Colloidal HgTe material for low cost detection into the MWIR

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Abstract: In this paper we report on HgTe colloidal based quantum-dot mid-infrared photodetectors. We demonstrate tuning the cut-off wavelength of this detector from the near infrared up to 7µm. Responsivity values are in the hundred $mA.W^{-1}$ range even at room temperature. The detectivity of the material is limited by a large *1/f* noise.

Keywords: colloidal quantum dot, HgTe, mid-infrared, Photo-detectors.

1. INTRODUCTION

II-VI semiconductors have been used for infrared imaging for 50 years. In particular the HgCdTe alloy is successfully used over a large range of wavelength from the SWIR[1] to the VLWIR[2]. In spite of this great maturity these detectors face two major issues: the cost of the growth and the limited operating temperature. Meanwhile II-VI semiconductors have been develloped in colloidal quantum dot (CQD) form[3,4]. These materials have been very successful in the visible wavelength range with applications such as LED[5], biolabeling[6] and solar cell[7]. In particular CQD materials offer the advantages of a low cost growth and they do not require epitaxial growth on an expensive wafer[8]. Most of the prior work with CQD involved cadmium or zinc based binary semiconductor quantum-dots. To tune the optical properties of this CQD into the infrared, it is necessary to use material with a lower band gap like those based on lead (PbS and PbSe)[9] or on mercury[10] (HgS or HgTe). Here we report on HgTe based CQD in which the energy band edge can be tuned over the 3-5µm atmospheric transparency window and up to 7µm[11]. We expect that this material will become a low cost alternative to current detectors in the mid-IR range.

The colloidal synthesis of quantum-dots is a suitable method to obtain particles in the nanometer scale. The particles are prepared through reaction of a mercury salt and a tellurium precursor in an organic solvent in the presence of coordinating ligands. We obtain particles which final sizes are in the 5 to 15 nm range. Electronic microscopy pictures of the films are shown on *Figure 1*(b).

2. INHERENT DIFFICULTIES OF THE USE OF COLLOIDAL MATERIAL

The success of colloidal material for photonic detection in the mid infrared was not guarantee *a priori*. Indeed to be stable the colloidal particles need ligands which are generally organic molecules with alkane chains and other chemical bonds such as S-H, N-H…. The main difficulty is that these bonds present vibration resonances in this range of wavelength. Thus the colloidal particle is a semiconductor core with a ligand shell, as shown in *Figure 1* (c). The semiconductor core is the optically interesting part with its controlled band-edge energy and the possibility to generate exciton. On the other hand the ligands also absorb the incident light, but do not generate photo-carrier. Ligand shell only acts as a filter, leading to a reduced amount of light on the detector. On lead-selenide particle it has been observed that the ligand absorption can be very detrimental for the CQD photoluminescence as the energy of the band edge is reduced[12]. *Figure 1* (a) shows the possibility to tune the cut-off wavelength of the CQD device from the SWIR (1.2µm) to the MWIR (above 5µm) at room temperature by adjusting the particle size. Moreover, due to the positive temperature dependence of the energy gap of HgTe, the cut-off wavelength was increased up to 7µm at low temperature (70K), see *Figure 2* (a). The obtained values of the responsivities are in the hundred $mA.W^{-1}$ range for absorption between 1.7µm and the MWIR band edge energy, see *Figure 2* (b).

3. PHYSICS OF THE CARRIER CHARGE GENERATION

Dark current I-V curves are shown in the inset of *Figure 3* (a). It is shown that the transport is in a linear regime at room temperature and starts to deviate from this behavior at low temperature. The temperature dependence of the dark current is thermally activated at least from 100K up to room temperature[13]. The measured activation energy is consistent with half of the band-edge energy. This means that the dark transport is limited by the thermal carrier generation, following the behavior of an intrinsic semiconductor (i.e. Fermi level in the middle of the gap). We can therefore model the density of carrier simply as $n = p = 2N_0 \exp(-E_G / 2k_B T)$ assuming that the number of states are equal to 2 for both electrons and holes. In this expression N_0 is the density of CQD. This expression can then be used to evaluate the mobility of the carrier which is found to be pretty high for unprocessed colloidal material in the 0.1 to 1

$cm^2V^{-1}s^{-1}$. We evaluate the interdot hopping time as 13ps. Such a short interdot transport time allows a fast dissociation of the exciton leading to reasonable responsivity by reducing the carrier transit time.

4. NOISE AND DETECTIVITY

The study of the noise is of great importance to use this material for detection. Indeed we expect that noise in the CQD based materials will be an important difference in competing with molecular beam epitaxy grown devices. In particular, the large interfacial areas and current crowding[14] are expected to lead to larger *1/f* noise. This is experimentally observed as shown on *Figure 3* (b). With these unoptimized films, detectivities, at room temperature, are typically of a few 10^7 jones. By cooling the sample values higher than 10^9 are achieved.

For our larger size dots, the optimal operating temperature is around 130K with a 6µm cut-off wavelength. We are now developing the synthesis of larger, more monodispersed quantum dots as well as exploring the processing of the films to optimize responsivity and reduce the noise.

5. FIGURES

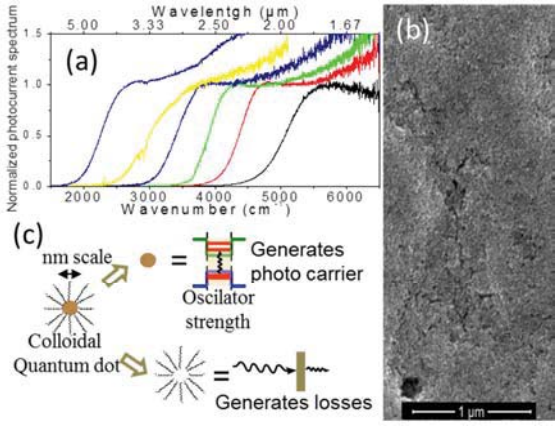

Figure 1 (a) Photocurrent spectra of films of HgTe CQD for different particle sizes. (b) Scanning electron microscope image of HgTe CQD film. One can notice the presence of cracks in the film due to shrinking after the ligand exchange. (c) Scheme of a CQD composed of a semiconductor shell acting as a confined area for the carrier and a ligand shell necessary for the colloidal stability of the particle in solution.

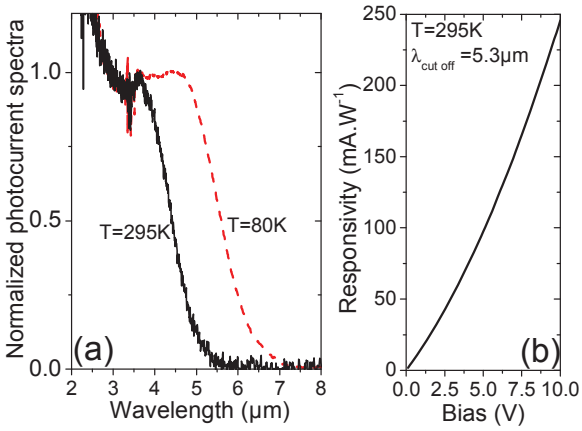

Figure 2: (a) Normalized photocurrent spectra at two different temperatures. (b) Responsivity of a 5.3μm cut-off wavelength device as a function of the applied bias at room temperature.

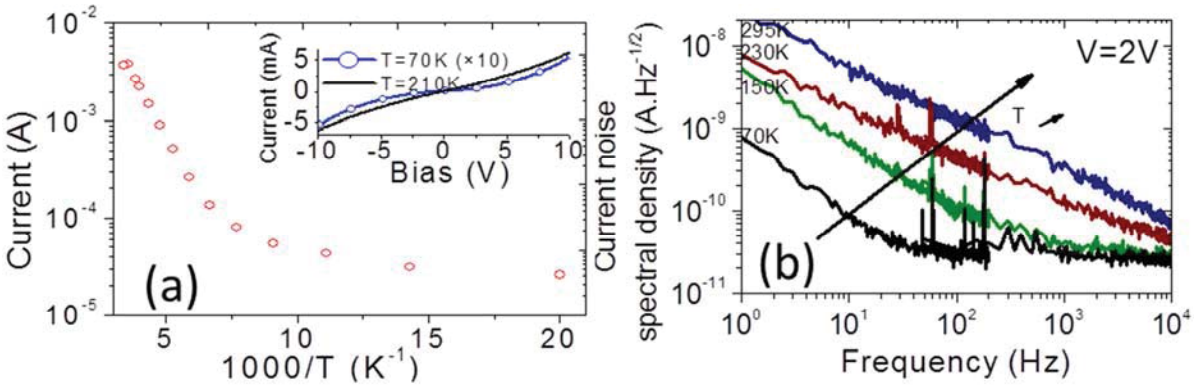

Figure 3: (a) Dark current for a 5μm cut-off wavelength sample, as a function of the inverse of the temperature. The inset shows the I(V) curve for the same sample for two different temperatures. (b) Noise current spectral density as a function of the signal frequency for a 5μm cut-off wavelength at different temperature.

6. REFERENCES

[1] R. Breiter et al., Proc. SPIE 7298, 72981W (2009). P. Chorier et al. Proc. SPIE 4369, 698 (2001).
[2] M. Z. Tidrow and W. R. Dyer, Infrared Physics & Technology **42**, 333 (2001).
[3] D. Talapin, J.S. Lee, M. Kovalenko and E. Shevchenko, Chem. Rev. **110**, 389 (2010).
[4] C.B. Murray, D.J. Norris, M.G. Bawendi, J. Am Chem Soc **115**: 8706 (1993).
[5] V. Wood and V. Bulović, Nano Reviews **1**, 5202 (2010)
[6] B. Dubertret, et al., Science **298**, 1759 (2002).
[7] A. J. Nozik, Physica E **14**, 115 (2002).
[8] M. Reddy et al., J. Electronic Materials **37**, 1274 (2008).
[9] G. Konstantatos, C. Huang, L. Levina, Z. Lu and E. H. Sargent, Adv. Func. Mater. **15**, 1865 (2005). J. M. Pietryga et al., J. Am. Chem. Soc. **126**, 11752 (2004). T. Rauch et al, Nature Photonics **3**, 332 (2009).
[10] M. V. Kovalenko et al., J. Am. Chem. Soc. **128**, 35163517 (2006).
[11] S. Keuleyan, E. Lhuillier, V. Brajuskovic and P. Guyot-Sionnest, Nature Photonics **5**, 489 (2011).
[12] H. Liu and P. Guyot-Sionnest, J. Phys. Chem. **114**, 14860 (2010).
[13] E. Lhuillier, S. Keuleyan, P. Rekemeyer and P. Guyot-Sionnest, J. Appl. Phys **110**, 033110 (2011).
[14] E.P. Vandamme and L.K.J. Vandamme, Microelectronics reliability **40**, 1847 (2000).