

Spray pyrolysed In_2S_3 thin films: A potential electron selective layer for large area inverted bulk-heterojunction polymer solar cells

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In this paper, we report the results of investigations on the potential of spray pyrolysis technique in depositing electron selective layer over larger area for the fabrication of inverted bulk-heterojunction polymer solar cells. The electron selective layer (In_2S_3) was deposited using spray pyrolysis technique and the linear heterojunction device thus fabricated exhibited good uniformity in photovoltaic properties throughout the area of the device. An MEH-PPV:PCBM inverted bulk-heterojunction

device with In_2S_3 electron selective layer (active area of $3.25 \times 3.25 \text{ cm}^2$) was also fabricated and tested under indoor and outdoor conditions. From the indoor measurements employing a tungsten halogen lamp (50 mW/cm^2 illumination), an open-circuit voltage of 0.41 V and a short-circuit current of 5.6 mA were obtained. On the other hand, the outdoor measurements under direct sunlight (74 mW/cm^2) yielded an open-circuit voltage of 0.46 V and a short-circuit current of 9.37 mA.

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1 Introduction Inverted polymer solar cells are quite promising from the point of view of stability and ease of fabrication. The underlying mechanism is such that electrons produced in the active layer, as a result of the photo-induced charge separation, are collected by the transparent conducting front electrode, usually ITO, and the holes are collected by the back electrode, usually silver. For the efficient functioning of this structure, an 'electron selective layer' is introduced between the active layer and ITO whereas an electron blocking layer is inserted between the metallic electrode and the active layer [1]. Advantage of the inverted structure is that it eliminates the use of low work function cathode which is usually highly reactive and gets easily oxidized in air. Furthermore, it avoids the possibility of an ITO/PEDOT:PSS interface which is quite reactive and degrades rather quickly [2]. Such inverted structures were shown to have power conversion efficiencies greater than 3% [3, 4]. However in most of these reports, the devices were fabricated on a laboratory scale with active areas less than 0.5 cm^2 . There have been only a few attempts on realizing such devices on a larger area [1, 5–8].

In inverted polymer solar cells, the most widely used electron selective layers are ZnO or TiO_2 thin films which are processed from solutions. However, preparation of these thin films is quite tedious and time consuming, even though they do not require any sophisticated equipments. For example, TiO_2 thin films are commonly prepared from a precursor solution which is coated onto ITO substrates and calcined at elevated temperatures ($450\text{--}500 \text{ }^\circ\text{C}$) for about 30–60 min [4, 9–11]. ZnO thin films, on the other hand, are prepared from their nano-particle solution/dispersion [3, 12], the preparation of which is again a tiresome process. Moreover a variety of preparation techniques are followed which points out the need for a standard and reliable process [10, 13–15]. Furthermore, to accomplish large area devices, the deposition technique should be such that it ensures uniformity of the film on the entire area in terms of its composition, morphology and thickness. Now from an industrial point of view, we must have a cost effective deposition process which is easy and less time consuming and which can be integrated onto a production line. It is at this point that we came across the relevance of spray pyrolysis technique. Several other

techniques such as ink jet printing, screen printing, etc. have already been demonstrated in this direction [1, 16]. The uniqueness of spray technique is that it is scalable, less time consuming and requires no elaborate procedures for preparing the precursor solution. Recently, Dedova et al. [17] have shown that nano-structured films could also be prepared using this technique.

In the present work, we report the use of spray pyrolysis technique for depositing indium sulphide (In_2S_3) as electron selective layer over larger areas for inverted polymer solar cells. In our earlier publication we had already reported the feasibility of spray deposited In_2S_3 as an electron selective layer by fabricating $\text{In}_2\text{S}_3/\text{MEH-PPV}$ heterojunctions [18]. An inverted bulk heterojunction configuration is tried in this work by using a blend of poly (2-methoxy-5-[2'-ethylhexyloxy]-1,4-phenylene vinylene) (MEH-PPV) with [6,6] phenyl C_{61} butyric acid methyl ester (PCBM). We have used MEH-PPV for ease and simplicity although it is well acknowledged that it is quite susceptible to photo-degradation under continuous illumination [19].

2 Experimental In_2S_3 thin films were deposited on ITO coated glass substrates (thickness 2000 Å, sheet resistance $10 \Omega/\text{cm}^2$) by using the spray pyrolysis technique. In this method, aqueous solution containing indium chloride and thiourea was sprayed at a rate of 2 ml/min on to the heated substrate kept at $350 \pm 5^\circ\text{C}$. At the substrate surface, the spray droplet vaporizes and leaves a dry precipitate, which instantly decomposes to form In_2S_3 . An indigenously developed automated spray pyrolysis unit was used for the deposition process. All the deposition parameters such as spray rate, substrate temperature, pressure of carrier gas, distance between spray head and substrate, can be controlled in this unit. More details related to automated spray unit and CSP technique has been described elsewhere [20, 21]. In the present work, we prepared In_2S_3 thin films with In/S ratio of 1.2/8, 2/3, 2.5/3 and 2/2 in the spray solution. This was achieved by varying the molarity of the precursors keeping the volume of solution fixed. Here an indium concentration of '2' corresponds to 0.025 M InCl_3 . All the ratios are derived from this fixed molarity value for InCl_3 . A total volume of 20 ml was sprayed in all the cases. Thickness of the films was measured using the Stylus Profilometer (Dektak-6M). Resistivity and photosensitivity [22] of the films prepared on glass substrates was measured using the two probe method employing a Keithley Source Measure Unit (SMU, K236).

Linear heterojunction was prepared by spin coating the solution of MEH-PPV in chlorobenzene (5 mg/ml), on top of the In_2S_3 film deposited on ITO substrates. MEH-PPV was synthesized as described elsewhere [23]. Layer thickness of MEH-PPV was approximately 100 nm. For fabricating the bulk-heterojunction devices, a chlorobenzene solution containing MEH-PPV and PCBM (purchased from Solenne BV) in the ratio 1:5 (wt:wt) and having a concentration of 20 mg/ml was spin coated on top of In_2S_3 . Layer thickness in this case was measured to be 120 nm. Electrical contacts

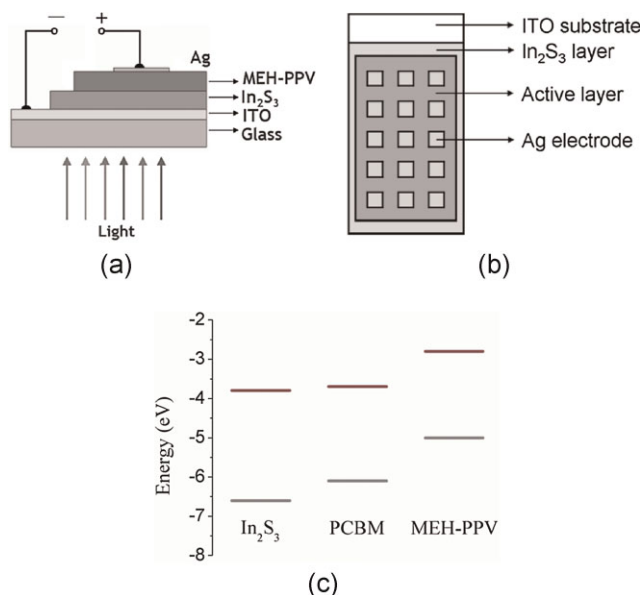


Figure 1 (online colour at: www.pss-a.com) (a) Device structure, (b) schematic of the top of the device and (c) HOMO-LUMO energy levels of MEH-PPV and PCBM, and the position of conduction band minimum and valence band maximum of In_2S_3 .

from the top were taken by depositing silver electrodes through vacuum evaporation (at a pressure less than 10^{-5} Torr) using a shadow mask. Except for electrode deposition, all the other deposition and characterization processes were carried out under ambient air atmosphere. The device structure is depicted in Fig. 1a.

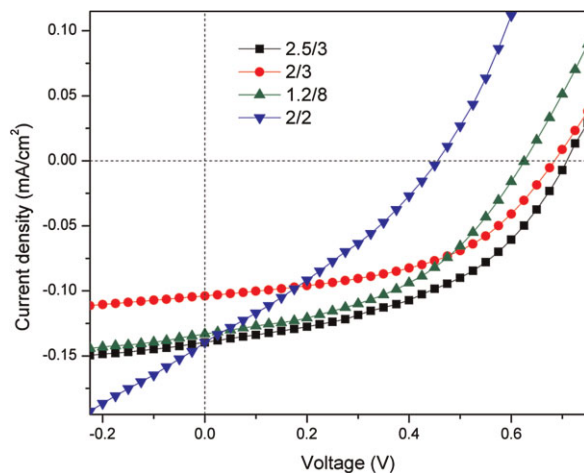
Dark and illuminated $J-V$ characteristics of the devices were measured using the Keithley SMU, K236 and Metric's Interactive Characterization Software (ICS). The devices were illuminated using a tungsten halogen lamp, with an intensity of $50 \text{ mW}/\text{cm}^2$, on the substrate surface.

3 Results and discussion In our previous study, we fabricated polymer heterojunction using In_2S_3 with In/S ratio of 1.2/8 in the precursor solution [18]. This bilayer device exhibits good photo-response compared to the single layer device employing the polymer alone which showed no photoactivity. Now as a continuation to this work, we varied the In/S ratio in the precursor solution used for preparing In_2S_3 and studied its effect on the photovoltaic performance of the heterojunction. In_2S_3 thin films on ITO substrates were prepared using precursor ratios such as 1.2/8, 2/3, 2.5/3 and 2/2 keeping the volume of solution sprayed at 20 ml. The films were found to be polycrystalline in nature except for the 2/2 ratio which was found to be amorphous. Thickness, resistivity and photosensitivity of the films were also measured and are given in Table 1.

Heterojunctions were fabricated by spin coating a 100 nm thick MEH-PPV layer over the In_2S_3 films. The $J-V$ characteristics of these devices are presented in Fig. 2 and the photovoltaic parameters are given in Table 2. From Fig. 2, it can be seen that an increase in open-circuit voltage

Table 1 Thickness, resistivity and photosensitivity of In_2S_3 thin films.

In/S ratio	volume of solution (ml)	thickness (nm)	resistivity ($\text{k}\Omega\text{ cm}$)	photosensitivity
1.2/8	20	200	238	100
2/3	20	330	342	99
2.5/3	20	350	416	557
2/2	20	210	161	116

**Figure 2** (online colour at: www.pss-a.com) J - V characteristics of the linear heterojunctions employing In_2S_3 thin films with different In/S ratios.

(V_{oc}) has been achieved by using an In/S ratio of 2.5/3. This increase in V_{oc} without any decrease in short-circuit current density (J_{sc}) may be attributed to the increase in both resistivity and photosensitivity of In_2S_3 (see Table 1). Typically, an increase in resistivity will naturally improve the open-circuit voltage, but at the expense of J_{sc} . This can be seen in the case of 2/3 ratio in which J_{sc} decreases to 0.1 mA/cm^2 . For the 2.5/3 ratio, however, it is apparent that the increase in photosensitivity could have saved J_{sc} from dropping due to increased resistivity of the film. In the case of device with 2/2 ratio, a reverse nature can be observed in which the V_{oc} drops due to the reduction in shunt resistance as a result of the decrease in resistivity of In_2S_3 [24]. The decrease in shunt resistance is evident from the nature of

Table 2 Photovoltaic parameters of the devices using In_2S_3 of different ratios.

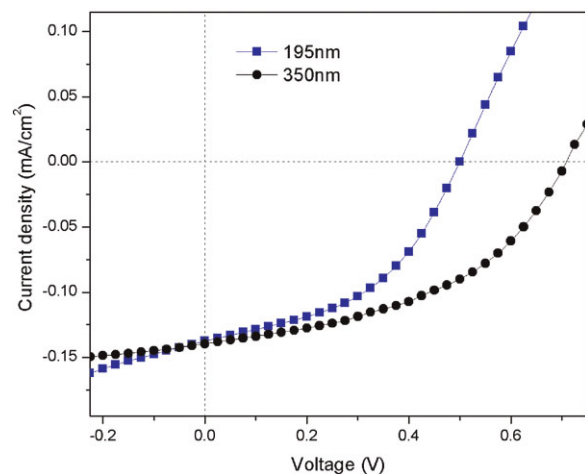
In/S ratio	V_{oc} (V)	J_{sc} (mA/cm^2)	fill factor, FF (%)	efficiency, η (%)
1.2/8	0.63	0.133	44.9	0.075
2/3	0.68	0.10	49.0	0.07
2.5/3	0.71	0.14	45.4	0.09
2/2	0.46	0.14	30.3	0.039

the characteristic around $V=0$. Now, the drop in V_{oc} has the effect that the fill factor also decreases resulting in decrease in efficiency of the device.

It may also be argued that an increase in thickness of In_2S_3 might also have contributed to improvement in V_{oc} . Hence in order to clarify this, we decreased the thickness of In_2S_3 keeping In/S ratio at 2.5/3. Now reducing the thickness by decreasing the volume of solution below 20 ml will result in discontinuous films and hence shorting of the device. Hence to overcome this problem, the volume was kept fixed at 20 ml and the molarity of the precursor was reduced to half. The deposited films were having a thickness of 195 nm. The resistivity and photosensitivity were $182\text{ k}\Omega\text{ cm}$ and 119, respectively. It may be noted that the film properties are comparable to that prepared with 2/2 ratio. This is also reflected in the J - V characteristic of the heterojunction fabricated using this film (see Fig. 3). This might be due to the fact that reduction in molarity keeping the volume fixed, causes lesser chance of sulphur being incorporated leading to a nature similar to that exhibited by 2/2 ratio. Hence it may be concluded that the optimum performance has been obtained for devices with the 350 nm thick film. Hence it has been used for fabricating devices for further studies.

In all these studies, the active area of the devices fabricated were only 0.12 cm^2 , i.e. only a very small area compared to the actual area of the sample (2.5 cm^2). Hence the variation of the photovoltaic parameters over the entire area of the sample was evaluated by measuring the J - V characteristics from 15 different points on the sample. For this, fifteen small electrodes of area 0.04 cm^2 were deposited at these positions as depicted in Fig. 1b. This helps to map the variation of the photovoltaic parameters over the entire area of the sample. The results are presented in Fig. 4.

In the figure, the X - and Y -positions represent the position of the electrodes along the width and length of the sample. The V_{oc} was observed to be fairly uniform throughout the entire area of the sample. Out of the 15 points selected, 12 showed V_{oc} in the range of 0.67–0.71 V. Maximum V_{oc}

**Figure 3** (online colour at: www.pss-a.com) J - V characteristics of the devices with different In_2S_3 thickness (2.5/3 ratio).

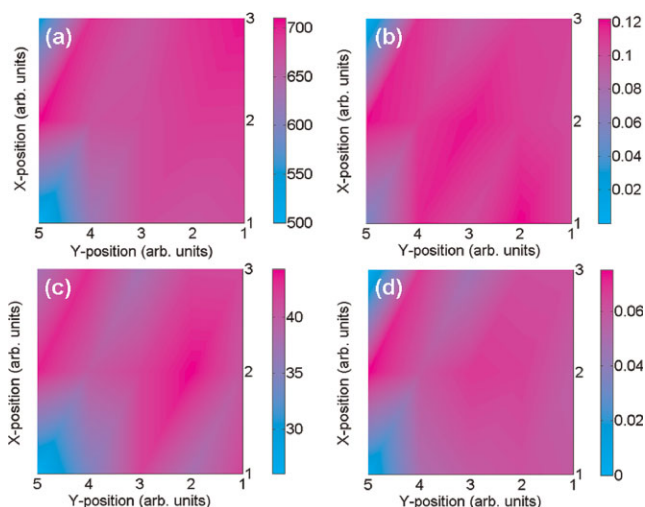


Figure 4 (online colour at: www.pss-a.com) 2D mapping of the photovoltaic parameters of the linear heterojunction (a) V_{oc} (in mV), (b) J_{sc} (in mA/cm^2), (c) fill factor (%) and (d) efficiency (%).

attained was 0.71 V with J_{sc} of $0.12 \text{ mA}/\text{cm}^2$, fill factor of 43.5% and efficiency of 0.75%. Significant variation in V_{oc} was found only towards the two corners of the sample. Similar is the case with other parameters such as J_{sc} , fill factor and efficiency. This result also indicates that the In_2S_3 layer is quite uniform and is free from pin holes or cracks. Further, any significant variation in the device properties could occur only at the edges and corners since the substrate temperature may drop quite easily at these places during the spraying process. This is also reflected in the photovoltaic properties of the device depicted in Fig. 4.

It may be noted that even though the V_{oc} is fairly high, all the devices were having a very low value for J_{sc} leading to very small efficiencies. This is because only the $\text{In}_2\text{S}_3/\text{MEH-PPV}$ interface contributes to the photocurrent generation and that the series resistance of the device is too high ($\sim 10^3 \Omega \text{ cm}^2$). An improvement in J_{sc} can be achieved by blending the polymer with an electron acceptor such as PCBM. Figure 5 shows the J - V characteristics of such an MEH-PPV:PCBM bulk-heterojunction device of active area 0.12 cm^2 , again employing In_2S_3 as electron selective layer. The J_{sc} of this device was in fact significantly improved. It increased to $0.87 \text{ mA}/\text{cm}^2$ at $50 \text{ mW}/\text{cm}^2$, i.e. there is almost a sixfold increase in the current density. This increase in J_{sc} leads to an increase in efficiency of the device to 0.25%. The open-circuit voltage of this device was found to be 0.54 V.

From Fig. 5, it can be seen that there is a point of inflection near V_{oc} and subsequent concavity in the fourth quadrant of the characteristic. This negative curvature causes a substantial reduction in the fill factor of the device. The fill factor decreases to around 27% for the bulk-heterojunction device. Gupta et al. [25] relates this concavity to a non-uniform contact or an incomplete coverage of metal over the polymer surface. However, this may not be true in the present case, since no such concavity was observed for the linear

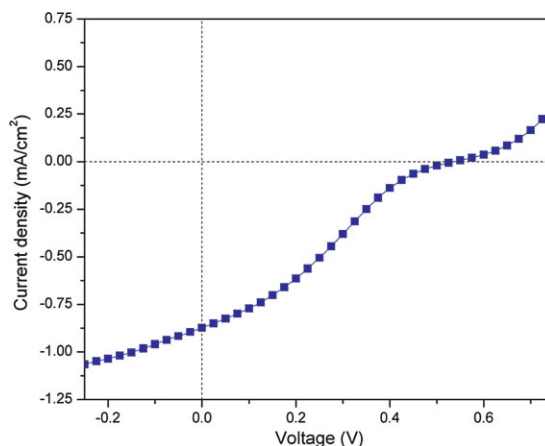


Figure 5 (online colour at: www.pss-a.com) J - V characteristics of the bulk-heterojunction device with an active area of 0.12 cm^2 at $50 \text{ mW}/\text{cm}^2$.

heterojunction device with the same metal electrode deposited under similar conditions. Hence it may be alleged that a counter acting diode is responsible for this inflection in the device characteristics. In our device structure, we used silver as the anode. It has already been found to serve as good positive contact [18]. However when used directly over the blend, both the donor and acceptor phases come in direct contact with the anode and leads to a counter injecting behaviour for the device. This can be overcome by using a hole collecting layer between the active layer and the metal anode. Weickert et al. [26] have shown that a significant improvement in the fill factor and efficiency could be achieved by introducing a hole transporting layer such as PEDOT:PSS.

Now a large area bulk-heterojunction device of dimension $4.5 \times 4.5 \text{ cm}^2$ with an active area of $3.25 \times 3.25 \text{ cm}^2$ was fabricated in order to demonstrate the potential of our spray technique to achieve large area uniform coating of thin films for polymer solar cells. The photograph of the fabricated cell is given in Fig. 6a. The cells were then tested both under indoor as well as outdoor conditions. As before, the indoor measurements were carried out using the Keithley SMU. Figure 6b shows the semi-logarithmic plot of the I - V characteristics of this large area cell under dark and $50 \text{ mW}/\text{cm}^2$ illumination. From the indoor measurements, we obtained a short-circuit current (I_{sc}) of 5.6 mA (current density of $0.53 \text{ mA}/\text{cm}^2$) and an open-circuit voltage of 0.41 V for this device. The fill factor and efficiency were calculated to be 27% and 0.11%, respectively.

On the other hand, the outdoor measurements yielded a short-circuit current of 9.37 mA and an open-circuit voltage of 0.46 V. The light intensity at the time of measurement was only $74 \text{ mW}/\text{cm}^2$. It should be noted that the large area device has smaller V_{oc} and J_{sc} compared to the small area device resulting in a decrease in the efficiency. A decrease in J_{sc} is expected since the series resistance will increase due to the collection of carriers using two contacts at the corners of the

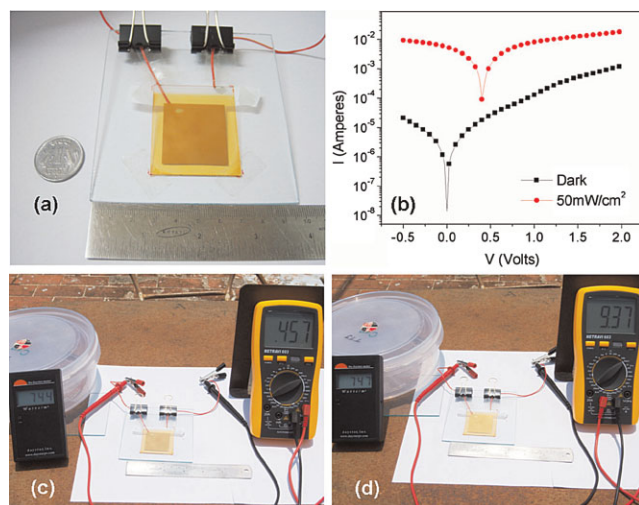


Figure 6 (online colour at: www.pss-a.com) (a) Photograph of the large area device fabricated, (b) semi-logarithmic plot of the I - V characteristics of the device under 50 mW/cm^2 illumination measured indoors, (c) and (d) photographs of the device under operation in direct sunlight (74 mW/cm^2).

device. The decrease in V_{oc} may be due to the non-uniform coating of the active layer which is a limitation of the spin coating technique when going for large area coating of films. Better results can hence be attained by using other solution coating techniques suitable for larger areas.

4 Conclusion From the present study it may be concluded that the chemical spray pyrolysis technique is quite suitable for the large area deposition of electron selective layers for inverted polymer solar cells. In_2S_3 electron selective layer was deposited over a larger area by this technique and inverted polymer devices were successfully fabricated using it. The device performance however has to be improved further by introducing a hole transporting layer and also by using a suitable polymer with lower band gap and better charge mobility than MEH-PPV.

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