Perylene diimide: Synthesis, fabrication and temperature dependent electrical characterization of heterojunction with p-silicon

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Abstract

A novel, n-type, organic semiconductor N-Butyl-N-(6-hydroxyhexyl)perylene-3,4,9,10-tetracarboxylic acid diimide (N-BuHHPDI) has been successfully synthesized in high yield. The compound has been characterized by atomic force microscopy (AFM) to understand the morphological properties of a new n-type organic semiconducting material. A 120 nm thin film of N-BuHHPDI has been sandwiched between Al and p-Si to form Al/N-BuHHPDI/p-Si device using the vacuum thermal evaporation technique. The electrical properties of sandwich type Al/N-BuHHPDI/p-Si device have been investigated. The current voltage (I-V) characteristics of the device, in dark, have been measured in the temperature range of 300–330 K. At room temperature, the device exhibits rectifying behavior with a rectification ratio of 51.5 at ±6.8 V. The device parameters such as ideality factor, barrier height, series and shunt resistances have been extracted using the conventional I-V characterization method. The effect of temperature on these parameters is also studied. Alternative electrical characterization methods such as Cheung’s functions and Norde’s techniques have been employed to measure the device parameters for comparison. The conduction mechanisms are investigated through the interface of N-BuHHPDI and p-Si.

Keywords:
- Organic-inorganic heterojunction
- Atomic force microscopy
- Electrical characteristics

1. Introduction

Organic semiconducting materials have gained great attention because of their potential applications as active materials in numerous electronic and optoelectronic devices, such as, junction diodes [1], sensors [2,3], organic field effect transistors [4], solar cells [5], etc. Very recently, fabrication and characterization of organic–inorganic interfaces have been the subject of intensive research [1,6]. The potential of these rectifying interfaces has been explored for the fabrication of many electronic devices [7–10]. In most of the earlier studies of organic–inorganic heterojunctions, p-type organic semiconductors have been extensively used. Provided research highlights are not as per the format mentioned in stylesheet/85 characters per bullet point. [11–15]. As far as we know, very little is known about their n-type counterparts which are the key components of organic p–n junction rectifiers, bipolar transistors and complementary integrated circuits [16].

In the research for rectifying contacts, the development of new n-type and p-type materials offering optimized thermal and photochemical stabilities, electrical and structural properties plays an important role. In the past few decades perylene tetra carboxylic diimides (PDI) and their derivatives have acquired much more attention due to their outstanding thermal and photochemical stabilities [17,18]. The electrical characteristics of the derivative of perylene tetra carboxylic diimide have been investigated for different heterojunction structures [19,20]. Perylene diimide derivatives are, particularly, a promising class of n-type organic semiconductors and have attracted much attention amongst small molecular organic semiconductors for a wide range of optoelectronic applications, such as, solar cells, field effect transistors, optical switches, chemical sensors, liquid crystal displays, organic light emitting diodes [21]. This has been mainly because of their interesting electrical and optical properties, such as, their strong absorption and emission in the visible range [22–24]. large carrier mobilities [25] and outstanding chemical and thermal stabilities [26,27]. The electrical characteristics of the rectifying contacts, usually measured at room temperature, do not provide detailed information about their conduction mechanism [28], therefore, temperature dependent electrical studies of these structures are very important in understanding the behavior of the p–n junction devices.

In this work, we report synthesis of a novel n-type organic semiconductor N-Butyl-N-(6-hydroxyhexyl)perylene-3,4,9,
10-tetra-carboxylic acid diimide (N-BuHHPDI) and electrical characterization of the N-BuHHPDI/p-Si organic–inorganic heterojunction, fabricated using vacuum thermal evaporation. The device demonstrated rectifying behavior. In order to check performance and suitability of N-BuHHPDI for the heterojunction device, temperature-dependent electrical characterization of the device has been carried out in temperature range of 300–330 K. The junction parameters are extracted using the conventional I–V characterization method, Cheungs’ function and Norde’s technique. The conduction mechanism and morphology of the thin film of (N-BuHHPDI) have also been investigated.

2. Experimental

2.1. Synthesis of N-Butyl-N’-(6-hydroxyhexyl)perylene-3,4,9,10-tetra-carboxylic acid diimide (N-BuHHPDI)

Perylene-3,4,9,10-tetra-carboxylic acid dianhydride (1) (1.96 g, 5 mmol) and potassium hydroxide (1.12 g) were dissolved in 25 ml of water at 363 K, with pH of the solution equal to 10. pH of the solution was maintained between 4.5–5.0 by drop-wise adding 4 ml of 31% hydrochloric acid over a period of two hours at 363 K. The mixture was further stirred for two hours at the same temperature. The mixture was then, cooled to room temperature and the precipitates were isolated by filtration and washed with hot water to obtain dark red powder of monopotassium salt of perylene-3,4,9,10-tetracarboxylic acid mono anhydride (2) (1.86 g). By making little modification in the procedure reported in the literature [29,30], monopotassium salt of perylene-3,4,9,10-tetra-carboxylic acid mono anhydride (2) (1.86 g) was added to the mixture of n-butylamine (1.26 g, 0.02 mol) in 25 ml of water. The contents were stirred first at room temperature for one hour and then at 363 K for another hour. Afterward, the mixture was acidified with hydrochloric acid and the precipitates were filtered. The residue was dissolved in 10 ml of 5% KOH solution at the temperature of 363–368 K and the di-potassium salt was precipitated by adding 1 g of KCl. The precipitates were filtered and washed subsequently with 5 ml of each 14% KCl and 1% KOH. The di-potassium salt was dissolved in boiling water and acidified to get black brown powder (1.6 g) of perylene tetracarboxylic acid mono anhydride monobutylimide on filtration. Then, a mixture of N-(n-Butyl)perylene-3,4-dicarboxiimide-9,10-dicarboxylic acid anhydride (3) (0.5 g, 1 mmol) and 6-aminohexanol (0.127 g, 1 mmol) in ethylene glycol was heated at 448 K for two hours. The mixture was cooled to 353 K and then diluted with 30 ml of methanol. The precipitates were filtered and then washed with 20 ml of methanol and 50 ml of water. Later, the product was dried in the oven at 383 K to obtain the required N-(n-Butyl)-N’-(6-hydroxyhexyl)-3,4,9,10-perylene tetracarboxylic acid diimide (N-BuHHPDI) (4) in the form of black brown powder with a yield of 71%, melting point at 573 K and molecular mass of 545.0 (M+).

The stepwise synthesis procedure is schematically shown in Fig. 1.

2.2. Device fabrication and measurements

A p-Si with orientation (100) was treated with HF:H2O having a solution strength of 1:10. Afterward, it was cleaned in acetone using ultrasonic bath for 5 min, which was followed by drying samples with stream of nitrogen gas. On the p-silicon substrate a 120 nm thin film of N-BuHHPDI was thermally deposited at a pressure of 10⁻⁵ mbar with a deposition rate of 0.1 nm/s. The thickness of the film was monitored by FTM5 Quartz Crystal Oscillator. Aluminum (Al) was used as a top electrode on N-BuHHPDI layer. Cross-sectional view of the fabricated Al/N-BuHHPDI/p-Si heterojunction is shown in Fig. 2. This device was kept on KARL SUSS PM5 probe station and varying the temperature using Temptronic Corporation Temperature-source, the current–voltage measurements were made on Keithley 237 SMU system. All the AFM measurements described here were performed with a NanoScope-IIIa SPM from Dimension TM 3100, Digital Instruments Veeco Metrology Group, which was operated in non-contact mode to prevent damages to the thin films. Height and phase images were recorded simultaneously.

3. Results and discussions

The surface profile of the N-BuHHPDI thin film is investigated using atomic force microscopy (AFM). Fig. 3 shows two dimensional representation of the N-BuHHPDI film on p-Si substrate at a...