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A Material Perspective on HgTe Nanocrystal-based Short Wave Infrared Focal Plane Arrays

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Abstract: After the use of nanocrystals as light down-converters, infrared sensing appears to be one of the first market applications where they can be used while being both electrically and optically active. Over recent years, tremendous progress has been achieved, leading to an apparent rise in the technological readiness level (TRL). So far, the efforts have been focused on PbS nanocrystals for operation in the near-infrared. Here, we focus on HgTe since its narrower band gap offers more flexibility to explore the extended short-wave and mid-wave infrared. We report a photoconductive strategy for the design of short wave infrared focal plane array with enhanced image quality. An important aspect often swept under the rug at an early stage is the material stability. It appears that HgTe remains mostly unaffected by oxidation under air operation. The evaporation of Hg, a potentially dramatic aging process, only occurs at temperatures far beyond the focal plane array's standard working temperature. The main bottleneck appears to be the particle sintering resulting from joule heating of focal plane array. This suggests that a cooling system is required, with a first role of preventing the material from sintering even before targeting dark current reduction.

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Introduction

Nanocrystals (NCs) have become viable building blocks for optoelectronics. Quantum confinement enables a straightforward tunability of their spectral properties. As a zero band gap semiconductor, HgTe^{1–6} offers a particularly broad tunability in the infrared with optical features varying from the visible to the THz range⁷. This has enabled the integration of HgTe as an optically active material in an extensive range of devices such as LEDs,^{8–10} lasers^{11–13}, photonic structures^{14–16}, infrared sensors^{17–24}, and cameras²⁵. Following their use as light down-converters in displays and farming, nanocrystals are now being integrated into infrared cameras^{25–28}, one of the first commercial applications in which the material is both electrically and optically active. So far, most reported cameras^{29,30} are based on PbS nanocrystals and operate in the near and short-wave infrared^{26–28,31–33}. HgTe holds more promises for the design of longer wavelength sensors in the extended short-wave and mid-wave infrared. On the other hand, there are to date only a few reports of imaging based on this material^{25,34–37}.

As devices based on HgTe NCs demonstrate ever-increasing performance, their stability is becoming a growing concern. The material's inherent stability must be compatible with air operations of the device (possibly after encapsulation) throughout a variety of operating conditions from low to high temperatures (-20 to +50 °C) with the ability to withstand traditional semiconductor processing (baking of resist, exposure to solvents). In the case of CdSe and InP nanocrystals, protecting the material with a Zn-based shell allows long-term operations of the nanocrystals, preserving high PL efficiency above 100 °C, under out-of-equilibrium operations and particularly under large incident photon flux³⁸. This improvement has enabled an extension of the display lifetime up to 30 000 hours. In the case of PbS, the surface chemistry has also been optimized to make the material able to sustain post-deposition fabrication, such as pixel etching³⁹ or deposition of non-reflective coatings⁴⁰. In the case of HgTe NCs, such a study is missing. Here, we aim to identify the strengths and weaknesses of HgTe NCs relevant for optoelectronics.

Our study builds on the recent reporting of photoconductive focal plane array based on HgTe NCs by Greboval *et al.*²⁵ They report a cost-effective strategy in which a single step of fabrication is required to infrared sensitize a CMOS read-out circuit (ROIC), with an in-plane applied electric field. Since such commercial cameras would require long-term operation, determining the limiting factors for the lifetime of sensors based on HgTe nanocrystals becomes crucial. After fabricating the device, we monitored its performance over time under various operation conditions and while encapsulating it. We then used X-ray photoemission to analyze the robustness of the material to operate in air and found that HgTe nanocrystals are far more stable than PbS nanocrystals that could easily form a PbO shell on their surface. Using thermogravimetric measurements, we then analyze how the temperature affects the film and determine the temperature at which ligands and mercury get removed from the material. Finally, we also study the impact of the particle sintering occurring when the film is exposed to mild annealing. We propose some strategies to overcome this limitation.

Results and discussion

We start by growing nanocrystals of HgTe using the Keuleyan's procedure,⁴¹ during which mercury chloride reacts with trioctylphosphine telluride in oleylamine used as coordinating solvent. The final particle size is driven by the temperature of the reaction (58°C) and the reaction duration (3 min). Eventually, dodecanethiol (Figure S1) is injected to quench the reaction and ensures the particle colloidal stability. The obtained particles present a branched aspect, see **Figure 1a**. This is chosen so that the band edge is close to that of InGaAs, which is traditionally used for short-wave infrared sensing. The absorption band edge appears at around 1.8 μm , while the material is luminescent and presents a PL peak at 2 μm , see **Figure 1b**. To render the material photoconductive, the native ligands are then replaced by shorter ones made of a mixture of HgCl₂ and mercaptoethanol^{42,43}. The latter procedure leads to a redshift of the band-edge, see **Figure 1c**, and the new cut-off wavelength reaches 2 μm . In the mid-infrared, the relative weight of the C-H bond peak is reduced (Figure S2), which is consistent with a reduction of the ligand length, and a broad peak at 3 μm is the signature of the O-H bond coming from the mercaptoethanol.

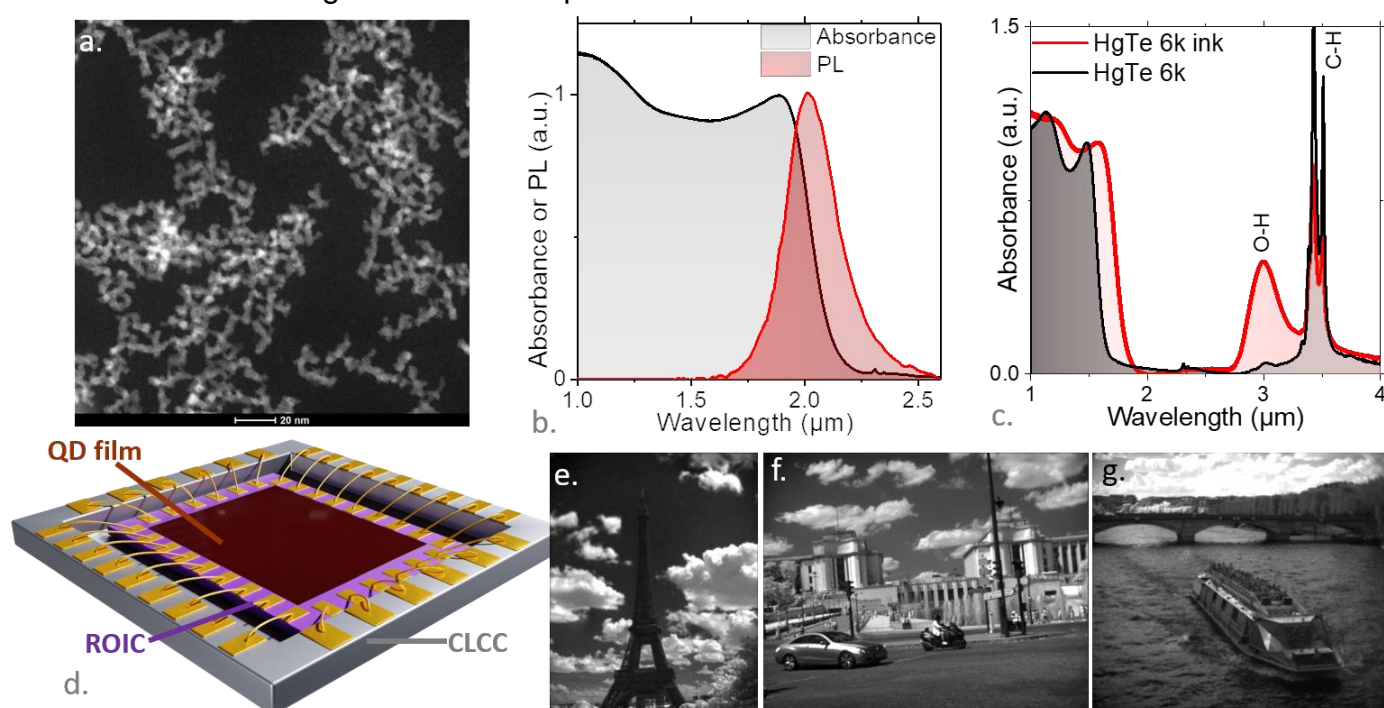


Figure 1 HgTe nanocrystals used for photoconductive focal plane array. a. STEM-HAADF image of the extended short wave infrared NCs. b. Absorption and photoluminescence spectra of the HgTe NCs. c. Absorption spectra of the HgTe NCs at the end of synthesis and once transformed under ink form. d. Schematic of the extended short-wave infrared sensor used as a photoconductive imager. Part d is adapted from ref 25 with permission from Copyright {2022} Royal Chemical Society. e-g Series of view of Paris city acquired with the HgTe NC-based sensor.

The obtained ink solution is then spin-coated onto a VGA format read-out circuit (ROIC – model 1601-quantum with planarized surface), **Figure 1d**. The aforementioned ROIC is chosen since it enables application of a different bias on consecutive pixels, leading to the formation of an in-plane electric field, while most ROICs are only compatible with a vertically applied electric field. This configuration allows for a photoconductive operation of the film, considerably easing the device fabrication as opposed to the design of a full homogeneous diode stack. However, this strategy comes at the price of halving the image's resolution. For more details on the operation and performances, see ref ²⁵ and Figure S3 for an image of the camera setup. Typical images acquired with the camera are given in **Figure 1e-g**.

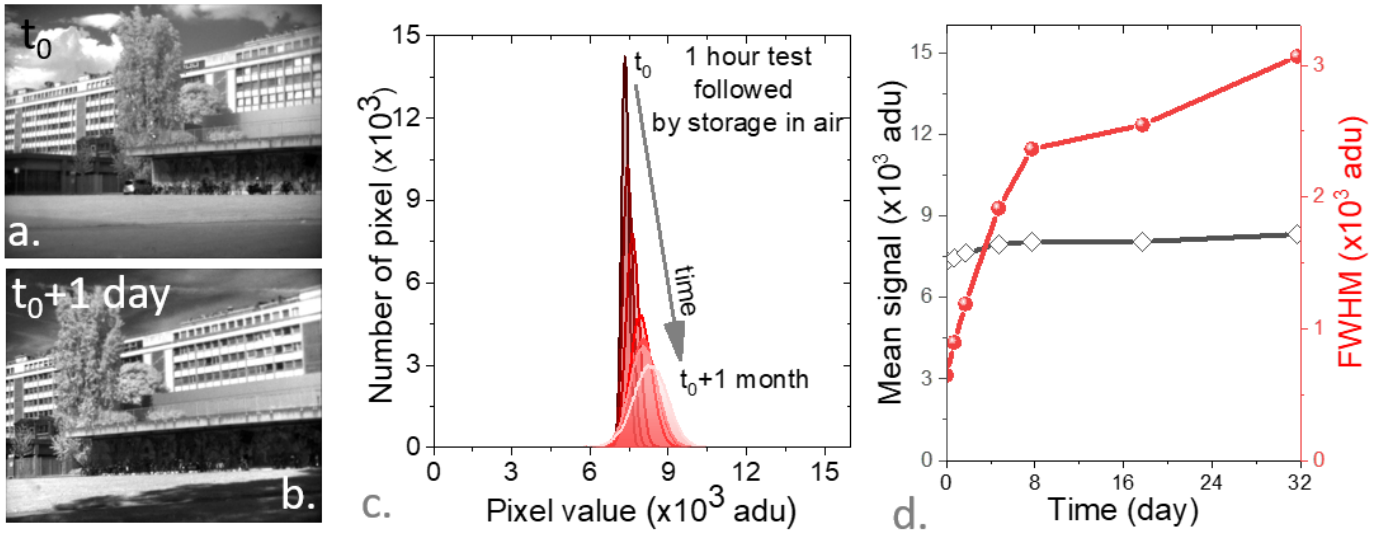


Figure 2 Aging of the sensor in air. In this experiment, discrete acquisitions, typically lasting 1h, are operated over one month. During this whole period the sample stays in air. a. (resp. b) image acquired, the first day (resp. the next day, with the same integration time) with the sensor operated without any cooling and in air. c. Histogram of the dark current count, acquired over $50 \mu\text{s}$, as a function of time. d. Average full width at half maximum of the dark current histogram quantized in adu (analog digital unit encoded over 14 bits corresponding to 16384 levels), as a function of time.

We monitored the ROIC's performance for nearly a month while the sensor was operating in air without any thermal management. The image quality is maintained, see **Figure 2a-b**. The histogram of the dark current is presented in **Figure 2c**, and we can only see a slight drift of the dark current over time, though the sensor also becomes less homogeneous, as pointed out by the rise of the histogram linewidth, see **Figure 2d**. To understand what is the origin of this evolution, we have followed the evolution for an encapsulated film of HgTe.⁴⁴ In this case, the film is covered by a PMMA and a PVA layer acting respectively as water and oxygen repellent. The same aging trend is observed, see Figure S4. This tends to suggest that the observed aging is not much due to exposure of the ROIC to air or moisture see Figure S4.



Figure 3 Aging of the sensor under continuous operation. In this experiment, the sensor is continuously operated for over one day in air. a. (resp. b) image acquired, the first day with $100 \mu\text{s}$ integration time (resp. the next day, with $40 \mu\text{s}$ integration time) with sensor operated without any cooling and in air. c. Histogram of the dark current count, acquired over $50 \mu\text{s}$, as a function of time.

While we observe minor damage as the device is punctually used and stored in air, we observe a stronger drop in the performance when the camera is continuously operated, see **Figure 3a-b**. After 1 day image gets more granulated and integration time has to be reduced from $100 \mu\text{s}$ to $40 \mu\text{s}$ due to the increase of dark current. After only 24h, the dark current has doubled (**Figure 3c**), and the

inhomogeneity (linewidth of the histogram) has increased dramatically. We also observe that in this condition, the film, due to Joule effect in the ROIC, is exposed to relatively high temperatures (see Figure S5). Therefore, in the remainder of the paper, we have used XPS to determine if HgTe gets oxidized and how temperature affects the structural properties of the film.

We used X-ray photoemission (XPS) as a surface-sensitive method to further investigate the HgTe NC surface chemistry. To avoid any charging effects (*i.e.*, a binding energy shift due to the accumulation of holes in the sample after the collection of photoelectrons in the analyzer), samples are systematically processed with short ligands to make them conductive, similar to the way they are made photoconductive. It enables electron reinjection from the substrate after the emission of the photoelectrons. We first use a conventional laboratory instrument to conduct these measurements. The survey spectrum, see **Figure 4a**, confirms the presence of Hg and Te contributions from the inorganic core and S and C from the capping ligands. It also reveals a first striking feature. Despite being prepared in air (*i.e.*, NCs washed in air and the films prepared in air) without any surface cleaning procedures (*i.e.*, films are only degassed under ultrahigh vacuum to conduct the XPS measurements, without further annealing or sputtering), nearly no contribution of oxygen is observed (the expected binding energy for O 1s state is 532 eV). This result contrasts with what has been observed for PbS NCs, which easily get oxidized,⁴⁵ leading to a blue shift of the band edge and consequently to the formation of a PbO shell around the PbS particles.

The resolved Te core level spectrum displays a single contribution (**Figure 4b** for Te 4d and Figure S6 for the Te 3d), excluding its oxidation as well.^{46,47} The structure of the S 2p states appears more complex with at least three contributions, see **Figure 4d**. There are two contributions on low binding energies (162.3 and 163.8 eV, respectively), compatible with sulfide and thiol forms of sulfur. This suggests that there might be a distribution of ligand coupling with Hg, where strongly bound ligands may appear as sulfides while weakly coupled or free ligands preserve their thiol oxidation state. On top of that, the S 2p states present a third contribution with a binding energy (169.3 eV) consistent with the one expected for oxidized sulfurs. This indicates that some sulfur atoms may be under sulfate form in the NC film. Kamath *et al.*⁴⁸ recently proposed to avoid such oxidized species by conducting the reaction in the dark since the oxidation process of the thiols may be photo-assisted.

Since II-VI semiconductor NCs are generally cation rich on their surface,⁴⁹ it is of utmost interest to conduct an XPS analysis of the cations while using more surface-sensitive conditions. This can be obtained by reducing the incident photon energy, which can be done through tunability over a wide energy range accessible with a synchrotron. In this case, the Hg 4f states (acquired with a photon energy of 1253 eV) display two contributions, see **Figure 4c**. The main one appears at a binding energy of 100.3 eV and can be attributed to Hg surrounded by Te atoms in this material. The second contribution appears with a binding energy of 101 eV, and its relative weight is larger as one uses a lower photon energy, see Figure S7. This suggests that this contribution is a surface one. The presence of Hg surface atoms connected to a second population matches with an Hg rich surface where atoms are bound to ligands. Furthermore, because S atoms from the thiolates have a higher electronegativity than Te, those Hg are less electron-rich, explaining why this contribution appears at a higher binding energy.

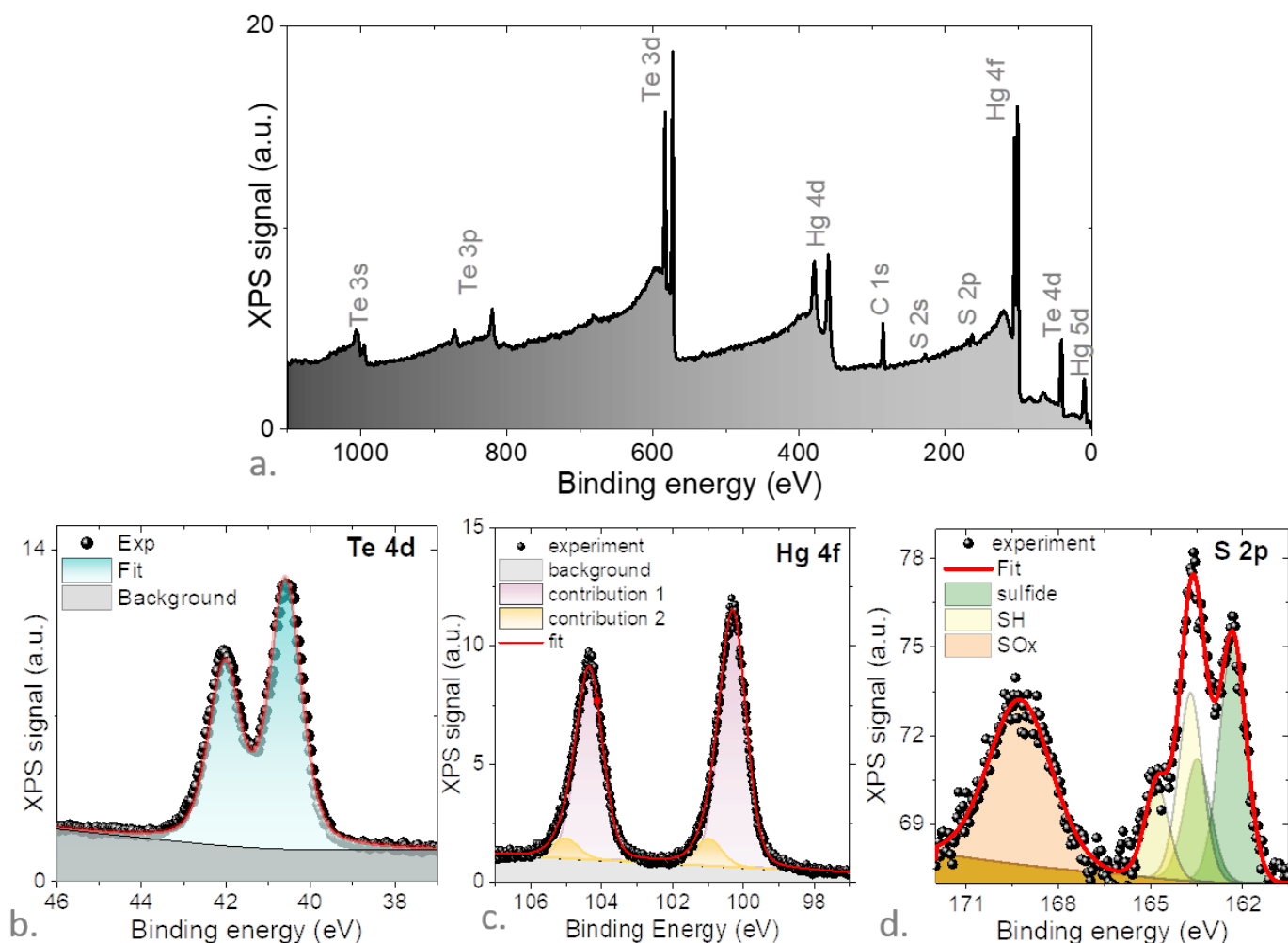


Figure 4 Surface chemistry probed by X-ray photoemission spectroscopy. *a.* XPS survey spectrum acquired using an Al K α line as source ($h\nu=1486$ eV) for a HgTe NCs film capped with EDT. *b.* Te 4d core levels for the same sample ($h\nu=1486$ eV). *c.* Hg 4f core levels for the same sample (acquired with a $h\nu = 1253$ eV), also see Figure S7. *d.* S 2p core levels for the same sample ($h\nu=1486$ eV).

Up to now, we have demonstrated that HgTe NCs appear fairly robust toward oxidation. Nevertheless, this phenomenon can still happen but will mostly occur at the ligand level leading to weaker surface passivation when thiols get oxidized into sulfates. Another relevant parameter to study regarding further integration in optoelectronics is the temperature and, particularly, we would like to determine the temperature range in which the material integrity is preserved. To answer this question, we performed TGA, see **Figure 5**. Starting from room temperature, the temperature is increased, resulting in weight loss, see **Figure 5a**. The first weight loss, around 100 °C, corresponds to solvent (toluene or DMF, depending on surface chemistry) evaporation. We then observe a second weight loss at around 260 °C that matches with the evaporation observed in the case of Hg thiolates only without being observed in the case of bulk HgTe. We can thus attribute it to the evaporation of the ligand shell. Finally, the last weight loss occurs in the 350-400 °C range, which is also observed in the case of bulk HgTe and can be attributed to the melting of the material followed by Hg evaporation.

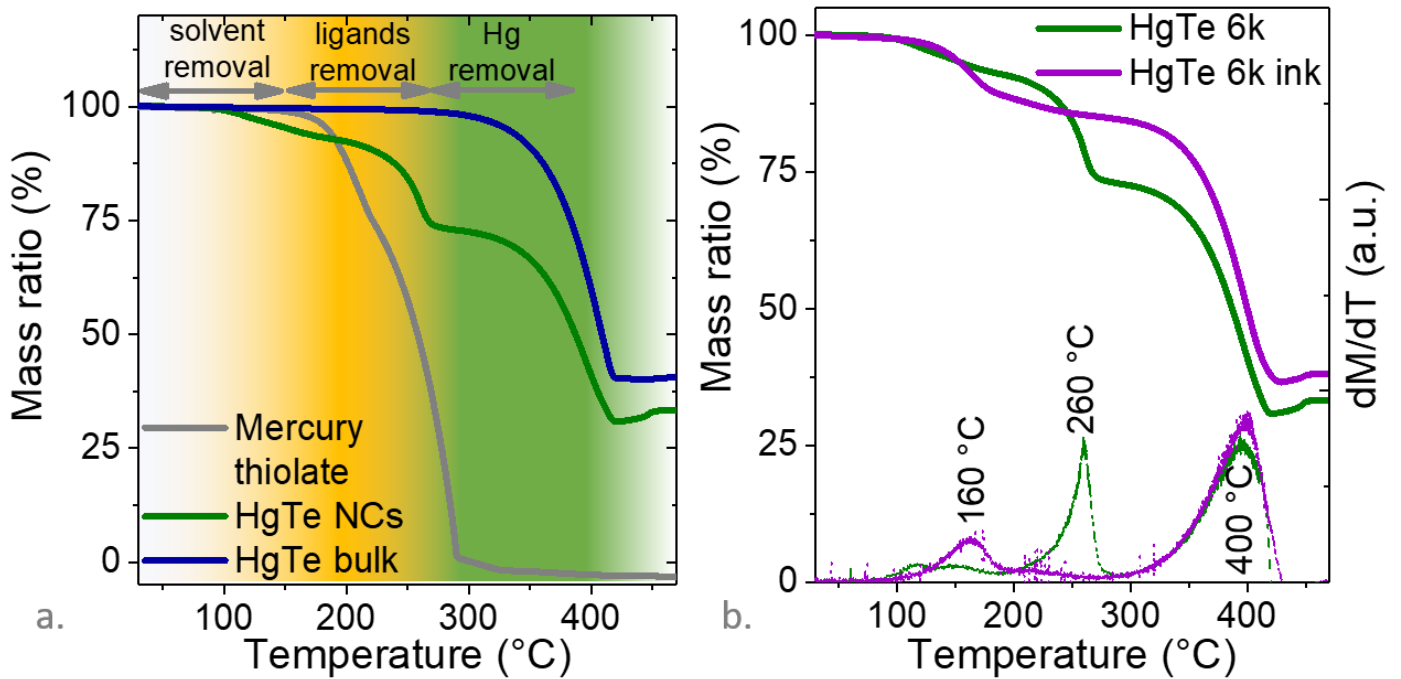


Figure 5 Thermogravimetric analysis of HgTe NCs. a. Mass ratio as a function of the temperature for mercury thiolate, HgTe 6k NCs and bulk HgTe. b. Mass ratio as a function of the temperature for HgTe 6k NCs with DDT and under an ink form. The curves at the bottom are the derivative curves to better highlight when the weight loss occurs.

Though particle sintering already occurs at lower temperatures, as discussed below, this ligand removal sets an upper bound for film processing. In the case of long ligands, the high boiling point of the long alkyl chain (275 °C for dodecanethiol) enables processing at 200 °C while preserving the ligand shell, that is, for example, compatible with atomic layer deposition processes. On the other hand, when the film is processed with shorter ligands, as it is the case in ink-based films, the ligands are removed at a much lower temperature (boiling point of mercaptoethanol at 157 °C), see **Figure 5b**, and the surface chemistry is lost as early as 160 °C.

Though the composition of the photoconductive HgTe NC thin film remains stable up to 160 °C, sintering of the particle can already occur under milder annealing conditions. We followed the absorption spectrum of HgTe films annealed at 50, 75, and 100 °C over time. This temperature range corresponds to the operating temperature of the ROIC, measured to be 57 °C after 15 min of continuous operation, see Figure S5. Note that this exact temperature depends on the operating conditions of the ROIC, and temperatures as high as 80 °C have been measured. While at 50 °C, the spectrum remains unaffected (see Figure S8), at 75 and 100 °C (**Figure 6a** and S8), we observe a large redshift of the spectrum, see **Figure 6b**. This redshift is the signature of a partial loss of quantum confinement induced by the sintering. Greboval *et al.* have¹ provided a sizing curve to link the band edge wavelength λ (in μm) to the equivalent spherical particle size d (in nm): $\lambda = 0.17 \cdot d^{1.49}$. The measured shift corresponds to an increase of the size from 4.7 nm before annealing to 5.2 nm after 15 min at 75 °C and 6 nm for the same annealing but conducted at 100 °C. Direct measurements of the structural change of the film can be obtained by following the narrowing of the diffraction peak as the film is annealed. The Scherrer size ($L = \lambda_{\text{XRD}} / (\text{FWHM} \cdot \cos\theta)$ with $\lambda_{\text{XRD}} = 0.154$ nm the wavelength of the X-ray line, FWHM the full-width at half maximum of the diffraction peak and θ the diffracted angle) extracted here from the (220) plane direction of the X-ray diffraction pattern, see **Figure 6c** and S9, shows an increase from 4 nm to above 6 nm for annealing at 100 °C.

Aside from the evident shift of the spectral response, this will result in a dramatic increase in the dark current of nanocrystal-based sensors due to its exponential dependence on the band gap. In Figure S10 and **Figure 6d**, we follow the current while the film is annealed in the same conditions as the absorption measurements. Dark current is unaffected by mild annealing at 50 °C and increases only by about a factor 3 after 15 min at 75 °C. On the other hand, at 100 °C, the rise of the dark current becomes dramatic and reaches a factor of 100.

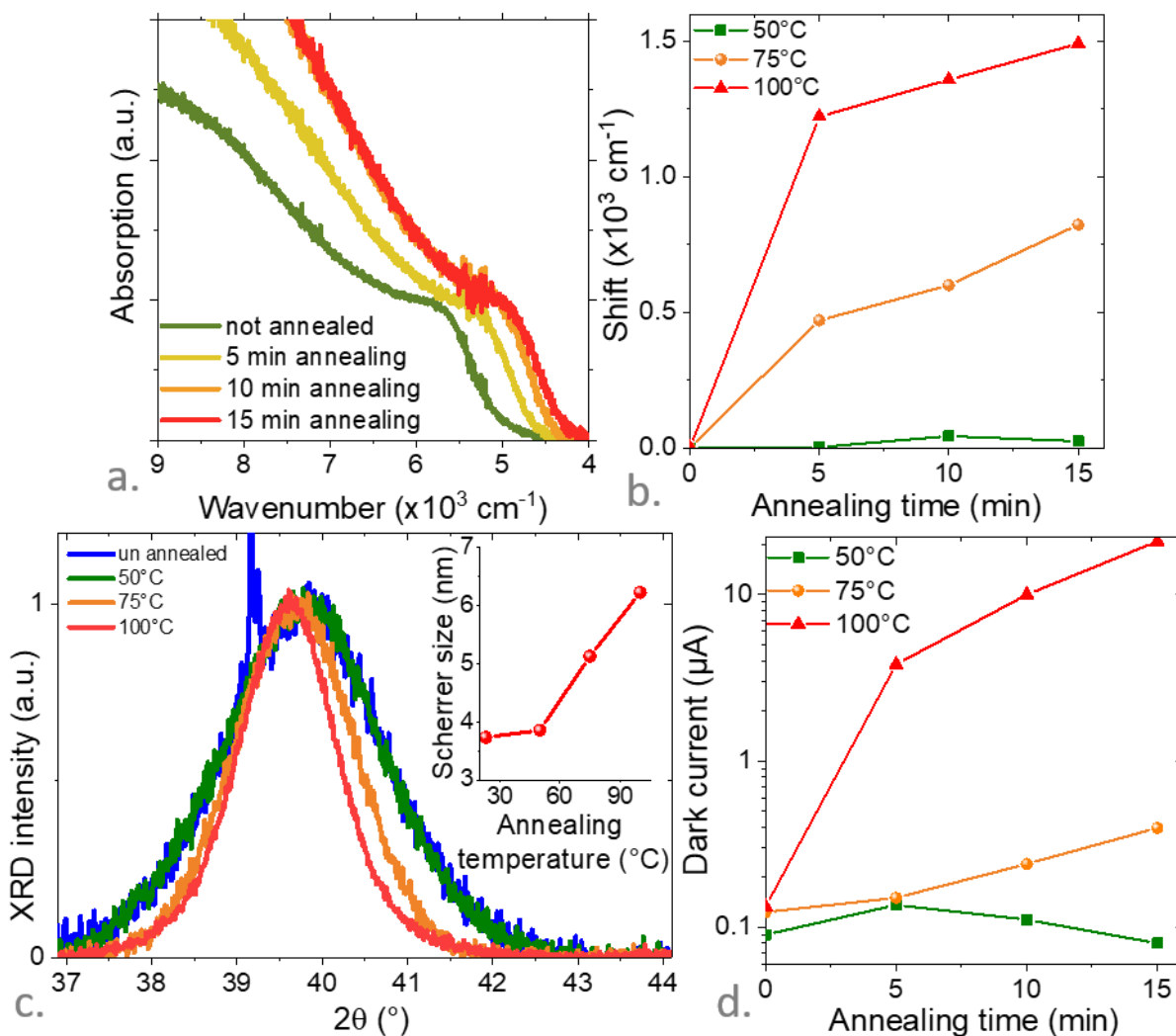


Figure 6 Effect of temperature on structural and optoelectronic properties of the HgTe NC film. a. Absorption spectra of a HgTe nanocrystal film annealed at 75 °C for various durations. Also see Figure S8 for annealing at 50 and 100 °C. b. Induced spectral shift of the band edge transition resulting from annealing at various temperatures as a function of the annealing duration. c. X-ray diffraction pattern around the (220) peak of the zinc blende phase of HgTe for HgTe NC films annealed at various temperatures. The inset shows the extracted Scherrer size for the HgTe crystallites as a function of the annealing temperature. d. Dark current within an HgTe NC film deposited on interdigitated electrodes and operated under 100 mV as a function of the annealing time at various temperatures. See Figure S9 for IV curves.

This result stresses the need for a temperature control in such camera. The latter will have a dual role: (i) control the dark current magnitude (reversible change) and (ii) to avoid particle sintering (irreversible change). In Figure S11, we have verified that once coupled to a Peltier stage, enabling temperature control in the -35°C to +30°C range, the dark current histogram stays unaffected over time, while it dramatically shifts and broadens when Joule heating is not counter balanced.

Alternatively passive strategies that ensure a higher thermal stability of the material may be considered. Atomic layer deposition (ALD) that infill the inter nanocrystal medium may be used as a possible strategy to prevent particle sintering⁵⁰⁻⁵², however the implementation of ALD may not

be straightforward since ALD is generally conducted under mild temperature (*ie* generally above the one leading to HgTe NC sintering) and early attempt of low temperature ALD on HgTe NC thin film has led to a loss of photoconductivity⁵³.

CONCLUSION

To summarize, we have investigated the performance stability of the HgTe NC-based focal plane arrays. Storage in air only leads to a slight drift of the dark current which can be addressed by conducting a two-point correction (dark and gain) of the image. This result is in line with the photoemission data showing that neither Hg nor Te gets oxidized by regular air exposure. Nevertheless, we notice that the ligands are the most prone to oxidation in the film and that oxidized sulfur are easily formed, which likely affects surface passivation. However, it appears that encapsulation is not the most crucial point to consider in order to improve the device stability. In addition, TGA measurement reveals a two-step process: first, a stripping off the ligands above 250 °C, then a mercury evaporation above 350 °C. This is relatively good news since none of these temperatures should be reached typical ROIC operation; thus, we can exclude user Hg vapor exposure. We observe that the primary source of performance drop in our system is the sintering of the particle. The latter starts to be problematic at temperatures ranging from 50 to 75 °C, which is probably high enough for the device to sustain passive storage. On the other hand, in the absence of thermal management strategies, the Joule effect resulting from the current passing in the ROIC can actually bring the device to temperatures where sintering occurs. Given the fact that the material seems to be able to sustain storage up to 50 °C, a simple solution will be the addition of a Peltier cooling stage. More than the reduction of the dark current, the purpose of the cooling stage would be first to prevent the particle sintering resulting from the Joule effect as the ROIC is operated. A long-term goal will be a modification of the material, probably through shelling^{48,54}, to prevent particle sintering. This objective remains challenging since mercury chalcogenide particles are incompatible with the high-temperature growth required by most shell growth methods.

Experimental section

Chemicals: Mercury chloride (HgCl₂, Strem Chemicals, 99%), mercury acetate (Hg(OAc)₂, Alfa Aesar, >98%), **Mercury compounds are highly toxic. Handle them with special care.** Tellurium powder (Te, Sigma-Aldrich, 99.99%), trioctylphosphine (TOP) (Alfa, 90%), oleylamine (OLA, Acros, 80-90%), dodecanethiol (DDT, Sigma-Aldrich, 98%), ethanol absolute (VWR), hexane (VWR, 99%), toluene (VWR, 99.5%), chlorobenzene (VWR), methanol (VWR, >98%), N,N dimethylformamide (DMF, VWR), 2-mercaptoethanol (MPOH, Merck, >99%). All chemicals are used without further purification, except oleylamine that is centrifuged before use.

1 M TOP:Te precursor: 6.35 g of Te powder are mixed with 50 mL of TOP in a three-neck flask. The flask is kept under vacuum at room temperature for 5 min before the temperature is raised to 100 °C. Degassing is conducted at this temperature for 20 min. Then, the atmosphere is switched to N₂ and the temperature is raised to 275 °C. The solution is stirred until a clear orange coloration is obtained. The flask is afterwards cooled down to room temperature and the color turns to yellow. Finally, this solution is transferred to a nitrogen-filled glove box for storage.

Mercury thiolate: 3.18 g of mercury acetate are dissolved in 150 mL of water. The mercury solution is then added to a solution of 5 mL of dodecanethiol in 250 mL of ethanol. Mercury dodecylthiolate is precipitated immediately as a white powder. After decantation, the solid product is filtered and

washed several times with ethanol (150 mL). The white powder is dried and recrystallized in hot toluene.

HgTe 6k nanocrystals: In a 100 mL three neck flask, 540 mg of HgCl_2 (2 mmol) and 50 mL of oleylamine are degassed under vacuum at 110 °C for 1h. Then, the atmosphere is switched to N_2 and the temperature stabilized at 58 °C. Meanwhile, 2 mL of TOP:Te (1 M) are extracted from the glove box and mixed with 8 mL of oleylamine. Then, the TOP:Te solution is quickly injected. After 3 min, 10 mL of a mixture of 10% DDT in toluene are injected and a water bath is used to quickly decrease the temperature. The content of the flask is split over 4 centrifuge tubes and MeOH is added and the solution is sonicated (3 min). After centrifugation the formed pellets are redispersed in one centrifuge tube with toluene. The solution is precipitated a second time with absolute EtOH and sonicated (3 min). Again, the formed pellet is redispersed in toluene. Then, the nanocrystals are centrifuged in pure toluene to get rid of the lamellar phase. The solid phase is discarded. The stable phase is transferred in a vial after filtration (0.22 μm pore size). The optical density of the NC solution is measured to be ≈ 1.5 at 400 nm after a 500x dilution, which roughly correspond to 50 $\text{mg}\cdot\text{mL}^{-1}$.

HgTe ink preparation: We dissolve 30 mg of HgCl_2 in a solution of 18 mL of DMF and 2 mL of mercaptoethanol. At each step the solution is stirred with a vortex and an ultrasonic bath. 900 μL of HgTe nanocrystal solution (same concentration as described above) are mixed with 1 mL of the exchange solution. Finally, toluene is added up to reach a global volume of 4 mL and the solution is centrifugated for 2 min at 6000 rpm to precipitate the nanoparticles. The supernatant is discarded and the formed pellet is dried using nitrogen flux and then redispersed in 175 μL of DMF in order to target a thickness of about 100 nm. The obtained solution is called ink. Before ink deposition, the substrate is placed in an oxygen plasma cleaner for 10 min to increase the wettability. The ink is spin-coated on the substrate at 4000 rpm (at 2000 $\text{rpm}\cdot\text{s}^{-1}$ acceleration) for 30 s. This gives a homogeneous film between 100 nm and 200 nm.

Infrared Absorption spectroscopy: For infrared spectroscopy, we use a Fischer Nicolet iS50 in attenuated total reflection (ATR) mode. The spectra are averaged over 32 acquisitions and have a 4 cm^{-1} resolution.

TEM: A drop of diluted NCs solution is drop-casted onto a copper grid covered with an amorphous carbon film. The grid is degassed overnight under secondary vacuum. Imaging is conducted using a JEOL 2010 transmission electron microscope operated at 200 kV.

X-ray diffraction (XRD) signals of thin films of nanoparticles drop-cast on a silicon substrate are recorded on a Phillips X'Pert diffractometer with a $\text{Cu-K}\alpha$ radiation. Measurements are performed at a working condition of 40 kV in voltage and 40 mA in current.

(Scanning)-Transmission Electron Microscopy ((S)-TEM) Characterization. Electron microscopy characterization is performed with a FEI Talos transmission electron microscope operating at 200 kV acceleration voltage. These characterizations include bright-field High-Resolution TEM (HRTEM), STEM (probe semi-convergence angle of 10.5 mrad).

X-ray photoemission measurements: Photoemission spectra are collected on an Omicron Argus X-ray photoelectron spectrometer, using a monochromated Al $\text{K}\alpha$ ($h\nu=1486.6\text{eV}$) radiation source having a 300 W electron beam power. The emission of photoelectrons from the analyzed sample is taken at a takeoff angle of 45° under ultrahigh vacuum (10^{-8} Pa). The spectra are collected with a 20 eV pass energy.

X-ray photoemission measurements on synchrotron: For photoemission spectroscopy, we use the Tempo beamline of synchrotron Soleil. Films of nanocrystals are spin-casted onto a gold coated Si substrate (the gold layer was 80 nm thick). The ligands of the nanocrystals are exchanged using the same procedure as for device fabrication to avoid any charging effects during measurements. Samples are introduced in the preparation chamber and degassed until a vacuum below 10^{-9} mbar is reached. Then samples are introduced in the analysis chamber. The signal is acquired by a MBS A-1 photoelectron analyzer equipped with a delay line detector developed by Elettra.^{43,55} The acquisition is done at a constant pass energy (50 eV) within the detector. Various photon energies from 150 to 1250 eV are used for the analysis of the core levels. A gold substrate is used to calibrate the Fermi energy. The absolute value of the incoming photon energy is determined by measuring the first and second orders of Au4f core level peaks. Then for a given analyzer pass energy, we measure the Fermi edge and set its binding energy as zero. The same shift is applied to all spectra acquired with the same pass energy. For the deconvolution of the XPS spectra, a linear background was subtracted and Voight function with 20% weighted Lorentzian contribution was used.

Thermogravimetric analysis (TGA): The TGA measurements are carried out on a TA Instruments SDTQ600. Solid samples are obtained as follows: 0.5 mL of the HgTe dispersion in toluene are precipitated by adding methanol, centrifuged and then dried under vacuum overnight. Between 5 and 15 mg of powder are used for each TGA measurement in a platinum crucible. Measurements are performed from 20 °C to 500 °C, with a heating rate of 5 °C/min under a flow of nitrogen.

Focal plane array fabrication: A ROIC packaged in a CLCC is cleaned in a O₂ plasma cleaner for 10 min. The ROIC is then placed on a spincoater and 30 µL of HgTe ink is spincoated at 1000 rpm and an acceleration of 500 rpm.s⁻¹ for 60 s and a drying step at 2000 rpm (1000 rpm.s⁻¹) for 120 s. The film is further dried for 2 hours under primary vacuum.

ASSOCIATED CONTENT

Supplementary material includes extra material discussing (i) surface chemistry probed by infrared spectroscopy, (ii) the focal plane array and its aging, (iii) XPS analysis of the HgTe NC film, (iv) effect of the sample annealing, (v) operation of the sensor with T control.

COMPETING INTEREST

The authors declare no competing financial interests.

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