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Electronic excitation induced modifications of optical and morphological properties of PCBM thin films

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ABSTRACT

Phenyl C_{61} butyric acid methyl ester (PCBM) is a fullerene derivative and most commonly used in organic photovoltaic devices both as electron acceptor and transporting material due to high electron mobility. PCBM is easy to spin caste on some substrate as it is soluble in chlorobenzene. In this study, the spin coated thin films of PCBM (on two different substrate, glass and double sided silicon) were irradiated using 90 MeV Ni^{7+} swift heavy ion beam at low fluences ranging from 1×10^9 to 1×10^{11} ions/cm^2 to study the effect of ion beam irradiation. The pristine and irradiated PCBM thin films were characterized by UV–visible absorption spectroscopy and fourier transform infrared spectroscopy (FTIR) to investigate the optical properties before and after irradiation. These thin films were further analyzed using atomic force microscopy (AFM) to investigate the morphological modifications which are induced by energetic ions. The variation in optical band gap after irradiation was measured using Tauc's relation from UV–visible absorption spectra. A considerable change was observed with increasing fluence in optical band gap of irradiated thin films of PCBM with respect to the pristine film. The decrease in FTIR band intensity of C_{60} cage reveals the polymerization reaction due to high energy ion impact. The roughness is also found to be dependent on incident fluences. This study throws light for the application of PCBM in organic solar cells in form of ion irradiation induced nanowires of PCBM for efficient charge carrier transportation in active layer.

1. Introduction

Nowadays the polymer-fullerene bulk heterojunction (BHJ) organic solar cells (OSC) are very promising source of photovoltaic (PV) devices because of their low cost, structural flexibility and improved efficiency compared to the other configuration of organic solar cells. In BHJ structure, two different materials are used, one is as electron donor and the other is as electron acceptor material to make a blend structure in the active layer. The donor material leads to the major light absorption in the visible region and a coulomb-bound electron-holes pair called exciton is generated. This blend structure of donor–acceptor material provides a large interface of sufficient potential gradient to dissociate the generated excitons into charge carriers within the exciton diffusion length (~10 nm). These charge carries thus transported towards the opposite electrodes through the acceptor material.

Recently, conjugated polymer Poly 3-hexylthiophene (P3HT) and fullerene derivative Phenyl C_{61} butyric acid methyl ester (PCBM) is widely used in the active layer of BHJ organic solar cells to get improved efficiency. The conjugated polymer P3HT acts as a donor material in the active layer of OSCs. P3HT consists of a π-conjugated backbone with polythiophene units and pendent alkyl side group. It has band gap about 1.9 eV (the Highest Occupied Molecular Orbital, HOMO lies at −4.8 eV and the Lowest Unoccupied Molecular Orbital, LUMO lies at −2.9 eV). In P3HT holes are the majority carriers which has mobility about 0.1 cm^2/Vs [1–3]. The other material PCBM acts as an acceptor and charge carrier transporting material [4,5] because of their high thermal stability, higher electron mobility and higher electron affinity. PCBM is a fullerene derivative which consists of phenyl ring and Butyric acid methyl ester side chain attached to a C_{60} cage. This side chain improves the solubility or solution processibility of PCBM molecules in different solvents such as chloroform, chlorobenzene and dichlorobenzene etc. than C_{60} molecules [6,7]. In present work, chlorobenzene has been used as solvent for PCBM

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solution. The mobility for PCBM molecules lies between 2×10^{-3} and 2×10^{-2} cm^2/vs. PCBM, being a versatile material, can also be used in thin film transistors [8,9], memory applications [10], fluorescence spectroscopy measurement of fullerenes [11] etc. as they have deep lying LUMO levels and n-type semiconducting nature. The other advantage of using PCBM as an electron acceptor is their high symmetry that leads to a good contact with neighboring molecules.

It has been reported that PV cells which are based on P3HT and PCBM material are very efficient and promising devices. To improve the device efficiency, many efforts have been made such as solvent annealing, consideration of different solvents for active layer [12,13], improved crystallinity and post annealing of the device [14,15]. It has been reported that the surface morphology is also an important factor for improved efficiency in PV devices [16]. Efforts have also been made on both the materials separately (electron donor and electron acceptor) using high energy ion irradiation technique to study the different properties under different perturbations. In the present study, focus is mainly on the electron acceptor PCBM material under swift heavy ion irradiation. A gradual shift in the LUMO and the HOMO levels of PCBM with increased electron fluence has already been reported by Seung Hwa Yoo et al. [17] and is explained on the basis of changes induced in molecular structure by electron irradiation. Yuta Maeyoshi et al. [18] have reported the fabrication of nanowires of 8–11 nm radius in fullerene C_{60}, methanofullerenes of C_{61} and/or C_{71} and indene C_{60} bis-adduct by using single particle nanofabrication technique (SPNT) using 490 MeV Os ion beam. Same group has also done studies on fabrication of nanowires in different polymers using SPNT [19–22]. The authors have explained that high energy ion beam irradiation can lead to the chain polymerization reactions in the host materials. These chain reactions are responsible for the high conductivity within the nanowires. The effect of high energy ion beam on the parent molecules of C_{60} and C_{70} (excellent electron acceptor material) has also been studied by several authors. The effect of 120 MeV Au swift heavy ions on fullerene C_{70} thin films has been investigated by R. Singhal et al. [23]. They have shown the decrease in optical band gap with increasing fluence and steep increase in conductivity beyond a fluence of 1×10^{12} ions/cm^2 fluence. Amit Kumar et al. [24] have investigated the ordering of fullerene C_{60} thin films under 200 MeV Au swift heavy ion beam impact at low fluence. A comparative study of ion induced damages in fullerene C_{60} and C_{70} have reported by R. Singhal et al. and found that C_{70} is more stable than C_{60} molecules under energetic ions impact [25].

All these studies show that the properties of fullerene molecules and its derivates can be altered using energetic ion irradiation. In order to investigate the effect of energy deposition on PCBM molecule, the spin coated PCBM thin films have been irradiated with 90 MeV Ni^{7+} ion beam in the present work. UV–visible absorption measurement, FTIR measurement and AFM image analysis studies have been carried out to observe the optical and morphological effect on pre and post irradiated PCBM thin films.

2. Experimental details

The PCBM ($C_{72}H_{14}O_2$) was obtained from Ossila, UK with purity 99.5% and molecular weight 911 g/mol. The solvent chlorobenzene used was taken from Merck (>99%). The PCBM solution (1.8 wt%) was prepared by dissolving PCBM powder in chlorobenzene and stirred. The solution of PCBM was spin casted on sequentially cleaned glass and double side polished Si substrates. During the spin coating, rotation rate was 800 rpm for 50 s. The substrates were sequentially cleaned in soap solution, de-ionized water, acetone and isopropanol for 15 min each with ultrasonication and then dried. After spin coating, films were post dried at 100 °C for 15 min to evaporate residual solvent. These thin films were irradiated using 90 MeV Ni^{7+} swift heavy ion beam obtained from 15 UD Pelletron Accelerator at Inter University Accelerator Centre, New Delhi. The incident particle number density was 1×10^9, 3×10^9, 1×10^{10}, 3×10^{10} and 1×10^{11} ions/cm^2 with current 0.2 pnA. A very small current was chosen to avoid heating effect during the irradiation. The electronic energy loss and nuclear energy loss of 90 MeV Ni^{7+} ions in PCBM films is 7736 eV/nm and 13.19 eV/nm respectively, which shows at this energy, electronic energy loss dominates over nuclear energy loss and modification produced in the material will be mainly due to electronic excitations. The range for Ni ion in the PCBM thin films is 16.6 μm. These energy losses and range was calculated by stopping and range of ions in matter (SRIM 2008) programme [26]. Films thickness is around 100 nm which is thin enough for the 90 MeV Ni^{7+} ions to pass through completely. The thickness of PCBM films was measured on glass substrate using a Dektak stylus surface profiler at Inter University Accelerator Centre (IUAC), New Delhi. Absorption spectra of pristine & irradiated samples on glass substrate was obtained using a Hitachi U-3300 spectrophotometer in the range 300–700 nm at IUAC, New Delhi. The FTIR spectra of pristine and irradiated thin films on double sided silicon substrate was observed using Perkin Elmer model no L1600401 spectrum and serial no 91606 made in Llantrisant, UK FTIR spectroscopy at National Physical Laboratory, New Delhi. To investigate the morphology of pristine and irradiated thin films, AFM analysis was done in tapping mode over double sided silicon substrate using Bruker Nano 5 AFM setup at Material Research Centre, MNIT Jaipur.

3. Result and discussion

3.1. UV–visible absorption spectroscopy

Fig. 1 shows the absorption spectra of pristine and 90 MeV Ni^{7+} irradiated thin films of PCBM on glass substrate. The incident fluences were 1×10^9, 3×10^9, 1×10^{10}, 3×10^{10} and 1×10^{11} ions/cm^2. The absorption spectrum of PCBM thin film is showing the absorption in the ultraviolet region (<400 nm wavelength) which is similar to the parent C_{60} molecule [27]. The absorption peak of PCBM films was found at 335 nm in the form of intense peak which arises due to interband transition among the π orbitals. A tail was also observed in the absorption spectra of pristine and irradiated thin films which is extending to 700 nm. This tail is not due to light scattering or some other experimental facts. The

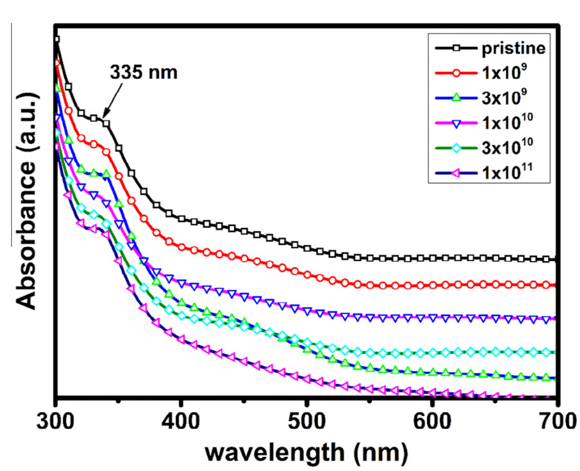

Fig. 1. UV–visible absorption spectra of pristine and 90 MeV Ni^{7+} ion beam irradiated PCBM thin films.