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Optical and Schottky diode performance of Au/4-hydroxy Coumarin/ITO heterojunction

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ABSTRACT

The current–voltage (I–V), micro-Raman and various optical properties of 4-hydroxy coumarin Schottky diode were studied. From its optical study, the optical band gap (E_g), transport band gap, binding energy and Urbach energy were found to be around 3.5 eV, 3.72 eV, 0.28 eV and 327 meV respectively. The given compound was following an indirect allowed transition. Photoluminescence of the current compound shows a various emission bands in UV region. From micro-Raman study, different modes related with the current structure were obtained and discussed. Some basic techniques related with device were carried out to find out different diode parameters. The observed properties shown by this molecule indicates its possible application for modern organic devices.

1. Introduction

Optoelectronic devices impact many areas of society, from simple household appliances and multimedia systems to communications, computing, spatial scanning, optical monitoring, 3D measurements and medical instruments. The driving force behind using organic materials in electronic devices is because of their easily tunable electronic and processing properties [1]. Recently various organic devices like Schottky diodes, organic light emitting diodes, organic field effect transistors, photovoltaic (PV) and solar cells, using organic semiconductors and their derivatives were fabricated and characterized [2]. Schottky diodes made by introducing a thin of organic layer on Si based structures have been shown to exhibit different potential features of these diodes [3]. Also, thicker organic interlayers of the conjugated organic molecules have also been successfully used to various desired diode properties [4].

Coumarins and its various derivatives are well known for various biological and medicinal activities [5]. Different conjugated coumarins and anthracene derivatives, having rigid structure, wide energy gaps and high fluorescent quantum yield, and are extensively used as fluorescence sensors for metal ions and biological compounds [6,7]. Various coumarin-based electro-luminescent materials have been demonstrated till today [8,9].

The structural, morphological, optical and electrical transport investigations taken on various coumarins were carried out by our group [10–16]. However, there is no device fabrication and characterizations of a any coumarin derivatives existing in the current literature. Therefore, in the present paper, we briefly described the first report on fabrication and characterizations (optical, Raman and electrical) of metal/4-hydroxy Coumarin/ITO heterojunction.

2. Experimental

The organic material/molecule (OM), 4-hydroxy coumarin were prepared by the method describe in elsewhere [17]. Inset of Fig. 4 shows the molecular structure of understudy material. After various basic characterizations of synthesized product, this material was used for fabrication of surface type diode. For diode preparations, the 4-hydroxy coumarin (OM) thin film (400 nm thickness) was deposited onto ITO (indium Titanium Oxide) coated glass (quartz) substrates by spin-coating (2000 rpm, 30 s, process repeated many time till desired film thickness was obtained) of this material solved in ethanol solution. Afterwards the OM/ITO hybrid heterostructures were transferred to a vacuum chamber and a semitransparent Au front contact (2×2 mm^2 by shadow masking) was deposited by thermal evaporation. During thermal deposition the chamber pressure was5.5×10^{-5} mbar. The thickness of the electrodes was 100 nm. The Cross-sectional view of Au/4-hydroxy coumarin/ITO surface-type Schottky diode is shown in inset of Fig. 5. Ultraviolet–visible (UV–Vis) spectroscopy of OM/ITO hybrid heterostructures was recorded on a Shimadzu UV-1601 spectrometer. Photoluminescence (PL) was done Shimadzu spectroflourometer RF-5301. Raman measurements were carried out by using Renishaw InVia Raman microscope. The Argon (Ar) laser

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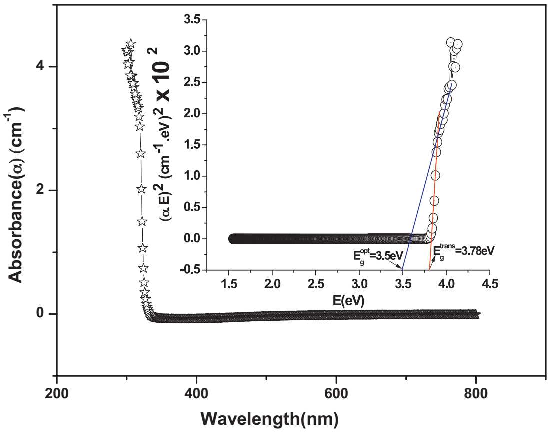

Fig. 1. Shows absorption spectra of the compound. Inset shows its Tauc plot for optical band gap determination.

(514 nm) was used for excitation and the laser power was kept 1 milli watt (mW), with 20× objective. The current–voltage (I–V) characteristic were taken with the help of Keithley 2400 source measurement unit at room temperature under darkness and vacuum. For photocurrent measurements, a short wavelength UV lamp (335 nm) fitted in UV cabinet (used for TLC illumination in open air) with a power density of 0.15 mW/cm^2 was used as an excitation source.

3. Results and discussion

3.1. UV–visible study

The Fig. 1 shows the UV–Vis spectrum of this organic film. The compound shows an absorption edge at around 330 nm. This band corresponds to π–π^* absorption transition. The peak is due to π–π^* (where π represents bonding orbitals and π^* represents anti-bonding orbitals) transition of the electrons of C═C bond in these type of systems [10–15]. The absorption band in the UV region is known as the Soret-band (B-band). Mostly, in case of aromatic cyclic conjugated π electron systems, the spectral features are because the aromatic compounds [18]. In these organic compounds, the vibrant electronic transitions seen in the ultraviolet and near visible regions are $\sigma \rightarrow \sigma^*$; $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ type [10–15]. Therefore, the present absorption edge (B-band) near UV region of the spectrum, may arise from a$_{2u}$ (π) highest occupied molecular orbital (HOMO) to E_g (π^*) lowest unoccupied molecular orbital (LUMO) transition [18].

The accurate information regarding optical band gap of materials is essential for various practical applications. The optical energy gap of this organic film was obtained by using the following expression [10–16].

$$\alpha h\nu = B(h\nu - E_g)^m \tag{1}$$

where "α" is absorption coefficient, "$h\nu$" is the energy (h is a Planks constant having value 6.625 × 10^{-34} J/s and ν is the frequency of incident photon in Hz) of the incident photon, E_g is the value of the optical energy gap between the valence band and the conduction band and "m" is the power which describes the electron transition process. Generally, the value of "m" is related to the distribution of the density states. It has discrete values 1/2, 3/2, 2 and 3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions respectively. The factor B depends on the transition probability and is supposed to be a constant within the optical frequency range (an energy-independent constant).

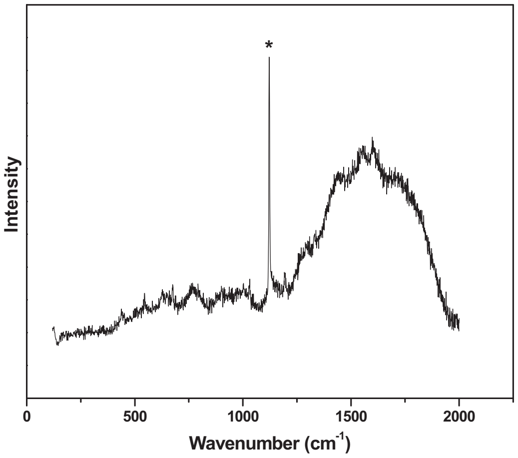

Fig. 2. Raman spectra of 4-hydroxy coumarin, where asterisk specifies the instrumental background.

In order to determine the more accurate value of energy gap, graphs of $(\alpha h\nu)^{1/m}$ against ($h\nu$) are plotted with m = 1/2, 3/2, 2 and 3 (Figure not shown here). From these plots, the best linear fit between $(\alpha h\upsilon)^{\mathrm{m}}$ as a function of $h\upsilon$ was obtained for n = 2 [see inset of Fig. 1]. According to Fig. 3, the present film has the value of two energy gaps. The low energy value is named the onset optical band gap (E_g^{opt}) and attributed to the generation of Frenkel exciton, or a bound electron–hole pair [6,7,10]. High energy value is the transport gap (E_g^{tran}) and corresponds to the energy difference between HOMO and LUMO [6,7,10,15]. The difference between E_g^{tran} and E_g^{opt} values are the binding energy (E_B). The E_g^{opt}, E_g^{tran} and E_B values of the current film were determined as 3.78, 3.50 and 0.28 eV, respectively.

The localized states near band edge can cause band tails [15]. The absorption edge is named as the Urbach tail [15]. The Urbach energy (E_u) is probably related to the effects of all possible defects. The Urbach energy is given in the following relation [15]

$$\alpha = \alpha_o \left(\frac{hv - E_0}{E_u} \right) \tag{2}$$

and the following relation is obtained by taking the logarithm of Eq. (2).

$$\ln \alpha = \frac{E}{E_u} \left[\ln(\alpha_0) + \frac{E_0}{E_u} \right] \tag{3}$$

In above expressions, E_0 and α_0 are constants and they are the Urbach bundle convergence point coordinates. The E_u of film are calculated from the slope of ln α versus $h\nu$ graphs (Figure not shown here) by using $E_u{}^{-1} = \Delta(\ln \alpha)/\Delta(h\nu)$. The determined E_u value of current sample is 327 meV.

3.2. Photoluminescence study

The Fig. 2 shows photoluminescence (PL) spectrum of this organic film (after excitation with 260 nm) in range of 290–400 nm. One can see various intensity peaks, the dominant one is at 330 nm possibly due to C═C bond and π–π^* transition of this molecule. Generally, the photo-exciting in coumarins, give rise to intramolecular charge transfer (ICT) from ring-I (donor) to ring-II (acceptor). The ICT can be associated by raising the HOMO energy level of the donor in ring-I or lowering the acceptor LUMO energy level in ring-II [6,7,10,12,13]. Mostly, these modifications in electronic band structure can be observed by fixing different chemical entities into both rings. As there is a change in HOMO or LUMO states, leading red shift to UV–Vis absorption and emission bands in these compounds. This occurs because less external energy is