Nano Scale Disruptive Silicon-Plasmonic Platform for Chip-to-Chip Interconnection

Operation of QD based photodetector with responsivity > 0.1A/W

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Executive Summary

A reproducible chemical synthesis of PbS QDs and photodiode fabrication processing has been developed. The most important qualitative and quantitative advance in the technology of PbS-QD based photodiodes was its solution-processing deposition by doctor-blading. In the most recent generations of PbS-QD Schottky photodiodes we demonstrate light photodetection in the telecom wavelength range (1300 – 1600 nm) that exhibits responsivities greater than 0.1 A/W (> 0.15 and 0.45 A/W at 1300 and 1550 nm, respectively). The Schottky concept is a very convenient device to be integrated in SOI technology, because photocurrent or photovoltage may be directly measured without needing polarization. A reasonable low noise current, 100 – 500 fA below 10 kHz of modulation signal (response time around 100 μs), and detectivity, in the range 10^{12}-10^{13} Jones, was estimated in our PbS-QD Schottky-heterostructure photodiodes. It is also worth noting that these devices, probed under AM1 solar illumination, were yielding photocurrent densities and open circuit voltages as high as 16-17 mA/cm^2 and 0.3 V, respectively, values that are of the order of the world maximum achieved with this technology.
Microgap and nanogap electrodes are currently fabricated by photolithography and ebeam-lithography, respectively, being the first (microgap) our test-model to develop an efficient PbS-QD layer to achieve a photoconductive detection concept that might be easily integrated together with photonic structures into Si-SiO_2 substrates, and the second (nanogap) the most ambitious target in Task 4.5.

Change Records

Version	Date	Changes	Author
1	2014-02-03	Description of synthesis and layer deposition	Pedro Rodríguez Cantó
2	2014-02-16	Electrical characterization	Juan P. Martínez Pastor
3	2014-02-17	First complete version	Pedro Rodríguez Cantó
4	2014-02-18	Revised version	Juan P. Martínez Pastor
5	2015-02-01	Updated version incorporating R > 0.1 A/W at 1550 nm	Juan P. Martínez Pastor

1. Introduction

The target in this milestone report is the fabrication of photodetectors operating at telecom wavelengths with responsivites in the order of or higher than 0.1 A/W. The photodetector is based on two different concepts: colloidal QDs deposited on a nano/micro-gap area between metal contacts and a Schottky-heterostructure design based on a QD thin solid film as absorber.

The Schottky photodiode design is very robust, easy to fabricate, and it can work without bias (photocurrent/photovoltage mode) with responsivities of the order of 1 A/W (depending on the thickness and absorption coefficient, mainly) or more using negative bias, but the footprint is larger, worse time response and it will be more difficult to integrate with planar photonics technology.

A micro-gap based photoconductor is also a very simple and robust design, even if distances between electrodes should be optimized accordingly to the low values of diffusion lengths in QD solid films (defined by photolithography). The most important advantage is the reasonably small footprint (depending if defined as a single micro-gap or interdigitated designs), easily integration in planar photonics technology, high photoconductive gain and fast operation (depending on the bias voltage). The main disadvantage can be the high bias voltage needed for this sufficiently high gain and fast operation.

An alternative to the micro-gap photoconductor is the most challenging nano-gap concept that comparatively can have many advantages, as the extremely small footprint, smaller bias voltage, faster operation and plasmonic effects can play a role for signal enhancement due to the small separation between metal contacts (antenna or electromagnetic field confinement effects). We should also mention some disadvantages, as the low electric signal expected due to the small area for photon absorption and the challenging fabrication by e-beam lithography.

In the present milestone we refer to the following achievements and progress:

- Synthesis of PbS QDs emitting at telecom wavelengths and preparation of QD thin solid films by doctor-blading in comparison to spin-coating used in previous work.
- Investigation of new ligand exchange procedures to improve device performance.
- Synthesis of alternative lead-free QD materials.
- Electro-optical properties of Schottky/heterostructure photodetectors.
- Photomask layout for fabrication of micro-gap photoconductors.
- Layout for fabrication of nano-gap plasmonic waveguide photoconductor by e-beam lithography.

2. Synthesis of IR QDs and preparation of QD-solids

a) Synthesis of PbS QD and QD-solids

In the last months we have carried out the synthesis of PbS QDs emitting at wavelengths around 1550 nm following the chemical route reported by Cademartiri [1]. This synthesis has been properly optimized to obtain QDs emitting at wavelengths around 1550 nm (Figure 1). Basically, this synthesis is based on lead chloride and elemental sulfur in oleylamine as precursors and using oleylamine as solvent and capping agent, simultaneously. After hot injection of the S(0)-oleylamine stock solution into the flask containing the Pb(II)-oleylamine precursor at elevated temperature monodisperse colloidal PbS QDs could be optimally produced and redispersed in octane. The size of the QDs was of around 8-10 nm in diameter as observed in TEM images (figure 1).

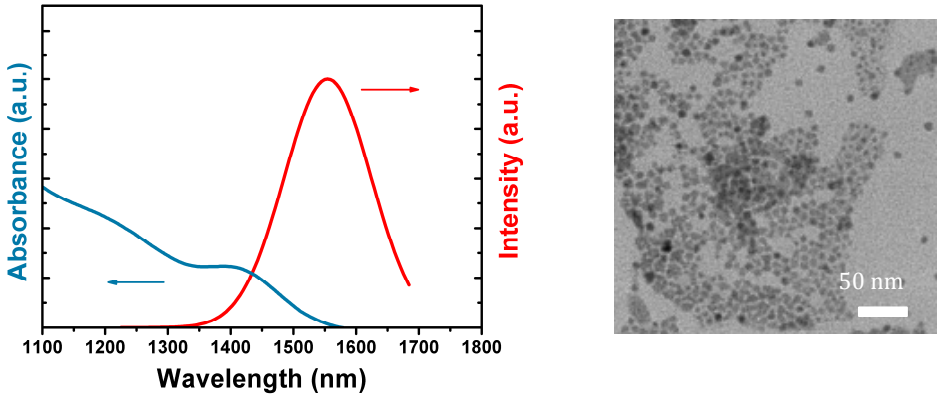

Fig. 1: Absorption and PL spectra (left) and TEM image (right) of oleylamine-capped PbS QDs in octane (left).

To date the production of QD-solids has been performed by using a solution-processing method called Layer-by-Layer (LbL) spin-coating, which was also extensively described in Milestone-18 and Deliverable 4.2. Even though this approach has several advantages, such as it allows a good control of the thickness and the fabrication of relatively smooth and crevice-free QD films (even if granurality is not disregarded) directly from the colloidal solution, it is not adequate to form thick layers that are required for the improvement of the diode and detector responsivity. For this reason, doctor-blading is an attractive alternative to conventional spin coating (Figure 2). This deposition technique is capable of achieving thicker films consuming far less material and expending less time than the spin-coating process. Besides, the QD packing density of thick films may increase if the solution evaporation is slowed down. Doctor-blading allows for slower solvent evaporation than spin coating because it does not introduce rapid air flow during film deposition. Hence, we have been able to form QD-solids at room temperature in a reproducible way with thicknesses between 300-800 nm. The resulting thin film thickness depends on the number of layer deposited. PbS QD films were typically deposited on glass (for micro-gap photoconductors), glass-(thin)ITO (for nano-gap photoconductors) or glass/ITO/PEDOT (for Schottky/heterostructure photovoltaic photodetectors) substrates. It is worth noting that the key parameter to get thick layers by this coating technique is to start from

highly concentrated PbS QD solutions. After deposition of the PbS QDs the samples were cured in a vacuum oven at 110ºC for 30 min.

Fig. 2: Doctor-blading equipment for the QD film formation.

The ligand exchange reaction has been mainly carried out using 3-Mercaptopropionic acid (MPA) instead of other organic ligands already tested such as ethanedithiol (EDT), oxalic acid, among others. The reason of that has been already explained in detail in Milestone-18. Basically, MPA passivation may enable significant enhancement of the carrier mobility-lifetime product in the PbS QD solid because of a lower density and energetic distribution of charge traps in MPA-processed PbS QD films [2]. As a result both the diffusion length of charge carriers and the photon conversion efficiencies increase significantly, and consequently, better responsivities can be attained.

The procedure to exchange the insulating oleylamine (2 nm long) with this bidentate ligand, consists of dipping the formed PbS-films into a solution of 10 % MPA in methanol for different times. We observed that a dipping step of 1 min was enough to efficiently carry out the ligand exchange reaction. Then, the layers were rinsed with methanol and dried with N_2. As aforementioned, the final thickness of the layers obtained with this doctor-blading approach ranged from 300 to 800 nm. Furthermore, the film quality was significantly improved obtaining smother and less granular films, as observed by a mechanical profilometer.

At the same time, we have started using other ligand exchange procedures that make use of monovalent halide anions (I^-,Br^-). This ligand exchange approach offers benefits in surface passivation, transport, and, lately, in device performance [3]. Here, we employ cetyltrimethylammonium bromide (CTAB) to cap the surface cations forming an all-inorganic halide anion-passivated PbS QD. The ligand exchange approach is similar of that used for MPA, that is, the oleylamine-capped PbS QD layer is dipped into a solution containing CTAB for efficient replacement of the ligands. This monovalent inorganic ligand passivation strategy enables good passivation of surface defects, high carrier mobility and good device stability. Even though we have already characterized some devices based on this approach we still need to optimize the thickness and the quality of the film. So far, we produced 500 nm-thick layers of Br-capped PbS QDs exhibiting a reasonably good film stability. We are currently carrying out the optimization of this new ligand exchange strategy in solution and in solid state.

b) Synthesis of Lead-Free QDs

In parallel, the synthesis of alternative lead-free QD materials were initiated with the aim to produce QD films for their application in IR photodetectors operating at telecommunication wavelengths. Hence, Ag_2X (X = S, Se, Te) heterostructures might be considered as an alternative to the standard IR materials containing Pb or Hg due to their low toxicity. Ag_2Xs exhibit different crystal structures, highly dependent on growth conditions and temperature. In their low-temperature structure, Ag_2Xs represent narrow band gap semiconductors with fundamental absorption edges at 0.15 eV for Ag_2Se, 0.67 eV for Ag_2Te, and 0.85 eV for Ag_2S. In this context, we are currently developing the synthesis of high-quality IR Ag_2S QDs and carrying out the corresponding optical and morphological characterization. Up to now monodisperse Ag_2S colloidal QDs with a diameter of 15-25 nm has been successfully synthesized (Figure 3). Characterization and optimal tuning of the required QD size corresponding to an absorption peak at 1500-1600 nm is under development.

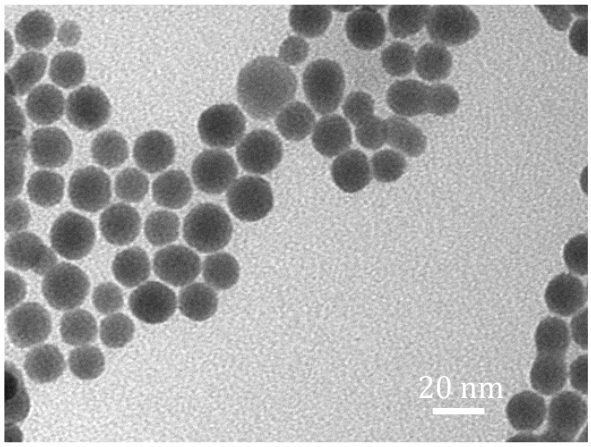

Fig. 3. TEM image of Ag_2S colloidal QDs.

3. Schottky/heterostructure photodetectors

For the fabrication of **Schottky photovoltaic photodetectors** (Fig. 4.a) we are using glass/ITO commercial substrates whose standard resistivity is in the order of 10-20 Ω.sq. A thin (100 nm) PEDOT layer is covering the ITO layer by spin-coating in order to reduce the ITO surface roughness and avoid shortcuts by high electric field conditions. The QD-solid is deposited after the PEDOT layer formation by Dr-blading and subsequent ligand exchange procedure. The structure is finished by a top silver ohmic contact in the form of 1 mm^2 square patterns (Fig. 4.a) that are contacted with silver leads for electro-optical characterization. For **micro-gap photoconductors** (Fig. 4.b) we are using glass and silicon-SiO_2 substrates where the QD-solid may be formed by either Dr-blading + ligand exchange or dropping, respectively. Figure 4.c shows a photograph of a contacted (silver leads glued with silver epoxy on evaporated Ag contacts on top of the QD-solid) micro-gap (45 ± 5 μm) photoconductor device made on glass; the electric field in these micro-gap photoconductors will be in the order of 22 kV/m for 1

V bias. In the case of micro-gap photoconductor devices made on silicon-SiO_2 substrates the interdigitated/micro-gap structures should be patterned by UV-photolithography and lift-off processing prior to the QD-solid formation to avoid its exposure to chemical agents. The PbS QD-solid may be prepared by simply dropping the QD colloidal solution on top of the interdigitated/micro-gap structures. We plan to characterize the device before and after a ligand exchange procedure by dipping the sample into the MPA solution.

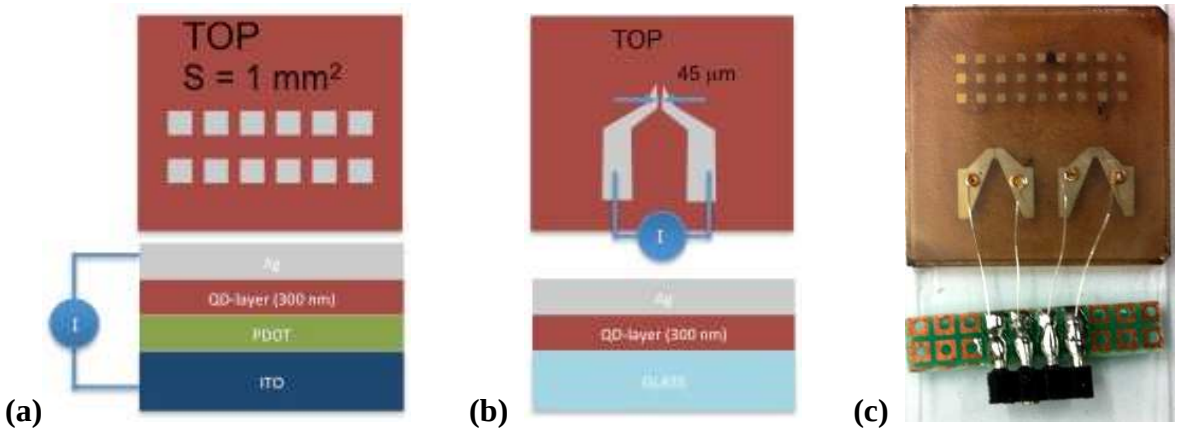

Fig. 4. Schottky/heterostructure photodiodes (a) and micro-gap photoconductor (b). Mask used for the Ag electrode deposition is the same for both designs (c); in the example contacts are made on the photoconductive design.

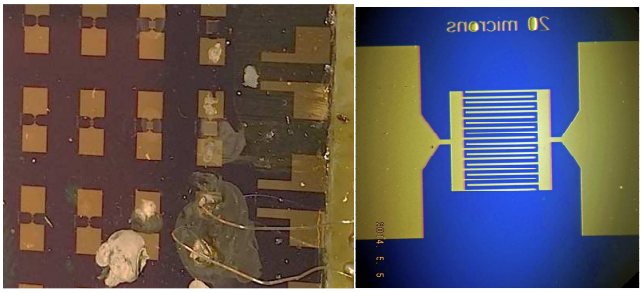

Fig. 5. Photograph of interdigitated photoconductors with a QD-layer on one of them and zoom image of one of them (20 µm gap).

a) Characterization techniques

So far, to measure the electro-optical properties of the photodevices at the visible (350 – 1100 nm) we have been using an in-house set-up based on a Xe-lamp (150 W) and monochromator 300 mm of focal length for illumination, a low-noise pre-amplifier and/or lock-in electronics for electrical signal amplification, other than a calibrated Si-photodiode to obtain responsivity values.

The measurement of the responsivity **at longer wavelengths (> 900 nm)** has been recently accomplished by a new characterization set-up that includes a Ge calibrated photodiode. The excitation source is a halogen lamp coupled into the monochromator (using 600 and 300 g/mm gratins with blaze at 1200 and 1500 nm, respectively) through an optical fiber. The power at the exit of the monochromator is of the order of 100 nW/nm and the electrical signal of the PbS QD-based photodetector was amplified by a factor 10^8 using a trans-impedance amplifier.

At the same time, we also use a Keithley 2400 source-meter for measuring I(V) characteristics under dark or illumination conditions (monochromatic light). The light leaving the monochromator is focused onto the device transparent surface (from glass substrate) through

a 20x objective or a short focal length lens. Then, we are able to measure weak and intermediate/large photocurrent signals by using the first and second type of measurements, respectively.

b) Electro-optical properties at the Visible

Figure 6 shows the comparison of the I(V) characteristics under dark and illumination (800/820 nm) for two QD-based Schottky photodiodes, one prepared by spin coating (Fig. 6a) and the other one newly produced by doctor blading coating technique (Fig. 6b). It is important to note here that both samples were prepared using MPA for the ligand exchange. As can be observed in the graphs, firstly, a big increase by more than a factor ten is observed in the open circuit voltage (V_{OC}). This improvement in V_{OC} is attributed to the new deposition technique that allows for a smoother film surface (reduction of the film granularity). As a result, the series resistance limitation is significantly reduced, as predicted in our previous report. The recorded photocurrent value is very similar, but this is an apparent value, because the incident power was slightly different in both measurements and the QD-film will exhibit a stronger absorption coefficient at 800 nm for the new device series (Fig. 6b). This is because of the bigger size of the PbS QDs showing an emission peak at 1550 nm, as aforementioned. These differences are included in the responsivity measured in the new series (0.04 A/W) that is enhanced by a factor ten compared to the old ones produced by standard spin coating.

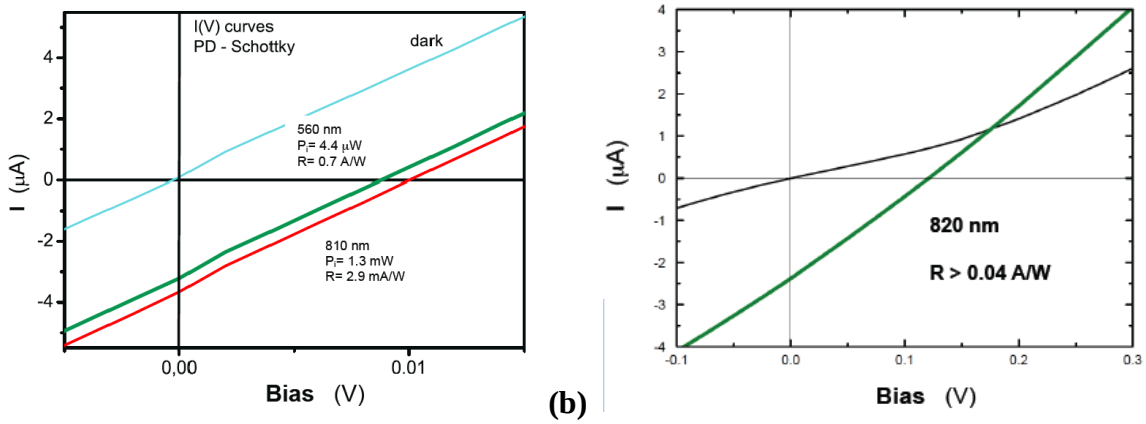

Fig. 6. Comparison of the I(V) characteristics of the best ITO/PDOT/PbS-QD-solid/Ag photodiodes: spin-coating (a, from previous report) and doctor blading (b). The QD-film thickness is very similar in both devices (360 nm).

Recently, we have also started investigating the electro-optical properties of PbS QD-based films using monovalent halide anions like Br- instead of MPA to replace the original oleylamine molecules. In Fig. 7 the I(V) curve for a micro-gap-based device with a 500 nm-thick QD-film deposited by doctor blading shows an excellent linear I(V) characteristic till 60 V of positive bias. This indicates a high resistance and great stability of the QD-film to electrical stimulation. Based on these results, this inorganic passivation strategy seems to be very promising since we are still optimizing the ligand exchange process what may lead to a significant increase in the device performance.

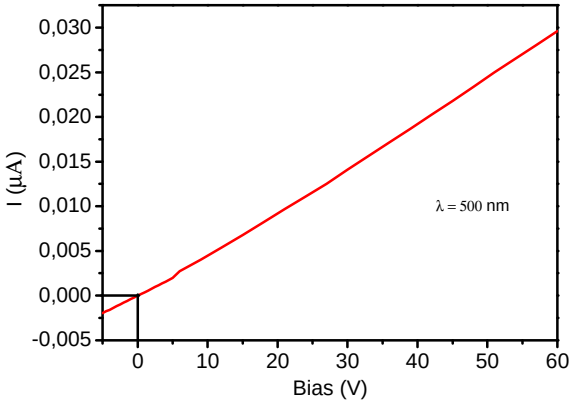

Fig. 7. I(V) characteristics of a microgap PbS-QD-solid(500 nm)/Ag photoconductor produced by doctor-blading and Br^- to replace the original oleylamine ligands.

c) Electro-optical characterization at the IR

The measurement of the responsivity at longer wavelengths (> 900 nm) has been recently accomplished by the new characterization set-up that includes a Ge calibrated photodiode, as above detailed. Figure 8 shows the responsivity curves for the first two generations of PbS QD-based Schottky photodiodes where the QD-solid was prepared by Dr Blading. In the first generation (Fig. 8a) nearly the maximum response was around 0.1 A/W at a wavelength around 1200 nm and decreases down to 0.07 A/W at 1550 nm, which is consistent with the observed absorbance and photoluminescence spectra of the colloid (Fig. 1-left), given that the QD(PbS)-film is relatively thin (300 nm) and light scattering by surface roughness is possibly smearing its absorbance spectrum (blue line in Fig. 8a). In the second generation we were able to use a PbS colloidal QD solution whose average size was slightly bigger than that used in the first generation of photodiodes. In this case the absorption spectrum clearly shows a maximum excitonic absorption band at around 1600 nm (blue curve in Fig. 8b), which is consistent with the observed maximum in the responsivity (red curve in Fig. 8b), now reaching a maximum value of 0.16 A/W, and decreases down to 0.11 A/W at 1550 nm, that is, above the target value in Navolchi.

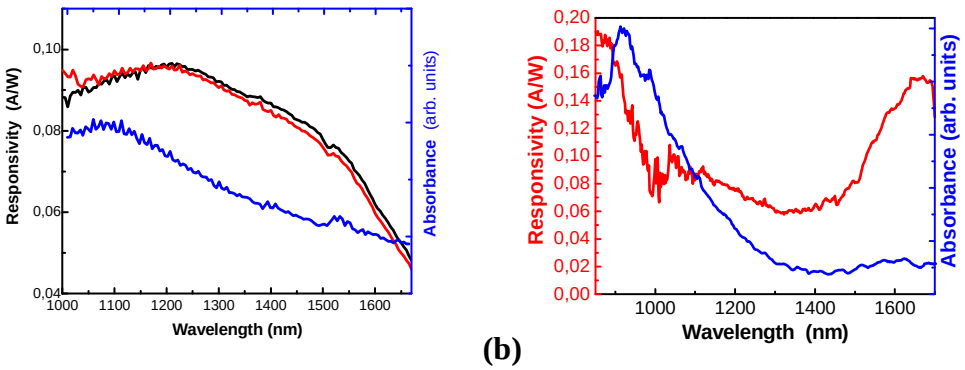

Fig. 8. Responsivity spectra for the first (a) and second (b) generations of glass/ITO/PEDOT/QD-film/Ag photodiodes (black and red curves in **a** and red curve in **b**) where the QD-films (300 and 500 nm for **a** and **b**) were prepared by Dr-blading and the corresponding absorbance spectra (blue curves).

In the case of the most recent generation of devices, peak responsivities were measured to be 0.48 and 0.15 A/W at around 1300 and 1550 nm (blue and green lines in Fig. 9a), respectively,

even if the ground state exciton absorption was outside our spectrometer range, *i.e.*, beyond 1650 nm. The observed peak responsivities at wavelengths shorter than that of the exciton peak are attributed to the different thicknesses of the PbS QD-solid film in the two diodes shown in Fig. 9a that give rise to different reflectance values in the examined wavelength region.

The time response of these photodiodes working in photocurrent mode is estimated to be around 100 μs, very similar to those reported in [4]. The photovoltage noise was measured to be of the order of 85 nV/Hz$^{1/2}$ at 1 kHz for the photodiode based in the 500 nm thick PbS QD film, whereas the photocurrent was perfectly linear over more than three orders of magnitude (constant responsivity). The detectivity is estimated to be very close to 10^{13} Jones. These photodiodes are stable in air during several weeks, even if electrical parameters degrade progressively (after one month in air the responsivity decreased a factor two, approximately).

Finally, it is also worth noting that these photodiodes, even if not made with an optimized architecture to be used as a solar cell, when illuminated under AM1 solar conditions, open circuit voltages (V_{oc}) are greater than 300 mV and short circuit currents (J_{sc}) in the range of 8-16 A/cm^2, which are in the range of the best expected and reported values for PbS QD films in solar cell structures of slightly smaller size [5]. Evidently, the solar cell efficiency is around 1% because of the low fill factor, as expected for the simple Schottky architecture used in the present photodetectors. In fact, this degradation of the I-V curve is even observed under monochromatic and low power excitations conditions at telecom wavelengths, as shown in Fig. 9b, which is attributed to a noticeable decrease of the diode shunt resistance due to and increased hole leakage towards the Ag contact.

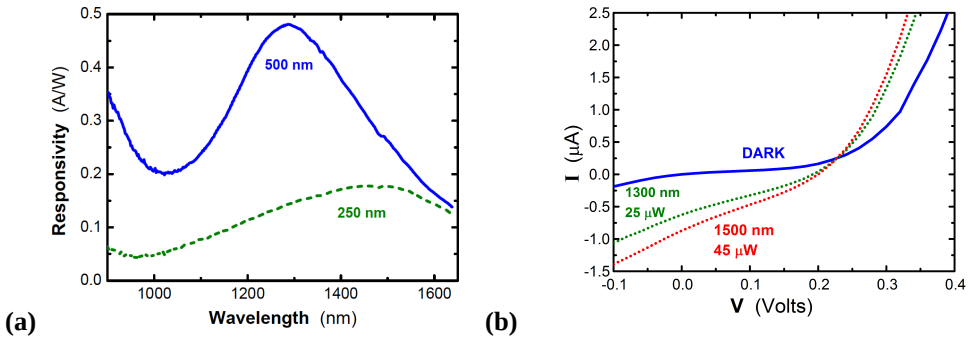

Fig. 9. (a) Responsivity curves in the most recent generation of photodetectors based on 250 (dashed green line) and 500 (continuous blue line) nm thick PbS QD-solid films (their absorption edge lies beyond 1600 nm in both cases). (b) I-V curves under dark and monochromatic excitation at 1300 and 1500 nm (the power indicated in both cases are measured by a power meter with detection area larger than that of the QD-photodetectors). This effect would be minimized by introducing a n-type ZnO transparent electrode on top of the QD-solid film [6].

4. Electro-optical properties of nano-gap and micro-gap photoconductors.

Concerning the nanogap design, we have already prepared together with TUE group the layouts and fabrication of the nanogap plasmonic waveguide photoconductor by means of E-beam lithography. The design includes gaps between 30 and 100 nm and electrode lengths between 2 - 5 μm (Fig. 10). Thus, by decreasing the gap we expect to reduce the response time for fast operation receivers through an efficient carrier extraction as well as through optimized

light absorption by resonant plasmonic field enhacement/confinement due to the small separation between metal contacts.

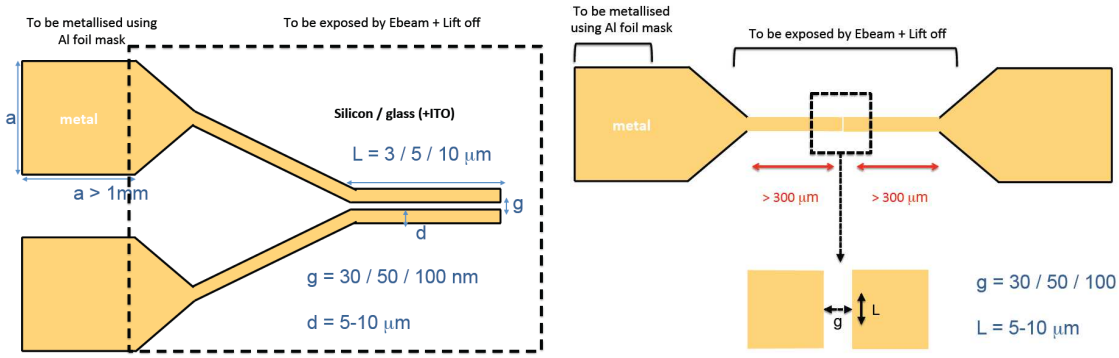

Fig. 10. Fabrication layouts for the fabrication of nanogap plasmonic waveguide photoconductors. In dotted area is indicated the fabrication by using ebeam lithography.

Simultaneously, we also considered the study of micro-gap photoconductors (Fig. 4b-c) because of the technical difficulty to achieve nano-gap distances and the possible difficulties to couple sufficient light leaving the plasmonic amplifier into this photoconductive device. First devices were made with an electrode-to-electrode distance ≈ 45 μm (Fig. 4b-c), but a first generation of micro-gap photoconductors were successfully fabricated on Si-SiO_2 substrates by lift-off processing as was illustrated in Fig. 5, for which appreciable photocurrent is measured at 1550 nm in preliminary tests, even if we are not satisfied with the ligand exchange protocol on small area QD-layers. As next steps we will try to improve microgap photoconductor devices by using the latest optimized PbS QD material and developing a processing protocol for ligand exchange in small area QD-films deposited on top of the micro-gap structure. In the case of plasmonic nanogap photoconductors is possibly more reasonable to use QD-layers deposited by micro-dropping of the colloidal solution without ligand exchange in order to avoid undesired short-circuits under the high electric fields between metal electrodes.

5. Conclusions and further work

In summary, the present results demonstrates that the use of PbS QDs deposited by doctor-blading coating on a glass-ITO substrate can be the basis to produce reasonably good and simple Schottky photodiodes exhibiting responsivities greater than 0.1 A/W at 1550 nm (target in NAVOLCHI project), as was demonstrated in the most recent generations of the devices (Fig. 9a). For this achievement, a reproducible chemical synthesis of PbS QDs and photodiode fabrication processing has been developed. The Schottky concept is a very convenient device to be integrated in SOI technology, because photocurrent or photovoltage can be directly measured without needing polarization (if amplification is not used).
Further improvement of the Schottky-heterostructure photodiode concept (fabricated on a Si-SiO_2 substrate) can be achieved by:
i) plasmonic scatterers as a substitute of an antireflective coating,
ii) more effective ligands for reducing surface trap levels,
iii) ZnO/Al as the top electrode of the photodiode for a further reduction of the dark current under illumination (at telecom wavelengths).

In the next future, after the above-demonstrated optimization of the QD and the QD-solid material in the Schottky-device, we will focus on the development of microgap and nanogap photoconductors. Both, microgap and nanogap electrodes are currently fabricated by photolithography and ebeam-lithography, respectively, being the first (microgap) our test-model to develop an efficient PbS-QD layer to achieve a photoconductive detection concept that might be easily integrated together with photonic structures into Si-SiO_2 substrates, and the second (nanogap) the most ambitious target in Task 4.5.

References

[1] L. Cademartiri *et al.*, *J. Am. Chem. Soc.* **128**, 10337 (2006).
[2] S. Jeong Kwang *et al.*, *ACS Nano* **6**, 89–99 (2012).
[3] Z. Ning *et al.*, *Adv. Mater.* **24**, 6295-6299 (2012).
[4] J. P. Clifford *et al.*, *Nature Nanotechnology* **4**, 40 (2009).
[5] W. Yoon *et al.*, *Scientific Reports* **3**, 2225 (2013).
[6] Bhola N. Pal *et al.*, Adv. Funct. Mater. **22**, 1741–1748 (2012).