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Quantum dots based broad spectral photodetectors with wavelength detecting ability

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ABSTRACT

Board spectral photodetectors are required for varied scientific and industrial applications, yet the studies of such devices are limited. In this work a CdSe/ZnS quantum dots (QDs) based photodetector with broad spectral detecting ability was fabricated through a simple approach. Due to the discrete electronic states of QDs, the photodetector was more sensitive to incident wavelengths than incident power densities, and the photocurrent decreased monotonously with increasing incident wavelength, which could also realize the wavelength detection of incident light. This character provides a new way to achieve color or image sensing, and it could also broaden the photodetection and photosensing applications of QDs and semiconductor detectors.

1. Introduction

Because of their insensitivity to magnetic fields, capability for high speed operation, good linearity and sensibility, semiconductor photodetectors are attracting increased attentions for potential applications in civil and military applications [1–8]. Yet most types of semiconductor photodetectors have the photoresponses only under a certain single wavelength or the light with a narrow range [9]. A photodetector with board spectral responses is required for broad applications including imaging, telecommunications, biomedicine, environmental monitoring and defence sensing [10–12]. In recent years, many efforts have been made to get broad spectral photodetectors by using small molecule materials [10], carbon nanotubes [11,13], narrow-bandgap semiconductor nanowires [9,14] and two-dimensional crystals [15] as functional layers. These devices have realized the wide response ranges, but the works that focus on the wavelength detecting abilities are limited. The relations between their responsivities and incident wavelengths are irregular [9–15], as a result, it is hard to predicate the incident wavelengths from the values of photocurrents, which has limited the color and image sensing applications of broad spectral photodetectors. A conventional way for photodetectors to achieve wavelength detecting is introducing absorptive filters in the device to get the red/green/blue response [16], but the filters require its own fabrication steps and meanwhile reduce the responsivities of the devices, a filter-free broad spectral detector with wavelength detecting ability is necessary. Because semiconductor quantum dots (QDs) have the quantum confinement effect of carriers in three-dimensionals, the electronic states will become completely discrete. As compared to continuous electronic states, the discrete electronic states will contribute to a regular and monotonous relation between photocurrent and incident wavelength, so using QDs as the active layer to fabricate photodetector will realize both broad spectral response and wavelength detecting ability. In this Letter, we designed a photodetector by using the colloidal CdSe QDs as functional layer, the surfaces of CdSe QDs were passivated by ZnS to improve its quantum yields [17] and enhance its quantum confinement effect [18]. We chose p-GaN and ZnO as p-type and n-type materials in the device because they all have wide band gaps and will not affect the photocurrent of QDs layer in the visible light region. Various strategies such as the self-assembled monolayer (SAM) method, Langmuir–Blodgett (LB) technique, layer-by-layer (LbL) assembly, exfoliation and synthetic techniques have been widely used for the preparations of semiconductor nanostructures or thin films [19,20]. For semiconductor QDs, the epitaxial growth method is hard to grow the QDs on large and flexible substrates [21]. For thin films, the metal organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) equipments are very costly. Here in this work, solution processable colloidal QDs were synthesized by wet chemical methods, and the ZnO film was prepared by the simple sintering method. The detector was assembled through a simple but efficient approach on the

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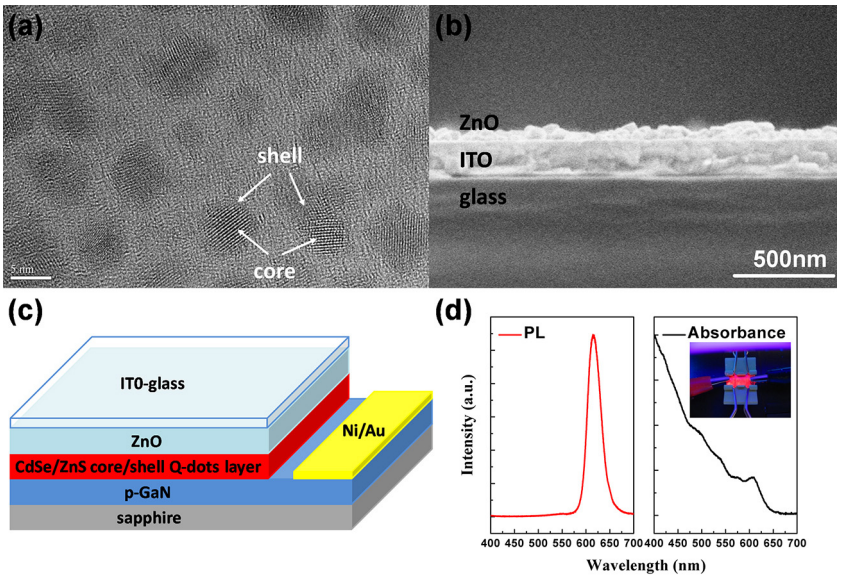

Figure 1. (a) HRTEM image of CdSe/ZnS core/shell QDs. (b) Cross-sectional SEM image of ZnO layer fabricated on ITO-glass. (c) Schematic configuration of the photodetector. (d) Room-temperature PL and the optical absorption spectra of the QDs. Insert is a photograph of the device under UV illumination.

basis of as-prepared materials, then broad spectral response and wavelength detection were observed.

2. Experimental methods

CdSe/ZnS core/shell QDs used in this work were synthetized by a two-step chemical method mentioned elsewhere [17]. The p-GaN thin film on sapphire substrate was prepared by MOCVD method. The Ni/Au contact on the GaN substrate was deposited by thermal evaporation method. The ZnO thin film used in this experiment was fabricated by a simple sintering method with following steps: First, ITO-glass substrates were cut into pieces of 1 cm × 1 cm, and strictly ultrasonic cleaned in acetone, ethanol and deionized water separately, 15 min for each. Then, zinc acetate ($Zn(CH_3COO)_2$) was dissolved in ethanol to form a solution with the concentration of 30 mg/ml. The zinc acetate solution was spin-coated on ITO glass substrates. Then the substrates were sintered at 400 °C in the tube furnace for 20 min. The process of spin-coating and sintering was repeated four times. The QDs based photodetector was fabricated as the following step: first, the ZnO coated ITO-glass and GaN thin film were clamped tightly by a binder clip. Then, the QDs solution was doped into the gap between ZnO and GaN layers. Due to the capillary action of liquid [22,23], the QDs solution formed a uniform layer between ZnO and GaN layers. Finally, the device was dried at 60 °C for 24 h to volatilize all the organic solvent, then the fabrication of the device was done.

The high resolution transmission electron microscope (HRTEM) in this work was obtained on a JEOL JEM-2100 F equipment. The morphology of samples was investigated by the field-emission scanning electron microscopy (FESEM, Hitachi S-4800). The photoluminescence (PL) measurement was carried out with a JY-630 micro-Raman spectrometer by using the 325 nm line of a He–Cd laser as the excitation source, and the absorption spectra were carried out using a Shimadzu UV-3101 PC spectrophotometer. The typical *I–V* curves were measured by a keithley 2611A measurement, and the time-resolved photo-current testing were carried out by using an optical chopper (EG&G 192) to turn on and turn off the light that illuminated on the device and using the 2611A measurement to record the time and corresponding photocurrent values. Commercial LEDs (400 nm, 470 nm) and UV lamp (365 nm) were served as light sources to carry out the *I–V* and time-resolved photocurrent characteristics of the device. To test the broad spectral detecting ability of the device, a monochromator (Shimadzu RF-520) equipped with a 150 W Xe lamp were served as light source to measure the responsivities and external quantum efficiencies under different wavelengths. The power densities of all driven light were evaluated by Ophir PD300R-UV power meter and calibrated by adjusting the applied bias to achieve a similar intensity to the UV lamp.

3. Results and discussion

Figure 1(a) shows the HRTEM image of the QDs, the CdSe single crystal core and the ZnS shell could be observed clearly in the picture. The average diameter of the QDs is about 5 nm. Figure 1(b) shows the FESEM image of the ZnO thin film that was sintered on the ITO glass. The thin film is consisted of ZnO crystal grains and the thickness of this film is about 50–60 nm. As can be seen in Figure S1, the photoluminescence (PL) peak of ZnO layer is located at 370 nm and the first exciton absorption peak of the film is centered at 360 nm. Figure 1(c) is the schematic description of the detector's sandwich structure, we use p-GaN and ZnO as p-type and n-type materials and the upper ITO-glass side is the light entrance side of the detector. Figure S2 shows the PL spectrum of p-GaN thin film used in this work, and the spectrum consists of two parts: NBE emission centered at 361 nm and a defective emission peak located at 377 nm. Figure 1(d) shows the PL spectrum and the optical absorption spectrum of QDs, the emission peak and the absorption edge of the CdSe/ZnS core/shell QDs are all located at about 625 nm. The insert of Figure 1(d) is a photograph of the detector under UV illumination. The uniform red color covering the whole device was originated from the photoluminescence of QDs layer, which means the QDs thin film was wholly and uniformly applied into the device by the method mentioned in this work.

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Figure 2 shows the typical *I–V* characteristics of the detector in dark and under the illumination of 400 nm light. When in the dark, the *I–V* curve shows that the detector behaves like an efficient diode with a current increasing rapidly under forward bias and blocking the current flow under reverse bias, which indicates the ZnO thin film fabricated in this work has good electrical