

Investigation of electrical properties of PANI/chalcogenide junctions

Research Article

Vinodini Shaktawat*, Dinesh Patidar, Kananbala Sharma,
Narendra S. Saxena[§], Thansewar. P. Sharma

*Semi Conductor and Polymer Science Lab, Department of Physics,
University of Rajasthan,
Jaipur, 302004, India*

Received 19 August 2008; Accepted 14 April 2009

Abstract: Pure Polyaniline (EB) and Polyaniline doped with different protonic acids (ESs) were chemically synthesized using ammonium peroxydisulphate (APS) as an oxidant. Junctions have been prepared by evaporating chalcogenide materials (ZnSe, CdSe) on conducting polyaniline (EB & ESs) pellets using a vacuum evaporation technique. I-V characteristics of junctions have been studied at room temperature using the Keithley electrometer 6517A. I-V measurements show the rectification effect. A junction of ES[PO₄³⁻] may be preferred over the other junctions due to its low ideality factor and maximum rectification ratio.

Keywords: Polyaniline • Emeraldine base (EB) • Emeraldine salt (ESs) • Protonic acids • Chalcogenide material • p-n junction • I-V characteristics

© Versita Warsaw and Springer-Verlag Berlin Heidelberg.

1. Introduction

Intrinsically conducting polymers such as polyaniline (Emeraldine base (EB) & Emeraldine salt (ESs)) have become very popular in the field of material science due to their promising applications such as energy storage devices, gas sensors, electromagnetic shielding, electrostatic charge dissipation, light emitting diodes, flexible display devices, anticorrosive material, electrochromic materials and electronic conducting fabrics [1].

They have electrical properties of semiconductors and at the same time, the processing advantages and mechanical properties of polymers. Among the conductive polymers, polyaniline (PANI) and its derivatives have attracted much attention because of their higher environmental, thermal and chemical stability along with high electrical conductivity. The electrical conductivity of these samples can be influenced both by the oxidation level of the main polymer chain and the degree of protonation. Several interesting modifications

of the oxidative polymerisation of aniline have been developed. Among these, redox doping and the acid-base doping are the major processes that are applied to Emeraldine base (EB). Extensive work has been reported [2] in the literature about the doping of EB with protonic acids to improve electrical conductivity. Such doping is achieved by simple protonation of the –NH group of emeraldine base by mineral or organic protonic acids, where positive charges become accumulated on the polymer backbone, and which are neutralized by the negatively charged counter ions of the dopant.

The heterojunction devices fabricated so far, highlight mostly the fabrication of junctions using various methods such as vacuum evaporation, chemical vapour deposition, molecular beam epitaxy, liquid phase epitaxy, vapour phase transport, flash evaporation, sputtering, etc [3]. These methods are highly expensive, time consuming and complicated. Electronic devices are not restricted only to the devices based on inorganic materials. In recent years, several types of electronic and optoelectronic devices, based on organic and

* E-mail: s_vinodini@rediffmail.com

§ E-mail: n_s_saxena@rediffmail.com

polymeric materials, including organic light-emitting diodes (OLEDs) [4-5], organic field-effect transistors (OFETs) [6], organic photovoltaic cells (OPVs) [7], and organic memory devices [8-9] have received considerable attention due to their advantages in terms of manufacturing cost, flexibility in terms of fabrication-methods, material variety and mechanical flexibility. The junction of conducting polymers and semiconducting films has been the subject of great interest to material scientists and physicists because of its physical and electrical properties. Conducting polymers exhibiting semiconducting properties are excellent candidate materials for opto-electronic devices. Therefore, the successful application of conjugated polymers to such devices requires an understanding of charge transport at their interfaces and bulk parameters [10-11]. In the recent past, many attempts have been made to modify the barrier height, form a rectifying contact and also to determine the characteristic junction parameters by using junctions of organic/inorganic semiconductor layers [12] at certain metal/inorganic semiconductors. In the passivation process [13], inorganic/organic semiconductor diodes may be sensitive probes that are useful for increasing the quality of devices. These devices have been fabricated using an organic/semiconductor in establishing processes for minimizing surface states, surface damage and contamination. Such studies not only make inorganic semiconductor/organic film interfaces potentially relevant in the fabrication of Schottky type diodes with actively tunable barrier heights, but also help in understanding the electronic processes at semiconductor interfaces.

For the present paper, an effort has been made to prepare the heterojunctions between PANI(EB & ESs) and chalcogenides material (ZnSe, CdSe) using a vacuum evaporation technique. The heterojunctions so prepared have been characterized through I-V measurement using the Keithley Electrometer 6517 A.

2. Material preparation

PANI is prepared by redox polymerization of aniline using ammonium peroxydisulphate $[(\text{NH}_4)_2\text{S}_2\text{O}_8]$ as an oxidant. For this, double distilled aniline (0.4 mol) is dissolved in 250 ml of precooled HCl (1 molar) solution. A calculated amount of ammonium peroxydisulphate (0.4 mol) is dissolved in 250 ml of precooled HCl (1 molar) solution, which is added dropwise to the stirred solution of aniline in HCl at 0°C. After keeping overnight, the dark green precipitate was obtained after which this ESs was first neutralized with NaOH 1 M solution, filtered

off, washed thoroughly (until the filtrate was pH 7), and dried under vacuum to obtain EB. This Emeraldine base form of polyaniline is re-doped with a protonic acid (0.4 mol) (HCl, H_2SO_4 , H_3PO_4 , $\text{H}_2\text{C}_2\text{O}_4$ and CH_3COOH) then filtered, washed thoroughly, dried under vacuum for 8 hours at 60°C and then ground to a fine powder using a mortar and pestle, to obtain the ESs.

Forelectrical measurements, thin films of chalcogenide materials (ZnSe (99.99%), CdSe (99.995%)) as obtained from Alfa Aesar) were deposited on bulk samples of PANI(EB & ESs) in the form of pellets (diameter 12 mm and thickness of approx 1 mm) prepared under a load of 6 tonnes. Thin films of chalcogenide materials (ZnSe (99.99%), or CdSe (99.995%)) were deposited using a vacuum evaporation technique at 2×10^{-5} Torr. The evaporation is performed at a temperature ca. 150°C for 3 minutes to obtain a thin film of the chalcogenide material with a thickness of 350 nm. The thickness is measured by using a Quartz Crystal Thickness monitor (CTM-200). Electrical contacts have been provided by a conducting paste of silver.

3. Results and Discussion

The I-V characteristics of heterojunctions between the PANI(EB & ESs) and chalcogenide material (ZnSe, CdSe) have been recorded using the Keithley electrometer/High resistance meter 6517A at room temperature and are shown in Figs. 1-2. The circuit diagram used for this study is given elsewhere [14]. This electrometer has an inbuilt capability of output independent voltage source of ± 1000 V. Accordingly, the same equipment was used to apply voltage across the sample and to measure the current through the sample.

The I-V characteristics of the PANI(EB & ESs)/chalcogenide junctions are asymmetric and non-linear. The forward current increases exponentially in the lower voltage region and linearly in the higher voltage region. These heterojunctions clearly exhibit rectification behaviour.

PANI(EB & ESs) are p-type semiconductors [15] and the chalcogenide semiconductors deposited on the pellet are n-type semiconductors. It is indicated that heterojunctions between PANI(EB & ESs) and chalcogenide semiconductors behave as p-n junctions. According to the theory, the work function of the chalcogenide must be smaller than that of the p-type PANI(EB & ESs) for the formation of a rectifying barrier at the interface [16]. If the work functions are in the reverse order (*i.e.* work function of chalcogenide is greater than the p-type PANI), an ohmic contact would exist.

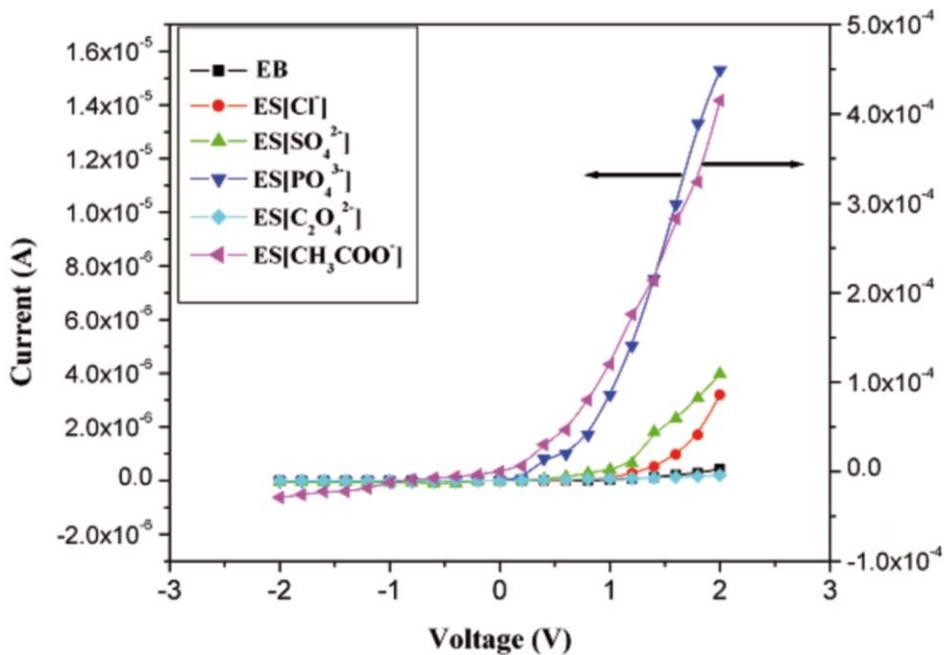


Figure 1. I-V characteristics of PANI/ZnSe heterojunctions

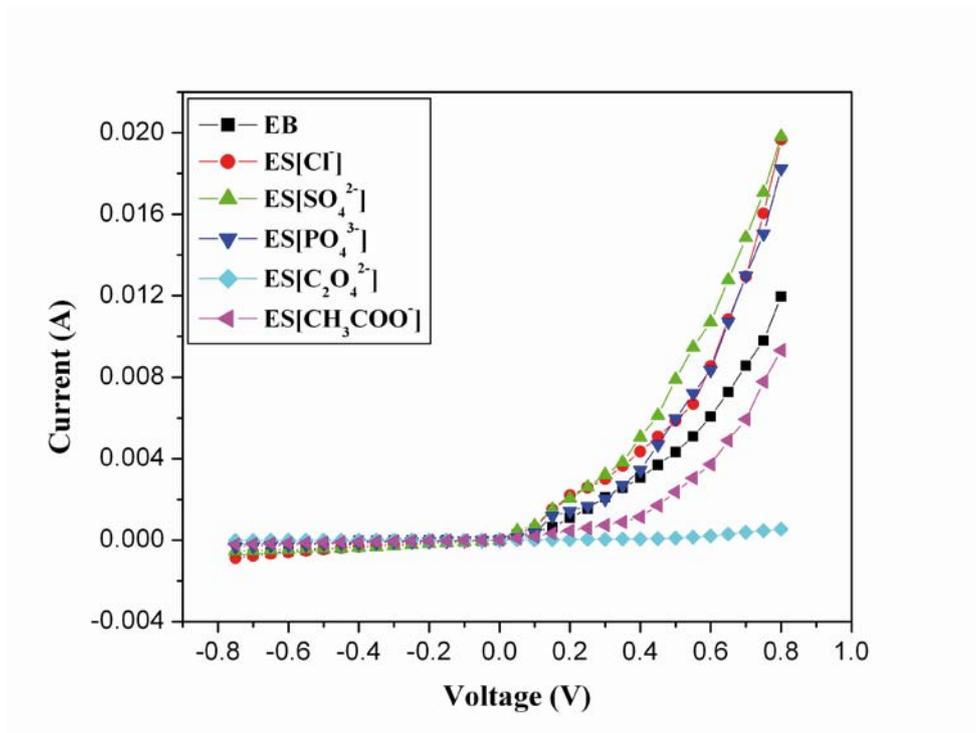


Figure 2. I-V characteristics of PANI/CdSe heterojunctions

The dependence of current on voltage is exponential which is given by the equation:

$$I = I_s [\exp (eV / nKT) - 1] \quad (1)$$

where I_s is the reverse saturation current, e is the electronic charge, n is the ideality factor, K is the Boltzmann constant and T is the absolute temperature.

The parameters I_s , n , rectification ratio (the ratio of forward to reverse current at a particular applied voltage) and series resistance (R_s) for the PANI(EB&ESs)/chalcogenide as calculated using the above equations are given in Table 1. This ratio is calculated at a fixed value of 0.2 volts. The exponential increase in the current in the low bias voltage region is due to a decrease in the width of the depletion region at the junction. In the higher voltage region, the depletion layer is minimized, leading to linear behaviour of the junction. This can be explained in terms of series-resistance effect, which may remarkably modify the actual rectifying junction-like behaviour at high bias voltages. An ohmic voltage term, IR_s , is usually included in the formula for such series resistance effect and eq. (1) is modified as:

$$I = I_s [\exp \{e(V - IR_s) / nKT\} - 1] \quad (2)$$

Therefore, the effect of bulk conduction in a device having a highly resistive semiconducting layer becomes important in a junction at high voltage in the forward direction and not in the reverse bias, where a rectifying junction-like behaviour should be dominant. Figs. 1 and 2 show that the forward and reverse characteristics of the heterojunctions are dissimilar, and the reverse current is much lower than the forward current. A slight saturating behaviour is observed in the reverse bias because the junction-like conduction process occurring in the depletion region would limit the measured heterojunction reverse current.

The junction parameter I_s is determined by interpolation of the exponential slope of the I-V curve at $V = 0$ and the diode ideality factors of these heterojunctions have been determined using Eq. 1. It is found that the diode ideality factor is from 2 to 5. These values are in good agreement with the values obtained by other workers [17-18].

The junction parameters extracted from the I-V characteristics (*i.e.* the saturation current, the rectification ratio and the ideality factor) are strongly influenced by the nature of the dopants. $ES[PO_4^{3-}]$ is more conductive in nature as the conductivity decreases in the order $\sigma (H_3PO_4) > \sigma (HCl) > \sigma (H_2SO_4) > \sigma (H_2C_2O_4) > \sigma (CH_3COOH)$. In the case of $ES[PO_4^{3-}]$, availability of H^+ ions required for formation of quinoid rings along the polymer backbone is enhanced and more and more anions are introduced throughout the matrix. This leads to an increased extent of doping, which initiates the formation of polarons and bipolarons, which are responsible for conduction. Therefore, more and more charge carriers are incorporated along the polymer matrix in $ES[PO_4^{3-}]$ *i.e.* charge carrier concentration can be controlled by the choice of dopant, and decreases in the order $ES[PO_4^{3-}] > ES[Cl^-] > ES[SO_4^{2-}] > ES[C_2O_4^{2-}] > ES[CH_3COO^-]$. The most optimal diode parameters, such as the rectification ratio and the ideality factor, were found for the $ES[PO_4^{3-}]$ /chalcogenide junction. The maximum value of the rectification ratio and the minimum value of the ideality factor found in the case of the $ES[PO_4^{3-}]$ /chalcogenide junction in comparison to those of other diodes are suggestive of the fact that the extent of doping is responsible for the higher contact potential at the p-n junction. This higher contact potential formed at the p-n junction, associated with a Fermi level pinning

Table 1. The various electrical junction parameters of PANI/chalcogenide heterojunctions

S.No.	Sample	I_s	n	Rectification ratio	R_s
ZnSe					
1.	EB	1.52E-09	5.14	1.05	4.63E-07
2.	ES[CH ₃ COO ⁻]	1.64E-06	5.09	1.89	2.94E-07
3.	ES[C ₂ O ₄ ²⁻]	2.18E-09	5.03	7.03	1.55E-07
4.	ES[SO ₄ ²⁻]	6.92E-08	4.97	9.91	4.19E-06
5.	ES[Cl ⁻]	7.66E-09	4.8	25.0	5.56E-06
6.	ES[PO ₄ ³⁻]	6.53E-08	3.37	81.4	1.25E-05
CdSe					
7.	EB	1.52E-04	4.0	5.16	2.48E-02
8.	ES[CH ₃ COO ⁻]	1.43E-04	3.98	6.84	2.55E-02
9.	ES[C ₂ O ₄ ²⁻]	8.32E-06	3.9	7.73	1.60E-03
10.	ES[SO ₄ ²⁻]	1.29E-04	3.7	8.24	3.93E-02
11.	ES[Cl ⁻]	1.98E-04	3.08	9.66	5.12E-02
12.	ES[PO ₄ ³⁻]	2.10E-04	2.8	10.7	4.43E-02

at the interface, or with a relatively large voltage drop in the interface region, results in the enhancement of the depletion layer width.

The maximum value of the rectification ratio and the minimum value of the ideality factor for the ES[PO₄³⁻]/chalcogenide junction is due to an increase in the concentration of the dopant anions incorporated in the polymer backbone. The decrease in the doping level in other samples causes a decrease in the Fermi level of PANI [19] and changes the diode parameters, *i.e.* a decrease of built-in voltage, depletion width of the junctions, and the rectification ratio, as well as an increase in the values of the ideality factors.

4. Conclusion

The junctions of PANI (EB&ESs) and chalcogenide (ZnSe, CdSe) show rectification behaviour. Ideality factors found in the present study are comparable with those

reported for inorganic-organic based semiconductor junctions. The maximum value of the rectification ratio and minimum value of the ideality factor found in case of ES [PO₄³⁻]/chalcogenide junction are suggestive of the fact that the extent of doping is responsible for higher contact potential at the p-n junction, which increases the width of depletion layer.

Acknowledgements

The authors are indebted to DRDO, New Delhi for providing financial assistance for this work. One of the authors Vinodini Shaktawat is also thankful to Mr. Kuldeep Singh Rathore, Ms. Deepika, Ms. Manasvi Dixit, Mrs. Sandhya Gupta and Mr. Praveen K. Jain for various help during this work.

References

- [1] C. Pratt, Applications of conducting polymers (2003), <http://homepage.ntlworld.com/colin.pratt/applcp.htm>
- [2] A. Sakouri, S. Li, Eighteenth International Conference on Thermoelectrics proceedings, ICT '99, IEEE Service Center, Baltimore Md., USA (Piscataway, NJ, 1999)
- [3] S.S. Joshi, C.D. Lokhande, J. Mater. Sci. 42, 1304 (2007)
- [4] W. Tang, S.A. Van Slyke, Appl. Phys. Lett. 51, 913 (1987)
- [5] J.H. Burroughs et al., Nature 347, 539 (1990)
- [6] F. Garnier, R. Hajlaoui, A. Yassar, P. Srivastava, Science 265, 1684 (1994)
- [7] N.S. Sariciftci, L. Smilowitz, A.J. Heeger, F. Wudl, Science 258, 1474 (1992)
- [8] L. Ma, J. Liu, S. Pyo, Y. Yang, Appl. Phys. Lett. 80, 362 (2002)
- [9] J.C. Scott, Science 304, 62 (2004)
- [10] K.P. Kamloth, Crit. Rev. Anal. Chem. 32, 121 (2002)
- [11] R. Singh, A.K. Narula, Appl. Phys. Lett. 71, 2845 (1997)
- [12] M.D. Migahed, T. Fahmy, M. Ishra, A. Barakat, Polym. Test. 23, 361 (2004)
- [13] J. Zhao, K. Uosaki, J. Phys. Chem. B 108, 17129 (2004)
- [14] V.K. Saraswat et al., Curr. App. Phys. 6, 14 (2006)
- [15] E.R. Holland, A.P. Monkman, Synth. Met. 74, 75 (1996)
- [16] R.K. Gupta, R.A. Singh, J. Polym. Res. 11, 269 (2004)
- [17] A.J. Franck, F. Glenis, A.J. Nelson, J. Phys. Chem. 93, 3818 (1989)
- [18] S.C.K. Misra et al., Appl. Phys. Lett. 61, 1219 (1992)
- [19] K.P. Kamloth, The Electrochemical Society, Inc., Abs. 892, 205th Meeting (2004), <http://www.electrochem.org/dl/ma/205/pdfs/0892.PDF>.