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Activation of boron-dopant atoms in ion-implanted diamonds

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Different ratios of boron to carbon ions were implanted into diamond maintained at liquid-nitrogen temperature. After implantation, the diamonds were heated to 500 °C by dropping them onto a platform situated in a vertical tube furnace, and then annealed for 1 h. This was followed by a further anneal at 1200 °C in an argon atmosphere. It was found that under suitable conditions optical and electrical properties could be obtained which correlated with those found in natural semiconducting diamond. Thermally activated electrical conduction could, for instance, be established at an activation energy of ~ 0.37 eV, which corresponds to the value measured for substitutional boron acceptors in diamond. Owing to the annealing cycle used, a relatively large amount of products resulting from radiation damage remained, which, in the carbon-ion-implanted diamond, manifested itself by increased optical absorption at short wavelengths. The results indicate that the product responsible for this absorption may be acting as a donor center situated at about 4 eV below the conduction band. Thermal electromotive-force measurements correlate with the movement of holes in the valence band.

I. INTRODUCTION

Since the discovery of naturally occurring *p*-type semiconducting diamond by Custers[1] in 1952, electronic devices in diamond, obtained by controlled doping of this material, have been an exciting possibility. Owing to the unique properties of diamond, such as its strong atomic bonding, chemical inertness, metastability, and high Debye temperature, the most promising route leading towards controlled doping seemed to be via the ion-implantation method.

During the past 20–25 years, many investigations have been conducted on ion implantation of diamond. This research rendered numerous interesting but mostly uncorrelated results. Progress in this field has been reviewed from time to time.[2–8] Although Vavilov *et al.* in their pioneering work established that electrical conductivity may be obtained in diamond by ion implantation,[9] it is now clear that their results were probably not caused by substitutional activation of the implanted dopant atoms, but were directly related to, or dominated by, the radiation defects introduced. Confusion was possible because the intrinsic radiation defects in diamond can also act as donor and/or acceptor, or compensation centers and at high enough densities may even lead to "impurity" band conduction by means of the hopping mechanism.[10–12] Thus, although it was reported that Hall-effect measurements on boron-implanted diamond showed *p*-type conductivity[13] and that weak rectifying junctions could be obtained by boron and phosphorus implantation,[14] no convincing proof of the presence of uncompensated dopant atoms was presented. One is tempted to conclude that these results were caused by some form of conduction between radiation-damage centers or electrically active complexes formed by the implanted atoms and the residual radiation damage.

Later, new enthusiasm was generated by a patent claiming that diamond growth occurs when carbon ions are implanted into diamond at temperatures between 400 °C and 1200 °C.[15] This could only mean that the implanted atoms take up substitutional positions in the diamond lattice. In a further patent it was claimed that substitutional doping may be obtained in the same temperature range.[16] Reviewing their results at a later stage, the investigators reported that the implantation-grown diamond layers contain a dense distribution of dislocations, and concluded that growth occurred as a consequence of the agglomeration of migrating point defects to form this dislocation array.[17] Although it is possible that implanted dopant atoms may have ended up on substitutional sites, the clustering of point defects could interfere with the electrical conductivity. In fact, studies by other investigators in the same temperature range using ESR (Ref. 18) and ion channeling techniques[19–21] indicated that not all possible dopant atoms necessarily occupy substitutional positions, and even if they do, the lattice damage which remains compensates any electrical activity. The latter defects, tentatively identified as multivacancy clusters, proved to be very stable and could not be removed even at an annealing temperature of 1400 °C. It seems unlikely that effective and controlled doping can be achieved in this manner, as claimed by the second patent.[16]

Below these temperatures an increase in ion dose to high enough values apparently causes enough randomization of the atoms to cause graphitization during subsequent annealing.[12,22] During implantation the layer discolors and eventually turns black at very high doses ($\sim 10^{16}$ cm^{-2}). It is generally assumed that amorphization sets in after reaching a critical dose[23,24] ($>5\times10^{15}$ cm^{-2}). Such layers conduct electricity by means of the variable range hopping mechanism, and it was speculated that the hopping centers may be graphitic bonds.[10,11] ESR (Refs. 25 and 26) and Mössbauer[27,28] studies also concluded that the layers are graphitic carbon dominated by sp^2 bonding. However, it was noted that such layers could retain some of their diamondlike characteristics like hardness[10,11] and high density.[28] The critical ion dose beyond which this irreversible "amorphization" sets in will obviously depend on the ion and implantation conditions used, but apparently sets an upper limit to the radiation damage which can be annealed in ion-implanted diamond. This is in contrast to silicon, where ion-amorphized layers tend to aid annealing and activation of the dopant atoms.[29] Although implantation of dopant ions into diamond held at these lower temperatures and at doses below the critical value allows some annealing of the radiation damage, very few if any dopant atoms end up in substitutional lattice sites.[22] This indicates that controlled doping of diamond by ion implantation at these temperatures may also not be possible.

Further gloom was spread when Maby, Magee, and Morewood found[30] that diamond implanted at room temperature with boron ions experienced a volume expansion at doses above 5×10^{15} ions/cm^2. They concluded that this expansion is caused by amorphization setting in, which, in turn, encourages diamond to convert to graphite or amorphous carbon. It is thus somewhat ironic that the first convincing experiment demonstrating effective doping of diamond by boron-ion implantation was achieved by Braunstein and Kalish[31] using a very large ion dose, viz., 1×10^{16} ions/cm^2, which, as expected on the basis of the discussed evidence, caused an irreversibly damaged layer to form. After implantation the diamond was annealed at 1400 °C, causing the ion-damaged layer to graphitize. Etching off this graphitic layer left a very thin p-type surface. Although this demonstrated that doping is possible, very little control over the number of dopant atoms and thickness of the doped layer can be exercised using the latter technique, which limits its applicability.

A study of hopping conduction in amorphized layers obtained by carbon-ion implantation at different energies into diamond held at ~250 °C led to the conclusion that some of the interstitials created in the collision cascades could move by means of diffusion while the vacancies were immobile.[32] Some of the diffusing interstitials recombine with vacancies while others can diffuse out of the damaged layer leaving behind a vacancy-rich area. A theoretical description of this process correlated with the experimental results and indicated that the onset of hopping conduction occurs at a certain uncompensated vacancy density and does not necessarily correlate with an amorphization threshold. It was subsequently found that the same theory could be applied to the volume expansion observed when implanting ions in the same temperature range.[33] The expansion is then a measure of the number of interstitials which diffused out of the ion-damaged layer. This was demonstrated by the rapid volume expansion already observed at low ion doses before reaching a critical ion dose. At high ion doses this expansion tended to saturate. A description of the expansion as a function of implanted ion dose was obtained by assuming that the probability P for a diffusing interstitial to recombine with a vacancy could be written as

$$P=\beta\left[\frac{n_v}{N}\right]=\beta\omega C_v\ , \tag{1}$$

where n_v is the total number of vacancies per cm^2 in the ion-damaged layer, N is the total number of carbon atoms per cm^3 in a perfect diamond, ω the ion-damaged width, and β a constant for a chosen target temperature; thus $C_v=n_v/(N\omega)$ is the atomic density of vacancies. At low ion doses the number of vacancies which has been created in the collision cascades is small, allowing many interstitials to escape, while at high doses P approaches unity, causing the volume expansion to saturate.[33]

In a previous study on the electrical conductivity of amorphized carbon-ion-implanted diamond, it was found that the layers obtained when implanting at very low temperatures, e.g., liquid-nitrogen temperature, differed markedly from those implanted above room temperature.[34,35] For example, the electrical resistance obtained after implantation at the low temperature was about 10^6 times higher than after implantation to the same ion dose at 250 °C. It seems possible that this difference arose because the interstitials, which formed in the collision cascades, cannot diffuse at liquid-nitrogen temperature. A further study on the volume expansion of diamond implanted at liquid-nitrogen temperature revealed that although, in this case, expansion still occurs at high ion doses, it only initiates after reaching a critical ion dose commensurate with an amorphization threshold.[36]

From the discussion above it is clear that the temperature at which diamond is maintained during ion implantation plays a crucial role and at least three distinct temperature regions can be distinguished.

(i) A high-temperature region where both the vacancies and interstitials formed in the collision cascades can diffuse. When implanting carbon ions at this temperature the diffusing point defects agglomerate to form extended defects, thus causing highly dislocated diamond growth.[17]

(ii) An intermediate-temperature region where the vacancies are immobile and interstitials can diffuse. In this case outdiffusing interstitials leave behind a vacancy-rich layer which can, after reaching a certain density, conduct electricity by hopping conduction.[32] Furthermore, this vacancy-rich layer manifests itself as a volume expansion.[33] Although undoubtedly a critical vacancy density should exist above which the ion-damaged layer may be considered amorphous, it is probably the low material density of this region which favors reversion to graphite when being annealed.[12,22] This type of damaged layer can be considered as diamond in skeletal form, which explains the retention of some diamondlike characteristics.[10,11,8]

(iii) A low-temperature region where both the vacancies and interstitials become "frozen in" during implantation, being unable to diffuse over large distances.[34,35] An amorphization threshold is reached after a certain number of crystal atoms have been displaced.

A combination of a low-temperature implant, which freezes in the radiation damage and implanted dopant atoms, with an intermediate- or high-temperature anneal presents interesting possibilities. For example, it might be possible to create enough vacancies and interstitials that at the annealing temperature [assuming Eq. (1) to be still valid] the initial value of P will be fairly large. Specifically, $\beta\omega C_v$ may be even larger than unity thus creating a "supersaturated soup" of interstitials with the corresponding strong driving force towards recombination with the vacancies. For P below unity recombination of interstitials with vacancies could still be enhanced in this way. If at the same time the implanted dopant atoms can also diffuse and compete with the self-interstitials to fill vacancies, it may be possible to end up having a high enough density of activated, substitutional dopant atoms and low enough residual radiation damage to obtain doping. Following this line of reasoning an investigation was launched using boron as the dopant atom.

II. THEORETICAL CONSIDERATIONS

Consider an ion-damaged layer in diamond of width ω obtained after implantation of a dose S/cm^2 at a temperature low enough to freeze in the vacancies and interstitials created, and the dopant atoms injected. The ion dose is, however, below the amorphization threshold and the layer has an average atomic density of C_{v0} vacancies, C'_{i0} self-interstitials, and C_{B} boron atoms.

After implantation, this diamond is heated to an intermediate temperature T at which both the self-interstitials and boron atoms in interstitial positions can diffuse, but not the vacancies. It is, of course, possible that some of the ion-injected boron atoms already ended up in substitutional positions during the implantation process. This fraction, which can be significant, will, for purposes of argument, be considered negligible and it is assumed that all the boron atoms occupy nonsubstitutional sites. It is further assumed that at the annealing temperature T, the interstitial boron atoms diffuse at the same rate and have the same β in Eq. (1) as the self-interstitials. In other words, a boron interstitial and a self-interstitial have an equal chance to combine with a vacancy. The latter assumption is probably not valid because one type of interstitial may be favored above the other, owing, for example, to the different charge states and diffusion rates they represent. However, for the present purpose, the self-interstitials and boron interstitials will be grouped together as C_{i0} interstitials.

At the annealing temperature T, the initial probability P_0 for interstitial-vacancy recombination follows from Eq. (1) in terms of β, ω, and C_{v0}. As already mentioned, it may even be possible to obtain values for the latter parameters such that $\beta\omega C_{v0} > 1$. In this case the interstitials will, at least in theory, not be able to diffuse out of the ion-damaged layer. During annealing, recombination will lower the vacancy density and at a critical density C_{vs}, P will just be unity where according to Eq. (1)

$$C_{vs} = (\beta\omega)^{-1} . \tag{2}$$

For $C_v < C_{vs}$ interstitials will escape, but recombination of interstitials with vacancies will still continue, lowering C_v even further. If dC_i interstitials are "lost" either by diffusing out of the layer or recombining with vacancies, the decrease of vacancies can be described by the following equation:

$$dC_v = P dC_i = \beta\omega C_v dC_i = \frac{C_v}{C_{vs}} dC_i . \tag{3}$$

Assuming that all possible interstitials can diffuse, integration renders the density of residual vacancies $C_{v\text{res}}$ after annealing ($C_i \rightarrow 0$) as

$$C_{v\text{res}} = C_{v0} \exp\left[-\frac{C_{v0}}{C_{vs}}\right] , \tag{4}$$

where C_{i0} has been equated with C_{v0}, because the number of interstitials created in the collision cascades is far greater than the implanted atoms in interstitial positions.

For $C_{v0} = C_{vs}$, Eq. (4) in conjunction with Eq. (2) becomes

$$C_{v\text{res}} = (\beta\omega e)^{-1} \tag{5}$$

and theoretically, the same number of residual vacancies will be obtained for any value of $C_{v0} > C_{vs}$. In practice this is probably not true because even for $\beta\omega C_{v0} > 1$ some interstitials may escape, owing to their large number, distribution, and diffusional motion. After all Eq. (1) is only an averaged probability function which was found adequate to describe interstitial-vacancy recombination during ion implantation in the intermediate-temperature range.[33]

After annealing, the atomic density of atoms which were initially interstitials but are now in substitutional positions is C_{ia}, where

$$C_{ia} = C_{v0} - C_{v\text{res}} , \tag{6}$$

and of these, the density of activated boron atoms $C_{\text{B}a}$ follows proportionally from the initial boron-to-self-interstitial ratio as

$$C_{\text{B}a} = C_{ia}\left[\frac{C_{\text{B}}}{C_{i0}}\right] . \tag{7}$$

Again for $C_{i0} \approx C_{v0}$, and combining Eqs. (6) and (7), a value for the ratio R of activated to implanted boron atoms may be obtained as

$$R = \frac{C_{\text{B}a}}{C_{\text{B}}} = 1 - \frac{C_{v\text{res}}}{C_{v0}} . \tag{8}$$

Thus the higher C_{v0} and the smaller $C_{v\text{res}}$, the nearer the activation ratio approaches unity, which seems to be a reasonable result. For $C_{v0} < C_{vs}$ Eqs. (4) and (8) give

$$R = 1 - \exp\left[-\frac{C_{v0}}{C_{vs}}\right] , \tag{9}$$

which clearly limits R to values smaller than $1 - e^{-1} \approx 0.63$. For $C_{v0} > C_{vs}$, the residual vacancy density is given by Eq. (5) which, when inserted in Eq. (8), renders

$$R = 1 - (\beta \omega e C_{v0})^{-1} \; . \qquad (10)$$

If these equations are correct, or approximately correct, the best possibility to obtain a large fraction of activated boron-dopant atoms ($R \sim 1$) and the lowest residual damage $C_{v\mathrm{res}}$, is to have the largest value of C_{v0} possible, preferably $C_{v0} > C_{vs}$. Obviously, the latter condition is more easily obtained for C_{vs} as small as possible, which according to Eq. (2) requires ω and β to be large. A study of hopping conduction in damaged layers obtained by carbon-ion implantation at different intermediate temperatures into diamond revealed that β increases with temperature and could be in the order of 25 to 30 $\mu\mathrm{m}^{-1}$ at 500 °C,[37] compared to about 8 $\mu\mathrm{m}^{-1}$ at 100 °C.[32] This result may be interpreted as a decrease with temperature of the mean free path for a diffusing interstitial moving through a distribution of vacancies, indicating a temperature-dependent "reaction cross section" or thermally activated recombination mechanism.

As a test of these ideas, it was decided to implant diamond at liquid-nitrogen temperature using a range of energies (to obtain a large ω) to a high dose but without crossing the amorphization threshold (for a high value of C_{v0}) followed by an anneal at 500 °C. The latter temperature was considered a reasonable choice to ensure diffusion of most, if not all, of the interstitials, without much movement of the vacancies. Furthermore, it allowed annealing to proceed in air without fear of graphitization. After this anneal, the residual vacancies were further diminished by heating at 1200 °C in an argon atmosphere.

III. EXPERIMENTAL PROCEDURE

Use was made of two high-purity, insulating (type-II*a*) diamond blocks which were cut from adjacent areas in the same parent stone. They were of the same size and orientation measuring $8 \times 4 \times \sim 1.5$ mm, with the large faces about 5 degrees off (100). Both gave identical optical-absorption spectra between 900- and 200-nm wavelength.

The diamonds were implanted while being held at liquid-nitrogen temperature using carbon or boron or both types of ions. During implantation, the diamonds were masked with a graphite disc defining a rectangular area of 7×3 mm. After a diamond had been implanted it was removed, while still cold, and kept in a liquid-nitrogen bath. A small vertical tube furnace with a horizontal platform in its middle was employed to effect the first anneal. The diamond was dropped, implanted face down, onto the platform, which was at 500 °C. After one hour it was removed and cleaned in a boiling acid solution, after which its optical-absorption spectrum was determined. This was followed by a further anneal at 1200 °C for another hour. Afterwards the diamond was again cleaned and examined in the spectrophotometer.

If after this procedure it was decided to test the diamond for possible electrical conduction, contact areas were effected by application of silver paste to preselected and prepared surface areas, followed by an anneal at 300 °C for about 2 h. Good reproducible linear contacts were obtained.

After the optical and electrical properties of an implanted layer had been determined, the layer was removed by careful polishing to prepare the diamond for another implantation. Before each implantation, the absorption spectrum was again measured.

The implanted layers were prepared using carbon- and boron-ion implantation in different ratios. An attempt was made to obtain the same amount and distribution of radiation damage, C_{v0}, while ending up with a different number of boron atoms for each case. The latter number was varied from zero, in which case only carbon ions were implanted, to a maximum, in which case C_{v0} resulted from boron-ion implantation alone. To prepare a large ion-damaged width ω, each ion was implanted at three different energies, i.e., 150, 80, and 50 keV for the carbon ions and 120, 70, and 45 keV for the boron ions. Initial calculations using data generated by the computer program TRIM-86 (Ref. 38) indicated that implantation at these energies for the two ions in an energy ratio of about 2.8:2.1 should result in a similar and fairly even distribution of radiation damage over a width of ~ 0.2 $\mu\mathrm{m}$. After the experiments were performed, a plot of the composite damage profile revealed that it was not uniform (see Fig. 1). However, this does not affect the validity of the conclusions arrived at during this study.

The same total number of vacancies for either ion requires a higher ion dose [about 14% according to TRIM-86 (Ref. 38)] for the boron owing to its lower mass. In order to obtain a reasonable number of vacancies C_{v0}, a preliminary scan of ion doses and anneals was done using carbon ions alone. Combining this with some educated guessing led to the choice of carbon-ion dose quantities (most probably not optimum) shown in Table I. The corresponding doses when only using boron ions are also displayed in the same table. Thus, the largest number of boron ions implanted was 5.8×10^{15} per cm^2, and in this case all the radiation damage was caused by these ions.

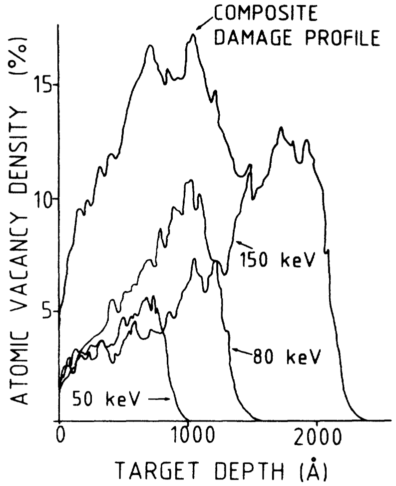

FIG. 1. Individual and composite vacancy-density profiles expected after ion implantation to the energies and doses used in this study. The profiles were generated using the TRIM-86 computer program (Ref. 38) assuming a displacement energy of 55 eV.

TABLE I. Ion doses and energies used when implanting only carbon or only boron ions into diamond to obtain the same amount of radiation damage for both ions.

Carbon ions		Boron ions	
Energy (keV)	Dose (cm^{-2})	Energy (keV)	Dose (cm^{-2})
150	2.4×10^{15}	120	2.8×10^{15}
80	1.8×10^{15}	70	2.0×10^{15}
50	8.8×10^{14}	45	1.0×10^{15}
Total dose=	5.08×10^{15}	Total dose=	5.8×10^{15}

For this reason an implantation under the conditions given for boron in Table I was termed a 100% boron implantation. An *X*% boron implantation comprised a total boron dose which was *X*% of 5.8×10^{15} ions/cm^2 distributed in the same ratio over the implant energies as the 100% implantation. Furthermore, part of this process was an initial implantation using (100-*X*)% of 5.08×10^{15} cm^{-2} carbon ions in the same ratio over the three carbon energies as given in Table I, before implanting the *X*% boron. This ensured that an *X*% boron-implanted layer contained about the same radiation damage for any chosen value of *X*. In all cases the dose rate used was $1.4\times10^{12}\ \mathrm{cm}^{-2}\,\mathrm{s}^{-1}$.

IV. RESULTS

A measure of the optical transmission through an implanted and annealed layer was obtained by dividing the transmission through the implanted diamond by the transmission at the same wavelength measured before ion implantation. Transmission measurements were made through a mask having a 1-mm-diam hole over the same area of the diamond. Even shifting the mask to other areas did not change the transmission significantly. Sometimes it was found that the transmission could differ when the light traversed the diamond in opposite directions. This effect, which seemed to be caused by the polished state of the diamond surface, could not always be prevented, and when it occurred, the average of the transmission in the two directions was used. Because of this uncertainty, no attempt was made to analyze the spectra quantitatively.

The optical transmissions between wavelengths of 900 and 200 nm, for the implanted layers studied, are shown in Figs. 2 and 3 after the 500 °C anneal and after the subsequent 1200 °C anneal, respectively. If the implantation did not affect the optical transmission, 100% transmission would have been recorded for all wavelengths measured. In both Figs. 2 and 3, the vertical scales were expanded above 80% to show up the results more clearly. It is interesting to note that in both cases there are some implanted layers which "transmitted" more than 100% for certain wavelengths. Although this may be a result of experimental error, the excess transmittance being only in the order of 4%, it is also possible that the implanted regions were acting as antireflecting layers or that luminescence occurred.

Even assuming an experimental error of 5%, it is clear that the amount of boron implanted affects the transmission in a regular manner. This is better illustrated in Fig. 4 where the transmission at 236 nm, just above the absorption edge, is shown as a function of the fraction of boron ions implanted for both of the annealed conditions studied. Owing to the relatively crude manner in which the 500 °C anneal was effected, no attempt was made to draw a smooth curve through the experimental points. Neither was an attempt made to obtain extra points in areas which seemed experimentally uninteresting. When only carbon ions were implanted, the transmission at 236 nm after the 500 °C anneal was only 41%. For low boron-ion fractions (up to 25%) the transmission stayed about the same. Between 25% and 50%, the transmission increased to 85% for the 50% boron fraction, whence it did not vary much for higher boron fractions up to 90%. Going from the 90% to the 100% fraction, the transmission dropping rapidly to a very low value and the layer became a dark brownish color.

After the subsequent 1200 °C anneal, the transmission at 236 nm showed a similar trend (see Fig. 4). When only carbon ions were implanted, the transmission was 80% compared to 41% after the 500 °C anneal. Again the transmission increased with increasing boron content and the highest transmission (92%) was measured for the 70% boron implantation. For the 80% implantation, the transmission dropped below 90%, and this drop in-

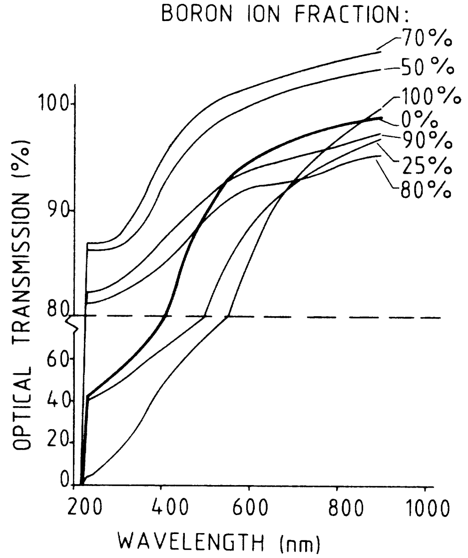

FIG. 2. Optical transmission spectra of the implanted diamond layers after annealing at 500 °C for 1 h.

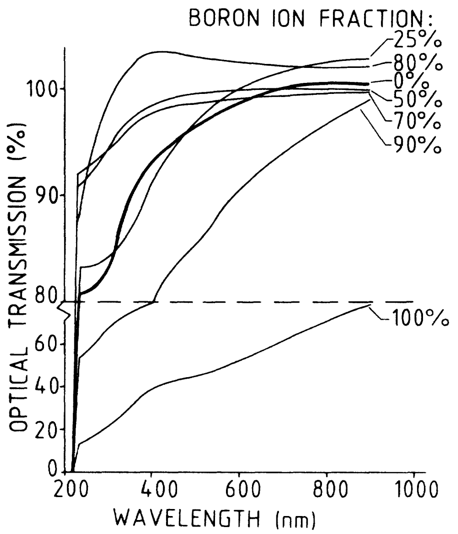

FIG. 3. Optical transmission spectra of the implanted diamond layers after annealing at 500 °C followed by a further anneal at 1200 °C for 1 h.

creased further for the 90% and 100% boron fractions. It is worthwhile to note that at the 90% boron fraction, the transmission measured after the 500 °C anneal was more (82%) than after the subsequent 1200 °C anneal (54%). After annealing, the layer obtained by boron implantation alone (100% fraction) displayed a charcoal-to-indigo smokey hue, indicative of the coloring one would expect of highly doped diamond.

Electrical contacts were applied to the 70%, 80%, 90%, and 100% boron-fraction layers and the sheet resistance measured. The results as a function of inverse temperature are displayed in Fig. 5. For the 100% implantation the resistance was very low and did not change much with temperature. The slope through the experimental points gave an average activation energy of 0.02 eV. For the 90% boron fraction the average slope was higher, giving an activation energy of 0.11 eV, and the curve started to bend over towards higher activation energies at high temperatures. More interesting results were obtained for the 80% and 70% implantations. In both cases certain definite activation energies could be measured in different temperature regions. Consider, for example, the resistance curve obtained for the 70% boron fraction. From room temperature to about 110 °C, the slope gives an activation energy of ~0.25 eV. Between 110 °C and 215 °C the activation energy measured is 0.37 eV. At 215 °C the slope changes drastically and gives a large activation energy of ~0.8 eV for higher temperatures. Similar regions, but shifted to higher temperatures, are observed for the 80% implantation, except that in this case the slope starts to change gradually below about 80 °C, bending over to lower activation energies. This could indicate that impurity band conduction is setting in. It would thus seem that at room temperature, the conduction mechanism for the 80%, 90%, and 100% boron implants is (hopping) impurity band conduction, and that this conduction correlates with the decrease in optical transmission (at 236 nm) seen in Fig. 4.

V. DISCUSSION

Since the discovery of naturally occurring, semiconducting diamond (also called type-II*b* diamond),[1] many studies have established that the dopant atom in diamond is boron and that this acceptor level is situated at ~0.37

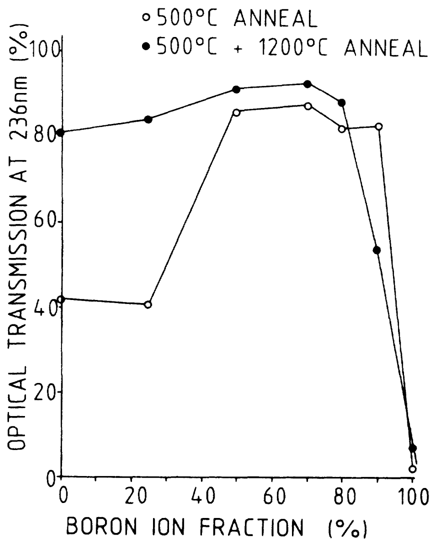

FIG. 4. Optical transmission at 236-nm wavelength through the implanted layers as a function of the boron-ion fraction implanted. Data are shown after the 500 °C and after the subsequent 1200 °C anneal.

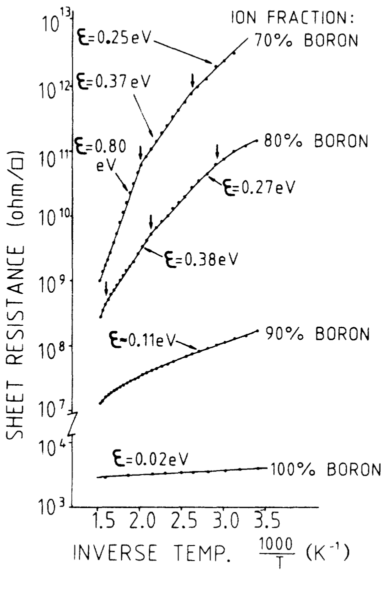

FIG. 5. Sheet resistance as a function of inverse absolute temperature for some of the boron-ion-implanted layers obtained in diamond.

eV above the valence band.[39] It is thus a reasonable approach to compare the implanted layers obtained in this study to the properties of naturally occurring type-II*b* diamond. In Fig. 6, the optical transmission spectrum of one of the type-II*a* diamonds used in this study is compared to the spectrum of a typical, lightly doped type-II*b* diamond of similar thickness. It is clear that the type-II*b* diamond absorbs more towards the longer wavelengths and much less for the shorter wavelengths than the type-II*a* diamond. Just above the absorption edge, at 236 nm, this specific type-II*b* diamond transmits about 50% more light than the type-II*a* diamond.

In the type-II*a* diamond the transmission gradually decreases with decreasing wavelength, transmitting the least just above the absorption edge. This decrease in absorption may vary in magnitude from one diamond to the other but is typical of type-II*a* diamonds, giving them a brownish hue. Clark, Ditchburn, and Dyer[40] suggested that this absorption may be attributed to small regions of amorphous carbon. In a previous study on ion implantation into diamond, it was suggested that these small regions were not amorphous, but rather vacancy-rich regions which may have condensed during cooling of the diamond when it was ejected during volcanic action.[32] If the latter or a related mechanism is responsible, one would expect similar regions in a type-II*b* diamond, which, if present, do not however show up in the optical spectrum (see Fig. 6).

It is interesting to note that the 0% boron fraction, where only carbon ions were used, leads to a transmission spectrum for the implanted layer which is similar in shape to the spectrum of a virgin unimplanted type-II*a* diamond. This is true after the 500 °C anneal and the subsequent 1200 °C anneal (see Figs. 2 and 3). It correlates with the assumption that this type of absorption is caused by vacancy-related defects, which according to the theory developed above (see the second paragraph) will be the residual radiation damage after annealing. No indication of the GR1 band, normally associated with individual vacancies, could, however, be found after either annealing procedure. This could be a consequence of too much residual radiation damage (forming effective vacancy-rich regions) remaining after the 500 °C anneal which then obscures the presence of this feature. In turn, after the 1200 °C anneal most vacancies may have clustered, leaving very few, if any, individuals behind.

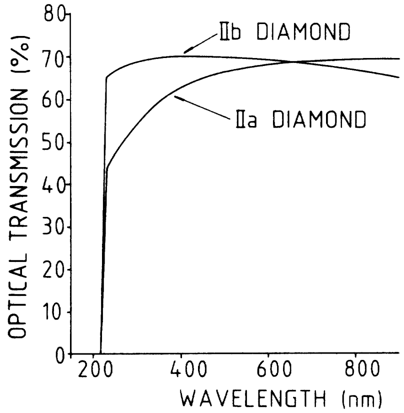

FIG. 6. Optical transmission spectrum for one of the type-II*a* diamonds used in this investigation as measured before ion implantation. For comparison the optical spectrum measured for a typical, naturally occurring type-II*b* diamond of comparable thickness is also shown.

With increasing boron content the optical transmission spectra of the implanted layers tend to become more II*b*-like in the sense that more transmission occurs at shorter wavelengths (see Figs. 3 and 4). This trend continued up to 80% implantation, beyond which, as indicated in Fig. 5, impurity band conduction probably ensued. Except for the 80% implantation, very little indication was found for more absorption at longer wavelengths caused by the presence of the boron. However, this absorption is the first feature that was found, by Dyer and Ferdinando,[41] to disappear when irradiating type-II*b* diamonds with electrons. Its absence in the results reported here most probably indicates still unacceptably high residual damage after annealing.

A noteworthy aspect of the optical measurements stems from the fact that the boron-to-carbon-ion ratios were chosen to result in the same residual radiation damage after annealing for all the layers studied. If it is assumed that this was achieved, the increase in transmission at low wavelengths with increasing boron content may be ascribed to charge transfer between this radiation damage and centers associated with the boron atoms. Taking cognizance of the results reported by Dyer and Ferdinando,[41] it seems possible that this damage, which causes optical absorption at short wavelengths when no boron is present, acts as donor centers which compensate boron acceptors when the latter have been introduced. This hypothesis explains the results in Fig. 4 well. Increasing boron content decreases the absorption measured after the 500 °C anneal allowing transmission of more than twice the amount of light after the 50% implantation compared to the boron-free layer (0% implantation). The same trend is found after the final 1200 °C anneal. An interesting result is the 90% boron-implanted layer which transmitted more light after the low-temperature anneal than after the subsequent 1200 °C anneal. Logically, it can be concluded that after the higher-temperature anneal, fewer donor centers remain to compensate existing acceptors, allowing a greater density of these uncompensated acceptors which are near enough to each other for increased absorption to occur.

If it is assumed that the centers responsible for the short wavelength absorption in type-II*a* diamonds, and the radiation damage centers which remained after ion implantation and annealing, are related; i.e., are vacancy-clustered regions in both cases, the absence of these features in the spectra of natural type-II*b* diamonds may be explained. These centers could be present where they act as compensating donors. It is even possible that they are the dominant donor centers in natural semiconducting diamond instead of substitutional nitrogen as has generally been assumed. If so, this will explain the results obtained by Horszowski[42] when he annealed semiconducting diamonds at various temperatures, and found that the number of uncompensated acceptors increased after each annealing cycle.

The interpretation of the optical measurements is supported by the resistance curves shown in Fig. 5. Firstly, it is clear that conduction takes place by means of thermally activated processes. Secondly, the electrical resistance at a given temperature increases with decreasing boron content showing that the conduction results from the presence of boron. Furthermore, at very high boron content (80%, 90%, and 100% fractions) the activation energies tend to be low and become less towards low temperatures, which indicates impurity band conduction as expected. However, for the linear portions obtained at 70% and 80% implantations, which may possibly be ascribed to holes being excited from acceptor centers to the valence band, three distinct activation energies were found instead of the single energy expected for substitutional boron, i.e., 0.37 eV. The fact that one of the three activation energies measured is indeed ~0.37 eV indicates that substitutional boron acceptors are present as expected. Further support for this conclusion was obtained by heating one of the contacts in this temperature region with a soldering iron. This contact developed a negative voltage relative to the colder contact, which is to be expected for conduction by means of holes. It seems logical to conclude that the activation energy of ~0.8 eV encountered at high temperatures results from the large number of donor centers which, in this study, remained after annealing, and which compensate the acceptors at lower temperatures. At a high enough temperature the compensating electrons can be excited from the acceptors back to the donors, in this way relieving them to excite holes into the valence band. In effect electrons are now excited from the valence band to the charged donors because the Fermi level has moved to a position above the acceptor energy. The donors must thus be situated at a minimum energy of ~0.8 eV above the acceptors, i.e., ~1.2 eV above the valence band. For a band gap of 5.4 eV they are accordingly deep but lie at most at ~4.2 eV below the conduction band. This correlates with the activation energy of 4.05 eV which was determined for donors in type-II*a* diamond by means of photo-Hall-effect measurements.[43]

The 0.25- and 0.27-eV regions found for the 70% and 80% implantations in Fig. 5 also depend on the quantity of boron implanted. For these experiments the activation ratio [Eq. (8)] was low, leaving many "unactivated" boron atoms which could have been trapped at suitable radiation defects. It is, however, more probable that these lower activation energies results from the very high level of compensation between the large number of donors and acceptors present. Hopping conduction of electrons between compensated and uncompensated acceptors may then already occur at high temperatures and this would be facilitated by an increase in the number of uncompensated acceptors, i.e., correlate with the quantity of boron implanted. One may speculate that in an unsuccessful doping experiment where many donor centers outnumber the boron acceptors, hopping conduction may occur between the neutral and charged donors, which in turn may be considered as the hopping of holes from the charged to the neutral donors. This could also occur at activation energies lower than 0.37 eV, and show some *p*-type characteristics. In this respect, it is worthwhile to note that the results reported by Vavilov *et al.* for boron-implanted diamond rendered activation energies in the order of 0.25 eV.[9,44]

Better annealing can be obtained by heating the diamond directly to a higher temperature than 500 °C. For example, introducing a boron-ion fraction of 6% (according to the scheme used in this investigation) into one of the type-II*a* diamonds used, and then heating the diamond directly to ~1200 °C, gave a similar conductivity to the 90% implantation.[37] However, the results reported in this study provide a better insight into the physics involved and may also become of historical value.

VI. CONCLUSION

This study shows that ion implantation of carbon and boron ions in a suitable ratio and to a suitable ion dose, at a temperature low enough to "freeze in" the radiation damage, followed by subsequent annealing which, as a first step, involves rapid heating of the diamond to the annealing temperature selected, can lead to optical and electrical properties which correlate with those of natural semiconducting diamond. The electrical conduction measured relates to the boron-ion dose and in an appropriate temperature interval renders an activation energy of ~0.37 eV, which is the energy expected for the substitutional boron acceptor in diamond. The high residual radiation damage present after applying the initial, relatively crude annealing cycle selected, enabled an activation energy to be measured from the electrical resistance curves which indicated the presence of compensating donors situated at about 4 eV below the conduction band.

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