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ZnO quantum dots-graphene composite for efficient ultraviolet sensing

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ABSTRACT

ZnO quantum dots-graphene (QDs-graphene) composite was synthesized using atomic layer deposition method. A photodetector fabricated from the ZnO QDs-graphene composite and polymers demonstrated high sensitivity to UV light with a maximum photoresponsivity of 247 A/W at 325 nm. The high photoresponsivity of this device is attributed to the high active surface to volume ratio of the ZnO QDs-graphene composite. In addition to the high photoresponsivity, fast transient response with response time on the order of tenth of milliseconds was achieved, which is attributed to high carrier transport and collection efficiency through the graphene.

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1. Introduction

ZnO is a promising candidate for UV photodetector applications due to its unique optical and electrical properties including direct wide band gap (3.37 eV), large exciton binding energy (60 meV) and strong resistance to high energy proton irradiation [1,2]. Various ZnO nanomaterials have been used for fabrication of ultraviolet (UV) photodetector with high photoconductive gain and high responsivity [3–5]. However, these UV photodetectors suffered poor transient response (with response time up to minutes), which is attributed to surface defects and oxygen adsorption/desorption process of ZnO nanomaterials. Therefore, it is highly desirable to improve the transient response of ZnO nanomaterial for fast UV sensing.

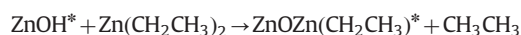
By now, different methods have been developed to improve the transient response of ZnO based UV photodetectors, which include hydrogen doping, oxygen plasma treating, deposition of carbon nanotube network, and graphene shell coating [6–9]. Among all of them, the combination of graphene with ZnO is one of the most promising methods, as it can effectively improve the carrier transport and collection efficiency of ZnO based UV photodetectors, leading to a high responsivity and fast transient response [9,10].

In this work, ZnO QDs-graphene composite was synthesized using the atomic layer deposition (ALD) method for UV photodetector applications. By using the ALD method, the ZnO QDs-graphene composite achieved very high active surface to volume ratio, which is preferable for photocurrent generation. In addition,

the high carrier mobility of graphene enabled efficient carrier transport and collection in the composite, leading to a high performance of this UV photodetector in terms of speed and photoresponsivity.

2. Experimental

ZnO ALD films were grown directly on graphene powders using a rotary ALD reactor [11]. For the ZnO ALD, diethyl Zinc ($\text{Zn}(\text{CH}_2\text{CH}_3)_2$) and high performance liquid chromatography (HPLC) grade H_2O were obtained from Sigma-Aldrich. The typical growth rate for the ZnO ALD chemistry is $\sim 2 \text{ \AA}$ per cycle [12,13]. ZnO ALD is performed using alternating $\text{Zn}(\text{CH}_2\text{CH}_3)_2$ and H_2O exposures:



where the asterisks represent the surface species. Without an adhesion layer that is provided by Al_2O_3 ALD, the ZnO ALD is expected to nucleate and grow at defects on the graphene surface [14]. Growth at these defects will result in a distribution of ZnO quantum dots instead of conformal ZnO thin film.

A UV photodetector was fabricated by sandwich the ZnO QDs-graphene composite in conductive polymers. All the chemicals were purchased from Sigma-Aldrich and used without further purification. First, a thin layer of N,N'-Di-[(1-naphthyl)-N,N'-diphenyl]-1, (1'-biphenyl)-4,4'-diamine (NPD) with thickness around 50 nm was deposited onto pre-cleaned ITO glass substrates through spin coating and then annealed in air at 120 °C for 10 min. The NPD act as a hole transport/electron blocking layer [15]. Then, the ZnO

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QDs-graphene composite was dispersed in dimethylformamide (DMF) solvent and spun coated on top of the NPD layer to form the active region of the device. After that, a thin layer of 2,9-Dimethyl-4,7- diphenyl-1,10-phenanthroline (BCP) with thickness around 30 nm was evaporated onto the top of the active region as an electron transport/hole blocking layer and annealed in air at 5 °C for 30 min [16]. Finally, aluminum contact with thickness of 150 nm was deposited on top of the device through e-beam evaporator.

A Carl Zeiss Ultra 1540 dual beam scanning electron microscope (SEM) was used to determine the morphology of the ZnO QDs-graphene composite. High resolution transmission electron microscopy (HR-TEM) studies were carried out in a HR-TEM microscope (JEOL 2011) at an operating voltage of 200 kV. X-ray diffraction (XRD, PANalytical) pattern of the ZnO QDs-graphene composite was measured at room temperature using Cu $K\alpha$ radiation. The typical I - V characteristics and transient response of the UV photodetector were measured using a HP4155B semiconductor parameter analyzer under dark and with UV illumination at 335 nm. The photoresponsivity of the device was measured by Shimadzu UV-vis 2550 spectrophotometer with a deuterium lamp (190–390 nm) and a halogen lamp (280–1100 nm).

3. Results and discussion

Material characterizations: The SEM images of the ZnO QDs-graphene composite are shown in Fig. 1A and B. It is clear from Fig. 1B that the ZnO QDs-graphene composite have very high active surface to volume ratio, as the ZnO QDs are uniformly deposited on

both top and sidewall of the shale like graphene sheet. Fig. 1C is the HR-TEM image of the composite structure. The average diameter of the ZnO QDs is estimated to be around 9 nm. The XRD pattern of the ZnO QDs-graphene composite is presented in Fig. 1D. All the peaks are identified and assigned according to the Joint Committee of Powder Diffraction Standards (JCPDS) data. The graphene shell has a broad (002) peak centered at around 24.5°, corresponding to an interlayer spacing of 0.37 nm [17]. The rest peaks can be well indexed to the wurtzite ZnO (JCPDS #36-1451).

Device characterizations: The structure and energy band diagram of the UV photodetector is shown in Fig. 2A and B, respectively. The typical I - V characteristics of the photodetector are shown in Fig. 3A. The photocurrent to dark current ratio at -10 V is approximately 230, which is more than 40 times higher than that of at 10 V. This is attributed to lower dark current under reverse bias condition, which can be understood by referring to the energy band diagram in Fig. 2B. Under reverse bias condition, the high barrier between BCP and Al together with BCP's hole blocking ability, can effectively impede hole injection from the Al contact. Similarly, electron injection from the ITO side can be greatly suppressed due to the high barrier between ITO and NPD, together with NPD's electron blocking ability. To the contrary, under forward bias condition, the electrons and holes can easily be injected from Al to BCP and from ITO to NPD, leading to higher dark current compared to reverse biased condition.

The transient response of the device is shown in Fig. 3B. The rise time and fall time of the device were measured to be around 14 and 11 ms, respectively. The fast transient response of the photodetector in this work is attributed to improved carrier transport process

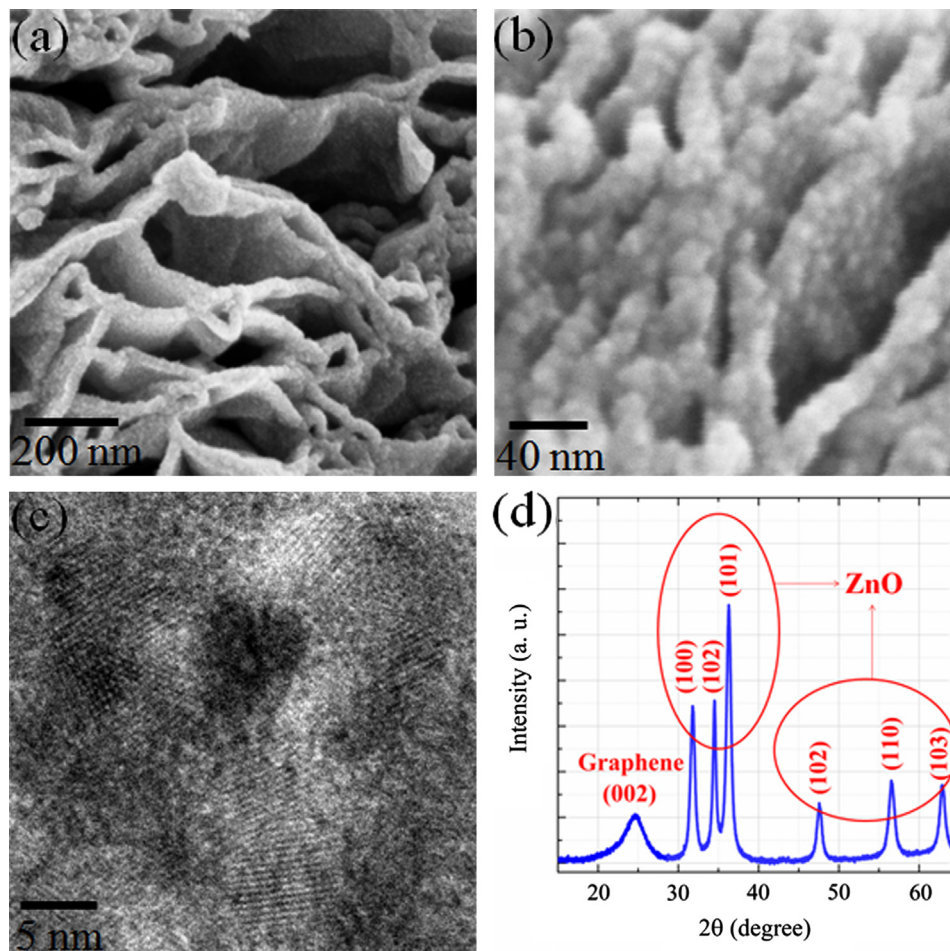


Fig. 1. (A and B) SEM images and (C) HR-TEM image of the ZnO QDs-graphene composite synthesized via ALD method. (D) XRD pattern of the ZnO QDs-graphene composite.

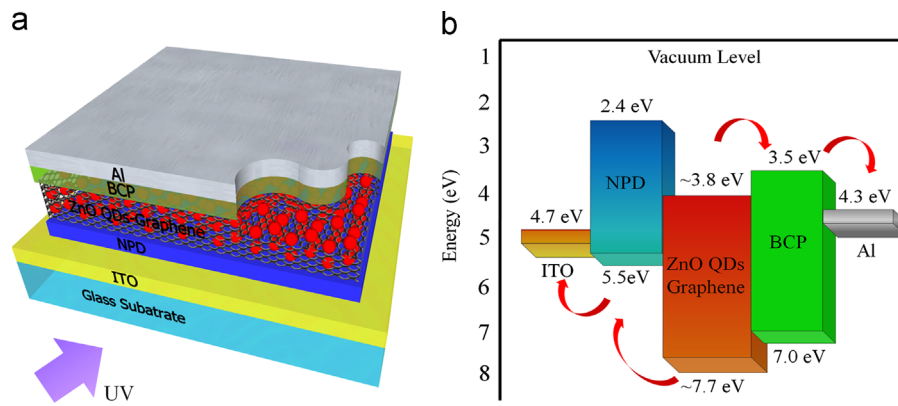


Fig. 2. (A) Schematic illustration of the hybrid UV photodetector fabricated from ZnO QDs-graphene composite material and polymers. (B) Energy band diagram of the device.

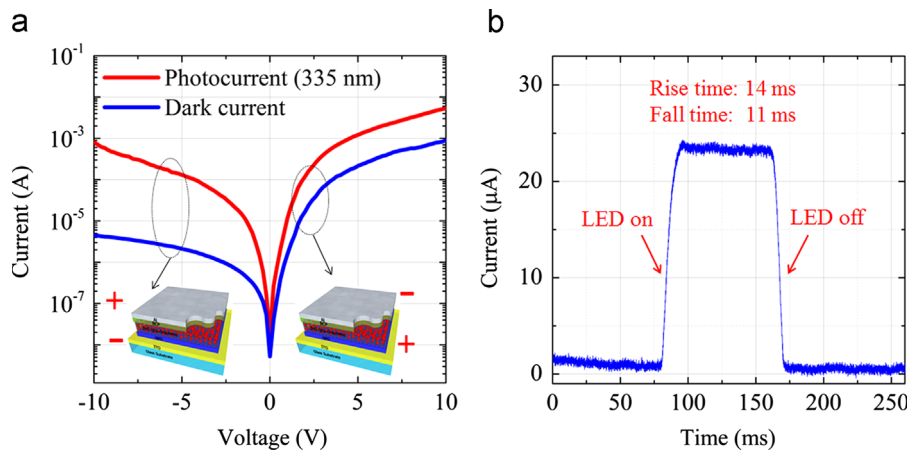


Fig. 3. (A) Typical I - V characteristics and (B) transient response of the hybrid UV photodetector fabricated from ZnO QDs-graphene composite and polymers.

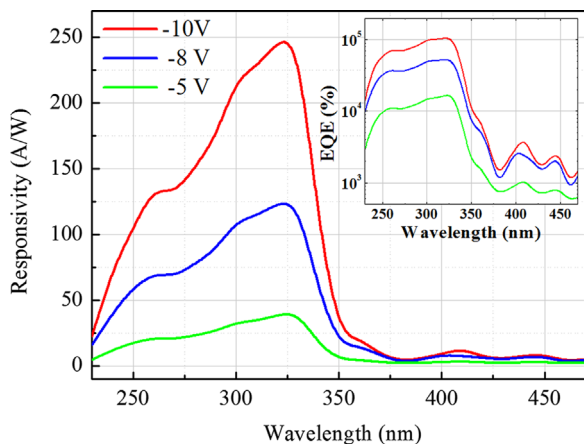


Fig. 4. Photoresponsivity spectra of the hybrid UV photodetector measured with varying bias voltages. Inset: EQE calculated for the hybrid UV photodetector.

between ZnO QDs and graphene, which has been reported in our previous work [9]. Briefly, it is energetically favorable for photo-generated electron to transfer from the conduction band of ZnO to the graphene due to the fact that the electron affinity of ZnO QDs is lower than the work function of graphene. Less accumulation of the electrons in the active region is expected because of the high carrier mobility of graphene. Therefore, the carrier transport efficiency can be improved, leading to a fast transient response.

The photoresponsivity of the device, defined as photocurrent per unit of incident optical power, is shown in Fig. 4. A maximum

photoresponsivity 247 A/W at 325 nm was observed under -10 V bias, which is more than three orders of magnitude larger than those of commercial GaN or SiC photodetectors (< 0.2 A/W) [4]. The high photoresponsivity of this device is attributed to the high active surface to volume ratio, together with the high carrier transport and collection efficiency through graphene. The inset of Fig. 4 shows the external quantum efficiency (EQE) of the photodetector calculated using the equation: $\text{EQE} = R \times hv/q$, where hv is the energy of the incident photon in electronvolts, q is the electron charge and R is the photoresponsivity of the UV photodetector.

4. Conclusion

In conclusion, ZnO QDs-graphene composite was synthesized using atomic layer deposition method. A UV photodetector fabricated from the ZnO QDs-graphene composite and polymers demonstrated fast transient response and high responsivity, which is attributed to high carrier transport and collection efficiency, together with the ultrahigh active surface to volume ratio of the ZnO QDs-graphene composite material.

Acknowledgments

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References

- [1] Chang CY, Tsao FC, Pan CJ, Chi GC, Wang HT, Chen JJ, et al. *Applied Physics Letters* 2006;88:173503.
- [2] Look DC, Coskun C, Clafin B, Farlow GC. *Physica B* 2003;340:32–8.
- [3] Soci C, Zhang A, Xiang B, Dayeh SA, Aplin DPR, Park J, et al. *Nano Letters* 2007;7:1003–9.
- [4] Jin YZ, Wang JP, Sun BQ, Blakesley JC, Greenham NC. *Nano Letters* 2008;8:1649–53.
- [5] Peng SM, Su YK, Ji LW, Wu CZ, Cheng WB, Chao WC. *Journal of Physical Chemistry C* 2010;114:3204–8.
- [6] Shao D, Yu M, Lian J, Sawyer S. *Applied Physics Letters* 2012;101:211103.
- [7] Liu M, Kim HK. *Applied Physics Letters* 2004;84:173.
- [8] Shao D, Yu M, Lian J, Sawyer S. *Applied Physics Letters* 2013;102:021107.
- [9] Shao D, Yu M, Sun H, Hu T, Lian J, Sawyer S. *Nanoscale* 2013;5:3664–7.
- [10] Shao D, Yu M, Lian J, Sawyer S. *Nanotechnology* 2013;24:295701.
- [11] George SM. *Chemical Review* 2010;110:111–31.
- [12] Cavanagh AS, Wilson CA, Weimer AW, George SM. *Nanotechnology* 2009;20:255602.
- [13] Lujala V, Skarp J, Tammenmaa M, Suntola T. *Applied Surface Science* 1994;82:34–40.
- [14] Yamada A, Sang B, Konagai M. *Applied Surface Science* 1997;112:216–22.
- [15] Schwartz G, Ke TH, Wu CC, Walzer K, Leo K. *Applied Physics Letters* 2008;93:073304.
- [16] Jung GH, Lee JL. *Journal of Material Chemistry A* 2013;1:3034–9.
- [17] Liu S, Wu J, Zhou Z, Gao L, Luo S, Xu X, et al. *Journal of Materials Science: Materials in Electronics* 2013;24:1298–302.