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Inverted ternary bulk hetrojunction hybrid photovoltaic device based on $AgInSe_2$ –polymer blend as absorber and PEDOT: PSS as hole transport layer

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ABSTRACT

For the first time Inverted ternary bulk hetrojunction hybrid photovoltaic device based on $AgInSe_2$ – polymer blend as absorber and PEDOT:PSS as hole transport layer was fabricated and characterized. Blends of MDMOPVV.PCBM.AIS (MDMOPVV-Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene], PCBM-(Phenyl-C61-butyric acid methyl ester), AIS-$AgInSe_2$) used as absorber layer. Bulk hetrojuction hybrid Photovoltaic device Ag/PEDOT:PSS /MDPVV.PCBM.AIS/ZnO/ITO was fabricated and tested with standard solar simulator and device characterization system as inverted cell configuration. The best performance and photovoltaic parameters, were obtained using an open-circuit voltage of about V_{oc} 0.24 V, a photocurrent of J_{sc} 0.56 J_{SC} (mA/cm^2), 28.4 (%) FF and an efficiency of 0.038 percent with a white light illumination intensity of 100 mW/cm^2. Further improvement efforts for better performance are on the way. Successful fabrication and working of this inverted device suggest further optimizations like spinning rate/thickness/solvents/depositions rates for active layers and proceeding further in light of knowledge of recombination studies and molecular modeling of AIS nanopowder with this organic system for better performance of a bulk hetrojunction hybrid solar cell.

Keywords: Bulk hetrojuction solar cell; hybrid electronics; blend photovoltaics; hole transport.

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Introduction

A conjugated polymer called poly (3, 4 - ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) is the most widely used organic material for hybrid devices. PEDOT:PSS is transparent, conductive (1000 S/cm) and as a hole transport layer in PEDOT:PSS can extract holes generated in blend out of the device **[1]**. Bulk hetrojunction photovoltaic cells are devices, known for fourth generation electronics which are believed to be dominating in energy sector in future. In this type of cell, the donor and the acceptor materials are mixed together to form the blend **[2]**. Various potential materials as active layers of blended bulk hetrojuction have been tried by researchers in past years **[3]**. Inorganic/organic hybrid solar cells have attracted a lot of interest due to their potential in combining the advantages of both components **[2]**. The maximum reported efficiency of such devices based on organic-organic and organic- inorganic bulk hetrojuction is around 6 % to the best of our knowledge **[4]**.

Chalcopyrite type $AgInSe_2$ is believed as a potential absorber material due to additional absorption edges due to crystal field and spit orbit splitting **[5]**. Blending such systems in organic matrix can be promising for future inorganic organic bulk hetrojuction hybrid photovoltaics. MDMOPVV (Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) and PCBM (Phenyl-C61-butyric acid methyl ester) are extensively being studied for possible donor accepter blends in bulk hetrojuction hybrid solar cells **[2]**. Blending with one of the inorganic component like $AgInSe_2$ can broad the absorption to NIR region, enhance the conductivity and help in better charge transfer due to photoluminescence quenching by AIS. Here we report bulk hetrojuction inverted hybrid photovoltaic device Ag/PDOT:PSS /MdPVV.PCBM.AIS /ZnO/ITO parameters for possible energy applications. In an inverted cell, the electric charges exit the device in the opposite direction as in a normal device. This happens because the positive and negative electrodes (which absorb the negative and positive charges, respectively) are reversed **[6]**. While inverted PVs enjoy longer lifetimes/stability compared to regular PVs, they typically don't reach yet efficiencies as high as regular PVs. The parameters of these devices were studied and are discussed here. To obtain good interfacial properties between the active layer and the electrode, poly(3,4-ethylenedioxythiophene):poly(styrene-sulfonate) (PEDOT: PSS), is used as a hole extraction layer (HEL) to increase the crystallinity of the subsequent layer as well as to enhance the extraction of holes **[7-8]**.

Experimental

The as synthesized $AgInSe_2$ (AIS) **[5]** was ball milled to miniaturize the crystal size to few nm. A high grinding energy planetary ball mill Pulverisette 6 (Fritsch, Germany) has been used. ZrO2 grinding bowls with 80 mL volume and charged with 25 ZrO2 balls of 10 mm in diameter were used. The details of ball milling procedure applied to obtain AIS nanostructure has been explained elsewhere in our earlier publication **[9]**. MDMOPVV (Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene) and PCBM (Phenyl-C61-butyric acid methyl ester) were purchased from sigma Aldrich and used without any further purification. The thickness of ITO films is about 135±15nm and its sheet resistance is about 15Ω/cm^2. The ITO substrates were patterned with 1MHCl and Zinc dust for 10 minutes and thoroughly washed with water. The patterned ITO substrates were cleaned with consecutively in ultrasonic bath with detergent powder, distilled water, acetone and isopropyl alcohol for 10 minutes in each and finally dried with pure dry N_2 gas. The dried substrates were further cleaned with Plasma cleaner for 10 minutes to remove organic contaminates and to improve surface roughness or wettability of substrate. To prepare 5ml of ZnO solution, 0.82g of Zinc acetate was weighed in top balance and dissolved in 4.8ml 2- methoxy ethanol and 0.2 ml ethanol amine. It was stirred with magnetic bar for 12 h and aged for 24h before use. The substrates were preheated about 50-60^{0}C for 2-3 minutes and spin-coated at the speed of 600-2000 rpm for 40 sec in ambient condition. The glass substrates coated with ZnO were transferred in to hot plate and baked at 150C for 30 minutes.

10mg MDMOPVV, 10 mg PCBM and 10mg of milled $AgInSe_2$ nano crystals were dissolved in 2ml chlorobenzene and stirred for 24 hr at 60C. The blend solution was spin coated at different spun speed at 1000rpm, 1500rpm and 2000 rpm for 50 seconds and annealed at 120C for 10 minutes (SCS G3 spin coater system). The contacts were cleaned with cotton sticks soaked with chloroform and finally poly (3 , 4 - ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) was also spin coated over it, then 100nm Ag were deposited in PVD (LC technology) at very low pressure at 1.6E-6mbar. The device (**Fig. 1**) was finally characterized by Keithly (Keithley 4200-SCS) system using of light of intensity 100mW/cm^2. The active area of tested device is 6mm^2. All layers were deposited one by one in glob box inert environment (N_2 gas, Lc technology) assembled at Queens University, Kingston, without breaking the vacuum to avoid contamination. It is important to mention here that device was fabricated and tested as inverted cell geometry. A set of devices with different spun speed for blend layer 1000, 1500, 2000 rpm were fabricated and studied for various solar cell parameters like short circuit current density (J_{sc}), open circuit voltage (V_{oc}), Fill factor (FF) ,series/shunt resistance (R_s, R_{sh}) and efficiency (E_{ff}).

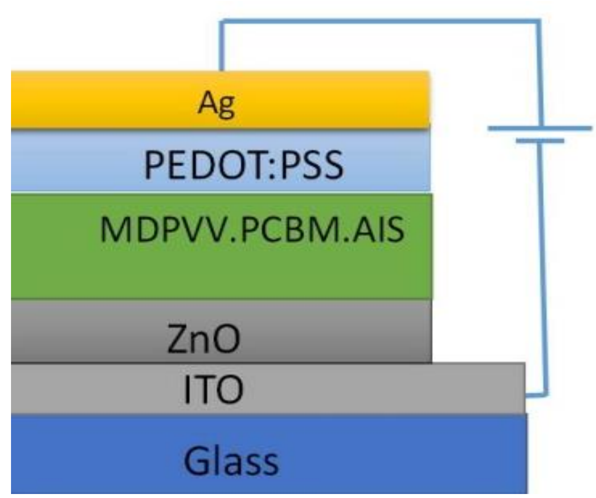

Fig. 1. Inverted ternary bulk hetrojunction hybrid photovoltaic device.

Results and discussion

Device structure and characterization

Fig. 2 shows Current density–voltage measurements for inverted devices Ag/PDOT:PSS/MdPVV.PCBM.AIS/ ZnO/ITO with different spun speed for active layers, without and with illumination. Our earlier communication with AIS microcrystal blend with MDMOPVV.PCBM **[2]** suggest a homogeneous dispersion of AIS in this polymer system with encouraging structural and optical feature for device application as studied by XRD, Optical microscopy, SEM, PL and UV-VIS spectroscopy. In this communication we present device performance of inverted hybrid cells with active layer blended with AIS nanostructures obtained by high speed ball milling and poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS), as a hole extraction layer (HEL) used to increase the crystallinity of the subsequent layer as well as to enhance the extraction of holes. PEDOT:PSS also serve as interfacial layer to improve the properties between the active layer and the electrode. The device is configured as inverted PVs geometry (**Fig. 1**) which is expected to enjoy longer lifetimes/stability compared to regular PVs. After a series of optimization out of best selected blends the device with configuration Ag/PEDOT:PSS/MDMOPVV. PCBM.AIS/ ZnO/ITO was fabricated and tested for efficiency and other cell parameters. **Table 1** shows the photovoltaic parameters of the devices with different spun speed. The Typical current–voltage (J–V) curves are shown in **Fig. 2(a-c)**. The J–V characteristics of the diodes have been obtained under white light with an irradiance of 100mW/cm^2 through the ITO side. In the MDMOPVV.PCBM.AgInSe$_2$ blends; PL is quenched as explained in our earlier communication **[2]**, which suggests that the excitons are splitting in these blends. A study to gain a detailed understanding of band structure and recombination in these systems is underway. The devices show series and shunt resistance of the order of 10^3 ohm. High series resistance of the device is also one of the reasons for poor efficiency. Series resistance in a solar cell has mainly three causes: firstly, the movement of current in the solar cell which can be further affected by various parameters like defects etc.; secondly, the contact resistance and finally the resistance of the top metal Contacts. The main impact of series resistance is to reduce the fill factor, although excessively high values may also reduce the short circuit current as observed here and tabulated in table **[2, 10]**. The sharp intercept on negative y axes show a significant short circuit current density on illumination. Maximum FF of 28.4 percent (maximum) which represent squareness of curve in fourth quadrant was calculated. We obtained an open-circuit voltage of about V_{oc} 0.24 V and a photocurrent density of Jsc 0.56 (mA/cm^2) and an efficiency of 0.038 percent using a white light illumination intensity of 100mW/cm^2. An optimum thickness is also important for optical layer; we see here decrease in short circuit current density and efficiency for the device layers which were deposited with more than 1000 rpm. High spinning speed results in very thin layers and absorb less intensity. It is proposed that for future optimization the layers must be spunned below speed 1000 rpm for these systems. Excitons separation and collection along with better band matching need to be explored for better performance. Further knowledge of recombination studies and molecular modeling of AIS nanopowder with this organic system may lead to better understanding of the various parameters in blended inverted solar-cell performance.

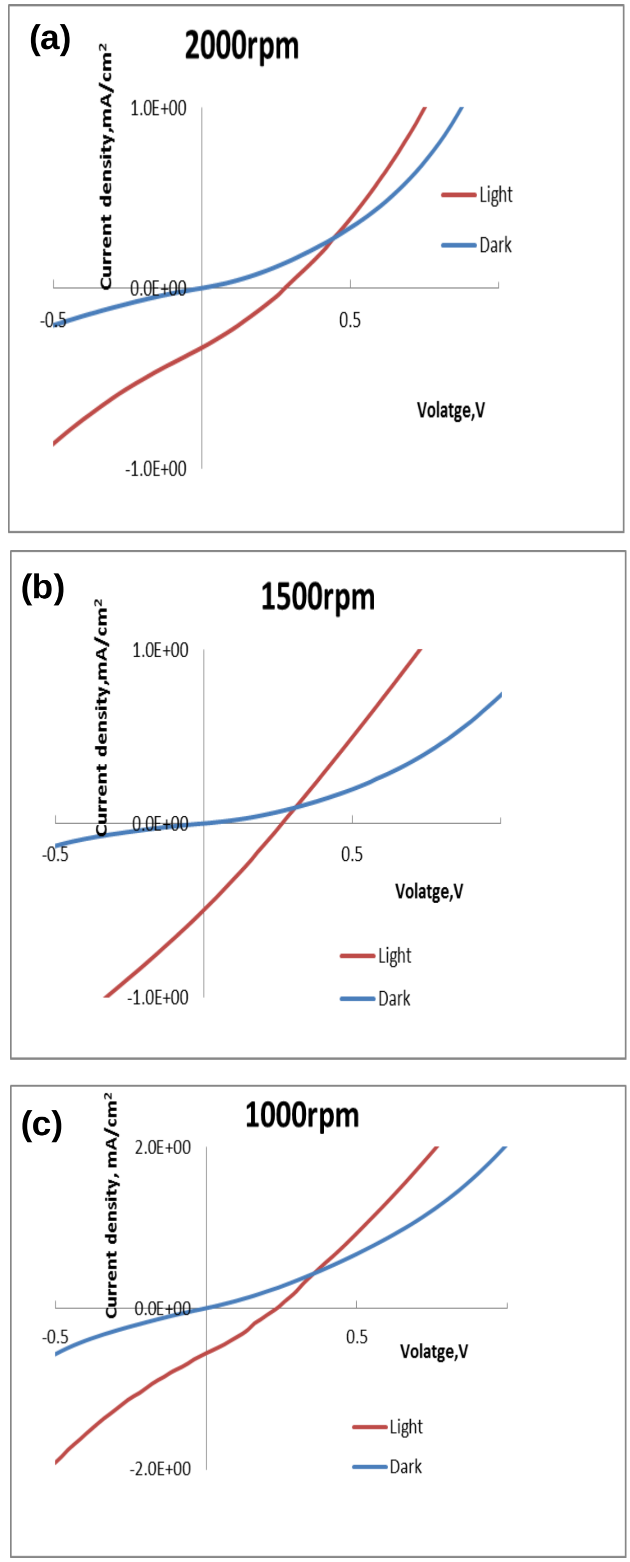

Fig. 2 (a-c). Current density–voltage measurements for inverted devices Ag/PDOT:PSS /MDPVV.PCBM.AIS/ZnO/ITO with different spun speed for active layers, without and with illumination. The best device has (Jsc) 0.56 mA /cm^2, (Voc) 0.24, (FF) 28.4%, and (EF) 0.038%.

Table 1. Photovoltaic parameters for devices.

SpunSpeed (rpm)	J_{SC} (mA/cm^2)	V_{OC} (V)	FF (%)	R_{SH} (Ohm)	R_S (Ohm)	E_{FF} (%)
1000	0.56	0.24	28.4	2.6E+03	1.9E+03	0.038
1500	0.50	0.26	26.7	2.9E+03	2.4E+03	0.034
2000	0.33	0.28	28.0	5.7E+03	2.9E+03	0.026

Conclusion

For the first time Inverted ternary bulk hetrojunction hybrid photovoltaic device based on $AgInSe_2$ – polymer blend as absorber and PDOT: PSS as hole transport layer was fabricated and studied for cell parameter. AIS nanopowder was obtained by high speed milling of as synthesized bulk microcrystals. Ar medium ball milled AIS nanopowder was dispersed in MDMOPVV and PCBM using chlorobenzene as a solvent. Inorganic organic blended bulk hetrojuction hybrid Photovoltaic device Ag/PDOT:PSS /MDMOPVV.PCBM.AIS/ZnO/ITO was fabricated and tested with standard solar simulator and device characterization system as a inverted cell geometry. To improve interfacial properties between the active layer and the electrode, poly(3,4-ethylenedioxythiophene): poly(styrene-sulfonate) (PEDOT:PSS), is used as a hole extraction layer (HEL) to increase the crystallinity of the subsequent layer as well as to enhance the extraction of holes. The best performance and photovoltaic parameters, we obtained with a spun speed of 1000 rpm was (Jsc) 0.56 mA /cm^2, (Voc) 0.24, (FF) 28.4%, and (EF) 0.038%. Our results are encouraging for carrying further the fourth generation inorganic organic hybrid bulk hetrojuction photovoltaics research for energy on these systems. More optimization after molecular modeling of AIS nanopowder with this organic system and with spinning rate/Thickness/solvents/ depositions rates for active layers etc. needed to be explored for improved photovoltaic response of these inverted bulk hetrojunction hybrid devices based on MDMOPVV.PCBM. $AgInSe_2$ nanopowder.

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