

Colloidal II-VI - epitaxial III-V heterostructure: a strategy to expand InGaAs spectral response

Adrien Khalili¹, Claire Abadie², Tung Huu Dang¹, Audrey Chu¹, Eva Izquierdo¹, Corentin Dabard^{1,3}, Charlie Gréboval¹, Mariarosa Cavallo¹, Huichen Zhang¹, Stefano Pierini¹, Yoann Prado¹, Xiang Zhen Xu³, Sandrine Ithurria³, Grégory Vincent², Christophe Coinon⁴, Ludovic Desplanque⁴, Emmanuel Lhuillier^{1*}

¹Sorbonne Université, CNRS - UMR 7588, Institut des NanoSciences de Paris, INSP, F-75005 Paris, France

²ONERA - The French Aerospace Lab, 6, chemin de la Vauve aux Granges, BP 80100, 91123 Palaiseau, France.

³Laboratoire de Physique et d'Etude des Matériaux, ESPCI-Paris, PSL Research University, Sorbonne Université Univ Paris 06, CNRS UMR 8213, 10 rue Vauquelin 75005 Paris, France.

⁴Univ. Lille, CNRS, Centrale Lille, Univ. Polytechnique Hauts-de-France, Junia, UMR 8520 - IEMN, F-59000 Lille, France

*To whom correspondence should be sent: el@insp.upmc.fr

Table of content

1. Device fabrication	2
1.1. HgTe Nanocrystal growth	2
1.2. InGaAs Nanowires growth	3
1.3. Hybrid structure fabrication	3
2. Electromagnetic simulations	5
3. Additional device characterization	6
4. References	8

1. Device fabrication

1.1. HgTe Nanocrystal growth

Chemicals: Mercury chloride (HgCl_2 , Sigma-Aldrich, 99%), **Mercury compounds are highly toxic. Handle them with special care.** tellurium powder (Te, Sigma-Aldrich, 99.99%), trioctylphosphine (TOP, Alfa Aesar, 90%), oleylamine (OLA, Acros, 80-90%), dodecanethiol (DDT, Sigma-Aldrich, 98%), acetone (VWR), isopropanol (IPA, VWR), ethanol absolute anhydrous (EtOH , VWR), methanol (VWR, >98%), hexane (VWR, 99%), 2-mercaptoethanol (MPOH, Merck, >99%), N,N dimethylformamide (DMF, VWR), toluene (VWR, 99.8%), lithium perchlorate (LiClO_4 , Sigma-Aldrich, 98%), polyethylene glycol (PEG, $M_w = 6 \text{ kg.mol}^{-1}$), methylisobutylketone (MIBK, VWR, >98.5%), ammonia (NH_3 , 30%, Carlo Erba Reagents). All chemicals are used without further purification except oleylamine that is centrifuged before use.

1 M TOP:Te: 2.54 g of Te powder are mixed in 20 mL of TOP in a three neck flask. The flask is kept under vacuum at room temperature for 5 min and then the temperature is raised to 100 °C. Furthermore, degassing of flask is conducted for the next 20 min. The atmosphere is switched to nitrogen and the temperature is raised to 275 °C. The solution is stirred until a clear orange coloration is obtained. The flask is cooled down to room temperature and the color change to yellow. Finally, this solution is transferred to a nitrogen filled glove box for storage.

HgTe NCs synthesis with band-edge at 6000 cm^{-1} : In a 100 mL three-neck flask, 540 mg of HgCl_2 and 50 mL of oleylamine were degassed under vacuum at 110 °C. At this stage, the solution was yellow and clear. Meanwhile, 2 mL of TOP:Te (1 M) was extracted from the glove box and was mixed with 8 mL of oleylamine. The atmosphere was switched to N_2 and the temperature was set at 58 °C. The TOP:Te solution was quickly injected and the solution turned dark after 3 min, 10 mL of a mixture of 10% DDT in toluene was injected and a water bath was used to quickly decrease the temperature. The content of the flask was split over 4 tubes and MeOH was added. After centrifugation, the formed pellets were redispersed in one tube with toluene. The solution was precipitated a second time with absolute EtOH. Again, the formed pellet was redispersed in toluene. At this step, the CQDs were centrifuged in pure toluene to remove the lamellar phase. The solid phase was discarded. The stable phase is transferred in a weighted falcon and finally precipitated using ethanol. Finally, CQDs are redispersed with a 50 mg.mL^{-1} concentration in toluene.

HgTe ink: 1.5 mL of the CQD solution in toluene is mixed with 1 mL of exchange solution as previously reported¹ and 1 mL of DMF to induce phase transfer toward polar phase. 5 mL of hexane is added to the solution and mixed with vortex and sonication. After a few seconds, two phases are clearly visible and the hexane one is removed. The solution is cleaned with hexane two times more. Then, the solution is precipitated by adding toluene and centrifuged at 6000 rpm for 3 min. Supernatant is discarded and the QDs are redispersed in 150 μL of DMF.

Material characterization: For TEM imaging, a drop of diluted NCs solution is casted on a copper grid covered with an amorphous carbon film. The grid is degassed overnight under secondary vacuum. A JEOL 2010F is used at 200 kV for the acquisition of pictures.

For infrared spectroscopy, we use a Fischer Nicolet iS50 in attenuated total reflection (ATR) mode. The source is a white halogen lamp, the beamsplitter made of CaF_2 and the detector is a DTGS ATR. Spectra are typically acquired between 10 000 and 2100 cm^{-1} with a $\approx 0.5 \text{ cm}^{-1}$ resolution and averaged over 32 spectra.

1.2. InGaAs Nanowires growth

InGaAs wires growth (Figure S 1a-c): Arrays of in-plane InGaAs n-doped nanowires are fabricated using atomic hydrogen assisted selective area Molecular Beam Epitaxy (MBE).^{2,3} The silicon dioxide mask, prepared by e-beam lithography and reactive ion etching on InP(100) semi-insulating substrate, consists of a 100 μm wide network of 200 [110]-oriented nano-trenches repeated every 500 nm and composed of 20 μm -long and 130 nm wide openings. These arrays are connected in parallel at one end by a larger 5x100 μm opening in the SiO_2 mask. Two other 100 μm long and 130 nm wide trenches are designed crosswise in the middle and at the other end of the NW arrays to anticipate some discontinuity of NWs and ensure electrical conduction. After mask preparation, the sample is introduced in the MBE chamber for InP surface deoxidization under atomic hydrogen and arsenic flux at 500 °C. The subsequent growth consists of the epitaxy of 50 nm InGaAs lattice matched to InP and n-doped with silicon. Atomic hydrogen exposure together with a nominal growth rate of 0.2 ML.s^{-1} ensures a good selectivity for the growth at 490°C. Van der Pauw measurements performed on a bare sample of the same thickness, under the same growth conditions but with no mask, reveal a Hall mobility of about 3100 $\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$ and an electron concentration of $3.5 \times 10^{18} \text{ cm}^{-3}$ at room temperature. At 77K, the conductance is slightly higher with a Hall mobility of 3500 $\text{cm}^2.\text{V}^{-1}.\text{s}^{-1}$ and the same electron concentration.

1.3. Hybrid structure fabrication

After the growth step, the sample is rinsed with acetone and isopropanol. An adhesion primer (TI-PRIME) is spin-coated onto the substrate and annealed for 2 min at 120 °C before AZ5214E photo-resist is spin-coated and baked at 110 °C for 90s. A MJB4 mask-aligner is used to exposed the sample to UV light for 1.5 s through a lithography mask. Then the sample is baked 2 min at 125 °C to invert the resist and flood-exposed for 40 s. The sample is dipped 30 s in a solution of AZ726 developer before being rinsed in pure water for 15 s. The patterned substrate is dried and cleaned with 5 min of oxygen plasma to remove resist residues. The sample is then dipped few seconds in a solution of NH_3 3% to prevent oxidation of the InGaAs wires. In a thermal evaporator, 5 nm of chromium are deposited as an adhesion promoter before 150 nm of gold are evaporated (Figure S 1d). Lift-off is conducted in an acetone bath for at least 1 h. Then, the substrate is rinsed with isopropanol before a layer of A6 PMMA 950 is spin-coated and baked 15 min at 150 °C. The sample is transferred in a Zeiss Supra 40 SEM with Raith ELPHYS Quantum device for electron beam lithography. The operating bias is set to 20 kV and the aperture to 20 μm . The current is measured at 100 pA. The dose is set at 260 $\mu\text{C}.\text{cm}^{-2}$. The PMMA is developed by dipping the film in a solution of MIBK:isopropanol (1:3) for 50 s and rinsed in pure isopropanol for 20 s. The sample is put under an O_2 plasma to remove residual resists. We dip the sample few seconds in a 3% NH_3 solution to prevent oxidation of the InGaAs wires. We then place the sample in an Alcatel sputtering chamber for a 50 min deposition of 100 nm of SiO_x (Figure S 1e). The lift-off is performed by dipping the film

in acetone overnight. Finally, a solution of HgTe QDs ink is spin-coated (Figure S 1f) following a two-step procedure: 1000 rpm for 120 s followed by 3000 rpm for 60 s. The final thickness is in the 200-400 nm range.

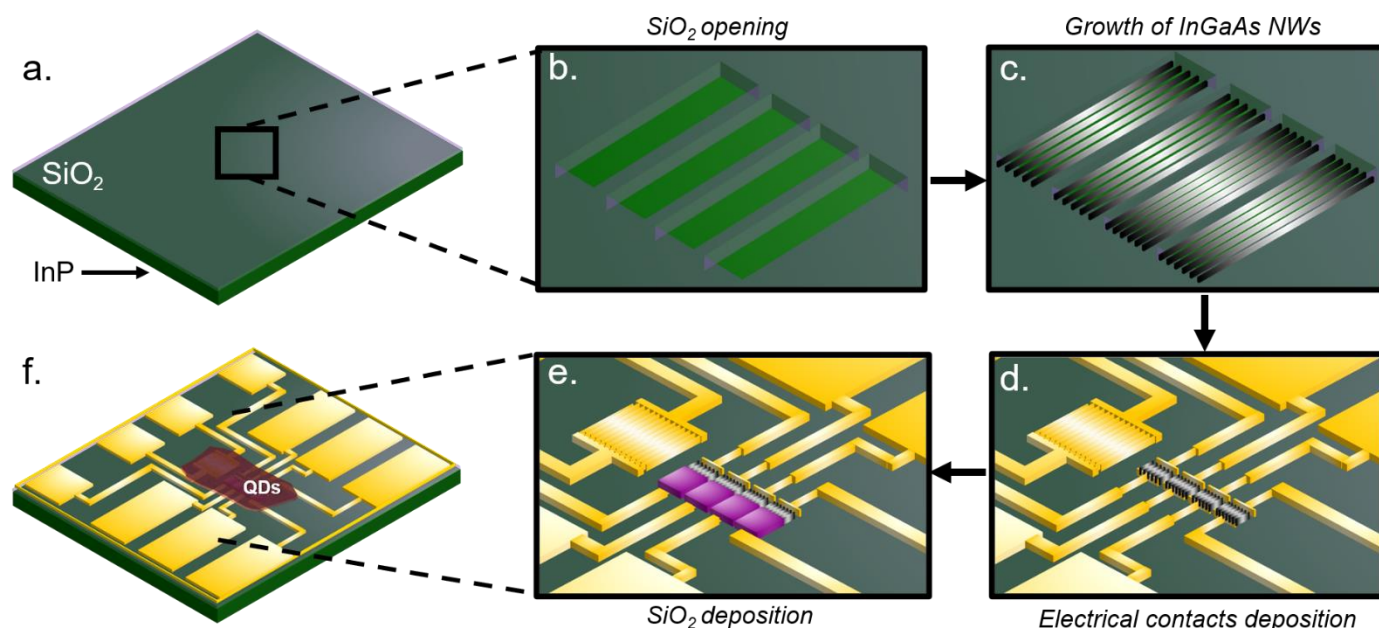


Figure S 1 Scheme of the six-step procedure for fabricating the InGaAs wires/HgTe NCs hybrid structure. a. Deposition of silica on InP substrate by sputtering. b. Opening of the silica layer by e-beam lithography and etching. c. Growth of the InGaAs wires by molecular beam epitaxy. d. Deposition of the metallic contacts after optical lithography. e. Protection of the metallic contacts by silica coating to avoid direct transport in the NC array. f. Deposition of the HgTe NC film

2. Electromagnetic simulations

Electromagnetic simulation: The complex optical index for InP, InGaAs,⁴ HgTe⁵ are respectively taken from ref. We assume that $n_{\text{SiO}_2} = 1.45$ and $k_{\text{SiO}_2} = 0$. Maps of the electromagnetic power loss density have been calculated with RF Toolbox from COMSOL commercial software based on the Finite Elements Method (FEM). Floquet periodicity is chosen as boundary conditions in the plane direction. Ports are implemented at the top and bottom limits and diffracted orders are considered. Mesh has a triangular pattern.

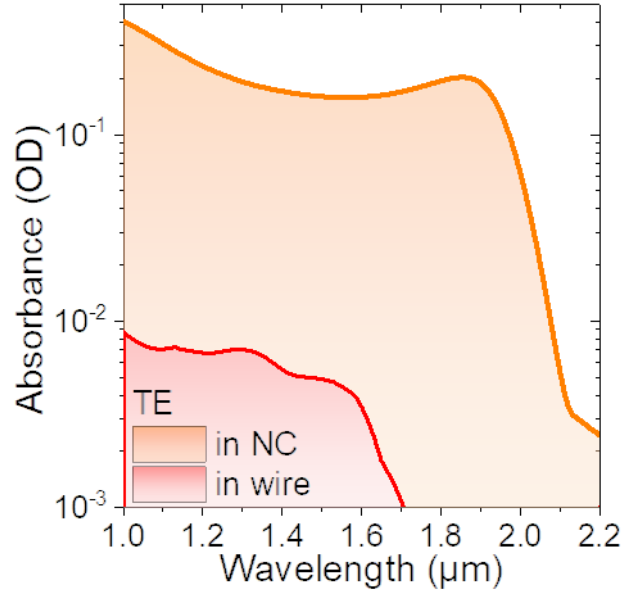


Figure S 2 Simulated absorption of the hybrid structure along the TE polarization within the InGaAs wires and within the HgTe NCs

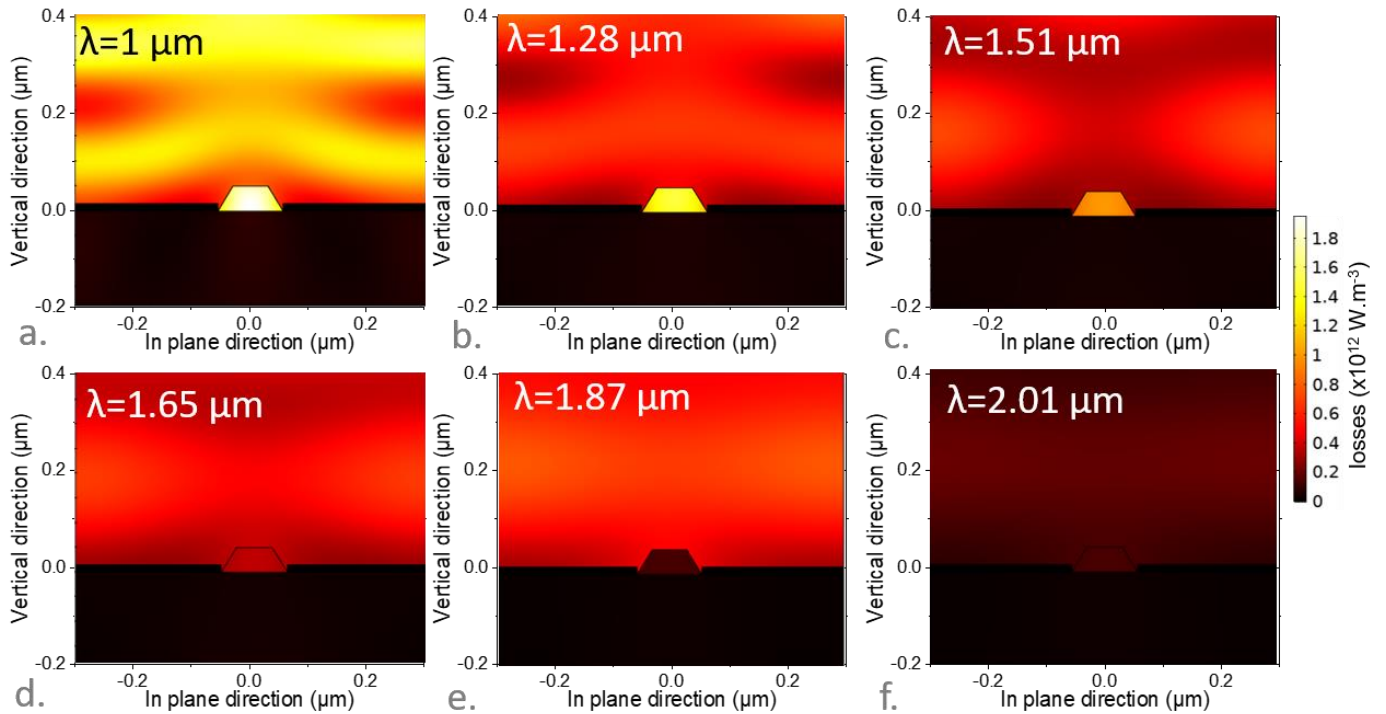


Figure S 3 Absorption maps of the hybrid structure in TE polarization at 1 μm (a.), at 1.28 μm (b.) at 1.51 μm (c.), at 1.65 μm (d.) at 1.87 μm (e.), at 2.01 μm (f.).

3. Additional device characterization

DC transport measurements: The sample is connected to a dual channel Keithley 2634b, which controls the drain bias (V_{DS}) and measures the associated current (I_{DS}). This measure is carried out in the dark or under illumination using a 1.55 μm laser diode.

Photocurrent spectra measurements: (see Figure S 4): The device is enclosed in a closed-cycle cryostat and cooled down to the desired temperature. The head of the cryostat is brought in the sample compartment of a Fischer iS50 FTIR spectrometer and illumination is provided by a white halogen lamp through two ZnSe windows (one on the outer cryostat enclosure and one on the cold shield). The photocurrent is amplified using a Femto DLPCA-200 transimpedance amplifier, which also serves as a bias source. Output of the amplifier is sent back to the FTIR spectrometer through the ad hoc external detector adapter. All spectra are normalized to the background spectrum, acquired with a flat-response DTGS detector in the same spectral range to account for source and optical path spectra.

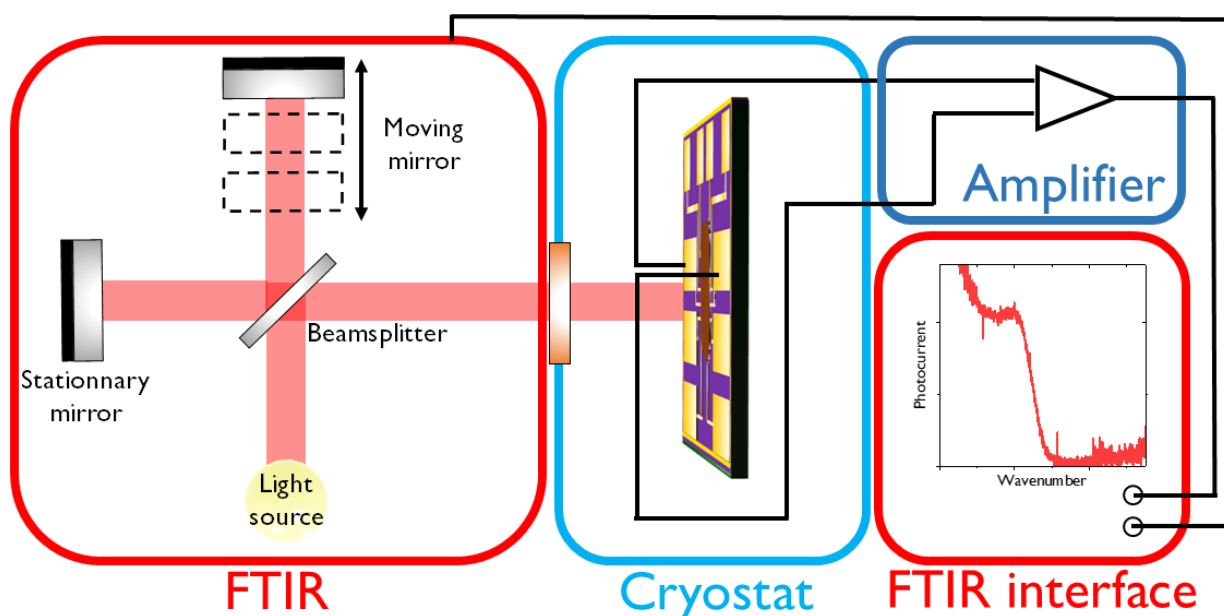


Figure S 4 Scheme of the experimental setup to measure the photocurrent spectra.

Activation energy measurements: Devices are mounted on the cold finger of a closed-cycle cryostat equipped with cold shield. The samples are cooled down to 80K, and current flow is measured with a Keithley 2634b source-meter which also applies bias to the sample. Temperature is measured with a Lakeshore 325 temperature controller using a calibrated sensor on the sample holder. Resulting $I(T)$ curves are fitted to an Arrhenius model ($I_0 = Ae^{-E_a/kT}$) between 300K and 80K, allowing for the extraction of the activation energy E_a .

Electrolyte gated field-effect transistor (FET): The electrolyte is prepared in a nitrogen-filled-glove-box. 0.5 g of LiClO_4 are mixed with 2.3 g of PEG ($M_w = 6 \text{ kg.mol}^{-1}$). The resulting mix is heated at 170 $^\circ\text{C}$ for 2 h until the solution turns clear, then cooled down overnight before use. In a nitrogen-filled-glove-box, the electrolyte is deposited on top of the device (see Figure S 5). The polymer gel is allowed to cool down overnight.

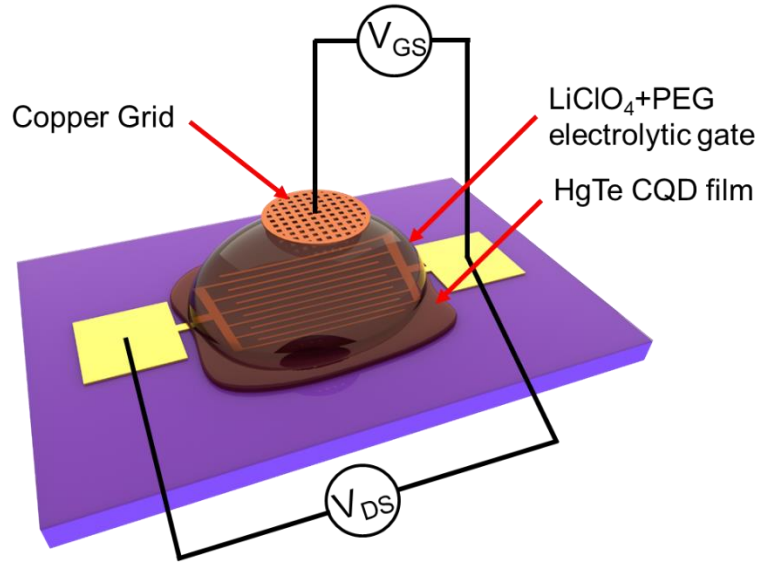


Figure S 5 Scheme of an electrolytic transistor.

Responsivity measurements (see Figure S 6): The source is a laser diode at $1.55\ \mu\text{m}$ with a spot size of $1.4\ \text{mm}^2$. The flux can be chopped from 1 Hz to 10 kHz. The photocurrent is measured using a Zurich Instruments MFLI lock-in amplifier. The sample is mounted on the cold finger of a close cycle cryostat.

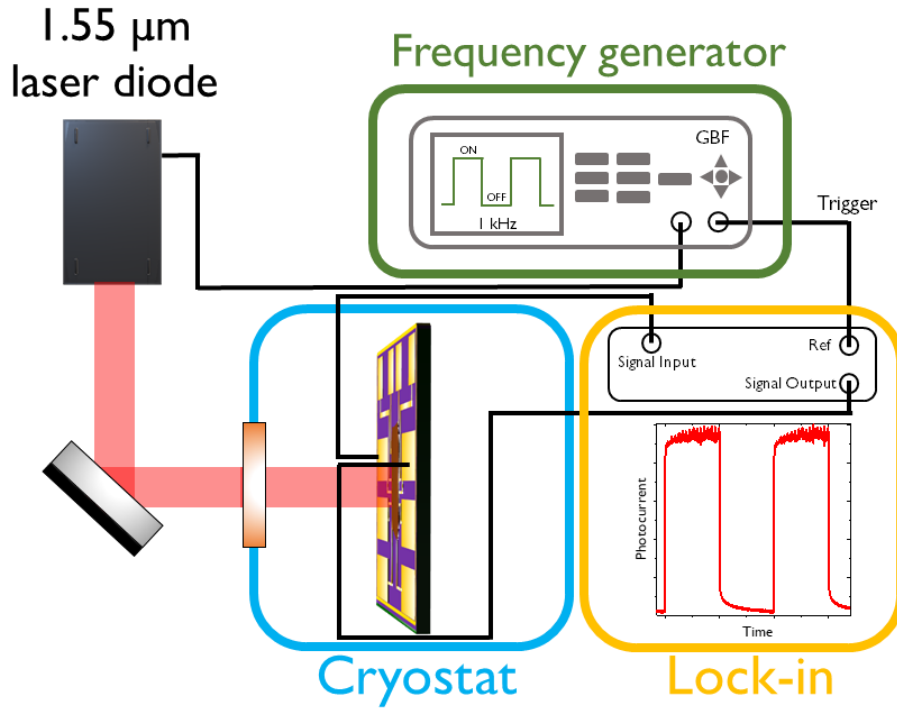


Figure S 6 Scheme of the experimental setup to measure the responsivity.

Time-resolved measurements (see Figure S 7): A pulsed laser (LD Pumped All-Solid-State Q-switched Laser MPL-H-1573) at $1.57\ \mu\text{m}$ is shone on the sample. The laser beam diameter is around $1.3\ \text{mm}^2$ (*i.e.*, poorly focused) to prevent excessive heating of the sample, which may lead to a drift

of the photoresponse. The pulses are 1.15 ns long and repeated every 10 ms (100 Hz). A photodiode is used to trigger the signal. Current from the device is amplified by a Femto Voltage Amplifier DUPVA-1-70, and fed into a GHz oscilloscope (Rhode & Schwartz RTE 1102).

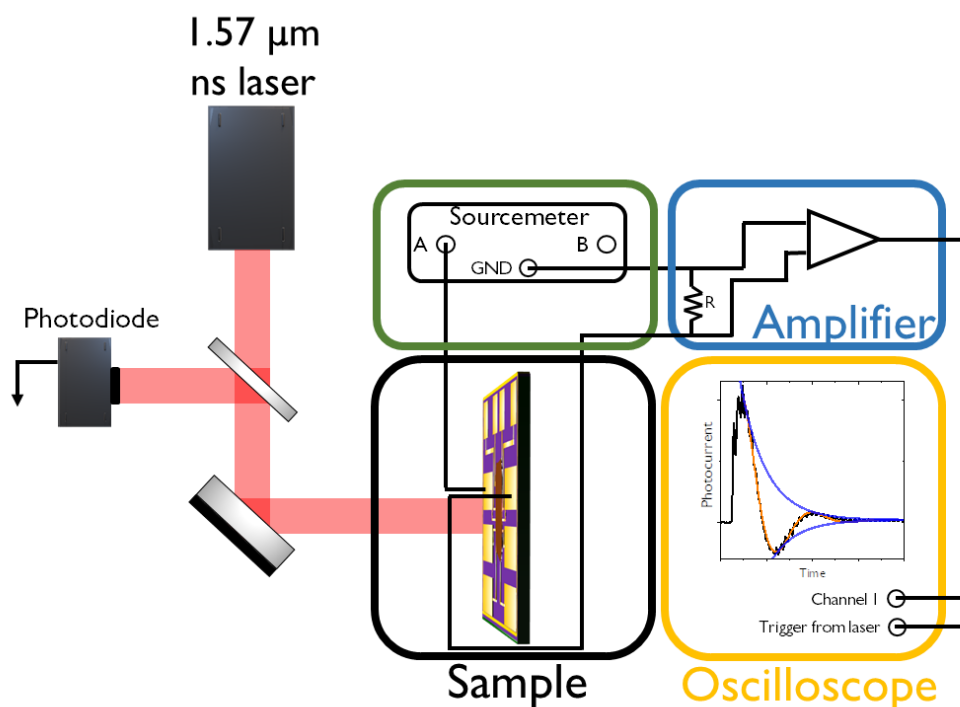


Figure S 7 Scheme of the experimental setup to measure the time-resolved photocurrent

Noise measurement: Current from the device is amplified by a Femto DLPCA-200, then fed into an SRS SR780 spectrum analyzer. The sample is mounted on the cold finger of a close cycle cryostat.

Detectivity determination: The specific detectivity (in Jones) of the sample is determined using the formula: $D^* = \frac{R\sqrt{A}}{S_I}$, where R (in $A.W^{-1}$) is the responsivity, S_I is the noise ($A/\sqrt{Hz}$) and A the area of the device (cm^2).

4. References

- ¹ B. Martinez, J. Ramade, C. Livache, N. Goubet, A. Chu, C. Gréboval, J. Qu, W.L. Watkins, L. Becerra, E. Dandeu, J.L. Fave, C. Méthivier, E. Lacaze, and E. Lhuillier, *Advanced Optical Materials* **7**, 1900348 (2019).
- ² A. Bucamp, C. Coinon, J.-L. Codron, D. Troadec, X. Wallart, and L. Desplanque, *Journal of Crystal Growth* **512**, 11 (2019).
- ³ A. Bucamp, C. Coinon, D. Troadec, S. Lepilliet, G. Patriarche, X. Wallart, and L. Desplanque, *Nano Res.* **13**, 61 (2020).
- ⁴ S. Adachi, *Journal of Applied Physics* **66**, 6030 (1989).
- ⁵ P. Rastogi, A. Chu, T.H. Dang, Y. Prado, C. Gréboval, J. Qu, C. Dabard, A. Khalili, E. Dandeu, B. Fix, X.Z. Xu, S. Ithurria, G. Vincent, B. Gallas, and E. Lhuillier, *Advanced Optical Materials* **9**, 2002066 (2021).