Optical Materials 85 (2018) 287–294

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Curtailed recombination rate and fast carrier transport in ZnPc/GaAs/ZnPc stacked hybrid structure

R. Rathes Kannan[a], P. Issac Nelson[a], S. Rajesh[c,*], T. Ponmudi selvan[a], A. Mohan[b], B. Vidhya[c], D. Nirmal[d], Arivazhagan[d]

[a] *Thin Film Laboratory, Department of Physics, Karunya Institute of Technology and Sciences, Coimbatore, 641114, India*
[b] *Department of Physics, St.Joseph's College (Autonomous), Bangalore, 560027, India*
[c] *Department of Nanoscience and Technology, Karunya Institute of Technology and Sciences, Coimbatore, 641114, India*
[d] *Department of Electronics and Communication Engineering, Karunya Institute of Technology and Sciences, Coimbatore, 641114, India*

ARTICLE INFO

Keywords:
Hybrid structure
Molecular orientation
Quenching
Decay time
Carrier transport

ABSTRACT

Hybrid organic-inorganic double-layered structures are fabricated from Zinc Phthalocyanine (ZnPc) and Gallium Arsenide (GaAs). The inclusion of GaAs interlayer widens the absorption spectrum of ZnPc. Photoluminescence (PL) shows that GaAs quenches emission from the ZnPc suggesting carriers transfer to GaAs. Time-resolved fluorescence spectroscopy shows the molecular orientation of ZnPc tunes fast charge transport. The ZnPc/GaAs/ZnPc hybrid structure possess the ability to a wide range of absorption as evident in ultraviolet–visible (UV–Vis) absorption studies and charge carrier extraction from PL analysis are suitable for solar cell application.

1. Introduction

A new class of organic-inorganic hybrid photovoltaic (PV) is an alternative for both pure organic and inorganic PVs with the incorporating advantages associated with both materials groups. Additionally, organic semiconductors have high absorption coefficients even in the very small dimension [1,2]. In recent works, most of the organic devices are based on phenylene vinylene (PPV), poly [2-methoxy-5-(2-ethyl-hexyloxy)-1,4-phenylene vinylene (MEH-PPV), poly (3-hexylthiophene-2,5-diyl) (P3HT) has shown the better efficiency [3–6]. However, the improvement in the efficiency has saturated due to the large band gap of polymer materials. Among the various organic materials, Zinc Phthalocyanine (ZnPc) was highly investigated organic-semiconductor as suitable for photovoltaic applications due to its higher absorption coefficient $> 10^5\,\mathrm{cm}^{-1}$ with strong visible region absorption [7,8]. It has advantages in the matter of high thermal and chemical stability, higher hole carrier mobility compared to the other class of organic materials [9]. It has been used in bulk heterojunction with a combination of ZnPc/C60 co-evaporated films. This class of devices provides a lager interface to simulate an enhanced charge extraction [10,11]. Moreover, the acceptor C60 has no significant contribution in light absorption. In the other case, its competent inorganic acceptor materials are more environmentally stable and potentially able to contribute in the light absorption than its counterpart. Example, The ZnPc/Cds nanoparticles hybrid structures showed significant improvement in the optical absorption [12]. Thus, a class of inorganic materials has been examined as acceptor materials with ZnPc. On the other hand, at low dimension (nanoparticles and quantum dots) inorganic semiconductors have shown excellent optical and electrical properties due to its discrete energy levels. It's well known if one of the dimensions of semiconducting materials has become comparable to of its exciton Bohr radius carrier, it undergoes quantum confinement [13,14]. As a matter of fact, GaAs based solar cells have a higher conversion efficiency of 28% than that of Silicon (Si) based cells [15]. In addition, it was highly investigated as an electron acceptor in organic/inorganic hybrid cells due to its high electron mobility ($\leq 8500\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{S}^{-1}$). It has an ability to enhance the power conversion efficiency as nanostructure rather than the bulk structure. Jiun-Jie Chao et al. (2012) has stated that vertically aligned GaAs nanowires and PEDOT: PSS heterojunction based cell of 9% efficiency [16]. Mariani et al. have reported 4% efficiency for the GaAs nanowire embedded bulk heterojunction with P3HT whereas only 1.44% was achieved with GaAs nanopillars coated with P3HT [17]. Ruiqin Ding et al. investigated quantum size effect in GaAs thin film, a reported band gap value is 2.0 eV for a thickness of 1–3 nm [18]. Thus, cumulative reports on GaAs thin layers insist its potential ability in photovoltaic and UV–Visible driven applications. In thermal evaporation, multilayer thin films have taken higher creditability in the formation of two-

---

* Corresponding author.
E-mail address: drsrajesh@karunya.edu (S. Rajesh).

https://doi.org/10.1016/j.optmat.2018.08.032
Received 2 April 2018; Received in revised form 8 August 2018; Accepted 11 August 2018

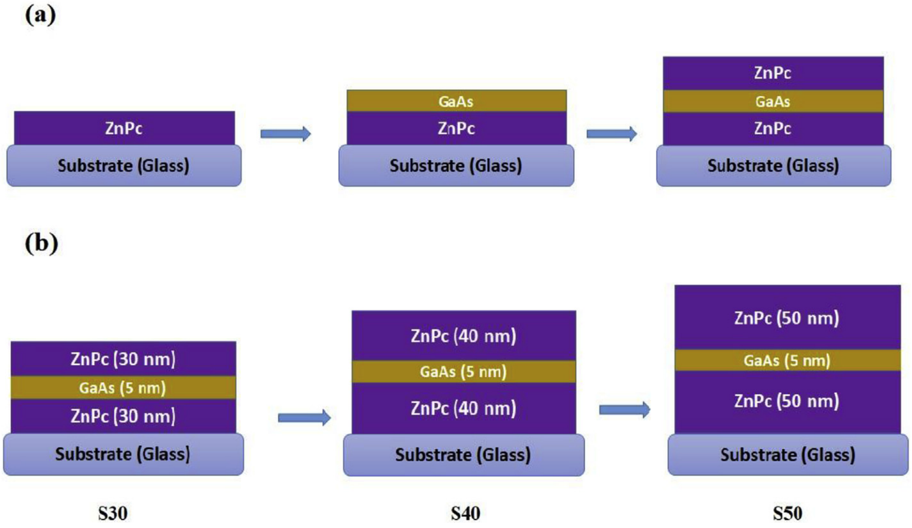

Fig. 1. Deposition steps of (a) ZnPc/GaAs/ZnPc stacked layers, (b) ZnPc/GaAs/ZnPc stacked layers with various ZnPc layer thickness.

dimensional semiconductor structures, in which two different semiconductors can be stacked as alternating layers [13]. The scintillating characteristics of ZnPc and GaAs have aroused our curiosity to examine its hybrid system in terms of optical transformation and a faster charge transport. Thus, in the present work, a very thin layer of GaAs (5 nm) is stacked between the organic ZnPc layers by a multilayer thin film approach.

2. Materials and methods

Thermal evaporation method was utilized to deposit ZnPc/GaAs/ZnPc hybrid structure by multilayer stacking on the ultrasonically cleaned glass substrates. High purity ZnPc (99.99%) (Sigma Aldrich) in the form of powder and GaAs in form of the ingot (Alpha Aesar) were placed in two individual molybdenum boats. Initially, ZnPc layer was deposited with a thickness of 30 nm over the glass substrate. Then, the two dimensional GaAs layer of 5 nm thickness was deposited and followed by successive deposition of ZnPc (30 nm thickness) layer deposited over the GaAs as shown in Fig. 1a. To characterize the effect of organic layer thickness in hybrid structure (Fig. 1b) three different samples with various ZnPc layer thickness of 30 nm (S30), 40 nm (S40) and 50 nm (S50) (with fixed GaAs layer thickness of 5 nm) were prepared. For comparison, reference ZnPc and GaAs films were prepared with a thickness of 100 nm. All the film depositions were carried out in a vacuum atmosphere of 10^{-5} mbar with controlled evaporation rate ranges from 1 to 2 Å/sec during the entire process. The layer thickness was controlled using a quartz crystal monitor.

The Fourier transform infrared (FTIR) spectra of ZnPc reference and S30, S40 and S50 films were recorded using Shimadzu between 700 cm^{-1} and 1800 cm^{-1}. The structural properties were carried out by X-ray diffraction analysis (Shimadzu XRD-6000 instrument) using Cu-Kα (λ = 1.5418) radiation in the range between 5° and 50°.The surface morphological properties were studied by using JEOL scanning electron microscopy. The UV–Visible spectroscopy and Photoluminescence spectroscopy were studied using Jasco-570 UV/VIS/NI and JASCO FP-8200 respectively.

3. Results and discussions

3.1. Vibrational analysis

The FTIR spectrum of reference ZnPc film in the range 600–1800 cm^{-1} is shown in Fig. 2a. In the fingerprint region, the intense peaks were observed at 725, 756 and 775 cm^{-1} and assigned to the C—H angular deformation, pyrrole stretching and macrocycle ring deformation respectively. These peaks also provide information about the crystalline nature of thermally evaporated ZnPc film. M.M.El-Nahaas et al. stated that the peak at 725 cm^{-1} indicates the presence of ZnPc in thin film form assigned to the α-phase of the monoclinic structure. The peaks at 756 and 775 cm^{-1} also indicate that the film is rich in α-phase [19].

The band at 1328 cm^{-1} is assigned to the pyrrole group in the plane of the macrocycle. This suggests that the organization of ZnPc molecules in the film is practically parallel to the substrate surface [20]. The FTIR spectrum of ZnPc/GaAs/ZnPc hybrid structure with different ZnPc layer thickness is displayed in Fig. 2b, c and 2d. The intense peak at 721 cm^{-1} of α-phase corresponding to C—H angular deformation out of the plane was observed in all the films. This indicates that the films exhibit similar crystalline structure. The perpendicular molecular orientation was affirmed in the S30 film by a strong pyrrole stretching band at 1334 cm^{-1} [21]. However, this band was slightly shifted to the lower frequency range (1330 cm^{-1}) in both S40 and S50 films, which implies the change in molecular orientation of ZnPc molecules from perpendicular to the parallel direction to the substrate surface in the films [20]. Overall, the vibrational peak of ZnPc central molecule was uninterrupted and there is no additional peaks were found.

3.2. X-ray diffraction analysis

Fig. 3 shows the diffraction pattern of ZnPc/GaAs/ZnPc hybrid structure with reference ZnPc film (100 nm). Fig. 3a shows the XRD pattern of ZnPc film, it possesses a broad single characteristic peak at 6.91° with (2 0 0) plane orientation corresponding to the α-phase of monoclinic ZnPc structure [22]. The crystalline structure of ZnPc/GaAs/ZnPc stacked layer with various ZnPc thickness can be observed from Fig. 3b, (c), (d) corresponding to the S30, S40 and S50 films respectively.

An intense peak was obtained at 7.1063° in S30 film, which corresponds to the (2 0 0) plane orientation of the monoclinic ZnPc structure. The same peak appeared in the S40 and S50 films with a slight shift in the peak position towards the lower angle region. The FWHM and the interplanar distance (d) of the peaks were increasing with respect to the ZnPc thickness (Table 1). It is known that the interplanar distance has a direct relationship with the molecular orientation of the ZnPc film. Senthilarasu et al. stated that the increase in the d-spacing value suggests that the tilt angle between the stacking axis and normal of the Phthalocyanine ring becomes smaller [22,23]. Further, the α-phase have usually lower tilt angle when compared to the β-phases ZnPc