ABSTRACT

The growing concern about our environment and sustainable development focuses attention on renewable energy sources. One of these sources is the direct conversion of sunlight into electricity by means of photovoltaic cells. Solar energy has the potential to fulfill an important part of the sustainable energy demand for future power generations. Thereby, low-cost organic photovoltaic systems have come into the international research focus during the past couple of years. This report demonstrates external power conversion efficiencies of above 2.3% under AM1.5 illumination (100 mW/cm²) and external quantum efficiency over 50% for organic thin-film photovoltaic cells using a phthalocyanine-fullerene (ZnPc/C₆₀) bulk heterojunction as an active layer, embedded into a p-i-n type architecture with doped wide-gap charge transport layers. The p-i-n architecture allows for the design of solar cells with high internal quantum efficiency where the photoactive region absorbs visible light and recombination losses at contacts are avoided. The current-voltage characteristics, power conversion efficiencies, the dependence of short circuit current on incident white light intensity, IPCE and the surface network morphology of these films by atomic force microscope (AFM) are discussed.

Keywords: Organic semiconductors; Photovoltaics; Solar energy conversion.

INTRODUCTION

Currently, the world consumes an average of 13 terawatts (TW) of power. By the year 2050, as the population increases and the standard of living in developing countries improves, this amount is likely to increase to 30 TW. If burning fossil fuels provides this power, the concentration of carbon dioxide in the atmosphere will more than double, causing substantial global warming, along with many other undesirable consequences. Therefore, one of the most important challenges facing scientists and engineers is finding a way to provide the world with 30 TW of power without releasing carbon into the atmosphere. The growing concern about our environment and sustainable development focuses attention on renewable energy sources. Renewable energy sources have experienced rapid growth in recent years as costs have improved.

The sun deposits 120,000 TW of radiation on the surface of the earth, so there is clearly enough power available if an efficient means of harvesting solar energy can be developed. The solar photovoltaic power generation utilizing clean and inexhaustible solar energy is expected to be the major domestic energy source in future in view of preventing global warming and climate change. For spreading the photovoltaic power generation, it is essential to reduce the cost of solar cells, and it has been argued what type of solar cells are to be put to practical use for this purpose. If the cost of producing solar cells could be reduced by a factor of 10, solar energy would be not only environmentally favourable, but also economically favourable.

One of the most promising candidates is organic thin-film solar cell, which can be produced at a reduced cost by printing on flexible plastic substrate. Organic materials are attractive alternatives to conventional semiconductors due to the relatively high cost for the input material. The processing of crystalline silicon wafers is high-level semiconductor technology, and as such expensive and very capital intensive. On the other hand, organic small-molecule and polymeric photovoltaic devices offer great technological potential as a renewable and alternative source of electrical energy in contrast to conventional silicon photovoltaic devices. In recent years, the power conversion efficiencies of thin-film organic photovoltaic cells have increased steadily and rapidly [1-14]. These significant improvements resulted from progress in material synthesis and purification methods and the introduction of novel
device concepts. Organic small-molecule and polymeric solar cell production use low-cost materials and demand a simpler, less energy-intensive manufacturing process than conventional solar cells. In addition, organic small-molecule and polymeric solar cells ultra-thin flexible material can be applied to large surfaces by printing or spraying, the material onto a roll of plastic, making it flexible, versatile and easy to install and require less capital investment than silicon-based devices and other thin-film technologies. Because of these advantages, the development of organic small-molecule and polymeric solar cells will have a major impact. These promising technologies are aimed at narrowing the gap between the cost of solar power and energy from fossil fuels. Seriously these affordable new generations of solar devices will be a boon for the energy needs of poor countries that do not have power grids or other infrastructure support. Most organic solar cells are currently running at conversion efficiencies as high as about 5 percent under simulated solar radiation of AM1.5 global [12,13]. These include flexible thin-film modules made of light-harvesting organic plastic polymers [14]. This is at the world top level among the organic thin-film solar cells. The outlook for organic solar cells is very bright and many are optimistic that 20% can be achieved by optimizing the processes described above.

A major problem with the plastic solar cells and organic solar cells in general is stability and long-lifetime. Apart from chemical decomposition of the organic molecules, organic solar devices can degrade from distortion, loss of adhesion of the layers, or the layers diffusing into each other. So, careful design of the device and engineering more stable molecules are needed to substantially improve the lifetimes of the device. Another challenge for organic solar cells has been the efficient capture and conversion of sunlight. The photons absorbed by a solar cell directly impact the power output. To achieve high power output, solar devices must take advantage of as much of the solar spectrum as possible. Most of the organic semiconductors investigated today absorb in the visible range, while the sun has its maximum photon density at around 700 nm [12].

Generally, the operation of an organic photovoltaic device comprises three consecutive fundamental steps: (1) absorption of light and creation of excitons, (2) creation of separate charges at the donor-acceptor interface, and (3) selective transport of the charges through the bulk of the device to the appropriate collecting electrodes. For the generation of electrical power by absorption of photons it is necessary to separate the electron-hole (e-h) pair generated by photoexcitation before recombination processes can take place. In conjugated polymers as well as in phthalocyanine, the stabilization of the photoexcited e-h pair can be achieved by blending these materials with an acceptor molecule, which has an electron affinity that is larger than the electron affinity of the polymer or phthalocyanine, but still smaller than its ionization potential. In addition, the highest occupied molecular orbital (HOMO) of the acceptor should be lower than the HOMO of the conjugated polymer or phthalocyanine. Under these conditions it is energetically favourable for the photoexcited donor molecule to transfer an electron to the acceptor molecule. Furthermore, in the case of donor-acceptor devices, an acceptor material with high electron mobility and a donor material with high hole mobility are ideal.

Phthalocyanine possesses good electron donating properties due to its large easily ionized π-electron system, whereas fullerene is a good π-electron acceptor, which can be connected with other organic molecules. Phthalocyanine-fullerene based molecular system is therefore a potential material candidate for a photovoltaic cell due to its large and flexible absorption combined with electrical properties similar to an organic semiconductor. Therefore, we have recently investigated the concept of p-i-n type bulk-heterojunction cells [5,6]. In the present work, we demonstrate employing materials for the transport layers with high mobilities and large band gap can significantly improve the efficiency of the p-i-n-bulk heterojunction photovoltaic cells. In the active layer of the device, holes are transported through the zinc-phthalocyanine, and electrons are transported by hopping between fullerene molecules. Based on this principle, it may be concluded that the newly developed p-i-n junction type organic thin-film solar cell can create good p-n junction, and has adequate potential for realizing higher efficiency organic thin-film solar cell.

EXPERIMENTAL

The schematic energy level diagrams of the p-i-n-bulk heterojunction photovoltaic devices together with the chemical structures of the materials used and details of the thin-film production technique have been reported earlier [5,6]. For the p-doped hole transport layer (HTL), we replaced the previously 4,4',4''-tris(3-methylphenylphenylamino) -triphenylamine (m-MTDATA) [5] with the N,N,N',N'-Tetrakis (4-methoxyphenyl) - benzidine (MeO-TPD). The devices have been fabricated on
Organic Thin-Film Solar Cells

RESULTS AND DISCUSSION

The calculation of the overall energy conversion efficiency, \( \eta_e \), has been performed using the equation:

\[
\eta_e = \frac{(V_{oc} \times I_{sc} \times FF)}{P_{inc}}
\]

where \( V_{oc} \), \( I_{sc} \), \( FF \) and \( P_{inc} \) are the open circuit voltage, the short circuit current density, the fill factor and the incident light power on the device as measured by a calibrated reference cell, respectively. We determine the value of the fill factor of the device, \( FF \), from the point \((V_{max} \times I_{max})\) in the 4th quadrant of the I-V characteristics with the maximum electrical power according to

\[
FF = \frac{(V_{max} \times I_{max})}{(I_{sc} \times V_{oc})}
\]

Figure 1 shows the device structure and performance of a series of samples with a photoactive layer of ZnPc:C60 (50 nm, molar blend ratio 1:2) embedded between different p-doped hole transport layers (HTLs) and n-doped electron transport layers (ETLs). The characteristics values of the sample A (fill factor and short circuit photocurrent) in Fig. 1(b) under illumination are seriously affected by the series resistance, determined by the low conductivity of doped m-MTDATA. This problem has been now overcome by replacing m-MTDATA with MeO-TPD as a matrix material for the p-doped HTL (device B). As compared to device A, the slope of the I-V characteristics, under illumination, for forward bias above 0.5 V is significantly increased leading to a higher fill factor, \( FF \) (0.5 instead of 0.33) and a higher short circuit photocurrent, \( I_{sc} \) (7 mA/cm² instead of 6.3 mA/cm²) under AM 1.5 illumination (Fig. 1(b)). However, LiF/Al cathode is a proper electrode for high fill factor.

A drawback of devices using MPP or 3,4,9,10-perylene-tetracarboxylic-bis-benzimidazole (PTCBI) as matrix material for the ETL is that the 50 nm thick layer of this dark red material absorbs a significant amount of light, while according to the low exciton diffusion length only a few nanometers close to the photoactive blend layer actually contribute to the photocurrent. Therefore, we replaced the single ETL of 50 nm n-doped MPP (devices A and B) by an undoped interlayer of 10 nm PTCBI followed by 50 nm n-doped C60 (device C). As the first absorption peak of C60 is at about 2.8 eV, it is basically transparent in the range of the first absorption peak of PTCBI at 2.2 eV. Therefore, it is obvious that device C should have much higher internal quantum efficiency in this spectral range than device B. However, as shown in Fig. 1(b), it exhibits also a significantly enhanced \( I_{sc} \). This is to be expected because device C, having a wide gap ETL, uses the light that is reflected at the Al top contact more efficiently than device B. Additionally, it might play a role that excitons in PTCBI that travel to the C60 interface are reflected there and have another chance to reach the interface of the mixed layer.
where they are separated into an electron on PTCBI and a hole on ZnPc.

![Device structure and characterization](image)

**Figure 1** Device structure and characterization
(a) p-i-n type bulk-heterojunction organic solar cells,
(b) Influence of charge transport layers on the I-V characteristics of p-i-n bulk heterojunction devices with the layer sequence ITO/PEDOT:PSS (40 nm)/ETL/50 nm ZnPc:C60 (1:2)/PTCBI/Al (70 nm).

Device A: HTL = p-doped m-MTDATA (50 nm), ETL = n-doped MPP (50 nm)
Device B: HTL = p-doped MeO-TPD (50 nm), ETL = n-doped MPP (50 nm)
Device C: HTL = p-doped MeO-TPD (50 nm), ETL = undoped PTCBI (10 nm)/n-doped C60 (50 nm). For all samples, p-doping is by admixture of 2mol% F4-TCNQ and n-doping by 2mol% rhodamine B. Fig. 1(b) under AM1.5 (100 mW/cm²) illumination.

Altogether, the characteristic parameters of device C in Fig. 1(b) are $I_{sc}$ of 8.5 mA/cm², open circuit voltage, $V_{oc}$ of 500 mV, FF of 0.55, and energy conversion efficiency of 2.33% under AM1.5 (100 mW/cm²) illumination. The benefit of embedding the intrinsic active layer system between doped organic wide gap materials is that one can design cells where only the photoactive layer absorbs light. Recombination losses at contacts or damage of the active layer by metal deposition are avoided and the cells make optimum use of the light reflected at the back contact electrode.

To investigate the short circuit current behaviour at higher light intensities, we have studied the dependence of the short circuit current on the incident white light intensity. As shown in Fig. 2, the short circuit photocurrents, $I_{sc}$ of devices B and C in Fig. 1(b) scale exactly linearly with the light intensity $I_{sc}$ up to more than 100 mW/cm², i.e. $I_{sc} \propto I_{sc}$ with the scaling exponent $\alpha = 1$. This proves that no non-linear effects like direct recombination of electrons and holes in the mixed layer or quenching of excitons by free carriers play a significant role.

**Figure 2** Dependence of the short circuit current versus incident light intensity of an ITO/PEDOT:PSS (40 nm)/p-MeO-TPD (50 nm)/ZnPc: C60 (1:2)/PTCBI (10 nm)/n-C60 (50 nm)/LIF (1 nm)/Al (70 nm) (solid squares) and ITO/PEDOT:PSS (40 nm)/p-MeO-TPD (50 nm)/ZnPc:C60 (1:2)/n-MPP (50 nm)/LIF (1 nm)/Al (70 nm) (solid circles) p-i-n bulk heterojunction devices. Lines are fits to a power law and are discussed in the text.

The photovoltaic external quantum efficiency or the spectrally resolved incident photon to converted electron efficiency IPCE (ε) is defined as the number of electrons flowing through an external circuit under short circuit conditions per incident
photon and is calculated from the spectrally resolved short-circuit current,

$$\eta_{\text{IPCE}}(\%) = \frac{1240/\lambda (\text{nm}) \times I_{\text{ph}} (\mu \text{A/cm}^2) / I_{\text{sc}} (\text{W/m}^2)}{L_{\text{int}}},$$

where \( L_{\text{int}} \) is the intensity of the incident light.

In Fig. 3 the result of the IPCE or the external quantum efficiency measurement for the same device C in Fig. 1 (b) is shown. A maximum external quantum efficiency or IPCE of 55% at a wavelength of 695 nm was observed, which comes mainly from ZnPc. In addition, a maximum in IPCE of 50% was reached at a wavelength of 405 nm, which results mainly from C60. Surprisingly, in a photoactive layer of ZnPc:C60 (50 nm, molar blend ratio 1:2) system, C60 contributed significantly to the photocurrent as efficient as ZnPc. The photocurrent contribution of C60 is generated from between \( \lambda = 400 \text{ nm} \) and 550 nm, while the ZnPc contributes from \( \lambda = 550 \text{ nm} \) to 800 nm, such that the solar spectrum at \( \lambda := 750 \text{ nm} \) is completely covered. The IPCE follows the absorption closely in the range where the ZnPc, C60 and PTCBl absorb [6]. Interestingly, these materials are well suited for p-i-n type bulk-heterojunction solar cells as they provide good coverage of the solar spectrum.

![Figure 3](image)

**Figure 3** Spectral resolved photon to electron conversion efficiency, IPCE of a p-i-n type bulk-heterojunction solar cell of device C in Fig. 1 (b) (i.e. ITO/PEDOT:PSS(40 nm)/ p-MeO-TPD(50 nm)/50 nm ZnPc:C60(1:2)/PTCBl(10 nm)/n-C60 (50 nm)/LiF (1 nm)/Al (70 nm)).

In addition, we have investigated the surface morphology of the film layers together with and without an intermediate layer of PEDOT:PSS using AFM. Figure 4 illustrates the surface morphology of (a) p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2)/PTCBl(10 nm)/n-C60 (50 nm) and (b) PEDOT:PSS (40 nm)/ p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2)/PTCBl(10 nm)/n-C60 (50 nm) of film layers as determined by atomic force microscope in tapping mode. The films for p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2)/PTCBl(10 nm)/n-C60 (50 nm) have a root mean square surface roughness (RMS) of about 8.0 ± 0.6 nm, whereas for PEDOT:PSS (40 nm)/ p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2)/PTCBl(10 nm)/n-C60 (50 nm) films RMS values of about 2.0 ± 0.5 nm are observed and a very homogeneous flat surface are showed in contrast to Fig. 4(a).

![Figure 4](image)

**Figure 4** AFM comparison of a) p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2 weight ratio)/PTCBl(10 nm)/n-C60 (50 nm) and (b) PEDOT:PSS/ p-MeO-TPD (50 nm)/50 nm ZnPc:C60(1:2 weight ratio)/ PTCBl(10 nm)/n-C60 (50 nm) film layers.

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Obviously, the surface roughness of the ITO glass substrate exerts a considerable influence on the thin film properties of the vacuum deposited organic films and this could be improved significantly using an intermediate layer of PEDOT:PSS which leads to lower the probabilities for shorts.

CONCLUSIONS AND RECOMMENDATIONS

In conclusion, efficient organic photovoltaic devices have been fabricated based on a p-i-n type bulk-heterojunction device architecture using doped wide-gap charge transport layers. For a device with a photoactive layer system consisting of a ZnPc:C60 blend and a neat PTCBI layer, an overall energy conversion efficiency of about 2.33% under 1 Sun, standard AM1.5 (100 mW/cm²) illumination were determined. Using AFM spectroscopy investigations we have directly demonstrated the relationship between film morphology and photovoltaic performance. Power conversion efficiencies are dependent on 3 factors: light absorption, exciton dissociation and charge collection. To gain high power conversion efficiency, organic layers should be thick enough to ensure high light absorption. Current organic layers used in photovoltaic (PV) devices are too thin to provide high light absorption. However, they cannot be made thicker due to poor exciton mobility. That is, exciton diffusion lengths cannot match optical absorption lengths. Triplet materials are good candidates since they possess longer exciton lifetimes compared with singlet ones. Long lifetime is also good for charge collection, especially for electron acceptor materials.

It is expected that further enhancement of light utilization efficiency by boosting the absorption of photons near the infrared frequency range and by building tandem structures will make it possible to improve the energy conversion efficiency substantially. Generally, it is expected that efficiencies exceeding 10% will be achieved in the future. "To enter large scale commercialization, the device efficiency will have to reach up to 15%, with a lifetime of up to 15-20 years. Organic photovoltaics have the potential of causing a revolution in the solar industry in the near future. Moreover, research and development on innovative organic photovoltaics solar technologies opens up the perspectives of high potential for cost reduction, to be flexible and semitransparent, to be manufactured in a continuous printing process, large area coating, substantial ecological and economic advantages, and new application fields in utilizing solar energy to improve quality of life and to help alleviate poverty and finally meeting the Millennium Development Goals (MDGs). Organic photovoltaics could be used for solar windows and solar awnings. Obviously, small-molecular-weight organic photovoltaic cells that can lead power conversion efficiencies >10% on flexible substrates could be achieved using double heterostructure and tandem organic PV Cells strategies. In general, this technology can also be used to provide solar power at a considerably lower initial capital expenditure. It also opens up entirely new applications such as providing electricity in remote areas in developing countries or operating large solar farms. Accordingly, our area of research in solar energy technology applications could be one of the most promising renewable energy sources for our future energy needs due to limited resources of traditional fuels and conventional energy sources and as well as environmental problems. Indeed, organic based solar cells have the potential to bring about a major breakthrough in reducing the cost of PV cells. In fact, organic semiconductors are relatively inexpensive and can be deposited on flexible substrates in high-throughput roll-to-roll coating machines, leading to low fabrication and installation costs and to a large variety of potential applications.

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