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Study of boron doping in MPCVD grown homoepitaxial diamond layers based on cathodoluminescence spectroscopy, secondary ion mass spectroscopy and capacitance–voltage measurements☆☆

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ABSTRACT

Boron incorporation from the gas phase was achieved in MPCVD grown (100)-oriented homoepitaxial diamond layers, either with or without a small fraction of oxygen in the gas phase, in addition to hydrogen, methane and diborane. From secondary Ion Mass Spectroscopy (SIMS), it is shown that the 0.25% of oxygen decreases the Boron concentration [B] by two orders of magnitude. In this way, we demonstrate that it becomes possible to control [B] with low levels of compensation and passivation down to the 10^{15} cm^{-3} range. Cathodoluminescence spectroscopy is systematically performed in seventeen samples under a 10 kV acceleration voltage at 5 K and the exciton bound to boron (BE_{TO}) intensity to the free exciton (FE_{TO}) intensity ratio is evaluated (I_{BETO}/I_{FETO}). A linear relationship between I_{BETO}/I_{FETO} and [B] with a coefficient of 3.5×10^{16} cm^{-3} is demonstrated for [B]$<3\times10^{17}$ cm^{-3} in single crystalline diamond, irrespective of the gas phase composition during growth.

1. Introduction

With its large indirect energy gap of 5.45 eV, diamond is well known to cumulate many superlative properties that makes it a very unique material for power electronic applications such as a breakdown electric field typically 30 times higher than silicon, a thermal conductivity 4 times higher than copper, and much larger mobility values for holes when compared to all other bulk semiconductor systems [1]. However, due to the intrinsic difficulties in achieving the n-type phosphorous doping of the material under good conditions, it is noteworthy to date that most of the applications of diamond to electronics rely on unipolar device technologies based on p-type doped diamond with boron [1,2], whose shallow acceptor energy level lies in the gap at 0.37 eV above the top of the valence band [3].

The Microwave Plasma Chemical Vapour Deposition (MPCVD) growth technique, where boron can be introduced in the gas phase as diborane (B_2H_6) or trimethylboron (TMB) species, is very efficient to incorporate boron in a controllable and flexible way during the diamond epitaxial growth of thin films. With a covalent radius that closely compares with carbon, boron substitutionally incorporates easily into the MPCVD grown diamond lattice even up to very high levels of concentrations of about 10^{21} cm^{-3} (and even slightly higher) without either producing structural damages in the bulk (graphitic phases micro-inclusions, etc.) or condensing as boron metallic clusters. It therefore gives the technical possibility to widely tune as a function of doping the diamond electrical properties from semiconductor to metallic, with a metal-insulator transition which typically lies at a boron concentration N_A of 4.5×10^{20} cm^{-3} for (100)-oriented homoepitaxial diamond [4]. On the other side, accurately controlling low levels of boron incorporation in diamond is a key issue for matching the requirements of device-quality MPCVD homoepitaxial diamond layers in electronic applications such as Schottky rectifiers or field effect transistors. In such devices, suitable boron concentrations in active layers typically lie in the 10^{16} cm^{-3} or 10^{15} cm^{-3} ranges. This property must be linked with a high chemical purity and a high crystalline perfection, involving a low density of extended defects (dislocations, stacking faults, …). If these characteristics are both achieved, low electrical compensation ratios N_D/N_A (where N_D is the donor concentration) allow to combine in such layers the advantages of optimal electrical carrier transport properties, low leakage currents and high breakdown electric fields. The MPCVD growth conditions with H_2/CH_4/TMB [5] have already proven their ability to obtain excellent device quality (100) oriented homoepitaxial boron doped diamond layers, down to the 10^{16} cm^{-3} range. We daily checked that $H_2/CH_4/B_2H_6$ plasmas make hardly

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achievable the control of boron concentrations below the few 10^{16} cm^{-3} range. This problem is real, even if very low levels of gaseous *B*/*C* ratios down to less than 0.1 ppm or even unintentional doping without any voluntary boron precursor introduced in the MPCVD machine. In such a context, introducing in such plasmas a small amount of oxygen (O_2/H_2 ratio in the 0.1–0.25% range) in the gas phase therefore looks extremely attractive. As shown in this work, it cumulates indeed the possibility to drastically divide the boron incorporation in the solid phase by a factor of 100 in the (100) oriented homoepitaxial diamond at a given *B*/*C* ratio in the gas phase [6,7], together with a significant decrease of the parasitic silicon and nitrogen incorporation [6,8] and a significant improvement of the structural properties of the diamond layers that appears to be mainly associated with much lower concentrations of parasitic phases [8–11]. Additionally, we recently experimentally demonstrated that the presence of oxygen at a 0.25% O_2/H_2 ratio during the MPCVD growth was yielding optimal electrical transport properties that could be considered as the signature of a low compensation by donors in the bulk. Notably, a room temperature 1870 cm²/V·s hole Hall mobility, very close to the intrinsic mobility limited by phonons, was obtained under such growth conditions in (100)-oriented homoepitaxial boron doped diamond with a SIMS boron concentration of 1.4×10^{16} cm^{-3}[12,13].

As long as the intentional bulk boron doping is considered in diamond growth, measuring the boron concentration in an accurate way remains recurrently as a very critical issue. In the case of low doping, the total boron incorporation in the lattice clearly includes three main separate components:

1. The substitutional single atom boron concentration, $[B]_S$. Such boron atoms correspond to the electrically active shallow acceptors, with the expected ionization energy level of 0.37 eV above the valence band [3].
2. The boron passivated by hydrogen concentration, [BH]. Such single substitutional boron atoms bound to hydrogen atoms are known to behave as electrically inactive species, all with deep energy levels in the gap [14–17].
3. The boron-point defect complexes, involving mainly vacancies, [BV complex]. Such boron atoms also give deep energy levels in the gap [18] and therefore are not electrically active.

Another important contribution to take into account is the total donor concentration N_D, as the capacitance–voltage ($C(V)$) measurement gives information on the $[B]_{CV} = N_A - N_D = [B]_S - N_D$ concentration, corresponding to the only non-electrically compensated boron atoms. Although destructive, the Secondary Ion Mass Spectroscopy (SIMS) technique is a very good tool to precisely determine the absolute total concentration of boron ($[B]_{SIMS} = [B]_S + [BH] + [BV\ complex]$), however with an instrumental low boron detection limit of 10^{16} cm^{-3}. Cathodoluminescence (CL) at temperatures close to the liquid He one, also quite convincingly appears as an efficient non-destructive tool for boron dosimetry. It is indeed able to extract even more accurately the same kind of information from the free and bound excitons optical features within a very large boron concentrations scale that ranges from 10^{15} cm^{-3} up to 10^{21} cm^{-3}[19–21]. Let us note however that as B–H pairs can be dissociated under the electron beam excitation with a 10 kV accelerating voltage [15] and beam current densities in the range 20–60 nA/μm^2 like we are using, the CL boron concentration must be written in our experiments as $[B]_{CL} = [B]_S + [BH]$. Data presented further will support this hypothesis.

In summary, the combination of these three boron concentration measurement techniques gives access to the total boron concentration in a given sample as well as to the compensated and the passivated ones, and therefore this helps to understand acutely the boron incorporation and activity in diamond epilayers. In this scope, this paper aims first at determining and discussing the positive active physico-chemical role of oxygen in the boron-doped homoepitaxial diamond MPCVD growth. In a second target, it reliably qualifies (for the first time with a large number of experimental points) the CL technique as a non-destructive tool for determining the absolute low boron concentration in the (100)-oriented diamond in the full 10^{14}–10^{18} cm^{-3} range, with the help of an analysis performed over a large series of samples and based on a close comparison with the SIMS boron concentration results.

2. Experimental techniques

I_b (100)-oriented $3 \times 3 \times 0.35$ mm^3 Sumitomo substrates were used in our studies. The diamond substrates were chemically cleaned prior growth in hot $HClO_4$:H_2SO_4:HNO_3 1:3:4 V/V, followed by a hot HF:HNO_3 1:1 V/V etching treatment. The diamond growth was carried out in a home-made NIRIM-type vertical MPCVD reactor, equipped with a 40 mm-diameter external cylindrical-shaped quartz growth chamber, fed with ultra-purified H_2, CH_4 and B_2H_6–H_2 mixture through a three stages dilution system. The 3×3 mm² diamond sample was supported on the top of a 25 mm-diameter internal quartz stage at the bottom frontier of the plasma ball, and was inserted into a silicon holder coated for passivation with non-intentionally doped polycrystalline diamond. The growth chamber was pre-evacuated overnight prior to growth down to the 10^{-6} Torr range using a secondary turbomolecular pumping. In order to perform the growth, metered amounts of H_2 purified in the ppb range, CH_4, B_2H_6 (and, eventually, additional oxygen) were introduced from the top side of the growth chamber, and the plasma excitation was produced using a 2.45 GHz microwave generator. The growth pressure was manually regulated at 50 Torr with a needle valve, and the growth temperature is measured with a single color pyrometer.

The calibrated boron concentration profiles were taken in a CAMECA IMS 4f SIMS equipment. Boron implanted diamond samples were used for calibration. The cathodoluminescence spectra were measured at 5 K in a Quanta 200 Scanning Electron Microscope (SEM) coupled through a mirror to the 100 or 50 μm-wide entrance slit of a HR 460 Jobin Yvon grating (600 g/mm) monochromator equipped with a liquid nitrogen-cooled CCD array. The spectra were excited with a 10-kV electron beam for epilayers with thicknesses of 1 μm or above. The pixel-to-pixel spectral spacing was 2.0 meV around 5.25 eV. Schottky diodes were processed in order to perform the $C(V)$ measurements, which remain meaningful as long as the reverse currents do not exceed 10 μA in our two experimental set-up. This condition has been carefully checked and fulfilled in all the diodes that we have measured. The diameter of each Schottky contact pad was generally 200 μm, resulting in capacitances in the range 1–10 pF for diamond doped in the 10^{16} B/cm^3 range. The ohmic contact (Ti/Pt/Au) was annealed at 700 °C for 1 h in high vacuum (10^{-8} Torr) before fabricating the Schottky contacts. The gap between the Schottky diode periphery and the ohmic contact results in a series resistance and a diode cut-off frequency, depending on the sample and temperature. Most samples comprise a p−/p+ stack and display series resistance amounting to few hundreds ohms at room temperature, which resulted in cut-off frequencies in the range 20–120 MHz, well above the measurement frequency of 1 MHz. For other samples, which consisted of only a low boron doping epilayer, concentrations are deduced from $C(V)$ at an adapted temperature for ensuring that the cut-off frequency of the diodes stays above ten times the measurement frequency, which can be eventually decreased in extreme cases down to 1 kHz. Well significant $C(V)$ measurements, performed in similar conditions, have been already analyzed and published in several works [18–20].

3. Results and discussion

3.1. Role of oxygen on the boron incorporation/compensation/passivation and on the homoepitaxial diamond crystal quality

Both $H_2/CH_4/B_2H_6$ and $H_2/CH_4/B_2H_6/O_2$ microwave plasmas were considered in our studies. The detail of the homoepitaxial growth