Journal of Colloid and Interface Science 416 (2014) 289–293

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Photoluminescence investigation about zinc oxide with graphene oxide & reduced graphene oxide buffer layers

Jijun Ding, Minqiang Wang *, Xiangyu Zhang, Zhi Yang, Xiaohui Song, Chenxin Ran

Electronic Materials Research Laboratory, Key Laboratory of Ministry of Education, School of Electronic and Information Engineering, International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

ARTICLE INFO

Article history:
Received 19 August 2013
Accepted 21 October 2013
Available online 8 November 2013

Keywords:
ZnO films
Graphene oxide
Reduced graphene oxide
Tunable photoluminescence

ABSTRACT

ZnO with graphene oxide (GO–ZnO) & reduced graphene oxide (rGO–ZnO) buffer layers were fabricated. Photoluminescence (PL) properties of GO–ZnO and rGO–ZnO compositions induced by oxygen vacancies defects were investigated using photoluminescence spectroscopy. The results showed that blue emission is quenched while yellow–orange emissions from GO–ZnO and rGO–ZnO compositions are significantly increased as compared to that of ZnO films. In stark contrast to enhanced yellow–orange emissions, PL spectra show three sharp, discrete emissions that characterize the dominant optical active defect, which is the oxygen vacancies and extended oxygen vacancies. Our results highlight the ability of GO & rGO buffer layers to modulate defect concentrations in ZnO and contribute to understanding the optical properties of deep-level defects, which is significant for development of long-wavelength photoelectric devices related with graphene materials.

1. Introduction

Graphene oxide (GO) is a graphene sheet modified with oxygen functional groups [1], and it exhibits interesting steady-state photoluminescence (PL) properties [2–4]. Such as, Eda et al. observed, in chemically derived GO, a relatively narrow PL peak centered at 390 nm and an apparently equivalent PL peak centered at 440 nm [5]. Luo et al. reported broadband visible PL from solid GO and discussed possible gapping mechanisms [6]. Mei and Zhang synthesized highly photoluminescent GO nanosheets and proposed a fluorescence “off-to-on” mechanism [7,8]. PL has been reported in chemically modified GO where the electronic structure has been modified [9].

Chien et al. reported tunable PL of GO with increased reduction [10]. Xin et al. also observed tunable PL of GO from near-ultraviolet to blue region through controlled hydrazine (N_2H_4) reduction [11]. In addition, reduced graphene oxide (rGO) also exhibits interesting steady-state PL properties. Cuong et al. demonstrated that optical emissions of rGO were ascribed to recombination of electron–hole pairs in localized electronic states [12]. Lui et al. observed significant light emission from graphene under excitation by ultrashort (30-fs) laser pulses [13]. Gokus et al. confirmed making graphene luminescent by oxygen plasma treatment [2].

ZnO is an II–VI semiconductor with a wide and direct band gap ($E_g = 3.37$ eV at 300 K), excellent chemical and thermal stability, and specific electrical and optoelectronic property of having a large exciton binding energy (60 meV) [14]. It possesses many important applications in electronic and optical devices [15,16]. Hybridization of carbon materials with ZnO offers a powerful way to obtain many interesting properties. Interestingly, optical properties of graphene & GO and ZnO composites have also been investigated. Such as, Yang et al. reported UV–vis absorption properties of functionalized graphene sheets (FGS)/ZnO nanocomposites exposed under UV light at regular time intervals [17]. Luo et al. presented UV–vis diffused reflectance spectra from RGO-hierarchical ZnO hollow sphere composites [18]. Kavitha et al. prepared graphene nanosheets decorated with ZnO nanoparticles which showed an emission peak at 400 nm associated with the recombination of excitons in ZnO [19]. Singh et al. investigated ZnO decorated with different molar ratios GO, and as the concentration of GO was increased, the PL quenching extent at 550 nm increased and observed large blue-shift of 0.15 eV in PL [20]. These ZnO decorated GO & rGO sheets display distinct optoelectronic characteristics, emitting near-ultraviolet to blue-green luminescence. However, other longer wavelength emission can also be expected for GO–ZnO and rGO–ZnO compositions, which is significant for development of low cost nanodevices. To our knowledge, there are no reports about the modulation of GO & rGO on larger wavelength range emission of ZnO. Also, PL mechanism in these compositions is still not clear.

In this paper, GO & rGO sheets were deposited on indium tin oxide (ITO) substrates by electrophoretic deposition (EPD), and then ZnO films were deposited on down-layer GO & rGO sheets

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* Corresponding author. Fax: +86 29 82668794.
E-mail address: mqwang@mail.xjtu.edu.cn (M. Wang).

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http://dx.doi.org/10.1016/j.jcis.2013.10.059

by magnetron sputtering technique to prepare GO–ZnO and rGO–ZnO compositions. The crystal structures, morphology, optical properties were analyzed by using X-ray diffraction (XRD) pattern, atomic force microscopy (AFM) and scanning electron microscopy (SEM) images, Raman spectra, PL and photoluminescence excitation (PLE) spectra. The effect of GO & rGO on PL spectra ranging from 300 to 800 nm of ZnO is investigated. PL mechanism in these compositions is proposed based on these experimental results.

2. Materials and experiments

Natural graphite (99.9%) powders are commercially available from Wodetai Ltd., Co., Beijing, China. ZnO target (prior to 99.99%, 3 inch in diameter) is commercially available from General Research Institute for Nonferrous Metals, Beijing, China.

GO–ZnO and rGO–ZnO compositions were fabricated by the following procedures. Firstly, GO was prepared from natural graphite by a classical Hummers method with some modification [21]. The exfoliated GO was obtained in the supernatant. The rGO used here was reduced from GO followed a convenient method under a low-temperature and atmosphere pressure in our previous work [22]. Finally, GO and rGO were dispersed to form solutions with an ultrasonic, followed by centrifuging at 4800 rpm for 30 min. Then, GO & rGO sheets were deposited on indium tin oxide (ITO) substrates by electrophoretic deposition (EPD). ITO was acted as working electrode and platinum plate was cathode that was kept 15 mm away from the counter electrode. The evenly dispersed GO & rGO solutions were used directly as electrolyte, and the concentration of GO & rGO in the solution was assigned to 0.5 mg/ml. A constant current of 0.2 mA was applied for 20 min to coat GO & rGO on the ITO substrates. Finally, ZnO films were deposited on down-layer GO & rGO sheets by magnetron sputtering technique. The base pressure for the system was 2×10^{-4} Pa and film growth was carried out in the sputtering ambient with $Ar:O_2 = 4:1$ (sccm) at a working pressure of 0.8 Pa. ZnO films were deposited on down-layer GO & rGO sheets with sputtering power of 100 W used during sputtering for 1.5 h.

XRD patterns were studied by using a D/Max-2400 X-ray diffractometer. AFM and SEM images were characterized by a Dimension Icon3 atomic force microscope and a FEI Quanta 250 scanning electron microscope, respectively. Raman spectra were investigated using a JY LabRAM HR800 laser Raman spectrometer from 1000 to 4000 cm^{-1} at room temperature. The 514.5 nm line of the laser was used as the excitation source. PL spectra within 350–650 nm measurements were carried out by a LS-55 fluorescence spectrometer under the 325 nm excitation wavelength. PL spectra within 450–800 nm were done using a SENS-9000 fluoroSENS fluorescence spectrometer under the 426 nm excitation wavelength. PLE spectra were measured using a SENS-9000 fluoroSENS fluorescence spectrometer monitored at 606 nm. All spectra were measured at room temperature in air.

3. Results and discussions

Fig. 1 shows XRD patterns of as prepared GO and rGO. As prepared GO shows a sharp diffraction peak centered at $2\theta = 10.8°$ corresponding to GO (002). In XRD pattern of as prepared rGO, GO (002) diffraction peak completely disappears and there occurs a broad diffraction band ranging from 10° to 30°, which indicates that the GO is completely reduced and there presents few defects in rGO during chemical reduction process.

Fig. 2 shows XRD pattern of ZnO films, GO–ZnO and rGO–ZnO compositions. In these XRD patterns, a major peak could be indexed to ZnO (002), indicating that all the compositions are single crystalline and oriented along c-axis of hexagonal structure [23]. Fujimura et al. [24] suggested that the surface energy density of the (002) orientation is the lowest in the ZnO crystal. This means that the (002) texture of the film may easily form. This texture growth results in good crystalline quality. Some minor peaks could be ascribed to ITO substrates. Generally, the above mentioned GO (002) and rGO (002) are theoretically expected to be observed in the XRD pattern of GO–ZnO and rGO–ZnO compositions. However, they did not appear in the corresponding compositions, indicating that the surfaces of rGO are fully covered by ZnO films [25,26]. Therefore, it can be seen that the diffraction peaks are mainly from the up-layer ZnO phase in the GO–ZnO and rGO–ZnO compositions.

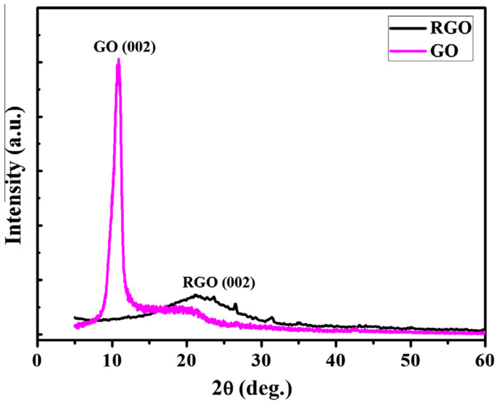

Fig. 1. XRD pattern of as prepared GO and rGO.

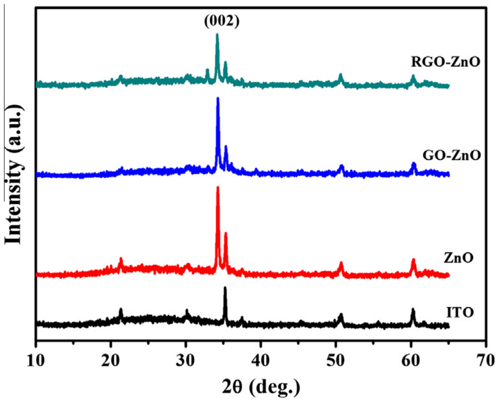

Fig. 2. XRD pattern of ZnO films, GO–ZnO and rGO–ZnO compositions.

Table 1 shows XRD parameters of ZnO films, GO–ZnO and rGO–ZnO compositions. The average crystallite size D was calculated by the following Scherrer formula [27]:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \tag{1}$$

where λ, θ and β are the X-ray wavelength (1.5406 Å), diffraction angle and the full width at half-maximum (FWHM) of the ZnO (002) peak. As can be seen from Table 1, GO–ZnO compositions have the minimum FWHM and the largest crystallite size.

Table 1
XRD parameters of ZnO films, GO–ZnO and rGO–ZnO compositions.

	FWHM (°)	D (nm)	σ (MPa)	d_{hkl} (nm)
ZnO films	0.216	38.1	1.0742	0.2614
GO–ZnO	0.200	41.1	1.0742	0.2614
rGO–ZnO	0.204	40.3	1.7007	0.2621