Colloidal Quantum Dot Photodetectors

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Abstract. We review recent progress in light sensors based on solution-processed quantum dots. We focus on visible-, near-infrared, and short-wavelength infrared photodetectors based on quantum-confined PbS nanocrystals. These devices have shown room-temperature D* values above 10^{13} Jones, while fully-depleted photodiodes based on these same materials have achieved MHz response combined with 10^{12} Jones D*.

Keywords: Photodetectors, colloidal quantum dots, photoconductive gain, photodiodes, solution-processed

I. Introduction

Materials that absorb light more effectively than silicon or where silicon does not are of great interest in photodetection and imaging. Strategies include top-surface detectors having 100% fill factor; and means of signal amplification within the photodetector itself, utilizing photoconductive gain [1].

These considerations motivate intense research activity in new materials and structures that expand the spectrum of absorption; minimize the thickness of semiconductor needed to absorb light completely; and amplify signal. Ideally, these materials should be integrable with silicon electronics or with flexible substrates, utilizing ink-jet printing, solution-casting, low-temperature evaporation, and layer-by-layer techniques which are very attractive alternatives to high-temperature epitaxial growth.

Here we discuss recent advances in light sensing, with materials compatible with low-temperature processing and large-area integration. We focus on colloidal quantum dots (CQDs)[2] in which nanoscale phenomena such as quantum confinement[3] play a major role in the optical and electronic properties of the semiconductor. Colloidal quantum dots are nanostructured materials synthesized and processed from solution phase which offer bandgap tunability through the quantum size effect. Rapid advances in colloidal quantum dot synthesis and photophysics have led to a high degree of control over nanoparticle size, shape, and composition [2]. We focus on two different types of photodetector (photodiodes and photoconductors); and discuss the device concepts, materials and physical phenomena that have underpinned these improvements in performance.

II. Photodiodes and Photoconductors

In a photodiode the electrons and holes generated by the incoming photons move to opposite electrical contacts, so the quantum efficiency of such devices cannot exceed unity. However, photodiodes can have fast response times determined by the transit time of the photogenerated carriers, and can be less than electron-hole recombination time, which are typically microseconds or less for the direct-gap semiconductors commonly used.

Photoconductors, on the other hand, are capable of high gain [4] because one type of charge carrier (say holes) is able to circulate through an external circuit many times before it recombines with its opposite carrier (say electrons), which remain trapped in the photoconductor bulk in the meantime. CQD photoconductors with responsivities in the range of 100 – 1000 A/W, corresponding to gains of 100 to 1000 have thus been reported [5, 6]. While these high gains increase responsivity and simplify the read-out circuits, they also reduce the bandwidth because of the long circulating carrier lifetimes involved.

The performance of a photodetector can be improved, not only by maximizing its electrical response to light, but also by minimizing the noise in its electrical output, which can obscure real signals. One can thus examine the noise-equivalent power (NEP), which reports the optical power at which the signal to noise ratio (SNR) is 1 (or 0 dB). The normalized detectivity D^* - equal to $(A_dB)^{1/2}R/i_n$ *(expressed in cm* $Hz^{1/2}/W$ *or Jones)* where A_d is the detector's active area, B is the noise measurement bandwidth, R the responsivity, and i_n the noise current - is a figure of merit that seeks to normalize for variations in device geometry and sampling conditions, thus providing a metric that enables comparison among different devices. The best solution-processed detectors have achieved D* values of up to $5x10^{13}$, which is comparable with the best values reported for single-crystal photodiodes.

III. Photodiode mechanisms and performance

Photodiodes rely on the use of two media - at least one of them a semiconductor - in which a significant difference in the materials' work functions produces a built-in potential. An internal field in the semiconductor depletion region near the junction propels electrons and holes in opposite directions. In the simple case of a fully-depleted device, high internal quantum efficiency is achieved if $t_{life} > t_{extract}$, where t_{life} is the lifetime of excess charge carriers, and $t_{extract} = L^2/\mu V_{bi}$ is the time taken to transport them to their respective contacts via the built-in field. In addition, L is the contact separation, μ is the mobility of the slower carrier, and V_{bi} is the built-in potential across the junction[36].

Solution-processed semiconductors exhibit carrier mobility in the range 10^{-5} – 10^{-3} cm^2/Vs and thus, even for a thin depletion region 100 nm thick and a typical built-in voltage of 1 V, drift times are in the range 100 ns – 10 us. Fortunately, some of the most promising semiconductors incorporated into colloidal quantum dots used in solution-processed photodetector realization have unusually long exciton lifetimes – greater than 1 microsecond [7] – that have led to excellent photodiode

quantum efficiencies, with even the first reports well above 50%. The high internal quantum efficiencies these findings entail also indicate that – when their surfaces are well-passivated using suitably-functionalized ligands – colloidal quantum dot solids achieve carrier lifetimes comparable to their exciton lifetimes: thus, well-passivated colloidal quantum dots incorporated into densely-packed solid-state films do not suffer from an excess of nonradiative recombination such as that assisted by midgap recombination centers [8]. Since the absorbance of many materials is in the 10^4-10^5 cm^{-1} range near the absorption onset, only reaching 10^6 cm^{-1} far above the bandgap, it is of interest to make devices that include light-absorption moieties as thick as micrometers. Typically, doping control in colloidal quantum dot solids has led to devices that are fully-depleted only if their thicknesses are 100-200 nm[9]. A majority of micrometer-thick devices will in this case be far from fully-depleted, demanding efficient transport through a quasi-neutral layer. In certain colloidal quantum dots solids, minority diffusion lengths in excess of 100 nm, and reaching as high as 200 nm, have been reported [7, 9] owing to the use of very short organic bidentate linker molecules. Minority electron mobilities of 10^{-3} cm^2/Vs combined with an absence of midgap traps thus extended diffusion lengths into to these very attractive lengthscales for solution-cast direct-gap optoelectronic materials.

A CQD PbS Schottky photodiode was reported in 2009 with excellent sensitivity out to 1.6 um ($D^* = 10^{12}$ Jones) and high bandwidth in the MHz range [9]. High sensitivity was achieved via the joint optimization of electron and hole transport, leading to high quantum efficiencies, as well as control over film morphology and defect passivation, which maximized the shunt resistance and minimized dark current. The MHz temporal response was achieved through the realization of a fully-depleted device, and this bandwidth further confirms that carriers are extracted via drift in these devices on the sub-microsecond timescale.

IV. Photoconductor mechanisms and performance

Photoconductors, unlike photodiodes, rely on a unipolar mode of conduction and the conductance increases upon illumination. The increased conductance state is determined by the carrier lifetime and thus if the lifetime exceeds the transit time of the flowing carrier through the device, many charges worth of current may be integrated for each photon absorbed. A leverage to control the carrier lifetime and thereby the gain is provided by the trap states. These traps serve both to delay band-to-band recombination, and also to impede the extraction of the trapped carrier, a condition necessary to photoconductive gain.

The first solution-cast optoelectronic device to outperform its epitaxial counterparts was a photoconductive photodetector reported in 2006 [5]. A key insight leading to this advance was the realization that excess noise could accumulate along the transport path if the interfaces between the nanoparticles making up the semiconductor film were randomly time-varying due to trapping and de-trapping effects from thermally- or optically-generated carriers [10]. This multiplicative noise, also known as transport noise, was obviated through a processing strategy wherein pure (trap-free) colloidal quantum dot films were first realized; and only once the electrical connections between adjacent nanoparticles were forged were the remaining exposed surfaces of the nanoparticles decorated with sensitizing centers.

Many advances in solution-cast photoconductor performance have since been reported. For example, PbS nanoparticles with a diameter of less than 3 nm can have a bandgap that is three times that of bulk PbS, and the resulting strong quantum confinement can be exploited to achieve high-detectivity visible-wavelength light sensing[6]. The quantum size effect affords wide spectral tunability within a single materials system and processing architecture, enabling multispectral detectors that monolithically integrate pixels sensitive in the visible, near infrared, and short-wavelength infrared.

Building on a long history of studies of bulk PbS photoconduction[1], recent reports have elucidated the chemical origins of traps having different energies, and different lifetimes, as a function of chemical species and nanoparticle size and preparation. This enabled the implementation of a single trap state lifetime and video-frame-rate-compatible photoconductor behavior[11].

V. Conclusions

Solution-processed light sensors offer a wide suite of advantages in imaging and photodetection. The convenient integration of light sensing materials with a variety of substrates enables separate optimization of each function: silicon electronics, ideally suited to volume manufacture, low-noise read-out, and a comprehensive array of analog and digital functions, can be augmented with a 100%-fill-factor, spectrally-tunable, optically dense, low-crosstalk light sensing layer customized for efficient conversion from the optical to the electronic domain. Ever-growing dexterity in manipulating materials at the nanoscale - the engineering matter on the quantum and plasmonic lengthscales - provides for an unheralded degree of customization and optimization in coming generations of light sensing arrays.

REFERENCES

[1] L. Sosnowski, *et al.*, "Lead sulphide photoconductive cells," *Nature* 159 (1947) 818-819.

[2] C. B. Murray, *et al.*, "Synthesis and characterization of nearly monodisperse CdE (E = S, Se, Te) semiconductor nanocrystallites," *Journal of the American Chemical Society* 115 (1993) 8706-8715.

[3] L. Brus, "Electronic wave functions in semiconductor clusters: Experiment and theory," *Journal of Physical Chemistry* 90 (1986) 2555-2560.

[4] R. L. Petritz, "Theory of photoconductivity in semiconductor films," *Physical Review* 104 (1956) 1508-1516.

[5] G. Konstantatos, *et al.*, "Ultrasensitive solution-cast quantum dot photodetectors," *Nature* 442 (2006) 180-183.

[6] G. Konstantatos, *et al.*, "Sensitive solution-processed visible-wavelength photodetectors," *Nature Photonics* 1 (2007) 531-534.

[7] K. W. Johnston, *et al.*, "Efficient Schottky-quantum-dot photovoltaics: The roles of depletion, drift, and diffusion," *Applied Physics Letters* 92 (2008) 122111-3.

[8] D. A. R. Barkhouse, *et al.*, "Thiols passivate recombination centers in colloidal quantum dots leading to enhanced photovoltaic device efficiency," *ACS Nano* 2 (2008) 2356-2362.

[9] J. P. Clifford, *et al.*, "Fast, sensitive and spectrally tuneable colloidal-quantum-dot photodetectors," *Nature Nanotechnology* 4 (2009) 40-44.

[10] A. Carbone, P. MAzzetti, " Grain-boundary effects on photocurrent fluctuations in polycrystalline photoconductors. *Physical Review B* 57 (1998) 2454–2460.

[11] G. Konstantatos, *et al.*, "Engineering the temporal response of photoconductive photodetectors via selective introduction of surface trap states," *Nano Letters* 8 (2008) 1446-1450.