

Organic Semiconductor: A Drastic change in Electronics

Nalini¹ & Vimal Saraswat²

¹Govt. Senior Secondary School, Sarada, Udaipur, India, 313902 ²Department of Physics, Bhupal Nobles' University, Udaipur, India, 313001 Email: nalini2008@hotmail.com, vimal@bnuniversity.ac.in

Received May 21, 2017; Revised June 28, 2017; Accepted July 10, 2017

Abstract

The fields of OS are attracting most of the researchers. The researchers are working on the devices in which OS are used and try to improve the efficiency of such devices. The television sets using technique of quantum dot give the best visibility. The ink-jet printers using OS give better printing quality in comparison to conventional inorganic semiconductor printer. In this way OS plays an important and vital role in current scenario of electronic devices. In present paper an important facts of OS are discussed so that a person, who want to work in this field can understand about it in better way.

Keywords: Semiconductor, Organic semiconductor, Solar cell, Quantum dots, OFET.

1. Introduction

It is well established fact that the semiconductors have the conductivity lower than the conductor and higher than the insulator. Initially inorganic semiconductors such as Si and Ge are used only as the semiconducting material [1], but in 1977 the first highly conducting polymer, chemically doped poly-acetylene was discovered [2]. This polymer could be used as electrically active materials as well as conducting and are known as organic semiconductor (OS) [3]. In this way there are two semiconductors, organic and inorganic. The OS are actually the solids, which are made from the π -bonded molecules or polymers, made by carbon and hydrogen atoms and also some other atoms like nitrogen, sulphur and oxygen. The OS exist in molecular crystals or amorphous thin films. In general these are electrical insulators, but when charges are injected from appropriate electrodes, by the method of doping or by photo-excitation then they become semiconducting [2, 4, 5].

It is found that in molecular crystals the energy gap, which is actually the energy separation between the topmost valence band and the bottom of the conduction band, is found to be about 2.5 to 4 eV, whereas in traditional inorganic semiconductor such as Si, Ge and

GaAs it is found to be about 0.6 to 2 eV [6]. At room temperature, these inorganic semiconductor posses free charge due to thermal excitation from valence to conduction band, and the concentration of charge carrier is given by $N = N_0 \exp(-E_g/kT)$, with N_0 be the effective density of conduction or valence band states and E_g be the band gap [7, 8]. The dielectric constant of these inorganic conventional semiconductors is found to be 11. This large amount of dielectric constant creates a dielectric screening and hence the Coulomb attraction between the electrons and holes are unimportant due to this screening effect [9]. In this way, we can say that the OS are basically insulators in the conventional sense and for semiconducting them, the charge carrier should be created by any method. This can also be done by the method of optical excitation. The primary optical excitations are however the neutral excitations and the Coulomb binding energy with them are found to be around 0.5 to 1 eV [10]. The main reason behind it that the dielectric constants of OS are 3 to 4 and it obstructs the efficient photo-generation of charge carriers in pure system. The efficient photo-generation can occur only in binary systems due to a part of transfer of charge between the donor and acceptor. If it does not happen then the neutral excitations decay to the ground state and emit

photoluminescence [11, 12]. In **Figure 1**, Jablonski energy level diagram is shown, which shows the principle luminescence process in an organic molecule. Here full and dotted arrows represent radiative and non-radiative process of neutral excitations [13].

The optical absorption edge of OS is nearly 1.5 to 3 eV, equivalent to a spectral range of the visible spectrum (700 to 400 nm). OS are special type of materials, which combine the electronic advantages of semiconducting materials with the chemical and also provide the mechanical benefits of organic compound (OC) like plastics. Thus, many properties of a material like absorbing light, conducting electricity, and emitting light is united with a material structure and these can be modified easily by the process of chemical synthesis. In this process we can entered the electronic property to the material like desired emission wavelength, to make it soluble, or to provide it mechanical strong, lightweight and flexible thin films.

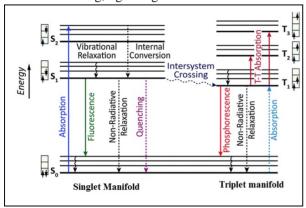


Figure 1: Jablonski energy level diagram showing principle luminescence processes in an organic molecule

2. History

Initially in 1862, Henry Letheby, when perform anodic oxidation of aniline in H₂SO₄, he got a material which is neither perfectly conductive nor insulating, it is partly conductive. This material may be poly-aniline. After it several researcher do their research in this field and finally in 1950, they discovered a polycyclic aromatic compound formed semi-conducting charge transfer complex salts with halogens and a high conductivity of 0.12 mho/cm in a complex peryline-iodine reported in 1954 [14]. This finding helps to show that an OC could carry current. Akamatu *et al.*, [15] discovered that an aromatic hydrocarbon become conductive, when blended it with molecular iodine due to the formation of a charge transfer complex compound. It helps to show that the crucial

parameter for controlling the conductivity is the work function of the electrode. So, we can replace the electrolyte by a solid semiconducting or metallic contact, having a suitable value of work function. Sano et al., [16] shows that when both the opposite charges holes and electrons are injected from opposite terminals in organic crystals they can combine radiatively, emitting electroluminescence. After it Kallmann and Pope found that a hole current can flow through anthracene crystal by connecting it with a positively biased electrolyte containing iodine. This time electrolyte works as a hole injector [17]. The first device incorporating an OS was produced by John McGinness. In Figure 2, an organic polymer voltage controlled switch is shown, which was discovered in 1974 and now it is a part of Smithsonian chip collection [18].



Figure 2

After it several researchers do the work on OC, Shirakawa *et al.* [3] found the high conductivity in oxidized and iodine-doped poly-acetylene and finally they got a Nobel Prize in Chemistry on their discovery and development of conductive polymer [19].

3. Organic Semiconductor Devices

The organic or non-metallic material exhibit the property of semiconductor comes into the category of OS. The conductivity (or semi-conductivity) in these materials are due to a single molecules, short chains of molecules and long polymer chains, which depends on the type of material using for it [20]. The organic materials pentacene, rubrene and anthracene included into small molecules, whereas fullerenes and its derivatives included into larger molecules [21]. The electronic devices, which include the OS, are known as OS devices. Some of them are describe here:

3.1. OTFT or OFET

Organic thin film transistors (OTFT) or organic field effect transistor (OFET) is shown in **Figure 3**. In this figure source and drain electrodes deposited directly on

the semiconducting layer. Its working is same as inorganic metal oxide field effect transistor.

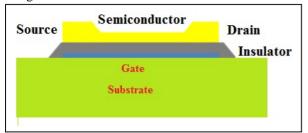


Figure 3: OFET

If no bias voltage is applied, then due to the difference in Fermi level between the metal electrode and semiconductor, a very small amount of charge carrier flows across the device and on applying a bias voltage to the gate, charge carrier collects at insulator-semiconductor interface. It lowers the Fermi level of the semiconductor, which creates a highly conductive layer at the interface through which charge carriers flow [22]. In **Figure 4**, a hetero-junction OTFT is shown. This devices use multiple types of organic materials to enhance the mobility of charge carriers to increase switching speed of the device [23].

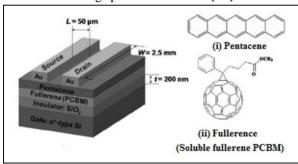


Figure 4: Hetero-junction OTFT

3.2. OPV and OD

Photovoltaic (PV) cells represent the building blocks of any solar panel; it converts the solar energy into electrical energy. The theoretical efficiency of conversion is about 32% but the real life efficiency is found only about 15%. Thus it is not a good source of energy on the basis of economic background. Several researchers claim that they have got the efficiency up to 28% in their laboratory conditions [24]. But its real-life performance has yet to be proved. When photons of the incident light hit the solar cell, then some of them, which have the energy of certain level can generate the free electrons and thus generate electrical current. The energy required to generate free electrons in the valence bond and send it into electrical circuit is known as dislocation energy (DE). If energy

of photon hitting PV cells is larger than DE, then remaining part of energy is converted into heat. An efficient PV cell is that cell, which convert the maximum amount of incident photo energy into electrical energy, without losing it into heat. The level of DE varies from 1 to 1.6 eV in efficient PV semiconductor [25]. The function of solar cell is shown in **Figure 5** [26].

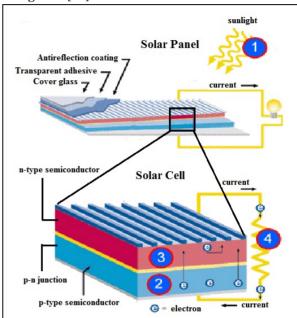


Figure 5: Function of Solar cell

Organic photovoltaic (OPV) cells are also solar cells in which organic polymers or organic materials are used as the active layer for absorbing light and charge transport. There are number of advantages and disadvantages in using organic materials semiconductor for solar cell. These materials are of low cost due to their structure being generally self-organized polycrystalline. However these have low energy conversion efficiency in comparison to inorganic solar cells. Now, in these days the researchers concentrate on improving the efficiency of OPV cells by optimizing such parameters as effective charge separation, charge mobility, crystal structure and minimizing impurities. Since the organic materials are more sensitive to oxidation effects and temperature variations and therefore it decreases the performance with the passes of time [27]. The most efficient solar cells having donor property is C₆₀ and its derivatives (phenyl-C61-butyric acid methyl ester or PCBM), and P3HT and MEH-PPV have the acceptor property [28].

The semiconductor particles of very small size (of the order of nanometers), so that their optical and

electronic properties differ from those of larger particles are called Quantum dots (QD) or semiconductor nano-crystals are called OD. These particles obey quantum mechanical principle of quantum confinement. On applying the electricity or light on QDs, they emit the light of specific frequencies depending upon the size, shape and material using in dots. In present days QDs are used in PV cells due to their high extinction coefficient. It increases the efficiency of cells and reduces the cost. QDs of PbSe (band gap of 0.27 eV) can produce more than one exciton from one high energy photon via the process of multiple exciton generation (MEG) or carrier multiplication [29]. In Figure 6, the semiconductor quantum dots of CdSe, ZnSe, ZnS and ZnO is shown [30].

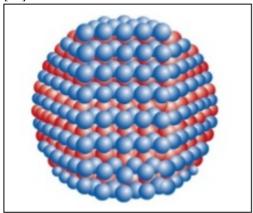


Figure 6: Semiconductor quantum dots

Aromatic self-assembled mono-layers (SAMs) (e.g. 4-nitrobenzoic acid) can be used at electrodes for better efficiency. This technique has provided a power conversion efficiency of 10.7% [31].

4. Conclusions

The fields of OS are attracting most of the researchers. The researchers are working on the devices in which OS are used and try to improve the efficiency of such devices. The television sets using technique of quantum dot give the best visibility. The ink-jet printers using OS give better printing quality in comparison to conventional inorganic semiconductor printer. The device using OS are low cost due to lower cost of material using in this device. Also such devices are of light weight. Thus in the present scenario OS plays a major role in electronic devices in reducing the size, weight and cost, and in improving their efficiencies.

REFERENCES

[1] Ioffe, A. F., "Physics of semiconductors," Academic

- Press Inc., New York (1960).
- [2] Chiang, C. K., C. R. Fincher, J. Y. W. Parker, A. J. Heeger, H. Shirakawa, E. J. Louis, S. C. GAU, and A. G. MacDiarmid, "Electrical Conductivity in Doped Poly-acetylene," *Phys. Rev. Lett.*, Vol. 39, No. 17, pp. 1098-1101, 1977.
- [3] Shirakawa, Hideki; E. J. Louis, A. G. MacDiarmid, C. K. Chiang, A. J. Heeger, "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x". *J. Chemical Society, Chemical Communications*, No. 16, pp. 578, 1977. DOI: 10.1039/C39770000578.
- [4] Kallmann, H., and M. Pope, "Bulk conductivity in organic crystals," *Nature*, Vol. 186, pp. pp. 31-33, 1960. DOI: 10.1038/186031a0.
- [5] Kumar, R., S. Singh and B. C. Yadav, "Conducting Polymers: Synthesis, Properties and Applications," *International Advanced Research Journal in Science*, *Engineering and Technology*, Vol. 2, No. 11, 2015. DOI: 10.17148/IARJSET.2015.21123.
- [6] https://application.wiley-vch.de/books/sample/3527332 928_c01.pdf.
- [7] https://people.eecs.berkeley.edu/~hu/Chenming-Hu_ch 1.pdf.
- [8] Hernandez, C. F., "Photorefractive Organic Materials and Applications," Springer Series in Materials Science 240, Springer International Publishing Switzerland 2016. DOI: 10.1007/978-3-319-29334-9 2.
- [9] Ortiz, R. P., A. Facchetti, and T. J. Marks, "High-k Organic, Inorganic, and Hybrid Dielectrics for Low-Voltage Organic Field-Effect Transistors," *Chem. Rev.*, Vol. 110, No. 1, pp. 205–239, 2010. DOI: 10.1021/cr9001275.
- [10] Newman, C. R., C. D. Frisbie, D. A. da Siva Filho, J.-L. Bredas, P. C. Ewbank, and K. R. Mann, "Introduction to Organic Thin Film Transistors and Design of n-Channel Organic Semiconductors," *Chem. Mater.*, Vol. 16, No. 23, pp 4436–4451, 2004. DOI: 10.1021/cm049391x.
- [11] Bakulin, A. A., S. D. Dimitov, A. Rao, P. C. Y. Chow, C. B. Nielsen, B. C. Schroeder, I. McCulloch, H. J. Bakker, J. R. Durrant, and R. H. Friend, "Charge-Transfer State Dynamics Following Hole and Electron Transfer in Organic Photovoltaic Devices," J. Phys. Chem. Lett., Vol. 4, No. 1, pp 209–215, 2013. DOI: 10.1021/jz301883y.
- [12] Lussem, B., M. Riede, and K. Leo, "Doping of organic semiconductors," *Phys. Status Solidi A*, Vol. 210, No. 1, pp. 9-43, 2013. DOI: 10.1002/pssa.201228310.
- [13] Xu, H., R. Chen, Q. Sun, W. Lai, Q. Su, W. Huang, and X. Liu, "Recent progress in metal-organic complexes for optoelectronic applications," Chem. Soc. Rev., Vol. 43, pp. 3259–3302, 2014. DOI: 10.1039/ C3CS60449G.
- [14] Naarmann, H., "Polymers, Electrically Conducting" *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2002. DOI: 10.1002/14356007.a21_429.

- [15] Akamatu, H., H. Inokuchi, and Y. Matsunage, "Organic Semiconductors with High Conductivity. 1. Complexes Between Polycyclic Aromatic Hydrocarbons and Halogens," *Bulletin of Chemical Society of Japan*, Vol. 29, No. 2, pp. 213 218, 1956. DOI: 10.1246/bcsj.29. 213.
- [16] Sano, Mizuka, M. Pope, and H. Kallmann, "Electroluminescence and Band Gap in Anthracene", Journal of Chem. Phys., Vol. 43, No. 8, pp. 2920, 1965. DOI: 10.1063/1.1697243.
- [17] Kallmann, H., and M. Pope, "Positive hole injection into organic crystals," *J. Chem. Phys.*, Vol. 32, No. 1, 1960. DOI: 10.1063/1.1700925.
- [18] McGinness, John, C. Peter, and P. Peter, "Amorphous Semiconductor Switching in Melanins", *Science*, Vol. 183, No. 4127, pp. 853–855, 1974.
- [19] Chemistry, 2000. http://nobelprize.org.
- [20] Mercier, J. P., G. Zambelli, and W. Kurz, "Introduction to material science," Elsevier, Paris, Amsterdam, New York, 2002. ISBN: 2842992865.
- [21] Yang, H., F. Gajdos, and J. Blumberger, "Intermolecular Charge Transfer Parameters, Electron–Phonon Couplings, and the Validity of Polaron Hopping Models in Organic Semiconducting Crystals: Rubrene, Pentacene, and C60", *The Journal of Physical Chemistry C*, Vol. 121, No. 14, pp. 7689-7696, 2017. DOI: 10.1021/acs.jpcc.7b00618.
- [22] Gomes, H. L., "Organic Field- Effect Transistors," Organic and Printed Electronics Fundamentals and Applications, pp. 147-197, 2016.
- [23] http://physics.usask.ca/~chang/homepage/Organic/files/ hetero-3-3.jpg

- [24] Fahrenbruch, A. L., and R. H. Bube, "Fundamentals of solar cells: photovoltaic solar energy conversion", Academic Press, New York, 1983.
- [25] https://www.smashingrobotics.com/electrical-power-sources-for-mobile-robots/.
- [26] http://solarcellcentral.com/ images/solar_ pv_ diagram. ipg.
- [27] Shaheen, S. E., D. S. Ginley, and G. E. Jabbour, "Organic-based photovoltaics: toward low-cost power generation," MRS bulletin, Vol. 30, No. 1, pp. 10-19, 2005. DOI: 10.1557/mrs2005.2.
- [28] Dang, M. T., L. Hirsch, G. Wantz, and J. D. Wuest, "Controlling the morphology and performance of bulk heterojunctions in solar cells. Lessons learned from the benchmark poly (3-hexylthiophene): [6, 6]-phenyl-C61-butyric acid methyl ester system," *Chemical reviews*, Vol. 113, No. 5, pp. 3734 -3765, 2013. DOI: 10.1021/cr300005u.
- [29] Schaller, R., V. Klimov, "High Efficiency Carrier Multiplication in PbSe Nanocrystals: Implications for Solar Energy Conversion," *Physical Review Letters*, Vol. 92, No. 18, 2004. DOI: 10.1103/PhysRevLett. 92.186601.
- [30] https://www.slideshare.net/hoangtienbk/quantum-dots-15108239.
- [31] Kim, Gi-Hwan, Arquer, F. Pelayo García de, Y. J. Yoon, X. Lan, M. Liu, O. Voznyy, Z. Yang, F. Fan, Alexander H. Ip, P. Kanjanaboos, S. Hoogland, J. Y. Kim, and E. H. Sargent, "High-Efficiency Colloidal Quantum Dot Photovoltaics via Robust Self-Assembled Monolayers," *Nano Letters*, Vol. 15, No. 11, pp. 7691-7696, 2015. DOI: 10.1021/acs.nanolett.5b03677.