Materials Research Express

PAPER

Optical, electrochemical and electrical properties of p-N,N-dimethyl-amino-benzylidene-malononitrile thin films

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Keywords: DABMN, optical properties, I-V characteristics, Mott-Schottky

Abstract

A donor-acceptor small organic molecule, p-N,N-dimethyl-amino-benzylidene-malononitrile (DABMN), has been synthesized and successfully prepared in thin films using spin coating technique. The thin film of DABMN exhibited semiconductor behavior with an optical band gap of about 2.27 eV. The photoluminescence spectrum was exhibited a strong red emission. The energy levels of lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) were determined by experimental calculation from cyclic voltammetry. The electrical performance of the ITO/DABMN/Al structure device was evaluated through current-voltage characteristics and showed a typical Schottky diode behavior with good charge mobility. The charge density associated with the DABMN film was calculated from the capacitance-voltage measurements.

1. Introduction

In recent years, the development of the solution-processable small \( \pi \)-conjugated molecules as semiconductor materials for optoelectronic and photonic applications has increased significantly due to their tunable optical, electrochemical and electrical properties [1–4]. This type of organic semiconductors offers many advantages such as simple synthesis, easy purification, high solubility and low cost [5–7]. Donor-Acceptor systems receive great attention in optoelectronic applications because of their binary charge transfer property and their charge trapping/detrapping process [8–10]. Molecular engineering have led to rapid progress in the field of the synthesis of donor-acceptor small organic molecules. The superelectrophile molecules are important materials for applications in synthetic organic chemical [11]. Recently, we have studied the opto-electrical proprieties of p-cyano-benzylidenemalononitrile as thin films and their results showed great importance for memory application [12]. Cyano groups were extensively used as electron-withdrawing group for dyesensitized solar cells [13, 14]. Further, the presence of cyano group in \( \pi \)-conjugated molecule reduces the both energy levels of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) and leads to the better stability and strong electron transport ability [15–17]. The modification of chemical structure from side functional groups selection is a very importance parameter in the improvement of optical and electrical characteristics [18, 19]. Therefore, in this work, we connected dimethylamino group as electron donor with electron withdrawing benzylidenemalononitrile ring in order to obtain donor-acceptor conjugated system. The optical, electrochemical properties of p-N,N-dimethyl-amino-benzylidene-malononitrile (DABMN) in thin films have been investigated. Then, DABMN was successfully applied in ITO/DABMN/Al structures and the electrical characteristics were evaluated.

2. Experimental section

2.1. Synthesis of p-N,N-dimethyl-amino-benzylidene-malononitrile

To a mixture of 4-dimethylaminobenzaldehyde (1.57 g) and malononitrile (0.63 g) in toluene (50 ml) were added piperidine (0.05 ml) and glacial acetic acid (0.1 ml). The mixed solution was heated under reflux for 12 h.
The solvent was removed under reduced pressure and the residue was separated using Et₂O. The Et₂O was washed with HCl (50 ml, 5%), then washed several times with water and followed by drying over anhydrous MgSO₄. The residue was further purified by recrystallization from a pentane/ethyl acetate mixture.

2.2. Structure elaboration
The Indium Tin Oxide (ITO) coated glass substrates with a resistance of 20Ω/square were purchased from Ossila. In order to elaborate the ITO/DABMN/Al device structure, we have pre-cleaned the substrates in an ultrasonic bath in acetone, isopropanol and de-ionized water successively and then dried by a nitrogen gas flow. DABMN was dissolved in chloroform at a concentration of 20 mg/ml. Then, the solution was deposited using spin coating at 2000 rpm for 25 s onto the ITO substrate, giving a thickness DABMN film of about 180–200 nm. Finally, an aluminum cathode was deposited by thermal evaporation under a vacuum (Pressure = 10⁻⁶ Torr). The schematic of ITO/DABMN/Al structure with the chemical structure of DABMN and band structure diagram of the ITO/DABMN/Al are shown in figure 1.

3. Results and discussions

3.1. Optical properties
UV–vis absorption spectrum of DABMN as thin film is presented in figure 2(a). DABMN film shows broad absorption in the wavelength range of 360–530 nm. The dominant peak at 448 nm was associated to π-π* electronic transition of the benzene ring, while the two shoulder peaks at 360 nm and 490 nm were assigned to intramolecular charge transfer (ICT) between dimethylamino group and malononitrile group. Optical band gap ($E_{\text{g}}^{\text{opt}}$) of DABMN was calculated by using the Planck-Einstein equation:

$$E_{\text{g}}^{\text{opt}} (\text{eV}) = \frac{hc}{\lambda_{\text{onset}(\text{nm})}} = \frac{1240}{\lambda_{\text{onset}(\text{nm})}},$$

where $h$ is the Planck constant, $c$ the speed of light and $\lambda_{\text{onset}}$ is the wavelength of the absorption onset. The calculated value for optical band gap is obtained as 2.27 eV.

The photoluminescence (PL) spectrum of DABMN film was measured under excitation wavelength of 375 nm (figure 2(b)). DABMN shows strong emission with a PL maximum peak at 615 nm. This peak is due to the radiative transition of photogenerated exciton from the excited state to the ground state. Furthermore, in comparison with BMN molecule, DABMN exhibited longer wavelength emission [11]. The Stokes shift is the difference between the wavelength of the absorption maxima and emission maxima. The long Stokes shift was observed in DABMN (167 nm) indicate the great importance for use the DABMN as active material in the OLED application [20, 21].

3.2. Electrochemical properties
Knowledge of energy levels in π-conjugated organic materials is essential for their application in optoelectronic devices. Therefore, the energy levels of the lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) of DABMN were extracted by using the cyclic voltammetry technique. The cyclic voltammetry were performed using three electrodes: working electrode (DABMN film spin-coated onto ITO,
substrate), reference electrode (Ag/AgCl) and counter electrode (Pt wire) in 0.1 M tetrabutylammonium tetrafluoroborate in acetonitrile at a scan speed of 50 mV s$^{-1}$. The estimations were done with the empirical relation [22]: $E_{\text{LUMO}} = [(E_{\text{red}} - E_{\text{ferro}}) + 4.8]$ eV and $E_{\text{HOMO}} = [(E_{\text{ox}} - E_{\text{ferro}}) + 4.8]$ eV. Ferrocene was used as external standard ($E_{\text{ferro}} = 0.98$ V). From the voltammogram results (figure 3), the onset reduction ($E_{\text{red}}$) and oxidation ($E_{\text{ox}}$) potentials of DABMN are -0.30 and 1.49 V, respectively. The energy levels of LUMO and HOMO are obtained as 3.52 eV and 5.31 eV, respectively and electrochemical band gap ($E_g = E_{\text{HOMO}} - E_{\text{LUMO}}$) is 1.79 eV. The difference between the values of optical band gap and electrochemical band gap (0.48 eV) of the DABMN molecule can be explained by the creation of free ions in the cyclic voltammetry experiment which reduced in the band gap [23].

3.3. Electrical properties
The current-voltage (I-V) characteristics of the ITO/DABMN/Al structure device are shown in figure 4. It is found that the forward current increases exponentially with the applied voltage, whereas the reverse current varies slowly with voltage. This result indicates a rectifying behavior, which is shown generally in the Schottky diode. Therefore, the dark I-V characteristics of an Schottky diode can be described using the following equation [24]:

$$I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]$$ (1)

Where $I_0$ is the saturation current, $q$ is the electronic charge, $V$ is the applied voltage, $k$ is the Boltzmann constant, $T$ is the temperature and $n$ is the ideality factor. The saturation current can be obtained from the intercept of the curve of ln(I)-V at $V = 0$ and is given by the following relation:

![Figure 2. Absorption (a) and photoluminescence (b) spectra of DABMN in thin film.](image)

![Figure 3. Cyclic voltammogram of DABMN at a scan speed of 50 mV s$^{-1}$.](image)
Where $A$ is the contact area, $A^*$ is the Richardson constant and $\phi_b$ is the barrier height. The value of $I_0$ is $6.63 \times 10^{-6}$ $A$ and by using equation (4), the value of $\phi_b$ is equal as 0.72 eV. The ideality factor checks the validity of the thermionic emission mechanism. The value of $n$ can be obtained from equation (3) and can be written as:

$$n = \frac{q}{kT} \frac{dV}{d \ln I}$$

For ideal diode, the value of the ideality factor ($n$) should be equal to the unity where the pure thermionic emission mechanism is the dominant conduction mechanism. However, for our device structure, the value of $n$ (4.1) is higher than the unity. Consequently, there can be other charge transport mechanism different from the pure thermionic emission mechanism. The high values of ideality factor were resulted to the interfacial states [25, 26].

To determine the dominant charge transport mechanism in the ITO/DABMN/Al structure device, $I$-$V$ characteristics were analyzed in log-log scale (figure 5). The dependence of the current on the applied voltage is described by typical power law ($I \propto V^m$), where $m$ is the slope value for each region of the applied voltage and provides information of the dominant conduction mechanism [27, 28]. The device structure, at low voltage, exhibits a slope close to unity ($m = 1.02$) indicating that the conduction is governed by the Ohmic. This conduction behavior is explained with the superiority of the density of thermally generated charge carriers in the DABMN film to the injected charge carriers from electrodes. In the second region ($m = 1.97$), with an increase in voltage, the injected carriers become larger than the thermally generated carriers. Consequently, the conduction mechanism switches from ohmic conduction to space charge limited current (SCLC) conduction. The additional increase of voltage leads to the linear rapid increase of the current, resulting in a slope equal to 4.34. Hence the charge transport is governed by the trap controlled space charge limited conduction (TCLC) [29]. The charge carrier mobility is a crucial factor for clarifying carrier transporting ability. According to the Mott-Gurney SCLC model, the charge carrier mobility in DABMN can be fitted, as bellow:

$$J_{SCLC} = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu_{eff} \frac{V^2}{d^3}$$

Where, $\varepsilon_0$ is the permittivity of vacuum, $\varepsilon_r$ is the relative dielectric constant, $d$ is the film thickness, $V$ is the applied voltage and $\mu_{eff}$ is the effective charge mobility. The effective charge mobility of the DABMN was calculated as $3.13 \times 10^{-5}$ $cm^2 V^{-1} s^{-1}$, which was comparable to literature [30].

To provide further insight into the charge transport behaviour, $C$-$V$ characteristics were measured at 100 Hz and the result is shown in figure 6(a). The voltage applied during the measurement ranged from $-3$ V to $+3$ V. $C$-$V$ characteristics confirmed the Schottky diode behavior for the ITO/DABMN/Al structure. In fact, the capacitance increases initially with bias, this is attributed to the increase of the injection of charge carriers from electrodes. Then, after the built-in voltage $V_B$ (the voltage which usually defines the difference between the work functions of anode and cathode) the capacitance slowly decreases with voltage increase. This decrease in the
capacitance is due to the charge carrier recombination at the DABMN/electrode interfaces [31]. In addition, C-V measurements provide information about built-in potential and carrier density of the structure. The C-V characteristic follows the Mott-Schottky relation given below [32, 33]:

$$C^{-2} = \frac{2(V_0 - V)}{A \varepsilon_0 \varepsilon_r q N_a}$$  \hspace{1cm} (5)

Where $V_0$ is the built-in voltage, $V$ is the applied bias voltage, $A$ is the active area and $N_a$ is the carrier density. Figure 6(b) shows the Mott-Schottky plot. The built-in voltage can be easily extracted from the linear portion of the $C^{-2}$-V plot. Furthermore, the carrier density is derived from the slope by means of the Mott-Schottky relation. The obtained values of built-in voltage and carrier density are 1.68 V and $2.9 \times 10^{16}$ cm$^{-3}$, respectively. The value of $N_a$ is comparable to the PCBM molecules [34, 35].

4. Conclusions

p,N,N-dimethyl- amino-benzylidene-malononitrile based donor-acceptor $\pi$-conjugated small molecule was successfully elaborated in thin film using the spin coating technique. The UV–vis absorption of DABMN was observed at 360–530 nm. The small molecule exhibits excellent red color emission at 615 nm. In comparison with BMN molecule, the incorporation of the dimethyl-amino group into DABMN molecule reduced the electrochemical band gap. Then, the ITO/DABMN/Al structure demonstrated an Schottky diode behavior. The
diode parameters such as the barrier height and the ideality factor were extracted from the current-voltage characteristics. From capacitance-voltage analysis, the carrier density in DABMN film was calculated and was $2.9 \times 10^{10}$ cm$^{-2}$. Our study suggests that the DABMN has good potential for application in organic optoelectronics.

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