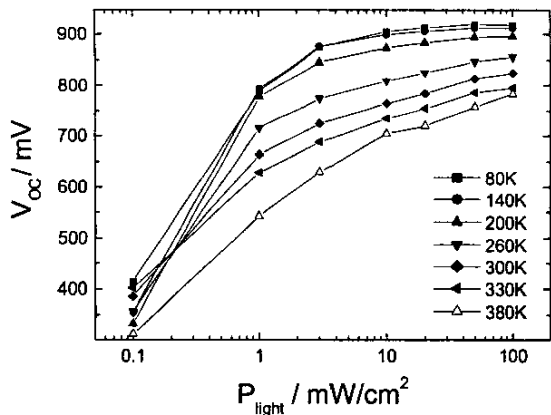


Fig. 8. Open-circuit voltage as a function of incident light intensity.

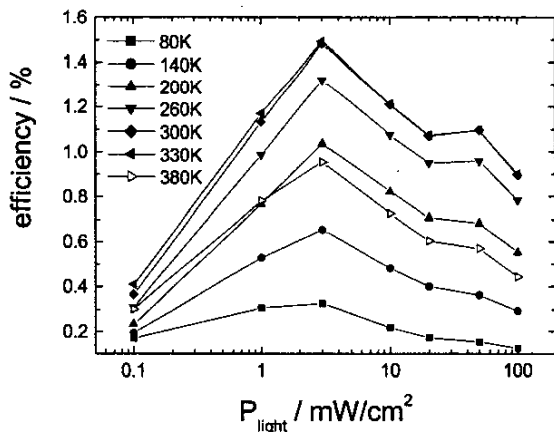


Fig. 9. Light intensity dependence of the device efficiency in a semi-logarithmic representation.

This may originate from a weak shift of the maximum power point of the J-V characteristics at different light intensities, which may be the result of poor conductivity of the absorber materials, as well as a not optimized active layer morphology.

4. Conclusion

We found that the device efficiency of polymer-fullerene bulk-heterojunction solar cells with an OC₁C₁₀-PPV:PCBM light absorber shows a strict positive temperature coefficient in the range 80K-330K independent of the incident light intensity. The transport properties of the respective semiconductors are strongly affected by temperature, resulting in positive slopes of the short-circuit current density and the fill factor. These overcompensate the decrease of the open-circuit voltage towards higher temperatures. However, a limiting factor for the investigated material is the glass transition at approximately T=60°C.

Concerning the influence of light intensity we found a nearly linear increase of J_{SC} with P_{light}, underlining that bimolecular relaxation of charge carriers is of minor importance. Although the fill

factor remains almost independent of P_{light} at temperatures close to 300K and the open-circuit voltage increases monotonically with P_{light}, the power conversion efficiency reaches the highest value at 3mW/cm². The loss mechanisms of the material used may be reduced by using conjugated polymers with enhanced transport properties, e.g. a less defect density, higher mobility and by improving the active layer morphology in order to create a larger geometrical interface between the donor and acceptor moieties.

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