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New organic semiconductor thin film derived from p-toluidine monomer

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ABSTRACT

p-Toluidine was used as a precursor to synthesize new organic compound [(E)-4-methyl-N^1-((E)-4-methyl-6-(*p*-tolylimino) cyclohex-3-en-1-ylidene)-N^2-(*p*-tolyl) benzene-1,2-diamine] (MBD) by oxidative reaction via potassium dichromate as oxidizing agent at room temperature. Spin coater was used to fabricate nano-size crystalline thin film of the MBD with thickness 73 nm. The characterizations of the MBD powder and thin film have been described by various techniques including Fourier Transform Infrared (FT-IR), Mass Spectra, X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), UV–Visible measurements and Atomic Force Microscope (AFM). The results revealed that the MBD as an organic material is semi-crystalline containing benzenoid (B_{en} −N− B_{en}) and quinonoid (Q_{uin} = N = Q_{uin}) structures. Various optical constants such as refractive index (n), and the absorption index, (k) of the MBD thin film were determined. The effect of temperature on the electrical resistivity of MBD film was studied by a Keithley 6517B electrometer. The energy band gap value of the MBD thin film was found to be 2.24 eV. Thus, MBD is located in the semiconductor materials range. In addition, structural and optical mechanisms of MBD nanostructured thin film were investigated. The obtained results illustrate the possibility of controlling the organic semiconductor MBD thin film for the optoelectronic applications.

1. Introduction

Recently, semiconductors with nanostructures have become attractive due to their abundant unique characteristics, which have potentially supreme functional components for optoelectronics applications [1–3]. The fabrication process of the thin film has been modified to meet the needs of the integrated circuit with low cost of photovoltaic systems [4–6]. Hence, awareness and detection of the functions and the properties of thin films can be modified for different applications in various areas [7]. Numerous methods to fabricate semiconductors' thin films have been developed, based on sophisticated techniques including radio frequency magnetron sputtering [8,9], spray pyrolysis [10,11], sol-gel [12,13], and pulsed laser deposition [14]. All these different processes are considered expensive because all are energy exhaustive and involve high temperature and consuming pressure. One of the most effective methods to deposit thin film is spin coating, because it is suitable for preparing uniform and highly homogeneous thin films [15,16]. Organic semiconductors with nitrogen and oxygen elements have also attracted much attention due to the weakness of the intermolecular forces between the molecules in the solid state. On the other hand, the organic materials display different properties of semiconductors based on their conjugation of single and double bond systems between their atoms. Therefore, the study of organic materials as a semiconductors has led to an expanded understanding of the fundamentals of the optoelectronic properties of the organic solids. Organic semiconductor materials have become more than an interest when they are photoconductive, especially in visible region illumination. These findings open new window to using the organic semiconductors in electrophotography and liquid crystal display (LCDs) applications. Thin films from organic conducting materials can be fabricated for use in solar cell application [17–19]. The polymerization of aniline monomer or aniline derivatives to give organic semiconductors of polyaniline or

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polyaniline derivatives have been investigated [20–24].

In the present manuscript, p-toluidine monomer as aniline derivative was used as a precursor to synthesize MBD new organic compound. Spin coating process was applied to fabricate thin film of MBD onto quartz substrate with thickness 73 nm. Different optical parameters of the MBD nanostructured thin film were determined (band gap = 2.24 eV). The electrical resistivity and the temperature coefficient of resistivity (TCR) values of MBD thin film were studied at temperature range of 320–440 K.

2. Experimental work

2.1. Raw materials

All materials' reagents were used without any further purification. p-*Toluidine* (Acros Organics: Thermo Fisher Scientific) potassium dichromate (Shanghai chemicals), ethanol (Aldrich), conc. hydrofluoric acid (HF), conc. nitric acid (HNO_3), acetic acid (CH_3COOH) and dimethyl sulfoxide-d6 (Merck) were used as purchased.

2.2. Synthesis of MBD powder [25]

The MBD was synthesized according to the method previously reported [25]. Typically, 2.14 g p-toluidine was dissolved in 50 ml ethanol at 25 °C. The resulting ethanolic p-toluidine solution was diluted by 50 ml distilled water. 4 ml concentrated hydrochloric acid was added to the p-toluidine solution under magnetic stirrer (600 rpm) at room temperature. Separately, 4.36 g potassium dichromate as an oxidizing agent was dissolved in 100 ml distilled water. A potassium dichromate solution was added drop-wise to the p-toluidine solution for 2 h, under the previous conditions. The violet color gradually appeared at the beginning of the addition of the dichromate solution to p-toluidine. The resulting compound was filtered by Buchner system and washed several times with distilled water. To purify the resulting compound, it was redissolved in ethanol under heating. The filtration process was applied to remove any impurities. The evaporation process was applied to the resulting ethanolic filtrate at low temperature until dryness. The resulting fine brownish powder was collected and kept.

2.3. Fabrication of MBD thin film

Heterojunction device of Au/MBD/p-Si/Al was fabricated by using a polished p-type single crystal Si wafer. The pore concentration of the Si wafer was 1.6×10^{23} m^{-3} with 400 mm. The native oxides from the surface of p-Si substrate was etched by mixture solution of the following acids HF: HNO_3:CH_3COOH for 10 s followed by rinsing with deionized water. An aluminum electrode was made by depositing aluminum films on the surface of the Si substrate. A thin film of MBD (around 73 nm) was deposited on another side of the Si wafer by the spin coating technique. A network from gold electrode was thermally deposited on MBD film. The gold and aluminum were selected as electrodes to make Ohmic contacts with the organic compounds. Fig. 1 shows the schematic diagram of the fabricated Au/MBD/p-Si/Al heterojunction diodes. The real cross-sectional area of the diodes was 1.04 cm^2. The thin film of MBD as organic material was fabricated according to the following steps: A 0.018 g of the MBD was dissolved in 0.5 ml DMSO solvent. The resultant MBD solution was stirred by a magnetic stirrer at 60 °C for 5 min. The substrate was coated by MBD solution using spin coater SPIN150 at a speed of 2000 rpm for 40 s. The resulting film was kept dry in clean environmental conditions (an evacuated desiccator) for testing. Au and Al films were evaporated individually using a tungsten filament. The film thickness was measured by M − 2000 Ellipsometer and found to be 73 nm.

2.4. Characterization

FT-IR spectra were recorded by a Perkin-Elmer FT-IR type1650 spectrophotometer in the range of 4000–400 cm^{-1} using KBr pellets. Mass spectra (ESI-MS) were detected using a JEOL JMS 600 spectrometer and electron-impact (EI). Scanning Electron Microscopy (SEM; Inspect S, FEI, Holland) was used to study the morphology of MBD powder. MBD powder and thin film were analyzed by A RIGAKUU Ultima IV XRD with utilized monochromatic Cu K α radiation ($\lambda = 1.5418$ Å) operated at 40 kV and 25 mA. The diffraction patterns were recorded automatically with a scanning speed of 6° min^{-1} per within the range of 5–85°. The divergence slit (DS) and the Receiving slit (RS) were adjusted at 1° and 0.2 mm, respectively. The surface roughness and morphology of MBD thin film were studied using an AFM (Bruker dimension icon taping mode).

3. Results and discussion

3.1. XRD of MBD powder and thin film

Fig. 2 Shows multi-peaks fit XRD spectra overlay of MBD powder and thin film. Two strong peaks are located at ≅ 19.93° and 24.16° indicates the semi-crystalline structure of MBD of powder and thin film respectively. This is characteristic for the Van der Waals forces between stacks of toluidine rings of MBD molecular structure. It implies that the MBD has clearly semi-crystalline nanostructural nature with expected high electrical conductivity. The broad peaks, which are located at 40.62° and 40.40°, can be attributed to the existing of methylenazo groups (C=N) in a quinonoid ring in the

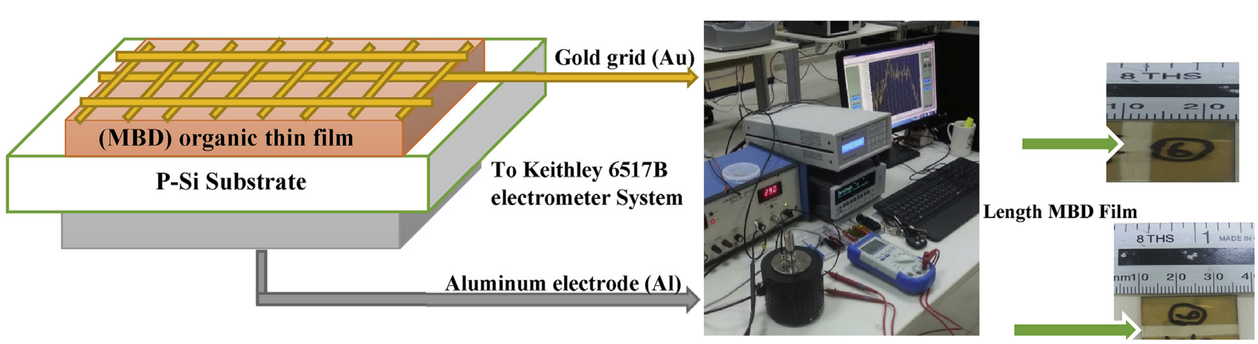

Fig. 1. Schematic representation showing Au/MBD/p-Si/Al heterojunction diode.