Study of interfaces in organic semiconductor heterojunctions

P Maheshwari¹, D Dutta¹, K Sudarshan¹, S K Sharma¹, S Samanta², A Singh², D K Aswal² and P K Pujari¹

¹Radiochemistry Division, ²Technical Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India.
E-mail: pujari@barc.gov.in

Abstract. The defect structure at the organic heterojunctions is studied using slow positron beam. The structural and electronic properties of heterojunctions are of technological and fundamental importance for understanding and optimization of electronic processes in organic devices. Interface trap centres play a significant role in the electrical conduction through the junctions. Depth dependent Doppler broadened annihilation measurements have been carried out in p- and n-type organic semiconductor thin films (30-80 nm) both single as well as multilayers grown on quartz substrate. The objective of the present study is to investigate the defect structure and to understand the behavior of positrons at the charged organic interfaces. Our result shows the sensitivity of positrons to the interfacial disorders that may be a convoluted effect of the presence of defects as well as the influence of the charge dipole in multilayers.

1. Introduction

Organic electronics has attracted worldwide attention due to the advantages of low-cost, ease of processing, compatibility with a wide range of substrates, large area and the ease of tailoring the material characteristics. The potential devices comprise of organic transistors [1], organic photovoltaic cells [2,3], organic light emitting diodes [4] and organic memory devices [5]. Organic heterojunctions are intrinsic to organic devices. Considerable work is focused on the heterojunctions towards understanding the physics of device operation and performance [6-9]. Many aspects of device operation are quite well understood. However, there is considerable knowledge gap in the understanding of structural and electronic properties of interfaces between organic and inorganic components which are important for understanding and optimization of electronic processes in these devices. Engineering of the interfacial properties to improve device performance by utilizing various surface modification schemes is another area of current interest.

In organic devices, energy level alignment and interfacial dipole has been observed at the interfaces due to charge transfer at the heterojunctions [10, 11]. The dependence of molecular orientation on charge transfer and interfacial dipole has also been reported [12, 13]. The molecular orientation near the interfaces, mainly governed by molecule-molecule and molecule-substrate interaction can be crucial for the device efficiency [14, 15]. Phthalocyanines are a class of low molecular weight organic molecules exhibiting semiconductor properties. They represent one of the most promising candidates for ordered organic thin films as these systems possess advantageous attributes such as thermal and chemical stability, and, excellent film growth characteristics [16]. The electronic and optical properties of organic semiconductor (OSC) thin films strongly depend on their structure and morphology [17].
The fabrication of heterojunctions involves controlled growth of OSC thin films. However, fabrication of hetero-multilayered structure is a challenge due to large anisotropy and relatively weak nature of interaction forces between organic molecules [16].

Beam based positron annihilation spectroscopy has been found to be a very sensitive technique to probe open volume defects present at the surfaces and interfaces, not possible by any other conventional defect characterization techniques. The unique repulsive force between positron and ion cores of the material makes positron ideal for probing defects, voids and free volumes. The presence of open volume defects/free volume manifests as increase in lifetime and narrowing of the momentum distribution. The latter is often described by a shape parameter, namely Doppler broadening S-parameter defined as the ratio of the number of counts in the central part of 511 keV gamma line to the total number of counts under the peak. The increase in S-parameter corresponds to an increase in number or size of the defect or void.

The morphology of OSC thin films as a function of temperature and the type of substrate as well as the thickness of the films has been reported by us earlier [18]. In the present work, microstructure of the organic-organic as well as organic-inorganic (film-substrate) interfaces of the heterojunctions has been studied. Doppler broadened S-parameter as a function of positron energy is seen to be sensitive to the interfacial microstructure. We have observed for the first time, sharp contrast in S-parameter at the interfaces in organic heterojunctions indicating the presence of considerable disorder contrary to the reported ordered superstructure obtained from X-ray measurements.

2. Experiment

Single layer and multilayer structure of n-type (copper-hexadecafluoro-phthalocyanine; F\textsubscript{16}CuPc) and p-type (cobalt-phthalocyanine; CoPc) OSC materials have been prepared on quartz substrate by thermal evaporation using Hind high Vac thermal evaporation system (model no-12A4T) under vacuum better than 10\textsuperscript{-6} mbar. The substrate was cleaned by sonication with trichloroethylene, acetone and methanol separately for 5 minutes each before the deposition. The films were deposited at the substrate temperature of 100°C and the deposition rate was 0.2 Å/sec. Single layer films of n and p-type material were 80 nm thick and the individual film thickness for p-n and n-p-n junction system was 60 nm and 30 nm, respectively. The thickness of the films was measured by quartz crystal monitor.

Depth dependent Doppler broadening measurements were carried out using slow positron beam at BARC in the energy range 200 eV-20 keV. A high efficiency high purity germanium detector with a resolution of 2 keV at 1332 keV photopeak of \textsuperscript{60}Co was used for Doppler broadening measurements and spectra with 2\times10\textsuperscript{5} counts were acquired at each energy. The ratio of integral counts within ~ 2
keV energy windows centered at 511 keV and total photo peak area was used to evaluate the $S$-parameter.

3. Results and Discussion
The variation of $S$-parameter as a function of positron energy for the single layer (p and n-type OSC) and multilayer films (p-n and n-p-n junction) are shown in figures 1-4, with solid lines as eyeguides. In general, there is a decrease in $S$-parameter with beam energy followed by an increase at the interface (organic-organic/organic-inorganic, as the case may be) and reaching the bulk value of quartz at higher energies. The most important observation is the enhancement of $S$-parameter at the interfaces.

Figure 1 and 2 shows the $S$-parameter variation as a function of depth for n-type and p-type OSC, respectively. The $S$-parameter variation for single layer n-type and p-type films of F$_{16}$CuPc and CoPc on quartz substrate reflects an organic-inorganic (film-substrate) interface. The energy corresponding to the maximum of $S$-parameter value indicates the mean depth of the interface between the film and the quartz substrate as calculated from the range-energy relation given by, $<z> = (40/\rho)^{1/1.6}$, where $\rho$ is the density of the material (1.7 g/cm$^3$ for OSC and 2.32 g/cm$^3$ for quartz) and $E$ is the energy of positron in keV. The observed $S$-parameter profile indicates the sharp contrasting interfacial characteristics between the film and the substrate. The high value of $S$-parameter at the interface indicates the presence of open volume defects/domains (trap centers) and reveals the sharp microstructure variation between organic and inorganic materials as indicated by the fall in $S$-parameter value thereafter. The epitaxial relation of film and the substrate is important not only in crystallographic sense but also for growth behavior. The organic molecules have large anisotropy and internal degrees of freedom due to low symmetry and extended size [16]. The effect of size difference of unit cells of organic molecules and the inorganic substrate as well as molecule-substrate interaction leads to translational and orientational domains, which are the sources of disorder [16]. The subsequent growth of the film is accomplished by the interplay of molecule-molecule and molecule-substrate interaction [19].

The organic-organic interfaces are distinctly clear in the case of multilayered structures; p-n and n-p-n heterojunctions. These interfaces experience weak van der Waals forces existing between the organic molecules. It has been reported in literature that these structures exhibit ordered arrangement of molecules across the heterojunction [20]. Also, energy level bending due to charge transfer at the heterojunction leads to the formation of charge accumulation layer and interfacial dipole [21]. However, the presence of defects/open volumes/domains of disorder are clearly revealed from our slow positron beam studies. Figure 3 shows $S$-parameter profile for p-n junction. This structure comprises of both an organic-organic (n and p-type OSC) and organic-inorganic (OSC-substrate)
interface. A sharp contrast in S-parameter can be seen at the two interfaces corresponding to energies 1.8 keV and 5.7 keV respectively. Similar interfacial characteristics have also been observed for n-p-n junction represented by the sharp oscillatory behavior of S-parameter near to the interfaces between n-p and p-n type OSC materials (bulk film) as well as film-substrate as shown in figure 4. The increase in S-parameter value near the interface is the convoluted effect of defects arising due to the growth behavior of different type of organic molecules and the intrinsic electric field due to interfacial dipole at the interface. It is to be noted that for energies higher than 1.8 keV, the standard Makhovian profile for positron implantation shows wide (in comparison to film thickness) and smoothly varying form and should not lead to sharp interfaces (as reflected from oscillatory behavior of S-parameter). However, electric field at the interfaces due to charge accumulation might have modified the standard Makhovian profile. This must be taken into account to explain the sharp oscillations in S-parameter.

The mean depths of these interfaces as calculated by positron implantation profile are observed to be shifted towards the larger depths. The shift in the depth appears to be due to the cumulative effect of increased diffusion of positrons on the substrate side, where diffusion length has been found to be high and leading to broadening of implantation profile. However, the role of electric field, especially in multilayers cannot be ruled out.

In conclusion, we have reported positron studies on the organic heterojunctions. A large degree of disorder or presence of open volume defects at the interfaces are seen which are believed to have ordered structure from X-ray studies. The observed contrast in the S-parameter at the interfaces makes the positron beam technique a potential characterization tool in organic electronics and, we believe, more detailed information on the heterojunction microstructure can be obtained through suitable modeling.

4. References

[1] Dodabalapur A, Katz H E, Torsi L and Haddon R C 1995 Science 269 1560
[2] Tang C W and Vanslyke S A 1987 App.l Phys. Lett. 51 913
[3] Peumans P and Forrest S R 2001 Appl. Phys. Lett. 79 126
[4] Tang C W and Vanslyke S A 1986 Appl. Phys. Lett. 48 153
[5] Ma L, Liu J, Pyo S and Yang Y 2002 App.l Phys. Lett. 80 362
[6] Akaik K, Kanai K, Ouchi Y and Seki K 2009 Appl. Phys. Lett. 95 113306
[7] Tang J X, Zhou Y C, Liu Z T, Lee C S and Lee S T 2008 Appl. Phys. Lett. 93 043512
[8] Liu Z T, Lo M F, Wang H B, Ng T W, Roy V A L, Lee C S and Lee S T 2009 Appl. Phys. Lett. 95 093307
[9] Brumbach M, Placencia D and Armstrong N R 2008 J. Phys. Chem. C 112 3142
[10] Haibo W, Liu Z, Ng T W, Lo M F, Lee C S and Lee S T 2010 Appl. Phys. Lett. 96 173303
[11] Rajagopal A, Wu C I and Kahn A 1997 J. Appl. Phys. 83 2649
[12] Chen W, Chen S, Huang H, Qi D C, Gao X Y and Wei A T S 2008 Appl. Phys. Lett. 92 063308
[13] Chen W, Chen S, Huang Y L, Huang H, Qi D C, Gao X Y, Ma J and Wei A T S 2009 J. Appl. Phys. 106 064910
[14] Kowarik S, Gerlach A, Sellner S, Schreiber F, Cavalcanti L and Konovalov O 2006 Phys. Rev. Lett. 96 125504
[15] Thayer G E, Sadowski J T, zu Heringdorf F M, Sakurai T and Tromp R M 2005 Phys. Rev. Lett. 95 256106
[16] Bruttling W, Physics of Organic semiconductors 2008 WILEY-VCH Verlag GmbH & Co. KGaA
[17] Ribic P R and Bratina G 2007 J. Vac. Sci. Technol. B 25 1152
[18] Maheshwari P, Dutta D, Samanta S, Singh A, Aswal D K, Reddy A V R and Pujari P K 2009 Phys. Stat. Solidi C 6 2589
[19] Debnath A K, Samanta S, Singh A, Aswal D K, Gupta S K, Yakhmi J V, Deshpande S K, Poswal A K and Surgers C 2008 Physica E 41 154
[20] Akimichi H, Inoshita T, Hotta S, Noge S and Sakaki H 1993 Appl. Phys. Lett. 63 3158
[21] Chen W, Chen S, Huang H, Qi D C, Gao X Y and Wei A T S 2008 Appl. Phys. Lett. 92 063308