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Effect of deposition rate on the charge transport in Vanadyl-phthalocyanine thin films

M. Raveendra Kiran*, Hidayath Ulla, M.N. Satyanarayan, G. Umesh

Optoelectronics Laboratory, Department of Physics, National Institute of Technology Karnataka, Surathkal, Mangalore, 575025, India

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ABSTRACT

We report fabrication of Vanadyl phthalocyanine (VOPc) based diodes with different deposition rates (0.1, 1 and 5 Å/s) in hole only device configuration: ITO/MoO_3/VOPc/MoO_3/Al. The dc and ac electrical conductivity of Vanadyl phthalocyanine based devices is investigated by employing Impedance spectroscopy measurements. The frequency dependence of conductivity indicates that the dominant mechanism for charge transport is the hopping type. Further, the dependence of conductivity on temperature and bias voltage clearly indicates that the hopping mechanism is described by the correlated barrier hopping (CBH) model. The thin layer (3 nm) of MoO_3 in our devices is seen to enhance the electrical conductivity. J-V measurements indicate that the current density J as well as the charge carrier mobility are higher for the devices fabricated at a relatively lower deposition rate (0.1 Å/s). Our results suggest that the VOPC films deposited at lower rates are more appropriate for the optoelectronic device applications.

1. Introduction

Metal-phthalocyanines (MPc) are one of the most important classes of organic semiconductor materials for optoelectronic applications. They have relatively good electronic properties, are inexpensive and possess high environmental stability [1–3]. The molecular electronic structure along with morphological, structural, optical and electronic properties of MPc thin films play crucial role in the device applications. Several investigations have been reported on charge transport and device applications of planar phthalocyanines (Copper phthalocyanines, CuPc and Zinc phthalocyanines) [4] and non- planar phthalocyanines (Boronsubtryphthalocyanine chloride, SubPc and Titanyl phthalocyanine, TiOPc). Non-planar phthalocyanine based devices are seen to offer better performance in comparison with planar phthalocyanines [2,5]. An example of such materials is Vanadyl phthalocyanines (VOPc) which has been used in several optoelectronic devices such as light emitting diodes (OLED), organic photovoltaic cells (OPV), organic field effect transistors (OFET) and sensors [6]. However, the charge transport in VOPc based devices has not been extensively investigated.

In order to achieve higher device performance, it is essential to understand the charge conduction mechanism that operates in these devices. Recently, our group investigated the influence of a buffer layer on the charge transport in VOPc using impedance spectroscopy [7]. In this paper, we report an investigation on the dependence of electrical conductivity with applied signal frequency, bias voltage and device temperature in order to understand the charge transport mechanism operative in these devices. Further, we discuss the effects of the deposition rates on the transport properties of VOPc in hole only devices with the configuration: ITO/MoO_3/VOPc/MoO_3/Al. These investigations have been carried with the motivation to identify the exact nature of the charge transport mechanism. In our devices, the dominant mechanism is hopping type.

2. Experimental

Pre-patterned ITO coated glass substrates (sheet resistance ~15 Ω/□, Kintec, Hong Kong) were cleaned using Labolene (detergent), sequentially ultrasonicated in acetone, isopropyl alcohol and DI water for 20 min each and dried in flowing ultrapure nitrogen. Prior to the deposition, UV-ozone treatment was done to the cleaned ITO surface for 15 min to avoid the possible electrical shorts and to increase its work function. We have used the thin layers (3 nm) of molybdenum Oxide (MoO_3) on both side of VOPc (100 nm) to assist hole injection and transport (ITO/MoO_3/

* Corresponding author.
E-mail addresses: kiran.phy85@gmail.com, kiran.phy85@nitk.ac.in (M. R. Kiran).

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VOPc/MoO_3/Al). The deposition rate of the MoO_3 was maintained at 0.1–0.2 A°/s for both bottom (ITO/MoO_3) and top (MoO_3/Al) layers, whereas, for VOPc, the films with the three deposition rates (0.1–0.2 A°/s, 1–2 A°/s and 5–6 A°/s) were deposited on MoO_3 layer (bottom layer). For simplicity, these deposition rates are denoted as 0.1 A°/s, 1 A°/s and 5 A°/s throughout this paper. Finally, a 100 nm thick Aluminium (Al, Sigma – Aldrich) layer was deposited at a rate of 5–6 A°/s on the top layer of MoO_3 using a shadow mask to function as cathode. The deposition rates and thickness of the films were controlled using a quartz crystal monitor. During the deposition, the substrates were maintained at room temperature under a vacuum of 8×10^{-6}mbar. The active area of the device was 0.016 cm^2.

The J-V characteristics of the devices were obtained using programmable Keithley 2400 SMU. IS measurements were performed using Agilent E4980A high precision LCZ meter in the frequency range of 100 Hz to 1 MHz by keeping an fixed ac amplitude of 100 mV. Surface morphology of the films were observed using Park XE7 Atomic Force Microscope. All the measurements were carried out without any encapsulation and at room temperature under ambient conditions.

3. Results and discussion

The surface morphologies (AFM images) of the thin films evaporated at different deposition rates are shown in Fig. 1. It is clearly observed that the film deposited at 0.1 Å/s shows elongated grain structure, whereas the films deposited at 1 Å/s and 5 Å/s show smaller nearly spherical grain structures, which has also been reported earlier [8]. The root mean square (rms) roughness of the films was estimated as 6.2 nm (0.1 Å/s), 4.5 nm (1 Å/s), and 4.3 nm (5 Å/s).

The schematic representation of the fabricated devices is shown in Fig. 2(a) and also the molecular energy level diagram is presented in Fig. 2(b). The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values of VOPc, the work function of ITO and Al electrodes have been taken from existing literature [7,9,10]. The disagreement in the HOMO-LUMO energy level values 2.3–5.3 eV and 6.7–9.7 eV for MoO3 in the literature are still under debate [11,12]. The sensitivity of UPS and/or other measurements for MoO3 energy level to surface states, the material purity, the thin film processing and the post treatment techniques determine the energy levels of MoO3. However, there is no discrepancy in the energy bandgap of approximately 3 eV. In our work, we have assigned the energy values as 2.3–5.3 eV as shown in Fig. 2(b). Insertion of thin layer of MoO3 is reported to increase the work function of ITO and Al electrodes [13]. This helps in achieving an ohmic contact between ITO and VOPc molecules. Fig. 2(c) shows the forward bias J-V characteristics for the device deposited at different deposition rates. For each deposition rate, four samples have been investigated for J-V characteristics. The results are reproducible within the experimental errors and are presented with the error bars in Fig. 2(c). The main observation drawn from Fig. 2(c) is that, there is no significant change in the current density in case of devices deposited at 1 Å/s and 5 Å/s. However, there is an improvement of ~40 A/cm2 (at 8 V) in case of 0.1 Å/s compared to the devices deposited at higher rates (1 Å/s and 5 Å/s). Fig. 2(d–f) depicts J-V characteristics of devices deposited at 0.1 Å/s, 1 Å/s and 5 Å/s in log-log scale and each plot exhibits three different regions. The power law which governs the current density in the three regions is [14]

$$J \propto V^{\delta} \tag{1}$$

where δ is the slope of the J-V characteristics in different regimes. The first is the ohmic region where δ ~1 (V <0.52 V for 0.1 Å/s, V< 0.33 for 1 Å/s and V< 0.26 for 5 Å/s). This implies that the electrical conduction in this region is due to the thermally generated charge carriers (excluding traps). Hence, in the ohmic region the current density of the device is given by [15]

$$J = p_0 e \mu \frac{V}{d} \tag{2}$$

where, p_0 is the concentration of thermally generated holes, e is the electron charge, μ is the hole mobility, d is the thickness of VOPc layer and V is the applied bias voltage. In the second regime, the gradient of the current density is δ ~2 (0.52 < V < 1.6 for 0.1 Å/s, 0.33 < V< 1.0 for 1 Å/s and 0.33 < V < 0.6 for 5 Å/s) indicating that the electrical conduction in this region follows SCLC mechanism given by [15]

$$J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{d^3} \tag{3}$$

where, ε_r (=3.6) is the dielectric constant of VOPc and ε_0 is the absolute permittivity. Our results demonstrate that, as deposition rate increases the extent of the SCLC region decreases. This is an indication of the rise in trap density with the deposition rate of VOPc. Further, the third region (δ > 2) represents the trap charge SCLC, which is governed by [16]

$$J = e \mu N_V \left(\frac{\varepsilon_r \, \varepsilon_o}{e P_0 k_B T_t} \right)^{l} \frac{V^{l+1}}{d^{2l+1}} \tag{4}$$

where N_V($\sim 10^{27}\ m^{-3}$) is the effective density of states at the valence band edge [14,17], P_0 is the trap density per unit energy range at the valence band edge, $l = \delta - 1$, $T_t = lT$ is a temperature parameter describing the exponential trap distribution and k_B is

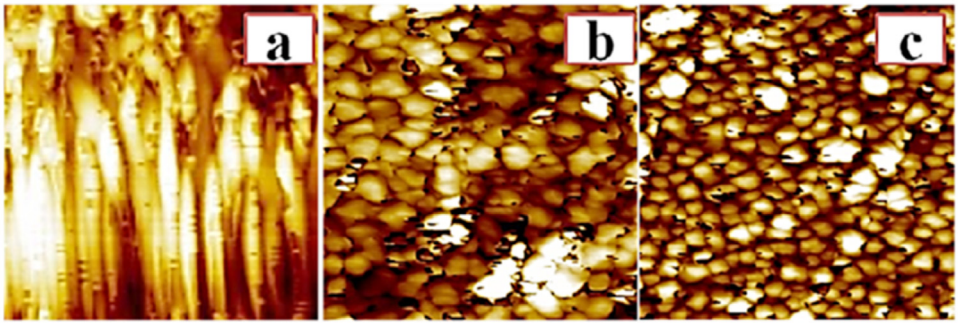

Fig. 1. Surface morphology of the VOPc thin films recorded at a scale of 2 μm × 2 μm for the deposition rate of (a) 0.1 Å/s; (b) 1 Å/s; and (c) 5 Å/s.