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Rectifying properties and photoresponse of CVD diamond p(i)n-junctions

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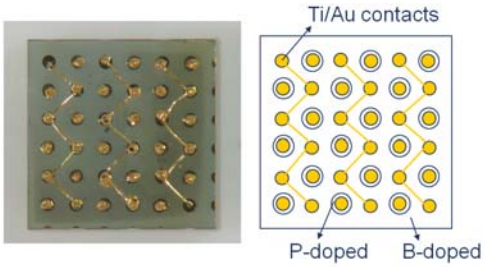
The current-voltage characteristics and photoresponse of mesa structured {111}-oriented homoepitaxial CVD diamond pin-junctions with different intrinsic layer thickness are investigated. When a sufficient thick intrinsic layer is present, a rectification ratio of 10^8 at ± 10 V could be obtained. Good rectifying diodes show a high photoresponse ratio between 210 nm (above bandgap) and 500 nm (below bandgap), making them suitable for UV detection purposes. The results are compared with similar measurements carried out on polycrystalline CVD diamond pn-junctions.



18 Diamond pin mesa structures (250 µm in diameter) based on a boron-doped/intrinsic/P-doped CVD layer stack deposited on a 2 x 2 x 0.5 mm³ {111} Ib HPHT diamond substrate.

1 Introduction

Since the first report by Koizumi *et al.* in 2001 on the formation of homoepitaxial CVD diamond pn-junctions based on boron and phosphorus doped diamond, a lot of progress has been obtained in optimising such structures on both the main crystallographic facets, {111} and {001} [1-3]. In fields like space weather, the use of diamond is envisaged for UV detection due to its so-called solar blindness. The low response to visible light compared to UV light, makes the use of filters for the visible part of the spectrum obsolete, enhancing the overall signal to noise ratio [4]. In the second half of 2009, the Proba2 satellite will be launched, containing a solar UV radiometer (LYRA) [5] based on diamond photodiodes [6] and photoconductors [7]. This paper investigates the influence of the intrinsic layer thickness on the current-voltage characteristics and the photoresponse of single crystal CVD diamond p(i)n-diodes, comparing results with promising large area polycrystalline pn-junctions.

2 Experimental

Four different sets of homoepitaxial p(i)n-junctions were deposited on {111}-oriented 2 x 2 x 0.5 mm³ HPHT Ib substrates from Sumitomo, Ltd, using a methane-to-hydrogen ratio of 0.05 %. As dopant precursor gasses trimethylboron (C_3H_9B) (TMB) and phosphine (PH_3) were utilized. All deposition processes were carried out at a pressure of 100 Torr, with the substrate temperature during B-doping being between 900 and 950 °C, while P-doped layers were grown between 870 and 900 °C. All the p(i)n-structures were deposited in two growth runs, using two two different ULVAC stainless steel chamber microwave plasma enhanced deposition reactors [1,8]. The difference between the four different structures can be found in Table 1. Based on experience and SIMS measurements carried out on similar samples, a growth rate of 0.5 µmh^{-1} was estimated for the 2nd deposition run, corresponding to intrinsic layer thicknesses of 1, 0.5 and 0.25 µm respectively for Set 1 to 3 [1,8].

Table 1 Growth steps used for the four different sets of {111} homoepitaxial CVD diamond p(i)n-junctions.

Growth step	Set 1	Set 2	Set 3	Set 4
B-doping [TMB]/[CH_4]	4 h – 1000 ppm			
	2 h – 100 ppm			
Intrinsic	2 h	1 h	0.5 h	–
P-doping [PH_3]/[CH_4]	0.25 h – 5000 ppm			1 h – 100 ppm
P-doping [PH_3]/[CH_4]	–			0.25 h – 2000 ppm

To create 18 mesa structured p(i)n-diodes per substrate, each 250 µm in diameter (see abstract picture), reactive ion etching (RIE) is used in combination with Al masks. This procedure, of which a detailed description can be found in ref. [8], enables contacting the previously buried bottom B-doped layer. Finally, Ti/Au stacks (Ø 150 µm) are used as Ohmic contacts to enable the collection of (photo)current.

Two different types of polycrystalline pn-diodes were created using two different P-doping procedures, with the main differences being the used deposition temperature and methane concentration. Full details on the growth can be found in Refs. [9] and [10]. In both cases, polished freestanding B-doped polycrystalline substrates were used of several hundreds of microns thickness. Contacts were applied on the bottom and top of the freestanding boron-doped/P-doped CVD layer stack.

The IV-characteristics are collected in the dark at room temperature using a wafer prober, applying the voltage with respect to the electrode on the p-type layer, hence addressing each mesa-structure separately. Photoresponse measurements are performed using ~ 13.33 Hz chopped light from a Xe and deuterium lamp in combination with a monochromator and lock-ins. For more details, see [11].

3 Results and discussion

In an attempt to correlate the rectifying properties with the photoresponse, all the structures were characterized with respect to their IV-characteristics. The best results obtained per set (2x 18 mesas) are depicted in Figure 1. It is obvious that Set 1 and 2, corresponding with an intrinsic layer thickness of 1 and 0.5 µm, yield the best result with respect to the rectifying properties of the p(i)n-diodes. At ± 10 V, a rectification ratio of 10^8 can be reproducibly obtained on several mesa structures of Set 1, with Set 2 showing a ratio nearly matching that, i.e. ~ 5 x 10^7. Due to the limitations of the measurement set-up, the minimum measurable current is limited to ~ 50 pA, explaining the similar current levels for the diodes of Set 1 and 2 for voltages below + 3.4 V. Hence, it can be assumed that lower current detection would yield results surpassing those currently obtained. Although the forward current is clearly influenced by a large series resistance, mainly coming from the P-doped layer, the rectifying properties at ± 10 V are similar to the ones recently reported by Oyama *et al.* on a p^+in^+-diode, where the use of heavily doped layers containing more than 10^{20} cm^{-3} B and P, leads to a much reduced resistivity due to hopping conduction [3].

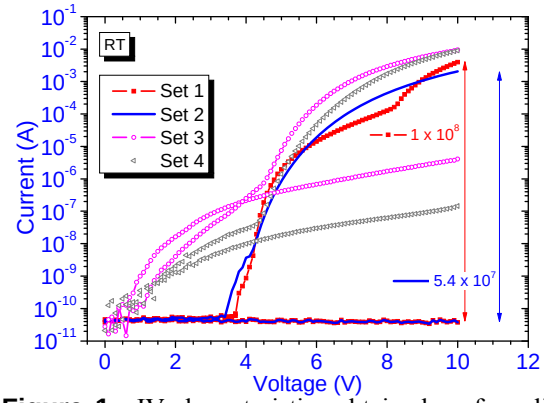


Figure 1 IV-characteristics obtained on four different homoepitaxial mesa structured p(i)n-diodes.

Figure 2 shows the relative photoresponse of single mesa p(i)n-diodes of each sample set. The same mesas used to obtain the data of Figure 1 were measured in photovoltaic mode. The absence of a bias voltage prevents detection of persistent photocurrent after excitation, guaranteeing devices with a response time below 75 ms. For reasons of comparison, all the data were put on the same value at 210 nm (~ 5.9 eV). The ratio between the response at 210 nm and 310 nm reaches a maximum value of 2 x 10^4 for the mesa of Set 2, with almost a similar value for the mesa of Set 1. As can be seen, most of the single mesas don't yield a measurable response below 3.6 eV, demonstrating very low sub band gap absorption. The data of Set 3 and 4 evidently show a worse response, i.e. more current in the unwanted region below the band gap. This current can be attributed to defect states in the gap induced by imperfections in the diamond lattice. The exact nature of these defects is not known at this stage, but they can be intrinsic (dislocations, …) or extrinsic (impurities,…). The presence of defects can also explain the poorer rectification ratio for these samples, with larger reverse currents as a result. By contrast, the combined response of three mesas of Set 1 can be measured for lower energies, yielding a photoresponse ratio of more than 10^5 for $I_{210\ nm}$ / $I_{500\ nm}$, suggesting even better results for a single mesa.

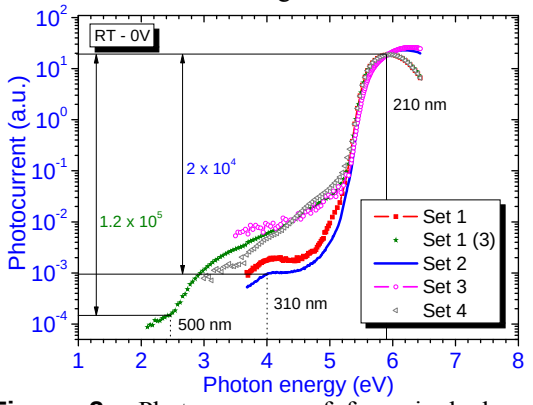


Figure 2 Photoresponse of four single homoepitaxial mesa p(i)n-diodes, and the combined response of three mesas of Set 1.

Based on an estimation of the light intensity impinging on the 250 µm in diameter mesa (of which the central part is covered with the Ti/Au contact of 150 µm Ø) and the corresponding current that is generated, the absolute responsivity of the best mesa is assessed as ~ 1 x 10^{-3} A/W @ 200 nm (6.2 eV). This value is only one order of magnitude lower than reported in literature for a 5 mm in diameter pin-diode which has more than two orders higher active area [6]. As it is much harder to get high quality large area HPHT diamond substrates, this directly influences the structural condition of the layers grown upon them, and thus also their (photo)electrical properties.

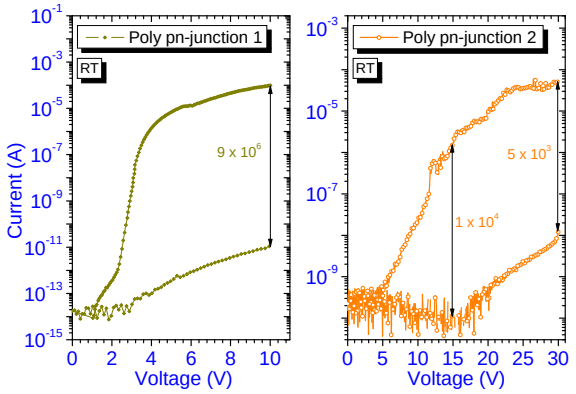


Figure 3 IV-characteristics of polycrystalline pn-diodes deposited using two different P-doping procedures.

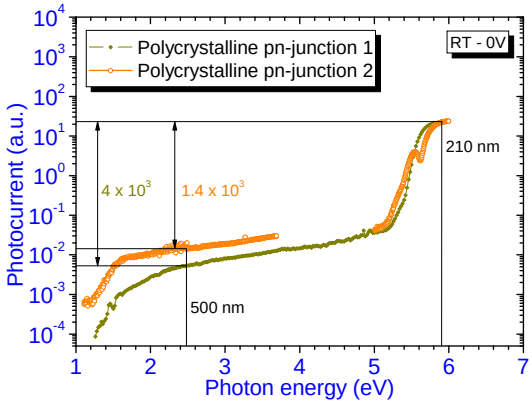


Figure 4 Relative photoresponse of the two polycrystalline pn-diodes used for Figure 3.

Finally, as single crystal diamond substrates are still expensive and limited in size, the possibility to use polycrystalline pn-diodes was investigated. Figure 3 shows the IV-characteristics of two different poly diodes as described in Section 2. Even though both junctions show clear rectifying behaviour, the 2nd type suffers from a very high series resistance and a noisy signal. This can be explained by the rather thick (~ 20 µm) P-doped layer, exhibiting a rough surface that influences the contact properties [12]. Being polycrystalline in nature, thus having grain boundaries, it can be expected that the rectification ratio is lower than those obtained for single crystal p(i)n-junctions. This is also reflected in the photoresponse, shown in Figure 4. The sub band gap absorption for polycrystalline diamond is proven to be higher than for single crystal diamond, mainly due to the presence of π and π* states in the band gap [13]. Even so, the photoresponse ratio $I_{210\ nm}$ / $I_{500\ nm}$ still reaches values of more than 10^3, which might be acceptable for certain applications given the highly reduced cost when working with polycrystalline materials that can be deposited over large areas. There is very little difference between the different poly pn-diodes in this respect.

4 Conclusions

The presence of an intrinsic CVD diamond layer of at least 500 nm, clearly enhances the rectifying properties of mesa structured {111}-oriented homoepitaxial CVD diamond pin-junctions. At ± 10 V a rectification ratio of more than 10^8 could be obtained. These diodes also show a > 10^5 photoresponse ratio $I_{210\ nm}$ / $I_{500\ nm}$. Although polycrystalline CVD diamond pn-junctions perform not as good as their single crystal counterpart, the results are encouraging for large area diamond electronic applications.

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