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Direct detection of 5 MeV protons by flexible thin-film devices based on organic semiconductors

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Summary. — The direct detection of 5 MeV protons by flexible organic thin film devices is here reported for the first time. Mechanical flexibility, portability, low cost of fabrication and human tissue equivalence are important properties which make this technology an excellent candidate for the development of wearable proton dosimeters to be employed in several areas such as in the medical field (*i.e.*, during proton therapy treatments). Moreover, by exploiting the coupling between the organic semiconductor and the plastic substrate, this class of detectors offers the unique possibility of operating them both in real-time mode and in integration mode by recording two different information items regarding the irradiation condition of the sensing system.

1. – Introduction

The development of detectors for protons is crucial not only for fundamental applications, but also for monitoring energy and fluences of particles in ion beam applications. Among the others, the most demanding application for which accurate measurements are needed is hadron therapy of cancer. In this application, ion beams are used for the controlled treatment of cancer by delivering the prescribed amount of dose to the tumor [1]. To ensure safe, effective and consistent radiation delivery, accurate monitoring of the beams and measurements of the absorbed dose are essential [2]. In particular, the detectors devoted to the monitoring of the absorbed dose by patients during treatments must satisfy some crucial requirements, such as the tissue equivalence to limit the perturbation of the beams and to avoid complex calibration procedures, the possibility of scaling up the system onto pixelated large-area and flexible 2D matrixes for the development of wearable dosimeters, and the real-time monitoring to improve treatment effectiveness. So far, a single detector which fulfils all these requirements does not exist, and different detectors are used for the monitoring of different aspects. For

instance, plane-parallel integrate circuits (ICs) are employed for point and longitudinal profile dose measurements [3] while radiochromic or radiographic films [4], scintillating screens [5], silicon microstrips, MOSFETs [6] and diamond array detectors [7] are mostly used to monitor transversal dose distribution. Despite the different advantages provided by all of these sensing technologies, some drawbacks are still present, like the impossibility to cover large-area and curved surfaces and to achieve real-time response. Here, the first demonstration of the direct detection of 5 MeV protons by organic semiconductor based 2 terminals co-planar devices is reported [8]. These devices allow overcoming the main limitations for proton detection as organic semiconductors can be deposited from solution at low temperature by easy-scalable techniques directly onto large-area and flexible substrates. Organic devices demonstrated to be operated both in real-time and in integration mode and offer the unique property to make these detectors human tissue equivalent in terms of ionizing radiation absorption, which is the most desirable property for a dosimeter to be employed in the medical field.

2. – Results and discussion

The organic detectors we fabricated and tested are depicted in fig. 1(A). The devices have a 2-terminal co-planar structure where the active semiconducting layer is an organic thin film (150 nm thick) of microcrystalline bis(triisopropylgermylethynyl)-pentacene (hereafter TIPGe-Pn), deposited from solution by drop casting onto two interdigitated gold electrodes (fig. 1(A)). We deposited and patterned gold electrodes by thermal evaporation on a 125 μm thick plastic substrate (*i.e.*, polyethylene naphthalate (PEN)), ensuring the mechanical flexibility of the system. The channel length (*i.e.*, the distance between the fingers of the electrodes) is $L = 30\,\mu$m and the width is $W = 45$ mm. TIPGe-Pn is an organic small molecule similar to bis(triisopropylsilylethynyl)-pentacene molecule (TIPS-Pn) by substituting the two silicon atoms with two germanium atoms [9]. TIPGe-Pn-based detectors have already been demonstrated to enhance the charge carrier mobility and the x-ray sensitivity with respect to TIPS-Pn based counterparts because of the increase of the attenuation fraction under ionizing radiation [10]. All fabrication steps to implement these detectors are scalable to large-area, low-temperature (<180°C) compatible processes, thus allowing obtaining large-area and flexible detectors (fig. 1(B)).

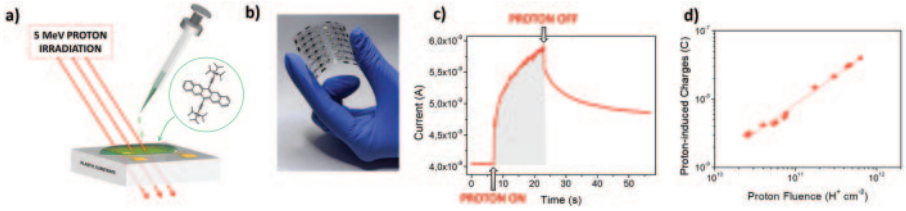

Fig. 1. – (a) Schematic of the 2-terminals device based on drop casted TIPGe-Pn active layer and tested under 5 MeV protons. (b) Mechanical flexibility of the organic thin film-based detectors. (c) Dynamic response of the organic based detector irradiated by 5 MeV protons. The arrows indicate when the irradiation cycle starts and ends. The grey shadow represents the photocharges generated by the energy deposited by protons in the active layer. (d) Plots of the collected charges as a function of the proton fluences in the range $[2.5 \cdot 10^{10}$–$6.3 \cdot 10^{11}]$ H^+ cm^{-2}.

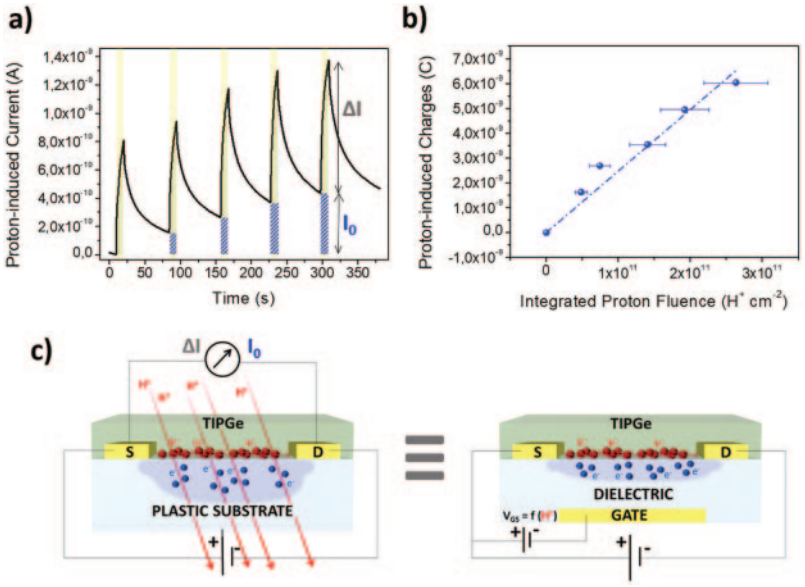

Fig. 2. – (a) Current response (black line) of the detector irradiated by different fluences of protons $[2.6 \cdot 10^{10}$–$7.1 \cdot 10^{10}]$ H^+ cm^{-2}. ΔI (grey shadow) is the real-time response proportional to the instantaneous dose and I_0 (blue shadow) represents the baseline shift due to the trapped charges generated in the plastic substrate. (b) Linear plot of the total charge generated in the plastic substrate as a function of the integrated dose. (c) Schematics of the model describing the detector integration-mode operation.

The detector response under proton irradiation was tested using a 5 MeV beam provided by the 3 MV Tandetron accelerator of the LABEC ion beam center (INFN Firenze, Italy). The intensity of the beam ($[2.5 \cdot 10^{10}$–$6.3 \cdot 10^{11}]$ H^+ cm^{-2}) is monitored and quantitatively measured using a rotating chopper [11], placed between the silicon nitride window and the sample. Although the energy of ion therapy beams is commonly above 70 MeV, the proton energy tested in this work is of the order of the end-of range values, in particular of the energies of scattered protons reaching internal healthy tissues surrounding the target. In fig. 1(C) the typical dynamic response recorded under 20 s proton irradiation is reported. The effect of protons is evaluated by monitoring the current flowing through the channel of the device while it is biased below 1 V. Due to the release of energy from the ionizing radiation beam in the semiconducting layer (1.55 keV for each proton), some electron/hole pairs are generated and an increase in current is observed. The slow rise and decay of this peak is the fingerprint of the detection by organic thin film-based devices ruled by the photoconductive gain mechanism already described in literature for x-ray detection [12]. By integrating the current peak it is possible to extrapolate the charges generated by protons in the organic layer and collected at the electrodes. The plot reported in fig. 1(D) demonstrates that the induced charges are linearly dependent on the proton fluences. By this curve it is possible to calculate the sensitivity of the detector as the slope of the fitting curve ($S = (5.15 \pm 0.13)$ pC Gy^{-1}).

In fig. 2(A), the response of the detector under multiple cycles of irradiation is reported (fluences in the range $[2.6 \cdot 10^{10}$–$7.1 \cdot 10^{10}]$ H^+ cm^{-2}). Here, two different contributions can be clearly observed: ΔI (grey shadow) is the real-time response proportional to the istantaneous dose (already described in fig. 1), while I_0 (blue shadow) represents a

persistent baseline shift due to the energy absorbed in the 125 μm thick plastic substrate (1590 keV for each proton). In fact, due to irradiation, negative charges are trapped in the polymeric substrate and they induce an increase of the semiconductor conductivity, leading to higher current in the organic thin film. In particular, the charges induced by this effect are linearly proportional to the integrated proton fluences, as shown in fig. 2(B). In fact, while the real-time contribution is due to the energy absorbed in the semiconducting layer and it is proportional to the istantaneous dose of irradiation, the latter effect results in an integrative process related to the longer relaxation time of the polymeric materials (*e.g.*, PET, PEN substrates). This effect can be modeled by considering what happens in an organic field effect transistor (OFET) structure, where the gate electrode is typically used to modulate the current flowing between the source and drain electrodes. In this case, the irradiated polymeric substrate of the sensor acts as the bottom-gate electrode of an OFET structure, creating a gating effect proportional to the integrated dose of irradiation.

3. – Conclusions

In conclusion, this study illustrates the direct detection of 5 MeV protons by organic thin-film devices realized on a plastic flexible substrate. The sensors demonstrate a stable and reproducible response to proton beams in a range of fluences $[2.5 \cdot 10^{10}$–$6.3 \cdot 10^{11}]$ H^+ cm^{-2}. By exploiting the structure of this sensor, two different operation modes can be effectively and independently used: 1) real-time sensing, where the amount of induced charges is proportional to the istantaneous released dose, and 2) integration-mode sensing, where the energy released in the polymeric substrate by protons generates trapped charges that induce an increase of conductivity in the semiconducting layer proportional to the history of irradiation of the sensor. To the best of our knowledge, this is the first study which demonstrates the potentiality of this new class of materials as flexible, portable, and human tissue equivalent proton detectors.

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REFERENCES

[1] Giordanengo S. *et al.*, *Phys. Med.*, **43** (2017) 79.
[2] Paganetti H., *Proton Therapy Physics* (CRC Press) 2012.
[3] Mirandola A. *et al.*, *Med. Phys.*, **42** (2015) 5287.
[4] Hara Y. *et al.*, *Nucl. Instrum. Methods Phys. Res. Sect. B*, **331** (2014) 253.
[5] Russo S. *et al.*, *Phys. Med.*, **34** (2017) 48.
[6] Legge K. *et al.*, *Radiat. Oncol.*, **12** (2017) 41.
[7] Akino Y. *et al.*, *J. Radiat. Res.*, **56** (2015) 912.
[8] Fratelli I. *et al.*, *Sci. Adv.*, **7** (2021) eabf4462.
[9] Sorli J. C. *et al.*, *Chem. Mater.*, **31** (2019) 6615.
[10] Ciavatti A. *et al.*, *Adv. Funct. Mater.*, **29** (2018) 1806119.
[11] Chiari M. *et al.*, *Nucl. Instrum. Methods Phys. Res. Sect. B*, **188** (2002) 162.
[12] Basiricò L. *et al.*, *Nat. Commun.*, **7** (2016) 13063.