Cathodoluminescence as a probe to study residual radiation damage in ion-implanted diamond

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Cathodoluminescence has been used to monitor the residual damage created in a type IIa diamond which had been implanted with carbon ions at a target temperature of $\approx$ 77 K followed by rapid thermal annealing to a temperature of 1200 °C. It has been found that a luminescence band with a width comparable to that of the blue "band A" band, typically observed in high purity type IIa diamonds, appeared in the ultra—violet at $\approx$ 4 eV. From doping studies, it is known that the residual damage which ensues when using this implantation—annealing route, acts electrically as donors situated at $\approx$ 4 eV below the conduction band. The results thus indicate that this new ultra—violet band is caused by transitions from the conduction band to the ground states of these donors.

1. INTRODUCTION

Diamond can be doped by means of ion implantation using the cold—implantation—rapid—annealing (CIRA) method [1,2]. Implantation is done at a low target temperature (typically liquid nitrogen) to inhibit diffusion of point defects, followed by rapid thermal annealing (RTA) to a suitable temperature where the point defects can, in contrast, diffuse and interact with each other. Implanted dopant atoms, for example boron, which combine with vacant lattice sites, become activated, while self-interstitial—vacancy recombinations, occurring at the same time, reduce the radiation damage which had been caused during ion-irradiation.

Owing to the finite width of the implantation—damaged layer, some of the self—interstitials can always diffuse away before annihilating vacancies. Damage, believed to be in the form of complex vacancy clusters [3], thus remains. Electrically, this damage manifests itself as deep—lying donor centres ($\approx$ 4 eV) [3] which can compensate lower lying boron acceptors and also scatter charge carriers [4].

Obviously, when doping diamond by means of ion implantation, an important object of the exercise is to reduce the donor centres, mentioned above, to a minimum. However, the choice of implantation—annealing parameters to achieve this objective, is not a trivial matter [5]. Ideally one needs a probe to study their formation.

It is well known that high purity type IIa diamonds display a broad blue luminescence band at $\approx$ 2.85 eV when excited by an electron beam [6]. This blue "band A" cathodoluminescence (CL) has been ascribed to donor—acceptor pair recombination [7], but recent results [8] indicate that this may not be the case. It is also known that this luminescence can be quenched by radiation damage when the diamond is subjected to high energy electrons [9]. It should thus be modified, either by changing the donor—acceptor pair densities or by strain quenching, when producing the donor centres discussed above. This may then provide the needed probe to study their formation and interactions.

This study reports on the preliminary results which have been found when measuring the CL spectrum from a type IIa diamond after sequential implantation steps with C^+—ions, each time using the CIRA route such that increasing quantities of the donor centres [10] were created without activating any acceptors, as would have been the case when using

B⁺—ions.

2. EXPERIMENTAL DETAILS

The preparation of the diamond, the implantation route and the annealing method have been described elsewhere [2].

The diamond was subjected to a series of consecutive implantation—annealing steps. During each of these implantation steps, the ions were implanted at different beam energies in order to create a uniform damaged layer from just beneath the surface to a depth of $\approx$ 0.25 μm [5]. The energies used, as well as the fractions of the total carbon ion dose implanted at these energies, are shown in Table 1. Also shown are the energies which would be required, according to the computer program TRIM92 [11], to obtain the same damage distribution when implanting B⁺—ions. Owing to the larger mass of the C⁺—ions, the total ion dose required to generate the same amount of damage, is less than for B⁺. In this study, the C⁺ dose step was 2.5×10^{15} cm^{-2}, which is equivalent to a B⁺ dose step of 3×10^{15} cm^{-2}.

After each C⁺ implantation step, the diamond was rapidly heated to 1200 °C and annealed for 5 minutes. It was then cleaned by boiling in an acid solution [2] followed by rinsing in distilled water, whence it was mounted for CL measurements.

The CL arrangement combined a standard Nuclide (Luminoscope) cold cathode electron gun and a McPherson, model 275, monochromator with a liquid nitrogen cryostat. By mounting the diamond at the focal point of a parabolic mirror, the light generated by the electrons could be collected and focused through a quartz lens on to the entrance slit of the monochromator. The light emerging from the exit slit was detected using a Hammamatsu model R928 photomultiplier tube. All measurements were done at liquid nitrogen temperature, and no corrections were made to the spectra for the response function of the latter device.

The electron beam of 0.3 mA could not be finely focused, and effectively covered the whole surface of the 8x4 mm² diamond face. It was possible to rotate the diamond relative to

Table 1
Ion energies and dose fractions used for each C⁺ implantation step of dose 2.5×10^{15} cm^{-2}. Also shown are the equivalent energies needed to generate the same distribution of damage with B⁺—ions, which require a dose step of 3×10^{15} cm^{-2} for the same amount of damage.

ENERGIES (keV)		DOSE:
C⁺	B⁺	Fractions of total
170	130	0.3750
140	110	0.1250
128	100	0.0625
116	90	0.0625
103	80	0.0625
90	70	0.0625
77	60	0.0625
64	50	0.0625
51	40	0.0625
37	30	0.0625

the electron beam, allowing the latter to intersect the surface at different angles and thus to penetrate to different depths. For the 10 kV electron beam used, an angle of 10° between the electron beam and diamond surface ensured that all the electron—hole pairs were generated within the ion—damaged layer [12].

3. RESULTS AND DISCUSSION

Each implantation—annealing step progressively quenched the blue "band A" CL. For the first few steps, the quenching was rapid, but it slowed down and seemed to approach a saturated value of $\approx$ 0.1x the original integrated intensity. However, at the same time a new broad luminescence band, centered around $\approx$ 4 eV, developed in the ultra—violet (UV) part of the spectrum. Initially, this band grew in intensity relative to the blue band.

In Fig. 1, the spectrum measured after the third implantation—annealing step is compared to the virgin spectrum which had been measured on the diamond before implantation en-
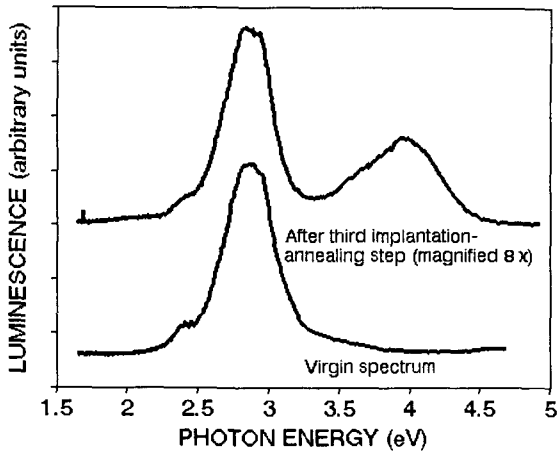
Figure 1. A comparison of the CL spectrum, with the virgin spectrum after three implantation—annealing steps.

sued. It can be seen that the UV band spans roughly the same energy interval as the well known 5RL band [13], but, in contrast, it shows no sharp zero—phonon lines. One cannot help to note that it peaks at ≈ 4 eV, which corresponds to the activation energy of the deep lying donors [3]. Owing to the fact that these donors had been deliberately created by the implantation procedure used in this study [10], it seems logical to assign this band to electron transitions between the conduction band and the ground states of these donors. If this is the case, it may indicate that the equally broad blue "band A" feature could also be due to transitions between band gap states and one of the carrier bands, for example the valence band, instead of donor—acceptor pair recombinations.

The integrated intensities were calculated by summing the measured intensities between photon energies of 2.5 and 3.3 eV for the blue band and 3.7 and 4.5 eV for the UV band. As a measure of the quenching, the integrated intensities for the blue bands measured after each implantation—annealing step, were normalized by dividing them with the corresponding value measured for the virgin diamond surface. The change in this parameter as a function of implantation—annealing steps can

be seen in Fig. 2. As already mentioned above, the quenching is quite rapid for the first few steps and then tends to slowly saturate at higher dose steps. From resistance measurements done previously [10], one expects that the residual vacancies, out of which the donors are assumed to be formed, will increase in a similar manner; initially rapidly, then tending towards saturation at higher implantation dose steps. It would thus seem that the quenching relates, at least qualitatively, to the increase in donors or rather the building blocks out of which they have formed. More measurements are needed to determine the relationship between the quenching and increase in vacancies, quantitatively.

At present the mechanism by which the donors cause the quenching, is not known. The measured spectra showed that, although the new UV band increased relative to the blue band, it also quenched with increasing implantation—annealing steps. If this band is a measure of the presence of the donor centres, as assumed above, it would indicate that their luminescence is quenched by the same mechanism responsible for the quenching of the blue band. Therefore, it seems probable that the quenching is caused by strain due to the presence of the radiation defects, even though these same defects seem to be responsible for
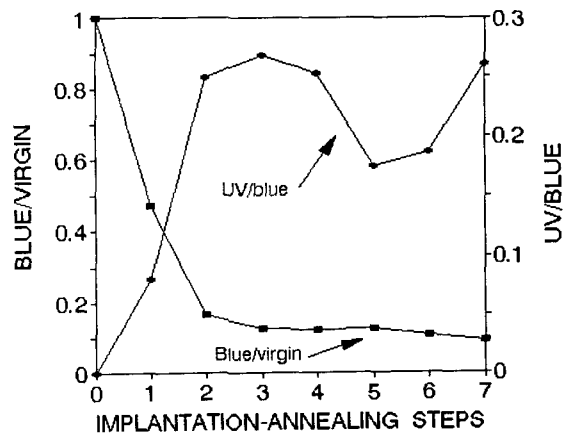

Figure 2. The ratios of the intensities of the blue band relative to the virgin value, and the UV band relative to the blue band, as a function of implantation—annealing steps.

the appearance of the UV band. Therefore, the ratio of the integrated intensity of the UV band to the blue band recorded in the same spectrum, was assumed to give a measure of the "growth" in the UV band with implantation—annealing dose steps; and this is also shown in Fig. 2.

As can be seen, the general tendency of the UV/blue ratio is to grow with increasing implantation—annealing steps. At this stage it is not known whether the relative decreases seen for steps 4 and 5 are real or caused by an experimental artifact. If not, it may give information on the manner in which the donor centres are being formed from the available vacancies. In this respect it should be noted that the 5 minute annealing steps chosen may be too short to allow all the vacancies created to form donor centres. Careful repetition of these measurements, as well as different implantation—annealing cycles, employing various temperatures and times, are needed to unravel the significance, if any, of this behaviour. However, the general tendency of the UV/blue ratio to increase with increasing donor centres, and the fact that this increase is rapid during the initial stages while slowing down at larger implantation—annealing steps, indicate that this ratio also relates qualitatively to the creation of the donor centres.

4. CONCLUSION

Although only isochemical carbon ions were used, these preliminary results indicate that CL may develop into a useful tool to study the residual radiation damage when subjecting diamond to different implanting and annealing cycles. The appearance of a UV band at ≈ 4 eV seems to relate directly to the deep lying donor centres, previously observed by electrical measurements, which form from the residual radiation damage during annealing. It is tentatively proposed that this band is caused by electron transitions from the conduction band to these donors.

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