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Investigation of reduced graphene oxide effects on ultra-violet detection of ZnO thin film

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HIGHLIGHTS

- The pure ZnO and reduced graphene-oxide (rGO) incorporated composite films were synthesized by dip-coating.
- By increasing the rGO content in composite films, the transparency and corresponding calculated band-gap of the films was a little decreased.
- The electrical resistivity of the samples was decreased by adding rGO.
- The addition of rGO regulated the sensitivity, time of response (and/or recovery) and corresponding signal to noise ratio.

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ABSTRACT

The reduced graphene oxide (rGO) incorporated ZnO thin films were fabricated by dip-coating method. The Raman and FT-IR spectra of 0.075 wt% incorporated composite film showed reduction of GO in composite film. The transmittance Prod. Type: FTP spectra have shown that rGO incorporation increase the visible light absorption of ZnO thin film while the calculated band gaps of samples were decreased from 3.28 to 3.25 eV by increasing the rGO content. The linear trend of *I–V* curve suggests an ohmic contact between ZnO and rGO. Besides, it was found that by increasing the rGO content, the electrical resistivity was decreased from $4.32\times10^{2}\ \Omega$ cm for pure ZnO film to $2.4\times10^{1}\ \Omega$ cm for 0.225 wt% rGO incorporated composite film. The composite photodetectors not only possessed a desirable UV photosensitivity, but also the response time of optimum sample containing 0.075 wt% rGO was reduced to about one-half of pure ZnO thin film. Also, the calculated signal to noise (SNR) showed that highly conductive rGO in composite thin films facilitate the carrier transportation by removing the trapping centers. The mechanism of photoresponsivity improvement of composite thin films was proposed by carrier transportation process.

1. Introduction

Semiconductor photodetectors have always shown a great promise for UV detection because of their cheapness and simplicity. Some important applications of an ultraviolet (UV) detector are in situ combustion monitoring gas, satellite-based missile plume detection, air quality monitoring, gas sensing, accurate measurement of radiation for the treatment of UV irradiated skin, etc [1,2]. Among the various studied semiconductors, ZnO has gotten more attention as an UV-detector because of its low cost, wide direct band gap (3.3 eV), and high exciton binding energy (~60 meV at room temperature) [3]. Besides, some benefits of ZnO thin film such as the high radiation and chemical stability propose it as a strong potential for ultraviolet (UV) detection or non-linear optical device in UV range [4]. Nevertheless, pure ZnO suffers from the low operating speed and the weak responsivity drawbacks. In order to solve these inadequacies for UV detection, it is convenient to synthesize the optimized UV sensitive layers whose strong photochemical stability can be tailored to considerable sensitivity.

Therefore, some of the recent studies have been focused on modification of the UV photosensitivity of ZnO either with doping by metallic (or non-metallic) elements [5–10] or fabrication of hierarchical nanostructures with improved physical properties [3]. Concerning the nonmetallic additives, carbonaceous allotropes have been proposed as a powerful candidate for improvement of UV photoresponsivity due to unique physical properties, exciton pair recombination inhibition, and low response time resulted by the presence of carbonaceous conductive pathway for careers [10–12].

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Recently, Chang et al. [9] have studied the UV photoresponsivity of a layer by layer fabricated ZnO/SWCNT hybrid system. Their results showed a fast response for hybrid films due to the rapid transportation of UV excited electron–hole (e/h) pairs by conductive SWCNTs. The same photodetector based on hybrid polymer–ZnO quantum dots (QDs)—graphene layer showed a significant improvement of UV-sensitivity [12]. However, a few works based on the ZnO/graphene composite thin film have been reported and that's the objective of this study to investigate the structural and optical characteristic of composite thin films. In this work, we synthesized the ZnO–rGO composite thin films with different graphene contents by sol–gel method. Afterward, in order to evaluate the feasibility of the samples as UV detector, the conductivity and UV photoresponsivity of the films were measured and a mechanism was proposed in this regard.

2. Experimental

2.1. Preparation of graphene oxide

The well-known modified Hummers method was used for preparation of graphene oxide (GO) [13]. In summary, 1 g of graphite powder was added to 25 ml sulfuric acid at 273 K. $KMnO_4$ was added drop wise and then, the solution warmed to 298 K and stirred for 30 min. Then, the slurry was warmed to 308 K and once again, it was kept stirring for 30 min. The slurry was then slowly diluted by 350 ml distilled water. After that, H_2O_2 (30%) was added to mixture until the color of mixture was turned to brownish yellow. The slurry was filtered and dried and then, the layers of GO were exfoliated by thermal shock at 1323 K. The GO nanosheets were collected and used without further treatments.

2.2. Preparation of thin films

In order to fabricate the composite films, the as synthesized GO powder was dispersed in ethanol (5 mg/ml) by 30 min ultrasonication until a very stable solution with brownish dark color was prepared. In a separate beaker, the ZnO sol was prepared by dissolving zinc acetate ($Zn(CH_3COO_2)\cdot 2H_2O$; Merck KGaA, 64271 Darmstadt, Germany) in ethanol (0.5 M) and subsequently adding diethanolamine (DEA/ZnAc=6/5) into the solution. Then, the resultant solution was stirred at 333 K for 30 min to yield a transparent and homogeneous sol which was considered for the dip-coating process.

The stable GO containing suspension was added dripped to already prepared sol while the ratio of GO to ZnO was adjusted between 0 and 0.225 wt%. Afterwards, the admixed sol was stirred again for 30 min. The films were coated by dipping a cleaned glass substrate in the prepared sol for 2 min and pulling up vertically at constant speed of 35 mm min^{-1}. The obtained samples were dried at 373 K for 10 min and this procedure was repeated 2 times to obtain a thicker and more uniform films. Then, the films were annealed at 623 K in air for 1 h to prepare pure and incorporated composite thin films. The annealing temperature of 623 K was selected for both (a) ZnO crystallization and (b) decomposition reduction of graphene oxide. Along this, Wang et al. [14] found that thermal decomposition of graphene oxide could be occurred at around 600 K under an ambient atmosphere.

2.3. Characterization

Crystalline structure of the prepared samples was characterized by X-ray diffraction (XRD) using a PW1800 Philips diffractometer. The surface morphology of the samples was characterized by a Hitachi SE4160 field emission scanning electron microscopy (FESEM) apparatus at working voltage between 15 and 30 kV. Moreover, the surface topography and height profile of GO nanosheets were studied by atomic force microscopy in tapping mode using a (AFM, Digital Instruments Nanoscope V). Raman spectroscopy was used to confirm both the reduction and presence of GOs in the composite thin films using a dispersive Raman Microscope Senterra–Bruker equipped by CCD detector. Fourier transform infrared (FTIR) spectrum in transmittance mode was recorded on a Nicolet spectrometer. The optical transmittance of the films was measured by UV–Vis spectrophotometer (Perkin Elmer) in the wavelength range of 200–600 nm. The optical band gap energy of the samples was calculated using the well-known Tauc method [15]. The electrical resistivity of the films was measured by the simple 2 electrode method.

2.4. UV detection measurement

UV photocurrent sensitivity of various samples was measured using a purpose-built dark box. The box has a vertically adjustable holder clamped to a 8 W Philips black-light UV-A lamp. The precise values of UV as well as visible light intensities were measured by UV light meter Lutron 340A and visible light meter pro TES 1339R, respectively. To measure the conductivity and UV photoresponsivity, the comb-like gold terminals with 1 mm spacing were sputtered on each sample and copper wires were bonded to the terminals by silver conductive adhesive. The samples connected to a known resistor in series and 2.0V-DC was applied through the circuit. The DC voltage across the known resistor was read out using a A/D converter interfaced to computer for further processing. The purpose-built box was equipped with a shutter unit for ultrafast opening/closing the light entrance aperture (Fig. 1).

Signal-to-noise ratio (often abbreviated SNR or *S*/*N*) is a measure used in engineering that compares the level of a desired signal to the level of background noise [16]. It is defined as the ratio of signal power to the noise power. Signal-to-noise ratio is sometimes used informally to refer to the ratio of useful information to false or irrelevant data. If the signal and the noise are

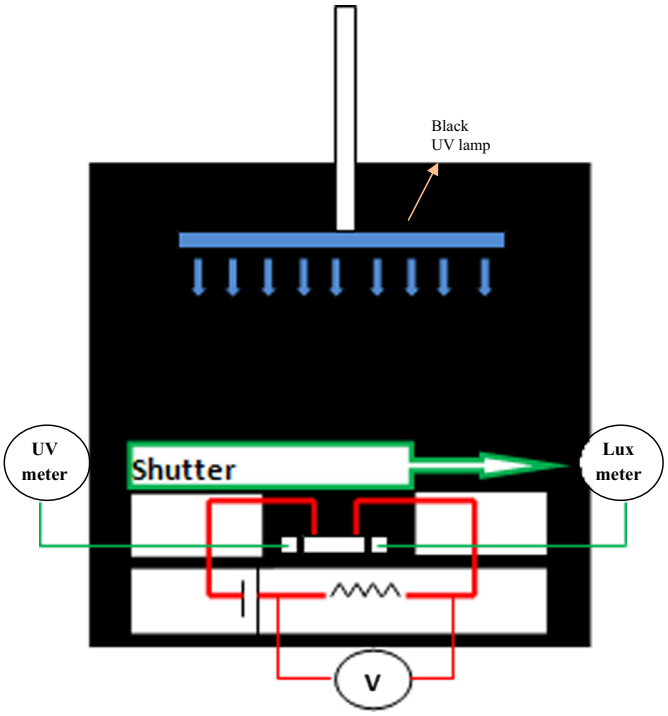

Fig. 1. Schematic view of the UV photocurrent measuring box.