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High performance organic-on-inorganic hybrid photodiodes based on organic semiconductor-graphene oxide blends

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ABSTRACT

Graphene has attracted considerable research interest due to its unique electrical and optical properties. In present work, we have utilized nanocomposites of poly(3,4-ethylene dioxythiophene):poly(styrene-sulfonate)/graphene oxide (PEDOT:PSS–GO) to fabricate the photodiodes. The current–voltage (*I*–*V*) characteristics of the PEDOT:PSS–GO/p-Si junctions having various compositions of GO were studied under dark and illumination conditions. It was observed that the photocurrent of the device increases with increase of GO concentration in the composite. The ideality factors of the diodes having 0.03, 0.05, and 0.1% of GO in the PEDOT:PSS–GO composites were obtained to be 5.43, 5.62, and 2.49, respectively. The diode having 0.1% of GO exhibited the highest photoresponse performance. The obtained results indicate that PEDOT:PSS–GO composites have high potential in photosensor applications.

1. Introduction

Transparent conducting electrodes have been widely studied because of their applications in flat panel displays, solar cell, metal/semiconductor diode [1–4]. Among various organic semiconductors, poly(3,4-ethylene dioxythiophene):poly(styrene-sulfonate) abbreviated as PEDOT:PSS is a very promising material because of its low sheet resistance, high optical transparency, and easy processability even on flexible substrates [5–7]. On the other hand, graphene films are also one of the most favorable candidates for next generation transparent conductive electrodes [8–10]. The high interest in graphene based materials is due to its unique electronic and optical properties.

The effects of temperature on morphological, optical and electrical properties of PEDOT-PSS films were reported [11]. The important finding of the work is that the electrical conductivity shows anisotropic behavior; the electrical conductivity being of about five order of magnitude higher in the direction parallel to the substrate. Kumar et al. [12] have investigated the effect of PEDOT:PSS interlayer on the Schottky barrier parameters of Pt/n-Ge Schottky contacts. It was observed that the PEDOT:PSS interlayer influences the space charge region of the Schottky junction, leading to increase in the barrier height. The effects of multiwall carbon nanotubes on the optical and electrical properties of PEDOT-PSS were studied [13]. It was reported that the reaction time has high influences on the electrical resistance of the films. High reaction time leads to low resistance of the films.

Recently, Shin et al. [14] have shown enhanced performance of organic light-emitting diodes by using hybrid anodes composed of graphene and PEDOT-PSS. The hybrid electrode can overcome low work function and high sheet resistance leading to enhance performance. The devices with hybrid anode showed the better performance of eight times in the luminance than single anode device. Wu et al. [7] have also reported that OLED based on doubled layer graphene/PEDOT-PSS electrodes showed better performance. Recently, we have utilized graphene oxide (GO) for fabrication of photodiodes [15].

In present study, we report the effect of graphene oxide on the diode characteristics of PEDOT-PSS/p-Si. The diodes were fabricated using spin coating technique on p-silicon substrate. The structural and electrical properties of the films were investigated in

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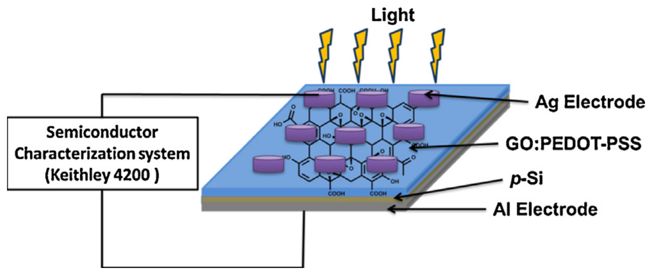

Fig. 1. Schematic diagram of the fabricated diode.

detail. The effects of light on the electronic properties of the diodes were also investigated. The present work suggests that these diodes could be used for photo sensing applications.

2. Experimental details

The graphene oxide was synthesized by the modified Hummers method as described in the literature [15,16]. The synthesized GO was dispersed in deionized water (1.5 mg/mL) using stirring for 10 min. After 10 min, it was ultrasonicated for 2 h to exfoliate GO sheets from the multilayer flakes. The nanocomposites of PEDOT:PSS and GO were prepared using PEDOT:PSS and GO solutions having different weight rations of GO (0.03, 0.05 and 0.1 at.% of GO). The films of PEDOT:PSS–GO were coated onto surface of p-Si substrate using a spin coater with 7000 rpm for 60 s. The thermal treatment was done at 260 °C for 1 h to reduce graphene oxide to graphene.

Before deposition of the PEDOT:PSS–GO composite, the native oxide layer of the silicon substrate was etched by HF and then rinsed in deionized water using an ultrasonic bath for 10–15 min. Finally, the silicon wafer was chemically cleaned according to method based on successive baths of methanol and acetone. Top contact of the diodes was prepared by Ag metal. For this, Ag metal was evaporated by thermal evaporation system in the form of circles with area of 3.14×10^{-2} cm^2. The schematic diagram of the fabricated diode is shown in Fig. 1. Surface morphology of the films was investigated using a PARK system XE 100E atomic force microscopy (AFM). The current–voltage (I–V) characteristics of the diode were performed with KEITHLEY 4200 semiconductor characterization system. Photoresponse measurements were performed using a solar simulator. The intensity of sun light was measured using a solar power meter (TM-206).

3. Results and discussion

The X-ray diffraction technique was used to check the synthesis of graphene oxide. The X-ray diffraction patterns of graphite flaks (starting material) and graphene oxide are shown in Fig. 2. As seen in Fig. 2, the XRD pattern of the graphite shows two distinct sharp characteristic peaks at $2\theta = 26.4°$ and 54.5°. The observed peaks for graphite are in good correlation with the hexagonal phase of graphite (JCPDS File: 00-041-1487). The peaks at 26.4° and 54.5° can be leveled as (0 0 2) and (0 0 4). On the other hand, the XRD pattern of graphene oxide shows a broad peak around 10.63°. This peak corresponds to the interlayer spacing of 8.32 Å. The presence of the peak at 10.63° indicates that oxygenated groups and H_2O molecules have been inserted in the in the interlayer of the graphite which causes increase in the interlayer spacing [17]. This result indicates that graphene oxide was successfully exfoliated from the graphite flaks [18].

The microstructure of the PEDOT:PSS–GO composite films were studied using atomic force microscopy (AFM). The AFM images of the films having different compositions are shown in Fig. 3. As seen in AFM images, the films having higher amount of graphene oxide shows sheet like structures.

The homogeneity of PEDOT:PSS–GO composite films was provided using optimum speed of spin coater with 7000 rpm for 60 s. For this rpm, the film indicates almost a homogenous surface on silicon substrate which was confirmed using AFM image. We coated the films under 7000 rpm for 60 s to find the same thickness. To confirm this, the film thicknesses of the films were determined using AFM and were found to be about 100 nm (Fig. 3).

The effects of light on the electrical properties of the diodes having different compositions were studied and compared with the electrical properties measured under dark as shown in Fig. 4. All the diodes show rectifying behavior in current–voltage measurements. It was observed that light has significant effect on the electrical properties of these devices. The reverse bias current increases by almost two order for the diodes having 0.1 and 0.05 at.% of GO in the composite films, whereas it increases about one order of magnitude for the composite having 0.03 at.% of GO. The current–voltage characteristics of the diodes can be expressed by the following relation,

$$I = I_0 \exp\left(\frac{q(V - IR_S)}{nkT}\right) \quad (1)$$

where V is the applied voltage, q is the electronic charge, n is the ideality factor, k is the Boltzmann constant, T is the temperature, R_S is the series resistance, and I_0 is the reverse saturation current. The reverse saturation current I_0 can be expressed as [19]

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

where A is the active device area, A^* is the Richardson constant (equal to 32 A/cm^{2}K^2 for p-type silicon) and ϕ_b is the barrier height [20]. The ideality factor is determined from the slope of the linear region of forward bias $\ln I$–V plot. The ideality factor of the diodes having 0.03, 0.05, and 0.1% of GO was observed to be 5.43, 5.62, and 2.49 respectively. The higher value of the ideality factor (ideal

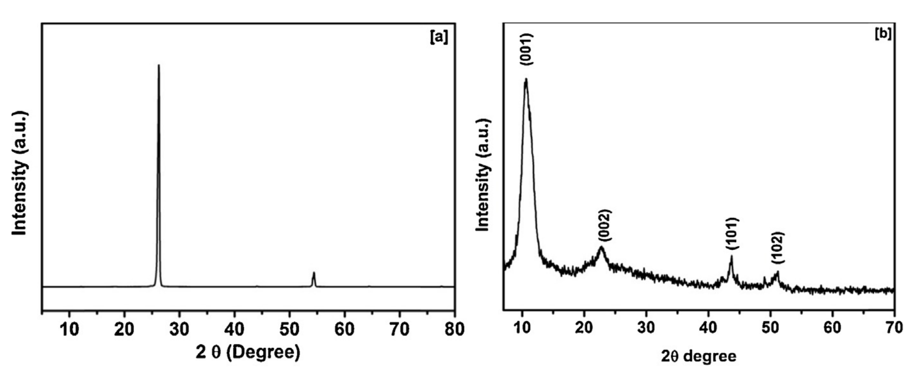

Fig. 2. XRD patterns of (a) graphite and (b) graphene oxide.