

PbS Colloidal Quantum Dot visible-blind photodetector for early indoor fire detection

Andrea De Iacovo, *Member, IEEE*, Carlo Venettacci, Lorenzo Colace, *Member, IEEE*, Leonardo Scopa, Sabrina Foglia

Abstract—We report on a novel optical fire detector based on a PbS colloidal quantum dot photodetector. The sensor is realized with a simple, cost effective, drop casting technique. The photodetector is characterized in terms of its electrical characteristics, responsivity and specific detectivity to monochromatic light. We demonstrate effective indoor fire detection at a distance exceeding 20m with a 120° field of view. We also show a twofold improvement of the detector signal to noise ratio exploiting a short focal lens.

Index Terms—Optical fire detector, PbS Colloidal Quantum Dot, near infrared photodetectors

I. INTRODUCTION

FIRE detection systems have been intensely investigated in the last years, accounting for an ever growing concern about safety and security. Nevertheless, in the last decade, the occurrence of fires has increased from 1.2 fires per 1000 inhabitants in 2004 to 2.5 in 2014; at the same time, in the USA, the average expense for fire protection in buildings reached the 0.26% of the GDP [1]. Despite the economic effort in fire prevention, more than 38% of the world fires are originated in buildings. Such statistics suggest that commercially available fire prevention systems and countermeasures are still too expensive and lack in effectiveness. State of the art devices for fire detection can be classified according to their working principle. Thermal detectors rely on thermoelectric, thermooptic or thermomechanical effect and are widely employed both for point detection (thermistors) and for long-range, distributed, detection (fiber optics systems)[2]. Thermal detectors are, usually, slow and trigger an alarm only when the ambient temperature already increased by several degrees with respect to normal conditions[3]. Better performance are obtained with thermooptic detection systems which, on the other hand, are quite expensive. The most common indoor fire detection systems are smoke detectors which can be divided into two sub categories: ionization current detectors and optical detectors. They are usually appreciated for the low cost and ease of installation; nevertheless they are prone to false alarms and, in the case of ionization current detectors, are often criticized for the presence of a radioactive source[3]. The last class of devices is based on the optical detection of flames in the early stages of a fire. These devices are usually based on semiconductor photodetectors operating from UV to infrared, always resorting to multiple wavelength detectors

in order to reduce false alarms and increase the immunity to ambient illumination [2]. Because of the materials and devices employed for their realization, however, such systems are still much more expensive with respect to smoke detectors and are employed in high-end applications where the superior performance justify the higher cost. Recently, a whole new class of optical detectors has been proposed, relying on image sensors and image processing algorithms for the detection of flames and smoke[4]. Such devices have been optimized to work even outdoor and to be solar blind in order to reduce the number of false alarms[5]; nevertheless, such systems are usually quite expensive and power consuming due to the need of a computer or an electronic board providing the real-time image processing capabilities. The optical detectors described so far, are all passive systems relying on the light emitted by the flames; in cases where there is a need to detect fires far away from the detection systems, however, active devices provide better results. Such detectors can either measure the optical absorption of gases produced by fires[6] or the light scattering due to smoke and dust[7]. In both cases detection range and sensitivity are extremely good at the price of an increased system complexity and cost. In this scenario, we propose a low-cost approach to the realization of a near infrared (NIR) photodetector for indoor flame sensing based on PbS Colloidal Quantum Dots (CQD). PbS is a semiconductor material with optical absorption in the near infrared spectral range ($1\mu\text{m}$ to $2.8\mu\text{m}$). In the form of quantum dots, PbS exhibits a size dependent bandgap and optical absorption due to quantum confinement effects; moreover, the magnitude of the absorption coefficient is dramatically increased[8]. PbS quantum dots have been effectively employed for the realization of high sensitivity photodetectors in the form of photoconductors, photodiodes and phototransistors [9][10][11]. In order to properly detect a fire in its early stage, a photodetector should be able to detect extremely low optical powers; in this sense, photoconductors are best suited for fire detection systems because of their large gain and responsivity even at low bias [10]. Photoconductors are slow if compared to photodiodes and phototransistor but their 3dB cutoff frequency (10-100Hz)[12] is usually large enough to allow a suitable response to the ignition of a flame. PbS quantum dots can be chemically synthesized with a well known, highly reproducible hydrothermal process[13] and they can be stabilized in a colloidal form. The synthesis process relies on standard chemical apparatus and does not imply the use of high vacuum technologies or high thermal budget process. The overall material production cost is, thus, very

Manuscript received xxxxxxxxxx; revised xxxxxxxxxx

A. De Iacovo, C. Venettacci and L. Colace are with University Roma Tre, Department of Engineering. L. Scopa and S. Foglia are with IMEM-CNR

low. Moreover, colloidal materials can be easily deposited onto several different substrates (silicon, SiO₂, glass) with a spinning or drop casting process, thus allowing the back-end integration of the photodetectors with Si electronics. Even if PbS CQD photoconductors are sensitive in the near infrared, they can also efficiently detect visible light. Therefore, in order to prevent false alarms due to ambient light, they must be provided with visible light optical filters. Fig. 1 shows the typical emission spectra of an LED lamp and of a fluorescent tube for indoor illumination together with the calculated spectrum of a flame at 1000°C. The latter was calculated by means of the Planck emission law and the flame temperature was chosen measuring the temperature of a wax candle flame by means of a pyroelectric thermometer. Lamp and flame spectra do not overlap for wavelengths greater than 0.9 μm ; thus, a photodetector equipped with a high pass filter and operating in the wavelength range shaded in figure can be effectively employed to detect a flame in indoor environments without interference from ambient illumination. In this work we report on the fabrication and characterization of a high sensitivity, visible-blind PbS CQD photoconductor for indoor flame sensing applications.

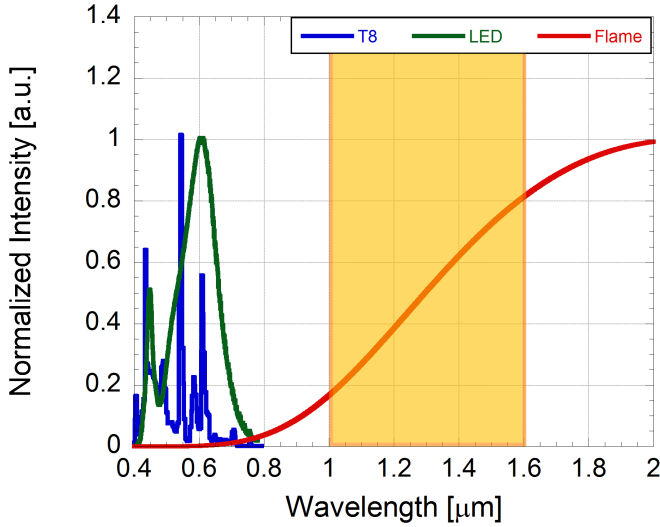


Fig. 1. Emission spectra of two different types of lamps for indoor illumination and a 1000°C flame. The shaded area represents the operating wavelength range for a visible-blind photodetector.

II. DEVICE FABRICATION

We developed the device fabrication process aiming at a future back-end integration of our photodetectors with standard CMOS silicon electronics. For this purpose, we completely avoided any thermal treatment or photolithographic process. We employed a commercial PbS QD solution with a density of 10mg/mL; PbS nanoparticles exhibit a mean diameter of 6nm and the first excitonic absorption peak is located at 1300nm. The absorption characteristics are given by the PbS producer and have been experimentally confirmed in our laboratory by means of optical absorption spectroscopy. QDs are diluted in toluene and are capped with oleic acid (OA). The OA is a long chained, monounsaturated fatty acid that links to the PbS

surface hindering steric and electrostatic interaction between nanoparticles thus stabilizing the colloid; unfortunately, oleic acid also inhibits electronic conduction between neighboring nanoparticles thus making them unsuitable for electronic device fabrication [9]. In order to obtain working photodetectors, we removed the oleic acid from the nanoparticles surface and substituted it with butylamine (details are reported elsewhere [10]). Butylamine capped nanoparticles were directly drop casted onto a couple of interdigitated gold contacts with a 5 μm spacing and let dry in vacuum until full solvent evaporation. The deposition was repeated several times to completely cover the gold contacts with a QD film. Once completely dried, the devices were soaked in methanol for 2 hours to completely remove butylamine and create a close packed nanoparticle film with a so called "necking" process[9]. Fig. 2 shows the resulting device structure and appearance. Fig. 3 shows

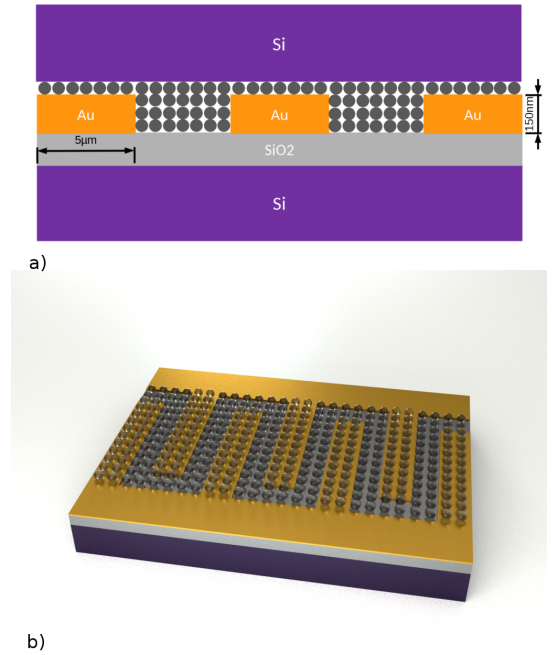


Fig. 2. Device schematic structure (a) and 3D artwork (b)

a SEM micrograph of the final device. It can be observed how the CQDs formed a dense film between all the metal fingers and partly covering them. Also some clusters are easily visible in the picture indicating a non-optimal deposition of the QDs. Cluster formation is typical of drop casting but their number can be reduced varying the density of the CQD solution and the number of deposited layers. Eventually, devices were left in ambient air for 24h to allow oxidation of the PbS nanocrystals surface and the resulting creation of electron trap states responsible for the photoconductive gain[14]. After oxidation, the photodetectors were sealed in a package provided with a polished silicon window as an optical filter for visible radiation. Recently, we realized similar devices as a first proof of concept for fire detection [15]; here we show a revised version of our photodetector obtained by means of a thorough optimization of the deposition and evaporation process aimed at improving the detectivity and

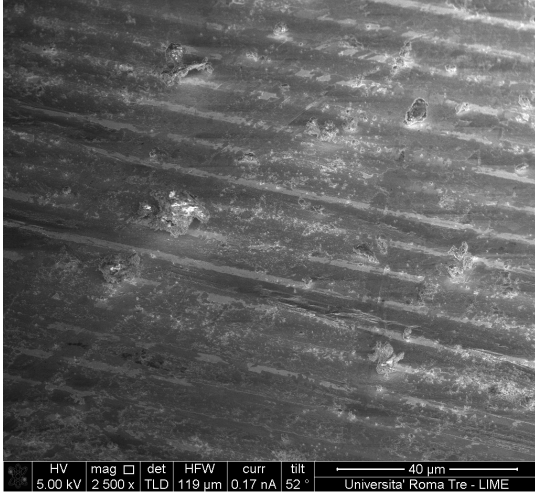


Fig. 3. SEM micrograph

the uniformity of the CQD film. In particular, we slowed down the evaporation of the QD solution to increase film uniformity and reduce the number of cracks (which are known to be responsible for high $1/f$ noise in similar devices[16])

III. RESULTS AND DISCUSSION

Photodetectors were characterized with a Keithley 2612B Source Measure Unit, applying a variable bias and measuring the resulting current both in dark and under illumination. For preliminary characterization, devices were illuminated with a $1.3\mu\text{m}$ laser to match the first excitonic absorption peak of the QDs. Fig. 4 shows the typical current vs. voltage characteristics of a PbS CQD photoconductor and its spectral response (inset). The device shows an ohmic behavior as expected from PbS CQD on gold. Dark current is 56nA at 1V bias and dark resistance is $18\text{M}\Omega$. Under $10\mu\text{W}$ monochromatic illumination, the device current increases by a factor of 40 with a responsivity equal to 0.2A/W at 1V bias. The normalized spectral response shows the expected excitonic peak at 1320 nm , a significant photoresponse up to $1.6\mu\text{m}$ and a cutoff around $0.9\mu\text{m}$ produced by the silicon window. Such spectral response exhibits a satisfactory overlap with the radiation spectrum from a flame and rejects shorter wavelengths from typical indoor illumination as shown in Fig.1. The responsivity of CQD photodetectors proved to be dependent on the incident optical power[17][18], thus we characterized our devices by means of a solid state laser at different bias levels and optical power densities. Fig. 5 shows the resulting responsivity. It should be noted how responsivity varies at low optical powers, increasing by almost two orders of magnitude in the $10\mu\text{W} - 10\text{nW}$ range. This behavior has been attributed to the filling dynamics of traps and recombination centers[14]. Long-lived traps are known to be responsible for gain in photoconductors. If the occupation of such trap levels is low (as at low optical intensity), they can capture photogenerated carriers and produce gain. At higher optical intensity, an increasing number of trap states are filled and there is a possibility for a couple of photogenerated carriers to be collected at the metal contacts without interacting with

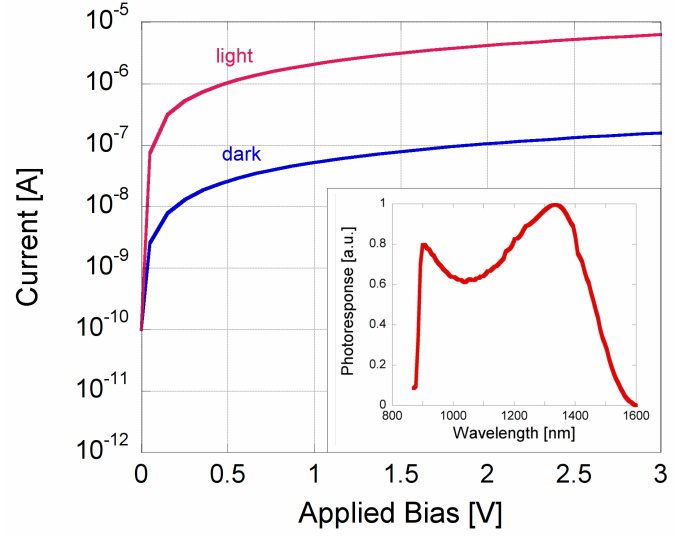


Fig. 4. Current vs. Voltage characteristic of a PbS CQD photoconductor in dark (blue line) and under $1.3\mu\text{m}$ illumination (red line)

any trap state. In this case, lower gain is produced and the overall responsivity drops. The power dependent behavior of

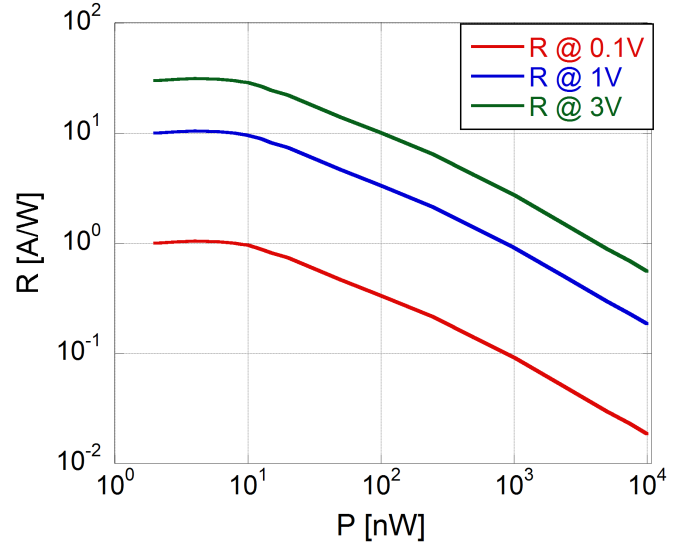


Fig. 5. Responsivity vs. incident optical power for three different biases.

the responsivity guarantees a very high dynamic range at the cost of a nonlinear response of the photodetector; in the case of a flame sensor, however, the extremely high responsivity at very low incident power enables detection of small flames far away from the device. We observed $1.3\mu\text{m}$ responsivity at low optical intensity as high as 30A/W and 10A/W at 3V and 1V bias, respectively. We also determined the specific detectivity of the photodetectors according to eq. 1 where R is the responsivity, A is the active surface of the detector, B is the measurement bandwidth and i_n is the noise current. The total noise spectral density depends on thermal, shot and flicker noise. Due to the large resistance of our devices (tens of $\text{M}\Omega$), the thermal noise contribution can be neglected.

Shot noise, stemming from the charge carriers overcoming potential barriers inside the QD film, has been proven to be the dominating noise source in similar PbS CQD photoconductors [9] and can be expressed as in eq. 2 where q is the electron charge and I is the total current in the photodetector. However, some authors showed that, depending on the morphological and electrical characteristics of the QD film, flicker noise should be taken into account[16].

$$D^* = \frac{R\sqrt{AB}}{i_n} \left[\frac{cm\sqrt{Hz}}{W} \right] \quad (1)$$

$$i_n = \sqrt{2qIB} \quad (2)$$

Our devices have been realized with a technique similar to the one proposed by Konstantatos [9], therefore, we assumed that the noise could be approximated with the shot noise calculated as in eq. 2. Fig. 6 shows the specific detectivity vs applied bias, measured for different optical powers; it should be noted that, at 1V bias, D^* is always larger than $10^{11} cm\sqrt{Hz}/W$ thus outperforming the detectivity of commercially available NIR photodetectors that exhibit D^* in the $10^9 - 10^{11}$ range[19][20]. In order to verify our assumption about shot

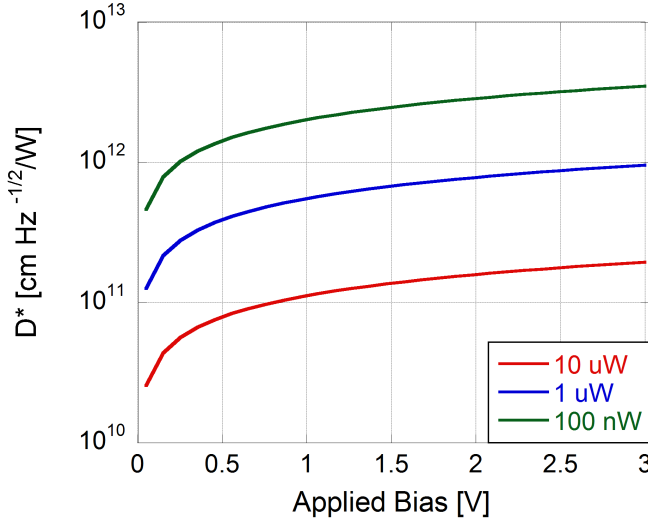


Fig. 6. Specific detectivity vs. applied voltage for different optical input powers.

noise, we measured the device total current at different bias levels over 60s timespans with different integration times. The total noise was, then, evaluated as the dark current standard deviation (rms). Unfortunately, the resulting noise was larger than the shot noise by about one order of magnitude. This can be attributed to both flicker noise and interferences or other noise sources within the measurement setup. Therefore, in the following characterizations, we will consider the measured standard deviation as the effective noise current in order to keep a conservative approach for the evaluation of the device performance as a fire detector. The flame response of the photodetectors was evaluated measuring the total current at 1V bias in presence of a candle flame. The flame was positioned at different distances from the detector surface and the test was

conducted indoor, in an ambient illuminated with fluorescent tubes that produced a mean light intensity of $35\mu W/cm^2$. Fig. 7 shows the measured current (dots) compared to the dark current (line); the inset shows an enlargement of the measured dark current over 0.5s acquisition. Clear and reproducible

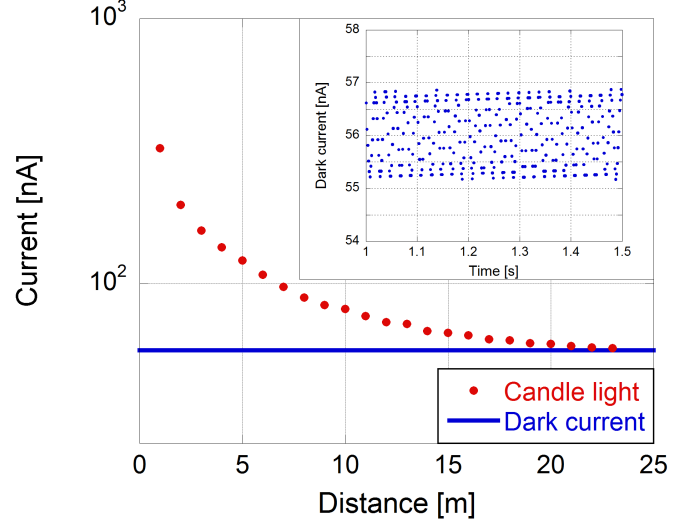


Fig. 7. Total current (red dots) and dark current (blue line) vs distance in case of illumination with a candle flame. Applied bias is 1V. Dark current variation over time is showed in the inset.

flame detection was obtained at a distance of 23m where a 6dB signal to noise ratio (SNR) has been estimated. Fig. 8 shows the SNR measured at different distances; the maximum distance was limited by the measurement setup, but an extrapolation on the SNR plot shows that the 3dB limit for the flame detection is at about 26m. The observed SNR dependence on

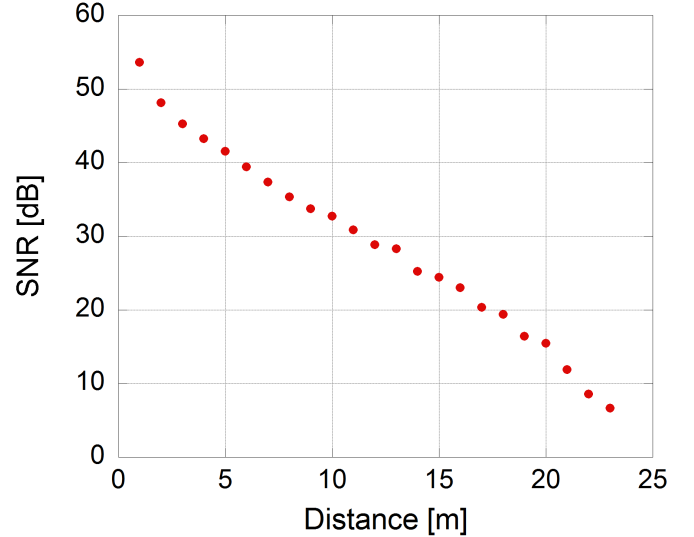


Fig. 8. Signal to Noise Ratio (SNR) vs. distance at 1V bias.

the flame distance is consistent with the $1/d^2$ decay of the light intensity combined with the device nonlinear response. We also evaluated the field of view (FOV) of the photodetector; measurements were taken putting the candle at 1m from

the device surface and then rotating the detector along two perpendicular axes. Fig. 9 shows the angular photoresponse of the flame detector. The resulting field of view (calculated as the full angle at half maximum) is 120° for both vertical and horizontal rotations. Such a wide view angle together with the high detection distance allows the employment of a single detector for the surveillance of a room larger than $100m^2$. The maximum detection distance can also be enhanced

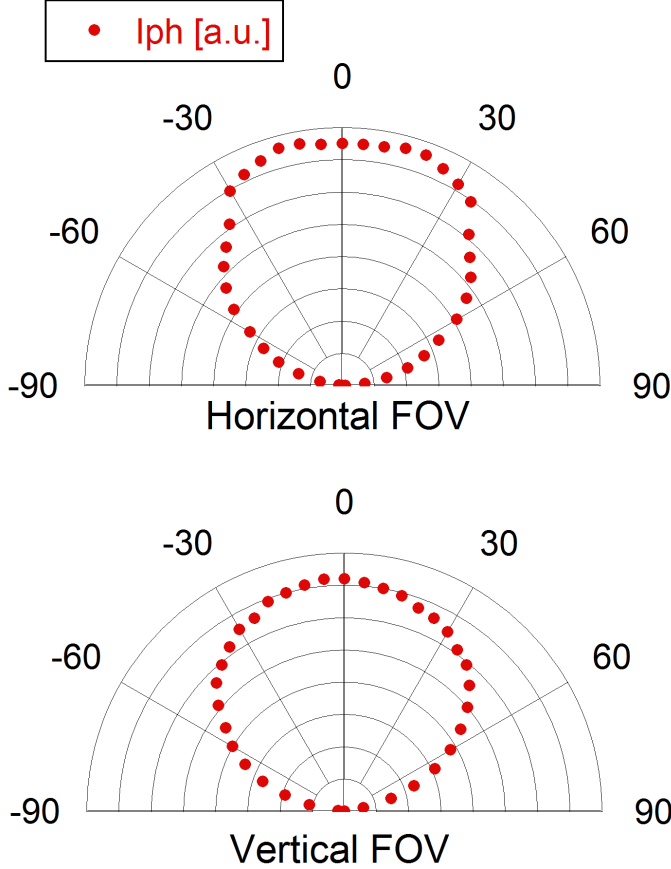


Fig. 9. Horizontal (top) and vertical (bottom) angular photoresponse of the flame detector.

using a lens in front of the detector. Employing a lens with 25mm focal length, we observed a twofold increase in the SNR value with an extrapolated 3dB detection limit of 47m. Such performance enhancement comes at the cost of a reduced FOV due to the low numeric aperture of the lens ($NA \approx 1.5$). Thus, depending on the environment where the fire detector should be installed and on the specific application, a trade-off between detection distance and FOV can be found selecting the suitable lens characteristics. Another important parameter of flame detectors is the time needed to trigger an alarm in case of fire. We analyzed the time response of our device using the same experimental setup employed for the measurements depicted in fig.7 and adding an electronic shutter in front of the device. This approach was used to simulate a fast ignition of the flame, thanks to the short switch time of the shutter ($\sim 100\mu s$) Fig. 10 shows the detector's current vs. time obtained at a 1V bias and with the candle at 2m, 6m and 10m from

the sensor's surface. The shutter was opened 1.5s after the beginning of the measurement. Rise time (calculated as the time taken by the signal to change from 10% to 90% of the maximum photocurrent) is always less than 2s. A slow temporal response is expected in PbS CQD photoconductors, however the measured rise time is more than satisfactory for fire detection applications. Moreover, we observed a significant reduction of the rise time at increasing optical power. This is expected because photoconductive gain is achieved thanks to trap states that produce carrier lifetimes larger than the transit time [21]. Since the time response of photoconductors is dominated by recombination, larger gain corresponds to slower time response, therefore larger optical intensity produces lower gain and faster response. Our devices typically undergo an initial significant change in both responsivity and dark current. Both the responsivity and the dark current decrease by about 50% in about one/two weeks. Nevertheless, the detectivity does not change significantly (due to its opposite dependence on the two parameters). After such period, performance are much more stable and the characterization was performed at this stage. Devices exhibit a dark current low frequency oscillation over two hours of less than $\pm 2\%$ and a long term (several days) dark current drift of about 0.3%/day. As previously

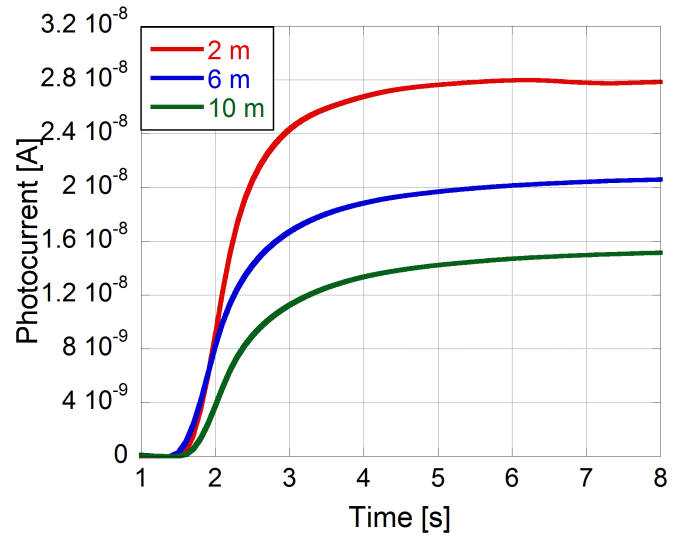


Fig. 10. Time response of the fire detector with the flame at different distances.

mentioned, all flame tests have been performed in an ambient illuminated with standard fluorescent tube. In addition, our devices proved to be completely immune to any change in ambient illumination as long as we employed fluorescent or LED lamps. Tungsten lamps or halogen lamps, conversely, emit radiation in the near infrared spectrum that may affect the detector operation depending on their intensity. However, it should be considered that both tungsten and halogen lamps have already been declared unsuitable for indoor illumination in many countries do to their low efficiency.

IV. CONCLUSIONS

We realized and characterized a flame detector based on PbS colloidal quantum dots; the device was realized with a simple,

cost effective, drop casting technique and was equipped with a silicon window to filter the visible light. The photodetector was characterized with monochromatic infrared illumination and with the light emitted by a candle flame. Responsivity at $1.3\mu\text{m}$ and low optical intensity is as high as 30A/W and 10A/W at 3V and 1V bias, respectively. Flame detection was achieved, in the presence of a standard indoor illumination (fluorescent tubes), at a 20m distance with a 120° field of view enabling the use of a single detector for the surveillance of environments wider than 100m^2 . We, also, demonstrated the possibility to extend the operation range of the photodetector employing a short focal lens at the cost of a reduced FOV. Such optical setup allowed a two fold enhancement of the SNR and a theoretical maximum detection distance of 47m. The rise time of the detector's photocurrent has been estimated always lower than 2s. Such results suggest that the proposed photodetector could be effectively employed for indoor flame detection; moreover, ease of fabrication and low cost are key feature for industrial technology transfer. Eventually, the proposed deposition technique is also CMOS compatible thus paving the way to the realization of photodetectors directly integrated with suitable readout electronics.

V. ACKNOWLEDGEMENTS

Authors would like to acknowledge Daniele De Felicis for technical assistance during SEM analyses, performed at the interdepartmental laboratory of electron microscopy of the University of Roma Tre, Rome Italy (<http://www.lime.uniroma3.it>)

REFERENCES

- [1] N. Brushlinsky, M. Ahrens, S. Sokolov, and P. Wagner, "World Fire Statistics 2016," International Association of Fire and Rescue Services, Tech. Rep., 2016.
- [2] R. Bogue, "Sensors for fire detection," *Sensor Review*, vol. 33, no. 2, pp. 99–103, 2013.
- [3] Z. Liu and A. K. Kim, "Review of Recent Developments in Fire Detection Technologies," *Journal of Fire Protection Engineering*, vol. 13, no. 2, pp. 129–151, 2003.
- [4] W. S. Qureshi, M. Ekpanyapong, M. N. Dailey, S. Rinsurongkawong, A. Malenichev, and O. Krasotkina, "QuickBlaze: Early Fire Detection Using a Combined Video Processing Approach," *Fire Technology*, vol. 52, no. 5, pp. 1293–1317, 9 2016.
- [5] A. Peyaud, A. Angelopoulos, C. Chelms, V. Costopoulos, M. Chica, I. Giomataris, A. Gongadze, T. Herbert, I. Kantemiris, S. Kirch, J. Mols, T. Papaevangelou, P. Pavlopoulos, and F. Quinlan, "The ForFire photodetector," *Nuclear Instruments and Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated Equipment*, vol. 787, pp. 102–104, 2015.
- [6] Y. L. Jiang, G. Li, T. Yang, and J. J. Wang, "Development of gas fire detection system using tunable diode laser absorption spectroscopy," *IOP Conference Series: Earth and Environmental Science*, vol. 52, no. 1, p. 012092, 1 2017.
- [7] A. B. Utkin, F. Piedade, V. Beixiga, P. Mota, and P. Lousã, "Scalable lidar technique for fire detection," M. F. P. C. Martins Costa and R. N. Nogueira, Eds. International Society for Optics and Photonics, 8 2014, p. 92860D.
- [8] V. I. Klimov, *Nanocrystal Quantum Dots*. Boca Raton: CRC Press, 2010.
- [9] G. Konstantatos, I. Howard, A. Fischer, S. Hoogland, J. Clifford, E. Klem, L. Levina, and E. H. Sargent, "LETTERS Ultrasensitive solution-cast quantum dot," *Nature*, vol. 442, pp. 180–183, 2006.
- [10] A. De Iacovo, C. Venettacci, L. Colace, L. Scopa, and S. Foglia, "PbS Colloidal Quantum Dot Photodetectors operating in the near infrared," *Scientific Reports*, vol. 6, no. 37913, 2016.
- [11] R. Saran and R. J. Curry, "Lead sulphide nanocrystal photodetector technologies," *Nature Photonics*, vol. 10, no. 2, pp. 81–92, 2016.
- [12] G. Konstantatos, J. Clifford, L. Levina, and E. H. Sargent, "Sensitive solution-processed visible-wavelength photodetectors," *Nature Photonics*, vol. 1, no. 9, pp. 531–534, 2007.
- [13] L. Cademartiri, J. Bertolotti, R. Sapienza, D. S. Wiersma, and G. A. Ozin, "Multigram Scale, Solventless, and Diffusion-Controlled Route to Highly Monodisperse PbS Nanocrystals," *Journal of Physical Chemistry B*, vol. 110, no. 2, pp. 671–673, 2006.
- [14] C. Hu, A. Gassenq, Y. Justo, K. Devloo-Casier, H. Chen, C. Detavernier, Z. Hens, and G. Roelkens, "Air-stable short-wave infrared PbS colloidal quantum dot photoconductors passivated with Al₂O₃ atomic layer deposition," *Applied Physics Letters*, vol. 105, no. 17, pp. 4–8, 2014.
- [15] A. De Iacovo, C. Venettacci, L. Colace, L. Scopa, and S. Foglia, "High Responsivity Fire Detectors based on PbS Colloidal Quantum Dot Photoconductors," *IEEE Photonics Technology Letters*, vol. 29, no. 9, pp. 703–706, 2017.
- [16] H. Liu, E. Lhuillier, and P. Guyot-sionnest, "1/f noise in semiconductor and metal nanocrystal solids," *Journal of Applied Physics*, vol. 115, p. 154309, 2014.
- [17] G. Konstantatos and E. H. Sargent, "Nanostructured materials for photon detection," *Nature Nanotechnology*, vol. 5, no. 6, pp. 391–400, 2010.
- [18] M. Böberl, M. Kovalenko, S. Gamerith, E. List, and W. Heiss, "Inkjet-Printed Nanocrystal Photodetectors Operating up to 3 μm Wavelengths," *Advanced Materials*, vol. 19, no. 21, pp. 3574–3578, 2007.
- [19] Hamamatsu, "InSb photoconductive detectors P6606 series," 2012.
- [20] THORLABS, "FDPS3X3 Lead Sulfide Photoconductor User Guide," 2005.
- [21] G. Konstantatos and E. H. Sargent, "PbS colloidal quantum dot photoconductive photodetectors: Transport, traps, and gain," *Applied Physics Letters*, vol. 91, no. 17, pp. 2013–2016, 2007.