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Electrical characterization of cobalt phthalocyanine/*n*-Si heterojunction

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ABSTRACT

We report fabrication and characterization of heterojunction diode based on organic semiconductor cobalt phthalocyanine (CoPc) with *n*-silicon. The electrical characteristics of the CoPc/*n*-Si junction, along with its photo response, are investigated by current–voltage (*I*–*V*) measurements. The morphological properties of the CoPc thin film are investigated using atomic force microscopy (AFM). The *I*–*V* characteristics of the junction show rectifying behavior with a rectification ratio of 145 at the bias voltages of ± 3.6 V. The diode parameters such as ideality factor *n*, barrier height φ_b and series resistance R_s were determined from the *I*–*V* characteristics, which were confirmed by Cheung's function. The conduction mechanism of the diode is also studied to calculate mobility of the CoPc film. The photo response of the device shows that it can be used as photo-sensor.

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1. Introduction

The fabrication and investigation of organic–inorganic heterojunctions have recently attracted great attention because of the availability of numerous organic semiconducting materials with interesting electrical and optical properties. Due to easy fabrication of organic–inorganic devices, these semiconducting materials have been employed in many electronic and optoelectronic applications, which include rectifying diodes [1], solar cells [2,3], nuclear radiation detectors [4], light emitting diodes [5], and field-effect transistors [6]. The fabrication and study of organic–inorganic hybrid heterojunctions open doors for new functional elements which have never been possible either by organic or inorganic materials, independently [7]. Organic–inorganic heterojucntions play important role in controlling the operation and performance of multi-layered organic optoelectronic devices [8,9].

Electrical properties of organic semiconductor based devices depend on ambient conditions, such as, temperature, light and humidity, etc., that is why they are considered very promising candidates for various types of sensors [10,11]. Metallophthalocyanines (MPcs) are a class of macrocyclic organic semiconductors, which have been extensively studied as bulk active materials in diverse applications [12]. Extraction of junction parameters for MPcs based heterojunctions, as investigated in [1,13], is important for assessing device performance. These materials continue to be the subject of increasing research interest due to potential applications of their bulk and nanoscaled species in emerging fields of molecular electronics, molecular spintronics, and molecular nanoelectronics. Due to high chemical and thermal stabilities and excellent optoelectronic properties, MPcs are most widely used and investigated [8,14]. MPcs may be deposited as thin films without dissociation and thus, are suitable for the preparation of thin film based devices through thermal deposition.

Cobalt phthalocynine (CoPc), a member of the MPcs family, exhibits *p*-type behavior [15]. Bulk and nanoscaled CoPc is a potentially interesting material for many applications, such as, biosensors and humidity sensors [16], etc. The electrical properties of other pthalocyanines, along with their derivatives, on *p*-silicon,

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n-silicon, and other inorganic semiconducting substrates have been widely studied [17,18] and there complementary data is available for future studies. Some work is also available on the electrical properties of CoPc [13,19].

In the present work, fabrication and study of electrical properties of Al/CoPc/n-Si/Al organic–inorganic heterojunction are reported. The objective of this work is to study the electrical properties of thermally evaporated CoPc thin film on heavily doped n-Si. The I–V characteristics showed good rectifying behavior. The values of ideality factor n, barrier height φ_b, and series resistance R_s of Al/CoPc/n-Si/Al have been extracted from the I–V characteristics. The device has been investigated in dark and under different illuminations at room temperature. It is important to extract junction parameters of the device under illumination for its potential application in photo-sensors.

2. Experimental

2.1. Synthesis

The active material CoPc was prepared in accordance with the method of Sakamoto and Ohno [20] but modified. Briefly, 20 g phthalicanhydride, 24.4 g of urea, 3.4 g cobalt chloride, and 0.04 g of ammonium molybdate were stirred in 40 g of diphenyl for 4 h at 180 °C. After the completion of reaction, diphenyl was removed by using n-hexane extraction in sauxhlet. The residues were washed with hot water and dilute HCl, filtered and dried to obtain cobalt phthalocyanine having a purity of more than 98% (yield 92%).

The obtained characteristics are: M.P: 300, Color: violet, IR KBr ν (cm^{-1}); 507, 570, 718, 760, 775, 770, 790, 850, 890, 880, 930, 1010, 1050, 1090, 1110, 1150, 1180, 1260, 1270, 1330, 1420, 1460, 1460, 1470, 14,820, 1499, 1510, 1545, 1550, 1600, 1620.Elemental analysis ($C_{32}H_{16}CoN_8$): C, 67.26; H, 2.82; N, 19.61; Co 10.31, found; C.67.21; H, 2.80; N, 19.59; Co 10.30.

2.2. Device fabrication and characterization

For the fabrication of Al/CoPc/n-Si/Al heterojunction, heavily doped n-silicon single crystal with (1 1 0) orientation was used as a substrate. The substrate was cleaned using acetone in ultrasonic cleaner, at room temperature, for 10 min and dried in atmospheric environment. Later, the substrate was plasma cleaned for 5 min in vacuum thermal evaporator. The purpose of cleaning process was to remove contamination and oxide layer. On the polished surface of n-Si, CoPc film of thickness 150 nm, was deposited using a shadow mask. The active layer of CoPc was thermally evaporated using Edward Auto 306 Thermal Vacuum Evaporator. The thickness of the deposited film was monitored by FTM5 quartz crystal oscillator. The growth rate was maintained at 0.2 nm/s under a pressure of 2×10^{-5} mbar during sublimation process. Finally, using shadow mask, aluminum contacts of thickness 200 nm were deposited on the CoPc and n-Si surfaces. The molecular structure of CoPc is shown in Fig. 1. A schematic diagram of the device is shown in Fig. 2. For surface morphological studies, a 150 nm-thick stand-alone CoPc film was grown on a glass substrate under the same deposition conditions as stated above. The I–V measurements were made in dark and under tungsten filament illumination, at room temperature, using Keithley 236 sourcemeter connected to a computer. The AFM images were obtained in tapping mode using Digital Instruments Veeco D3000 microscope.

3. Results and discussions

Fig. 3 shows 3-D AFM micrograph of the CoPc film deposited on glass substrate, at a height of 10 nm. The image exhibits non-uniform rather rough surface with sharp-peak like structure. The root mean square roughness of the film is 1.9 nm. The average grain size is 4700 nm^2. The discontinuity of the CoPc film is obvious from pores present in the film surface, which is responsible for charge trapping and thus lowering the diode current.

The I–V characteristics of the CoPc/n-Si heterojunction have been measured to obtain valuable information about the junction properties, such as rectification ratio 'RR', ideality factor 'n', barrier height 'φ_b', reverse saturation current 'I_0', and series resistance 'R_s', The I–V curves have also been analyzed to investigate the transport properties which control conduction in the device.

The linear forward and reverse bias I–V characteristics, obtained at room temperature to study the rectifying behavior of CoPc/n-Si, are shown in Fig. 4. The nonlinear and asymmetric characteristics exhibit exponential increase in the forward direction which provides evidence for the formation of barrier between n-Si and CoPc. Two important parameters turn on voltage and rectification ratio have been extracted from the graph. It can be observed form Fig. 4 that the turn on voltage, which is the voltage where rectification begins, is 1.2 V. The RR, defined as the ratio of forward to reverse current at the same voltage, is obtained as 145 @ $\pm$3.6 V from the I–V curves.

For the analysis of our rectifying contact, thermionic emission theory is used and is given by the following expression:

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

where I_o is the saturation current, given by:

$$I_0 = AA^{*}T^2\exp\left(\frac{-q\varphi_b}{kT}\right) \tag{2}$$

q is the charge of electron, V is the applied voltage, A^* is the effective Richardson constant equal to 112 $A/cm^2 K^2$ for n-Si, A is the effective diode area (3.083 mm^2 for our device), T is the absolute temperature, k is the Boltzmann constant and n is the ideality factor, which is determined through the following relation:

$$n = \frac{q}{kT}\frac{dV}{d(\ln I)} \tag{3}$$

The reverse saturation current I_o is determined from the extrapolation of semi-log I–V curve of Fig. 5 to zero bias and is found equal to 1.2×10^{-6} A.

The barrier height that exists at the organic–inorganic interface can be expressed by:

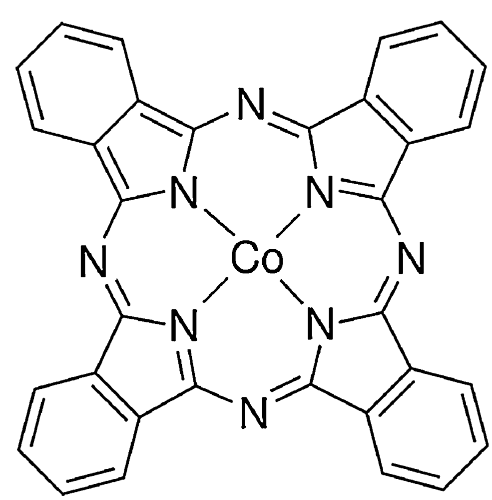

Fig. 1. Molecualr structure of CoPc.

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