Luminescence of impurity-defect complexes containing nitrogen i ion-implanted layers of natural diamond

A. M. Zaĭtsev, A. A. Gippius, and V. S. Vavilov

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

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The cathodoluminescence spectra of natural diamond crystals containing nitrogen impurities introduced by ion implantation were found to include specific lines associated with complexes containing nitrogen atoms. An analysis of these cathodoluminescence spectra, including those obtained under uniaxial deformation conditions, was carried out using the concept of "compliance" of the luminescence centers. The results of this analysis and the dependences of the line intensities on the implantation dose and annealing temperature were used to identify or determine more accurately the microstructure of some of these complexes. It was found that a strong disorder of the lattice created by ion implantation facilitated transformation of the nitrogen-containing complexes during annealing.

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1. INTRODUCTION

We used the cathodoluminescence method to investigate diamond layers containing implanted nitrogen atoms. Nitrogen is a special impurity in diamond: the amount of nitrogen is one of the main criteria for the classification of natural diamond crystals. The presence of nitrogen has a very strong influence on many physical (including optical) properties of diamond. The absorption and luminescence spectra have revealed structures many of which are associated with either nitrogen atoms or nitrogen–defect complexes.[1] In spite of the relatively large amount of work done on this topic, the nature of some of the optically active centers in diamond and the mechanism of their formation are still not clear. Ion implantation provides an opportunity for clean and quantitatively controlled introduction of impurities into solids. Implantation of nitrogen ions in diamond gives rise to specific groups of luminescence lines. An analysis of the luminescence spectra carried out under various experimental conditions in the study described below allowed us to obtain new information on the nature of nitrogen-containing centers and on the behavior of nitrogen in diamond.

2. EXPERIMENTAL PROCEDURE

Our samples were platelets of type IIa diamonds (these are known as "nitrogen-free" crystals because the nitrogen concentration is below 10^{18} cm^{-3}, as deduced from the infrared absorption and photoconductivity spectra), as well as type Ia diamonds (with nitrogen concentrations in the range $\geq 10^{19}$ cm^{-3}). Implantation of nitrogen ions of energies up to 350 keV in doses necessary to produce the required impurity distribution profile took place at room temperature. The ion source was an accelerator made by High Voltage Engineering Europa.

The ion-implanted layers were annealed in a graphite container in 10^{-5} torr vacuum where temperatures from 500 to 1400°C (in steps of 100°C) were applied for 2 h. The cathodoluminescence excited by beam electrons of energies 2-10 keV (the beam current was ≈ 5 μA) was investigated at 80°K in the spectral range 300-900 nm. The piezospectroscopic measurements were carried out using a special device which made it possible to bond the sample and to create uniaxial compressive or tensile in a thin ion-implanted layer.[2]

3. RESULTS AND DISCUSSION

The cathodoluminescence spectra of the original ples consisted of a wide A band whose position and were different for samples of different kinds (Fig. 1a). This band was associated with nonradiation defects locations or platelet defects containing nitrogen[3,4] was used as a reference standard, exactly as in Ref i.e., the intensities of the lines and bands appearing result of implantation and annealing were measured

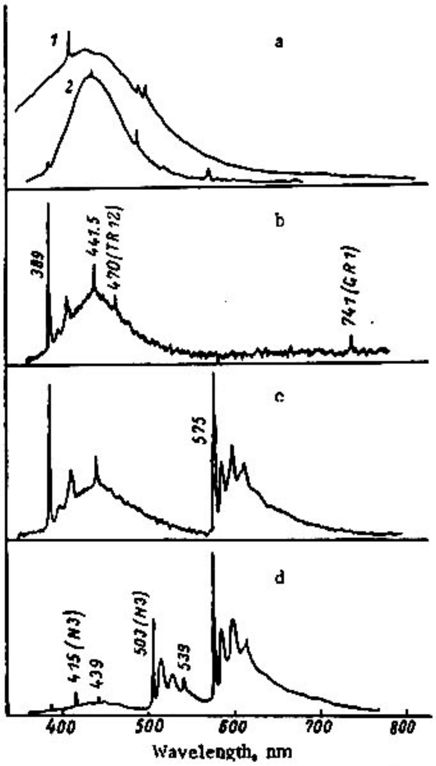

FIG. 1. Cathodoluminescence spectra: a) original type samples; b-d) samples containing implanted nitrogen atoms ing (b), after annealing at 600°C (c), and after annealing at

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the intensity of the A band and this eliminated the ence of changes in the nonequilibrium carrier life- e

The cathodoluminescence spectra of the samples con- ing implanted nitrogen atoms included not only rela- ely weak lines of intrinsic GR1 and TR12 defects,[1] but o specific groups of lines (usually consisting of a nar- zero-phonon line and a more or less intense phonon g associated with centers which we identified in ac- dance with the wavelength of the zero-phonon line. The ters we associated with the 389 and 441.5 nm lines ap- red immediately after implantation; then, after anneal- at T > 500°C we observed the 575 nm center. Anneal- at T > 1000°C destroyed the 389 and 441.5 nm centers well as the intrinsic GR1 and TR12 defects) and gave to new 415 and 503 nm centers. Finally, at T ≈ 0°C we observed 439 and 539 nm lines. Since all these ters appeared in the spectra of the nitrogen-free type crystals only after implantation of nitrogen (we in- tigated the influence of implantation of 23 elements), concluded that these centers contained nitrogen atoms. ortant evidence in support of the nitrogen origin of se centers was also the shift of all the zero-phonon s toward shorter wavelengths as a result of implanta- of ions of the ^{15}N isotope.

The structure of the nitrogen-containing centers can deduced from the dependences of the intensities of the responding lines on the implantation dose and annealing perature, and from the piezospectroscopic measure- ts. In the latter case, in addition to the usual infor- ion on the symmetry of the centers we employed a pa- eter representing the response of the optical centers niaxial deformation. This parameter we called "com- nce" and defined it as $s = (\Delta h\nu_{\max}\ h\nu_0\sigma)\cdot 10^{12}$ Pa^{-1}, re $\Delta h\nu_{\max}$ is the shift of the most strongly split-off ponent of the zero-phonon line from its position $h\nu_0$ in absence of deformation and σ is the applied elastic ess. The compliance of an optical center, representing relative change in the transition energy caused by a stress, clearly depends on the relative deformation of electron orbitals (at least in the orientational degener- case) and can therefore be used to judge the value of latter. The deformation of the orbitals, i.e., the de- nation of the defect under the action of elastic stresses depends on how a given defect alters the local elastic constants of a crystal. It is known that a vacancy loosens the lattice locally, i.e., it makes it softer, whereas an interstitial atom increases the elastic constants.[6] This means that the defects containing vacancies are deformed by a given stress more than the defects consisting of interstitial atoms and, consequently, the compliance of the optical centers can be higher in the former case than in the latter. These predictions are confirmed by an analysis of the available experimental data. It is found that in the case of the vacancy defects such as the 741 nm (known as GR1 and representing isolated vacancies[7]) and 638 nm (vacancy plus a substitute and nitrogen atom[8]) centers, the compliance s is 4.5 and 4.1 Pa^{-1}, whereas in the case of the 736 nm centers containing two silicon atoms we have $s < 0.1$ Pa^{-1} (Ref. 9) irrespective of the positions of these centers in the lattice (not yet determined accurately); it is known that the 736 nm centers harden the lattice considerably because the covalent radius of Si is 1.5 times greater than that of C. Therefore, knowing the value of s, we can draw qualitative conclusions on the structure of the optical centers, i.e., on whether they consist mainly of vacancies or interstitial atoms. In the intermediate cases, i.e., for the centers consisting either of substituent atoms with radii differing little from the carbon atoms or those containing both vacancies and interstitial atoms we should have intermediate values of the compliance $s \approx 1$ Pa^{-1}.

We shall now consider the individual luminescence centers in the order of their appearance after implantation and annealing. Our conclusions about these centers will vary in respect of their reliability. Nevertheless, a study of the formation and properties of these centers in ion-implanted layers has made it possible to obtain information on the processes of formation and changes in the defect—impurity complexes in strongly disordered diamond crystals.

3.1. Centers Associated with the 389 and 441.5 nm Lines

As pointed out earlier, these centers appear immediately after implantation of nitrogen in nitrogen-free crystals at room temperature. In the case of our ion-implanted layers we found, in agreement with Ref. 10, that there was no ESR signal associated with the substituent isolated nitrogen atoms. Consequently, the formation of the 389 and

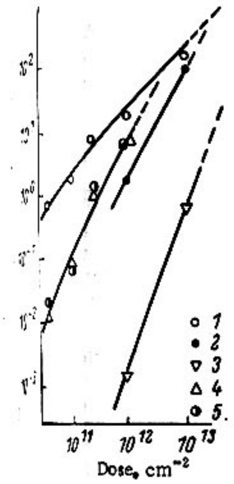

FIG. 2. Dependences of the intensities of the cathodoluminescence lines of nitrogen-containing centers on the implanted dose of nitrogen atoms: 1-3) results obtained for the 575 nm, 503 nm (H3), and 415 nm (N3) centers, respectively, in type IIa crystals; 4, 5) results for 503 nm (H3) and 494 nm (H4) centers, respectively, in type Ia crystals.

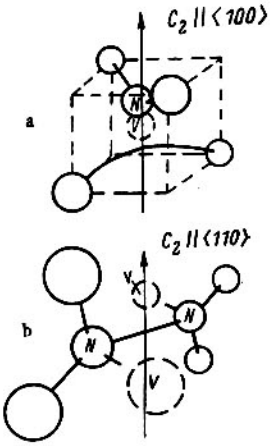

FIG. 3. a) Model of a 575 nm center. b) Model of a 503 nm (H3) center.[20]

441.5 nm centers involves interstitial nitrogen atoms, as confirmed by the very low compliance ($s < 0.1$) of these centers. This makes it impossible to determine the type of symmetry of these centers from the piezospectroscopic measurements. Therefore, we can only postulate that the 389 and 441.5 nm centers are either interstitial nitrogen atoms in different configurations or they are complexes formed from these atoms themselves or from nitrogen and accidental impurities; both kinds of complexes are stable in ion-implanted layers right up to ≈ 1000°C.

3.2. Center Associated with the 575 nm Line

The 575 nm center appears in the nitrogen-free crystals after implantation of nitrogen and subsequent annealing at 500°C or after irradiation with electrons of energies amounting to a few kiloelectron-volts. The luminescence associated with these centers is of orange-red color. The linear dependence of the intensity of this luminescence on the implantation dose (curve 1 in Fig. 2) shows that each such center contains one nitrogen atom. Uniaxial deformation along the ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions splits the zero-phonon line into two, two, and three components, respectively. According to the theory of Kaplyanskii[11] and Runciman,[12] such splitting corresponds either to a transition between nondegenerate states of a defect of the orthorhombic-I symmetry with the $C_2 \parallel \langle 100 \rangle$ axis or to a transition between the A and T states of a defect of the tetrahedral symmetry. This symmetry is exhibited only by single atoms at regular sites or in tetrahedral interstices. However, as pointed out earlier, the ion-implanted layers did not contain substituent nitrogen atoms and the tetrahedral interstitial position in the diamond lattice was unstable (at least for the carbon atoms themselves[13,14]). Therefore, we shall assume that the 575 nm center has the orthorhombic-I symmetry with the $C_2 \parallel \langle 100 \rangle$ axis.[1)] The 575 nm center has a an intermediate (compared with vacancies and interstitial centers) compliance ($s = 1.3$). Therefore, we may conclude that it contains both an interstitial atom and a vacancy. The presence of a vacancy is confirmed by the fact that the phonon structure of the spectrum is governed by the interaction with a quasilocal vibration associated with a vacancy ($\hbar\omega = 43$ meV).[16] These properties of the 575 nm center fit a model in which a nitrogen atom is located in a ⟨100⟩ − split interstitial position and is bound to the nearest vacancy along the ⟨100⟩ axis (Fig. 3a). The 575 nm center has the point symmetry group C_{2v} and is an analog of the A center (i.e., of a complex formed by an oxygen atom and a vacancy) in silicon.[17]

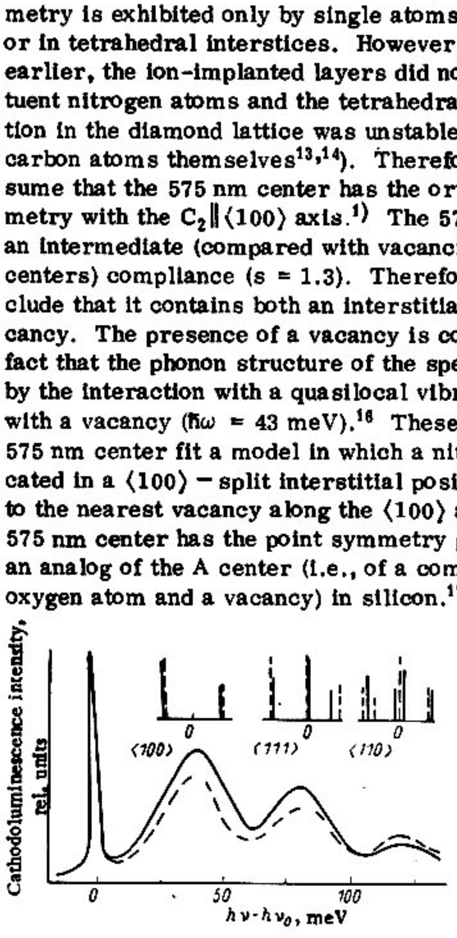

FIG. 4. Phonon structure and splitting (caused by uniaxial deformation) of zero-phonon lines of the 503 nm (H3) and 496 nm (H4) centers (continuous and dashed lines, respectively).

3.3. H3 (503 nm), H4 (496 nm), and N3 (415 nm) Centers

According to the published data, the 503 nm cente (known as H3) originates from the A form of nitrogen (two neighboring substituent atoms) and a radiation de In view of the conflict between the data on the symmet of this center,[18,19] the structure has until recently bee regarded as controversial. According to Davies,[18] the center has the orthorhombic-I symmetry and consists two nitrogen atoms located at the sites of an elementa tetrahedron and bound to a vacancy at the center of th tetrahedron. According to this model, the A form of ni trogen is transformed when such centers are generate On the other hand, according to Sobolev,[20] the H3 cente appears as a result of the capture of two vacancies by A form of nitrogen and this produces the VH_2V-transc figuration with the monoclinic-I symmetry (Fig. 3b).

Ion implantation provides a means for a controlle introduction of impurities into a crystal and for obtain additional data on the structure of the resultant center We find, first of all, that the quadratic dependence of intensity of the 503 nm line on the nitrogen ion dose re ceived by nitrogen-free crystals (curve 2 in Fig. 2) con firms that the H3 center contains two nitrogen atoms. Moreover, bombardment of the Ia type crystals (conta ing "blanks" of the H3 centers inside the A configurat of nitrogen in a concentration of ≈ 10^{19} cm^{-3}) also res in a quadratic dependence of the 503 nm line on the ra ation dose (curve 4 in Fig. 2); this shows that each H3 center contains two radiation defects. The large val the compliance of the H3 center ($s = 4.9$ Pa^{-1}) shows th these defects are vacancies. This is supported by the teraction of the 503 nm electronic transition with quas local vibrations associated with a vacancy ($\hbar\omega = 43$ me Finally, our measurements indicate that the symmetr the H3 center is monoclinic-I. Thus, all our data conf fully the VN_2V-trans model of the H3 center proposed Sobolev.[20]

It is known that whereas the H3 (503 nm) center or inates from the A form of nitrogen, the H4 (496 nm) ce ter appears as a result of the capture of a radiation de fect by the B_1 form of nitrogen, i.e., by a macroscopic cluster of nitrogen atoms representing two parts of the nearest atomic layers located in the (111) plane.[21] Th coupling of the H4 center to a macroscopic cluster of radiation origin is confirmed by the fact that, in contra to the H3 centers, it is not possible to generate the B centers by implantation of nitrogen in nitrogen-free c tals with the same concentrations (≈ 10^{20} cm^{-3}) after nealing at such temperatures (≈ 1400°C) that signific

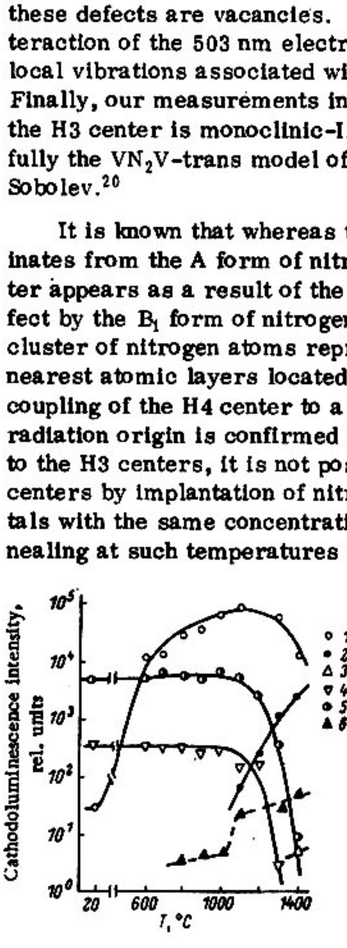

FIG. 5. Dependences of the ties of the cathodolumines on the annealing temperatu results for the 575 nm, 503 n 415 nm (N3), 441 nm, and 3 centers, respectively, formed sult of implantation of nitrog type IIa crystals; c) results fo nm (N3) centers in type Ia

migration of defects and changes in their structure takes place (see Sec. 3.5). However, the H3 and H4 centers are similar because they have the same phonon structure of the spectra, similar values of the compliance (s = 4.9 and 4.5 Pa^{-1}, respectively), very similar splitting patterns of the zero-phonon lines under uniaxial deformation (Fig. 4), and zero-phonon line photons differing by just ≈ 1.5%. All these similarities indicate that the molecular structure of these two kinds of center is the same (i.e., VN_2V-trans) and the difference lies in the location of the H4 centers near the platelet (V_1) form of nitrogen, which has a perturbing influence on these centers.

According to the data of many authors, the 415 nm (N3) center contains three substituent nitrogen atoms located in the (111) plane. Models proposed for this center are different: in one case it is suggested that a triplet of nitrogen atoms is bound to the nearest carbon atoms along the (111) axis,[22,23] whereas others postulate the presence of a vacancy.[20,24] Our results confirm that the 415 nm center consists of three nitrogen atoms (the luminescence intensity is a cubic function of the nitrogen ion dose received by nitrogen-free crystals, as demonstrated by curve [illegible] in Fig. 2). Moreover, the fairly large compliance (s = [illegible] Pa^{-1}) of the center shows that it contains a vacancy, in agreement with Refs. 20 and 24.

3.4. Centers Associated with the 439 and 539 nm Lines

Both these centers appear after implantation of nitrogen ions in nitrogen-free crystals and subsequent annealing at 1400°C. The 439 nm center has the monoclinic or the trigonal (A → E transition) symmetry, whereas the 539 nm center has the tetragonal symmetry. The fairly large compliance of these centers (3.5 Pa^{-1} for the 439 nm center and 3.4 Pa^{-1} for 539 nm) indicates that they contain vacancies. However, the available data are insufficient to propose microscopic models of these centers. We can simply say that their structure is fairly complex. In fact, the 439 nm center is observed in nitrogen-free crystals only after large implantation doses. The same center appears after the implantation of any ions in the type Ia diamonds after annealing at T > 1100°C and the rate of its introduction rises strongly on increase in the ion mass. Irradiation of diamonds with 2.2 MeV electrons produces hardly any centers of this kind. It follows that the formation of the 439 nm centers requires strong disordering of the lattice.

The 539 nm center contains not only nitrogen atoms and vacancies but also some accidental impurity or nonradiation defect because the intensity of the 539 nm line varies strongly from sample to sample.

3.5. Changes in the Structure of Nitrogen-Containing Centers

The data on the structure of the nitrogen-containing centers and on the conditions of their appearance allows us to identify some features of the process of changes in the state of the implanted nitrogen atoms during the annealing of diamond crystals and the appearance of increasingly larger complexes consisting of these atoms and intrinsic defects. Immediately after implantation at room temperature the implanted nitrogen atoms are at interstitial positions, as indicated by the absence of the ESR signal associated with the substituent atom. The appearance of the 575 nm center after annealing at T > 500°C or after electron irradiation suggests some changes in the implanted atoms and/or defects. Such changes may involve those occurring within the existing "blanks" of the 575 nm centers or the formation of complexes after thermal diffusion or athermal migration (as a result of interaction with an electron beam) of nitrogen atoms in interstices.

Beginning from T ≈ 1000°C the concentration of the centers containing single nitrogen atoms (389, 441, 575 nm) decreases and complexes consisting of two (H3) and three (N3) nitrogen atoms and vacancies are formed (Fig. 5). The available data are insufficient to draw any conclusions about the details of the atomic changes which accompany the formation of such centers. We can simply say that at T ≈ 1000°C the mobile particles in ion-implanted layers are both interstitial nitrogen atoms and vacancies because otherwise the formation of many-particle complexes would require that all the components of the complexes (for example, two vacancies and two nitrogen atoms in the case of the H3 center) should appear after implantation within practically the same unit cell of a crystal, which is extremely unlikely. In general, the temperature at which the formation of complexes begins can be regarded as the activation energy of the motion of the components of these complexes as well as the barrier impeding the formation of complexes. This may apply to the appearance of the complex 439 and 539 nm centers at T ≈ 1400°C.

It is interesting to compare our data with the results of other investigations reporting transformations in nitrogen-containing centers in diamond. Formation of double (A form) and triple (N3) complexes of nitrogen from single substituent atoms in the type Ib diamond crystals at temperatures 1700–2000°C and pressures of 55 kbar is reported in Ref. 25. Transformation of the 638 nm centers (consisting of a single substituent nitrogen atom and a vacancy) into the H3 centers (two nitrogen atoms in two vacancies) in electron-irradiated diamonds of the Ib type is described in Ref. 26. This process occurs at 1500°C under normal pressure. In the case of ion-implanted layers investigated by us the transformations of the nitrogen-containing centers occur already at temperatures as low as ≈ 1000°C. Therefore, radiation treatment of crystals facilitates the transformation of nitrogen-containing complexes. In the case of ion-implanted layers this may be due to a strong disorder of the lattice or due to the fact that the implanted nitrogen atoms are in interstitial positions.

4. CONCLUSIONS

The application of ion implantation, which is a clean and precision doping method, made it possible to obtain new data on the properties of nitrogen impurities which have a very strong influence on diamond. An analysis of the results obtained by recording the cathodoluminescence spectra (including those recorded under uniaxial deformation conditions) after implantation and annealing under various conditions made it possible to identify or obtain details of the microstructure of some of the complexes containing radiation defects and nitrogen atoms, and to establish the features of the transformation of these complexes during annealing in the presence of a strong disorder of the lattice created by ion implantation.

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[1)] Our data on the symmetry of the 575 nm center differ from the results of Davies.[15] The origin of this discrepancy is not clear. A similar discrepancy occurs between the data of the various authors on the symmetry of the 503 nm center (see Sec. 3.3).

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Formation, annealing, and interaction of defects in ion-implante layers of natural diamond

A. A. Gippius, A. M. Zaitsev, and V. S. Vavilov

P. N. Lebedev Physics Institute, Academy of Sciences of the USSR, Moscow

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The cathodoluminescence method was used to determine the characteristic features of the formation and annealing of defects in diamond subjected to ion implantation. It was found that these features could be explained on the basis of the existing ideas on the properties of disordered regions created by ions. A specific influence of nitrogen on the formation of defects in ion-implanted layers was discovered. It was found that the defect environment influenced the annealing of the luminescence centers created by different types of radiation.

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1. INTRODUCTION

Ion implantation doping is used to alter the properties of diamond in a desired manner and, in particular, to obtain layers exhibiting semiconducting properties. This doping method is particularly important because other methods for doping diamond have not yet been developed sufficiently. In principle, to realize the advantages of ion implantation as an effective method of clean precision doping one should know the implantation and annealing conditions which ensure that the properties are governed by the newly introduced impurities and not by the radiation defects created as a result of implantation. One should point out that although ion implantation has been used to prepare semiconducting layers of diamond,[1] the characteristic features of the formation of defects in the co of ion implantation in diamond have not been investig much, particularly in respect to the nature of specific fects. The main attention has been concentrated on th electrical activity of the implanted impurity[1,2] and sh have been made of the influence of defects on the mac scopic properties of ion-implanted layers.[3] Relative little information can be gained by the application of t ESR method to ion-implanted layers of diamond. It h been found that the implantation temperature influenc the signal associated with dangling bonds or with the "amorphous phase," and anisotropic ESR centers hav been observed (but only after the implantation at rel high temperatures) some of which are likely to be va cancies.[4,5] We investigated defects in ion-implanted

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