Superlattices and Microstructures xxx (2017) 1–11

Contents lists available at ScienceDirect

Superlattices and Microstructures

journal homepage: www.elsevier.com/locate/superlattices

Optoelectronic properties of hybrid diodes based on vanadyl-phthalocyanine and zinc oxide

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

Optoelectronics Laboratory, Department of Physics, National Institute of Technology, Karnataka, Surathkal, Mangalore, 57502, India

A R T I C L E I N F O

Article history:
Received 17 August 2017
Received in revised form 27 September 2017
Accepted 19 October 2017
Available online xxx

Keywords:
Impedance spectroscopy
Cole-cole plot
Charge transport
Hybrid diode
Phthalocyanine
Mobility

A B S T R A C T

We report an investigation of the optoelectronic properties of a hybrid p-n diode device fabricated using ZnO film prepared by sol-gel technique on which a VOPc organic film is deposited by vacuum evaporation. The charge transport properties of devices having the configurations ITO/ZnO/Al and ITO/ZnO/VOPc/MoO_3/Al were investigated at different annealing temperatures (150 °C, 250 °C, 350 °C and 450 °C) by Impedance Spectroscopy (IS). The structural, morphological, optical and electrical properties were also studied at different annealing temperatures. The parameters related to the ITO/ZnO and ZnO/VOPc interfaces such as ideality factor (n), barrier height ($q\phi_B$) and rectification ratio (RR) of the diodes were determined from current density-voltage (J-V) characteristics. IS measurements suggest that the large photocurrent generated is due to the decrease in bulk resistance of the device on account of the generation of electron-hole pairs in the organic active layer when exposed to light. The RR and the photocurrent responsivity (R_{ph}) values obtained from the J-V characteristics compare well with those obtained from the IS measurements. It was observed that the absolute value of R_{ph} (470 mA/W) for the p-n diode with ZnO annealed at 350 °C is high compared to that of diodes with different ZnO annealing temperatures. These values also agree well with the values obtained for p-n diodes of other phthalocyanines. Our studies clearly demonstrate that a p-n diode with ZnO film annealed at 350 °C exhibits much better optoelectronic characteristics on account of increased grain size, improved charge injection due to the reduction of barrier height and hence higher (up to 5 orders) charge carrier mobility.

1. Introduction

Organic-inorganic hybrid diodes have been of interest in optoelectronic applications in recent years. They are seen to play a prominent role in devices such as light emitting diodes, solar cells and photodiodes [1–4]. In such hybrid diodes, one can exploit the advantages of both organic and inorganic materials. Inorganic semiconductors, such as Zinc Oxide (ZnO) and Titanium oxide (TiO_2), are stable n-type semiconductors and have high electron mobility (5–6 $cm^2\ V^{-1}\ s^{-1}$) compared to organic semiconductors (10^{-5} to 1 $cm^2\ V^{-1}\ s^{-1}$) [5]. On the other hand, organic p-type semiconductors (phthalocyanines, pentacene, and P3HT) are known to have broad absorption spectra in the visible region which can lead to high efficiency in photodiodes and solar cells [6–8]. Moreover, these devices can be easily fabricated at low cost, even on flexible substrates [9].

* Corresponding author.
E-mail address: kiran.phy85@gmail.com (M.R. Kiran).

https://doi.org/10.1016/j.spmi.2017.10.023

Hybrid interfaces of ZnO with organic semiconductors have been recently studied by several groups to explore their suitability in applications such as photodiodes [4,8,10–14].

Apart from planar interfaces with ZnO films, various nano structures of ZnO (particles, rods, tubes, wires, belts etc.) have been explored due to their potential applications in various miniaturized devices. Due to the ease of synthesis, high surface area and superior optoelectronic properties, ZnO nanoparticles have been widely exploited. Since a p-n junction is fundamentally important in all semiconductor devices, it is imperative to understand the role of quality of the junction on charge transport, in order to achieve high device performance. In devices involving ZnO/organic semiconductor interfaces, the effect of annealing of ZnO layer on the interface properties have not been explored much.

In this work, we have investigated the optoelectronic properties of hybrid diodes involving ZnO and Vanadyl-phthalocyanine (VOPc), a well-known metal phthalocyanine (MPc). MPcs possess relatively good electronic properties, are inexpensive and exhibit high environmental stability [15,16]. ZnO/MPc photodiodes have been well investigated [17–19]. Our specific choice of VOPc was based on the fact that it is a non-planar phthalocyanine molecule and is known to offer better performance in comparison to planar phthalocyanines [20–22]. Further, VOPc is commonly employed as a hole transport material [23]. To the best of our knowledge, photodiodes based on ZnO/VOPc combination has not been investigated so far. In an earlier work on hole transport through the VOPc thin films, we have shown that films deposited at low rates are better for optoelectronic applications [24]. Here, we first investigate the effect of ZnO film annealing at different temperatures on the charge transport properties of ITO/ZnO/Al electron only devices. Subsequently, we also report the fabrication and electrical characterization of p-n junctions with the configuration, ITO/ZnO/VOPc/MoO_3/Al, under dark and illuminated conditions. These investigations were carried out with the motivation of understanding charge carrier dynamics at ITO/ZnO and ZnO/VOPc interfaces and its effect on the charge transport.

1.1. Experimental details

The schematic of the proposed devices is shown in Fig. 1.

1.2. Preparation of ZnO thin films and fabrication of electron only devices

ZnO nano-particulate thin films were prepared by sol-gel spin coating technique similar to the method used in our previous study [25]. The precursor was prepared by dissolving 4 g of zinc acetate dehydrate [Zn $(CH3COO)_2 \cdot 2H_2O$] in 50 ml of 2-methoxy ethanol. This colloidal solution was stirred for 1 h on pre-heated hot plate (70 °C), and 1.2 ml of monoethanolamine (MEA; acts as a stabilizer) was added drop-wise for about 10 min and the mixture was stirred for about 2 h. The resulting clear solution was aged (48 h) at room temperature to form a gel. The aged sol-gel was spin coated on pre-cleaned and UV-Ozone treated (15 min) patterned ITO coated glass substrates at a spin rate of 500 rpm for first 30s and 1000 rpm for next 30s. The deposited film was baked at 120 °C for 10 min and the process is repeated three times to achieve desired thickness. These films were further annealed in air at either 150 °C, 250 °C, 350 °C or 450 °C for about 1 h. Thickness of the films was about 200 ± 10 nm as measured by spectral reflectometry technique.

For the fabrication of single layer devices, a 100 nm thick aluminium (Al) electrode layer was thermally evaporated on the pre-coated (and annealed) ZnO at a rate of 5–6 Å/s using a shadow mask.

1.3. Fabrication of hybrid p-n junction diode

VOPc (dye content > 85%) was procured from Alfa Aesar and was used without any further purification. A 100 nm thick VOPc layer was deposited on ZnO thin films by thermal evaporation at a base pressure of 8×10^{-6} mbar at a deposition rate of 0.1–0.2 Å/s. Subsequently, a thin layer of Molybdenum Oxide (MoO_3, 3 nm) was deposited at a rate of 0.1–0.2 Å/s to facilitate better hole injection. Finally, a 100 nm thick Al layer (electrode) was deposited as described earlier for the electron only devices.

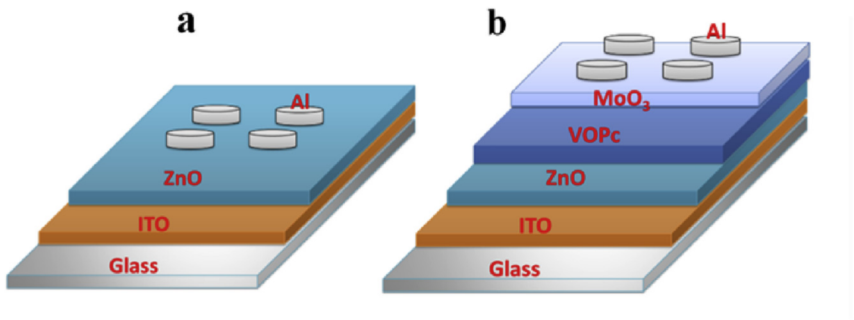

Fig. 1. (a) Schematic of electron only device and (b) schematic for hybrid diode.

Please cite this article in press as: M.R. Kiran et al., Optoelectronic properties of hybrid diodes based on vanadyl-phthalocyanine and zinc oxide, Superlattices and Microstructures (2017), https://doi.org/10.1016/j.spmi.2017.10.023