Extreme UV single crystal diamond Schottky photodiode in planar and transverse configuration

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ARTICLE INFO

Article history:
Received 31 July 2009
Received in revised form 28 October 2009
Accepted 5 November 2009
Available online 11 November 2009

Keywords:
Single crystal diamond
UV detectors
Schottky photodiode
Extreme UV

ABSTRACT

We report on the study of the performances of two extreme ultraviolet (EUV) photovoltaic single crystal diamond Schottky diodes based on metal/intrinsic/p-type diamond junction developed at the University of Rome "Tor Vergata" and having different contact geometries. One detector operates in transverse configuration with a semitransparent metallic contact evaporated on the intrinsic diamond surface, while the second one operates in planar configuration with an interdigitated contact structure on the growth surface of the intrinsic diamond layer. Both devices can work in an unbiased mode by using the built-in potential arising from the electrode–diamond interface and show excellent rectifying properties with a rectification ratio of about 10^6. The devices have been characterized in the EUV spectral region by using He–Ne DC gas discharge radiation source and a toroidal grating vacuum monochromator, with a 5 Å wavelength resolution. The extremely good signal-to-noise ratio, the reproducibility of the device response, the absence of persistent photoconductivity and undesirable pumping effects suggest the high quality of our CVD diamond for UV applications. The external quantum efficiency (EQE) as well as the responsivity have been measured in the spectral range from 20 to 120 nm and opposite behaviours for the two different geometries proposed have been observed.

1. Introduction

Diamond appears to be a promising material for UV radiation detection. Its wide band-gap, 5.5 eV, results in a very low leakage current and its electronic properties as high carrier mobility allow fast time response [1]. Besides, it has a large breakdown electric field (~ 10 V/μm), a low dielectric constant (i.e. low capacitance), chemical inertness and low intrinsic carrier density, which makes cooling for noise reduction unnecessary [2]. Its extreme radiation hardness is well known and another interesting feature, again related to the wide band-gap, is its selective sensitivity to radiation with wavelengths shorter than 225 nm (visible-blind detectors) [3]. Several attempts have been made to build up UV detectors from natural or synthetic diamonds. A detector often reported in literature is the photodiode structure [6,7] with a contact on the diamond growth surface and a backside contact on the silicon substrate. However, the CVD diamond performance is limited in this case by the polycrystalline structure due to defect states in the band-gap introduced by the grain boundaries [8,9], which affect the photoelectric properties and alter the detection characteristics. On the other hand, detector grade natural diamonds are extremely rare and expensive, while high pressure high temperature (HPHT) diamonds have their performance strongly worsened by defects and impurities [10]. Finally, a more promising approach is to use a planar Schottky photodiode fabricated on homoepitaxially grown p-type diamond epilayer as reported by Koide et al. [11].

A few years ago, at the University of Rome “Tor Vergata” laboratories, single crystal diamond films grown by chemical vapour deposition (CVD) were used to obtain a new class of detectors with a layered structure. The performances of a photodetector based on CVD single crystal diamond in a p-type/intrinsic/metal (PIM) configuration with a grid-shaped Al contact were reported in a previous publication [12]. In order to allow the comparison among the proposed PIM structure and the configuration most reported in literature, i.e. interdigitated electrodes, two different configurations of the PIM device have been tested.
A first detector operates in a planar configuration with interdigitated fingers on the diamond surface. One set of fingers is made of aluminium and the second one is made of p-type diamond. The second one has been designed in transverse configuration, but at variance with Ref. [12], instead of the grid-shaped contact a semitransparent electrode was deposited on the diamond surface in order to improve the electric field homogeneity.

2. Experimental

The PIM diamond detector consists of a multilayered structure obtained by a three step deposition process. A conductive boron-doped diamond homoepitaxial layer with approximately 5 Ω cm resistivity, used as a backing contact, is deposited by Microwave Plasma Enhanced CVD (MWPECVD) on a commercial low-cost synthetic HPHT type Ib single crystal diamond substrate, 4×4×0.5 mm³ in size. After that an intrinsic diamond layer is homoepitaxially grown on the doped one and is used as the detecting layer. Due to the small penetration depth of UV radiation in the 10–200 nm range [13], the detecting region of diamond has a thickness of approximately 2 µm. The intrinsic layer is deposited by using a separate reactor in order to avoid any boron contamination. The intrinsic diamond surface is oxidized, after the growth, by isothermal annealing at 500 °C for 1 h in air, in order to remove the hydrogenized surface conductive layer. Finally, a semitransparent Al electrode (3 mm in diameter) with a thickness of about 10 nm is deposited on the diamond surface by thermal evaporation, while annealed silver paint is utilized in order to provide an ohmic contact with the B-doped layer.

For the second diamond detector with interdigitated finger electrodes (IDT-PIM in the following), two steps of a standard photo-lithographic technique are used for the fabrication process. First, an intrinsic diamond layer is homoepitaxially grown by MWPECVD on a commercial HPHT single crystal diamond substrate. As previously mentioned, annealing in air is employed in order to remove the surface conductive layer of the as-grown diamond film. After the annealing process, p-type diamond interdigitated fingers are selectively grown on the top of the intrinsic diamond layer by using a patterned Cr plasma-resistant coplanar mask. After removal of the chromium mask by wet etching, the interdigitated Al electrode is fabricated using a second mask which is aligned to the pattern previously obtained. The Al fingers are patterned by a standard lift-off photo-lithographic technique and by thermal evaporation on the CVD intrinsic diamond surface. The width and the gap between two fingers are both 20 µm. A SEM image of the IDT-PIM device and a scheme of PIM device are shown in Fig. 1.

Both devices have been tested over the extreme UV spectral region from 20 to 120 nm, using He–Ne DC gas discharge as radiation source and a toroidal grating vacuum monochromator (Jobin Yvon model LHT-30) with a 5 Å wavelength resolution. The dimension of the optical aperture was 0.25 × 6 mm²; a manual shutter was used to switch on and off the UV radiation. The photoresponse measurements have been performed in a vacuum chamber, at a pressure of 0.03 mbar. By using a three dimension mechanical (X–Y–Z) stage powered by stepper motors, it is possible to locate the photodetector in front of the beam light and to compare its response with that of a calibrated NIST silicon photodiode [14] placed in the same position, which measures the absolute photon flux. A hole, 2 mm in diameter, is used to collimate the radiation on the sensitive area of the detectors and to obtain the same illuminated area on the silicon photodiode. The photocurrent is measured by an electrometer (Keithley 6517A), using the internal voltage source. The detectors are reverse biased with a negative voltage on the boron-doped contact while the Al contact is grounded. It must be noticed, however, that the particular detector structure used is also able to work in an unbiased mode, by using the internal voltage drop at the electrode–diamond junction.

Because of the different geometries adopted for the two devices, they are measured differently. The PIM detector is encapsulated in a copper/vetronite shielded housing with a 2 mm pinhole. In such housing, the Al contact is grounded and the photocurrent is measured from the p-type diamond electrode so that the signal is not affected by the possible presence of secondary electron emission current from the illuminated contact. In the case of the IDT-PIM, secondary electron emission cannot be shielded because the signal is collected from the contacts on the irradiated surface. Therefore the measured photocurrent of IDT-PIM detector can contain both photoconductive current and photoemission current arising from the Al fingers and from the p-type diamond exposed to the UV irradiation.

3. Results and discussion

Fig. 2 shows the I–V characteristics of the two diamond Schottky diodes measured from −3 V to 10 V at room temperature in a vacuum chamber at a background pressure of 10⁻⁶ mbar. The dark current is lower than 10⁻¹³ A for reverse bias voltages for both devices. A very good rectification ration of about 10⁴ was observed for both devices at ±3 V. The photocurrent vs. applied voltage is also reported in the same figure when the devices are exposed to UV radiation from a He–Ne lamp and at 30.4 nm (He line) and 73 nm (Ne line). Both devices operate in the reverse bias mode because when operating in the forward bias mode, the photocurrent is masked by the dark current [15]. It is evident that the devices show a photocurrent response even at zero voltage bias. The photocurrent is almost constant with increasing positive voltage, while the dark current increases by about two orders of magnitude. Remarkably, thus, the best signal-to-dark current ratio is obtained at zero bias voltage, so that in the following, the devices have been operated with no external bias voltage applied.
The detector time response, upon exposure to UV radiation, has been measured by opening and closing a manual shutter during the acquisition. The temporal response of the tested devices is reported in Fig. 3(a) under UV illumination of the He–Ne DC gas discharge radiation source. The response is reproducible and undesired effects such as persistent photocurrent and priming or memory effects, which are often observed in diamond UV detectors [16–18], are not present. Fig. 3(b) shows rise and fall times of the signal of about 60 ms, which correspond to the acquisition rate of the used electronic chain.

The normalized emission spectra of a DC discharge He–Ne lamp measured in an unbiased mode by the detectors are reported in Fig. 4. All spectral lines are clearly resolved and observed with a good signal-to-noise ratio, demonstrating the high photodetection capabilities of the CVD single crystal diamond grown in the extreme UV spectral region. In particular, the weak intensity lines of the He–Ne spectrum in the wavelength range 20–30 nm [19] are easily resolved by PIM detector (see Fig. 5).

The absolute spectral response of the detectors is measured by comparison with a calibrated photodiode exposed to the same source on the same optical area of about 1 mm².

The spectral responsivity, expressed in amperes per watt (A/W), is defined as the photocurrent per unit incident optical power and can be evaluated from the relationship $R_d = R_s I_d / I_s$ where $R_s$ is the responsivity of the calibrated silicon photodiode at a given wavelength, $I_s$ and $I_d$ are the photocurrents measured by the silicon photodiode and the diamond detector, respectively.

The absolute spectra responsivity curves of the two devices are shown in Fig. 6.

The responsivity of the PIM device decreases monotonically as the wavelength increases up to about 80 nm, but at 120 nm an increment is observed. At 98 nm the signal is below the noise level so that only an upper limit can be provided (see error bar in Fig. 6). However, the presence of a minimum in the responsivity at around 100 nm can be clearly deduced from Fig. 6.

The responsivity of the IDT-PIM detector is much lower than that of the PIM detector at short wavelengths (below 50 nm), with a maximum at about 73 nm. The increased sensitivity of the IDT-PIM device at intermediate wavelengths could be ascribed to the contribution of photoemission current as already reported in the literature [20]. For both devices the absolute responsivity measured at around 50 nm is comparable to results recently reported in literature for diamond based EUV detectors [21].

Fig. 6 also reports the responsivity of an unshielded detector, tested in a previous publication [12], that operates using a third contact geometry, i.e. in a transversal configuration using an Al grid-shaped contact instead of a semitransparent homogeneous Al contact. The new PIM proposed in this paper a much higher responsivity than the previously tested device at $\lambda<60$ nm. The continuous electrical contact generates an electric field near the detector surface more uniform and parallel than that generated by the grid-shaped contact improving the responsivity at low wavelengths. On the other hand,
the response of the grid-shaped contact detector is rather flat and a higher sensitivity with respect to the PIM device is observed above 60 nm. However, it should be pointed out that the grid-shaped device was not encapsulated and the improved sensitivity observed above 60 nm could be due to secondary photoemission current contribution.

The External Quantum Efficiency (EQE) spectrum, estimated by
$$\text{EQE} = 1240 \cdot \frac{R}{\lambda} \left[ \text{nm} \right],$$

is reported in Fig. 7 for the PIM devices. To understand the different behaviours of EQE for the two devices, a physical analysis of the detection process should be performed. Because of the particular geometry of the device, this is very difficult for the IDT-PIM case. Moreover, as mentioned above, the photocurrent measured by IDT-PIM detector includes the photoemission current, which also depends on the wavelength [20]. On the contrary, the shielded PIM device is not affected by secondary electron contribution, and the more homogeneous electric field configuration of the PIM device allows a simple analysis of the detection process. The physics of the device is clearly based on the existence of a Schottky barrier generated at Al–diamond interface, as demonstrated by the fact that the detector is able to operate even with no external bias applied.

The EQE depends on the absorptance $A(\lambda)$ (number of photon absorbed) of the diamond active layer and taking into account the PIM structure (see Fig. 1(b)), we can simulate the experimental data by the following equation:

$$\text{EQE}(\lambda) = g \cdot \eta(\lambda) \cdot A(\lambda) = g \cdot \eta(\lambda) \cdot \left(1-R(\lambda)\right) \cdot e^{-\alpha_{Al}(\lambda) d_{Al}}$$

where $g$ is a photoconductive gain, $\eta(\lambda)$ internal quantum efficiency, $R(\lambda)$ the reflectivity of aluminium/diamond structure [22], $\alpha_{Al}(\lambda)$ the Al absorption coefficient, $d_{Al}$ (~10 nm) the thickness of Al contact. The number of electron–hole pairs created per absorbed photon $\eta(\lambda)$ is unity for $\lambda > 95.4$ nm and it has a value of $95.4/\lambda$ for $\lambda < 95.4$ nm [21,23], since for higher photon energies, secondary ionization is energetically possible.

The curve expressed by Eq. (1) is reported in Fig. 7 from 40 nm to 120 nm for $g = 1$. Clearly it does not reproduce the experimental data. Changing the value of $g$ (see the $g = 0.1$ curve in Fig. 7), would only produce a vertical shift of the curve therefore not improving much the fit. One reason for this lack of agreement could be that the $R(\lambda)$ values are accurate only in the ideal condition of a perfectly smooth surface. However, such a strong discrepancy suggests the occurrence of a different process. The penetration depth of diamond shows a deep minimum at about 100 nm whose trend is qualitatively similar to the responsivity curve observed in Fig. 6. This suggests the existence of a dead layer located at the diamond surface, probably related to the recombination of photo-generated carriers close to the metal–diamond interface [21]. Introducing such a dead diamond layer in the simulation, we can indeed reproduce the experimental behaviour. Under this assumption, Eq. (1) must be multiplied by the additional term $\exp(-\alpha_{diam}d_{diam})$, where $\alpha_{diam}(\lambda)$ is the diamond absorption coefficient and $d_{diam}$ is the thickness of the dead diamond layer.

$$\text{EQE}(\lambda) = g \cdot \eta(\lambda) \cdot A(\lambda) = g \cdot \eta(\lambda) \cdot \left(1-R(\lambda)\right) \cdot e^{-\alpha_{diam}(\lambda) d_{diam}}$$

Fig. 4. He–Ne emission spectrum measured by the two devices.

Fig. 5. He–Ne spectrum measured by PIM detector in the range 20–30 nm.

Fig. 6. Responsivity of both devices.

Fig. 7. External quantum efficiency (EQE) of the PIM device between 20 and 120 nm. The dotted and solid lines correspond to Eq. (1) for $g = 1$ and $g = 0.1$ respectively. The dashed curve corresponds to Eq. (1) with $g = 1$ and adding a 10 nm thick dead diamond layer.
The efficiency curve reported in Fig. 7, calculated by using $d_{\text{diamond}} = 10 \text{ nm}$, now shows a good agreement with the experimental data.

4. Conclusions

Two detectors were fabricated at the University of Rome “Tor Vergata” with a structure that acts as a metal/intrinsic/p-doped diamond photovoltaic Schottky diode. The two detectors operate in different configurations: one in transverse geometry and the other in planar configuration.

We have measured the electrical characteristics and tested the performances under continuous vacuum UV photon irradiation of the two devices. A general result of our experiments is that diamond detectors exhibit a low dark current and a very good signal-to-noise ratio. The responses are reproducible and undesired effects such as persistent photocurrent, priming or memory effects are negligible for both devices. The response time could not be measured, being much lower than the acquisition rate of the used electronic chain ($\sim 60 \text{ ms}$).

These results indicate the high quality of our CVD diamond grown for UV applications.

The responsivity and the EQE of the two devices show an opposite behaviour as a function of the radiation wavelengths due to the different operative configurations. In particular the PIM detector is more efficient at lower wavelengths and presents a drop of sensitivity at approximately 100 nm. The IDT-PIM is less efficient at low wavelengths and has a maximum efficiency at about 73 nm. Moreover, the measured EQE of the PIM detector was compared with the theoretical curve taking into account the detector structure. The simulation results seem to indicate that the presence of a thin dead diamond layer at the diamond–metal interface should be taken into account. Work is in progress to study the influence of the metallic contact material upon the detection performance of the devices.

References