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Alpha-voltaic battery on diamond Schottky barrier diode

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ABSTRACT

A diamond Schottky alpha-voltaic nuclear battery (DSAB) is fabricated, and the alpha-particle degradation test is performed. The device is formed on oxygen-terminated intrinsic CVD diamond epitaxially grown on B-doped HPHT diamond. An open-circuit voltage of 1.13 V and a short-circuit current of 53.4 pA are measured under a low-activity alpha source with 8.85 μCi/cm^2 irradiation, and a total conversion efficiency of 0.83% is obtained. The DSAB simultaneously has better open-circuit voltage and short-circuit current stability than Si and SiC diodes, which means that DSAB has the highest potential for achieving high and stable conversion efficiency.

1. Introduction

A radioisotopic battery is a device that converts radiant energy into electricity. The isotope decay process is not affected by the environment. Its energy release process is stable and reliable, and it has high energy density, which makes the design life of the radioisotopic battery relatively long (mainly depending on the half-life of the radioisotope), with a large power density (from a hundred to thousand times larger than that of a chemical power source, depending on the type of the radioisotope). Recently, the demand for implantable medical devices for long-time power supplies and microbatteries has increased [1]. Several energy-conversion mechanisms are available, such as thermoelectric effect [2], thermionic effect [3], alpha-voltaics [4], beta-voltaics [5], and photon-intermediate direct energy conversion [6]. Radioisotope thermoelectric generators have been widely used in aerospace applications. However, they suffer from a severe weakness, namely, lower power density. In other words, they are difficult to miniaturize while maintaining a given power. To meet the requirement of microelectromechanical systems for batteries with high power density, miniaturization, and stability, alpha-voltaics and beta-voltaics have been extensively studied. Nuclear batteries based on wide-bandgap semiconductors have been fabricated, such as gallium nitride (GaN) [7] and silicon carbide (SiC) [4]. Among the many semiconducting materials, diamond has the widest bandgap of 5.48 eV, whereas those of Si, Ge, SiC, and GaN are 1.12, 0.68, 2.9, and 3.39 eV, respectively [8]. A particle with an energy of tens to hundreds of kiloelectron volts emitted by an isotope that penetrates a semiconductor can create many electron-hole pairs. The theoretical maximum energy conversion efficiency can be estimated by $E_g/(2.8E_g + 0.5\text{eV})$, which implies that the larger the bandgap, the higher is the possible efficiency [9]. The theoretical maximum energy-conversion efficiency of diamond is 34.6%, whereas that of Si is 30.8%. The energy required to displace the host atom from a crystal lattice (displacement energy) is a material property that reflects the material's radiation hardness. Diamond has a displacement energy of 43 eV, whereas the displacement energy values of Si, Ge, SiC, and GaN are 19, 30, 28, and 24 eV, respectively [8,10], which indicates that diamond is the best radiation-hard material among common semiconductors. Diamond nuclear batteries have recently attracted much attention. Microwave plasma-assisted chemical vapor deposition (CVD) diamond-radiation energy-conversion devices with a total conversion efficiency of 0.2%–0.4% were fabricated by Trucchi et al. [11]. Bormashov et al. developed ^{63}Ni, ^{147}Pm, and ^{90}Sr-^{90}Y beta-voltaic and ^{238}Pu alpha-voltaic nuclear microbatteries with total conversion efficiencies of 0.6%, 1%, 0.004%, and 3.6%, respectively [12]. A single-crystal CVD diamond-membrane beta-voltaic cell was reported by Delfaure et al., and a total conversion efficiency of 9.4% was obtained under electron-beam-induced current measurement [13]. A p-i structure diamond Americium-241 (^{241}Am) alpha-voltaic battery with an open-circuit voltage (V_{oc}) of 0.62 V and short-circuit current (I_{sc}) of 40 pA was developed by

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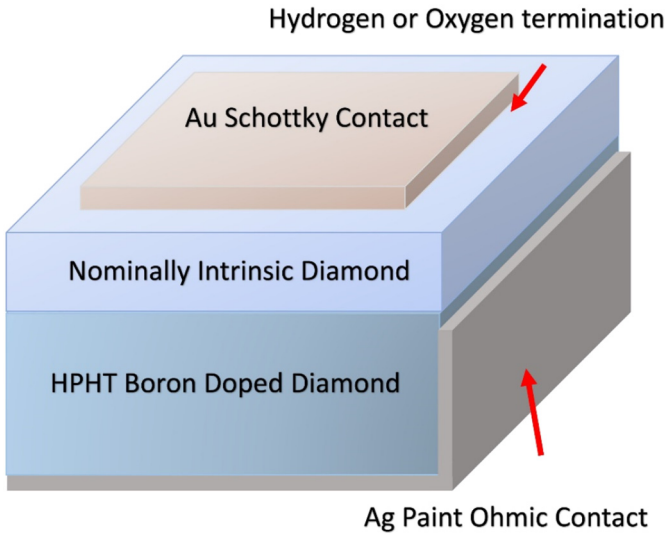

Fig. 1. Structure of the PIM diamond Schottky diode.

Rodionov et al. [14] The n-type diamond is known to be difficult to obtain; thus, a Schottky barrier diode is a better choice for diamond-based devices. In addition, the Schottky barrier diode exhibits better radiation hardness to high-energy radiation particles than a p-n junction [15], and diamond Schottky barrier diodes with better performance can be fabricated more easily.

In the present study, we developed a diamond Schottky alpha-voltaic battery with a total efficiency of 0.83% under a low-activity ^{241}Am irradiation and illustrated the importance of oxygen termination in forming a high open-circuit-voltage battery. Then, the radiation tolerance test of the diamond nuclear battery was performed, which demonstrated the high resistance of diamond to nuclear radiation and its superiority in the field of nuclear batteries.

2. Materials and fabrication procedure

2.1. Realization of the PIM structure

A p-type/intrinsic/metal (PIM)-structure diamond Schottky diode was fabricated, as shown in Fig. 1. Schottky diodes form built-in electric field in the junction region which can separate excess carriers to the electrodes. Excess carriers in depletion region could be separated and collected effectively leading to a high charge collection efficiency. An α particle with energy of 4.5 MeV will propagate approximately 10 μm in the diamond which is estimated by the software SRIM [16]. However, the depletion width of diamond diodes will not exceed 0.6 μm even with a low acceptor-impurity density level (10^{16} cm^{-3}) at zero bias estimated by formula [17]:

$$W = \sqrt{\frac{2\varepsilon_s V_{bi}}{qN_A}} \quad (1)$$

where ε_s is permittivity of diamond (5×10^{-11} F/m), V_{bi} is the built-in potential assuming a maximum value of 5.5 V, q is the electron charge and N_A is the acceptor-impurity density. The presence of the intrinsic layer will effectively widen the depletion region improving the performance of the device. Thus, the PIM Schottky structure is selected. The thickness of the depleted active region is a little larger than that of the intrinsic layer, approximately 16 μm.

Microwave plasma-assisted CVD was used to perform the epitaxial growth of the diamond intrinsic layer on a 3×3 mm^2 boron-doped high-pressure high-temperature diamond substrate. The diamond substrate purchased from Zhengzhou Sino-Crystal Diamond Co. is light blue and has a low resistance, indicating the existence of boron [18]. The uncompensated acceptor concentration (N_A-N_D) ≈ 2×10^{16} cm^{-3} was determined from infrared absorption spectrum, as measured with Perkin Elmer Frontier FTIR spectrometer. The integral intensity of boron-related absorption band at 2800 cm^{-1} was converted to B concentration according to a calibration taken from Ref. [19]. The substrate resistivity of ~5×10^3 Ωcm was evaluated by sputter coating two Au electrodes (0.15 mm wide, 0.5 mm long spaced by 0.85 mm) on the diamond surface and measuring the resistance under a bias of 200 V.

Before growing, the substrate was sequentially cleaned in acetone, deionized water, and alcohol by ultrasonic cleaning. The growth of diamond intrinsic layer was performed in a 2.45 GHz, 5 kW microwave plasma CVD (MPCVD) reactor PLASSYS SSDR 150 [20]. Before epitaxial diamond growth, the substrate pretreatment was performed in H_2 plasma at 800 °C for 40 min to etch surface defects. The diamond growth was achieved with the gas pressure of 230 mbar, feed flow of 194 sccm hydrogen and 6 sccm methane with a methane-to-hydrogen ratio of 3:97, microwave power of 3200 W and substrate temperature 800 °C. The substrate temperature was measured by a two color pyrometer (Willamson Pro 92-40-C). After a 2-h growth, an ~16-μm intrinsic layer was obtained. Methane was switched-off at the end of the growth process, and the sample was immersed in pure hydrogen plasma for 15 min, waiting when methane was completely removed from the chamber. Therefore the diamond surface was H-terminated. A 20-nm Au layer was deposited on the as-grown diamond intrinsic layer to form a Schottky contact, and Ag paint was used as an Ohmic contact [21,22]. Au electrodes were fabricated with a sputter coater Cressington 108 at sputtering current of 30 mA with an aluminum foil mask. In order to reduce the impact of the hydrogenation on shunt resistance, the diode was illuminated by a 250 W mercury lamp for 10 min in air [23]. Then, the photovoltaic test was performed using a DH-2000 Deuterium & Tungsten Halogen ultraviolet (UV) lamp. The nominal power of the lamp is 25 W and a peak wavelength located around 220 nm. To create a high Schottky barrier height (SBH) diode, the oxygen termination of the diamond intrinsic layer was performed by heating the structure in a nitric and sulfuric mixture solution for an hour after the removal of the Au layer from the aqua regia. Similarly, Au Schottky and Ag paint Ohmic contacts were produced, and a photovoltaic test was performed. The current–voltage (I–V) characteristics of the diamond Schottky alpha-voltaic nuclear battery was investigated using a Keithley 4200-SCS semiconductor characterization system.

2.2. Surface-termination selection

In general, diamond surfaces exhibit hydrogen or oxygen termination, which strongly influences the properties of the Schottky diode. In this section, we demonstrate the reason why we experimentally and theoretically choose oxygen termination. Fig. 2 shows the photovoltaic measurement of the oxygen and hydrogen terminations of the PIM diamond Schottky diode under deuterium lamp illumination. At bias $U = -2$ V the dark current as low as 10^{-11} A is measured, while under UV illumination the current increased by five orders of magnitude, up to 4×10^{-6} A (Fig. 2).

The results listed in Table 1 demonstrate the oxygen-terminated surface, which exhibits better photovoltaic performance. The open-circuit voltage of the oxygen-terminated device is 110 times higher than that of the hydrogen-terminated one. Theoretically, V_{oc} is dominated by the development of the electric field, i.e., for a Schottky cell, the larger the SBH, the larger is V_{oc}.

For diamond, different terminations display different electron affinities (χ). The surface of a diamond prepared by CVD is terminated by hydrogen, which exhibits a negative electron affinity of −1.3 eV [24], whereas a diamond with oxygen termination exhibits a positive electron affinity of 1.7 eV [25]. The relationship between χ and SBH is expressed as follows [26]: