CHIN. PHYS. LETT. Vol. 27, No. 2 (2010) 027302

# Low-Cost UV-IR Dual Band Detector Using Nonporous ZnO Film Sensitized by PbS Quantum Dots

SHAO Jia-Feng(邵佳锋)[1], A. G. U. Perera[2], P. V. V. Jayaweera[2], HE De-Yan(贺德衍)[1*]

[1]*School of Physics Science and Technology, Lanzhou University, Lanzhou 730000*

[2]*Department of Physics and Astronomy, Georgia State University, Atlanta, Georgia 30303, USA*

(Received 23 July 2009)

*A low-cost photoconductive dual-band detector was prepared using a nanoporous ZnO film sensitized by PbS quantum dots (QDs). At room temperature the device shows a UV response in the wavelength range of 200–400 nm with a 370 nm peak responsivity of* $4.0 \times 10^5$ *V/W and a vis-NIR response from 500 to 1400 nm with a 700 nm peak responsivity of* $5.4 \times 10^5$ *V/W. By increasing the size of the PbS QD, the response can be extended up to 2.9 μm. It is suggested that the UV response is a result of interband absorption of UV radiation by ZnO and the IR response comes from the absorption of PbS QDs.*

*PACS: 73. 21. La, 73. 22. −f, 73. 63. Bd, 73. 25. +i* DOI: 10.1088/0256-307X/27/2/027302

A single detector capable of sensing two or more spectral regions (dual or multi bands) helps to reduce the cost and size of detection systems and will be useful for specialized applications such as mine detection or identifying the origin of fires. Several dual/multi band detectors based on quantum wells,[1] quantum dots,[2] dots-in-the-well,[3] superlattices[4] and heterojunctions[5] have been reported recently. Most of the UV-IR dual band detectors were prepared using wide-band-gap semiconductors such as GaN or AlGaN, and designed to use interband absorption for UV sensing and intersubband transitions for IR sensing.[6] All of the wide-band-gap semiconductors were deposited by thin film epitaxial growth techniques including molecular beam epitaxy and metal-organic chemical vapour deposition.

On the other hand, wide-band-gap oxide semiconductors can be fabricated using relatively simple techniques and sensitized by quantum sized semiconductor particles.[7,8] The sensitization principle of the wide-band-gap semiconductors has been intensively investigated with organic dyes specially for visible region of the spectrum. Utilizing size quantized band-gap modulation, quantum dots (QDs) of semiconductors with low effective carrier mass can be sensitized to the electromagnetic spectrum ranging from UV to far IR.[9] Of the wide-band-gap oxide semiconductors, ZnO has some advantages over its competitors: it is inexpensive, relatively abundant, chemically stable, easy to prepare and nontoxic. More importantly, ZnO is sensitive to UV radiation[10] and nanoporous ZnO films can be grown by low-cost techniques such as sol-gel, spray-pyrolysis and doctor blading.

In this work, a dual band photoconductive detector was prepared using a nonporous ZnO film sensitized by PbS QDs. It is shown that the UV response with a threshold corresponding to the bandgap is a result of interband absorption of UV radiation by the ZnO film. Absorption of PbS QDs leads to a vis-NIR response with a tunable response threshold wavelength $\lambda_t$.

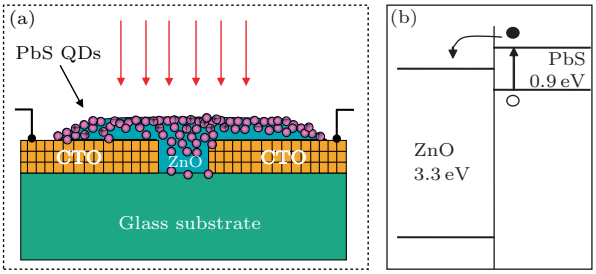


**Fig. 1.** (a) A schematic diagram illustrating the sample geometry used for the dual band detector. (b) The band diagram of the detector.

The photosensitive nanoporous ZnO films in this study were prepared by a process as described below. A fine diamond point was used to engrave a ∼ 30-μm-thick scribe on the surface of F-doped ZnO (CTO) coated glass plate with a sheet resistance of 12 ohm/square ($1 \times 2\,\mathrm{cm}^2$ in area). The ZnO coating was then ultrasonically cleaned in a solution of KOH and propan-2-ol, followed by rinsing with diluted nitric acid, deionized water and immersion in boiling propan-2-ol. ZnO paste was coated by screen painting on top of the etched area ($1 \times 1\,\mathrm{cm}^2$) as shown in Fig. 1(a). ZnO paste was prepared by grinding 1 g of ZnO powder (Fluka) with a few drops of acetic acid and the surfactant Triton X100, and then adding sufficient ethanol. The coated paste was dried under ambient conditions and then sintered in air at 450°C for 20 min. The resultant ZnO layer was about 10 μm thick and the electrical contacts were inserted as shown in Fig. 1(a). In order to embed PbS QDs into the coated ZnO layer, one drop of (about 50 μl)

*To whom correspondence should be addressed. Email: hedy@lzu.edu.cn

lead (Ⅱ) acetate [$Pb(CH3COO)_2{\cdot}3H_2O$] saturated solution in absolute ethanol was absorbed onto the ZnO layer and exposed to $H_2S$ for 30 min at room temperature. The layer has a brownish-black tint due to the formation of PbS QDs. The size of PbS QD was chosen so that the band gap is widened to $\sim 0.9$ eV from 0.42 eV of the bulk PbS. With such a band structure design, the band alignment between the two materials allows photo-induced electron transfer from PbS to ZnO as shown in Fig. 1(b).

The current-voltage ($I-V$) characteristics of the devices were measured using a Keithley 2400 source meter and a UV-vis-NIR monochromator, a lock-in-amplifier and chopper system was used to ascertain the spectral response. The sampling resistance was 2 MΩ and a battery contacted in series. A set of cut-off filters were used to block the higher orders of the grating monochromator output. Monochromator output light intensity was calculated using calibrated Si and InGaAs photodiodes.

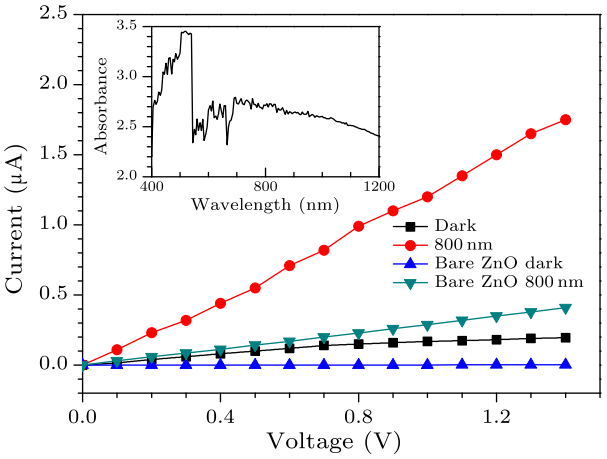


**Fig. 2.** $I-V$ characteristics of the PbS-coated ZnO sample and the bare ZnO film in the dark and under illumination of 850 nm monochromatic radiation with intensity 6.3 μW/cm$^2$, respectively.

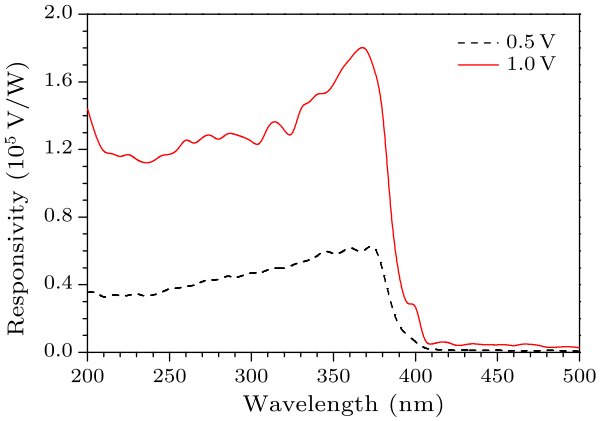


**Fig. 3.** Responsivity of the ZnO detector before introducing PbS QDs.

Figure 2 shows the $I-V$ characteristics of the detector measured in the dark, and under 850 nm monochromatic light with an intensity of 6.3 μW/cm$^2$. The calculated absorbance of the detector based on the measured transmission spectrum is shown in the inset of Fig. 2. The linear $I-V$ curves indicate the ohmic nature of the detector. It is noted that the conductivity of the PbS-sensitized ZnO film is significantly higher than that of the bare ZnO film, indicating that the embedded PbS QDs in the pores improves the transport properties of ZnO films.

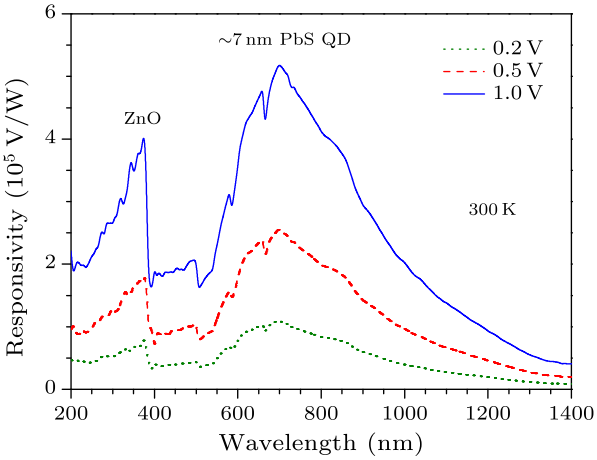


**Fig. 4.** Responsivity of the PbS QD embedded ZnO dual band detector under three different applied biases (0.2 V, 0.5 V, and 1 V) at room temperature.

Figure 3 shows the responsivity of the ZnO detector before introducing PbS QDs over a wavelength range from 200 nm to 400 nm at two different biases. As is expected, a sharp edge at 380 nm can be observed, which corresponds to band-gap absorption in ZnO and matches the band gap energy 3.3 eV of ZnO. The same detector was used to embed PbS QDs. The full spectral responsivities of the QD embedded sample from 200 nm to 1400 nm at three different biases are shown in Fig. 4. It can be seen that the responsivity in the UV and NIR regions increases with bias up to 1 V (corresponding to an electric field about 333 V/cm over the channel), and above 1 V the signal becomes noisy and unstable. It is interesting that the presence of PbS QDs has enhanced the UV responsivity by a factor of about 3. There are many factors that can lead to this phenomenon, maybe the enhancement of the UV responsivity of ZnO film is due to the interface structure between the quantum dots and ZnO film. The vis-NIR response with a peak at $\sim$ 700 nm over the wavelength from 500 nm to 1400 nm clearly shows that the response does not come from the interband absorption of the bulk PbS, which has a band gap of 0.42 eV (corresponding to $\lambda_t = 2.9$ μm). As shown in Fig. 1(b), PbS can absorb photons and inject excited carriers into the conduction band of ZnO. Since the detector is biased in photon

conduction mode, the increasing carrier concentration in the ZnO layer increases the current through the circuit as a photon response.

Table 1. Expected threshold wavelengths of the detectors sensitized with different-sized PbS QDs.

| Diameter of the PbS QD (nm) | Photo response threshold wavelength (μm) |
|---|---|
| 7 | 1.4 |
| 10 | 1.8 |
| 20 | 2.5 |
| 30 | 2.7 |

It is noted that there is significant decay in the photon response with time. Photon response reduces to 10% of its initial value by keeping the sample for one week under a normal room environment. This is due to the conversion of PbS into $PbSO_4$ in the presence of environmental oxygen and moisture. The fact that a sample kept inside a vacuum desiccator does not show this response decay is circumstantial evidence. Based on the absorption spectra reported by Wang *et al.*[8] for PbS QDs in different sizes embedded in polymer films and bandgap energy of PbS QDs calculated with a finite depth potential model,[13] the average diameter of PbS QDs in the present sample was estimated to be about 7 nm (because the wavelength of the peak responsivity is 700 nm, it corresponds to the bandgap of the PbS quantum dot $\Delta E = 0.9$ eV. According to Ref. [8], the relationship between the bandgap and the size of the quantum dots is as follows: $\Delta E = (E_g^2 + 2\hbar^2 E_g(\pi/R)^2/m^*)^{1/2}$, $E_g = 0.42$ eV is the bandgap of bulk PbS, $m^*/m_e = 0.085$, $R$ is the radius of the quantum dot, so the size of the quantum dot is about 7 nm). The value agrees with that of the PbS-QD-based detector reported by Konstantatos *et al.*[14] Expected threshold wavelengths for PbS QDs of different sizes are listed in Table 1. As PbS is transparent to UV and ZnO opaque to NIR, the uppermost region of the film shows sensitivity to NIR radiation. However, the interpenetrated PbS QDs increase the conductivity of the film and permit lower biasing voltages.

In summary, a low-cost, dual band response and easy wavelength-tailorable detector has been prepared based on PbS-QD-sensitized nanoporous ZnO film. At room temperature, it shows a UV response with a peak responsivity of $4.0 \times 10^5$ V/W at 370 nm, and an IR response with a peak responsivity of $5.4 \times 10^5$ V/W at 700 nm.

## References


[1] Liu H C, Song C Y, Shen A et al 2000 *Appl. Phys. Lett.* **77** 2437
[2] Chakrabarti S, Su X H, Bhattacharya P et al 2005 *IEEE Photon Technol. Lett.* **17** 178
[3] Krishna S, Raghavan S, Winckel G et al 2003 *Appl. Phys. Lett.* **82** 2574
[4] Li J, Choi K K and Tsui D C 2005 *Appl. Phys. Lett.* **86** 211114
[5] Ranga C J, Ariyawansa G, Dietz N et al 2008 *Opt. Lett.* **33** 2422
[6] Ariyawansa G, Rinzan M B M, Alevli M et al 2006 *Appl. Phys. Lett.* **89** 091113
[7] Vogel R, Hoyer P and Weller H 1994 *J. Phys. Chem.* **98** 3183
[8] Wang Y, Suna A, Mahler W et al 1987 *J. Chem. Phys.* **87** 7315
[9] Hoyer P and Konenkamp R 1995 *Appl. Phys. Lett.* **66** 349
[10] Moon T H, Jeong M C, Lee W et al 2005 *Appl. Surf. Sci.* **240** 280
[11] Black K, Jones A C, Chalker P R et al 2008 *J. Cryst. Growth* **310** 1010
[12] Xu Z Q, Deng H, Xie J et al 2006 *Appl. Surf. Sci.* **253** 476
[13] Nosaka Y 1991 *J. Phys. Chem.* **95** 5054
[14] Konstantatos G, Clifford J, Levina L et al 2007 *Nature Photon.* **1** 531