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Homoepitaxial {111}-oriented diamond pn junctions grown on B-doped Ib synthetic diamond

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Boron- and phosphorus-doped diamond layers were grown successively by microwave plasma-assisted chemical vapour deposition on {111}-oriented boron-doped Ib substrates. The resulting diodes were studied electrically with and without metallization. Although cathodoluminescence results showed that the material quality of the p-type {111} layer could still be improved, Electron Beam Induced Current imaging (EBIC) provided evidence for a space charge region. At room temperature, I(V) characteristics yielded a rectification ratio at +/– 25V varying between 10^4 and 10^9. In some cases, this figure remained greater than 10^6 up to 200 °C, despite a marked increase of the reverse current with temperature.

1 Introduction

Many fundamental properties of diamond make it an attractive material for active semiconducting layers in specific electronic devices to be used under extreme conditions of pressure, temperature, wear or radiation, as well as in chemically aggressive environments. In spite of early announcements [1], the considerable difficulty of achieving a suitable and controlled n-type conduction in this material has hindered the practical production of bipolar diamond devices, and most applications under development are using p-type diamond and a Schottky diode design. Nevertheless, the remarkable progress in n-type doping of diamond [2–4] observed since 1997 in various laboratories has led to a few reports of pn junctions [5–8] with rectification ratios between 10^3 [5] and 10^5 [6, 7]. Under high forward bias these devices have been shown to emit excitonic and defect-related electroluminescence in the UV and visible range respectively [6–8].

Earlier work convinced us that despite the difficulties of {111}-oriented growth [9], a proper control of n-type doping could be obtained during the plasma-assisted growth of diamond in the presence of phosphine [2, 3, 7]. We thus grew phosphorus-doped epilayers on top of p-doped {111}-oriented homoepitaxial films, with the aim of obtaining higher rectification ratios under high dc bias (20–30 V). In this paper we report on the electrical and cathodoluminescence characteristics of some pn junctions produced by this method.

2 Experimental

The boron-doped and phosphorus-doped diamond epilayers were grown successively in two independent NIRIM-type vertical silica tube reactors by Microwave Plasma-enhanced Chemical Vapour Deposition

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(MPCVD). The Ib diamond 2 × 2 mm^2 commercial substrates (either boron-doped or nominally undoped) were placed on a diamond-coated silicon substrate holder in the centre of the plasma ball. Two different sets of conditions led to two series of diodes.

In order to determine the boron incorporation on {111}-oriented surfaces, a control layer (sample CN58, 1 µm-thick) was deposited on a HPHT type Ib substrate in the reactor dedicated to the growth of p+ and p-type diamond. The growth temperature was 950 °C and the total pressure was set at 50 Torr with a 0.25% CH_4/H_2 gas mixture flowing at 200 sccm. Eventhough there was no intentional introduction of diborane into the plasma, an incorporation around 3×10^{18} B/cm^3 was detected by Secondary Ion Mass Spectroscopy. This was attributed to the residual boron content resulting from previous runs in this cold wall reactor. Despite this high value, a first attempt at producing a pn junction was made: a thinner p-type epilayer was deposited under the same conditions on a B-doped Ib-type {111}-oriented substrate, before a second layer was grown in another chamber dedicated to n-type diamond. In this case, phosphorus incorporation resulted from adding phosphine to a 0.15% CH_4/H_2 mixture with a $(P/C)_{gas}$ atomic concentration ratio of 500 ppm. Growth pressure and temperature were the same as for p-type layer epitaxy. Examination under the optical micoscope of the surface of the resulting bilayer (CN59, nominally 0.4 µm n-type on 0.5 µm p-type) showed that it was free of cracks although a major part of its surface was rough, probably because of the high deposition temperature and/or the high methane content.

For that reason, when the second bilayer (sample CN69) was deposited on the same type of substrate as sample CN59, both layers were prepared with a low methane concentration (0.15%) and at a lower temperature (880 °C) resulting from a weaker plasma power (250 W). For the p-type layer, unintentional residual boron contamination was minimized and diborane was introduced in the chamber with a relative $(B/C)_{gas}$ ratio of 0.2 ppm. The $(P/C)_{gas}$ ratio for the n-type diamond growth was 650 ppm. A square array of 36 circular metallic dots (150 µm in diameter) was then evaporated on the smooth surface of this sample, in the following order: first, 40 nm Ti to ensure adhesion, then 25 nm Al to prevent interdiffusion, and last 55 nm Au as capping layer.

For the electrical measurements performed in vacuum (around 10^{-4} Torr) with a Keithley 236 Source Measurement Unit, silver/epoxy paste was used to contact gold wires on individual metallic pads. The cathodoluminescence (CL) spectra were collected at 5 K in a FEI-Quanta 200 Scanning Electron Microscope (SEM) at high injection (spot size 8, i.e. around 50 nA) with a home-made mirror coupled to the 50 µm-wide entrance slit of a HR 460 Jobin Yvon monochromator (600 gr/mm) equipped with a liquid N_2-cooled CCD array. The Electron Beam Induced Current (EBIC) images were obtained at room temperature with a home-made isolated sample holder adapted to the same SEM.

3 Results and discussion

3.1 Cathodoluminescence

Figure 1 shows the CL spectra of samples CN58 and CN59 taken with electron beam acceleration voltages low enough to result from the radiative recombination processes taking place within the film(s). The absence of a free-exciton related peak FE^{TO} and the width (40 meV) of the boron-bound exciton peak $^{B}BE^{TO}$ detected at 5.195 eV in the spectrum of the p-type layer (CN58) confirmed the poor quality and rather high boron concentration of this {111}-oriented layer. The spectrum of the associated n/p stack of layers (CN59) was somewhat richer, with even broader features and both a high and a low energy shoulder on the aforementioned 5.195 eV peak, not clear enough to be attributed to the free exciton, or to the phosphorus-bound exciton $^{P}BE^{TO}$ and its zone centre phonon replica $^{P}BE^{TO+O}$ which have been detected in other P-doped films [10].

Evidence for the presence of a space charge zone was obtained by plane view EBIC investigations of the metallic circular dots on sample CN69, as shown by Fig. 2. In Fig. 2b, only the pad contacted with a gold wire (see the secondary electron image in Fig. 2a) yielded a strong contrast. This corresponds to the electron–hole pairs generated near or at the junction by the 30 kV electrons having penetrated through the metallic layer stack. The other contacts can also be identified in Fig. 2b, but only as a result of the absorption current mode. The lateral decay of the EBIC signal at the edge of the contacts provide some

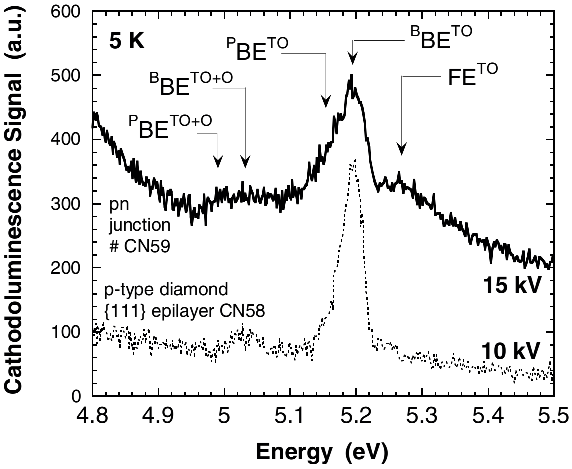

Fig. 1 CL emission spectra in the excitonic range (225–260 nm) taken at 5 K on the control layer CN58 (dotted line) and on the n/p bilayer CN 59 (upper continuous trace). Spectra were vertically offset for clarity.

indication on the minority carrier diffusion length and thus on the μτ product. More local observations at 5 kV showed the diffusion length to be below 1 μm at room temperature. Cross-section EBIC investigations are under way, which should bring more quantitative information about the junction, as already published in previous reports on diamond [1, 11].

3.2 I(V) characteristics

The simplest way to characterize electrically a pn junction such as sample CN59 was to put a polarized tungsten tip in contact with the phosphorus-doped upper layer. Under vacuum conditions, rather high d.c. bias (+/–120 V) could be applied to this structure and the resulting I(V) characteristic, shown in Fig. 3a for a temperature of 125 °C, was clearly rectifying. However, the rectification ratio at +/– 25 V was only one order of magnitude and the reverse bias behaviour obviously non ohmic at high voltages. These features may be due to the high contact resistance on the n side, which limits the forward current (negative d.c. bias), and to the probable leakage (at low bias) and tunnelling on localized states (at higher bias)

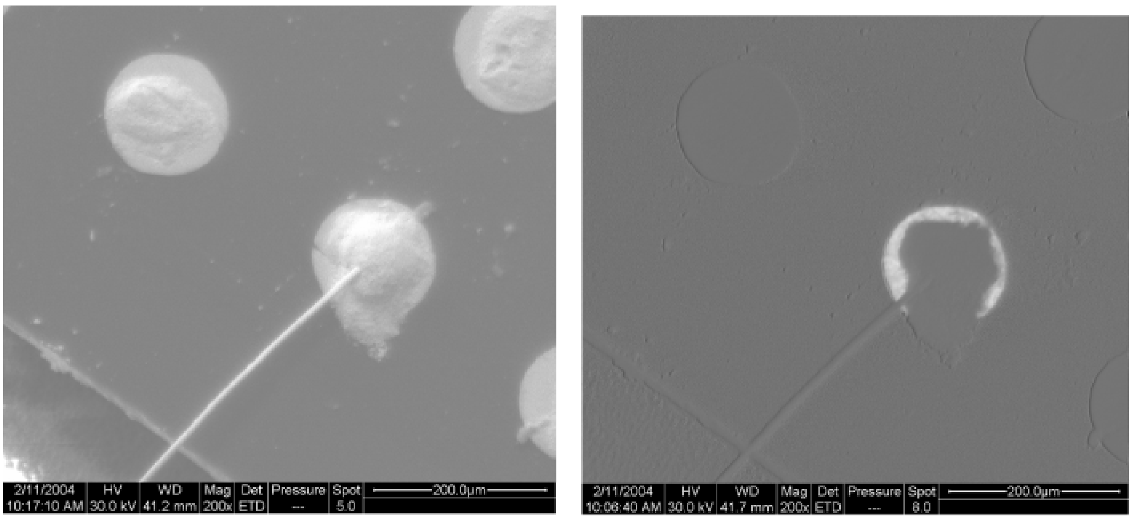

Fig. 2 a) Secondary Electron SEM 0.6 × 0.5 mm^2 image at 30 kV of sample CN69, with a gold wire pasted to the surface of the pad of diode d5. b) EBIC images of pad d5 in plane view at room temperature. The non-contacted diodes and the wire and paste barely yield any contrast.

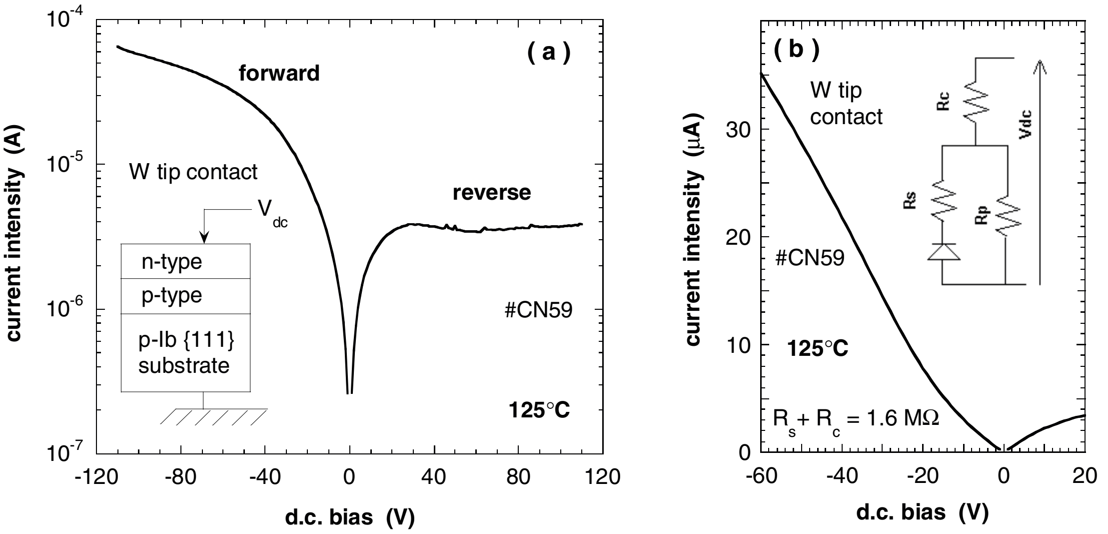

Fig. 3 Logarithmic (a) and linear (b) I(V) characteristics of bilayer CN59 measured directly with a tungsten tip at 125 °C; the sign of the reverse current has been inverted. Definition of the contact resistance R_c and of both the series R_s and parallel R_p resistances on the corresponding electrical circuit.

which affected strongly the reverse current. More precisely, using a simple equivalent circuit also represented in Fig. 3, the sum of the contact resistance R_c and of the series resistance R_s of the device was about 1.6 MΩ as deduced from the forward I(V) dependence, which was linear (see Fig. 3b) rather than exponential.

A much stronger rectification was observed with the diodes defined on sample CN69 by evaporated metallic contacts for which the contact resistance R_c was considered negligible in comparison to the device impedance. In Fig. 4, the I(V) characteristic measured at 0 °C in vacuum is shown for one of the evaporated dots (d1). The reverse current was in the sub-nA range, and its linear dependence on the d.c.

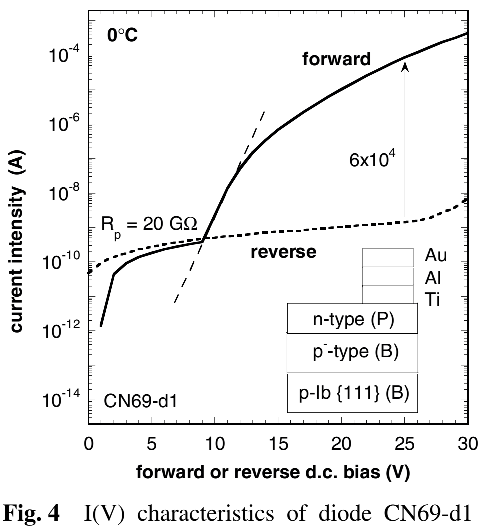

Fig. 4 I(V) characteristics of diode CN69-d1 recorded at 0 °C under vacuum conditions, and a schematized cross-section of the diode structure. The sign of the reverse current has been inverted. Estimates are proposed for the parallel resistance and the rectification ratio.

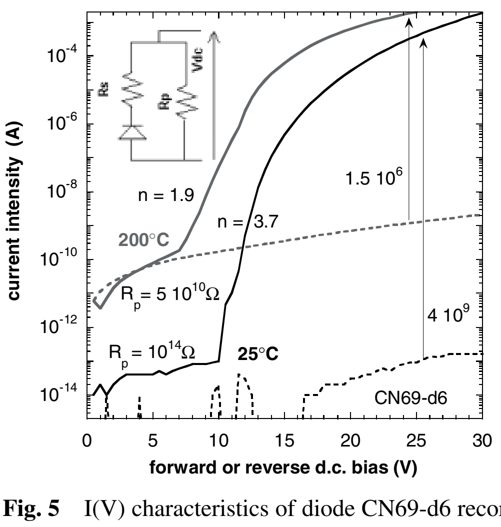

Fig. 5 I(V) characteristics of diode CN69-d6 recorded at 25 °C and 200 °C in vacuum for reverse (dotted) and forward (continuous) bias. Estimates for the parallel resistance, the rectification ratio and the ideality factor n are also given.

reverse bias (no tunnelling here) led to a parallel leakage resistance of a few 10^{10} Ω. The forward current was strongly limited by the series resistance, so that the exponential I(V) behaviour could be observed only in a restricted V_{dc} range around 10 V (too narrow to allow a proper determination of the ideality factor n). The rectification ratio at +/– 25 V was equal to 6×10^4 for this particular diode (d1), in agreement with most previous reports on diamond pn diodes [5–7]. This figure varied from 10^4 to 10^9 from dot to dot over the whole 2 × 2 mm^2 bilayer surface. Such an I(V) characteristic showed moreover that the depletion region detected by EBIC below the metallic contacts was due to the pn junction and not to a Schottky barrier.

As shown in Fig. 5, in a more favourable case (d6) the reverse current at room temperature was barely measurable (10^{-15} to 10^{-13} A range), and the value of the parallel resistance was around 100 TΩ. The rectification ratio for this device was 4×10^9 at +/– 25 V, a figure to our knowledge comparable to the best value yet reported: a 10^{10} ratio obtained recently at +/– 10 V on similar but mesa-etched pn structures [12]. The ideality factor at room temperature was close to the value of 3.5 reported for mesa-etched diodes [12].

When the operating temperature was raised, the diamond pn junction maintained a rectifying behaviour at least up to a temperature of 400 °C in vacuum. However, the reverse current increased markedly, as illustrated by the I(V) characteristic of the same diode CN69-d6 measured at 200 °C, where the parallel leakage resistance has dropped from 10^{14} to 5×10^{10} Ω. The resulting rectification ratio was still around 10^6 at this temperature, while the ideality factor dropped to 1.9, in agreement with the variations observed on mesa-etched devices [12]. Preliminary estimates of the activation energy of the reverse current at 15 V yielded a value of 0.1 eV suggesting that the reverse current was not flowing through the pn junction.

4 Conclusion

In conclusion, we have shown that n-type phosphorus-doped diamond layers deposited on unoptimized p-type boron-doped {111}-oriented epilayers form pn junctions with a space-charge zone detected by EBIC. Electrical measurements have demonstrated that promising rectification ratios around 10^9 could be obtained at room temperature under vacuum conditions even without mesa-etching, and that a rectifying behaviour could still be observed at 400 °C. we believe that these performances could still be notably improved if the growth of the p-doped layer on {111} conditions was optimized further.

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