High- quality polycrystalline CVD diamond for conformal radiotherapy applications

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Abstract - A bidimensional dosimeter made with a state-of art polycrystalline Chemical Vapour Deposited (pCVD) diamond for applications in clinical radiotherapy has been manufactured in the framework of the DIAPIX project (INFN-CSN5). It is constituted by a large area ($2.5 \times 2.5 \text{cm}^2$) pCVD diamond film equipped with in-house electrical contacts on the front and rear surfaces in transverse geometry. Upper contact, made on the growth side of the film, is in form of a squared matrix of 24x24 pixels, pixel size 0.8 mm x 0.8mm, 300nm thick, pitch 1mm. Optimization of the operational conditions has been performed studying a few pixels along the matrix. Instability effects due to trapping-detrapping mechanisms were observed to be negligible at low bias. These results confirm that the pCVD diamond device is suitable for mapping the bidimensionally conformed dose in an Intensity Modulated Radiation Therapy (IMRT) treatment.

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1. Introduction

Conformal radiotherapy, as X-photons Intensity-Modulated radiotherapy (IMRT) [1], represents a major development in clinical treatments. With IMRT it is possible to deliver a highly conformed dose to an irregularly shaped tumor volume while sparing the surrounding healthy tissue as much as possible. In IMRT treatments, very accurate dosimetric verifications are mandatory and represent a major challenge for clinical dosimetry, due to the high-dose gradients, elevated variability in space and time of the dose rate and of the beam spectral composition. This imposes strict requirements to the detectors, in terms of high sensitivity, stability and velocity of response, independence of energy and dose rate.

Many of the outstanding chemical and physical properties of diamond make this material potentially attractive in this respect. Due to its atomic and mass numbers it is considered an almost tissue-equivalent material. Dosimeters made with natural diamond are already commercially available [2] but extremely expensive due to the difficulty in selecting stones with the proper dosimetric characteristics. Polycrystalline Chemical Vapor Deposited (pCVD) diamond films have been proposed in their stead, due to the potential low cost of this material and much effort has been devoted worldwide to produce pCVD diamond films with properties suitable for dosimetry in radiotherapy. In past, a major drawback of pCVD detectors concerned the slow rise and decay times and the poor response stability [3]. In the conventional mode of using high-quality pCVD diamond dosimeters, (average applied electric field of the order of $1V/\mu m$) the dynamical response of these devices is, in fact, still affected by trapping dynamics, originating rise and decay times typically of the order of a few seconds and the occurrence of pumping effects [3]. To reduce the effect of native defects on response stability, single-crystal diamond films, grown on high temperature high pressure (HPHT) diamond substrates by a CVD method (scCVD), have been proposed [4]. Nonetheless, large-scale bidimensional dosimeters, as those needed for IMRT [5], cannot be foreseen with this kind of material: due to the limited size the HPHT diamond seed, wafer maximum size achievable has approximately 1cm diameter. On the contrary, current state-of-art technology demonstrates that segmented devices can be processed on high quality polycrystalline CVD diamond 4-6" wafers [6]. Recently it has been shown by some of the authors that a considerable improvement of the performance of the pCVD diamond dosimeters can be obtained using them in zero-bias conditions [7]. Nonetheless, applying an external bias, low enough to prevent unwanted polarization effects in the device, can be useful in view to preselect the polarity of the output current. This paper presents first experimental results obtained with such a prototype in view to get an optimization of its operational conditions under radiotherapy beams.

2. Materials and methods

2.1. Experimental details

A large area (2.5x2.5cm^2) pCVD diamond film, 300μm thick, made by Diamond Detectors Ltd, UK, with a certified high-purity electronic grade (Detector Premium Grade) was used to manufacture the prototype. Optimization of the electronic quality of the pCVD diamond material has been obtained by the company using a material removal procedure, performed from the substrate side, where the density of grain boundaries is higher due to the typical columnar growth of the diamond microcrystals. Both diamond surfaces are lapped, roughness due to residual polycrystalline stresses was tested by Atomic Force Microscopy in the range of a few tens of nm. The diamond film has been equipped with in-house made Cr/Au electrical contacts

on the front and rear surfaces in transverse geometry. Before metallization diamond surfaces were cleaned in a highly oxydising and corrosive environment leaving the diamond surface oxygen terminated. Chromium deposition on oxygen terminated diamond surface was used in order to achieve a good mechanical adhesion and, as discussed in [8], to create a built-in potential barrier at the metal-semiconductor interfaces. The upper contacts, made on the growth side of the film, is in form of a squared matrix of 24x24 pixels, pixel size 0.8 mm x 0.8mm, 300nm thick, pitch 1mm. Back contact is a square pad of about the dimension of the diamond film. A photograph of the diamond dosimeter equipped with the matrix of pixels is shown in fig.1.
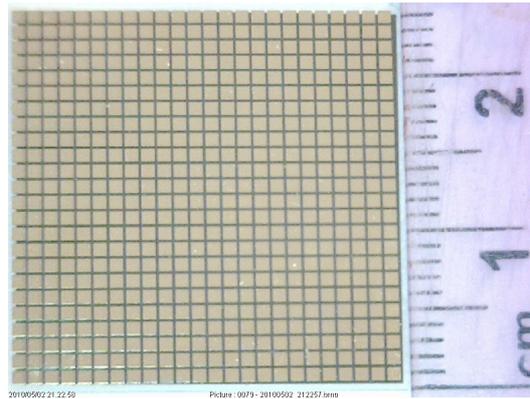
Figure 1: Picture of the first prototype of bidimensional dosimeter manufactured in Florence using a pCVD diamond film
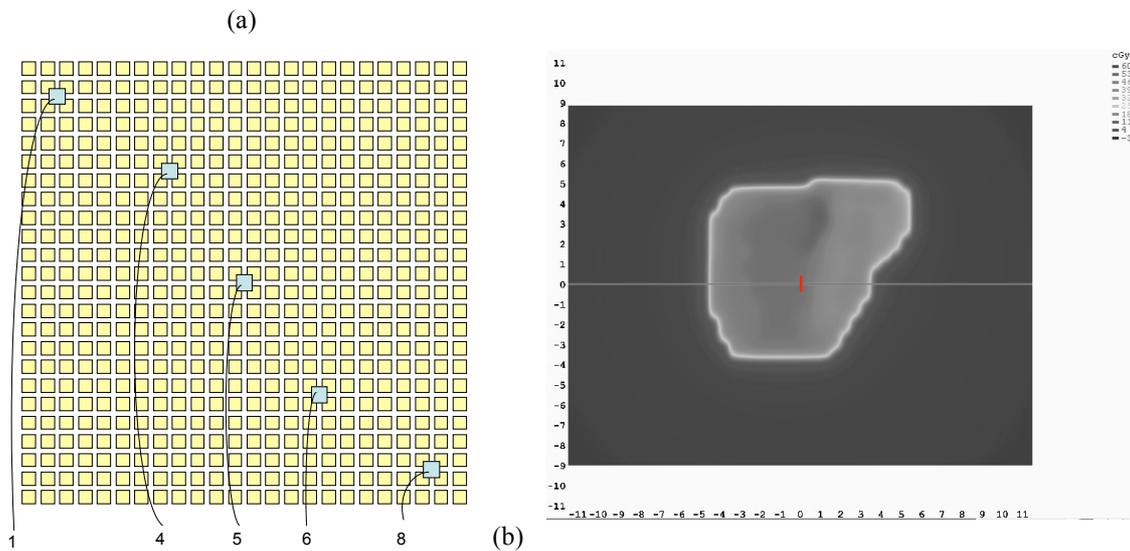
Figure 2: (a) Position of the 5 point of measurement tested in this study. ;(b) Field map of the IMRT treatment plan, the line indicates the profile tested in this study and the red marker the treatment isocentre.

A Farmer type Ionization Chamber NE 2571 (IC) connected to an UNIDOS electrometer was used as the reference dosimeter with conventional beams in order to take into account of beam instabilities and to determine the absolute dose.

During exposure, samples were placed in a PMMA slab phantom at a water-equivalent depth of 5-10cm. The dosimetric performance of the pCVD diamond has been investigated measuring both current and charge signals, by means of a Keithley 6517A electrometer. Preliminary measurements on the performance of the prototype as a dosimeter have been carried out at a few different positions in the matrix. A map indicating the 5 points of test is shown in fig 2 (a). Every pad is made of four adjacent pixels, so the active area of each pad is 1.8mmx1.8mm.

The dosimetric characteristics of the pCVD diamond dosimeter have been investigated at the Radiotherapy Unit of the University of Florence by means of an Elekta Synergy LINAC, both with conventional 6-10 MV photon beams in a 10x10 cm^2 field size (sample placed at the isocentre) and with a 10MV IMRT field. During irradiations with conventional beams the IC was placed 2.5 cm apart from the pCVD diamond at the same water-equivalent depth and irradiated simultaneously. In modulated intensity beams the photon fluence impinging on the patient varies point to point inside the radiation field. Such a modulation is obtained thanks to a Multi Leaf Collimator (MLC) mounted on the linear accelerator. At the Radiotherapy Unit of the University of Florence the step-and-shoot IMRT modality is used, i.e. the desired non uniform fluence distribution is obtained for each beam by a sequence of numerous static irradiations (segments) each characterised by a different MLC configuration; the beam is switched off during the MLC rearrangement. The width of the leaves (projected at the isocentre plane) of the Elekta Synergy LINAC is 4 mm. In IMRT measurements, a 10 MV photon beam for prostate treatment in step-and-shoot modality was released, obtained by a sequence of 12 segments with a nominal dose rate of 400MU/min.

2.2. Choice of device operative configuration

It is well known that the work function of diamond is strongly dependent on its surface treatment, with a hydrogen terminated surface work function value of 4.8 eV and an oxygen terminated surface value as high as 5.8 eV [8]. Due to the high surface conductivity, time instability and high superficial leakage currents of H-terminated surfaces [9] oxygen terminated surface is preferred for detecting devices. To get oxygen terminated surfaces diamond films are cleaned in a highly oxydising and corrosive environment using a saturated solution of sulfuric acid and potassium dichromate (chromic solution) at boiling temperature. Chromium deposition on oxygen terminated diamond, used in order to achieve a good mechanical adhesion, brings to the formation of chromium carbide on the oxygen terminated surface. Since the work function of chromium is 4.5 eV, at the metal-diamond interface a junction with a potential difference of the order of 1 volt is created [10]. Considering the sandwich configuration of our samples, the diamond dosimeter will result in a metal-semiconductor-metal (MSM) device in transverse configuration with two back-to-back Schottky barrier contacts.

In figure 3 the charge density (a), electric field profile (b) and band diagram (c) of our device at null bias are shown following the model given in [11] and considering that the polycrystalline CVD diamond bulk has a slightly p-type character [12]. A negative charge is confined at the Cr-carbide interfaces, while bulk of the material [x1,x2] is neutral. Values of barriers at the two contacts (VD1 and VD2) are generally different, as they depend on the specific amount of oxygen-terminated bondings at both surfaces. This will result in an asymmetric band bending at the two contacts. With short-circuited electrodes, the generated charged carriers are driven by the built-in electric field and recombine causing a redistribution of the charge at the contacts; the current response is due to the displacement of the zero-field

plane [13]. In other words, the external current is due to the net flow of charge between the two contacts which react at the change of the internal charge distribution, i.e. at the zero-field plane motion.
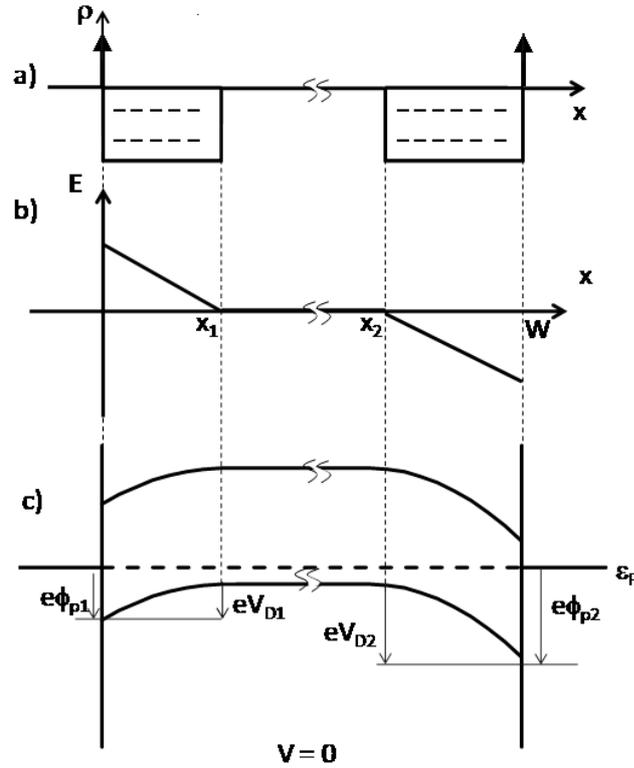
Figure 3: (a) space charge, (b) electric field profile and (c) band diagram of the diamond device at null bias

Recently it has been shown by some of the authors that a considerable improvement of the performance of the pCVD diamond dosimeters can be obtained using them in zero-bias conditions [7]. Nonetheless, the choice of null-bias has as a drawback that current polarity of the pCVD diamond samples during exposure to irradiation in null bias could be either plus or minus, depending on which of the two Schottky barriers in fig. 3 is prevailing on the other. In particular, the polarity of the current could in principle vary along the pixel matrix, which undoubtedly represents an effect increasing the complexity of the read-out electronics. To select the polarity of the current sign it is then necessary to apply an external bias to the sample.

In fig. 4 we report the charge density (a) , electric field profile (b) and band diagram (c) of our device at low bias. When a positive voltage is applied to the metal-semiconductor contact #2 with respect to contact #1 the barrier ϕ_{p2} is reverse biased while ϕ_{p1} is forward biased: due to this effect most of the voltage drop will occur across the depletion region of contact No. 2. The applied voltage is shared between the two contacts $V = V_1 + V_2$: as the voltage applied increases, the sum of the two depletion regions increases and eventually, at the reach-through voltage V_{RT}, equals the total thickness of the device. For $V << V_{RT}$ the current is mainly due to the thermionic emission from the reverse biased contact. The internal neutral region, due to negligible diffusion length of carriers in polycrystalline diamond, is not contributing to the

signal. For sufficiently low biases (typically such as $V < E_g/q$ with $E_g = 5.5eV$ and q electronic charge) the external current would still be mainly due to the zero-field plane motion inside the sample, with negligible contribution from the dark current.
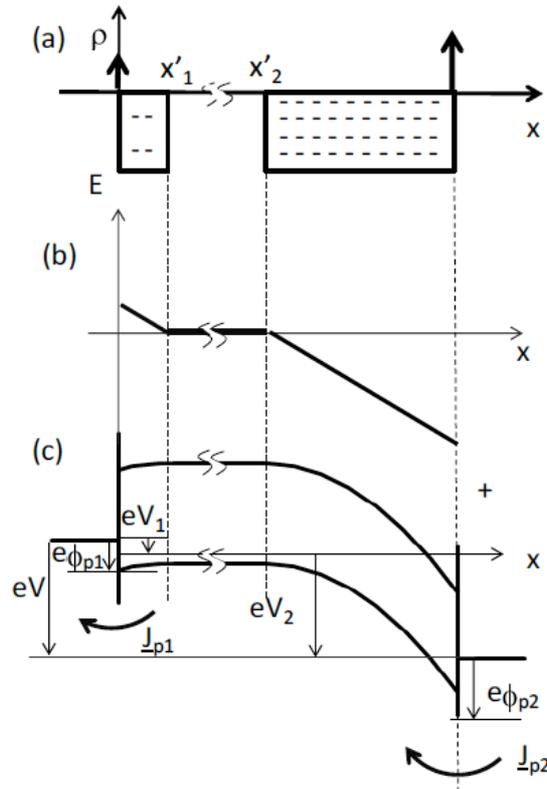
Figure 4 : (a) space charge, (b) electric field profile and (c) band diagram of the diamond device at low bias.

3. Experimental results

3.1. Measurements under radiotherapy beams

Our study was aimed at verifying that, applying a low external bias, the signal would not be affected by trapping/de-trapping phenomena from the neutral bulk. For this reason we studied the performance of our device at null bias and with an external voltage up to 5V applied on the rear (nucleation side) contact (current is read-out from the growth surface contact). Fig. 5 (a) shows the current response of pad #6 at 0V and 5V under a conventional beam of 10 MV photons at a nominal dose rate of 400Gy/min. The current signal, negative at null bias, switched to positive at 5V, as expected when a low voltage is applied the current response is higher. The sensitivity of a pad made up of four pixels at 5V is about 38 nC/Gy and it reduces to about 5nC/Gy at 0V. The current signal of pad #6 has been measured several times during the same experimental session with a constant dose rate and no significant variations in the response have been observed, furthermore no relevant changes in the dynamics were observed between the signals at 0 and 5 Volts. Fig. 5(b) shows the current response of pad #5 when placed in the position indicated in fig.2 (b) inside an IMRT field for prostate cancer treatment. For better comparison, the two signals have been normalized to their highest value and the current

response measured at 0V is shown in absolute value. From the plot we see that all the segments of irradiation are well distinguishable, with absence of both persistent current and polarization effects. Rise and decay times appear to be compatible with the IMRT procedure.
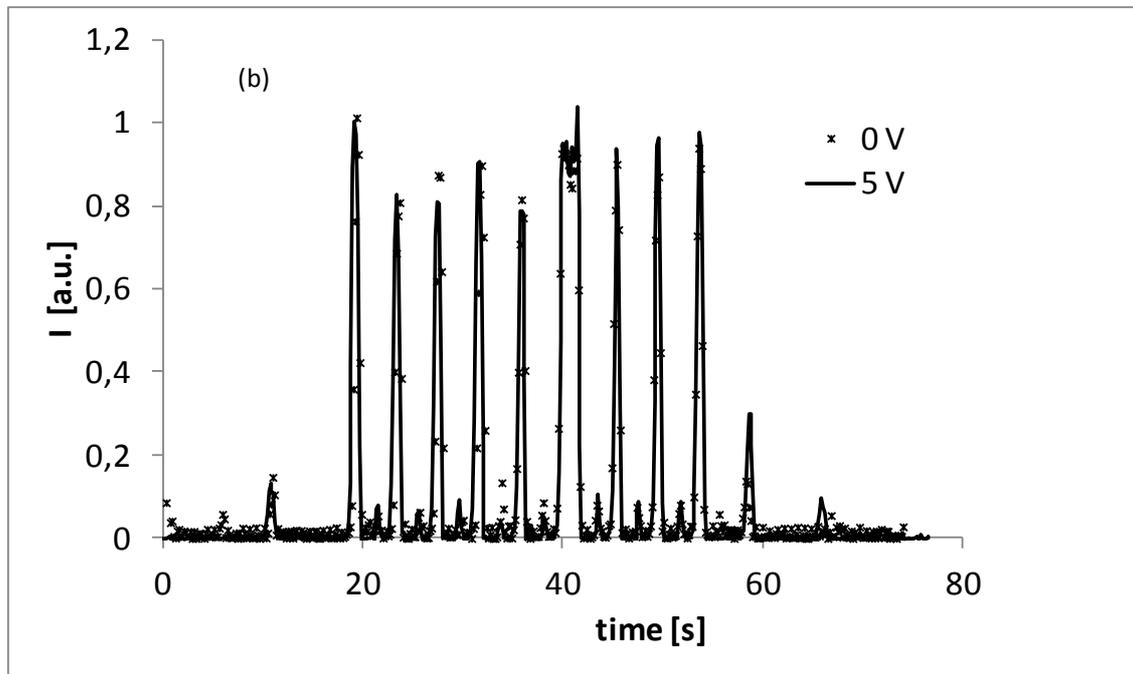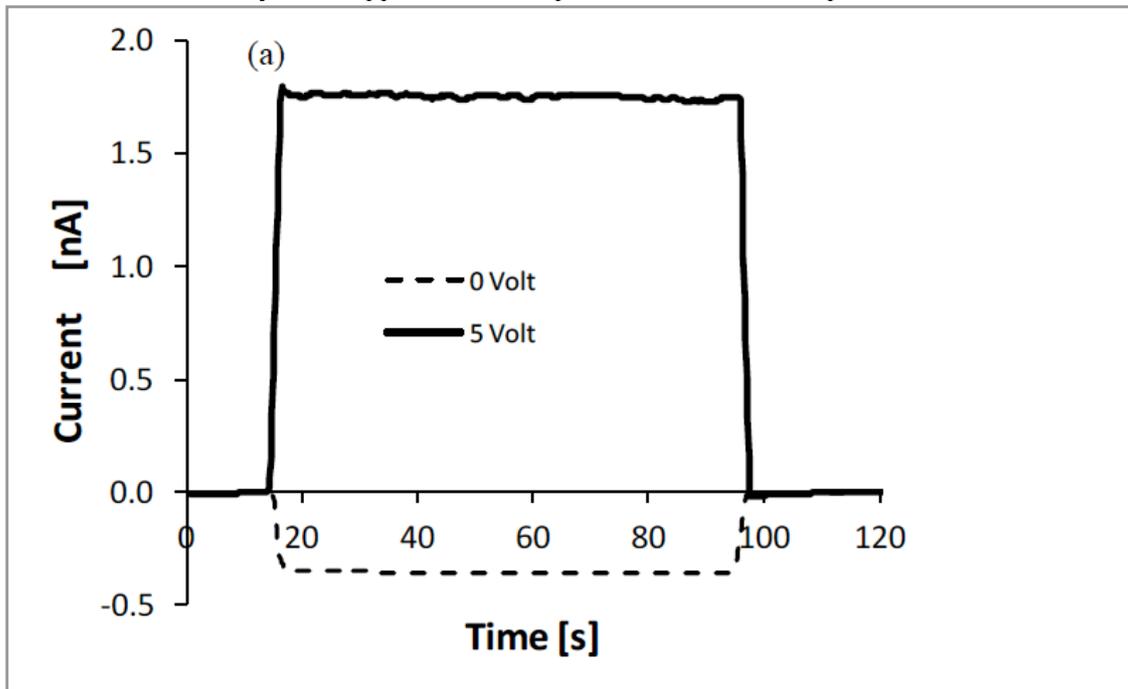
Figure 5: Comparison of the current signal measured at null bias and 5V under (a) conventional 10MV X photon beam (pad #6) and (b) IMRT beam: pad #5 positioned in the cross as indicated in fig. 2b.

We further investigated the use of our device with a low voltage applied. As an example, in fig. 6 we show the current response of pad #5, during irradiation with a conventional 10MV X-photon beam with different dose rates in a linear plot, best way to evidence stability of response and absence of priming.
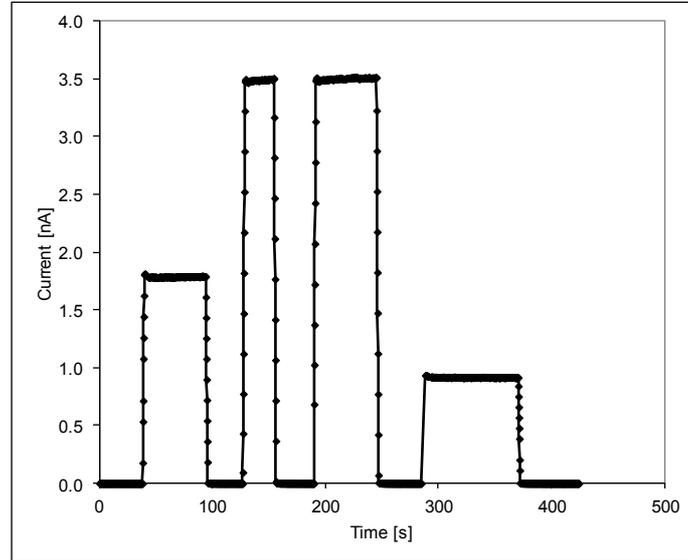
Figure 6: Current response of the central pad (#5) to different irradiation cycles with nominal dose-rates: 200Mu/min, 400Mu/min, 400Mu/min, 100Mu/min.

A collection of rise and decay times observed under radiotherapy beam of 6MV with nominal dose rates of 100, 200, and 400 MU/min for the five pads is shown in table 1. Each value is within the time range 1.1-2.1 with an uncertainty of ± 0.2 s.

	# 1		# 4		# 5		# 6		# 8	
Dose rate [cGy/min]	t_{rise} [s]	t_{decay} [s]	t_{rise} [s]	t_{decay} [s]	t_{rise} [s]	t_{decay} [s]	t_{rise} [s]	t_{decay} [s]	t_{rise} [s]	t_{decay} [s]
100	1.5	1.5	1.4	1.2	1.8	1.6	1.3	1.6	1.4	1.4
200	1.4	1.5	1.5	1.8	1.4	1.8	1.6	1.4	1.4	1.4
400	1.1	1.1	1.4	1.4	1.9	2.1	1.1	1.1	1.4	1.3

Table 1: Rise and decay times measured with different dose rates under a 6MV X photon beam.

A linear current versus dose rate dependence is equivalent to a charge-dose response independent of dose rate. In the case of solid-state dosimeters in on line configuration equipped

with ohmic contacts, it is possible to apply the Flowler [14] model: $I = I_{DARK} + RD_r^\Delta$.

Dose rate dependence of our sample has been investigated by changing the Pulse Repetition Frequency (PRF) of the accelerator. The current signal for different dose rates, as shown in fig. 6 for pad #5, has been fitted according to this model for each pad under study.
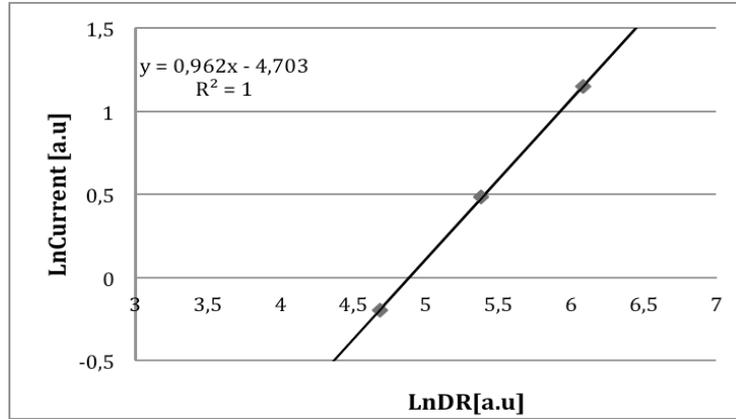
Figure 7: Current response of pad #6 as function of dose rate in log-log scale with the linear fit superimposed.

Figure 7 shows the behavior of the current response of pad #6, together with the linear fit (in a log-log scale). The Δ factors that result from the analysis on the signal of each pad are given in table 2. We observe that values are always very close to 1, indicating a quasi linear behavior in the range of interest for IMRT.

	# 1	*# 4*	*# 5*	*# 6*	*# 8*
Δ	*0.94±0.01*	*0.96±0.02*	*0.96±0.02*	*0.96±0.01*	*0.96±0.01*

Table 2: Δ factors measured with the five pads under a 6 MV X photon beam.

4. Conclusions

A first prototype of bidimensional dosimeter made on high-quality polycrystalline CVD diamond film has been manufactured and preliminary tested. A large area (2.5x2.5cm^2) pCVD diamond film, 300μm thick, made by Diamond Detectors Ltd, UK, with a certified high-purity electronic grade (Detector Premium Grade) was used to manufacture the prototype. The diamond film has been equipped with in-house electrical contacts on the front and rear surfaces in transverse geometry. Chromium deposition on oxygen terminated diamond surface was used in order to achieve a good mechanical adhesion and, to create a built-in potential barrier at the metal-semiconductor interfaces. The upper contacts, made on the growth side of the film, is in form of a squared matrix of 24x24 pixels, pixel size 0.8 mm x 0.8mm, 300nm thick, pitch 1mm. Back contact is a square pad of about the dimension of the diamond film.

In this paper we investigated the use of the pCVD diamond dosimeter with an applied voltage low enough to prevent the creation of unwanted polarization effects. The use of a small external voltage, allowing us to set the sign of the current signal, is beneficial as it permits the use of a non-bipolar electronics. We verified that, in these operative conditions, the contribution of trapping mechanisms at defects in the diamond bulk is still negligible: the current signal is stable and rise/decay times are compatible with the machine characteristics.

In order to perform preliminary tests on the device, the response of few points of measurement along the matrix, has been evaluated. The results on sensitivity, response dynamics and linearity of the current response with dose-rate show that our device is compatible with IMRT applications.
The device shows performances comparable to those reported for synthetic single crystal diamond (scCVD) dosimeters [15], which operated in null-bias as well.
Authors in [15] attribute this behavior to the high crystalline quality of the single crystal material: our results suggest that a significant contribution to the performances could be as well attributed to the null-bias operation of the device.

We are now in the process to develop the electronic read-out to be interfaced with our prototype, in view to be able to read the signal from the overall matrix pixels. The full system is presently under development and results will be presented in forthcoming works.

Acknowledgments

References

[1] S. WEBB, Intensity Modulated Radiation Therapy, Eds Orton, Spaan, Webster, IOP Publishing Bristol and Philadelphia, 2001

[2] PTW-Freiburg GMBH, Lörracher Str. 7 79115 Freiburg, Germany, http://www.ptw.de.

[3] C. De Angelis, M. Casati, M. Bruzzi, S. Onori and M. Bucciolini, Present limitations of CVD diamond detectors for IMRT applications, Nucl. Instrum. Methods Phys. Res. A, 583 (2007) 195-203

[4] J. Isberg, J. Hammersberg, E. Johansson, T. Wikstrom, D.J. Twitchen, A.J. Whitehead, S.E. Coe, G.A. Scarsbrook, High Carrier Mobility in Single-Crystal Plasma-Deposited Diamond, Science, 297 (2002) 1670-72.

[5] D. Menichelli, M. Bruzzi, M. Bucciolini, C. Talamonti, M. Casati, L. Marrazzo, M. Tesi, C. Piemonte, A. Pozza, N. Zorzi, M. Brianzi, A. De Sio, Design and development of a silicon-segmented detector for 2D dose measurements in radiotherapy, Nucl. Instrum. Methods Phys. Res. A, 583 (2007) 109–113.

[6] H. Kagan, Recent advances in diamond detector development, Nucl. Instrum. Methods Phys. Res. A, 541 (2005) 221–227.

[7] M. Bruzzi, C. De Angelis, M. Scaringella, C. Talamonti, D. Viscomi, M. Bucciolini, Zero-bias operation of polycrystalline chemically vapour deposited diamond films for Intensity Modulated Radiation Therapy, Diamond and Related Materials, Volume 20, Issue 2, February 2011, Pages 84-92

[8] H. Gamo, M. N. Gamo, K. Nakagawa, and T. Ando, "Surface potential change by oxidation of the chemical vapor deposited diamond (001) surface," *J. Phys.: Conf. Series*, vol. 61, pp. 327–331, 2007

[9] H. Kawarada, Hydrogen-terminated diamond surfaces and interfaces, Surface Science Reports 26 (1996) 205-259.

[10] A. Galbiati, S. Lynn, K. Oliver, F. Schirru, T. Nowak, B. Marczewska, J. A. Dueñas, R. Berjillos, I. Martel, and L. Lavergne, IEEE TRANSACTIONS ON NUCLEAR SCIENCE, 56, 4, 1863, (2009).

[11] S. M. Sze, d. J. Coleman, jr. And a. Loya CURRENT TRANSPORT IN METAL-SEMICONDUCTOR-METAL (MSM) STRUCTURES, 1971 Solid-State Electronics Vol. 14, pp. 1209-1218.

[12] S. M. Hearne, E. Trajkov, D. N. Jamieson, J. E. Butler, S. Prawer, J. Appl. Phys. 99 113703 (2006).

[13] Bernhard Gross and Martin M. Perlman, ShortCircuit Currents in Charged Dielectrics and Motion of ZeroField Planes, J. Appl. Phys. 43, 853 (1972).

[14] Fowler J F 1966 Solid state electrical conductivity dosimeters Radiation Dosimetry ed F H Attix and W C Roesch (New York: Academic).

[15] Almaviva S, Ciancaglioni I, Consorti R, De Notaristefani F, Manfredotti C, Marinelli M, Milani E, Petrucci A, Prestopino G, Verona C, Verona-Rinati G, Synthetic single crystal diamond dosimeters for conformal radiation therapy application , DIAM RELAT MATER, 2010, 19-2-3.

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