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Diamond Detectors for Radiotherapy X-Ray Small Beam Dosimetry

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Many new X-Ray treatment machines using small and/or non-standard radiation fields, e.g., Tomotherapy, Cyber-knife, and linear accelerators equipped with high-resolution multi-leaf collimators and on-board imaging system, have been introduced in the radiotherapy clinical routine within the last few years. The introduction of these new treatment modalities has led to the development of high conformal radiotherapy treatment techniques like Intensity Modulated photon Radiation Therapy, Volumetric Modulated Arc Therapy, and stereotactic radiotherapy. When using these treatment techniques, patients are exposed to non-uniform radiation fields, high dose gradients, time and space variation of dose rates, and beam energy spectrum. This makes reaching the required degree of accuracy in clinical dosimetry even more demanding. Continuing to use standard field procedures and detectors in fields smaller than 3×3 cm^2, will generate a reduced accuracy of clinical dosimetry, running the risk to overshadowing the progress made so far in radiotherapy applications. These dosimetric issues represent a new challenge for medical physicists. To choose the most appropriate detector for small field dosimetry, different features must be considered. Short- and long-term stability, linear response to the absorbed dose and dose rate, no energy and angular dependence, are all needed but not sufficient. The two most sought-after attributes for small field dosimetry are water equivalence and small highly sensitive (high sensitivity) volumes. Both these requirements aim at minimizing perturbations of charged particle fluence approaching the Charged Particle Equilibrium condition as much as possible, while maintaining high spatial resolution by reducing the averaging effect for non-uniform radiation fields. A compromise between different features is necessary because no dosimeter currently fulfills all requirements, but diamond properties seem promising and could lead to a marked improvement. Diamonds have long been used as materials for dosimeters, but natural diamonds were only first used for medical applications in the 80 s. The availability of reproducible synthetic diamonds at a lower cost compared to natural ones made the diffusion of diamonds in dosimetry possible. This paper aims to review the use of synthetic poly and single-crystal diamond dosimeters in radiotherapy, focusing on their performance under MegaVoltage photon beams. Both commercial and prototype diamond dosimeters behaviour are described and analyzed. Moreover, this paper will report the main related results in literature, considering diamond development issues like growth modalities, electrical contacts, packaging, readout electronics, and how do they affect all the

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dosimetric parameters of interest such as signal linearity, energy dependence, dose-rate dependence, reproducibility, rise and decay times.

Keywords: diamond, radiotherapy dosimetry, small field, cvd, polycrystalline, single-cristal, bidimensional dosimeter

1 INTRODUCTION

The most commonly adopted solution (about 50% of cases) for cancer treatment as a unique cure, or in combination with chemotherapy and/or surgery, is radiotherapy [1]. Radiotherapy aims to deliver the prescribed radiation dose to the tumor and targets tissues while minimizing the dose and toxicity to nearby healthy tissues. Many non-standard delivery machines, like CyberKnife, Tomotherapy, and other modern linear accelerators, have been recently developed and implemented for routine clinical use to achieve this goal. Intensity-modulated radiotherapy (IMRT) and its natural evolution Volumetric Modulated Arc Therapy (VMAT) and stereotactic radiotherapy (SRT), have enabled a rapid advance of the precision radiotherapy concept. Such techniques facilitate greater conformity, reduce planning margins and increase the delivered dose to the target volume. However, highly-conformal, high-dose radiotherapy is challenging due to the possible introduction of uncertainties in each step of the treatment process. All these considerations pose new challenges, including from the dosimetric point of view. Dosimetry was a well-established field up until a few years ago; however, the latest technologies have imposed dealing with small non-uniform fields with high dose gradients, time and space dose rate and beam energy spectrum variations. Therefore, to calculate the dose delivered to the patient, new procedures and detectors to measure percentage depth doses, output factors, and beam profiles are necessary. Accurate calculations of a dose using treatment planning systems (TPS) depends on the quality of the measured data used to configure the beam model. Usually, a field size less than 3×3 cm is considered small; however, according to [2] three equilibrium factors determine if a radiation field can or cannot be considered small. The first is the size of the beam source that is viewable from the detector location. If the detector views only a part of the source area, due to the reduced field size, the output is lower compared to field sizes where the entire source is viewable from the detector. Moreover, using the full width at half maximum to measure the field size when partial occlusion of the radiation source occurs, the field size is overestimated with respect to the actual field size. The second factor is the electron range in the irradiated medium. It relates to lateral charged particle disequilibrium in the photon beam, i.e., the beam radius becomes small compared to the maximum range of secondary electrons influencing the transverse beam profile and the dose on the central axis. The last equilibrium factor is related to the size of the detector used during measurements. Due to its finite size, the signal is averaged over its volume, and for a small beam size, the effect is an underestimation of the dose near the field center and an overestimation of the dose around the penumbra region. Moreover, the detector's electron density is different from the water ones, thus perturbing the secondary electron field (density effect) [3]. Quantification and correction of the combination of volume averaging and density effects (volume effect), can be addressed using MonteCarlo simulation to calculate correction factors to relate the detector's signal to the dose in water [4, 5]. Therefore, volume averaging with source occlusion and lack of lateral electron equilibrium can cause a reduction of linac output and of measured output. Moreover, source occlusion may also result in a modified energy spectrum, compared to a beam with no source occlusion [6] Field size definition and Bragg-Gray cavity theory, valid for larger fields, do not hold for small fields. Negligible geometric and dosimetric aspects of dose delivery at large fields need special attention for small fields. Acceptable approximations used in planning systems can introduce significant errors in the prediction of delivered doses to the patients. To manage these dosimetric issues, which represent new challenges for medical physicists, a new code of practice and formalism has been published [7, 8]. Moreover, devices used with larger fields could not be assumed to perform optimally with small ones because different detectors have different dosimetric advantages [9]. Small beam fields characteristics like high dose gradients and energy spectrum space and time variations mean that the ionization chambers (the gold standard detector in radiotherapy dosimetry) are no longer suitable for dosimetric measurements. An ideal dosimeter fulfilling all requirements does not currently exist. Commonly used dosimeters in small fields are small volume ionization chambers [10], radiochromic films [11], silicon diodes [12], and diamond detectors [13, 14] reports operation principles of solid-state dosimeters and their applications in modern radiation therapy with X-Ray beams while [15] describes the advantages and potential drawbacks of each kind of dosimeter available for small field dosimetry. Point-like detectors are usually used for small field relative dosimeters, while taking into account variations in space and time of the beam spectrum 1D-2D detectors are desirable [14]. Radiochromic films could be a valid choice for small field dosimetry because they are almost tissue equivalent and have little energy dependence, high spatial resolution, dose rate independence, and no angular dependence. Unfortunately, there are several drawbacks; they are expensive and intrinsically off-line dosimeters, and before developing, after film exposure, it is necessary to wait up to 24 h. Furthermore, the developing procedure is cumbersome and time-consuming. [16] describes the physics and operation modes of silicon detectors. Due to their real-time readout, high spatial resolution, and small size, silicon dosimeters have been widely used in small-field dosimetry. However, the silicon sensitivity is not energy independent due to its atomic number ($Z = 14$) higher respect to the human tissue's one ($Z \sim 6/7$). This therefore leads to an overestimation of the silicon response for low energy photons

and an underestimation for small fields, caused by the reduced low energy photon contribution to the small field dose [17]. Radiation damage affects the sensitivity to radiation and the dose per pulse dependence of silicon diodes. Moreover, the sensitivity degradation with an accumulated dose can be controlled [18] and to some extent the dose per pulse dependence too [18–20]. Readers can learn more about the accumulated dose and dose rate topics in [14]. Moreover, silicon detector signal suffers from directional dependence which is important in measuring beam profiles and PDDs [21]. In small field applications, in the absence of equilibrium, unshielded diodes are used since the effect of spectral changes is less important than the volume averaging [22]. Furthermore, new generation silicon dosimeters present improved stability, dose linearity and radiation hardness [14]. Thanks to its material properties, diamonds get quite close to satisfying almost all ideal dosimeter requirements. In the late 40 s of the 20th century, diamonds began to be used as a dosimeter, but it was only in the 80 s when natural diamonds were first used for medical applications. Its high spatial resolution, water equivalence, high-dose response, and directional independence makes it suitable for small field dosimetry. It is also energy independent due to the almost constant stopping power and mass-energy absorption ratio [21, 23–25]. Natural diamond crystals with the desired electric properties are rare and expensive. The fabrication of synthetic diamonds made reproducible and low-cost substrates available and allowed for the greater diffusion of diamond in dosimetry. The first studies describing the proprieties of chemical vapor deposition (CVD) and the high-pressure high temperature (HPHT) diamond detectors and their performances as dosimeters are reported in the literature [26, 27]. Finally, [14, 15] report further developments in diamond detectors and their applications related to small field dosimetry. Compared to the abovementioned papers, this manuscript draws attention to radiotherapy applications of single and poly-crystalline CVD diamond dosimeters, focusing on their performance under photon MegaVoltage beams. Special emphasis is placed on growth modalities, electrical contacts, packaging, and signal readout and their influence on detector behaviour. These aspects are not considered in the abovementioned reviews. The paper also considers all the parameters of interest for relative dosimetry such as reproducibility, signal linearity, energy dependence, dose-rate dependence, rise, and decay times. Both commercial and prototype synthetic diamonds are described and compared, reporting in detail on the published results. An overview of recent advanced research and development projects is also provided.

2 MATERIALS

In the last few years, the fabrication of diamond substrates, followed by transformation into externally biased or self-biased devices generating a signal when exposed to therapeutic beams, have undergone some significant modifications. First, unlike in the past, the task of growing the substrate is almost always left to firms. This trend is a consequence of the required level of specialization and standardization, too high to be handled efficiently by any research group focused on dosimetry. Besides the historical firm [28] it should be underlined that the number of vendors, such as [29–31] has increased in the past decade. The next important development is the growing diffusion of a commercial dosimeter, the PTW60019 microDiamond, which has become a reference dosimeter after many comparative studies with other types of dosimeters [32–36].

2.1 Diamond Fabrication

The standard production procedures for artificial diamond substrates are High-Pressure High-Temperature (HPHT), homo-epitaxial, and hetero-epitaxial Chemical Vapor Deposition (CVD). In the HPHT process temperatures over 1300°C and pressures of several GPa are reached inside the reaction chamber to access the region of phase space where, from a diamond seed, using a source of carbon atoms the diamond crystal could grow [37]. In dosimetry, the crystal impurity content, which strongly depends on the fabrication process' optimization, is a relevant parameter for substrate performances [38].

Using the micro-wave plasma-enhanced Chemical Vapour Deposition (CVD) technique it is possible to grow CVD synthetic diamonds starting at a much lower temperature (~700°C) [39]. By means of very precise control of growth parameters, substrate qualities and the derived detection properties, are reproducible to a high degree. There are essentially two main types of homo -epitaxial CVD diamonds: the single crystal (scCVD), where for the CVD growth, an HPHT diamond is used as a seed, and the polycrystal (pcCVD) where the seeds are diamond nano-crystals or scratches produces by diamond powder [40]. The resulting pcCVD diamond bulk contains grain-boundaries corresponding to the junction of crystal growth from different seeds. These structural defects act as free charge carrier trapping centers. Because of the limited area of the HPHT seeds, the corresponding area of scCVD is below 1 cm^2, while with the pcCVD seed matrix, even tens of cm^2 could be obtained. Like Diamond-On-Iridium (DOI) where the iridium seeds form the initial matrix, the hetero-epitaxial CVD process uses a non -diamond initial matrix. DOI substrates have sizes, charge collection distance (CCD) and defect concentration in between pcCVD and scCVD standard substrates [41]; Finally, to fabricate wider and thicker substrates, while maintaining an excellent quality, an optimization of the CVD process which applies new concepts in the growth phase is in progress. A new configuration of microwave modes allows obtaining a wider area of the plasma over the substrate with 5% film thickness uncertainty [42]. Introducing oxygen in the gas mixture and controlling the distance between the discharge region core and the substrate top surface, thicker substrates (up to 6 mm) have been produced [43].

2.2 Characterization Techniques

Intrinsically, every artificial diamond substrate has a certain level of defects, both shallow and deep. The shallow levels are unstable at room temperature and will be filled up during irradiation until

an equilibrium state between trapping and detrapping is reached. The detrapping must be as slow as possible to permit a measurement session without relevant photosensitivity modification. On the contrary, deep levels, which are stable at room temperature, are filled at the beginning of the irradiation and remain filled for a longer time [44]. Irradiation before starting a measurement session (priming) is therefore mandatory, and the needed dose and dose-rate depend on the substrate type and quality. According to this, it is relevant to characterize the substrate with a variety of techniques customarily used.

- Raman spectroscopy is used before metal electrode fabrication to analyze the crystal structure and the presence of defects and/or contaminants other than diamonds (graphite, sp2 and disordered sp3 carbon compounds) [45]. It is possible, for example, to understand if the crystal structure is pure (peak at 1,332.8 cm^{-1}) or if there are other contributions due to vacancies that could act as a trapping center for charges (other peaks). For the pcCVD substrate, the level of defects could also depend on the large concentration of grain boundaries [46–49]. This analysis is sometimes complemented by optical spectrophotometry or FTIR methods to detect substitutional defects in the diamond lattice.
- Charge Collection Distance (CCD) is related to the free mean path of a charge carrier inside the diamond. In other words, it is a measurement of the charge collection efficiency of a device. CCD For Optical Grade CVD diamond substrates is (30 μm) and for detector grade substrates one order of magnitude higher. The CCD value can be extracted depositing a known amount of energy inside the diamond and measuring the generated signal. Standard sources of radiation for this measurement are α emitting radio-nuclide, either single-peak (^{241}Am or similar) or multi-peak like triple radioisotopes [50, 51].
- Deep and shallow defect levels could be evaluated using the thermally stimulated luminescence (TL) and, less frequently, the photoluminescence techniques. A sensor irradiated with a known dose increases its temperature gradually at a constant rate. The shallow defects will detrap at the beginning of the thermal stimulation while the deeper ones detrap progressively while increasing the temperature [52, 53].
- Another type of information that could be obtained concerning the class of electronically-active defects are their density and energy position. The methods used are a thermally-stimulated current (TSC) [54] and the transport of photogenerated carriers [55].

2.3 Diamond Dimensions and Electrodes Geometry

Detector dimensions and the presence of extra components like electrodes and packaging in diamond dosimeters are crucial because they may alter the tissue equivalence and affect measurements with the volume effect. On these factors depends on the quality of dose measurements. Diamond detector dimensions are crucial, especially in small beam dosimetry, where the detector should have a small detection volume compared to the irradiation beam size, because of the lack of lateral electronic equilibrium. A dose measurement with high spatial resolution is possible using a small diamond sensitive volume. Dosimeters made with scCVD diamond films show excellent dosimetric properties, but the wafer maximum achievable size (1 cm diameter) makes the construction of large-scale dosimeters with this kind of material impossible. On the other hand, due to its potential low cost, pcCVD diamond films with a maximum achievable size of 25 × 25 mm^2 surface can be produced and, using different electrode geometries, large sensitive area high spatial resolution devices are obtainable. Diamond dosimeters design is generally a parallelepiped solid-state ionization chamber in two main configurations: with interdigitated electrodes on the same side (3D configuration) [56–59] or electrodes both on front and back sides (called planar or "sandwich" configuration) [60–64].

The most standard configuration for diamond detectors is the "sandwich" geometry. This configuration can be operated in photoconduction (ohmic behaviour) and photovoltaic (Schottky barrier configuration) modes. In the first operation mode, two electrodes are deposited on the diamond film surfaces and a constant external bias is applied: the incident radiation generates a current in the biased structure which is a measure of the absorbed dose. These diamond devices are generally operated using an electric field of 1 V/μm (operation ranges 10–1000 V) for drift velocity saturation. In the presence of an external voltage, charged carriers drift and are trapped by defects within the bulk, generating unwanted polarization effects which influences both the dynamic response stability and the device rise and fall times. It can practically act as an ideal dosimeter only with sufficiently high bias voltages but needs to be improved for better charge collection efficiency, temporal response, and uniformity for applications when a very fast response to following the beam variations is necessary. In the second configuration, due to the settlement of the Schottky barriers at the metal and diamond interface, an active volume is present also without an external polarization voltage. The built-in electric field at electrodes can then be used to collect the incident radiation generated charge in such active regions. Electrons and holes generated by an ionization event, start to drift due to the presence of the built-in electric field (of around 1 V/nm [65]), inducing a current signal in the readout electronics. In the absence of external bias, and thus of an electric field driving the generated charges through the diamond volume, trapping mechanisms in the diamond bulk are negligible. Consequently, the response dynamics becomes mostly unaffected by impurities and less dependent on the overall substrate crystalline quality [65–67]. However, for these kind of geometries, in the absence of a perfect ohmic contact between the metal and diamond, it is also possible to have a partial drift and thus residual signal formation, with a reduced CCE [66].

For planar diamond detectors, electrodes covering the whole surface are recommended because, with a partial electrode covering, the sensitive volume is not well defined. The electric field outside the volume under the electrode is therefore not

uniform and is too weak to fully collect the generated charge. The full coverage electrodes also improve the dose rate linearity and the charge collection efficiency [68]. However, electrical contacts that are too large (too close to the plate lateral faces) may induce unexpected leakage conduction at high fields through a large density of defects situated on the lateral sides of the diamond substrate. A 3D electrode geometry may overcome possible volume averaging effects (detector size) fabricating high-resolution detectors for small field dosimetry. The electrode geometry is crucial in defining the sensitive volume of the detector (material between the electrodes). For this new type of detector, by means of a pulsed laser technique [48], the electrodes are fabricated directly inside the diamond, bulk creating a 3D column structure with rectangular cells that are of a small size ~80 × 120 μm^2 [48, 69, 70]. Groups of connected cells can then form pixels or strips of potentially very small sizes. The sensitive area scales down with the decreasing electrode spacing while the depth of the sensitive volume remains unchanged. Using interdigitated electrodes, detectors with very small sensitive areas but with quite high sensitive volumes are fabricated, allowing highly segmented devices with a high signal to noise ratio [56–59].

2.4 Diamond Contacts

The performance of diamond detectors strongly depends on the metal diamond interfaces. Different contact fabrication techniques lead to Ohmic or Schottky electrical contacts. Notwithstanding several studies done in the past years about the metallic electrode manufacturing on diamond substrates, both ohmic or Schottky type, [71–75] diamond contacting is still a challenging task. The difference between the work functions of diamond and metal being in contact, provoke the electrons to flow from the lower to the higher work function. As a consequence, one material becomes slightly positively charged and the other slightly negatively charged creating an effective barrier. After the passage of ionizing radiations, charge accumulation occurs within the crystal and immobile carriers establishing an electric field which acts in a direction opposite to the applied field produced by the external polarization voltage.

Different approaches have been proposed to solve the polarization problems, providing at the same time a method to obtain a durable and stable ohmic contact on the diamond. First, the diamond surface must be prepared before metallization. Ohmic contacts may be obtained on an H-terminated diamond surface, but the drawbacks of a hydrogenated surface are mostly represented by the lack of a strong adhesion of the metal film electrodes on the hydrogen termination and by its thermal instability [72, 76]. It is therefore highly desirable to develop a deposition process of ohmic contact starting from an oxygenated diamond surface–well known to be very stable [51, 67]. The metallic diamond contact could present non-ohmic electrical behaviour or an ohmic one with high specific contact resistance. However, in many cases, it is possible to improve the electrical conduction at the diamond/metal interface by inducing a graphitic layer underneath the diamond substrate surface [77]. Preferred materials for diamond dosimeters electrodes are Al [68, 78, 79], Cr/Au [65, 67, 80], Ag [81]. Amorphous carbon blended with nickel (C/Ni) electrodes for polycrystalline and monocrystalline diamonds are also used to produce near-tissue equivalent detectors [51, 82]. Moreover, to have better adhesion and a detector closer to tissue-equivalence, diamond-like carbon (DLC) contacts have been produced and tested [61, 83]. DLC is a form of amorphous carbon in between a diamond and graphite, containing a significant portion of sp^3 bonded atoms in the matrix. The novel contact consists of a very thin (1–3 nm) diamond-like carbon film obtained on a diamond substrate. The extremely thin DLC layer works by charge carrier tunneling, thus avoiding space-charge effects for a wide polarization voltage range. Moreover, it becomes a seed for the sputter deposition of high work function noble metals (Pt, Au) allowing metals to stick on the diamond surface [84]. demonstrated that diamond-like-carbon multi-layer contacts permit the fabrication of devices with a remarkable sensitivity to very low dose rates using the bias voltage as a key operative parameter for different dose rate ranges. Concerning the importance of contact shape, both circular [68, 79, 81] and square contacts [85] are widely used without evidence of advantages of one over the other.

2.5 Detector Readout

Diamond detector response is read out through different standard and dedicated systems divided into two large groups: single channel and multichannel readout electronics. Usually, for the single output detectors, electrical connections to external electronics are carried out through the use of standard triaxial connectors and the measurements of the current are performed with Keithley electrometers(s), which also serve as the power supply to apply the appropriate polarization between the electric contacts [61, 63, 86, 87]. The signal of the commercial diamond dosimeter SCCD-PTW can be read out with any electrometers available in a Radiotherapy unit. To obtain a radiotherapy beam mapping, with high resolution for beams that are generally characterized by strong spatial gradients, the use of diamond dosimeters with high spatial resolution is necessary. To read out more than one channel at a time is therefore necessary in a multichannel system. The natural evolution toward a matrix of sensitive elements read out synchronously is a possible solution. However, the corresponding increase in the number of readout channels is not straightforward. The measurement setup commonly used for the single output, due to the size of the connections and the size and cost of the measurement devices, is hardly usable with more than a single device at a time. Using an integrated multi-channel readout chip, placed the closest possible to the detector, it is possible to solve the problem by reducing the overall sensor size. Several authors studied high-resolution small volume detector developments to design new devices for accurate dosimetry in high energy narrow photon beams. Multichannel detectors consist of pixel matrixes or strips [78, 88]. The energy released in every single active area, generates charges, collected with a specific efficiency by independent readout channels connected to a single pixel or a strip, and is then converted into counts. In more advanced applications, with technologies such as advanced Application-Specific Integrated Circuits (ASICs), analogue to digital converters (ADC) and registers

are also included [89]. Every channel designed and fabricated in a 0.18 μm CMOS process, includes a charge integrator and an A/D converter. This readout architecture permits storing the digitized signal and avoids dead times. Real-time operations are also efficiently accomplished through field-programmable gate arrays (FPGAs). The use of FPGAs guarantees high flexibility, fast, and deterministic data processing like in [90] where an onboard Xilinx FPGA handles the chips readout. Furthermore, very fast readout circuits with an analogue front end for pulse-by-pulse beam intensity measurements have also been developed. The dose deposited by the single pulse is important for dynamic treatments, and its measurement is also possible due to the very fast diamond detectors response [83].

2.6 Detector Housing

To obtain an exact estimation of the absorbed dose studying the detector's current profile is crucial to knowing the detector's active volume and the detector's housing contribution. Because the charge induced by radiation outside the sensitive volume will be collected in addition to the charge released in the detector's sensitive volume, to correctly model the detector's response a detailed geometrical knowledge of the solid-state detector housing used is necessary [91–93]. The exact knowledge of the detector support structure is crucial in particular to correctly calculate small field output correction factors with Monte Carlo simulation [94–96]. The detector housing also affects its directional dependence; it therefore seems to be very important to verify the response of the detector in the given set-up. This is true for silicon diodes [97], and for diamond detectors [98, 99]. A suitable diamond dosimeter must be incorporated into a suitable probe's housing which should not introduce energy dependence. Detectors with metallic shielding overestimate of values [62], therefore, choosing the right material for diamond housing is of crucial importance. The most commonly used housings for diamond dosimeters are cylindrical or tubular [61, 63, 64], but rectangular shape holders are also used [86]. The holders are made of different water equivalent materials like, but not limited to, Perspex, PMMA, and Solid Water GAMMEX 457 etc. [61, 63, 81]. To minimize the presence and effects of ambient light on diamond sensors, some authors use a thin opaque layer [86, 100]. This choice obviates the need to pre-irradiate the detector before dose measurements. The similarity in the atomic composition of all three media (diamond holder, diamond bulk, electrodes) should be beneficial for the design of an energy-independent dosimeter.

3 RADIOTHERAPY APPLICATIONS

In the 1990s significant research activity in the field of diamond dosimetry was devoted to the development of synthetic diamond detectors to overcome problems related to dosimeters using natural diamond stones [101]. Natural diamond detectors for radiotherapy applications were commercially available, but not widely used due to high cost, inadequate stones availability, and difficulties with result reproducibility. However, thanks to new diamond synthesis developments, both CVD and HPHT diamond are actively considered for radiotherapy dosimetry [47, 61, 102–105]. HPHT crystals resulted in not being suitable for applications on small field dosimetry because they exhibit electronic defects that alter the detector response. Furthermore, early papers on CVD diamond dosimeters underlined some problems related to a non-optimized quality of the crystals, electric contacts, and encapsulation [106, 107]. These drawbacks, not only related to structural properties of the material, did not allow their use in radiotherapy and, in particular, but their application in small field dosimetry was also not considered viable. Afterwards, some studies demonstrated that it was possible to grow single crystal diamonds with a chemical vapor deposition (CVD) process that better satisfy the dosimetric requirements than polycrystalline ones [64, 108].

A description of some of the most cited dosimeters, built according to different designs, focusing on the intensity-modulated applications and small field dosimetry is given in the following paragraphs. **Table 1** reports the main proprieties of those dosimeters, while **Table 2** lists the advantages and potential drawbacks for small field application.

A CVD synthetic diamond, developed at CEA-LIST, was obtained from an oriented HPHT substrate, which was removed by laser cutting after growth [64]. The device, with an active volume of 0.534 mm^3, was first studied to test its potential use as a radiotherapy dosimeter, obtaining a sensitivity of 215 $nC\,Gy^{-1}\,mm^{-3}$ at a bias voltage of −50 V. The detector signal showed good linearity with dose, and the stability and repeatability of the signal result was well below 0.5%, the threshold limit that is in agreement with the IAEA dosimetric requirements [114]. Investigating the current dependence from the dose rate, the Fowler model's Δ parameter [115] was obtained and found to be 1.04 ± 0.04 in the range 1–8 Gy/min. Clinical tests under IMRT beams were performed using the treatment plan of a naso-pharyngeal carcinoma. Point measurements were obtained with the CEA-SCDD dosimeter and an ionization chamber (IC) and compared with the point dose calculated by TPS. The observed difference between TPS calculations and CEA-SCDD measured data were found to be below 2.5%. This study demonstrated that the detector was a good candidate for dose measurements of high conformal techniques, but better results could be obtained with smaller devices.

In 2013 Marsolat et al. [62, 110], a detector (SCDDo) based on a commercially available single crystal CVD diamond with a detection volume of 0.165 mm^3, suitable for small field dosimetry, with fast response and high signal-to-noise ratio was developed. The detector was characterized using clinical photon beams and results compared to those of a diode and a small ionization chamber, both commercially available. The calculated Δ value of 0.975 ± 0.003 was in agreement with those obtained, in the same operational conditions, with the natural diamond of PTW dosimeter [116] and the CEA-SCDD dosimeter [64]. Cross-line dose profiles were measured with SCDDo up to the smallest field size 0.6 × 0.6cm^2, and the 20–80% penumbras from dose profiles resulted in 1.6 mm for SCDDo and 1.8 mm for the silicon diode. SCDDo was considered a suitable detector for small field dosimetry due to its spatial resolution. Output Factors

TABLE 1 | Properties of diamond dosimeters.

Name	Type cristal	Single/poly	Active volume	Bias (V)	Ref
CEA-SCDD	CVD	single	3.14 mm^2 × 170 μm	–50	[109]
SCDDo	CVD	single	1.mm^2 × 165 μm	50	[62]
PTW-SCDD	CVD	single	3.79 mm^2 × 1.μm	0	[108]
DIAPIX	CVD 2D	Poly	4 mm^2 × 300 μm	0	[65]
3DOSE	CVD	Poly	70 × 114 μm × $^{-2}$500 μm	10	[58]

TABLE 2 | Advantages and potential drawbacks of diamond dosimeters used in small field dosimetry.

Name	Advantages	Drawbacks	Ref
CEA-SCDD	Good spatial resolution	Dose rate dependance	[64]
SCDDo	Good spatial resolution	OF small field	[110]
PTW-SCDD	Commercial dosimeter	use for field size >1 cm	[111]
DIAPIX	Large area detector	pixel size	[112]
3DOSE	High spatial resolution	Encapsulation processes	[113]

(OF) measured with SCDDo were compared to those obtained with a small IC for a field size ranging from 0.6 × 0.6 to 10 × 10 cm^2. The results obtained with SCDDo were higher than those obtained with the IC, with a maximum difference of 7% for the smallest field size. These results were promising and encouraged the use of SCDDo for small field dosimetry even if additional work was needed to conclude that the device could provide the exact OF values in small beams.

A single-crystal diamond prototype, working as a Schottky diode with no bias applied, provided more than promising results. The prototype was developed at the University of Tor Vergata (Rome, Italy), and is presently also commercially available (PTW 60019 MicroDiamond). The prototype had a small sensitive volume (0.004 mm^3), and it was tested for relative dosimetry with different beam qualities RX (from 1.2–10 MeV) and electrons (from 6 to 18 MeV) [108]. Ciancaglioni et al. (2012) [117] observed linearity of the response as a function of the absorbed dose of about 1.2 cGy with a deviation from linearity less than 0.5% in the range (0.04–50) Gy. The dose rate dependence was studied in the range 1–6 Gy/min obtaining Δ = 0.9997. They measured the sensitivity in 6, 10 MV photon beams and 6, 9, 12, 15, and 18 MeV electron beams, and it was constant for each radiation quality. The disagreement of PDDs, output factors, and beam profiles with those measured with a reference IC was below 1%. Moreover, tests using PTW-SCDD as a dosimeter for IMRT [118] and Volumetric Arc Therapy [111] were performed. In the first paper, using a water phantom, the dose delivered during a prostate cancer IMRT treatment in different positions was measured and compared with the doses measured by two ionization chambers. The agreement found between PTW-SCDD and IC measurements was within 2%. In the second paper, PTW-SCDD was used to measure dose profiles for a VMAT treatment of pulmonary disease. These dose profiles are in good agreement with those measured by an IC and those calculated by TPS. Moreover, PTW-SCDD dose profiles demonstrated a better accuracy in the regions of high gradient dose. Several studies found in the literature [13, 119–121] use PTW-SCDD with standard linear accelerators, MRI-linac, CyberKnife and GammaKnife with different beam energies and collimation systems, which demonstrate the good performance of the PTW-SCDD down to small field sizes. In particular, most of them report the measurement of relative output ratios for very small fields. It is very difficult to compare all these data since they were collected with different experimental setups. However, it is a general opinion that no output correction factors have to be applied to the PTW-SCDD measurements for field sizes larger than 1 cm. On the contrary, the literature reports inconsistencies among the results reported for field sizes smaller than 1 cm. This is mainly due to the different experimental setups and different collimating systems used to conform the X-Ray beam, both in the measuring section and Monte-Carlo simulation. Moreover, small discrepancies are more evident in a field size below 1 cm since the compensation between volume averaging and density effects are lost. In [122–124] authors reported a dose over-estimation of PTW-SCDD response, while in [125–131] dose under-estimation is reported. In the IAEA-AAPM International Code of Practice [7], OF data of different dosimeters published from 2000 to 2015 have been collected and fitted to provide output correction factors also for the PTW-SCDD. Moreover, Casar et al. [132] published new data about PTW-SCDD, which are a supplement to [7]. At present this is the only commercial diamond dosimeter used in Radiotherapy Units for small field relative dosimetry.

Single crystal devices demonstrated good performance, whereas polycrystalline films can be grown to larger sizes but with a lower quality mainly due to the presence of structural defects and recombination traps. In the beginning, Polycrystalline CVD detectors, due to their slow response dynamics, could not follow the sharp transients of intensity-modulated fields [133]. Nonetheless, important improvements have also been made using polycrystalline substrates. A dosimetric characterization with 6 MV clinical X rays of CVD dosimeters fabricated from a range of commercially available synthetic diamonds was reported by S. P. Lansley et al. [106]. Devices obtained with substrates from Diamond Materials and Element Six demonstrated high sensitivity, low priming doses, low dark currents and linear relation between current response and dose rate.

Shortly after, a fundamental step forward in the use of these devices was made when a polycrystalline CVD dosimeter was operated with a very low bias voltage [65]. Authors demonstrated that dosimeters made of a polycrystalline diamond operated at null or very low bias voltage, performing well both for relative

dosimetry measurements and for pretreatment verification [67, 111]. At present, to our knowledge, the DIAPIX dosimeter manufactured within the DIAPIX Italian project described in [18, 90] is the only large area pixelated diamond dosimeter successfully operated for relative dosimetry and plan verification. the matrix consists of 12 × 12 pixels, 2 mm pitch, covering a total area of (2.5 × 2.5 cm^2). Pixels and pitch's dimensions are a trade-off between spatial resolution and read-out channels, so improving electronics means an increase spatial resolution. Pointlike detector's spatial resolution is determined by the scanning system and the size of the dosimeter. Instead in 1D-2D dosimeters, the resolution is determined by the pitch between the sensitive volumes in the array and the sensitive volumes' size. The basic idea to use a 2D-1D instead of pointlike dosimeter comes from the fact that beam fluencies vary in time in the new treatment techniques, and it is not possible to measure them with a pointlike dosimeter. Therefore, 2D dosimeters are appealing, also due to their flexibility. Different configurations could be explored to develop prototypes for pretreatment verification, transmission detectors upstream of the patient, or between the patient and the couch considering all the additional complexities in terms of dose rate, energy, and angular dependence during the transition from single point like detectors to 2D arrays of single point-like detectors [97]. In [90] the authors reported the dosimetric characterization of the DIAPIX detector composed of two pcCVD matrices, each with area 2.5 × 2.5 cm^2 and a thickness of 300 μm. The measured rise and fall times are of the order of 0.5 s and 0.1 s, respectively, for all the pixels of both matrices in a dose rate range of 50–500 cGy/min. The dose rate dependence was investigated obtaining the Δ value, with an average value over all the pixels of DIAPIX is 0.9832 ± 0.0015. The reported sensitivity averaged over all the DIAPIX pixels is 24.02 ± 0.27 nC Gy^{-1}. Moreover, the authors studied the dose distribution of a lung VMAT clinical plan. A quantitative evaluation of the comparison between measured and calculated 2D dose was performed with the gamma analysis. Using a γ-index 3%/3 mm, and a threshold of 10%, the γ passing rate was found to be about 95% excluding the bad pixels and those corresponding to the matrix edge [112]. Results are promising, and the performance of the device could be improved working on the pixel contact quality, which will ensure a higher uniformity of the device response.

Recently, as described in paragraph 2.3, to tackle very small field dosimetry problems, the 3Dose INFN group proposed a bidimensional polycrystalline diamond prototype with columnar electrodes, also known as 3D detector [58]. Thin columnar electrodes, developed inside the bulk of the crystal, were fabricated perpendicular to the detector surface using laser pulses creating small cells (70 × 114 μm^{-2} × 500 μm). Small sensitive volume pixels (n × 4 10 mm^{-3}) were created connecting more cells in parallel. The basic idea is to develop a highly segmented large polycrystalline diamond dosimeter to obtain complete field profiles in a single measurement, hence reducing the uncertainty of the delivered dose. A first prototype was tested using a clinical 6 MV beam, showing a linear dose response with a maximal deviation from linearity of 2% and a high sensitivity of about 80 nC Gy^{-1}. The diamond detector response did not depend on photon beam energy within a range of 6–10 MV. Authors [58, 59], reported the preliminary results of the 3Dose characterization. 3Dose demonstrated good time stability and repeatability with less than 0.6% signal variation. An array of nine pixels was built, and the response of each pixel studied under a standard 6 MV 10 × 10 cm^2 photon beam. Each pixel of the array biased at 10 V presented a different sensitivity to the radiation beam ranging from 25 to 95 nC Gy^{-1}. The signal was linear and stable, allowing for the extraction of the different calibration factors to be applied for the overall detector response. The detector signal rise and fall time were 0.5 and 0.3 s, respectively. The response of 3Dose is therefore sufficiently fast to follow in real-time the radiation beam intensity changes. The dose rate dependence was also studied measuring a Δ value of 0.999 for each pixel [56]. Moreover, new tests were performed to test 3Dose dealing with small fields. The 3Dose detector confirmed its performance in terms of time stability and repeatability and demonstrated a deviation from linearity of 2% at low dose rates. A comparison of uncorrected output factor values with the single crystal PTW60019 and the plastic scintillator detector EXRADIN W1 shows a good agreement between measurements, even if some additional effort must be put in the encapsulation processes [113].

4 CONCLUSION

Diamond dosimeters are ideal candidates for small field dosimetry, but besides the high-quality material, substrate type, dimensions and geometry, they must exhibit several additional characteristics. When choosing the electrode material, readout system used, and dosimeter housing, some caution is mandatory. Over the years, researchers have developed increasingly better devices. At present, single-crystal diamond dosimeters are commercially available and are routinely used in hospitals with costs comparable to those of other detectors. However, dose measurements in field sizes below 1 cm must be corrected following the international code of practice since measurements are still not accurate enough. Moreover, profile measurements in the penumbra regions performed with single diamond detectors suffer from volume averaging effects while small commercial silicon dosimeters perform better. To overcome these drawbacks diamond detectors of increasingly smaller dimensions have been developed in the last decade; the most promising ones are designed with a three-dimensional graphitic path structure in the diamond bulk, at the same time creating pixels with sufficient sensitive volume and very small size. Large area detectors have also been developed to provide reliable dose maps, which would be very challenging or even impossible using a point-like detector, and, even more difficult, a dose map that varies with time. Polycrystalline pixel matrices, for example, have proven to be adequate for both relative dosimetry and pre-treatment verifications even if attention must be paid to the fabrication of pixel contacts and pixel calibration. Broadly speaking, for radiotherapy applications, an overall trend of evolution is observed towards energy independent all-carbon dosimeters. These new types of dosimeters partially overcome problems such as the reduced polarization voltage, the need for pre-irradiation, and the use of correction factors, but there are still several issues that need to be solved.

AUTHOR CONTRIBUTIONS

CT was main editor of the review and wrote the following sections: abstract, introductions, Radiotherapy Application, Conclusion. KK wrote the Diamond contacts and Diamond dimensions and electrodes geometry sections. SP collected papers and reviewed the final manuscript. LS wrote Detector read out, housing and conclusion sections and he reviewed the final manuscript. All authors discussed and contributed to the final manuscript.

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