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Single crystal CVD diamond membranes for betavoltaic cells

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A single crystal diamond large area thin membrane was assembled as a p-doped/Intrinsic/Metal (PIM) structure and used in a betavoltaic configuration. When tested with a 20 keV electron beam from a high resolution scanning electron microscope, we measured an open circuit voltage (V_{oc}) of 1.85 V, a charge collection efficiency (CCE) of 98%, a fill-factor of 80%, and a total conversion efficiency of 9.4%. These parameters are inherently linked to the diamond membrane PIM structure that allows full device depletion even at 0 V and are among the highest reported up to now for any other material tested for betavoltaic devices. It enables to drive a high short-circuit current I_{sc} up to 7.12 μA, to reach a maximum power P_{max} of 10.48 μW, a remarkable value demonstrating the high-benefit of diamond for the realization of long-life radioisotope based micro-batteries. *Published by AIP Publishing.*
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Recent progress in modern microsystems and microelectromechanical systems (MEMS) has enabled the fabrication of highly functional devices, but autonomy and standalone functionality requires on-board power. In 1991, Sony commercialized the first Li-ion cell based on chemistry that led to the fastest growing battery on the market. However, the storable energy remains near the 1 A.h.cm^{-3} value, and this limit seems hard to be overtaken although the market is in need of smaller and more powerful energy devices. One of the alternatives is the use of radioisotope batteries, which directly convert nuclear decay products (alpha or beta particles) into electricity. They appear as a reliable alternative to chemistry batteries with longer lifetime and reduced size. In fact, the approach is not new, and nuclear-based energy sources exist since the late 1950s,[1] where Si junctions were irradiated with a SrY-90 beta source. These approaches opened up the way to medical power (cardiac stimulation), and still today they appear as viable alternative devices for spatial, aeronautics, and submarine applications where long-term stability and high performances in harsh environments are required. The key to a feasible radioisotope battery is an efficient nuclear-to-electrical conversion mechanism and a high tolerance to the radiation damage.

In many previous works, studies based on alpha-, betavoltaic approaches[2–15] have demonstrated the gain in using wide bandgap semiconducting materials, such as Si, GaN, and SiC. Here, we propose to demonstrate that diamond is a very promising alternative since its large band-gap enables a significant improvement of the internal efficiency of such devices.[15] First hints about the use of diamond for beta-cells can be found in the pioneering work from Ref. 16. More recently, the interests of diamond were confirmed by Ref. 17. The main advantages of diamond as a direct converting material includes (i) its low Z implying low electrons backscattering, and bremsstrahlung generation, thus better coupling of the beta source to the diamond beta-cell, and no radiation damage, (ii) high electronic density thus higher stopping power (thinner layers can be used to reduce the device volume), (iii) high mobility of both electrons and holes[18,19] with a high diffusion length enabling lower recombination rate in highly doped regions, thus increased CCE, and (iv) p-doped diamond layer as an entrance electrode provides an electrochemically active layer on which radioactive isotopes can be directly precipitated from liquid solution with no beta-cell degradation.[20] These properties combined with its outstanding radiation hardness[21,22] and the significant progress in the chemical vapor deposition (CVD) synthesis of high purity single crystal (scCVD) make diamond the perfect candidate for betavoltaic alternative miniature energy sources.

In the recent work from Ref. 17, the fabrication of a diamond based betavoltaic cell by combining 130 scCVD-based Schottky barrier cells over 15 cm^2 was demonstrated. Several beta sources (Ni-63, Pm-147, and Sr-90/Y-90) could be used to allow the fabrication of a betavoltaic battery with a conversion efficiency up to 5% and a typical open-circuit voltage of 0.8 V (characterized with an SEM at 20 keV). This value remains low and was here attributed to a poor distribution of the Schottky barrier height within the battery over the numerous individual scCVD cells. We report here on the development of a single betavoltaic cell based on a high purity scCVD diamond membrane with almost a twice higher conversion efficiency.

In previous works we demonstrated the possibility to fabricate self-supported scCVD thin diamond membranes (1–10 μm thickness) using an argon/oxygen plasma etching method, and applied it to commercially available scCVD diamond samples.[23,24] Such a membrane was combined with a thin layer of highly boron doped diamond which has been first grown on top of the sample by microwave enhanced plasma chemical vapor deposition (MPECVD),[25] and an aluminum backcontact at the bottom allowing the formation of a fully depleted p-doped/Intrinsic/Metal (PIM) structure with a high built-in potential, which renders direct nuclear-to-electrical conversion possible with high efficiency. We used an electronic grade scCVD diamond from *ElementSix* with a lifetime of excess charge carriers approaching microseconds.[18] Figure 1(a) displays a picture of the device tested.

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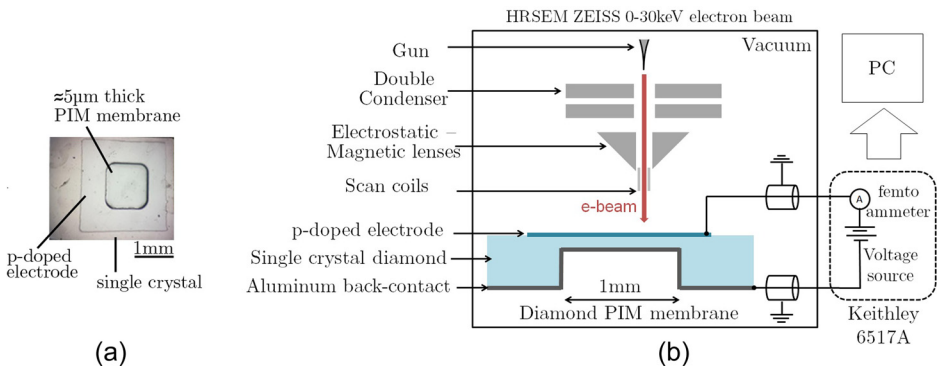

FIG. 1. (a) Optical micrograph (top view) of the scCVD membrane arranged into PIM structure, (b) Sketch of the EBIC set-up for measurements of scCVD membrane beta-cell characteristics in the HRSEM.

The larger square ($2 \times 2\,mm^2$) represents the 200 nm thick boron doped diamond entrance electrode (boron concentration: $[B] \sim 10^{21}\,cm^{-3}$) that is grown over the $1 \times 1\,mm^2$ square 5 μm thick membrane in the center. The growth proceeds in a homemade CVD reactor and the conditions are as follows: $[CH_4]/[H_2] = 0.55\%$, $(B/C)_{gas} = 2 \times 10^4$ ppm, 438 W, 120 mbar, and 870 °C. An aluminum bottom electrode (200 nm thick) was deposited on the entire back surface using RF physical vapor deposition (RF PVD) sputtering. The thick edge of the membrane with 40 μm thickness provides mechanical stability and handling convenience to the thin active central device. This particular membrane configuration may further allow easy vertical stacking of multiple PIM structures. The surface area of the membrane could also easily be extended on larger crystals allowing much higher active areas.

We use an HRSEM ZEISS SUPRA 40 to simulate the electrons emitted by a Ni-63 radioactive source and probed their interaction with the diamond beta-cell using an electron beam induced currents (EBIC) set-up. The scCVD PIM membrane is mounted on a printed circuit board inside a Faraday cup providing electrical connections to the membrane electrodes and electrical shielding, further to probing the direct primary e-beam current. The top p-doped diamond electrode is connected to a Keithley-6517A femto-ammeter and the bottom aluminum electrode is connected to the bias source (as indicated in Fig. 1(b)). All measurements (including dark characteristics) are done in vacuum below 10^{-5} mbar inside the HRSEM chamber. The primary e-beam energy was tuned to 20 keV, being close to the average energy of beta particles emitted by a Ni-63 source.[26] Electrons impinge the PIM membrane through the p+ diamond electrode and enter the membrane. The penetration of electrons into the structure is evaluated to be 2.1 μm at this energy, according to the Monte-Carlo simulations done with *Casino* software.[27] In such geometrical configuration the backscattering of electrons is minimized to a few percent due to the low atomic number of carbon, compared with other semiconducting materials (e.g., Si ~ 15% or GaN ~ 25%).

The total efficiency of the beta-cell is the product of three terms: the source efficiency η_b related to the fraction of energy that is actually impinging the semiconductor surface; the coupling efficiency η_c that is related to the absorption of beta particles in the diamond and its collection efficiency; and the internal efficiency of the semiconductor η_s (see Refs. 15 and 28 for details). The first depends on the radioisotope used to fabricate a beta-cell. The latters have the form

$$\eta_c = (1 - r)Q, \tag{1}$$

$$\eta_s = \frac{qV_{OC}FF}{\varepsilon}, \tag{2}$$

where r is the reflection coefficient of beta particles from the surface of the device and Q refers to the CCE of the semiconductor. In Equation (2), q refers to the elementary charge and ε to the ionization energy of the material. Thanks to the EBIC setup we were able to test only the internal efficiency with some hints to the coupling efficiency due to the backscattering and absorption of electrons in the p+ layer. Figure 2 presents the dark current–voltage characteristics of the PIM diamond membrane (black triangles) and its response under 20 keV electron beam irradiation (red squares). From the dark I-V characteristics the quality of the PIM junction can be deduced. In the reverse mode the leakage current ($<10\,nA/4\,mm^2$) was negligible up to 250 V measured. In forward mode, the current of the bias source was quickly saturated at biases below 6 V. A remarkable diode rectification ratio of 10^{10} was obtained at 6 V.

Prior to the beta-cell characteristics measurements, the electron-beam current is measured by means of the Faraday cup. We measured values of 5.19 nA at 20 keV electron energy. This gives us an injected power P_{in} which amounts to $P_{in} = I_{ebeam} \times E_{ebeam} = 103\,\mu W$. The activity of a corresponding Ni-63 beta source would be 32.40 Gbq.

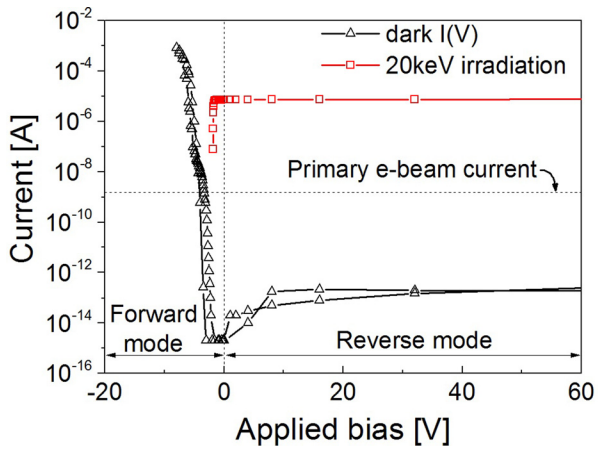

FIG. 2. Current–voltage (I-V) characteristics of the PIM scCVD diamond membrane: (black triangles) dark characteristics; (red squares) under 20 keV electron beam illumination. The primary SEM beam current of 5.19 nA was measured with a Faraday cup and is indicated in the graph (horizontal black dashed line).

The I-V characteristics of the diamond beta-cell under electron irradiation is presented in Figure 2 (red squares). A constant current flows at positive biases (reverse mode), a strong indication of complete CCE, as observed in detector configurations.[23] Assuming that full collection is achieved at biases above a few volts in reverse mode, one can note that about 98% charge is already collected at 0 V. This very high collection efficiency comes from the high purity of the crystal combined with the full depletion of the device that is made achievable in such thin diamond membranes. Comparing the value of measured EBIC current (at maximum measured bias) with the primary beam current measured by the Faraday cup, an amplification factor of 1450 is probed, implying that each 20 keV electron from the primary beam creates 1450 thermalized e-h pairs within the diamond bulk. From this factor an average energy for e-h pair creation in diamond is calculated to be $\varepsilon = 13.8$ eV/pair, a value comparable with the excess charge carriers ionization values.[19,29] This ionization energy can be slightly overestimated, since we do not perform the correction for e-h pair recombination in the p+ layer (few percent) and for the backscattering of electrons. As the current is measured with a large positive applied bias, no secondary electrons are escaping from the surface. We used the *CASINO* software to estimate the fraction of backscattered electrons. At 20 keV, the backscattered coefficient is about 3%–4% and only slightly varies with the energy of the beam. Since all the electrons are stopped in the membrane volume, the absorption of electrons is only affected by the backscattering and the recombination in the p+ layer. Assuming an approximate effective absorption of 90% and a CCE of 98%, the coupling efficiency of the HRSEM set-up can be estimated to be about 88%.

A more detailed view of the EBIC current, so called photovoltaic mode (for solar cells) or betavoltaic mode in this case, in the diamond membrane is plotted in Figure 3 together with the electrical power flowing through the device. The beta-cell performance can be extracted from this curve where an open-circuit voltage of 1.85 V and a short-circuit current of 7.12 μA are measured. The maximum power of 10.48 μW is reached at a forward polarization of −1.5 V and the fill factor is calculated to be 80%. Taking into account these parameters and the ionization energy previously expressed, the internal efficiency η_s of the device is calculated to be 10.7%. And the total conversion efficiency $\eta_{conv} = \eta_c \cdot \eta_s$ of the cell is 9.4%. This value is relevant when compared with the ratio of the maximal electrical power output of the device to the available power in the electronic beam (10.2%), and despite higher efficiency for other devices in recent papers,[30–32] this result is the best conversion efficiency measured in diamond betavoltaic cells. This result shows that the efficiency of a betavoltaic cell of a given material and with a given beta source depends strongly on the CCE and on the V_{oc} parameters. Since the CCE is approaching intrinsic 100% and could not be further improved, only the increase of V_{oc} allows here the improvement of the beta-cell efficiency. Although the open circuit voltage has been almost doubled in this study compared with the literature, the influence of the fabrication process on V_{oc} must still be understood. As mentioned in the work of Ref. 17 the open-circuit voltage could be strongly related to the Schottky barrier height and thus to the surface preparation and to the choice of the metal for the electrode.

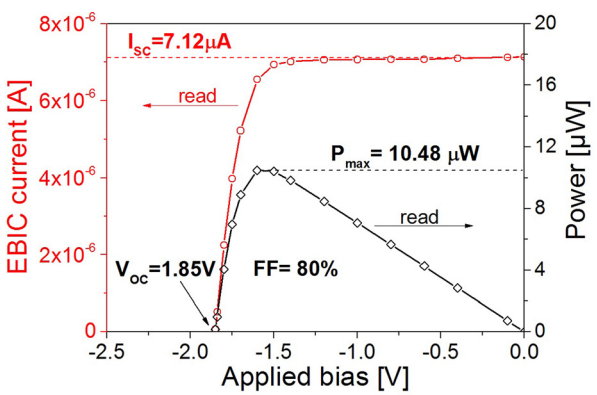

FIG. 3. The diamond membrane beta-cell characteristics under 20 keV e-beam irradiation. The I-V betavoltaic characteristic is plotted with red circles and the power characteristics is represented with black diamonds. The crucial parameters of a beta-cell are indicated in the graph including the fill-factor (FF) and the maximum power output.

A betavoltaic device has been fabricated using a single crystal diamond membrane etched in a high purity *ElementSix* diamond electronic grade crystal. The PIM structure is based on a p+ boron doped diamond epilayer on one side and an aluminum electrode on the other side. The membrane is 4 μm thick and totally covered by the contacts. This device has been characterized using a commercial ZEISS SUPRA 40 HRSEM with a 20 keV electron beam to simulate the exposure to the beta radiation from a Ni-63 source and by measuring the EBIC current flowing through the cell in forward mode. The device shows extremely promising results with one of the highest reported open-circuit voltage of 1.85 V and a high conversion efficiency of 9.4%. These results origin from (1) the full depletion of the membrane which gives a CCE approaching 100% at 0 V (2) the low absorption of the top electrode which is here made of boron-doped diamond (3) and a drift region made of a high purity scCVD diamond. These results give a good insight on the behavior of the diamond PIM structure regardless of the source and will be useful for the future fabrication of a complete beta-cell including a radio-emitter. Such betavoltaic diamond cells made of large area and thin membranes appear as ideal candidate to provide long-standing, reliable, and powerful micro current sources.

[1]P. Rappaport, "The electron-voltaic effect in p−n junctions induced by beta-particle bombardment," Phys. Rev. **93**, 246–247 (1954).
[2]C. Eiting, V. Krishnamoorthy, S. Rodgers, T. George, J. Robertson, and J. Brockman, "Demonstration of a radiation resistant, high efficiency SiC betavoltaic," Appl. Phys. Lett. **88**(6), 064101 (2006).
[3]M. Chandrashekar, C. Thomas, H. Li, M. Spencer, and A. Lal, "Demonstration of a 4H SiC betavoltaic cell," Mater. Sci. Forum **527–529**, 1351–1354 (2006).
[4]J.-P. Clarkson, W. Sun, K. Hirschman, L. Gadeken, and P. Fauchet, "Betavoltaic and photovoltaic energy conversion in three-dimensional macroporous silicon diodes," Phys. Status Solidi A **204**(5), 1536–1540 (2007).
[5]T. Kosteski, N. Kherani, P. Stradins, F. Gaspari, W. Shmayda, L. Sidhu, and S. Zukotynski, "Tritiated amorphous silicon betavoltaic devices," IEEE Proc. Circuits, Devices Syst. **150**(4), 274–281 (2003).

[6]M. Lu, G. Zhang, K. Fu, G. Yu, D. Su, and J. Hu, "Gallium nitride Schottky betavoltaic nuclear batteries," Energy Convers. Manage. **52**(4), 1955–1958 (2011).
[7]S. Yao, Z. Song, X. Wang, H. San, and Y. Yu, "Design and simulation of betavoltaic battery using large-grain polysilicon," Appl. Radiat. Isot. **70**(10), 2388–2394 (2012).
[8]C. D. Cress, B. Landi, and R. Raffaelle, "InGaP alpha voltaic batteries: Synthesis, modeling, and radiation tolerance," J. Appl. Phys. **100**, 114519 (2006).
[9]H. Chen, L. Jiang, and X. Chen, "Design optimization of GaAs betavoltaic batteries," J. Phys. D: Appl. Phys. **44**(21), 215303 (2011).
[10]W. Sun, N. Kherani, D. Hirschman, L. Gadeken, and P. Fauchet, "A three-dimensional porus silicon p-n diode for betavoltaics and photovoltaics," Adv. Mater. **17**, 1230–1233 (2005).
[11]D.-Y. Qiao, "Demonstration of a 4H SiC betavoltaic nuclear battery based on Schottky barrier diode," China Phys. Lett. **25**, 3798 (2008).
[12]G.-Q. Wang, H. Li, Y.-S. Lei, W.-B. Zhao, Y.-Q. Yang, and S. Luo, "Demonstration of Pm-147 GaN betavoltaics cells," Nucl. Sci. Tech. **25**, 020403 (2014).
[13]T. Wacharasindhu, J. Kwon, D. Meier, and J. Robertson, "Radioisotope micobattery based on liquid semiconductor," Appl. Phys. Lett. **95**, 014103 (2009).
[14]Z. Cheng, X. Chen, H. San, Z. Feng, and B. Liu, "A high open-circuit voltage gallium nitride betavoltaic microbattery," J. Micromech. Microeng. **22**, 074011 (2012).
[15]L. Olsen, "Review of betavoltaic energy conversion," in Proceedings of the 12th Space Photovoltaic Research and Technology Conference, Washington, 1993.
[16]D. Trucchi, E. Capelli, and P. Ascarelli, "Designing CVD diamond betavoltaic batteries," in Proceedings of the 13th Italian Conference on Sensors and Microsystems, 2009.
[17]V. Bormashov, T. Sergey, V. Alexander, T. Sergey, E. Korostylev, A. Golovanov, M. Kuznetsov, D. Teteruk, N. Kornilov, S. Terentiev, S. Buga, and V. Blank, "Development of nuclear microbattery," Phys. Status Solidi A **212**(11), 2539–2547 (2015).
[18]J. Isberg, J. Hammersberg, E. Johansson, T. Wilström, D. Twitchen, and S. Whitehead, "High carrier mobility in single-crystal plasma-deposited diamond," Science **297**, 5587 (2002).
[19]M. Pomorski, E. Berdermann, M. Ciobanu, A. Martemyianov, P. Moritz, M. Rebisz, and B. Marczewska, "Characterisation of single crystal CVD diamond particle detectors for hadron physics experiments," Phys. Status Solidi A **202**(11), 2199–2205 (2005).
[20]J. De Sanoit, T. Q. Tran, M. Pomorski, S. Pierre, C. Mer, and P. Bergonzo, "Design of an electrochemically assisted radiation sensor for α-spectrometry of actinides traces in water," Appl. Radiat. Isot. **80**, 32–41 (2013).
[21]C. Bauer, I. Baumann, C. Colledani, J. Conway, P. Delpierre, F. Djama, W. Dulinski, A. Fallou, K. Gan, and R. Gilmore, "Radiation hardness studies of CVD diamond detectors," Nucl. Instrum. Methods Phys. Res., Sect. A **367**(1–3), 207–211 (1995).
[22]M. Angelone, M. Pillon, A. Balducci, M. Marinelli, E. Milani, M. Morgada, G. Pucella, A. Tucciarone, G. Verona-Rinati, K. Ochiati, and T. Nishitani, "Radiation hardness of a polycrystalline chemical-vapor-deposited diamond detector irradiated with 14 MeV neutrons," Rev. Sci. Instrum. **77**(2), 023505 (2006).
[23]M. Pomorski, B. Caylar, and P. Bergonzo, "Super-thin single crystal diamond membrane radiation detectors," Appl. Phys. Lett. **103**, 112106 (2013).
[24]V. S. N. Grilj, M. Pomorski, W. Kada, and N. Iwamoto, "An ultra-thin diamond membrane as a transmission particle detector and vacuum window for external microbeams," Appl. Phys. Lett. **103**, 243106 (2013).
[25]P.-N. Volpe, J.-C. Arnault, N. Tranchant, G. Chicot, J. Pernot, F. Jomard, and P. Begonzo, "Boron incorporation issues in diamond when TMB is used as precursor: Toward extreme doping levels," Diamond Relat. Mater. **22**, 136–141 (2012).
[26]I. L. Preiss, R. W. Fink, and B. L. Robinson, "The beta spectrum of carrier-free Ni^{63}," J. Inorg. Nucl. Chem. **4**(5), 233–236 (1957).
[27]D. Drouin, A. Couture, D. Joly, X. Tastet, V. Aimez, and R. Gauvin, "CASINO V2.42 - A fast and easy-to-use modeling tool for scanning electron microscopy and microanalysis users," Scanning **29**, 92–101 (2007).
[28]A. Sashenko, A. Shkrebtii, R. Korkishko, V. Kostylyov, M. Kulish, and I. Sokolovskyi, "Efficiency analysis of betavoltaic elements," Solid-State Electronics **111**, 147–152 (2015).
[29]J. Kaneko, T. Tanaka, T. Imai, Y. Tanimura, M. Katagiri, T. Nishitani, H. Takeuchi, T. Sawamura, and T. Iida, "Radiation detector made of a diamond single crystal grown by a chemical vapor deposition method," Nucl. Instrum. Methods Phys. Res., Sect. A **505**, 187–190 (2003).
[30]C. Thomas, S. Portnoff, and M. G. Spencer, "High efficiency 4H-SiC betavoltaic power sources using tritium radioisotopes," Appl. Phys. Lett. **108**(1), 013505 (2016).
[31]K. Zhang, G. Gui, P. Pathak, J.-H. Seo, J. P. Blanchard, and Z. Ma, "Quantitative modeling of betavoltaic microbattery performance," Sens Actuators, A **240**, 131–137 (2016).
[32]Q. Zhang, N. Wang, P. Zhou, C. Chen, H. San, K. Wang, and X. Chen, "A betavoltaic microbattery using zinc oxide nanowires under build in potential difference," in 2016 IEEE 29th International Conference on Micro Electro Mechanical Systems (MEMS), 2016.