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Thermal properties of mid-infrared colloidal quantum dot detectors

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Abstract

HgTe colloidal quantum dot films are studied for photodetection over the 3-5 μm atmospheric transparency window. The temperature dependence of the conductivity indicates that the material behaves approximately as an intrinsic semiconductor. In photoconduction, the responsivity can be as high as several hundred mA W^{-1} at room temperature. The dark current presents $1/f$ noise which is larger than for homogeneous conductors, and this noise decreases with temperature. A specific detectivity of 2×10^9 Jones is obtained for a sample with a 6 micron cut-off wavelength at 130K. These values are obtained for the thickest films studied (~ 400 nm) and whose thicknesses are still much less than the optical absorption length. The time response can be faster than 100 nanoseconds.

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18 **I. INTRODUCTION**

19 Colloidal quantum dots (CQD) have been studied over more than two decades, and they have
20 potential for various optoelectronic applications¹. While sharing the advantages of liquid
21 processing with organic molecular compounds, they have a very unique advantage in the infrared
22 due to weaker vibrational absorption and well defined infrared electronic absorption. They have
23 already been extensively investigated in the near-IR for photodetection,^{2,3,4,5,6} . PbS and PbSe
24 quantum dots are potential materials in the near-IR^{7,8,9,10}. For longer wavelengths, HgTe should
25 be a better choice since it is a gapless semiconductor^{5,11}. As CQD, this material had already been
26 shown to function well for near infrared photodetection^{12,13} and we recently extended the
27 material's response into the mid-IR.¹⁴

28 CQD may address current demand for a decrease of the cost of the infrared focal plane array and
29 an increase in operating temperature. Already established technologies in the mid infrared, such
30 as InSb or MCT or even promising detectors such as type II superlattices, achieve excellent
31 performances but fail to provide a low cost solution. In part, the high cost is due to the
32 requirement of epitaxial growth. HgTe CQD material can thus bring ease of processing and much
33 lower costs.^{15,16,17} Moreover the development of HgTe CQD benefits from the extensive
34 knowledge of HgCdTe, making this material easily transferable to MCT foundry.

35 In this report we present an initial study of the temperature dependent conductivity and
36 photoconductivity characteristics of the HgTe CQD with mid-IR gaps. We report measurement of
37 the dark current, spectral response, responsivity and noise as a function of bias and temperature.
38 The efficiency of the CQD based detectors is evaluated and their optimal operating temperature
39 identified. We identify possible pathways for optimizing the material as a photodetector.

62

63 II. EXPERIMENTAL

64 A. MATERIAL AND FILMS PREPARATION

65 The synthesis of the QD particles uses the previously published method.¹⁴⁴⁰ Briefly, 13mg of
66 tellurium are dissolved in 2mL of butanol and 0.1mL of trioctylphosphine. The mixture is heated
67 to 90°C for 20 min under Ar to dissolve the tellurium. The temperature is then adjusted based on
68 the desired particle size, with higher temperatures leading to larger particles. The smallest
69 particles with band gaps reaching the visible region were obtained at temperatures as low as 0°C
70 while the largest particles were prepared at 90°C. Meanwhile mercury acetate is mixed with 2mL
71 of butanol and 2mL of pyridine. This solution is then quickly injected into the flask, immediately
72 forming a dark solution. Finally the reaction is stopped after several minutes by extracting to a
73 room temperature solution of 10% dodecanethiol in tetracholoethylene (TCE).

74 The diameters of the dots in this study are in the 6 to 12nm range. Particles with a ~8nm diameter
75 (respectively 10.5 nm) present a band edge energy corresponding to 3μm (5μm). Figure 1
76 Figure 1 gives a transmission electron microscopy (TEM, Tecnai F30, 300kV) image showing
77 aggregated particles. Dynamic light scattering (DLS, Malvern, Zetasizer) measurements suggest
78 the nanocrystals are similarly aggregated in colloidal solution. The aggregate size distribution
79 follows approximately a log normal distribution typical, with a mean size which is typically 20
80 times larger than the single dot diameter. However the optical absorption shows confinement
81 which varies only with the dimensions of the individual particles in the aggregates.

82 Films of dots are obtained by drop-casting the TCE CQD solution on interdigitated Pt electrodes
83 on a glass substrate (ABTech IME 1050, 50 periods, 100nm thick, 10 μm width and spacing).

Mis en fo

Films of HgTe CQD film studied here are a few hundred nanometers thick and we also investigated thinner films made by using more dilute solutions. For all the following measurements, the samples are mounted on the cold finger of a closed cycle He cryostat (Coldedge SDRK 101D) operating between 3 and 300K. Three samples are under investigation in this study with the following cut-off wavelength at room temperature 2.8 μ m (sample A), 3.4 μ m (sample B) and 5.3 μ m (sample C).

B. EXPERIMENTAL SETUP

$I(V)$ curves are measured using a Keithley 6487 pico-ammeter. The sample is illuminated by a tungsten light-bulb. Its temperature, measured with a pyrometer, is adjusted in the 1400 to 2100°C range, giving an incident power of a few mW on the sample.

A home-made Michelson interferometer is used to measure spectral responses. A SiC lamp (equivalent to a 1200°C blackbody) serves as broadband light source and is chopped at a frequency in the kHz range. The detector signal is amplified using a Keithley 6487 and a PAR model 124 lock-in.

The transient response of the detector is obtained by illuminating the sample with short pulses (10ps, 25Hz) of a Nd:YAG laser at 1.06 μ m. The transient photocurrent is recorded using a 100MHz digital oscilloscope (Tektronix, TDS 1012B).

Noise measurements are performed with a spectrum analyzer (HP 3561a). The sample is biased with a battery in order to limit the input noise. The mean signal is removed using a resistor bridge and the noise current is then input to a low noise operational amplifier (LF356N, National

Semiconductor). The current amplification is typically in the 10^4 to 10^7 range before input to the spectrum analyzer. All the noise measurements were conducted in the cryostat with the optical shutter closed.

III. RESULTS AND DISCUSSIONS

A. AN INTRINSIC SEMICONDUCTOR

Dark $I(V)$ curve for sample C are presented in [Figure 2](#)~~Figure-2~~. The dark $I(V)$ curves present almost no hysteresis. They are generally linear at high temperature and become less linear as the temperature decrease. The dark current as a function of temperature is also presented in [Figure 2](#)~~Figure-2~~. The transport decreases about two orders of magnitude from the room temperature value, with an Arrhenius law $I(T) \propto \exp\left(-\frac{E_a}{k_B T}\right)$, with E_a an activation energy, k_B the Boltzmann constant, and T the temperature until settling to a lower slope. Activation energies are reported in [Table 1](#)~~Table-1~~ for sample A, B and C.

135

136 Table 1 : Activation energies for the dark current of the three samples. This value is compared to
 137 the half value of the optical gap at room temperature. N_0 is the estimated random close packed
 138 density of CQDs with the range based on a 20% standard deviation of the diameter. The carrier
 139 density, n , is estimated based on a model for intrinsic thermal activation. .

Sample	$\lambda_{\text{cut-off}}$ (295 K) (μm)	$\lambda_{\text{cut-off}}$ (70K) (μm)	E_a (meV)	$E_G/2$ (meV) From optical measurement	N_0 ($\times 10^{18}$ cm^{-3})	n ($\times 10^{16}$ cm^{-3})	α (10^{-4} eV.K^{-1})	β (K)	$E_G(0\text{K})$ (eV) From Varshni's fit
A	2.8	3	273 ± 10	221 ± 44	2.6-7.6	0.08-0.3	1.5	500	0.43
B	3.4	4.35	201 ± 10	182 ± 36	1.5-5	0.2-0.8	7	500	0.33
C	5.3	6.6	106 ± 10	117 ± 20	0.6-2	1-4	7	500	0.23

140

141 The activation energy is in each case close to half of the energy gap value (at room temperature),
 142 the latter being determined as the edge of the photoresponse described below measured at room
 143 temperature. Such a relation between the energy of thermal activation of carriers and the gap is
 144 expected for an intrinsic semiconductor. At room temperature, we therefore conclude that the
 145 carrier density is dominated by the intrinsic properties. There may of course be some carrier
 146 doping in our samples, but given the thermal behavior of the dark current, it must be much less
 147 than the density of intrinsic carriers at room temperature. In the intrinsic case, the carrier density
 148 can be determined as $n = p = N_0 \sqrt{N_c \cdot N_v} \exp(-E_G / 2k_B T)$ where N_0 is the number of
 149 nanocrystals per volume, and N_c and N_v are the numbers of electron and hole states respectively
 150 in the nanocrystals that are thermally accessible. Given that much of the confinement energy is in
 151 the electron states, we take $N_c=2$. For the more massive holes, we will also take $N_v=2$ even

though it may be somewhat more. The estimated carrier densities at room temperature are then shown in Table 1.

The measured resistivities of the samples allow an estimate of the mobility using $\rho^{-1} = ne\mu$, which typically leads to value in the $0.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ range for sample C. For the discussion later, we also provide an estimate of the hopping time between nanocrystals. Using Einstein's relation, the hopping time between nanocrystals and the mobilities are related by $\tau_{hop} \approx \frac{2eR^2}{3\mu k_B T} \approx 13 \text{ ps}$ in sample C. Hopping times faster than recombination times are helpful for efficient operation.

B. EFFECT OF THE TEMPERATURE ON THE OPTICAL PROPERTIES

Figure 3 shows the spectral response for the three samples. By changing the size and temperature of the particles, the cut-off wavelength tunes from 2.8 to almost 7 μm . Shorter cut-off wavelengths are accessible by growing smaller particles but are not in the scope of this work. In samples B and C, some features in the spectral response are due to vibrational absorption of the C-H bonds from the ligands (3.5 μm), H₂O (3 μm) and CO₂ (4 μm) coming from water vapor and carbon dioxide in the interferometer.

For all the samples, a decrease in temperature results in a red-shift of the spectral response, as shown in ~~Figure 3~~ and ~~Table 1~~. This is consistent with bulk HgTe, where thermal dilation of the HgTe lattice leads to a reduced gap with decreasing temperature.^{18,19}

The thermal dependence of the energy gap is captured quite well with an empirical parabolic fit. Alternatively, Varshni's²⁰ expression, given by equation ~~(1)~~, is often used.

$$E_G(T) = E_G(T = 0K) + \frac{\alpha T^2}{\beta + T} \quad (1)$$

Here, the α parameter is linked to the thermal dilation coefficient. β was originally associated with the Debye temperature although it can deviate significantly^{20,16}. The parameter values for bulk HgTe are poorly known and reported values cover a wide range, with $\alpha = 2.7 \times 10^{-4} \text{ eV} \cdot \text{K}^{-1}$ to $8.5 \times 10^{-4} \text{ eV} \cdot \text{K}^{-1}$.^{18,14,19,15} Our experimental points are compared with a Varshni's law fit for the thermal dependence. As shown in ~~Figure 2~~Figure-2, the fit is imperfect and is in fact not very sensitive to the choice of β , set at 500K, but the coefficient α is reasonable. Table 1 lists the parameters. With more monodispersed samples it will be important to determine these parameters with more accuracy than in the bulk and to extract their size dependence²¹ since the red shift with temperature is relevant to the mid-IR detection.

Increasing the bias increases the magnitude of the response but it does not change its spectral shape. The relative responsivity as a function of temperature is shown in Figure 4b and is obtained by the integral of the photocurrent spectrum. At sufficiently high temperature, the responsivity reaches a regime where it is independent of the detector temperature. However, at a low enough temperature, the responsivity decreases exponentially.

The responsivity is proportional to the exciton ionization efficiency of a single dot multiplied by the gain over the structure which is the ratio of the carrier lifetime over the carrier transit time,²² as given by equation ~~(2)~~(2).

191 $R \propto \eta \frac{\tau_{LT}}{\tau_{transit}} \quad (2)$

192 Future measurements of each of these parameters will be needed. At present we speculate that the
 193 ratio of carrier lifetime and transit times is a constant independent of temperature and bias. This
 194 will be the case if carrier trapping plays a significant role. A possible example of traps could be
 195 very large dots with therefore vanishing gaps. In this case, the major contributor to the
 196 temperature variation of R is the ionization efficiency η . We then consider that the ionization rate
 197 is thermally activated $k_I = k_{I0} \exp(-E/k_b T)$ and competes with a fixed recombination rate k_r
 198 due to radiative and nonradiative processes within one dot. The ionization efficiency is then

199 $\eta_{\text{single QD}} = \frac{e^{-E_I/kT}}{k_r/k_{I0} + e^{-E_I/kT}} \quad (3)$

200 Fitting the experimental data with such an expression leads to a strong discrepancy at the lowest
 201 temperature since it predicts $\eta = 0$ at 0K. Such a deviation may result from the distribution of
 202 activation energies. For a collection of dots, we choose a Gaussian energy distribution such that

203 $\eta_{\text{ensemble}}(T, E_i, \sigma) = \int_{-\infty}^{\infty} \eta_{\text{single QD}}(T, E) \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{(E - E_i)^2}{2\sigma^2}\right) dE \quad (4)$

204 This provides a better fit with values of the mean activation energies of 160meV for sample A,
 205 100 meV for sample B and 34 meV for sample C. The broadening of the ionization energies are
 206 within 20-50%. In this model, the saturation of the ionization efficiency at moderate temperature
 207 implies that the time required for charge separation becomes smaller than the recombination time,
 208 radiative and non-radiative, and therefore that the quantum yield of charge generation is already

close to unity. This is compatible with the fast hopping time mentioned earlier at room temperature.

The origin of these activation energies for charge separation may lie in the disorder associated with the size inhomogeneity and in an energy barrier associated with charge transfer, even in the absence of disorder. To estimate the latter, we use Marcus theory²³ considering that the electron (or hole) transfers from an exciton in a sphere with binding energy E_{ex} to a neighboring sphere.

The Exciton binding energy is given by²⁴ $E_{ex} = 1.8 \frac{e^2}{\epsilon R}$, with R the radius of the dot and ϵ their dielectric constant. Assuming a value of $\epsilon=20$ in HgTe^{25,26}, this is estimated as 32 meV and 24 meV for samples B ($R=4$ nm) and C ($R=5.3$ nm). The Marcus expression for the energy barrier is

$\Delta G_0 = \frac{\lambda_0}{4} (1 + \frac{E_{ex}}{\lambda_0})^2$ where λ_0 is the reorganization energy. For electron transfer in a two-sphere

model $\lambda_0 = e^2 \left(\frac{1}{R} - \frac{1}{R + \delta} \right) \left(\frac{1}{\epsilon_\infty} - \frac{1}{\epsilon_0} \right)$, where R is the dot radius, and δ is the matrix thickness

between the dot surfaces estimated as ~ 1 nm for the dodecanethiol. The dynamic and static dielectric constants, ϵ_∞ and ϵ_0 , refer to the matrix. This is unknown for the matrix material, mostly bound alkane thiol, but we take $\epsilon_\infty = 2.1 \ll \epsilon_0$. This gives energy barriers of 32 meV and 25 meV for samples B and C respectively. Energy disorder due to size inhomogeneity could easily be a larger effect, and may explain the discrepancy with measured values above.

C. RESPONSIVITY

Using the $I(V)$ curves under illumination, as described in reference [1410](#), we can extract the absolute responsivity of our detectors. To proceed, we first identify a temperature at which the

dark current is far below the photocurrent in our range of flux (room temperature for the A sample, 190K for the C sample). We then measure two $I(V)$ curves under illumination at this temperature, for two different amounts of incident flux. This latter is evaluated as in equation

~~(3)~~ ~~(3)~~

$$\phi(T_{BB}, \alpha, \beta) = A_d \pi \cdot \cos \beta \cdot \sin^2 \alpha \int_{\lambda_{\min}}^{\lambda_{\text{cutoff}}} \frac{2hc^2}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda k T_{BB}}} - 1} d\lambda, \quad (3)$$

Where A_d is the active area of the sample (0.1 cm^2), α is the half angle of view of the detector and β is the angle between the normal of the detector and the incident light, h is the Planck constant, c the speed of the light, and T_{BB} the equivalent black-body temperature of the light source.

Finally the responsivity is given by equation ~~(4)~~ ~~(4)~~

$$R = \frac{I_{\text{total}}(\phi_1) - I_{\text{total}}(\phi_2)}{\phi_1 - \phi_2} \quad (4)$$

We thus obtained the absolute responsivity at one temperature and the relative responsivity in ~~Figure 4~~ ~~Figure 4~~ (b), for the other temperatures. Finally the responsivity as a function of the applied bias is plotted in ~~Figure 5~~ ~~Figure 5~~. The responsivity appears linear with bias.

D. NOISE AND DETECTIVITY

The spectrum analyzer provides the voltage noise density (v_n). The current noise density (i_n) which is the useful quantity to evaluate the detectivity, is then obtained by $i_n = \frac{v_n}{G \cdot BW}$, where G is the current amplification and BW is the bandwidth of the spectral acquisition.

The noise for sample C is plotted in ~~Figure 6~~Figure-6 (a) and (b). At all biases and temperatures, a non-white noise prevails at low frequency, and follows a power law with an exponent in the -0.4 to -0.7 range consistent with $1/f$ noise. As temperature and bias increase, the dark current and the noise both increase.

$1/f$ noise can be modeled using the Hooge's law²⁷,

$$i_{1/f}^2 = \frac{\alpha_H \cdot I^2}{N \cdot f} \quad (5)$$

where N is the number of carriers, I the average current through the sample, f the frequency and α_H is a parameter which describes the magnitude of the $1/f$ noise. Hooge reported that in most metallic materials, this parameter is rather close to 2×10^{-3} . While we do not know of reported values of α_H for bulk HgTe, α_H has a value in the 10^{-3} to 10^{-5} range for HgCdTe detectors^{28,29} (with a cadmium content in the 0.17 to 0.3 range), also much smaller than observed here. We

extract $\frac{\alpha_H}{N} = f \frac{i_{1/f}^2}{I^2}$, shown in ~~Figure 6~~Figure-6 (c) for $f=10\text{Hz}$. The number of carriers can be

evaluated as the product of the carrier density, which was estimated in table 1, and the volume of

the sample. This gives 4×10^{10} carriers for sample C. Since the value of $\frac{\alpha_H}{N}$ is typically 10^{-11} for

sample C, α_H is therefore around 0.4, two decades above the Hooge value. The larger value of

the Hooge constant therefore suggests that our CQD samples are possibly about 10 fold noisier

than they need to be. One possibility is that the sample inhomogeneity induces current

crowding^{30,31} such that the actual number of carriers should not be related to the total volume of

the sample. Whether the noise level is intrinsically related to the nanoparticle assembly or more

specific of the particular samples that we have studied, and in particular the aggregation discussed in section I, Figure 1, remains unknown and is a target of further study.

Finally, by combining the responsivity and noise measurements we evaluate the specific detectivity of the samples, using equation ~~(6)~~(6).

$$D^* = \frac{R\sqrt{A_d}}{i_n} \quad (6)$$

Maps of the detectivity as a function of the operating temperature and applied bias are presented in ~~Figure 7~~Figure 7.

These maps show that the HgTe CQD material is able to reach detectivity above 10^9 Jones. The optimal operating temperature is just below room temperature (270K) for sample A ($\lambda_{cut-off} = 2.8\mu\text{m}$) and is around 130K for sample C (with a $\lambda_{cut-off} \approx 6\mu\text{m}$ at this temperature). The applied optimal biases are respectively for sample A and C 19V (corresponding to an electric field of 8kV cm^{-1}) and 8V (19kV cm^{-1}), which is above the applied bias of the regular read-out circuit (generally a few volts). Nevertheless this optimal bias can easily be reduced by changing the spacing of the electrodes.

E. INFLUENCE OF THE THICKNESS

The thickness of the CQD film is an important parameter determining some of the detector properties. In particular, based on bulk optical properties of HgTe, the absorption depth of films of CQDs is expected to be around 5 microns, which is an order of magnitude larger than the thickest samples studied. Correspondingly, the optical densities of the samples were rather small,

of the order of 0.1. Thicker films will directly lead to improved responsivities. While making uniform thick films will require a dedicated effort, it is interesting to explore how the response of thinner films varies with thickness. Therefore, three samples based on sample C of respective thickness 15, 35 and 450nm have been studied. Their properties are summarized in [Table 2](#). The thickness is measured using an Atomic Force Microscope, scanning a groove made with a sharp razor blade.

Table 2: Properties of the three films based on sample C ($\lambda_{\text{cut-off}} \approx 5\mu\text{m}$) and of different thicknesses. The time response is the 1/e decay time.

	Thick film	Medium film	Thin film
Appearance	Brown	Barely colored	Colorless
Thickness (nm)	450	35	15
Dark Current, at 10V (mA)	22	0.56	0.031
Resistance (room T) at 10V (k Ω)	0.5	17	320
Responsivity (normalized by thick film value)	1	7%	0.2%
Decay time (ns)	63	2×10^3	5×10^5

Even the thinnest film provides a measurable mid-IR photoresponse, while being very transparent and only a couple layers of dots. Generally the thicker the film the smaller the resistance, see [Figure 8](#) (a). An increase of the thickness also results in greater absorption which leads to a higher responsivity ([Figure 8](#)(c)). In parallel, the noise also increases with sample thickness. According to Hooge's expression, we expect the current 1/f noise to increase as the

square root of thickness while the responsivity increases linearly with the thickness as long as it remains much smaller than the absorption length. Therefore, there should be a net increase of the detectivity with square root of the thickness. A square root fit is then used as a guide to the eye in [Figure 8](#) (e).

The measurement of the transient photocurrent has been used to probe the density of states inside the gap of several materials.^{32,33} Here, we focus on the transient photocurrent decay, which is related to the cut-off frequency of the detector. Surprisingly, an increase in film thickness gives a faster response of the detector, see [Figure 8](#) (b). It is also observed that an increase of the bias leads to a faster response, both for the rise and decay time while the incident beam energy only slightly affects the transient shape. Increasing the operating temperature of the detector, from 250K to 295K, also leads to a faster response. While these effects are not completely understood, they likely arise from capacitance associated with space charge at the contacts³⁴. While this capacitance is constant for a given electrode geometry, the resistance of the devices drops with increasing film thickness, bias and temperature, leading to a decreased RC time constant. Compared to PbS CQD detector⁹ operating in the near-IR, the HgTe times response are much faster but the responsivities are also lower, in accordance with equation [\(2\)](#).

Since the optimal detectors need to have thicknesses larger than the thickest one studied here in order to saturate the absorption, we expect that the speed of the detector will be much faster than required for usual imagery application for which the typical integration time is in the 1ms range.

IV. CONCLUSION

The conductivity and mid-infrared response photoconductivity of HgTe CQD solid films are investigated as a function of temperature. By changing the size of the particle and the temperature, the cut-off wavelength has been tuned from the near infrared up to $7\mu\text{m}$. The measured responsivity already competes with existing devices such as QWIP³⁵ or type II superlattices^{36,37} and further improvements are expected with optimized thicker films.

The dark current is thermally activated with an activation energy close to half of the energy gap. This suggests that, at room temperature, most carriers are thermally generated. From the estimated carrier density, the mobility is extracted and is relatively large at room temperature, of the order of $0.1\text{-}1\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, especially given that the material is a simple drop-cast film of CQDs without any attempt to eliminate or replace the ligands. These mobility values will need to be confirmed by direct measurements. We observe that the temperature dependence of the responsivity is much weaker than that of the dark current, being essentially constant around room temperature and dropping only at lower temperatures. We interpret this behavior as arising from already efficient charge separation at room temperature. The films show $1/f$ noise at low frequency with values of the Hooge's constant that are two orders of magnitude larger than for clean homogeneous metals, although the noise decreases with temperature leading to an optimum operating temperature. The best detectivity values for a 450 nm thick film are $\sim 2\times 10^9$ jones at 130K and the fastest response times are below 100 ns at room temperature. We stress again that these results have been obtained with no processing of the films other than simply drop-cast from solutions.

Since the mobility and carrier generation efficiency are already high it seems that further improvement will rather come from the improved optical absorption edge, longer carrier lifetime, and reduced noise. Improved optical properties come from thicker films, and materials with

improved monodispersivity. Higher monodispersivity will also reduce the concentration of large dots which may act as recombination centers. Reducing the noise will involve investigating the effect of film processing to possibly reduce the crowding effect which maybe the source of excess $1/f$ noise. It is expected that detectivities above 10^{10} Jones in the mid-IR will be achievable while maintaining a fast response time and moderate cooling temperatures consistent with imaging operation.

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451

452 Figure 1: (a) TEM image of the HgTe material. (sample C) Scale bar is 10 nm. The inset shows a
453 high resolution image of a single dot. (b) Diameter distribution of single dots for sample C
454 measured from TEM imaging (c) Hydrodynamic radii distribution in solution (sample C)
455 obtained by dynamic light scattering (DLS), and a log normal fit of the distribution with a 220
456 nm mean value.

457

458 Figure 2: Dark current for sample C, as a function of the inverse of the temperature, for three
459 different biases. The inset shows the $I(V)$ curve for the sample C for two different temperatures.

460

461 Figure 3: Normalized spectral response for the sample A (top), B (middle) and C (bottom) for
462 different temperatures. These spectra have been acquired while the samples were respectively
463 biased by 2V, 1V and 0.3V.

464

465 Figure 4 (a) Position of the long-wavelength half maximum of the spectral response as a function
466 of the temperature for the sample C. (b) Relative responsivity (integral of the photocurrent
467 spectrum), normalized to the room temperature value as a function of temperature for samples A,
468 B and C. The solid lines are associated fit as discussed in the text.

469

470 Figure 5: Responsivity for samples A, B and C as a function of the applied bias for different
471 temperatures.

472

473 Figure 6: (a) Current noise spectral density for a 2V bias at temperatures: 70, 110, 150, 190, 230,
474 250 and 295K for sample C. (b) Current noise spectral density at 250K at applied bias: 0.5, 2 and
475 5V for sample C. (c) Ratio of the α_H Hooge's parameter over the number of carriers as a function
476 of the detector temperature at 10V for sample C at 10Hz.

477

478 Figure 7: Map of the specific detectivity as a function of temperature and applied bias for sample
479 A (top) and C (bottom).

480

481 Figure 8: (a) Dark current as a function of the applied voltage for three films. (b) Transient
482 photocurrent in response to a short (10ps) laser pulse of 1.06 μ m wavelength, with 7V bias (c)
483 Relative responsivity as a function of the applied bias, (d) noise current spectral density, at a 7V
484 bias and (e) Detectivity (at 7V) as a function of film thickness for three films of different
485 thicknesses based on the material of sample C. All measurements were conducted at room
486 temperature. In the graphs a, b, c, d, the solid line is for the 15nm film, the dashed line for the
487 35nm film and the dotted line for the 450nm film.

488

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- ¹ For a recent review see D. Talapin, J.S. Lee, M. Kovalenko and E. Shevchenko, Chem. Rev. **110**, 389 (2010).
 - ² G.I. Koleilat, L. Levina, H. Shukla, S.H. Myrskog, S. Hinds, A.G. Pattantyus-Abraham, E.H. Sargent, ACS Nano. **2**, 833 (2008).
 - ³ J. Tang, E. H. Sargent, Advanced Materials **23**, 12 (2011).
 - ⁴ I. M Tsidilkovski, Electron spectrum of gapless semiconductors, Spinger series on solid state sciences 116, Springer, Heidelberg, 1997.
 - ⁵ G. Nimtz and B. Schlicht, Narrow-gap semiconductors, Springer tracts in modern physics 98, Spinger, Heidelberg, 1983.
 - ⁶ T. Rauch, M. Böberl, S. F. Tedde, J. Fürst, M. V. Kovalenko, G. Hesser, U. Lemmer, W. Heiss, O. Hayden, Nature Photonics **3**, 332 (2009)
 - ⁷ E. H. Sargent, Adv. Mater. **17**, 515 (2005).
 - ⁸ G. Konstantatos, C. Huang, L. Levina, Z. Lu and E. H. Sargent, Adv. Func. Mater. **15**, 1865 (2005).
 - ⁹ G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina and E. H. Sargent, Nature **442**, 180 (2006).
 - ¹⁰ J. M. Pietryga, R. D. Schaller, D. Werder, M. H. Stewart, V. I. Klimov, and J. A. Hollingsworth, J. Am. Chem. Soc. **126**, 11752 (2004).
 - ¹¹ I. M Tsidilkovski, Electron spectrum of gapless semiconductors, Spinger series on solid state sciences 116, Springer, Heidelberg, 1997.
 - ¹² M. Kovalenko, E. Kaufmann, D. Pachinger, J. Roither, M. Huber, J. Stangl, G. Hesser, F. Schaffler, and W. Heiss, J. Am. Chem. Soc. **128**, 3516 (2006).
 - ¹³ M. Böberl, M. V. Kovalenko, S. Gamerith, E. J. W. List, and W. Heiss, Advanced Materials **19**, 3574 (2007).
 - ¹⁴ S. Keuleyan, E. Lhuillier, V. Brajuskovic and P. Guyot-Sionnest, Mid-infrared HgTe colloidal quantum dot photodetectors, submitted to Nat. Photonics (2011).
 - ¹⁵ L. Kim, P. O. Anikeeva, S. A. Coe-Sullivan, J. S. Steckel, M. G. Bawendi and V. Bulovic, Nano Lett **8**, 4513 (2008).
 - ¹⁶ V. Wood, M. J. Panzer, J. Chen, M. S. Bradley, Jonathan E. Halpert, M. G. Bawendi, V. Bulović, Advanced Materials **21**, 2151 (2009).
 - ¹⁷ T. Kim, K.Cho, E. K. Lee, S. J. Lee, J. Chae, D. H. Kim, J. Kwon, G. Amaratunga, S. Y. Lee, J. Kim , B. L. Choi, Y. Kuk , J. M. Kim and K. Kim, Nat. Photonic **5**. 176 (2011).
 - ¹⁸ C. S. Guenzer and A. Bienenstock, Phys. Rev. B **8**, 4655 (1973).
 - ¹⁹ M. Dobrowolska, A. Mycielski and W. Dobrowolski, Solid State Comm. **27**, 1233 (1978).
 - ²⁰ Y. P. Varshni, Physica **34**, 149 (1967).
 - ²¹ A. Olkhovets, R.-C. Hsu, A. Lipovskii, and F. W. Wise, Phys. Rev. Lett. **81**, 3539 (1998).
 - ²² E. Rosencher and B. Vinter, in *Optoelectronics (Cambridge University Press, Cambridge, 2002)*.
 - ²³ R.A. Marcus, Pure and Appl. Chem. **69**, 13 (1997)
 - ²⁴ L. E. Brus, J. Chem. Phys. **79**, 5566, (1983).

-
- ²⁵ K. Ortner, X. C. Zhang, A. Pfeuffer-Jeschke, C. R. Becker, G. Landwehr, and L. W. Molenkamp, Phys. Rev. B **66**, 075322 (2002).
- ²⁶ V. Radhakrishnan and P. C. Sharma, Phys. Rev. B **23**, 3004 (1981).
- ²⁷ F. N. Hooge, IEEE Trans. Elec. Devices **41**, 1926 (1994).
- ²⁸ R.J. Westerhout, C.A. Musca, J. Antoszewski, J.M. Dell and L. Faraonen, J. Electronic Materials **36**, 884 (2007).
- ²⁹ C.T. Elliot, N.T. Gordon, R.S. Hall, and T.J. Phillips, C.L. Jones and A. Best, J. Electronic Materials **26**, 643 (1997).
- ³⁰ E.P. Vandamme and L.K.J. Vandamme, Microelectronics reliability **40**, 1847 (2000).
- ³¹ A. Mercha, L.K.J. Vandamme, L Pichon, R carin and O. Bonnaud, J. Appl. Phys. **90**, 4019 (2001).

33

- A. Rose, Phys. Rev. **97**, 1538 (1954).
- ³⁵ V. Guériaux, A. Nedelcu and P. Bois, J. Appl. Phys. **105**, 114515 (2009).
- ³⁶ E. Plis, J.B. Rodriguez, G. Balakrishnan, Y.D. Sharma, H.S. Kim, T. Rotter and S. Krishna, Semicond. Sci. Technol. **25**, 085010 (2010).
- ³⁷ M. Walther, R. Rehm, F. Fuchs, J. Schmitz, J. Fleissner, W. Cabanski, D. Eich, M. Finck, W. Rode, J. Wendler, R. Wollrab and J. Ziegler, J. Elec. Mat. **34**, 722 (2005).