Energy transfer in ZnO-anthracene hybrid structure

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Abstract: Anthracene dispersed in Polyphenylsiloxane (PPS) glass was synthesized on epitaxially grown zinc oxide (ZnO) to realize organic/inorganic hybrid semiconductors for efficient energy transfer. The photoluminescence (PL) from ZnO was modified by the presence of anthracene molecules due to resonant energy transfer. The UV-visible emission from anthracene molecule was also influenced due to resonant coupling with the excitonic and defect bound excitonic states in ZnO. Temperature dependence of PL of the hybrid system showed quenching of the defect bound emission of the ZnO to be due to energy transfer from anthracene. The PL lifetime in ZnO-anthracene/PPS hybrid structure at 4 K is relatively shorter and becomes comparable to the PL lifetimes in ZnO at 77 K. However, at room temperatures the PL lifetime of the hybrid structure is significantly longer than in ZnO and is comparable to the recombination lifetime in anthracene.

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Inorganic/organic hybrid materials have the potential of paving the way for developing new

photonic systems [1]. The dipole-dipole coupling in inorganic/organic structures enables

exciton energy transfer from a donor to an acceptor. In recent years, these hybrids have

attracted extensive attention due to their potential applications for optical and electronic

devices [2–6]. The energy transfer is more efficient when the donor molecules in the hybrid

system is in the vicinity of the acceptor species and have overlapping exciton emission energy

with the absorption energy of the acceptor [7].

III-nitride based semiconductors are much likely to be playing a major role in blue- UV

solid-state lighting due to wide bandgap energy and large exciton binding energy at room

temperature [8–10]. The lack of suitable lattice matched or high quality substrate makes it

relatively expensive compared to GaAs or InP based III-V semiconductor devices. Zinc oxide

(ZnO) offers an economically viable alternative wide bandgap semiconductor for solid-state

lighting with an energy gap of 3.37 eV (at room temperature). It is classified as one of the

wide band-gap semiconductor with a large exciton binding energy (60 meV) compared to

GaN or the other II–VI group semiconductors. This large exciton binding energy results in

stable excitonic emission at room temperature. This property of ZnO provides the impetus for

developing novel optical/electronic devices, inclusive of light emitting diodes (LED), solar

cells, and photodetectors [11]. In addition, ZnO has defect energy levels corresponding to the

visible wavelength, which can influence the bandedge optical properties. A reduction of the

nonradiative recombination process from the bandedge to the defect level state can be

engineered by saturating the population of the defect level states.

The nitrides also have the potentiality of broadband white light emitters. The incorporation

of Al and In within GaN which can extends the bandgap emission from the UV to the near-

infrared regime [12]. However, UV emitting ZnO-based system does not have a viable

inorganic ternary system for covering the whole visible spectrum. An efficient light emitting

solid state organic molecule is an alternate option.

Anthracene (C_{14}H_{10}) is a polycyclic aromatic compound exhibiting absorption and

luminescence in the blue region of the visible spectrum. Polyphenylsiloxyene (PPS) glass has a

low softening temperature which serves as a host material capable of dispersing anthracene

molecules homogeneously without thermal degradation [13,14]. The energy levels of the

anthracene molecules dispersed in this host material are in close proximity of the bandedge

and the defect levels of ZnO, which can facilitate efficient resonant energy transfer. This

particular feature motivated the present study of the optical properties of hybrid structures

composed of the PPS glass homogenously dispersed with anthracene molecules and its cast on

ZnO thin films to realize a stable and robust hybrid semiconductor complex for integrated

phononics. It was observed that the UV emission from ZnO is enhanced by an order of

magnitude at 15 K and the visible emission is quenched at 15 K by the anthracene molecules

being in physical proximity to the ZnO surface. The UV-VIS emission from anthracene is also
modified by ZnO. In this work, the origin of the modification of the emission properties of the hybrid structure has also been investigated using temperature dependent and time-dependent PL spectroscopy.

2. Sample preparation and experimental procedure

ZnO thin films were grown by molecular beam epitaxy (MBE) on α-sapphire substrates. ZnO growth was carried out at 550 °C following the deposition at 200 °C and annealing up to 650 °C of a low temperature ZnO buffer layer under oxygen rich conditions. ZnO-anthracene/PPS hybrids were prepared by casting of anthracene/PPS solution in a 9/1 acetone/cyclohexane mixed solvent on the ZnO films. PPS was prepared separately using a technique reported in [13,14]. The required masses of PPS and anthracene were dissolved in this mixed solvent for spin-coating. The structure of the hybrid material is depicted in Fig. 1(a). The thickness of the ZnO thin film was about 200 nm, and the anthracene/PPS film cast/dried on the ZnO film had a thickness ~2 µm.

The temperature-resolved PL measurements were carried out with a continuous wave He–Cd laser ~325 nm (~3.81 eV) in a closed cycle helium cryostat at various temperatures ranging from 15 K to 300 K. The time-resolved PL measurements were performed with a 80 MHz Ti-sapphire pulse laser system (pulse width of 80 fs) at the excitation wavelength of 350 nm (~3.54 eV).

Figure 1(b) shows the transmission spectra of the anthracene/PPS composite glass (without ZnO) and the PL emission spectra of this composite and the bare ZnO thin film at room temperature. PL spectrum of the bare ZnO thin films shows the oxygen vacancy related deep level emission band, which indicates fairly good optical quality of ZnO thin films. The ZnO film prepared in this study had a rough surface (revealed by a preliminary scanning electron microscopy not shown here) to exhibit a deep level emission related to oxygen vacancy. However, this feature in turn offers a method of tuning the emission from rough ZnO surfaces with anthracene molecules, as discussed later in more detail. The symmetric (mirror-image) features of the transmission and PL spectra of anthracene are observed as distinct peaks having similar vibrational energy levels of $S_0$ and $S_1$. These peaks are assigned to the absorption from the lowest vibrational level of $S_0$ to higher vibrational levels of $S_1$ and the emission from the lowest vibrational level of $S_1$ to lower vibrational levels of $S_0$ [7]. We also note that the high energy states of anthracene and bandedge excitonic states of ZnO have large overlap at 3.2 - 3.4 eV. The oxygen vacancy related defect level emission in ZnO around 2.3 eV is also resonant with the absorption levels in the anthracene molecules to some extent. The higher energy states of the anthracene molecules in close vicinity of the ZnO film (within ~10 nm separation) can act as a donor for the excitonic or bandedge state of ZnO. Close coincidence of those resonant energy levels can result in nonradiative transfer of an electronic excitation from anthracene to ZnO [4].
3. Results and discussion

Figure 2 shows the PL spectra of ZnO and the anthracene/PPS hybrid on sapphire and the ZnO-anthracene/PPS hybrid on the same substrate, measured at 15 K. For interpretation of the spectra changes on the hybridization, it is very useful to refer to the energy levels depicted in Fig. 3 [3,8,15]. There are states in anthracene molecules that are energetically higher than the bandedge excitonic states in ZnO. These states can act as donor states for the ZnO bandedge states which then accept the photoexcited carriers due to close proximity of the ZnO and anthracene molecules. Optically induced carrier transfer occurs efficiently at 3.20 eV, when the 0-0 transition energy of $S_1 \rightarrow S_0$ in the anthracene molecules is resonant with the conduction bandgap energy of ZnO. These electrons then rapidly decay to the ground state by radiative recombination as luminescence. There is also the possible energy transfer from the vibrational $S_1$ state of the anthracene molecules to the defect level states in ZnO. The resonance in the energy level is evident from the overlap of the broad absorption in anthracene with the defect level emission peak of ZnO at 2.21 eV in Fig. 1(b). The resonant energy transfer from the $S_1$ states in anthracene to defect states in ZnO can result in saturation of the trapping sites for the electrons. The saturation of available defect level states $S_n$ is likely to prevent the nonradiative recombination of electrons from the conduction band or excitonic state in ZnO. This results in decrease in green emission from the ZnO-anthracene/PPS hybrid as shown in Fig. 2.

As shown in Fig. 2, the intensity of the green (2.21 eV) emission band of ZnO, assigned to its defect level emission (cf. Fig. 3), is reduced by an order of magnitude on hybridization with the anthracene/PPS. This reduction can be attributed to the coupling between the resonance of the energy states of anthracene ($S_1 \rightarrow S_0$ transition) and ZnO. Similarly, the blue (2.98 eV) emission bands of ZnO is quenched significantly on hybridization, possibly due to the resonant energy transfer between anthracene and ZnO. The proximity of the broad absorption state in anthracene molecules resonant to the defect level state related oxygen vacancy in ZnO molecules result in the modification of PL for the donor (anthracene) and acceptor (ZnO), respectively. Although higher quality epitaxial ZnO thin films with relatively low defect levels can be grown by maintaining the growth temperature at 600 °C, this enhancement of the ZnO emission due to the suppression of defect level emission by anthracene might be highly effective in chemically synthesized ZnO nanoparticles [16] and ZnO nanowires [17] where the surface defects dominates the green emission process.
Fig. 2. Comparison of PL spectra of ZnO, anthracene/PPS, and the ZnO-anthracene/PPS hybrid at 15 K. The emission of ZnO at 2.21 eV is reduced significantly whereas the emission of ZnO at 3.37 eV is enhanced due to resonant energy transfer.

Figure 3. Schematics of energy levels for ZnO and anthracene in eV range.

Figure 4 shows temperature-dependent PL spectra of the ZnO, the anthracene/PPS composites, and the ZnO-anthracene/PPS hybrid material at 15 - 300 K. The near bandedge emission of the ZnO layer shown in Fig. 4(a) is dominated by acceptor-bound exciton ($A^\circ X$) emission in the entire range of temperatures, $T$. The shoulder on the donor bound exciton D$^\circ X$ (3.365 eV) peak and the FX (3.377 eV) emission peak are also observed [18]. The integral PL intensity $I(T)$ usually decreases with $T$ due mainly to thermal quenching and can be described [19] by,

$$I(T) = \frac{I_0}{1 + A \exp \left( \frac{-E_a}{k_B T} \right)}$$

where $E_a$ is the activation energy of the thermal quenching process, $k_B$ is the Boltzmann constant, $I_0$ is the intensity at 0 K, and $A$ is a constant. The natural logarithm of the integrated intensity of FX versus $1/T$ plot from the data in Fig. 4(a) estimates $E_a$ to be 36.7 meV. The peak position of A$^\circ X$, 3.359 eV at 15 K, exhibits a redshift to 3.278 eV at 215 K due to...
narrowing of the bandgap with increasing $T$. The linewidth of the dominant $A^0X$ emission at 15 K and 215 K is 6.8 meV and 72 meV, respectively [19,20]. This broadening of peaks with increasing $T$ is primarily attributable to the exciton–phonon scattering.

Figure 4(b) shows the PL emission of anthracene/PPS which indicates that there are three emission peaks at 3.221, 3.054 and 2.883 eV corresponding to 0-0, 0-1 and 0-2 of $S_1 \rightarrow S_0$ transition (the emission peak at 2.883 eV is not shown in Fig. 4(b)). When temperature increases, the intensities of these emissions is reduced due to the thermal broadening and the peak position is not so much changed. An increase in temperature results in a decrease in exciton-phonon coupling which results in relaxation of carriers from the excited state due to phonon scattering. A high energy emission at -3.35-3.45 eV observed at 15 K has not been studied in previous studies and its assignment is not clear at this moment. However, one possibility is the charge-transfer exciton in solid state anthracene crystals [21]. Figure 4(c) shows the band edge PL emission spectra of ZnO-anthracene/PPS hybrid structure. The PL spectrum exhibits sharp peaks of $A^0X$ (3.359 eV), $D^0X$ (3.365 eV) and $FX$ (3.377 eV) at 15 K. As temperature increases further the $A^0X$ and $D^0X$ diminishes, however, $FX$ persists and dominates in the entire temperature range. This indicates that the free exciton recombination dominates in the ZnO-anthracene/PPS hybrid structure and is accountable for the UV emission. The redshift of emission peak of $FX$ is due to electron phonon coupling, lattice distortion, localization of charge carriers due to interface defects and point defects. The $E_a$ for $FX = 55.0$ meV was estimated from the linear portion of the plot according to Eq. (1). The $E_a$ for $FX$ is higher than $A^0X$ or $D^0X$ in the ZnO-anthracene/PPS hybrid system unlike in case of bare ZnO semiconductors.
To observe the changes in the free exciton recombination process of the ZnO-anthracene/PPS hybrid structure, time-resolved PL (TRPL) measurements, at various temperatures using a laser power of ~500 mW at 355 nm and corrected emission from 365 to 380 nm, were conducted for ZnO, anthracene/PPS, and ZnO-anthracene/PPS hybrid structure. In general, PL decay rate is a sum of the radiative (R) and nonradiative (NR) decay rates: \( \tau^{-1}_{\text{PL}} = \tau^{-1}_{\text{NR}} + \tau^{-1}_{\text{R}} \), where \( \tau_{\text{PL}} \), \( \tau_{\text{NR}} \), \( \tau_{\text{R}} \) are PL, NR and R decay time constants, respectively. Figure 5 shows TRPL measurement results at 4, 77 and 300 K. The PL decay time is relatively longer in anthracene (> 2.0 ns), whereas the carrier recombination in ZnO is relatively shorter (~in the ps domain) due to the strong exciton binding energy and due to the effect of LO phonon mediated interband transitions at higher temperatures. At low temperatures, the PL process in the hybrid system appears to be dictated by the recombination channels in ZnO. The PL decay time in the ZnO-anthracene/PPS hybrid at low temperatures is similar to that of the excitonic or carrier recombination lifetime in ZnO. At 4 K, the PL lifetime in the hybrid system is shorter (0.021 ns) than in ZnO (Fig. 5(a)) and it becomes comparable (~0.025 ns) at 77 K (Fig. 5(b)). As the temperature is increased to 300 K, the PL...
decay time in the hybrid structure is over two orders of magnitude longer (~2.39 ns) compared to that at 4 K (~0.02 ns). The emission process at 300 K is dominated by the energy transfer from the ZnO to the anthracene molecules as evidenced by a comparable PL lifetime in the hybrid system and the anthracene molecules (2.33 ns). The PL lifetime of ZnO also exhibits a shorter lifetime (0.274 ns) which can be attributed to the nonradiative recombination process in ZnO at room temperature. The nonradiative recombination process is evidently enhanced due to the presence of the defect level states at 2.21 eV. In the ZnO-anthracene/PPS hybrid structure, these defect levels in ZnO are saturated due to the resonant energy transfer from adjacent donor states in the anthracene molecules (Fig. 1(b)). It results in a single component long PL lifetime from the hybrid structure with negligible nonradiative recombination process. It consequently leads to the enhancement of the PL at 3.37 eV, which is significantly more than it is observed in Fig. 2. The increase in PL intensity does not account for the reduction in the incident pump photons and the emitted PL due to the absorption by the 2 µm-thick anthracene/PPS film overlayered on the ZnO film.

![Graphs](image)

Fig. 5. Time-resolved PL measurement for ZnO, anthracene/PPS, and ZnO-anthracene/PPS hybrid structure at various temperature (a) 4 K, (b) 77 K, and (c) 300 K.

4. Conclusion

Optical properties of ZnO-anthracene/PPS hybrid structures were studied by temperature and time-resolved PL measurements. The band edge PL exhibited enhanced UV emission due to resonant energy transfer from anthracene fluorophore to ZnO fluorophore at low temperature. The suppression of the defect level emission without the passivation of the actual ZnO defect states at low temperature is due to the saturation of the defect level population in the presence of resonant coupling of donor and acceptor energy levels in ZnO and anthracene. TRPL measurement results at various temperatures suggested efficient energy transfer from ZnO to anthracene at 300 K. At room temperature the carrier recombination is dominated by the nonradiative recombination process as evident by the low emission intensity. As the bandedge emission in ZnO red-shifts and is thermally broadened with temperature in addition to being reabsorbed by the anthracene composite, the room temperature PL enhancement cannot be ascertained. The integrated PL intensity over the UV-blue regime is significantly enhanced in the ZnO-anthracene/PPS hybrid structures. This approach of light harvesting using organic/inorganic hybrid systems may pave the way for the development of new photonic systems.

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