

Photovoltaic Effect in Polymer–Semiconductor Heterojunction

N. A. BAKR

Polymer and Semiconductor Laboratory, Physics Department, Faculty of Science, Mansoura University, Mansoura, Egypt

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ABSTRACT: A heterojunction of poly(4-methylstyrene) and ZnTe was prepared on a glass substrate coated with SnO₂. ZnTe was deposited by a semiclosed space technique (SCST), while a pure and iodine (1% wt)-doped polymeric layer was deposited, on the front surface of the ZnTe film, by the spin-coating method. The junction characteristics are discussed in view of the morphological surface of ZnTe obtained at different substrate temperatures and UV absorption spectra. The photovoltaic parameters were explored from current–voltage (I–V) measurements under dark and illumination conditions. The results were interpreted according to the formation of the rectifying junction at the polymer–semiconductor interface. A rectifying heterojunction and a photovoltaic effect are improved for the iodine-doped polymer layer and a substrate temperature of 350°C. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 79: 2425–2430, 2001

Key words: photovoltaic; heterojunction; polymer–semiconductor; morphology; optical absorption

INTRODUCTION

The study of semiconductor heterojunctions (SHJ), prepared from a wide band gap of several binary compounds of II–VI and III–V classes, are promising to be extremely useful in both scientific and technological applications. In recent years, considerable attention has been focused on the investigation of a new classes of heterojunctions, such as polymer–metal Schottky barriers, polymer–semiconductor composites, polymer–porous silicon, and polymer–semiconductor heterojunctions (PSHJ), due to the unusual nature of their contacts as well as the potential new devices to which these heterojunction contacts can be applied.^{1–14}

ZnTe is one of the widest band gap material of II–VI, as a *p*-type compound, which has a direct band gap of 2.26 eV at room temperature^{15,16} and 2.39 eV at 10 K.¹⁷ This type of semiconductor

offers an immense potential for advanced optoelectronic device applications.

It is known that, through chemical and/or mechanical doping, polymeric materials can be generated with electrical conductivities that vary over a wide range from insulator to metalliclike materials. Therefore, several types of junctions are possible when contact is made between a polymer and a semiconductor, where a rectifying barrier can be formed at the interface.

Poly(4-methylstyrene) (PMS) is nonpolar material having π -electrons in the phenyl rings. The addition of iodine (I₂), at low concentration, will increase its conductivity due to the introduction of cationic states in the polymer backbone. Hence, doping produces a local attractive iodine either dispersed in the polymer matrix or attached to the phenyl group.^{7,18–20} It was the purpose of the present work to fabricate a photovoltaic sandwich cell based on the iodinated PMS and ZnTe system and to investigate its photovoltaic characteristics.

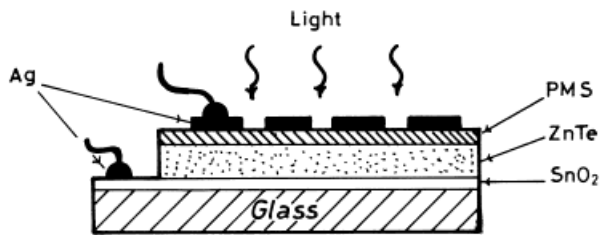


Figure 1 Schematic representation of the PSHJ structure.

EXPERIMENTAL

A thin layer of ZnTe was evaporated by the semi-closed space technique^{21,22} under a vacuum of 10^{-5} Torr, using an Edward 360 A coating unit. A transparent glass coated with a thin transparent conductive layer of SnO₂, as a lower electrode (having 0.05- μm thickness), was used as a substrate for the deposition of ZnTe films. Different samples of ZnTe with a nearly constant thickness of 5 μm was obtained at different substrate temperatures ($T_{\text{sb}} = 300, 350, 380^\circ\text{C}$) at a constant evaporation temperature of the material source of $T_{\text{ev}} = 600^\circ\text{C}$ for a constant evaporation process time of $t_{\text{ev}} = 5$ min.

The upper layer of the fabricated heterojunction is a thin layer of PMS with a thickness of 3 μm . The pure polymeric material and that doped with a low concentration of iodine (1% wt) were dissolved in a toluene solvent for 1 week in the dark at room temperature. The doped and undoped polymeric solutions were deposited on the upper surface of the ZnTe layer by the spin-coated method at the same conditions. The obtained structures were dried, in an oven regulated at 100°C for 2 h to thoroughly remove the residual solvent. A thin layer of Ag was evaporated on the outside surface of the polymeric layer, in a finger-like structure, as an upper electrode. A cross-section diagram of the obtained heterojunction system is represented in Figure 1.

The surface morphology investigation was carried out using a polarized Zeiss Laboval 4 optical microscope. UV-absorption spectra, in the range of 200–900 nm, were obtained at different temperatures ranging from room temperature up to 80°C with an ATI Unicame UV/VIS spectrometer UV2 (Vision software V 3.2). To study the photovoltaic effect of the prepared heterojunction, the current was measured by a Keithly picometer 485. The samples were illuminated with the full intensity of a tungsten lamp source (100 mW/

cm^2) on an active area of 0.28 cm^2 . The PMS side was illuminated to act as a window to the ZnTe layer.

RESULTS AND DISCUSSION

The surface morphology dependence of ZnTe thin films on the glass substrate temperature (T_{sb}) are shown in Figure 2. A polycrystalline feature was obtained for all substrate temperatures ranging from 300 to 380°C . A large and shallow triangle structure is observed, with the best fine structure at $T_{\text{sb}} = 350^\circ\text{C}$. For lower and higher substrate temperatures, that is, at 300 and 380°C , a rough and random polycrystalline phase, in shape and size, is observed. For lower T_{sb} (300°C), the evaporation energy increased as well as did the condensation energy. Since the vapor pressure of Zn atoms is higher than that of Te atoms,²³ the obtained film with a small grain size has an excess of Zn atoms. As T_{sb} increases ($T_{\text{sb}} = 350^\circ\text{C}$), the condensation energy of the substrate increases²² and the number of Zn atoms which will arrive at the substrate surface decreases. These will yield a thin film having a structure near the stoichiometric composition with a nearly real triangle structure with a large grain size [as seen in Fig. 2(b)]. For a higher T_{sb} value (380°C), the condensation energy decreases more and the possibility of the re-evaporation process of Zn atoms from the substrate surface led to the formation of nonstoichiometric polycrystalline ZnTe film with a high degree of randomness and a small grain size. Furthermore, the surface resistance (R_s) dependence on the substrate temperature is illustrated in Table I. These grain boundaries can operate as defects. As the grain size increases, the surface resistance of the evaporated ZnTe films decreases.

The UV spectrum of ZnTe (dashed line) and PMS (solid line) are shown in Figure 3. The optical band gap of ZnTe films was calculated from the absorption edge of the UV spectra (Fig 3), taken at room temperature and found to be 2.15 eV. This value was found to be very close to that reported.^{15,16,21} A very low absorbance, $\lambda > 350$ nm, was observed for PMS. This means that PMS has a high transparency for both visible and near IR regions. For $\lambda < 350$ nm, an abrupt increase in the absorbance took place due to the high absorption coefficient in this range. The band gap of the material was calculated from this edge and found to be 3.5 eV. A high transparency and a large band gap offers the possibility of using this ma-

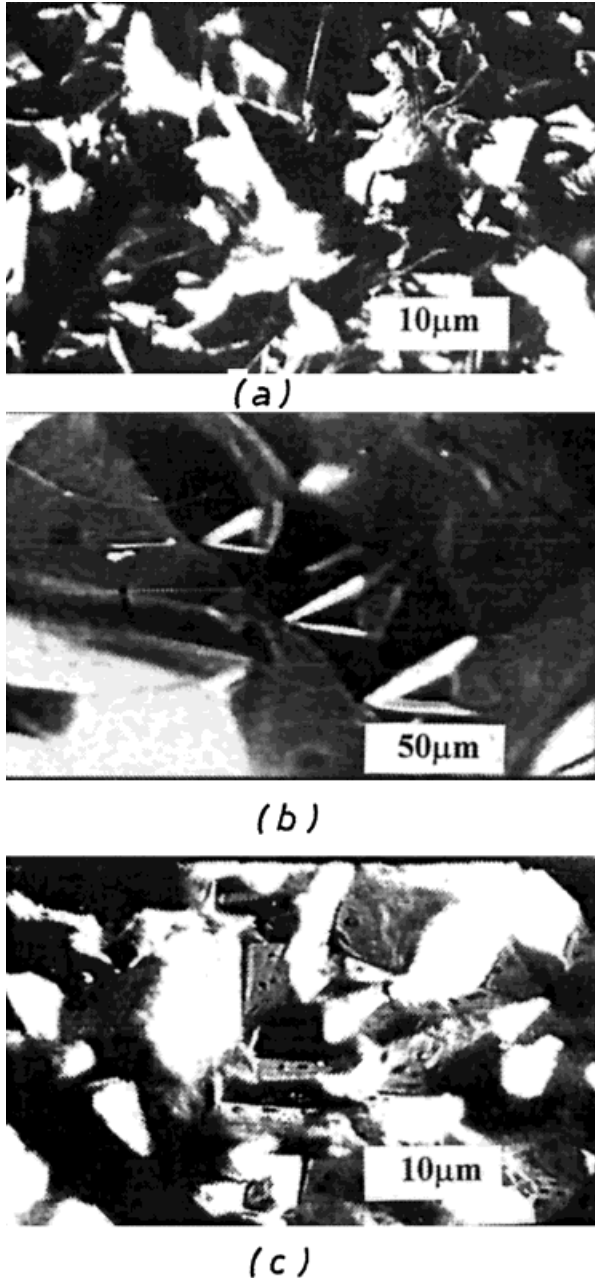


Figure 2 Top-view image of ZnTe thin-film surface deposited at different glass substrate temperatures: (a) 300°C; (b) 350°C; (c) 380°C.

material as a front-wall illumination (window) which to be transparent to the sub-band gap radiation. On the other hand, the thermal stability of PMS was examined by measuring the UV spectrum at different temperatures ranging from room temperature to 80°C. In this temperature range, the material proved to be thermally stable, indicating that the structure has not been changed.

Figure 4 illustrates the UV spectra, taken at room temperature, for pure PMS (curve a) and doped with a low concentration of iodine I_2 (1% wt) (curve b). On the doping of PMS with I_2 , new shoulder bands at 370 and 700 nm appeared. These bands can be attributed to the PMS- I_2 complex and free I_2 ,⁷ respectively. It is important to observe that there is no change in the absorption edge of the spectrum. This indicates that the addition of I_2 does not lead to a remarkable change in the calculated optical band gap that was found to be 3.54 eV. On the other hand, curve c in Figure 4 shows the UV spectra of an I_2 -doped polymer measured at high temperature (80°C).

A shoulder band at 370 nm was found to increase in intensity at the expense of that located at 700 nm. This can be explained as a result of the gradual elimination of free I_2 from the polymeric matrix as the measurement temperatures increase. At the same time, the I_2 -polymer complex concentration increases and leads to the remarkable increasing in the band intensity at 370 nm.

The absorbance spectra of the PMS- I_2 /ZnTe system as a heterojunction, taken at different temperatures, from room temperature to 80°C, are shown in Figure 5. A broad band in the interval $500 > \lambda > 350$ nm is observed. This broad band gives evidence for the formation of new interfacial structure at the polymer-semiconductor interface, with a graded band gap ranging from 2.48 to 3.20 eV. This interfacial layer can arise from the mechanism of intercalation of a polymer through the ZnTe grain boundaries during the process of polymer deposition. This large broadening range with the abrupt increase in the ab-

Table I Photovoltaic Parameters of PMS- I_2 /ZnTe Heterojunction at Different Substrate Temperatures

T_{sb} (°C)	R_s (Ω)	V_{oc} (volt)	$J_{sc} \times 10^{-4}$ amp cm^{-2}	FF	$\eta \times 10^{-2}\%$
300	8.2×10^6	0.72	0.2	0.415	0.6
350	1.1×10^2	0.75	0.63	0.48	2.24
380	7.3×10^5	0.54	0.48	0.39	1.0

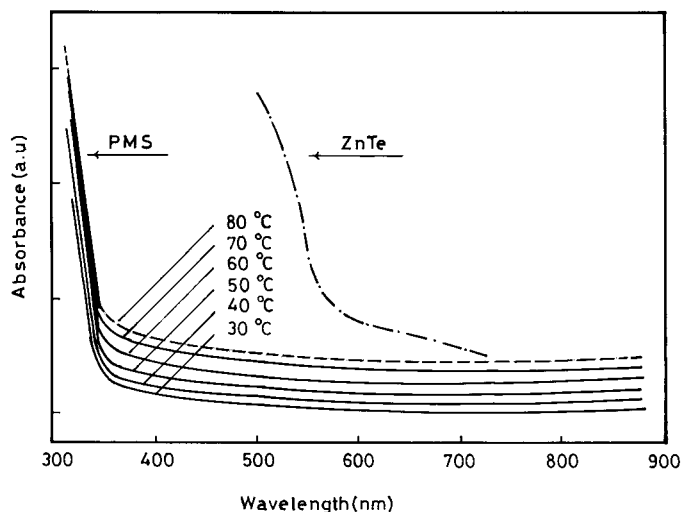


Figure 3 Optical absorption spectra of (dashed line) as-deposited ZnTe thin film measured at room temperature and (solid lines) PMS thin film measured at different temperatures.

sorbance, $\lambda > 280$ nm, suggests that the interfacial layer structure formed at the interface between ZnTe and PMS extends nearly over the whole film thickness. It is observed that, as the temperature increases, the intercalation mechanism of PMS-I₂ through the ZnTe grain boundaries increases, and, consequently, the thickness of the graded structure increases. As a result, the absorbance increases without any structural change of the polymer complex and the semiconductor.

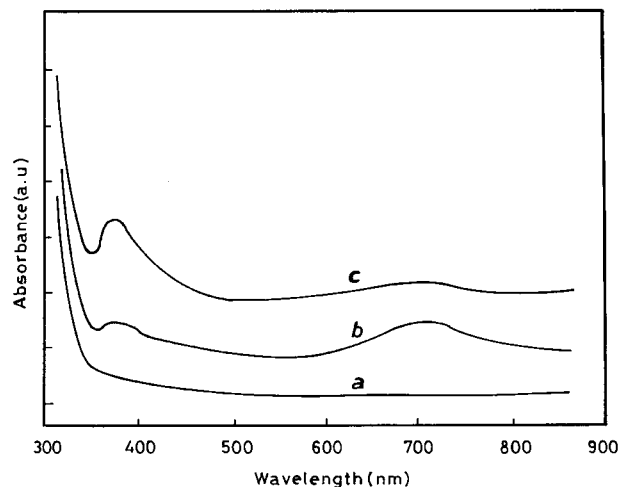


Figure 4 Optical absorption spectrum, measured at room temperature, for (a) pure PMS and for iodinated PMS measured at (b) room temperature and (c) 80 °C.

Figure 6 shows the current–voltage characteristics, for a relatively small forward and reversed bias, in the dark and under illumination for both PMS/ZnTe [Fig. 6(a)] and PMS-I₂/ZnTe [Fig. 6(b)] heterostructures. The observed behaviors, in general, are similar to the most crystalline semiconductor heterojunction, confirming that iodine plays the role of an electron supply in the polymeric matrix and, consequently, acts with ZnTe film (*p*-type) as a rectifier. This rectifying behavior is obviously observed with rectification ratios 50 and 100 for the PMS/ZnTe and PMS-I₂/ZnTe

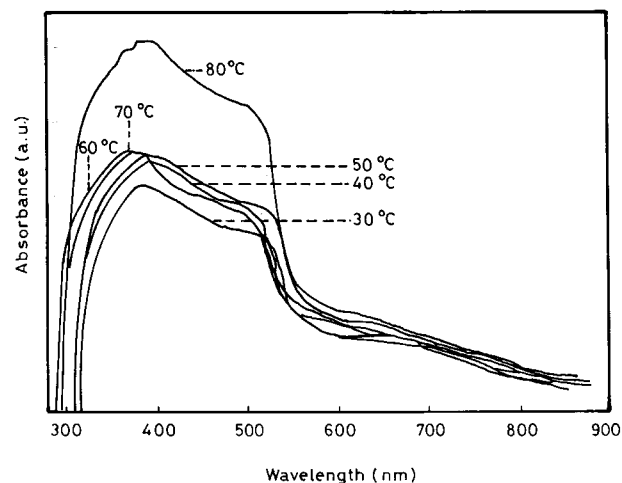


Figure 5 UV spectra of PMS:I₂/ZnTe heterojunction system [T_{sb} (ZnTe) = 350 °C] measured at different temperatures.

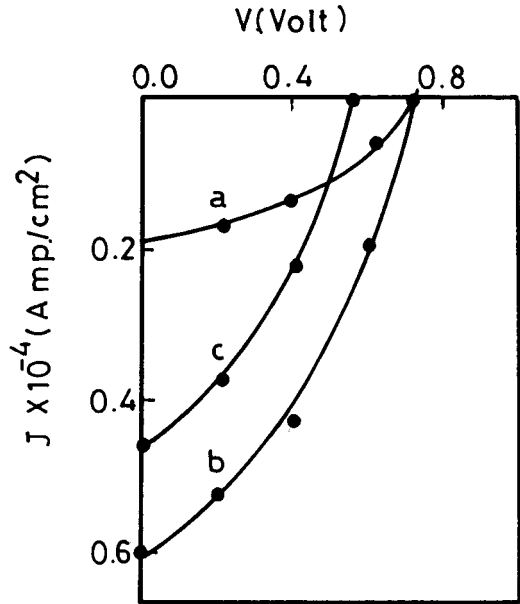
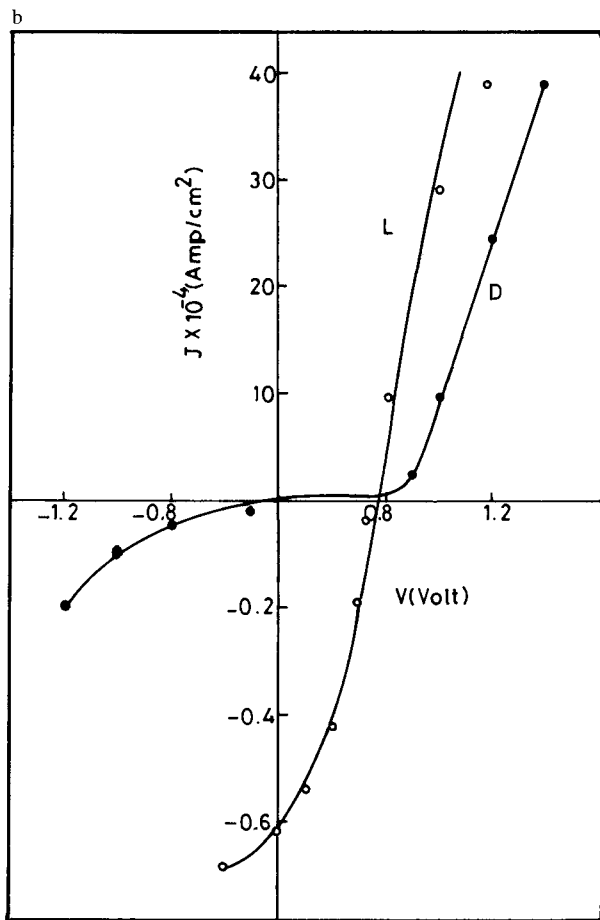
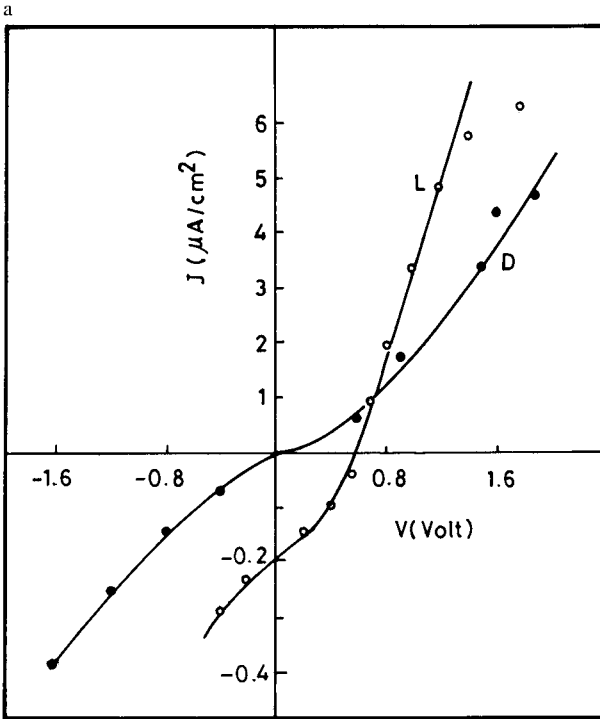


Figure 7 Illuminated I-V characteristics of PMS:I₂/ZnTe heterojunction devices for different glass substrate temperatures: T_{sb} (ZnTe) = (a) 300°C, (b) 350°C, and (c) 380°C.

heterostructure systems, at 1 V, respectively. The large difference in the rectification factor can result from the addition of iodine and the formation of a polymer complex and, consequently, increases the conductivity. Hence, the polymer-polycrystalline SHJ, with a large difference in the band gap, may be described as a Schottky barrier type when PMS in its doped state (with I₂) behaves like a metal and then photocarriers are generated in the semiconductor.

The I-V characteristics of the PMS-I₂/ZnTe system as a function of the substrate temperature (T_{sb}) during the evaporation process of ZnTe, in the photovoltaic mode, obtained at constant full light intensity, are shown in Figure 7. The most important device parameters of the obtained cells can be calculated by analysis of the data given in Figure 7 for the doped polymer/semiconductor system. The fill factors (FF) and the corresponding power conversion efficiencies of the cells (η), can be given by the relations^{8,21}:

$$FF = J_m V_m / J_{sc} V_{oc} \quad (1)$$

Figure 6 (D) Dark and (L) illuminated I-V characteristics for (a) PMS/ZnTe and (b) PMS:I₂/ZnTe heterojunctions (T_{sb} (ZnTe) = 350°C).

and

$$\eta = J_{sc} V_{oc} FF \times 100 / P_{in} \quad (2)$$

where J_m and V_m are the current density and voltage at maximum power input, respectively, and J_{sc} and V_{oc} are the short-circuit current and open-circuit voltage, respectively. Finally, P_{in} is the input light power. These parameters are found to be strongly dependent on the substrate temperature (T_{sb}) of the condensation of ZnTe films as a substrate to the polymeric layer. The evaluated parameters are listed in Table I. It was found that the calculated conversion efficiencies (η) is very small in comparison with that of ideal SHJ cells^{23,24} and showed a reasonable agreement with that reported for polymer–semiconductor and/or polymer–metal cells. On the other hand, it is found that doping PMS with I_2 increases the calculated conversion efficiency in comparison with that obtained for an undoped polymer ($\eta = 4 \times 10^{-5}\%$) as an upper layer in a heterojunction system.

CONCLUSIONS

ZnTe was evaporated on a SnO_2 -coated glass substrate at three substrate temperatures (300, 350, 380°C). PMS, without and with I_2 doping, was deposited onto ZnTe. The optical absorbance, current–voltage characteristics, and photovoltaic properties of this structure were discussed. The formation of a rectifying heterojunction was confirmed between a typical *p*-type semiconductor ZnTe thin film and PMS.

It has become evident that the junction parameters markedly depend on the substrate temperature during the deposition process of ZnTe thin films. But, in general, it must be stressed that the conversion efficiency of the obtained cell is very small. These have been attributed to the large series resistance of the cell expected principally from the possible formation of an interface barrier and a trap level, originating from ZnTe defects, which govern the barrier behavior. However the photovoltaic effect is improved by the doping of the polymeric matrix with a low concentration of iodine (1% wt).

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