Synthetic Metals 209 (2015) 164–172

Contents lists available at ScienceDirect

Synthetic Metals

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

Graphene-oxide doped 2.9.16.23-tetrakis-4-{4-[(2E)-3-(naphthalen-1-yl)prop-2-enoyl]phenoxy}-phthalocyaninato cobalt(II)/Au photodiodes

R.O. Ocaya[a], A. Dere[b], H. Tuncer[c], Ahmed A. Al-Ghamdi[d], Derya C. Sari[c], F. Yakuphanoglu[b,d,*]

[a] Department of Physics, University of the Free State, South Africa
[b] Department of Physics, Faculty of Sciences, Firat University, Elazig, Turkey
[c] Department of Chemistry, Faculty of Science, Firat University, Elazig, Turkey
[d] Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

ARTICLE INFO

Article history:
Received 11 June 2015
Received in revised form 8 July 2015
Accepted 10 July 2015
Available online 29 July 2015

Keywords:
Graphene oxide
Cobalt phthalocyanine
Photodiode

ABSTRACT

The device parameters of Al/GO:CoPc/p-Si/Au Schottky diodes were investigated using direct current–voltage (*I–V*), photocurrent and impedance spectroscopy. The ideality factor of the diode was found to depend significantly on GO content. The calculated barrier heights had low variance over the range of illumination intensities per doping level and averaged 0.575 for the undoped diode, and 0.769 ± 0.001 eV taking all the diodes having GO content. Capacitance–voltage (*C–V*) measurements show that the capacitance decreases with increasing frequency, suggesting a continuous distribution of interface states over the surveyed 100 kHz–1 MHz frequency range. The photocurrent characterizations show that the photocurrent increases with illumination intensity suggesting that the devices are suitable for photosensor applications.

1. Introduction

There is currently much theoretical and practical interest in graphene oxide hybrid structures, particularly those that are used in conjunction with organic compounds as scaffolding structures. The interactions between GO and Metallo Pc nanocomposites have been studied in detail by various researchers using varied methods in the literature. It has been shown that the interactions do not follow a simple donor–acceptor mode, but follows a complicated two-way process. Firstly, there is the transfer of electron from the graphitic domain to the adsorbed/intercalated CoPc. It is then followed by feedback from the Co ions through the ligand-like attacking of oxygen functional groups of GO to the central cobalt ions [1,2]. It has also been shown that the adsorption of cobalt phthalocyanine on functionalized graphene yields a tunable hybrid material that allows sensing because of the intrinsic electrical properties provided by functionalized GO and CoPc [3]. Understanding the mechanisms of transfer may open up applications of the nanocomposites to solid-state sensing applications. In this paper, we synthesized a novel naphthylchalcone substituted cobalt phthalocyanine (CoPc) for the first time and graphene oxide doped CoPc nanocomposites with varying contents of graphene oxide. The resulting Schottky diodes have the structure Al/GO_x:CoPc/p-Si/Au where (x) is the weight fraction of GO in the hybrid. The device parameters are established through the use of different characterization methods. Through detailed characterizations using standard methods we show that the constructed devices have a clear potential in photosensing applications.

2. Experimental

2.1. Synthesis of 2.9.16.23-tetrakis-4-{4-[(2E)-3-(naphthalen-1-yl)prop-2-enoyl]phenoxy}-phthalocyaninatocobalt (2)(II)

4-{4-[(2E)-3-(Naphthalen-1-yl)prop-2-enoyl]phenoxy}benzene-1,2-dicarbonitrile, 1 [4] (0.25 g, 0.625 mmol), metal salt Co $(OAc)_2 \cdot 4H_2O$ (0.0778 g, 0.3125 mmol) and 2–3 drops DBU ((1,8-diazabicyclo [5.4.0] undec-7-ene) were heated at 170 °C with 4 mL dry DMF in a sealed glass tube, and stirred for 24 h under argon atmosphere. After cooling to room temperature, the dark green solution treated with DMF (5 mL) and the mixture was poured into 150 mL of ice-water. The precipitate was filtered off and washed with distilled water throughly until the filtrate was neutral. Then product was purified by extraction with tetrahydrofurane,

* Corresponding author: Tel.: +90 424 2370000 3496; fax: +90 424 2330062.
E-mail address: fyhan@hotmail.com (F. Yakuphanoglu).

http://dx.doi.org/10.1016/j.synthmet.2015.07.016
0379-6779/© 2015 Elsevier B.V. All rights reserved.

dichloromethane, acetonitrile, acetone, ethylacetate, ether. Synthesized phthalocyanine is soluble in dimethylformamide, dimethylsulfoxide and chloroform (Scheme 1).

CoPc (2): Yield: 0.2488 g (24%); m.p.: >300 °C. IR υ_{max} (cm^{-1}) (KBr): 3057–3025 (Ar—H), 1654 (C=O), 1595–1485 (HC=CH), 1269 (Ar—O—Ar). ^1H NMR [DMSO-d_6,δ(ppm)]: 6.90–8.55 (m, broad, 64H, ArH). UV–vis (DMF) λ_{max} (log ε) (nm): 670 (4.93), 612 (4.20), 330 (5.15). Anal. Calc. for $C_{108}H_{64}N_8O_8Co$ (1660.64): C, 78.11; H, 3.88; N, 6.75%. Found: C, 78.80; H, 3.99; N, 6.63%. MS (MALDI-TOF) m/z: 1660.925 $[M]^+$, 1662.925 $[M+2]^+$.

The graphene oxide (GO) was synthesized by the modified Hummers method as described in the literature [4,5]. The

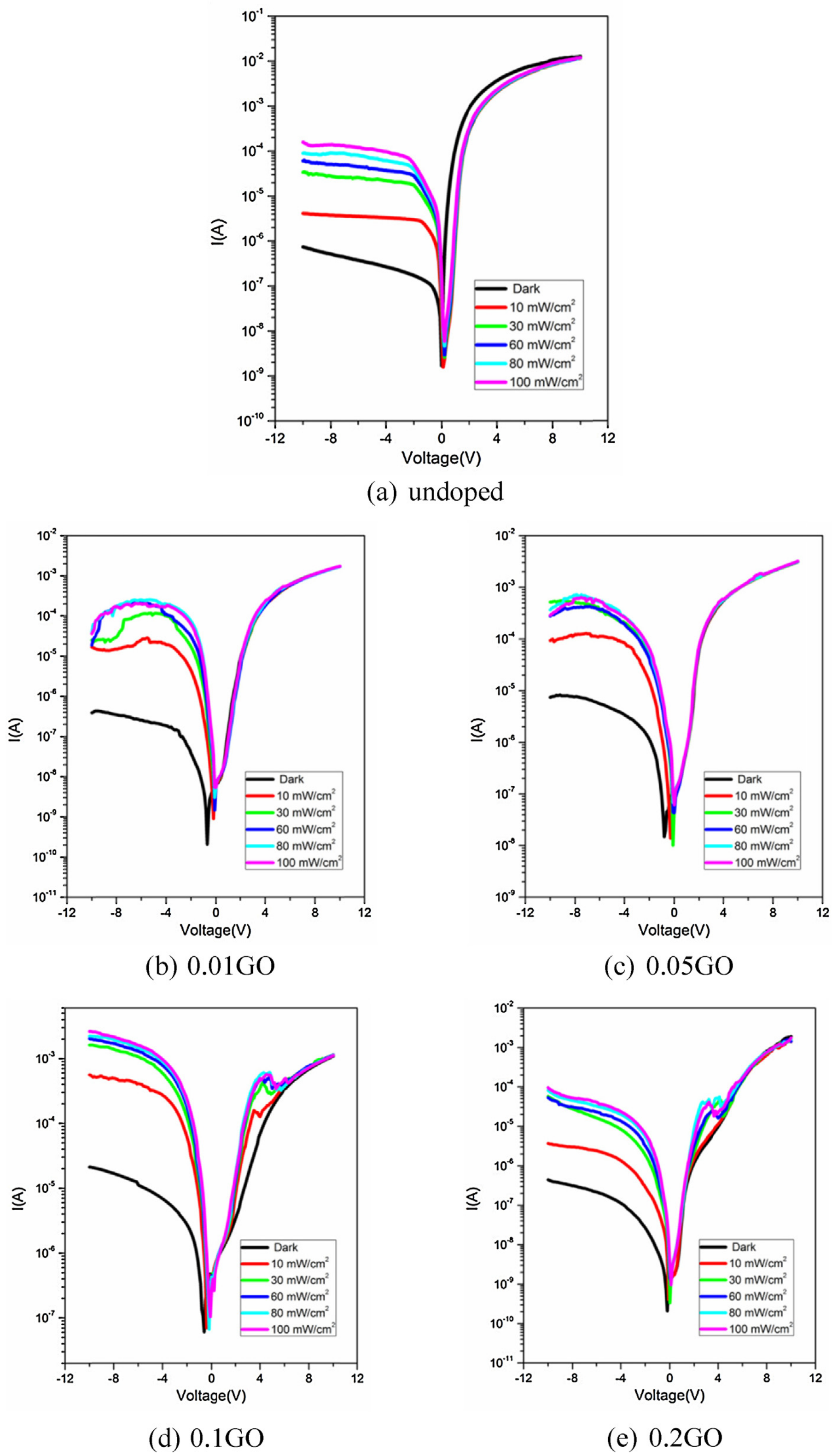

Fig. 1. Current–voltage characteristics of the diode under different illumination intensities and GO doping levels.