An ultraviolet photodetector with an active layer composed of solution processed polyfluorene:Zn_{0.71}Cd_{0.29}S hybrid nanomaterials

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ABSTRACT

An ultraviolet photodetector with an active layer of solution processed polymer:quantum dot hybrid is introduced. Poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl] represents the polymer and Zn_{0.71}Cd_{0.29}S is the quantum dot used for the device. Photophysical studies showed that an electron transfer from the polymer to the ternary quantum dot is thermodynamically favored. Quenching experiments performed between the polymer and quantum dot indicates the formation of a non-fluorescent complex with an association constant of $4.6 \times 10^4 \text{ M}^{-1}$. The device structure of ITO/PEDOT:PSS/ADS231BE: 50 wt% Zn_{0.71}Cd_{0.29}S/Al yielded a photoresponsivity value of 324 mA/W at -4 V under 1 mW/cm^2 illumination at 365 nm at room temperature and this value is further increased to 380 mA/W as a result of annealing at 75°C .

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1. Introduction

Photo multiplier tubes, thermal detectors and Si based UV photo detectors (PDs) are used to detect UV radiation. Generally, UV detection is achieved by wide band gap materials such as GaN, AlN, MgZnO, AlGaIn, ZnO, TiO₂ [1,2]. Unfortunately, the manufacturing processes to modify the optical and electrical properties of these inorganic semiconductor nanoparticles is very complicated and consequently expensive [2]. However, the material variability and solution processability of organic semiconductors and their hybrids has the potential of reducing the manufacturing costs.

In recent years, due to the possibility to change the photo physical properties through simplified chemical synthesis and easy thin film processing, quantum dots (QD) and polymer:QD hybrids attract a lot of attention in UV-PD applications [1–8], as well as the other photonic applications, such as biological imaging and contrast agents [9,10], light-emitting devices (LEDs) [11,12] photovoltaic [13–15], etc. Most of the QDs used in UV-PDs are binary systems, the band gap of which are tuned by varying the diameter of the nanoparticle [1–5,7,8,16]. However in ternary QDs, the band gap may be tuned by the relative composition of materials used

as well [6,17]. Nonetheless to the best of our knowledge, there is only one report existing in the literature involves the utilization of a ternary QD, i.e. CuInSe₂, in a hybrid UV-PD [6]. Likewise, the studies focusing on the photophysical interactions between the polymer and QD nanoparticles are also limited [7,8].

In this study, we used a commercially available blue emitting polymer, i.e. poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl], with a ternary alloy, i.e. Zn_{0.71}Cd_{0.29}S nanoparticle as the active layer of a solution processed UV-PD and examined the donor–acceptor relationship between those two components. A photoresponsivity value of 380 mA/W under 1 mW/cm^2 irradiation at 365 nm is reported and it is shown that the working mechanism of the UV-PD depends on the non-radiative complex formation between the ADS231BE and Zn_{0.71}Cd_{0.29}S.

2. Experimental

2.1. Materials

Cadmium acetate, zinc acetate, sulfur powdered, oleic acid and octadecene used in the synthesis of nanoalloy were purchased from Sigma Aldrich and Fluka, respectively. Indium tin oxide (ITO) coated glass substrates with sheet resistance of $4\text{--}10 \Omega/\square$ were obtained from the Delta Technologies. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) and

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aluminum (Al) were purchased from Sigma Aldrich. ADS231BE (poly[9,9-di-(2-ethylhexyl)-fluorenyl-2,7-diyl]) polymer was purchased from American Dye Source.

2.2. Synthesis of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$

$\text{Zn}_x\text{Cd}_{1-x}\text{S}$ ternary nanoalloys were synthesized by modifying the one-pot synthesis approach introduced by Zhong et al. [18]. A mixture of 0.086 mmol cadmium acetate (CdAc_2), 0.28 mmol zinc acetate (ZnAc_2), 3.17 mmol oleic acid, and 20 ml non-coordinating solvent octadecene were heated at 100 °C under N_2 atmosphere for 1 h. Then the mixture was heated to 250 °C to initiate dissociation of metal precursors CdAc_2 and ZnAc_2 . At the same time sulfur (S) solution was prepared by dissolving 0.0754 mmol S in 4 ml octadecene under sonication. After obtaining clear colorless solution of metal precursor, the prepared S solution was swiftly injected into the hot solution of metal precursors. As soon as S addition was completed, the temperature of reaction mixture was lowered to 230 °C for the subsequent growth and annealing of the resulting nanocrystals. The reaction was stopped by cooling the solution. The excess oleic acid and the un-reacted metal precursor were separated from the dispersion of nanoalloys by extraction of the reaction solution with an equal volume of $\text{CHCl}_3:\text{CH}_3\text{OH} = 1:1$. Upper part of the extract was separated and precipitated by means of ethanol.

2.3. Device preparation

ITO substrates were etched by hydrochloric acid and ultrasonically cleaned in detergent solution, deionized water, and acetone, blow-dried with nitrogen gun and then treated with O_2 plasma for 5 min. After the cleaning process, PEDOT:PSS was spin-coated at 3000 rpm for 1 min and dried in vacuum oven at 100 °C for 30 min which yielded in a film thickness of 45 nm. Thin films of ADS231BE: $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ hybrids with a thickness of 80 nm were obtained by spin coating at 2500 rpm on to the PEDOT:PSS layer. The total material concentration was 10 mg/ml in chlorobenzene and doping ratios of 25, 33, 50, 66 and 75 wt% of nanoalloy were used. The thickness of the active layer was independent from the nanoalloy content. Following the organic layer coatings, Al cathode (100 nm) was deposited through a shadow mask by the use of a vacuum evaporator, attached to an MBRAUN 200B glove box system, at a rate of 0.5 Å/s and at 3×10^{-6} mbar pressure. The UV-PD device structure studied was ITO/PEDOT:PSS/ADS231BE: $x\text{wt}\%\text{Zn}_x\text{Cd}_{1-x}\text{S}/\text{Al}$ with an active area of 12 mm². Five parallel measurements were performed for each device. The cross sectional device configuration and the energy levels of the used materials are given in Fig. 1a and b, respectively.

Effect of annealing the active layer was also studied for the device presented maximum photoresponse. Spin coated polymer:nanoalloy blends were kept in vacuum oven for 15 min at 50 °C, 60 °C, 75 °C, 80 °C and 90 °C and subsequent cathode evaporation was performed. Photodetector characterizations were performed under nitrogen environment in glove box system.

2.4. Instruments

Size of the nanoalloys was measured by Malvern Zetasizer Nano ZS. X-ray powder diffraction pattern of the nanoalloy was obtained by using a Philips X'pert Pro Materials Research Diffractometer. The grounded samples were placed on a zero-background silicon sample holder. Data were collected by using $\text{CuK}\alpha$ ($\lambda = 1.5406$ Å) radiation at settings of –45 kV and 40 mA for 45 min. The scan rate was 0.1°/s and the data were collected for 2θ values of 5° to 65°. Composition analysis was carried out by Varian ICP 96 model Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES).

Glass transition temperature (T_g) of ADS231BE polymer was determined by Perkin Elmer Pyris6 Differential Scanning Calorimeter (DSC) with a heating rate of 10 °C/min from –10 °C to 300 °C and found to be at around 75 °C. Absorption, photoluminescence (PL) and lifetime measurements were performed by Perkin Elmer UV-Vis-NIR, Edinburg FLS920P spectrophotometers and with an excitation source of 368 nm laser-LED, respectively. CH Instrument 660 B potentiostat equipped with a Ag/AgCl reference electrode, platinum wire and nanoalloy or ADS231BE on ITO glass as counter and working electrodes, respectively and 0.1 M TBAPF₆ in acetonitrile as electrolyte was used in cyclic behavior determinations. Ferrocene was used as the internal standard in all cyclic voltammetry measurements.

Laurell WS-400B-6NPP-LITE spin coater was used for the preparation of organic coatings and the thickness of thin films was determined by Ambios XP-1 high-resolution surface profilometer. Film morphologies were monitored by AmbiosQScope 250 model atomic force microscope (AFM) and Phillips XL-305 FEG scanning electron microscope (SEM). Current–voltage (I – V) and impedance characteristics of the photodetectors were obtained with Keithley 2400 source meter and IM6 ZahnerElektrik impedance analyzer, respectively. Electrical characteristics were performed in dark and under 1 mW/cm² illumination intensity at 365 nm measured by Nova II versatile laser power energy display that contains a calibrated silicon photodiode. Illumination provided from a solar simulator attached to MBRAUN 200B glove box system that also contains a vacuum evaporation system with a quartz crystal thickness monitor. Solar simulator irradiation is filtered through 365 nm bandpass interference filter with 10 nm full width at half maximum obtained from Edmund optics.

3. Results and discussion

3.1. Compositional characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$

Quantitative measurements of metals in the nanoalloys were achieved by ionizing the sample with inductively coupled plasma and separating them by Atomic Emission spectrometer (ICP-AES). Standard solutions were prepared in order to obtain calibration curves of Cd^{2+} and Zn^{2+} individually. Nanoalloys were disintegrated by 2.5% HNO_3 solution. Cadmium to zinc mole ratio was determined as 0.41 and the composition of nanoalloys were estimated as $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$. The presence of characteristic (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3) and (1 1 2) peaks (Fig. 2a) in XRD pattern resulted the Wurtzite structure of the nanoalloys.

The uniformity and size distribution of the synthesized nanoparticles were measured by SAXS and DLS. The DLS data inserted in Fig. 2b verify the hydrodynamic size of nanoalloys as 4.3 nm and SAXS measurements resulted in a crystalline size of 3.7 nm. The reason of the bigger value of DLS then SAXS data is that DLS contains scattering from surfactants and solvent molecules surrounding the crystalline size of the nanoalloys.

The molecular mass (M_a) of nanoalloy was determined by using the equation below:

$$M_a = \frac{[4\pi(x/2)^3 m_a]}{3}$$

where x is the size of nanoalloy divided by the lattice distance of it and m_a is the formula mass of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ (111 g/mole). Ramasamy et al. have both measured and calculated the lattice distance of $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ quantum dots with different compositions and reported this value to be between 0.31 nm and 0.33 nm [19]. Therefore, the lattice distance of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ was taken as 0.3 nm in the equation.

Fig. 1. (a) Cross sectional device structure and (b) the energy diagram of ITO/PEDOT:PSS/ADS231BE: Zn_{0.71}Cd_{0.29}S/Al.

3.2. Spectroscopic and electrochemical characterization of Zn_{0.71}Cd_{0.29}S

Fig. 2c shows the normalized absorption and PL spectra of the nanoalloy in chlorobenzene. The absorbance variation of the nanoalloy with its concentration was measured for five different values and the molar extinction coefficient of Zn_{0.71}Cd_{0.29}S at 410 nm was calculated as $1.8 \times 10^5 \text{ L/M}^{-1} \text{ cm}^{-1}$. Although more complicated experimental determinations of extinction coefficient

exist in literature, the reported values are close to our ternary system [20].

The nanoalloy emitted light via both, band-edge (at 425 nm) and surface-trap states (broad peak at around 550 nm). Excitation spectrum of Zn_{0.71}Cd_{0.29}S resulted in two absorption peaks at 315 nm and 350 nm. The emission wavelength and shape of PL spectrum was independent from the excitation wavelength used (data not shown here). The relative fluorescence quantum yield (ϕ_f) of Zn_{0.71}Cd_{0.29}S was calculated as 0.14 by using the equation

Fig. 2. (a) X-ray powder diffraction patterns, (b) Size distribution by DLS, (c) Normalized absorption and PL spectra and (d) PL decay curve of exciton emission of Zn_{0.71}Cd_{0.29}S nanoparticles (inset: Fluorescence lifetime values and their relative percentages. χ^2 value is 1.110).

given in literature [21] and perylene as the standard (ϕ_f of perylene in benzene is 0.89) [22]. The characteristic PL decay profile of nanoalloy is provided in Fig. 2d. The PL decay curve successfully fits the multi-exponential model. Fluorescence decay traces with relative amplitudes are seen in the inset of Fig. 2d. The four exponential fitting yields, shorter lifetime components with of several nanoseconds (τ_1 :1.4 ns, τ_2 :7.6 ns) and longer lifetime components with several tens of nanoseconds (τ_3 :29.8 ns, τ_4 :143.3 ns). Average excited state lifetimes (τ_{AV}) are calculated by using the equation below [23]:

$$\tau_{AV} = \frac{\sum_{i=1}^n \alpha_i \tau_i^2}{\sum_{i=1}^n \alpha_i \tau_i}$$

where α_i is the amplitudes of the components at $t=0$, τ_i is the decay times and n is the number of decay times. τ_{AV} for $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$

nanoparticles is calculated as 129 ns in chlorobenzene. This value is decreased to 72.4 ns for the nanoparticles in film phase which is attributed to the aggregation and/or concentration quenching.

3.3. Determination of energy levels and electrochemical behavior of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$

Cyclic voltammogram of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ resulted in a reversible reduction peak with a peak potential of -0.97 V and an onset potential of -0.77 V which is used as ϕ'_n in the equation below for the calculation of conduction band (CB) of the nanoalloy [24,25].

$$E_{CB} = -e(\phi'_n + 4.4)$$

The valance band (VB) energy level of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ is simply estimated from the CB and optical band gap obtained from absorption spectrum offset (3.02 eV) as -6.65 eV. Electrochemical measurement of the polymer resulted in a single oxidation peak with an onset potential of 1.34 V that corresponds to the highest occupied molecular energy level (HOMO) of -5.74 eV and addition of the optical band gap gave a lowest occupied molecular energy level (LUMO) of -2.73 eV. These values are in good accordance with the fluorene type polymer literature [26,27].

PL and τ_{AV} variations of drop casted $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ nanoalloy on ITO substrate with anodic and cathodic potentials were studied under atmospheric conditions. Under anodic potentials, the PL intensity changed dramatically and more than 50% reduction in τ_{AV} value was obtained (Fig. 3a) whereas no significant change is

Fig. 3. PL spectra of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ drop casted films on ITO under (a) forward and (b) reverse bias (inset: life time decays).

Fig. 4. Absorption and PL spectra of ADS231BE and $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ in chlorobenzene.

Fig. 5. (a) Absorption and (b) ϕ_f deviation of 10^{-7} M ADS231BE with the addition of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ in chlorobenzene (inset: Stern–Volmer plot).

Fig. 6. Current density–Voltage characteristics of ITO/PEDOT:PSS/ADS231BE: x wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ ($x = 25, 33, 50, 66$ and 75 at RT) and ITO/PEDOT:PSS/ADS231BE: 50 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ at annealing temperatures of RT, 50°C , 60°C , 75°C , 80°C and 90°C , (a) and (b) in dark and (c) and (d) under $1\text{ mW}/\text{cm}^2$ at 365 nm irradiation, respectively.

detected with cathodic potential application (Fig. 3b). The decrease observed under anodic potential was expected as the $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ nanoparticle is an n -type semiconductor [28]. The observed electrochemical change was irreversible. Under cathodic potential a significant PL intensity increment was expected as the stability of valence band electrons would also increase and the surface traps would be passivated. However, only slight enhancements were observed. As stated above, the measurements were performed under atmospheric conditions and the oxygen content of environment may have prevented the PL intensity improvement [29,30].

3.4. Photophysical studies of ADS231BE and $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$

The absorption and PL spectra of ADS231BE and $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ in chlorobenzene solvent are given in Fig. 4. The absorption of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ nanoalloy substantially overlapped with the PL spectrum of polymer. The ϕ_f value of ADS231BE was calculated with the same procedure applied for $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ and found to be 0.32 in chlorobenzene. The possible donor–acceptor relationship between the polymer and nanoparticle was studied by increasing the concentration of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ in the polymer solution which resulted in an increase in absorbance (Fig. 5a) and a dramatic decrease in ϕ_f value of ADS231BE (Fig. 5b), whereas no significant deviation in the τ_{AV} value of polymer is detected. This observation addresses that the nature of the quenching is static [31] and occurs as a result of the formation of non-fluorescent complex between $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ nanoparticle and ADS231BE polymer. Here the non-complexed polymer was unperturbed and the only fluorescence comes from this fraction. The static quenching constant (K_s) was calculated from Stern–Volmer equation:

$$\frac{F_0}{F} = 1 + K_s[Q]$$

where the “ F_0 ” and “ F ” is the photoluminescence intensity in the absence and presence of quencher, respectively and $[Q]$ is the concentration of the quencher ($\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ nanoalloys) [31]. K_s is calculated as $4.6 \times 10^4\text{ M}^{-1}$ (Fig. 5b inset). Static quenching constant is also named as the association constant that indicates the complex formation tendency of donor and acceptor species and a value around 10^4 points out the strong interaction between the ADS231BE and $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$.

The possibility of complex formation via electron transfer from the polymer to the nanoparticle is investigated thermodynamically. The redox properties of the QD and the polymer reveal that ground state electron transfer from ADS231BE to $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ is forbidden as the Gibbs free energy change (ΔG_{ET}) calculated by using the given equation is positive ($\Delta G_{\text{ET}} = 2.05\text{ eV}$) [32]:

$$\Delta G_{\text{ET}}(\text{eV}) = E_{(\text{D}/\text{D}^+)} - E_{(\text{A}/\text{A}^-)} - 0.06$$

However, upon illumination electron transfer becomes thermodynamically favored since its ΔG_{PET} equals $\Delta G_{\text{ET}} - E_{\text{D}^*}$ where E_{D^*} is the band gap of the polymer (3.01 eV) obtained from the offset of the absorption spectrum. The calculated ΔG_{PET} is -0.91 eV and the negative value indicate that the interaction is spontaneous. Furthermore, the “rule of thumb” suggest quenching via electron transfer when $\Delta G_{\text{PET}} \leq 0.2\text{ eV}$ [32].

Stability of the nanoparticle under cathodic potential, increment of the polymer absorbance accompanied by PL quenching and thermodynamically allowed electron transfer from the polymer to the QD directed us to use this non-fluorescent complex as the active layer in UV-PD.

Fig. 7. Absorbance (at 365 nm) and responsivity values of ITO/PEDOT:PSS/ADS231BE: 50 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ device at different annealing temperatures.

3.5. The electrical characteristics of UV-PD

The electrical characteristics of the PDs were studied for the voltage range of -4 V to 4 V . Current density (J , mA/cm^2) versus voltage curves obtained at RT for illumination of $1\text{ mW}/\text{cm}^2$ at 365 nm and in the dark are given in Fig. 6. The RT photoresponse of the PDs at -4 V were gradually increased from $195\text{ mA}/\text{W}$ to $324\text{ mA}/\text{W}$ with increasing fraction of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ in the Polymer:QD mixture up to $50\text{ wt}\%$. Then the photoresponse was decreased to $174\text{ mA}/\text{W}$ and $157\text{ mA}/\text{W}$ for higher amounts of doping i.e. $66\text{ wt}\%$ and $75\text{ wt}\%$, respectively. The maximum photoresponse of $380\text{ mA}/\text{W}$ is obtained from the PD, when the active layer of which was annealed at 75°C and has the maximum absorption value at 365 nm (Figs. 6 and 7 and Table 1). The course of the absorption values at 365 nm and photoresponsivity values obtained at different annealing temperatures were the same. The temperature of 75°C corresponds to the T_g of the polymer and enhancing the photoresponse as a result of annealing at T_g is known in literature [33,34]. The ratio of the photocurrent to the dark current for all doping fractions and annealing temperatures is around 10^4 .

The mechanism of ultraviolet sensing not only in polymer:QD hybrid UV-PDs but also in bare organic UV-PDs is not clear yet. Recently, Guo et al. have shown that the electrons transferred from the polymer to the QD are trapped in the QD and under illumination those electrons shift to the LUMO energy level of the polymer and align the Fermi energy level of the active layer with that of the cathode [8]. This explanation is supported by (i) the lifetime measurements performed in this study; both in solution and film phase the τ_{AV} value of ADS231BE was not effected from the increase in $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ concentration (Table 2) and (ii) the open circuit voltage (V_{oc}) deviation with the nanoparticle doping amount; the devices that contain $25\text{ wt}\%$ and $33\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ have V_{oc} values of 0.95 V and 0.75 V , respectively. This value reaches a minimum of 0.55 V for $50\text{ wt}\%$ doping and a significant back increment to 1.0 V is detected for $75\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ doping. Actually, it may also provide a sufficient explanation on the photoresponsivity increase up to a certain $\text{wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ doping and drastic loss of

Table 2

Time resolved fluorescence intensity decay properties of the films at 420 nm with different $[\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}]$ wt% content [$\lambda_{\text{ext.}} = 368\text{ nm}$; τ_{AV} is the average fluorescence lifetime (ns)].

Film $[\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}]$ content	0 wt%	25 wt%	33 wt%	50 wt%	66 wt%	75 wt%
τ_{AV}	1.8	1.6	1.5	1.5	1.6	1.7
χ^2	1.1	0.9	1.0	1.0	0.9	1.0

photoresponse obtained from the devices that contain $66\text{ wt}\%$ and $75\text{ wt}\%$ of QD. As the concentration of ADS231BE is constant in all devices for the $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ doping ratios higher than $50\text{ wt}\%$ the strong electron quantum confinement effect in the QD may become dominant. Although the mechanism suggested by Gua et al. succeeds in explanation of the electrical characteristics and responsivity values, it still cannot describe why and how an electron at the excited state of QD would shift to the LUMO of polymer that has a higher potential of energy state. We think that as the donor–acceptor relationship between the polymer and QD has the strong evidence of non-fluorescent complex formation under illumination, the electron at the Fermi level of this complex is collected from the cathode.

Further electrical characteristics of the PDs are investigated by impedance spectroscopy. The impedance curves of the PDs that contained different amounts of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ and that contained $50\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ and annealed at different temperatures are given in Fig. 8. The measurements are done under $1\text{ mW}/\text{cm}^2$ and

Fig. 8. Impedance characteristics of ITO/PEDOT:PSS/ADS231BE: $x\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ devices under $1\text{ mW}/\text{cm}^2$ at 365 nm irradiation (a) $x = 25, 33, 50, 66$ and 75 at RT and (b) when $x = 50$ and annealed at RT, 50°C , 60°C , 75°C , 80°C and 90°C (inset figures: equivalent circuits of systems and $V_{\text{appl.}} = 0\text{ V}$).

Table 1

Responsivity values of ITO/PEDOT:PSS/ADS231BE: $x\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ ($x = 25, 33, 50, 66$ and 75) and ITO/PEDOT:PSS/ADS231BE: $50\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ at different annealing temperatures.

$x\text{ wt}\%$ $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$	25	33	50	66	75	ADS231BE: $x\text{ wt}\%$
Responsivity (mA/W)	195	251	324	174	158	$\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$
Annealing Temp.	50°C	60°C	75°C	80°C	90°C	ADS231BE: $50\text{ wt}\%$
Responsivity (mA/W)	344	368	380	287	234	$\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$

Fig. 9. AFM images of ADS231BE: x wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ films ($x=25, 33, 50, 66$ and 75) at RT where roughness values of (a) to (g) are 0.73 nm, 6.54 nm, 2.38 nm, 2.44 nm, 2.34 nm, 2.79 nm, 2.87 nm, respectively.

365 nm UV illumination. The single semicircle curves addressed a serial resistance (R_s) that is the resistance of ITO and polymer interface, with a parallel resistance (R_p)-capacitance circuit generating from the bulk of PD. The R_s values were almost the same for all doping ratios and annealing temperatures, a reduction of only 80Ω is detected when the doping ratio is increased from 25 wt%

to 50 wt% and no difference was detected between the applied annealing temperatures. However, the R_p values reached a minimum of 25 k Ω for the device that contains 50 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ and further increase in the doping ratio increased this value to 68 k Ω that corresponds a two times higher value than that of the device contained 25 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$. Slope shaded phase mode

AFM images of the films are given in Fig. 9. The root mean square (RMS) values were in the range of 2.98 and 3.6 nm for the hybrid films. Almost no deviation is observed between the RMS values of these films and no phase separation is detected. However, the formation of island like clusters with the increase in QD concentration was obvious. It is assumed that those clusters consist of $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ agglomerates and act as the trapping centers for the electrons. Annealing the 50 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}$ doped active layer at the T_g of ADS231BE caused a reduction to 17.7 k Ω in the bulk resistance of the device and allowed reaching a photoresponsivity of 380 mA/W.

Obviously, annealing the active layer until the T_g of polymer does not affect the complex formation tendency, but increase the photoresponsivity through reduction of bulk resistance. However, whenever the annealing temperatures over T_g are applied, the complex formation is disrupted. To the best of our knowledge, this study is the first example that brings a mechanistic explanation that follows the complex formation between the polymer and QD on the working steps of a UV-PD.

4. Conclusion

UV-PD device based on the physical structure of ITO/PEDOT:PSS/ADS231BE: 50 wt% $\text{Zn}_{0.71}\text{Cd}_{0.29}\text{S}/\text{Al}$ is introduced. The photoresponsivity values reported in this study are either comparable or higher than that of GaN (230 mA/W at 356 nm) [35] and SiC (130 mA/W at 270 nm) based UV-PDs [36] and has potential applications in environmental and biological monitoring. Contrary to the approaches followed in literature which explain mechanism in polymer:QD blends, i.e. accepting the polymer and QD as two separate species, this study shows that the polymer and QD may form a non-radiative complex under illumination and this complex may exhibit electron transfer and exciton dissociation tendency different from the parent compounds.

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