Displacement currents in semiconductor quantum dots embedded dielectric media: A method for room temperature photon detection

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It is shown that the high electronic polarizability of quantum dots can be utilized to devise photon detectors by embedding quantum dots in dielectric media to form capacitors. Modulated light generates displacement currents and an expression is obtained for responsivity in terms of the properties of the quantum dot, the dielectric, and the detector geometry. A model detector constituted of PbS quantum dots embedded in paraffin wax is devised to illustrate the principle, giving ~0.6 A/W as an upper limit for the responsivity. As these systems sense only the variations of the light intensity, they could be operated at ambient temperature. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2768305]

The unique properties of low dimensional semiconductors offer opportunities for application in almost all areas of electronics.[1–5] Many concepts have been extensively studied identifying potential applications. Quantum dots (Qds) are used in photon detection,[1–3,6] especially the near infrared and infrared (IR) regions of the spectrum.[7–10] Utilizing size quantized band gap modulation, Qds of low effective carrier mass semiconductors can be sensitized to the electromagnetic spectrum from ultraviolet to far IR. Photovoltaic and photoconductive photon detectors have been made from QD blended conducting polymers.[11–13] In photovoltaic detectors, interpenetrating networks of polymer and Qds communicate with two electrodes. The excitons generated by the incident photons decompose at the interface into electron-hole pairs which separate into the two regions creating a photocurrent and a photovoltage. Photoconductive type operates by derivation of a current by an external voltage via movement of carriers across the polymer medium. Properties of individual Qds are greatly obscured by clustering and aggregation, and also obtaining electronic contacts to Qds would not be an easy task. The photoconductive detectors, where the Qds are homogeneously impregnated into a solid substrate, avoid the above problem. In this letter we show that by embedding Qds in a film of high dielectric material to form a capacitor, the displacement current generated by modulated light can be used as a signal to detect photons. As in pyroelectric detectors,[14] this technique has the advantage that only the intensity modulated light generates signals enabling room temperature operation for sensing IR radiation. Again as in photoconductive QD-polymer detectors, their fabrication does not require electrical connections to the Qds. We illustrate the principle by designing a capacitor with PbS Qds embedded in paraffin wax [Fig. 1(a)].

PbS Qds embedded paraffin wax films were prepared by the following method. Water insoluble lead oelate was synthesized by mixing equal volumes of lead acetate (0.1 M) and sodium oelate (0.2 M) solutions. The white precipitate of lead oelate was separated, washed with water, and dried in a vacuum. A weighed amount of lead oelate was dissolved in molten purified paraffin wax (melting point ~64 °C, dielectric constant=2.4) and a thin layer of wax was spread on the surface of a conducting glass plate (1.5×1 cm^2). After solidification of wax, the plate was inserted into a N_2 atmosphere containing H_2S (~20% by volume) and propan-2-ol vapor and left there for 2 h. H_2S diffuses into the wax impregnating it with oleic acid capped PbS Qds. The presence of the vapor of a slightly polar liquid (propan-2-ol) facilitates this diffusion controlled reaction. The absorption spectrum of the film is presented in Fig. 1(b) and the spectrum of the film material dissolved in hexane was also recorded. These spectra suggest a polydispersion PbS Qds in wax with a median diameter of ~8 nm. To form the capacitor, the plate is warmed to melt the wax and another conducting glass plate posed above to cover an area of 1 cm^2 and fill the capillary space with molten wax. When wax solidifies, plates hold together and leads are connected to the two protruding ends of the conducting glass plates (see inset of Fig. 1). The measured capacitance (200 pF) of the system was nearly of the same order as that of a capacitor of same dimensions (area =1 cm^2, thickness=10 μm) with a film of pure wax and the resistance exceeded 1 GΩ.

Calculations indicate that Qds have several orders of magnitude larger polarizabilites than that of atoms and molecules.[15,16] This has been confirmed by quantum confined stark effect[17,18] and measurement of the electronic polarizability of optically generated excitons in quantum dots.[19]

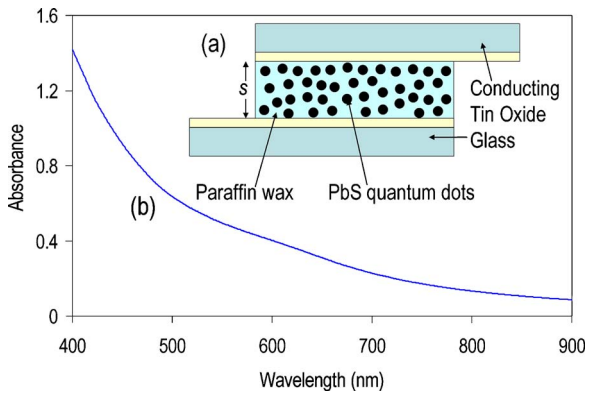

FIG. 1. (Color online) (a) Absorption spectrum of the suspension of PbS quantum dots. (b) Cross section of the device experimentally tested.

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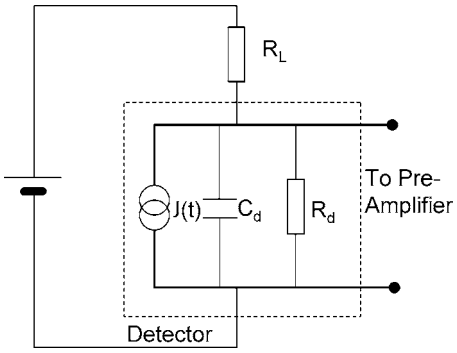

FIG. 2. equivalent circuit of the detector and the circuit used for measurement of the photoresponse (C_d=detector capacitance, R_d=detector resistance).

Using effective medium theory,[19,20] the electric susceptibility χ of the QD-dielectric composite can be expressed a

$$\chi = \varepsilon_0 n \kappa \alpha, \tag{1}$$

$$\kappa = \frac{9\varepsilon^2}{(\varepsilon_{QD} + 2\varepsilon)^2}, \tag{2}$$

where n is the number density of excitions per QD, α is the exciton polarizability, ε is the dielectric constant of the composite, and ε_{QD} is the dielectric constant of the QD material. Hence, if a capacitor of thickness s consisting of N Qds of given size per unit volume is placed in a constant electric field E, the displacement current density $dD/dt=J(t)$ originating from time variation of n can be written as

$$J(t) = \frac{dD}{dt} = sN\varepsilon_0 \kappa \alpha E \frac{dn}{dt}. \tag{3}$$

For simplicity we analyze displacement current response of the system assuming that the photon flux incident on the capacitor modulates as $I=I_0(1+\sin \omega t)$. Thus the rate of exciton generation is given by

$$\frac{dn}{dt} = \phi I_0[1 + \sin(\omega t)] - kn, \tag{4}$$

where ϕ is the quantum efficiency of exciton formation and k is the exciton recombination rate constant. Solving Eq. (4) for n and combining with Eq. (3), the displacement current density can be expressed in the form

$$J(t) = \frac{\phi N E I_0 \omega \kappa \alpha \varepsilon_0}{\sqrt{\omega^2 + k^2}} \left(\sin(\omega t + \delta) + \frac{k e^{-kt}}{\sqrt{\omega^2 + k^2}} \right), \tag{5}$$

where $\tan \delta = k/\omega$ and we have set the initial condition $J(0)=0$, $t=0$. When the transient in Eq. (5) decays, the detector output current density simplifies to

$$J(t) = \frac{\phi N E I_0 \kappa \alpha \varepsilon_0 \omega \sin(\omega t + \delta)}{\sqrt{\omega^2 + k^2}}. \tag{6}$$

Setting $E=V/s$ (V is the applied voltage bias), we obtain the current (A/W) and voltage (V/W) responsivities of the detector (R_L and R_d as indicated in Fig. 2),

$$R = \frac{\sqrt{2}\phi(\nu)\omega V N \kappa \alpha \varepsilon_0}{h\nu s\sqrt{\omega^2 + k^2}},$$

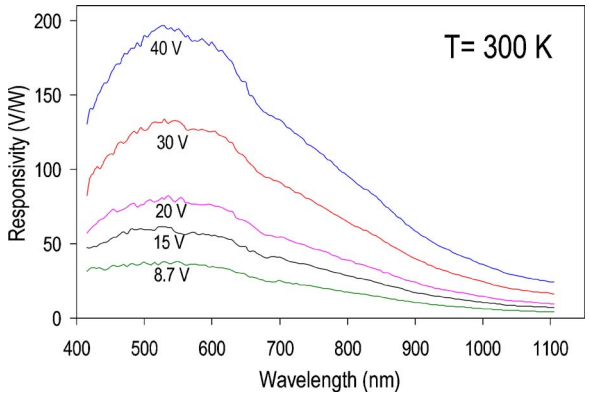

FIG. 3. (Color online) responsivity of the detector under different bias voltages. (85 MΩ resistor was used as load resistor R_L and the chopping frequency was 57 Hz).

$$R_V = \frac{\sqrt{2}\phi(\nu)\omega V N \kappa \alpha \varepsilon_0}{h\nu s\sqrt{\omega^2 + k^2}} \times \frac{R_L \times R_d}{R_L + R_d}. \tag{7}$$

The circuit used for the measurement of the photoresponse, including the equivalent circuit of the detector is shown in Fig. 2. The effect of the parasitic capacitance in the circuit is not very strong at low chopping frequencies (i.e., $\omega < [R_d C_d]^{1/2}$) The plot of responsitivity versus wavelength at different bias voltages (8.7–40 V) and a fixed chopping frequency of 57 Hz is shown in Fig. 3. Despite the simplicity of the system, the response extends from 400 to 1100 nm.

For (7) enables calculation of the intrinsic responsivity of the detector in terms of the properties of the Qds, the embedding dielectric medium, the thickness of the film, and the bias voltage. Responsivity depends on several factors, i.e., size and the number density of Qds, their polarizability, the thickness of the capacitor, and the applied bias. The response increases linearly with the applied bias according to Eq. (6) up to ~20 V and deviation from linearity is seen thereafter. A higher bias will also increase the noise and, at biasing values exceeding the field ionization threshold, the motion of dissociated electrons and holes will also contribute to the displacement current, causing deviation from the linear variation. Formula (7) involves the recombination rate constant k which is sensitive to the structure of the dot (i.e., capping, size, and shape) and its environment. Under optimum conditions (i.e., absence of trapping of the carriers) the exciton recombination is slow (approximately millisecond range) and the condition $\omega \gg k$ should be satisfied. The constant k can be readily estimated from photocurrent transients (when radiation of constant intensity is interrupted, the transient signal takes the form $sN\kappa\alpha E\phi I_o e^{-ikt}$) and the value obtained is of the same order of magnitude (i.e., milliseconds). For optimization of the responsivity, the quantum dots need to be densely packed keeping the film thickness s comparable to the mean free path of photons. However, in general, conductor-insulator composites exhibit percolation thresholds[21] when the packing fraction of the conducting material exceeds a critical value $N=N_C$. In the present system such a threshold would depend on the size of the quantum dots. We did not succeed in determining this threshold for monodispersions of PbS Qds in paraffin. When the total amount of PbS incorporated into the wax reached ~15% by weight, PbS begins aggregating masking the detection of this effect. Almost complete absorption of incident radiation

avoiding any percolation threshold would be possible by increasing the film thickness. In general, near percolation thresholds, systems tend to be noisy[21] and therefore optimization should be achieved keeping N well below N_C and appropriate adjustment of s. In the present investigation no attempt was made to optimize the system.

In the measurement reported, bias voltage was varied from 1 to 40 V with a 85 MΩ load resistor (R_L). Figure 3 gives the plot of voltage responsivity versus the wavelength of the incident radiation and the responsitivity at the peak absorption (λ=540 nm) was found to be 195 V/W at a bias of 40 V and the specific detectivity under the same condition was determined as 3×10^8 cm $\mathrm{Hz}^{1/2}$/W.

The responsivity of the present system can be compared to that of a photoconductive detector of the same bulk material as follows. As photoconductive current density is $J_c = en\mu E(\mu = e\tau/m$, with μ the mobility, τ the scattering time, m the carrier effective mass, and taking low frequency molecular exciton polarizability $= e^2/\varepsilon_0 m\omega_0^2$ (ω_0 exciton binding energy/$\hbar$), we obtain $J/J_C = \omega sNA/\tau\omega_0^2 \sim 10^{-5}$ (with A the detector area=1 cm^2, ω=57 Hz, $N=10^7$, and exciton binding energy=10 meV). Due to the less than ideal coverage of Qds in the dielectric (i.e., $N=10^7$) the responsivity is very low compared to a photoconductive detector. Owing to its low melting point and brittleness, paraffin wax is not the best material to embed Qds. However, due to the simplicity of the preparation, paraffin wax was selected as the dielectric instead of any other dielectric material including silica, glass, or polymers. Better methods of preparation of PbS Qds and use of other embedding dielectrics should improve the performance, when N is increased by several orders of magnitude. It is straightforward to extend the concept proposed here to Qds of other materials and nanowires. Carbon nanotubes which possess high polarizabilities[22] with band gap taliorability would provide an option to fabricate multiband detectors. Thus more versatile photon detectors may be developed if nanotubes are used instead of quantum dots. An additional merit is the sensitivity to polarized radiation if the nanotubes are aligned in the dielectric medium. Furthermore, large aligning torques can be applied to carbon nanotubes, in a highly resistive dielectric medium compared to a conducting medium. The effects of multiexciton production will also be reminiscent in these detectors, especially if PbS is replaced by PbSe. In PbSe-conducting polymer photon detectors, enhancements in quantum efficiency originating from impact ionization have been observed.[23]

The optimization of the detectors based on this technique requires further studies on quantum dot/nanotube impregnated dielectric media and assessment of noise and ways minimizing it. It is also important to test the room temperature operability using Qds that absorb longer wavelengths. Displacement current measurements in QD embedded dielectric media could also give useful information on properties of low dimensional semiconductors.

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