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Enhancement in electrical properties of ITO/PEDOT:PSS/PTCDA/Ag by using calcium buffer layer

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ABSTRACT

This paper reports on electrical characterization of ITO/PEDOT:PSS/PTCDA/Ca/Ag device based on 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) and calcium (Ca) buffer layer with improved junction properties. The *I–V* characteristics have been utilized to extract various electrical parameters such as ideality factor (n), barrier height (ϕ_B) and series resistance R_s, which are found to be 1.9, 0.79 eV and 2.5 kΩ, respectively. The device shows good rectifying behavior, with a rectification ratio of 528, and also field-lowering mechanism with a linear dependence of log I on $V^{1/2}$. The device reported in the present work shows 50% improvement in the rectification ratio and ideality factor as compared to our previously fabricated device. It appears from the experimental data that the transport mechanism in the PTCDA thin film is dominated by the Poole–Frenkel model of thermionic emission, which may be associated with high density of structural defects or traps present in the film.

1. Introduction

Organic semiconductors have acquired great attention, in recent years, for their wide applications in electronics [1]. These materials offer attractive features of low cost fabrication processes, low material consumption for thin films and easy processability, which lead to cost-effective production of electronic devices [2]. On the contrary, conventional inorganic materials require high-temperature and high-vacuum deposition processes and fine photolithographic patterning techniques, due to which they are processed through very expensive and complex manufacturing techniques [3]. The properties of organic semiconducting materials, stated earlier, give them an edge over the existing high-cost and much complex processes involved in conventional Si technology [3]. Moreover, due to mechanical flexibility of organic materials, which make them compatible with flexible substrates, they can be used for the manufacturing of lightweight flexible electronic products [4,5]. In addition to cost-effective fabrication processes, organic semiconductors offer a variety of properties which include thermal and photochemical stability [6] and large absorption coefficient [7] etc. Owing to numerous electronic and optoelectronic properties, organic semiconducting materials and their derivatives have been investigated as Schottky diodes, organic light emitting diodes, solar cells and field effect transistors [8–13]. To achieve improved device performance, it is mandatory to have a better insight of physical phenomena of the organic semiconductor based devices which include various junction properties, charge transport and mobility etc. [14,15]. Employing thin films of organic materials such as porphyrin, phthalocyanines (Pcs), perylene etc. on semiconductors or metals, result in the properties of reactivity, ultra-fast optical response, chemical sensing, and biocompatibility [16–19].

Among a plethora of organic semiconductors, perylene and its derivatives constitute a family of promising candidates due to their electronic, optical and electrochemical properties [20]. A detailed study on thin films of perylene tetracarboxylic-dianhydride (PTCDA) has shown its use in a variety of electronic and optoelectronic applications [21,22]. Due to the organic semiconducting behavior, PTCDA has been employed in the application of organic thin film transistor (OTFT), organic light emitting diodes (OLED) and organic solar cells (OSC) [23–25]. PTCDA, which belongs to a small aromatic molecular system, has high thermal and photochemical stability and low vapor pressure [26]. It has also been reported that PTCDA has a high crystallinity and low

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intermolecular distance, which lead to promising transport properties [27]. Many researchers have explored PTCDA for its electronic properties on different substrates, film thicknesses and growth conditions [10]. During the last decade 3,4,9,10-perylene tetracarboxylic dianhydride (PTCDA) has been successfully used to alter properties of Schottky contacts [28]. Junction properties of PTCDA in Schottky diode through current–voltage (I–V) characteristics, have been studied in [26-29]. PTCDA has been, recently, used to improve Schottky barrier height and enhance electronic transport properties [28-30]. So far, many approaches have been used to improve the device performance but the most notable technique is the introduction of buffer layer between acceptor and metallic top contact, which provides a useful means in efficiency breakthrough [31].

In the present work, we report on the fabrication and study of electronic properties of ITO/PEDOT:PSS/PTCDA/Ca/Ag diode. The I–V characteristics showed excellent rectifying behavior. The values of ideality factor n, barrier height ϕ_B, and series resistance R_s of ITO/PEDOT:PSS/PTCDA/Ca/Ag have been extracted from the I–V characteristics. Generally, electronic parameters are extracted at room temperature by assuming only thermionic emission which is responsible for the flow of charge carriers. Herein, we also report on the study of other current transport processes in PTCDA thin film, which are responsible for the flow of electrons. The present work shows 50% improvement in the rectification ratio and ideality factor as compared to our previously fabricated device [29].

2. Experimental work

Organic semiconducting material, Perylene tetracarboxylic-dianhydride (PTCDA), having molecular mass of 546.23, is used for the fabrication of ITO/PEDOT:PSS/PTCDA/Ca/Ag diode. The molecular structure of PTCDA is shown in Fig. 1. A substrate used in the device is Indium Tin Oxide (ITO), which is treated with HF:H_2O having a solution strength of 1:10. Afterwards, it is cleaned in acetone using ultrasonic bath followed by drying with nitrogen gas for 5 min. Spin coating technique was adopted to deposit a 20 nm thick layer of PEDOT:PSS on cleaned ITO at the rate of 2000 rpm for 20 s. Then, the PEDOT:PSS layer was annealed at 50 °C for 2 h using hot plate, in the nitrogen environment, to allow moisture to evaporate from the layer, completely. Later, the active layer of PTCDA was sublimed on pre-coated PEDOT:PSS layer, at a pressure of 10^{-5} mbar and deposition rate of 0.1 nm/s. Thickness of the film was 150 nm, which was measured by in situ FTM5 Quartz Crystal Oscillator with a least count error of 0.01%. A 20 nm Ca buffer layer was deposited by thermal evaporation on top of the active layer. Finally, an Ag metal contact, having a thickness of 50 nm, was deposited on the Ca layer through a shadow mask. Thin films of the three materials PTCDA, Ca and Ag were deposited sequentially in situ in the vacuum thermal evaporator (in the glove box) without breaking vacuum. The evaporator contained multi boats and the materials were separately loaded in three different boats. For deposition of thin film of the desired material film growth, the corresponding boat was made active. Schematic diagram of the fabricated ITO/PEDOT:PSS/PTCDA/Ca/Ag device is shown in Fig. 2. Current–voltage measurements were carried out by Keithly SMU 236 system. The I–V measurements were repeated 10 times and very similar results were obtained for all the sweeps. The acquisition time was one data point per second with a step-size of 0.1 V in the voltage range of -7 to $+7$ V. Morphology of the film was examined by atomic force microscopy (AFM). The AFM measurements were performed by a NanoScope-IIIa SPM from Dimension TM 3100, Digital Instruments Veeco Metrology Group, which was operated in tapping mode (non-contact) imaging technique to prevent damage to the thin films.

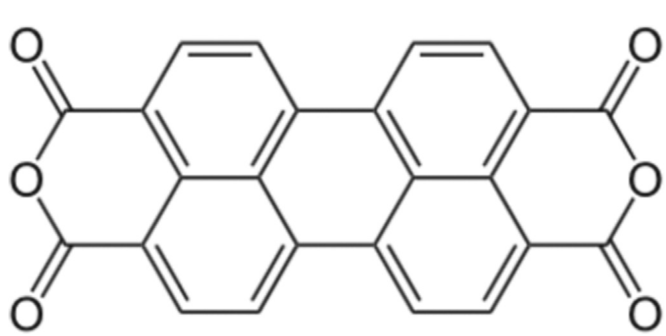

Fig. 1. Molecular structure of PTCDA.

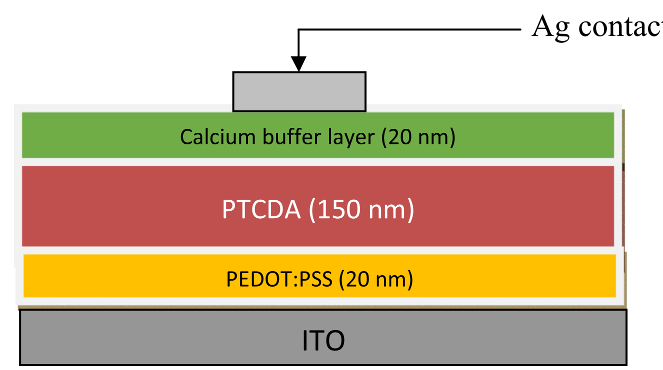

Fig. 2. Cross-sectional view of ITO/PEDOT:PSS/PTCDA/Ca/Ag diode.

3. Results and discussions

Fig. 3 shows a 3-D AFM micrograph of the PTCDA thin film, with a scan size of 5 μm × 5 μm, prepared on an ordinary microscope glass slide under normal ambient conditions. The sharp peak-like projections of the film suggest non uniform and rough surface, having valleys distributed over the surface of film. Such

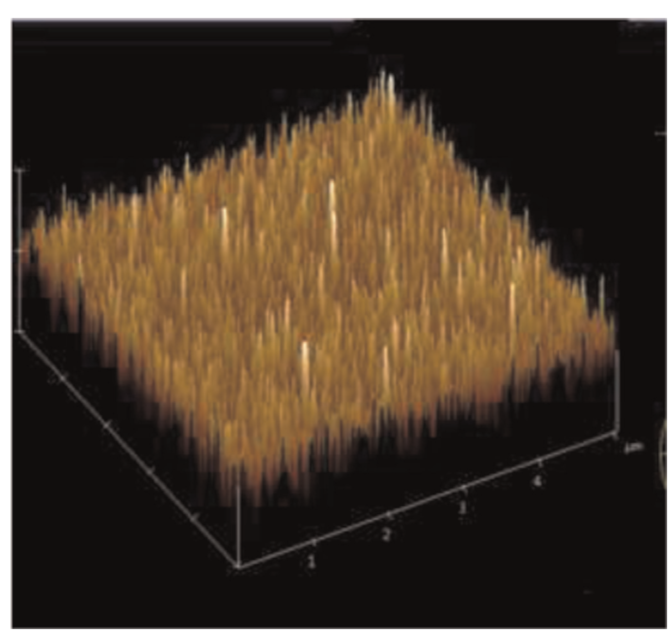

Fig. 3. A 5 μm × 5 μm 3-D AFM micrograph of the PTCDA thin film prepared on glass substrate.