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Volume expansion of diamond during ion implantation

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A study was made of the volume expansion obtained during ion implantation of 170-keV fluorine ions into diamond under ambient temperature. By concluding that the expansion is not related to the onset of amorphization or graphitization of the ion-damaged layer, a simple theoretical description of the phenomenon could be developed taking into account only the creation and interaction of the point defects resulting from the collision cascades. The results support the view that the so-called "amorphous" layers obtained in diamond under these implantation conditions are primarily vacancy-rich regions which to a large extent retain their diamond characteristics in skeletal form.

I. INTRODUCTION

After exposing a diamond to a 17-MeV fluorine-ion beam, the irradiated spots were found to have extruded well above the original diamond surface.[1] Using lower-energy fluorine ions (170 keV), similar large expansions could be obtained when implanting at room temperature.

Volume expansion of diamond during ion implantation has also been reported by Maby, Magee, and Morewood when they implanted diamond with boron ions.[2] They measured significant irreversible expansion when the dose exceeded 5×10^{15} ions per cm^2 and suggested that it be attributed to amorphization of the ion-damaged layer which in turn favors a diamond to graphite density change (3.51 to 2.24 g cm^{-3}) owing to the metastability of diamond. Below this ion dose they could not measure any expansion within the accuracy of their data. A secondary-ion mass spectroscopy (SIMS) analysis of the implanted boron profile also showed up appreciable broadening of the profile to greater depths below the surface after reaching the dose of 5×10^{15} ions per cm^2.

It has also been observed by Hauser and Patel[3] that when diamond "amorphizes" at these high ion doses the implanted layer can conduct electrically by means of hopping conduction, but that the ion-damaged diamond retains many of its diamondlike characteristics such as a high degree of hardness. In a follow-up study, Hauser, Patel, and Rodgers[4] estimated that if the hopping centers are graphite bonds, their number relative to the remaining diamondlike bonds is in the ratio of $10^{20}/10^{22}=0.01$ when the highest density of hopping centers is reached at a carbon ion dose of 6×10^{16} ions per cm^2. If correct, this means that at this high ion dose the transition of diamond to graphite should be only of the order of 1%.

In contrast, Maby, Magee, and Morewood found from their SIMS data for boron implantation below a dose of only 5×10^{15} cm^{-2}, an (unexpanded) range straggling of $\Delta R_p=0.05$ μm. To obtain the surface extrusion measured by them at 2.5×10^{16} cm^{-2} (the highest dose used by them but still a factor of 2 less than used by Hauser, Patel, and Rodgers) would require a diamond layer (density 3.51 g cm^{-3}) of thickness $4\Delta R_p=0.2$ μm to convert *totally* to graphite (of density 2.24 g cm^{-3}). Furthermore their data do not show any saturation indicating that larger expansions could have been measured at doses above 2.5×10^{16} cm^{-2}.

We have investigated this phenomenon more closely by extending our measurements for 170-keV fluorine ions from low to very large ion doses (up to 7.6×10^{17} ions per cm^2).

II. EXPERIMENT AND RESULTS

Use was made of a type IIa diamond on to which a flat area of approximately 150 mm^2 was polished. Different spots for irradiation were masked off using a stainless steel disc with a 2-mm-diameter hole in it and each spot implanted at ambient temperature to a different dose using 170-keV fluorine ions at a rate of 2.2×10^{13} cm^{-2} s^{-1}. For some implantations, a thermocouple was mounted just under the mask on top of the diamond surface. It was found that the surface temperature increased very rapidly at this dose rate, to exceed 100 °C. After each implantation the step height of the implanted spot was measured with a Taylor-Hobson Surtronic 3 profilometer. The implanted dose was varied from 3×10^{15} to 7.6×10^{17} ions per cm^2.

The results obtained are displayed in Fig. 1. It can be seen that at low ion doses (up to about 5×10^{16} cm^{-2}) the volume expansion is very rapid. At higher doses the expansion rate decreases and becomes constant giving a linear increase in volume with dose. Furthermore, it does not seem as if the expansion occurs suddenly above a critical dose as proposed by Maby, Magee, and Morewood,[2] but starts as soon as implantation is initiated. Indeed, extrapolation of the curve down to zero step height indicates that the most rapid expansion occurs at the lowest ion doses, and that this rate of expansion gradually slows down as a dose of 5×10^{16} cm^{-2} is approached.

Part of the volume expansion must occur to accommodate the fluorine atoms which were injected into the diamond crystal and this expansion should be approximately linearly related to the ion dose. It seems thus reasonable to deduce that the linear slow increase in expansion ob-

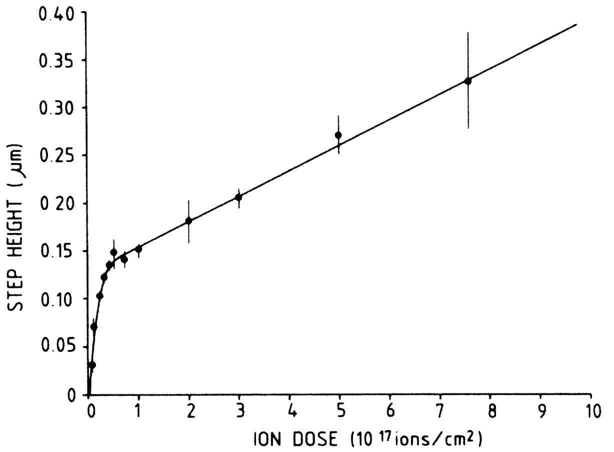

FIG. 1. Dose dependence of the step height on a diamond surface caused by the volume expansion during implantation of 170-keV fluorine ions.

served at high ion doses is caused by this accommodation. The slope measured for this linear portion is equivalent to a volume increase of 26 $Å^3$ for each injected ion. Each carbon atom in the diamond lattice occupies a volume of only 5.7 $Å^3$. Thus in the linear region, the expansion obtained is about 4.6 carbon atom volumes per impinging ion. Taking cognizance of the fact that a fluorine atom has a smaller radius than a carbon atom indicates that the large expansion of 26 $Å^3$ may contain data on the chemical accommodation of the fluorine atoms in the implanted diamond or further ion-to-target ballistic information (see Discussion, below). Subtraction of the linear expansion from the measured data renders the curve shown in Fig. 2. This graph illustrates the rapid increase in volume at low doses leading to saturation; it does not relate linearly to ion dose and thus needs a different interpretation.

From the computer program TRIM–86,[5] the distribution of total target vacancies expected (not taking into account possible volume expansion or subsequent annealing) when implanting diamond with 170-keV fluorine ions can be obtained, and the result after 1400 incident ions is given in Fig. 3. The distribution consists of two superposed parts, i.e., a high-density peak centered around a depth of about 0.13 μm and a lower-density tail extending out to the surface. To obtain a step height of 0.126 μm through graphitization would require virtually the whole damaged width (peak and lower-density tail) to graphitize completely. Again, this would not correspond to the possible partial graphitization suggested by the results of Hauser and Patel,[3] and Hauser, Patel, and Rodgers[4] for high-dose carbon ion implantation into diamond.

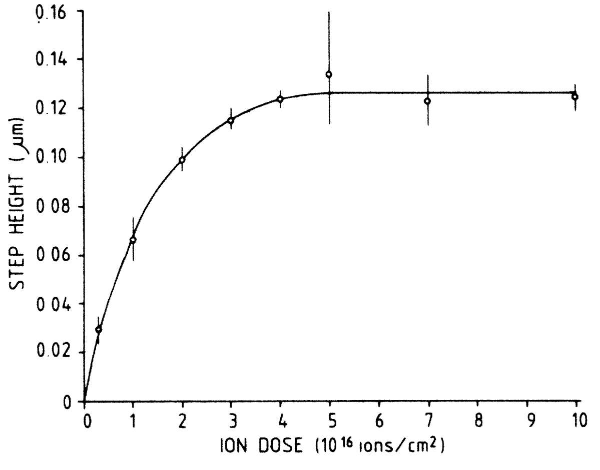

FIG. 2. Dose dependence of the rapid volume expansion observed at low ion doses after subtraction of the linear expansion which is prevalent at high ion doses.

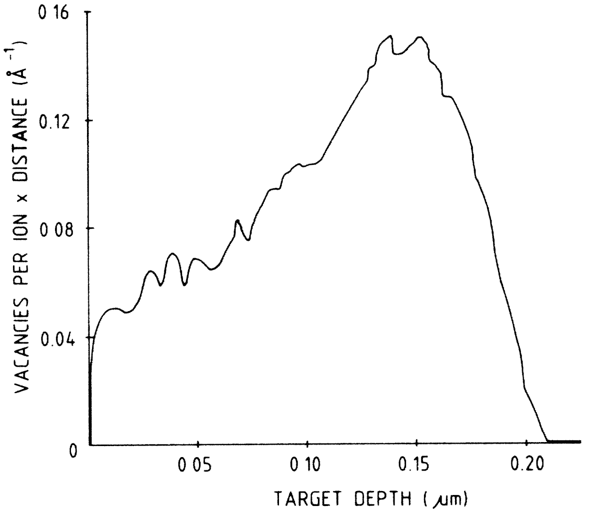

FIG. 3. Unannealed vacancy distribution in diamond after implantation with 170-keV fluorine ions as simulated by the TRIM-86 (Ref. 5) computer program.

III. THEORETICAL MODEL

A previous investigation into the onset of hopping conduction in diamond implanted with carbon ions while being maintained above room temperature (at 250 °C), but below the temperature at which diamond growth occurs, indicated that the onset of conduction correlates with the density of immobile vacancies remaining in the ion-damaged region after their corresponding interstitial atoms have diffused out of this layer.[6] Large-scale diffusion of interstitial atoms during ion implantation seems to occur above about 50 °C.[7,8] For temperatures between 50 and 500 °C it was accordingly assumed that, whereas the vacancies formed in the collision cascades are immobile, the interstitials, or at least a substantial fraction of them, can diffuse out of the layer being implanted, leaving behind a corresponding number of vacancies. It would seem thus quite logical to suggest that the initial rapid expansion observed during the present investigation (Fig. 2) is caused by the same mechanism. As observed, ion beam heating caused the diamond surface temperature to exceed that needed to allow interstitial diffusion. This should induce some of the interstitials to diffuse out of the damaged region towards other sinks, which may even be the nearby surface. In this case the expansion at low ion doses (Fig. 2) should be a direct measure of the corresponding number of immobile vacancies remaining in the damaged layer after out-diffusion of the interstitial atoms.

Let each ion being implanted dislodge on average a cascade of α host atoms in the nuclear stopping region. After the cascade has subsided, an atom which has cascaded will be found either again in a lattice position, or (more probably) in a nonlattice site. Depending on the temperature the latter atoms, or at least a fraction of them, may now diffuse and in so doing either recombine with a vacancy or get trapped at a site in the damaged layer or diffuse out altogether.

The probability that an atom in a cascade will be trapped by a vacancy before it can escape from the damaged layer, either ballistically or by diffusion, will obviously depend on the availability of vacancies. As their number increases so will this probability, and it seems reasonable to assume that the expansion saturates when it approaches unity, i.e., each cascade will in effect create as many vacancies as are subsequently filled by the cascading atoms. This probability should be a function of the relative density of the vacancies and the width of the implant, which when multiplied, gives the total number of vacancies n_v per cm^2 divided by the number of atoms per cm^3 (N) resident in a perfect diamond lattice. Accordingly, a simple probability function P for a cascading atom to recombine with a vacancy and not to leave the ion-damaged region may be assumed as

$$P=\beta\frac{n_v}{N}\ . \tag{1}$$

β has been found to increase with increasing target temperature.[9]

Increasing the ion dose by dS ions per cm^2, causes $\alpha\, dS$ new vacancies (or cascading host atoms) of which $P\alpha\, dS$ will be filled by the cascading atoms during ballistic or diffusional motion. Accordingly the increase in vacancies with increase in ion dose dS will be

$$dn_v=\alpha\, dS-\beta\left[\frac{n_v}{N}\right]\alpha\, dS\ . \tag{2}$$

Integration gives the total number of vacancies n_v obtained after ion implanting to a dose of S ions per cm^2. Each one of these vacancies represents a host atom which has escaped to add to the volume increase and each such host atom represents a volume of N^{-1} in the diamond lattice. From Eq. (2) the step height H at a vacancy density n_v, can be derived, ignoring any effect which may result from lattice relaxation after vacancy creation, as

$$H=\frac{n_v}{N}=\beta^{-1}\left[1-\exp\left[-\frac{\alpha\beta S}{N}\right]\right]\ . \tag{3}$$

For large ion doses, H saturates to become β^{-1}. From Fig. 2 the saturated step height has been obtained as 0.126 μm, which immediately renders a value for β of 7.9×10^4 cm^{-1}. Using this value and the experimentally determined step heights shown in Fig. 2 for doses below saturation it is possible to display the expression $\ln[(1-\beta H)^{-1}]$ as a function of ion dose in Fig. 4. A linear relationship is found supporting the validity of Eq. (3). The measured slope of the straight line is

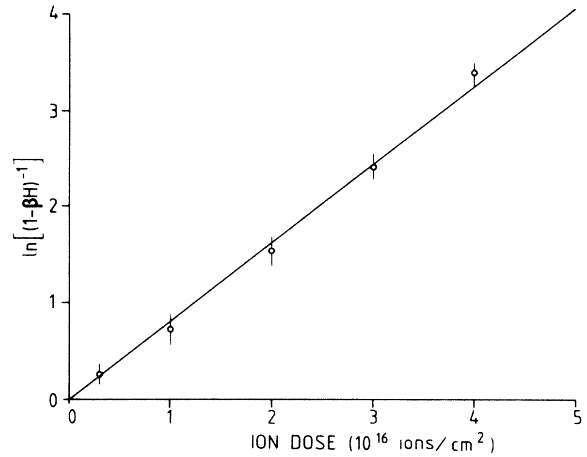

FIG. 4. The linear relationship found between $\ln[(1-\beta H)^{-1}]$ and ion dose for 170-keV ions into diamond. H is the step height on the diamond surface. The inverse of β gives the saturated step height observed above an ion dose of 5×10^{16} ions per cm^2.

$$\frac{\alpha\beta}{N}=8.25\times10^{-17}\ \text{cm}^2\ \text{per ion}\ .$$

Using $\beta=7.9\times10^4$ cm^{-1} and $N=1.77\times10^{23}$ atoms/cm^3 gives $\alpha=184$.

In the literature, two values are quoted for the threshold energy needed to displace a carbon atom from its normal site in diamond: i.e., 80 eV (Ref. 10) and 35 eV (Ref. 11). Using these two values in executing the program TRIM-86 (Ref. 5) for implantation of 170-keV fluorine ions into diamond gives the average number of vacancies created per ion as 123 and 282, respectively. These two values straddle the value of 184 found for α above. A displacement energy of 55 eV causes the number of vacancies per ion to correspond to $\alpha=184$.

Obviously, lattice relaxation around the vacancies may affect the step height measured, causing it to be lower than it would have been without it. This can be taken care of in a simple way by multiplying the right-hand side of Eq. (3) by a factor $\gamma<1$. Then $\beta/\gamma=7.9\times10^4$ cm^{-1}. Assuming a value for $\gamma\sim0.9$ gives $\beta=7.1\times10^4$ cm^{-1} and $\alpha=206$, indicating a possible lower displacement energy than 55 eV.

IV. DISCUSSION

Further support for the model was obtained by applying it to the measurements made by Maby, Magee, and Morewood[2] for 200-keV boron ion implantation into diamond. Unfortunately they did not measure to high enough ion doses which could have established the value of the saturated volume expansion expected. In order to find a possible value for α, the program TRIM-86 (Ref. 5) was again executed, in this case for boron ion implantation into diamond. For a realistic comparison to the fluorine case, use was made of a displacement energy of

55 eV which gave $\alpha = 101$. With this value a good description of the boron data could be obtained for $\beta = 5.0 \times 10^4$ cm^{-1} as shown in Fig. 5. Compared to the value of β obtained for the fluorine data, this number seems to be reasonable, in view of its temperature dependence (see below).

It is possible to ascribe the absence of expansion below a boron ion dose of 5×10^{15} cm^{-2} as reported by Maby, Magee, and Morewood,[2] to insufficient ion beam heating as indicated by their lower β. Their diamond holder may have been a better heat sink than ours and/or their dose rate low enough to limit this heating at low total doses. At higher doses (above 5×10^{15} ions per cm^2) the implantation time would be longer allowing a temperature to be reached at which substantial interstitial diffusion could occur. The fact that the same investigators found from SIMS analysis that the boron profile broadened in sympathy with the external expansion measured might indicate, contrary to the model proposed here, that expansion due to phase relaxation does indeed occur in the implanted layer. However two other mechanisms may rather account for this broadening. Firstly, the outdiffusion of interstitial atoms from the ion-damaged layer will decrease the density of atoms available to take part in the collision cascades caused by subsequent impinging ions. This should enlarge the average distance traveled by the cascading atoms which, in turn, would have the effect of broadening the damaged width in inverse proportion to the decrease in density. For n_v vacancies and width w, the density of remaining material ρ should be proportional to $N - n_v/w$. If the initial density was ρ_0 (proportional to N) the ratio of the damaged width w to the undamaged initial width w_0, should be

$$\frac{w}{w_0} = \frac{\rho_0}{\rho} = \frac{N}{N - n_v/w} .$$

Solving for w gives

$$w = w_0 + n_v/N . \tag{4}$$

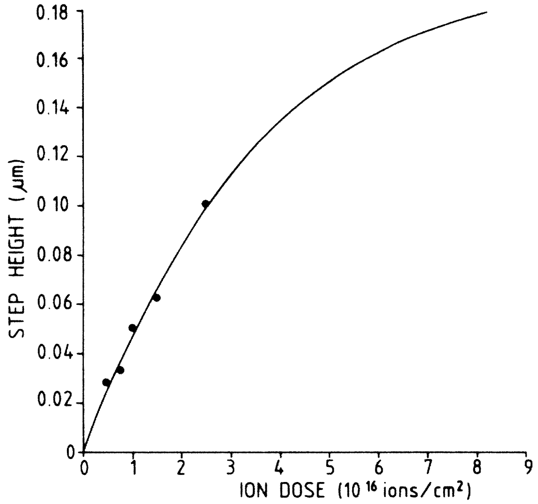

FIG. 5. Correspondence obtained between the results measured by Maby, Magee, and Morewood (Ref. 2) for 200-keV boron ion implantation into diamond, and the proposed theoretical model when choosing $\alpha = 101$ and $\beta = 5 \times 10^4$ cm^{-1}. The calculated curve has been extended to high ion doses illustrating the expected onset of saturation in volume expansion.

Secondly, at least some of the interstitials which egressed from the damaged layer may add on to the exposed surface being implanted. This will have the effect of lengthening the path from the surface to the layer where most of the nuclear stopping occurs. Subsequent ions will thus stop on average at a position nearer to the original surface, in this way also broadening the width of the ion-damaged layer. For example, if all the escaped interstitials add on to the surface the effective range is lengthened by the same amount as the step height $H = n_v/N$. If both processes operate the total width increase may be written as

$$w = w_0 + \lambda n_v/N , \tag{5}$$

where $1 < \lambda < 2$.

It is interesting to note that if either process were to operate, the effect would be to increase the apparent average range R_p of the ions. This is exactly what Maby, Magee, and Morewood[2] observed from their SIMS profiles for a dose of 5×10^{15} cm^{-2}, where broadening occurred. According to their data, the range at 3×10^{15} ions per cm^2, where no step was observed, was $R_p = 0.24$ μm and the straggling $\Delta R_p = 0.05$ μm whereas at 5×10^{15} ions per cm^2, with a step height of just under 0.03 μm, R_p was 0.28 μm and $\Delta R_p = 0.06$ μm. Subtraction of $(R_p + \Delta R_p)$ for the lower ion dose from the same distance for the larger dose gives 0.05 μm which is almost twice the step height measured at the latter dose.

With the aid of Eq. (5) it is possible to calculate the average immobile vacancy density N_v (per cm^3) remaining in the damaged layer as

$$N_v = \frac{n_v}{w} = \frac{n_v}{w_0 + \lambda n_v/N} . \tag{6}$$

The saturated vacancy density N_{vs} is then reached when $n_v = N/\beta$, giving

$$\frac{N_{vs}}{N} = \frac{1}{\beta w_0 + \lambda} . \tag{7}$$

From TRIM-86,[5] the FWHM values for the ion-damaged layers could be obtained as 0.12 and 0.10 μm for the fluorine and boron ions, respectively. Using these values for w_0 in conjunction with the values determined for β above, and assuming $\lambda = 2$, the expected average densities at which saturation should occur could be calculated from Eq. (7) and found to be 0.34 and 0.40 for the fluorine and boron ions, respectively.

Obviously, the probability P in Eq. (1) will never be exactly unity. Interstitial atoms created near the edge of the damage distribution will have a better chance to escape than the ones created further in. Thus, even after saturation has been achieved some interstitial atoms will still escape when increasing the ion dose. Furthermore, if the implanted ion competes with the cascading host atoms to fill vacancies, an extra interstitial per impinging ion will on average be created which can then also escape. If these escaping atoms now again add on to the surface, the effective range will be increased still further and this will cause extra width of lower vacancy density to be added to the existing damaged width. This extra width, in turn, will supply further interstitials which can escape. Thus even after saturation has been reached, the impinging ions could still liberate atoms which escape and add to the volume. In such a steady-state case the number of atoms released would be proportional to the number of incoming ions. This may explain the 4.6 atomic-volume increase per ion observed after saturation has been reached for fluorine above a dose of 5×10^{16} cm^{-2} (see Fig. 1).

It is interesting that such a simple probability function, as chosen in Eq. (1) should lead to a theoretical model which describes the observed volume expansion to such an apparently satisfactory degree. One expects that a more accurate function should exist which will improve the theory. To date, other functions which intuitively seemed physically more reasonable, gave worse descriptions. A better understanding of the mechanics involved during diffusion assisted interstitial-vacancy recombination could undoubtedly lead to a better choice for the probability P. Furthermore, the number of vacancies per ion, α, although an average quantity, may not be constant over the whole range of the implant. The decrease in density in the damaged layer with increasing vacancies should disturb the bonding between the remaining atoms, thus lowering the threshold displacement energy with an accompanying increase in α. A better choice for the function P should reflect such an occurrence.

If this model is correct, implantation at a temperature where no interstitial diffusion can occur should severely limit the expansion, as shown in the low-dose results of Maby, Magee, and Morewood.[2] Implantation of fluorine ions at liquid-nitrogen temperature showed no expansion below a dose of 1×10^{16} ions per cm^2.[12] At and above that dose, expansion did occur which gave a different type of curve and may be ascribed to amorphization as originally proposed by Maby, Magee, and Morewood.[2]

This theoretical model is based on the same arguments as were used to explain the onset of hopping conduction in ion-implanted diamond.[6] In that study it was assumed that hopping conduction starts when the vacancy density reaches a certain value. It was further speculated that the vacancy rich layer may form a type of "low-pressure" region which facilitates relaxation to a partly graphite bonded structure, which in turn provides the hopping centers. Although the present results do not exclude some form of relaxation at very high vacancy densities, they indicate that the hopping centers may be directly related to the vacancies, even after onset of conduction.

V. CONCLUSION

This study indicates that the expansion observed in diamond implanted above room temperature can be explained by a theoretical model which only takes into account the creation and movement of point defects resulting from the collision cascades without having to invoke an amorphization threshold nor having to consider the possible conversion to graphite of the diamond layer being implanted. The so-called amorphized layer obtained in diamond at high ion doses is in many cases probably a vacancy rich crystal lattice which to a large extent retains its gross integrity as diamond.

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