Materials Research Bulletin xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Materials Research Bulletin

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

ZrO_2 quantum dots/graphene phototransistors for deep UV detection

Xiaoqin Shi, Xuhai Liu, Haibo Zeng*

MIIT Key Laboratory of Advanced Display Materials and Devices, Institute of Optoelectronics & Nanomaterials, College of Materials Science and Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

ARTICLE INFO

Article history:
Received 5 April 2017
Received in revised form 7 May 2017
Accepted 25 May 2017
Available online xxx

Keywords:
A. Optical materials
A. Semiconductors
B. Optical properties
D. Electrical properties
D. Electronic structure

ABSTRACT

ZrO_2 is a promising material for deep-UV detection application, yet the low carrier density and high crystal lattice defects hinder the device performance. Graphene is an attractive material for photoactive and charge transport layers in photodetectors, but the photoresponsivity have been limited by the weak light absorption, no wavelength selectivity. Here, we demonstrate heterostructure phototransistors consist of graphene as the conducting channel, which is covered by a film of ZrO_2 quantum dots as the light absorption layer. Light absorption in the quantum dots layer creates electron-hole pairs. Under the built-in electric field, the electrons are trapped in ZrO_2 acting as an additional light tunable gate, whereas the holes are transferred towards the graphene. The ZnO_2/Graphene heterostructure, with a high photoresponsivity of 22 AW^{-1} and wavelength selectivity to deep UV wavelength range (220–250 nm) at low operating voltage, is promising to be integrated into solution processed and low-cost optoelectrical devices.

1. Introduction

Zirconium oxide (ZrO_2) nanoparticles are promising candidates for optical engineering, photocatalysis and high-κ dielectrics [1–4] It possesses great potential for deep-UV detection applications due to its wide bandgap of 5.0 eV. However, the responsivity of ZrO_2 phototransistor is still not satisfactory due to the low density and mobility of charge carriers, and the high crystal lattice defects [5–7].

Graphene (Gr) has been developed for broadband detection from the ultraviolet (UV) to infrared (IR) due to its unique properties, such as the ultrahigh carrier mobility (up to 10^6 cm $V^{-1}S^{-1}$) at room temperature, and the excellent electrical conductivity [8–10]. However, Gr is not suitable for phototransistor application owing to the weak light absorption, no wavelength selectivity and the extremely short exciton life-time. Recently, the implementation of photoconductive gain and enhancement of the light absorption in graphene was realized by modifying the graphene transistor with quantum dots (QDs) [11–14], which was regarded as being essential for ultrasensitive graphene-based photodetection [15,16].

Herein, we report a deep-UV photodetector with a heterostructure channel consisting of a ZrO_2 QDs layer and a Gr layer. The mechanism of UV response and the origin of the efficient charge transfer between ZrO_2 QDs and Gr layers have been clarified. Gr acts as the carrier transport channel while the ZrO_2 QDs are used as the photon absorbing material.

With the presence of Gr, the photo-generated holes are prone to transfer from the valence band of ZrO_2 to Gr. Since Gr possesses a high carrier mobility, less accumulation of the electrons on the graphene side can be expected. Therefore, the carrier transport efficiency can be effectively improved, leading to a fast photoresponse. The as-prepared field-effect transistors (FETs) based on Gr channel can be also operated at the lower gate and drain biases for lower power consumption. Therefore, the ZrO_2 QDs-Gr heterostructure is a highly efficient photoelectrical material that can achieve a responsivity to deep UV as high as 22 AW^{-1}.

2. Experiments

2.1. Synthesis of ZrO_2 QDs

40 mL of $ZrOCl_2 \cdot 8H_2O$ (0.08 g mL^{-1}, AR, Sinopharm Chemical Reagent Co.) aqueous solution was added into 25 mL of sodium oleate (0.06 g mL^{-1}, Beijing Chemical Reagent Co.) ethanol solution. After 20 min of stirring, we added 40 mL of cyclohexane to extract zirconyl oleate and kept stirring for another 20 min. The upper

* Corresponding author.
E-mail address: zeng.haibo@njust.edu.cn (H. Zeng).

http://dx.doi.org/10.1016/j.materresbull.2017.05.049
0025-5408/

organic layer was separated, and the cyclohexane was distilled off. Zirconyl oleate was obtained after washing the residues with water and drying. Yttrium oleate was prepared in a similar way using $Y(NO_3)_3{\cdot}6H_2O$.

The previously prepared mixture of zirconyl oleate/yttrium oleate (weight ratio is 20:1) was added into a solution of oleic acid, oleylamine, *n*-octane (AR) and ethanol (volume ratio is 1:2.5:25:10) to form a 0.03 g mL^{-1} mixture. The mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 200 °C for two days. After the mixture was cooled down, a large amount of ethanol was added to precipitate the white product, which was then collected by centrifugation. Finally, the white product was further washed twice by cyclohexane and ethanol, and redispersed in cyclohexane to form a clear solution for device fabrication.

2.2. Fabrication of graphene FET

Heavily *p*-doped Si with 300 nm SiO_2 was used as the substrate. Cr/Au (5/80 nm) as source and drain electrodes were deposited on precleaned Si/SiO_2 substrate by thermal evaporation with a shadow mask. The channel length and channel width were 20 μm and 2 mm, respectively.

The CVD graphene grown on copper foil was transferred by poly methyl methacrylate (PMMA)-assisted wet process onto the abovementioned substrate between the source and drain electrodes. $FeCl_3$ solution was used to etch the copper substrate. After the transfer, the substrate with metal contacts and PMMA/graphene film was dried overnight at room temperature. PMMA was then removed by warm acetone, followed by annealing at 300 °C to remove the residues.

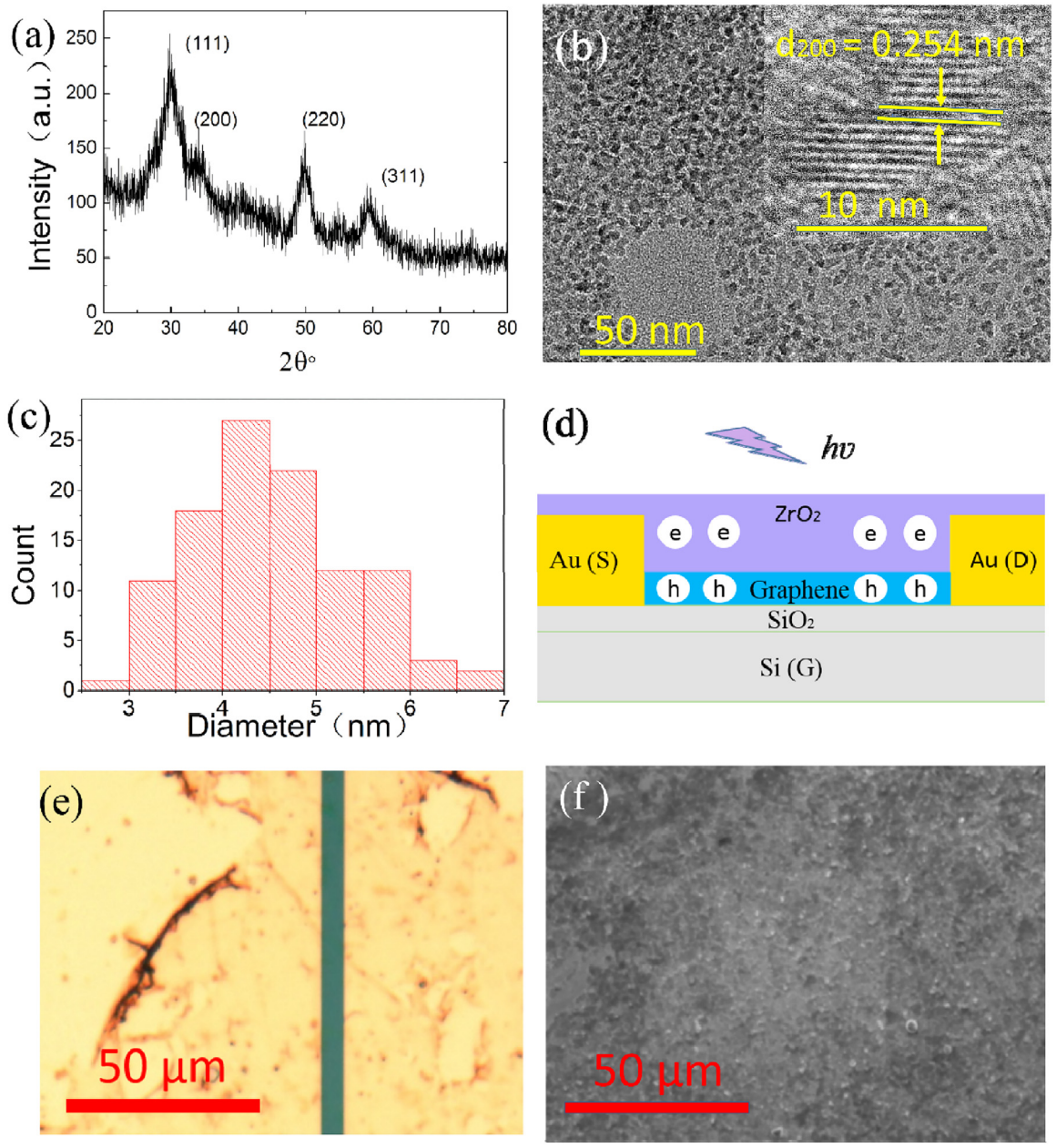

Fig. 1. (a) XRD patterns of the ZrO_2 QDs. (b) Low-resolution TEM image. Inset: the corresponding high-resolution images. (c) Size distribution histogram of the QDs. (d) Schematic illustration of the graphene–ZrO_2 quantum dot heterostructure photodetector. (e) Optical image of the graphene transferred onto the electrodes. (f) SEM image of ZrO_2 QDs film on graphene.

Please cite this article in press as: X. Shi, et al., ZrO_2 quantum dots/graphene phototransistors for deep UV detection, Mater. Res. Bull. (2017), http://dx.doi.org/10.1016/j.materresbull.2017.05.049