n-type semiconducting diamond by means of oxygen-ion implantation

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By a judicious choice of implantation and annealing conditions, an *n*-type conducting layer with activation energy of about 0.32 eV has been created in oxygen-implanted diamond. This conclusion was reached as a result of performing three similar implantations in identical, high-purity (type IIa) diamonds. They have been implanted with O^+, C^+ and $(B^+ + C^+)$ ions to respectively create the same density and distribution of radiation damage in each diamond. The density and distribution of dopant atoms were the same for the O^+- and $(B^+ + C^+)$-implanted layers. After implantation at liquid-nitrogen target temperature, the diamonds were rapidly heated to 500 °C and maintained there for 30 min. Electrical measurements showed that the O^+ and $(B^+ + C^+)$ diamonds conducted orders of magnitude better than the C^+-implanted diamond. Thermal-emf measurements were used to determine *n*- and *p*-type conduction. The resistance behavior was in both cases commensurate with that of a highly compensated, extrinsic semiconductor. After more O^+ implantation steps to lower the resistance further, Hall-effect measurements confirmed that this diamond became *n*-type conducting.

Semiconducting diamonds containing boron acceptors are found in nature. They can also be grown or be generated by means of ion implantation.[1] The activation energy for hole conduction is 0.37 eV.[2] Although substitutional nitrogen atoms act as donors in diamond, their electronic energy level is situated at about 1.7 eV below the conduction band.[3] This is too deep to allow substantial *n*-type conduction at room temperature. Over the years, many attempts have been made to generate donor states in diamond with lower activation energies.

Since diamonds have been grown by plasma-assisted chemical-vapor deposition (PACVD), attempts have been made to incorporate phosphorus atoms substitutionally during growth. Although a high density of phosphorus could be incorporated into the bulk of the diamond, the required *n*-type conduction could, for many years, not be obtained. Only recently, incontrovertible proof was obtained that diamond can be doped *n* type by the incorporation of phosphorus during homoepitaxial growth.[4] Evidence that diamond can also be doped by means of P^+-ion implantation was obtained by using very low ion doses,[5] and by driving ion-implanted P atoms into a region containing a low density of vacancies.[6] It was, however, found that annealing at too high a temperature deactivated the P-atom donors.[6,7] This can be ascribed to vacancies diffusing to and becoming trapped at the impurity sites.[7,8] Similar vacancy interactions also occur in the case of nitrogen donors.[1]

The average activation energy measured for the phosphorus-doped diamond layers was about 0.5 eV,[4,7] which is still too high for room-temperature applications. Cathodoluminescence measurements indicate that the true ionization level is situated even deeper at 0.65 eV below the conduction band.[9] In order to develop useful *n*-type electronic devices in diamond, an activation energy, which is at least comparable to or better than that for the boron acceptor, is preferable. It is known that diamond is a negative electron affinity (NEA) material.[10] If there is no band bending at the surface, the bottom of the conduction band will lie ≈0.5 eV

above the vacuum level.[11] This means that for any dopant atom which forms a shallow donor, the donor level must lie higher than the vacuum level (assuming zero band bending at the surface). Such an atom will be in a higher energy state than it will be in when it is outside of the diamond. It is improbable that atoms like these will be incorporated within the diamond lattice during growth, unless driven in by large nonequilibrium events.

Theoretically, oxygen atoms could form donors if they can be made to occupy substitutional sites within the diamond lattice. This elemental gas can be injected into the plasma during PACVD growth of diamond with very few, if any, of its atoms being incorporated into the bulk of the layer being grown. It seems logical to conclude that an oxygen atom in the bulk, whether substitutional or interstitial, will be in a higher energy state than it will be when outside.

Ion implantation injects ions, such that their corresponding atoms end up within the bulk of a material. They are thus forced into sites with high formation energies. It is known that when a diamond is implanted at a low enough temperature (typically liquid-nitrogen temperature), and low enough doses to prevent the formation of large stresses, the point defects created within the collision cascades become effectively ''frozen'' into the positions they end up in after their ballistic movements.[12] It may thus be possible that oxygen atoms, that had been injected at low enough target temperatures, may find themselves in high-energy states relating to substitutional and interstitial positions. If they could, such atoms would prefer to escape from the diamond crystal or to relax into states with lower energies. In both cases, the processes will require atomic movements involving the scaling of activation barriers. Such processes are temperature dependent. By a judicious choice of the annealing temperature, it may thus be possible to increase the density of those high energy sites which act as shallow dopant levels within the band gap. It is clear that such a temperature must be relatively low. It should probably be lower than the temperature at which vacancies can start to diffuse [≈ 600 °C (Ref. 13)]

TABLE I. Ions, energies and doses used to implant three diamonds with O^+, C^+, and (C^++B^+) ions, respectively, such that the radiation-damage density and distribution will be the same in all three cases. The coimplanted B^+ diamond layer contained the same density and distribution of implanted B atoms as the implanted O^+ layer contained O atoms.

O^+		C^+		(C^++B^+)			
Energy (keV)	Dose (cm^{-2})	Energy (keV)	Dose (cm^{-2})	Energy (keV)	Dose (cm^{-2})	Energy (keV)	Dose (cm^{-2})
170	1.0×10^{13}	130	1.5×10^{13}	130	6.7×10^{12}	102	1.0×10^{13}
155	1.0×10^{13}	120	1.5×10^{13}	120	6.7×10^{12}	93	1.0×10^{13}
140	1.0×10^{13}	108	1.5×10^{13}	108	6.7×10^{12}	84	1.0×10^{13}
125	1.0×10^{13}	98	1.5×10^{13}	98	6.7×10^{12}	76	1.0×10^{13}
110	1.0×10^{13}	86	1.5×10^{13}	86	6.7×10^{12}	67	1.0×10^{13}
95	1.0×10^{13}	76	1.5×10^{13}	76	6.7×10^{12}	59	1.0×10^{13}
80	1.0×10^{13}	63	1.5×10^{13}	63	6.7×10^{12}	48	1.0×10^{13}
65	1.0×10^{13}	51	1.5×10^{13}	51	6.7×10^{12}	40	1.0×10^{13}
50	1.0×10^{13}	40	1.5×10^{13}	40	6.7×10^{12}	32	1.0×10^{13}
35	1.0×10^{13}	27	1.5×10^{13}	27	6.7×10^{12}	25	1.0×10^{13}

in order to prevent the latter defects from diffusing to oxygen-donor states. Such vacancies may deactivate these states as happens in the case of nitrogen and phosphorus.

In order to test the reasoning above, three identical, high-purity (type IIa) diamonds were used in a comparative experiment. All three diamonds were first subjected to anneals at 1600 °C, and then boiled in an oxidizing solution of acids[12] to clean them. Their faces, which were implanted, had identical sizes of 8×3.6 mm^2. Each diamond was subjected to the CIRA (cold-implantation-rapid-annealing) (Ref. 12) implantation-doping routine, in which the implantations at liquid-nitrogen target temperatures were followed by rapid thermal annealing (RTA) to 500 °C, where they were maintained for 30 min. The first diamond was implanted with O^+ ions, the second with C^+ ions, and the third with both C^+ and B^+ ions. The ion energies and doses used are given in Table I. In each case, these energies and doses created, according to the simulation program TRIM,[14] exactly the same amount and distribution of damage, as shown in Fig. 1. Furthermore, the O^+ diamond and the (B^++C^+) diamond contained, according to TRIM, the same number and distribution of implanted O and B atoms, respectively. Before doing the doping implantations, the contact areas of the diamonds were CIRA implanted using the same ions, respectively, in order to create a range-profile of dopant atoms which increases sharply as the surface is approached from the interior of the diamond. It has been found that such implanted regions facilitate the preparation of ohmic contacts.[7]

The resistance behavior as a function of temperature for the three diamonds is compared in Fig. 2. It is clear that both the O^+ and the (B^++C^+) diamonds had lower resistances than the C^+ diamond. Because all three diamonds should have, within experimental error, nearly the same residual radiation damage, the lower resistances can only be ascribed to the presence of the impurity atoms. The hysteresis observed between the heating and cooling cycles for the C^+ diamond can be explained in terms of charge transfer between vacancies that are in different charge states.[15] This is consistent with the theory of the CIRA routine,[12,16] from which it is expected that the residual damage, after annealing to 500 °C,

will consist primarily of isolated vacancies. The C^+ and (B^++C^+) diamonds should also contain the same density and distribution of vacancies in addition to the band-gap states which relate to the presence of the oxygen and boron atoms, respectively. Although the (B^++C^+) diamond also tended to show some hysteresis (Fig. 2), it was small compared to the C^+ diamond. In contrast, the O^+ diamond showed, within experimental error, no hysteresis within the temperature window used for the resistance measurements.

Vacancies can compensate boron acceptors[17] by forming positively charged states at ≈1.2 eV above the valence band.[18,19] It is also known that for the shallow implanted depths used in this study (see Fig. 1) many self-interstitial atoms will diffuse out of the layer before annihilating vacancies. This effect becomes more important at low annealing temperatures.[16] If enough boron acceptors have been activated in the (B^++C^+) diamond to generate hole conduction
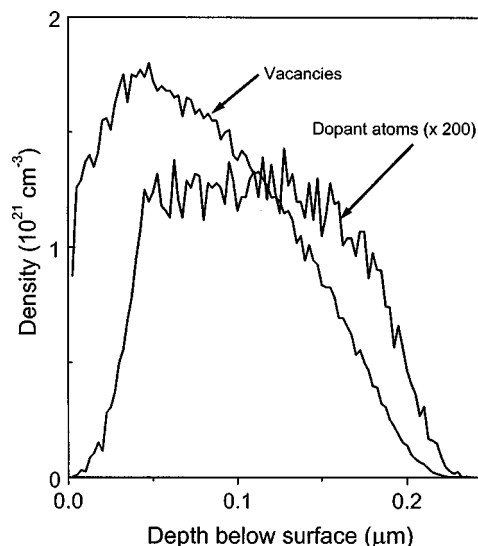

FIG. 1. TRIM simulations of the density and distribution of the vacancies and dopant atoms created in the collision cascades (assuming a displacement energy of 35 eV). See Table I for the ion energies and doses used.
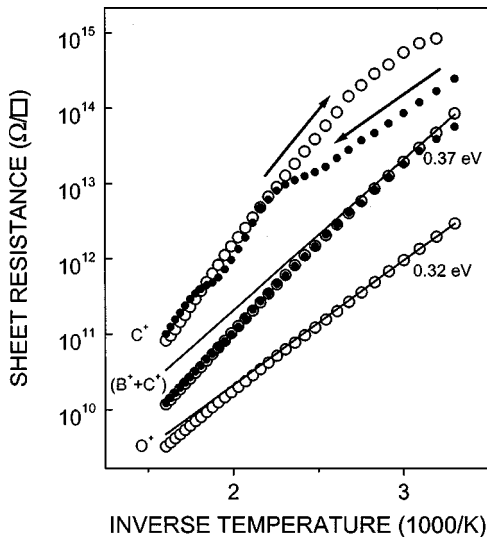
FIG. 2. A comparison of the electrical resistance behavior of the three diamonds which were implanted according to the CIRA process, which included a rapid thermal anneal from liquid-nitrogen temperature to 500 °C. O^+, C^+, and (B^++C^+) ions were used, respectively. The filled data points were measured during heating, and the open data points during subsequent cooling of the substrates.

FIG. 3. The change in resistance behavior for three sequential CIRA implantation anneals. The results measured on the O^+- and C^+-implanted diamonds are shown. The corresponding data for the (B^++C^+) diamond was similar to the O^+-diamond data.

in the valence band, one will expect the doped layer to act like a highly compensated semiconductor. This is exactly what is observed in Fig. 2. At low temperatures, conduction occurs with an activation of 0.37 eV, as expected for boron acceptors, and at higher temperatures the activation energy increases owing to the movement of the Fermi level towards a position halfway between the acceptor and positive vacancy states.[20] When this data was plotted as a function of $T^{-1/4}$, no linear relationship could be obtained. This shows that the change towards a steeper gradient with increasing temperature in Fig. 2 is not the result of variable-range-hopping conduction. Thermal-emf measurements, while maintaining a stationary temperature gradient between the contacts, showed p-type conduction.

The thermal-emf measurements on the O^+ diamond revealed n-type conduction. Furthermore, the behavior of this layer also corresponded to that of a highly compensated semiconductor. At low temperatures, conduction occurred with an activation energy of ≈ 0.32 eV, while at higher temperatures the Fermi level started to move towards compensating acceptorlike states. Vacancies can accept electrons to form ND1 centers,[21,22] which are situated at least 3.2 eV below the conduction-band states at $\mathbf{k}=0$ or ≈ 2.6 eV below the lowest band states. The results are thus commensurate with the formation of oxygen-related donor states situated at ≈ 0.32 eV below the conduction band which are compensated by vacancies that accept electrons to form ND1 centers.

Because the negative vacancy states (ND1 centers) lie much further from the conduction band than the positive vacancy levels lie from the valence band, the movement of the Fermi level away from the dopant levels is expected to occur at a higher temperature for the n-type layer (O^+ diamond) than for the p-type layer. This is exactly the case in Fig. 2. It should, however, be remembered that an oxygen atom at a substitutional site can theoretically donate two
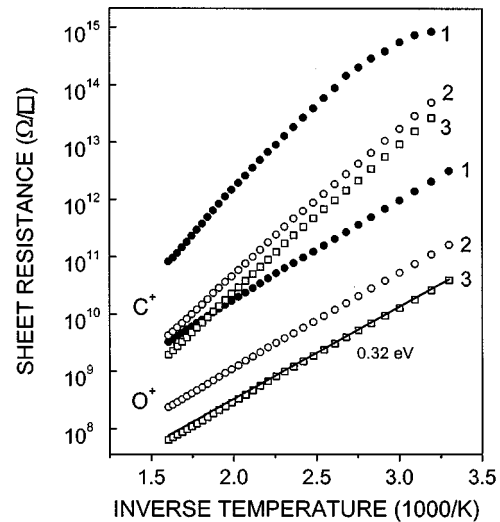
electrons. The deviation for the n-type layer may thus be a movement of the Fermi level from the first ionization level to the second. Alternatively, the first ionization level may be even lower than 0.32 eV. Lower temperature measurements, which could not be done owing to equipment limitations, should verify this possibility.

It is interesting to note that the O^+ diamond had an even lower resistance than the (B^++C^+) diamond. This may indicate that more oxygen donors became activated than boron acceptors. Alternatively, it may indicate that the electrons in the conduction band have a higher mobility than the holes in the valence band. Both possibilities may be occurring.

Further CIRA implantation steps were used to increase the density of activated dopant atoms. Although, the residual damage (in the present case the vacancies) also increases, it is known that this density tends faster towards a saturated upper limit than the dopant density.[23] The results for three identical CIRA steps (as described above) on the O^+ and C^+ diamonds are compared in Fig. 3. Only the results measured during cooling are displayed for the C^+ diamond. It is clear that in both cases the resistances decreased after each step, but that the resistance for the C^+ diamond stayed orders of magnitude higher than for the O^+ diamond. The linear behavior of the C^+-diamond layer during cooling can be explained by assuming that holes are excited from positive vacancies into the valence band.[15] It should be noted that after each O^+-CIRA step, the diamond still conducted with an activation energy of ≈ 0.32 eV at low temperatures, and that this behavior extended to higher temperatures as the number of CIRA steps increased from one to three. This is exactly what one will expect when the density of activated donor atoms increases faster than the density of compensating acceptor states. The (B^++C^+) diamond showed similar behavior owing to a faster increase in acceptor-density relative to the vacancy density.

After the third step, the resistance of the oxygen-doped diamond was low enough that a Hall-effect measurement could be attempted. A van der Pauw configuration for the contacts[24] was used. The Hall constant showed n-type con-

duction that confirmed the thermal-emf measurement. The density of electrons at room temperature and the mobility of these carriers were determined to be $n \approx 5 \times 10^{11}$ cm^{-3} and ≈ 40 cm^2/V s. The latter value is acceptable for a layer containing a very high density of vacancies. It is estimated that the residual vacancy density will decrease when MeV ion energies are used to drastically increase the width of the implanted layer.[25] It is expected that such implantations should improve the quality of these layers. These experiments are currently in progress. Even though it is expected that the oxygen donors will become deactivated for anneals above 600 °C, such doped layers, with lower compensation ratios, may be useful to generate electronic devices which operate below this temperature.

In conclusion, it is clear that n-type layers can be generated in diamond by means of oxygen-ion implantation and low-temperature annealing. The activation energy of these donor states is comparable to, and tends to be even lower than, the activation energy for boron acceptors.

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