Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information for

Inside a nanocrystal-based photodiode using photoemission microscopy

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Table of content

1. Planar pn junction fabrication

Sample preparation: 5 nm of Cr and 80 nm of Au were thermally evaporated on an Si substrate. The substrate is then sonicated in acetone, rinsed with isopropanol and finally cleaned using O_2 plasma. SnO_2 is spin-coated on top of Au at 4000 rpm for 30 s. Then, AZ5214E photoresist is spin-coated on the surface, baked at 110°C for 90 s and an interdigitated pattern is created by UV lithography through a mask. Ag_2Te is spin-coated on top of the pattern followed by the photoresist lift-off using acetone and rinsing in deionized water. The top layer of HgTe ink is spin-coated on top of the interdigitated pattern with a targeted thickness of 40 nm.

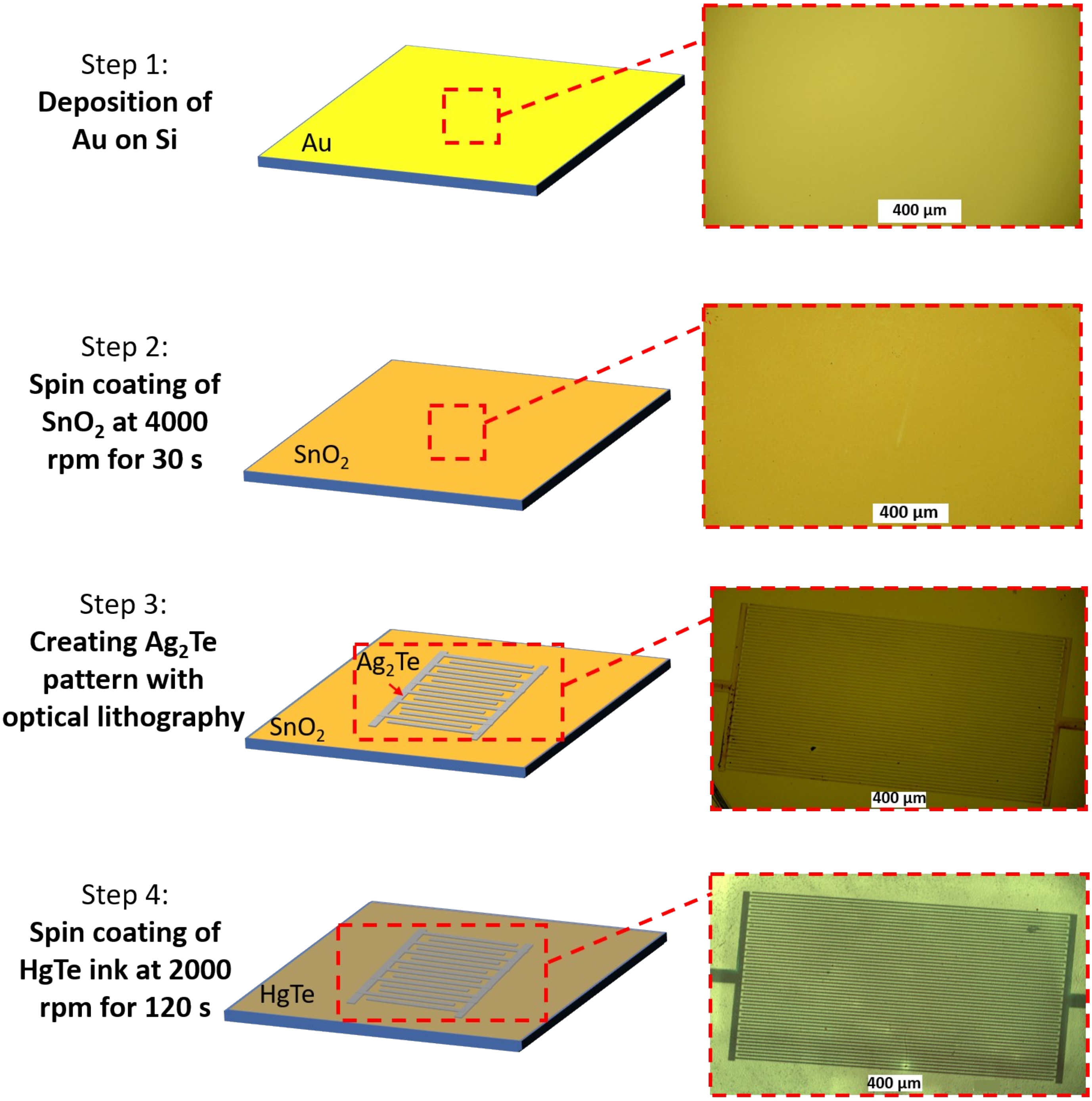

Figure S 1 Fabrication steps of the planar p-n junction. Left side describes the concept whereas right part provides optical microscopy image at each step.

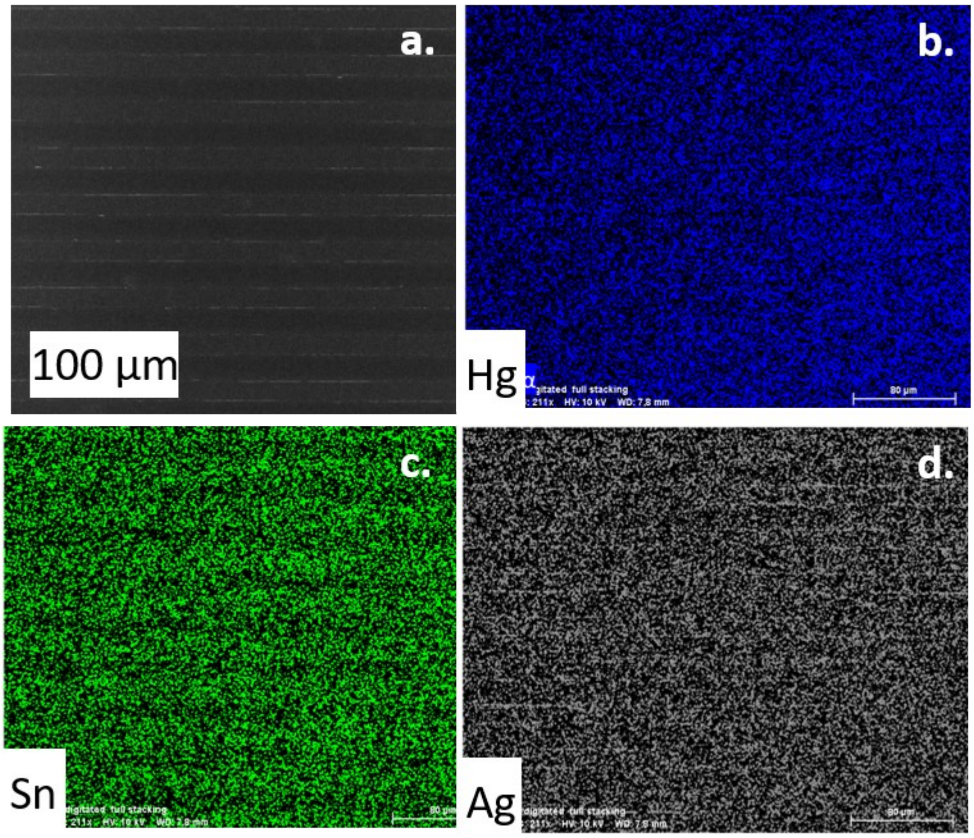

Figure S 2 Chemical mapping of the interdigitated electrodes. a. Scanning electron microscopy image. Images b to d are respectively EDX maps for Hg, Sn and Ag.

2. Photoemission

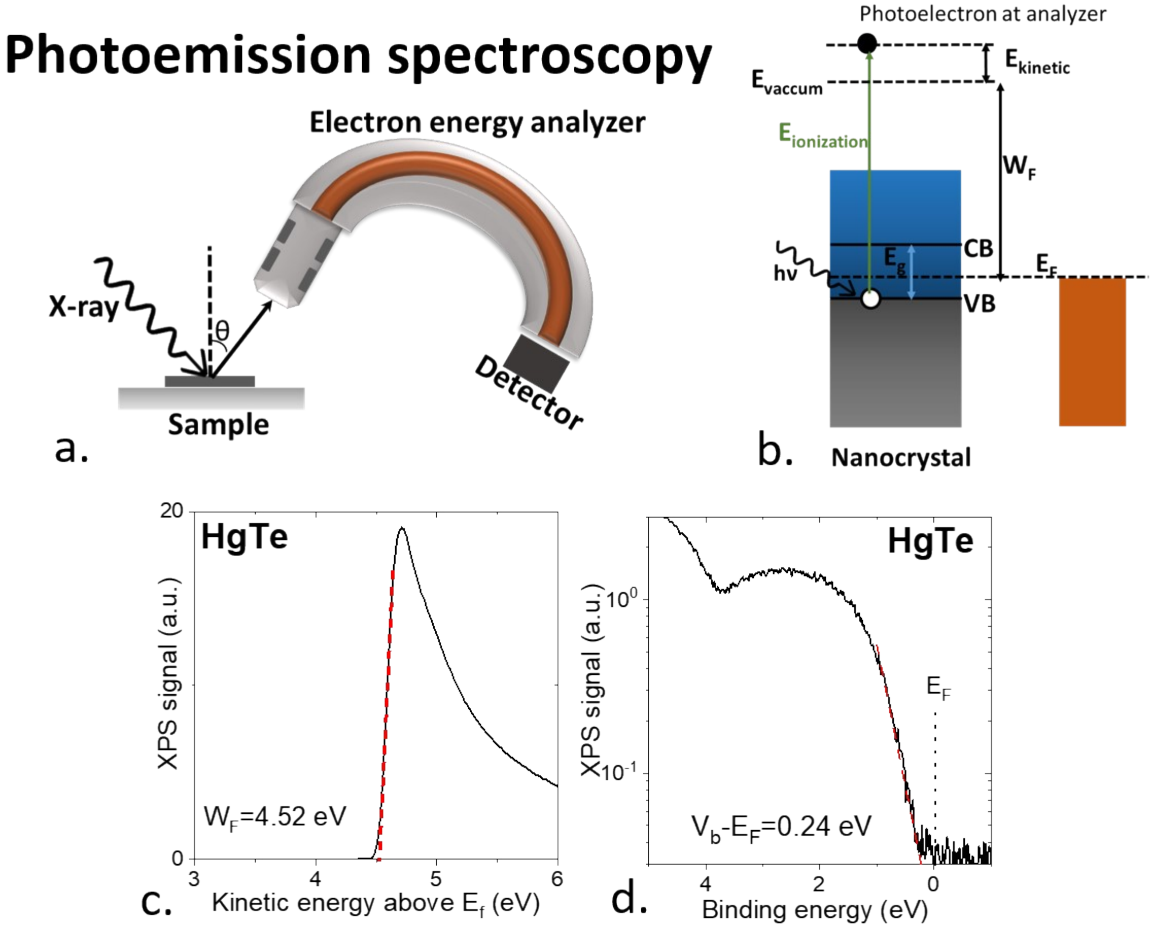

Figure S 3 a. Schematic of X-ray photoemission experimental technique. b. Representation of energy level diagram demonstrating the principle of X-ray photoemission. X-ray photoemission spectrum relative to the cut-off of the secondary electrons (c.) and from the valence band (d) for a HgTe nanocrystal film. The band energies are determined from the intersection of an extrapolation from the signal to the baseline. The figure is adapted with permission from ref[1] *Copyright (2017), American Chemical Society.*

The concept of photoemission spectroscopy used to unveil a semiconductor band alignment is illustrated in Figure S 3. Soft X-ray beam is illuminated on the sample enabling electrons to escape, see Figure S 3a. These electrons are collected with an electron analyzer which measures their kinetic energy. Energy conservation gives $h\nu = E_{BE} + E_K + WF_{analyzer}$ where $h\nu$ is the photon energy and $WF_{analyzer}$ the work function of the analyzer. This equation is then used to convert the experimental scale E_K into a material scale in binding energy E_{BE}. The cut-off of the secondary electrons (i.e., the low kinetic part of the photoemission spectrum) is measured to determine the sample work function, see Figure S 3c. The work function corresponds to the relative position of the vacuum level with respect to the Fermi level. The high kinetic energy of the spectrum (and thus the low binding energy part, see Figure S 3d) is used to determine the relative position of the valence band with respect to the Fermi level that is set, by convention, as the zero of energy. In practice, the Fermi edge of a metallic sample is measured and we shift its energy to be zero. Then, all later spectra will be shifted the same way. Finally, we use the optical band gap to determine the conduction band energy with respect to the valance band. This actually neglects any coulombic corrections, but the latter are small in high dielectric constant materials (such as HgTe) compared to the experimental resolution (50-100 meV). The same set of experiment has been performed for various size of HgTe NCs keeping the surface chemistry unchanged, see Figure S 4.

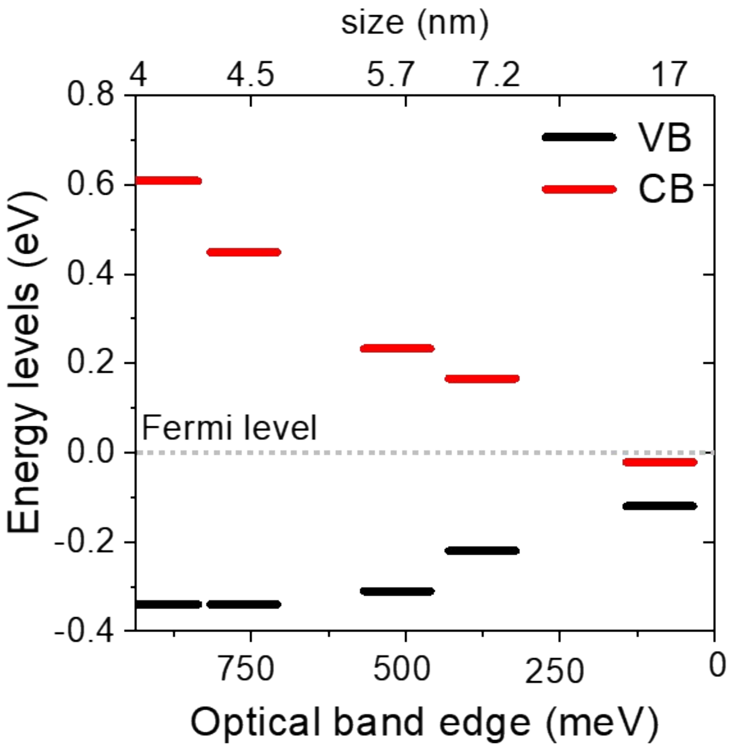

Figure S 4 Band alignment for HgTe NCs with various optical band gap. Data are adapted from ref [2]*.*

3. REFERENCES

1 C. Gréboval, A. Chu, N. Goubet, C. Livache, S. Ithurria and E. Lhuillier, *Chem. Rev.*, 2021, **121**, 3627–3700.

2 A. Jagtap, B. Martinez, N. Goubet, A. Chu, C. Livache, C. Gréboval, J. Ramade, D. Amelot, P. Trousset, A. Triboulin, S. Ithurria, M. G. Silly, B. Dubertret and E. Lhuillier, *ACS Photonics*, 2018, **5**, 4569–4576.