Molecular Dynamic Simulation for the NV-N Center Formation by Means of N_2 Beam Implantation into a Diamond

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We have searched for an optimum condition to form a specific defect center called NV-N (nitrogen-vacancy-nitrogen) in a diamond, which is of interest, because of the possibility of a NOT system in a quantum computer. It is composed of one NV center made of a substitutional nitrogen (N) coupled with an adjacent vacancy (V) and an associated N atom. The second N is located at a mean distance (R_{N-N}) of ~ 2 nm. Considering the cohesive potentials we performed an empirical molecular dynamic simulation for the low-energy N_2 beam implantation into a diamond. The identification of a NV center was performed by a crystallographic analysis called the pixel-mapping (PM) method based on crystallography. We found that impact energy E_0 could be decisive for the mean distance R_{N-N}, while temperature T was decisive for the formation of NV centers. The optimum set of conditions to form an NV-N center is a compromising choice of (E_0, T). The formation probability of the NV center exceeded 20 % when using (E_0, T) = (200 (eV/atom), 1000 K), however, the mean value $<R_{N-N}>$ was below 1.5 nm. A little higher energy than 200 (eV/atom) will be necessary for ideal NV-N centers.

1. INTRODUCTION

A quantum computer (QC) is a breakthrough as the ultimate algorithm of vector computation. The qubit (quantum bit) supports its basis. For a realistic QC to be available at room temperature a solid-state QC has to be developed. The NV (substitutional nitrogen (N) and adjacent vacancy (V)) center in diamond, whose bonding is along the <111> orientation, is such a promising candidate that can produce a set of three-state qubit [1]. In the NV center, an excess electron supplied by a N atom (V group element) in a diamond (IV group one) is localized at the vicinity of the adjacent V site. If the electron-spin is coupled with some nuclear spin and the interaction lasts long, the entangled quantum states can be a useful unit for quantum cryptography [2, 3].

Furthermore, in order to set up the logical circuit of a QC, a quantum NOT logic gate is necessary. A model for the NOT has been demonstrated, by adding nitrogen in the neighbor- hood of NV center [1], which is called a "NV-N" center [4]. The intrapair distance between the two N atoms, R_{N-N}, is essential. The second N atom has to be located at an "appropriate distance of R_{N-N} ~2 (nm)" from the NV center [5]. When a NV-N center is produced under ion beam implantation, the formation process can be either 1) one NV center is first formed, later an additional N atom might stop at the appropriate distance from the NV center, or 2) two N atoms are located at the appropriate distance to each other, and afterwards a migrating vacancy approaches either of them and forms the NV center. For the formation model 1), we had simulated the formation process of NV-N using a Molecular dynamics (MD) simulation [6]. A single N atom entered the MD box representing a diamond lattice in which one NV center was positioned at its center. The depth of the MD box was about 2 times larger than the mean projected range of 200 eV N into C. The mean projected range of 1.2 nm was obtained using a Monte-Carlo (MC) simulation called SRIM [7]. The MD calculations were performed at low temperatures below 30K. In most cases the NV center did not survive the bombard- ment and finally none of the two N atoms was at a substitutional site. Thus it was almost impossible to form NV-N centers.

For the formation model 2), it is essential whether one can manipulate the allocation sites of N atoms, i.e., R_{N-N}. Gaebel et al. [8] proposed that the R_{N-N} could be tunable if N_2 implantation, making use of a MC simulation, was done. Therefore, in this article we will

examine the model 2) and use a N_2 beam at higher temperatures than before [6], close to annealing temperature (ca. 1073 K). We search for the optimum condition to produce a NV-N center making use of MD calculations combined with the Pixel Mapping (PM) method [9], not by the MC. The reasons are threefold. The first is to adopt a cohesive potential for atoms forming a molecular beam and to trace the simultaneous interaction due to molecular ion impact. Such consideration is beyond MC capacity assuming binary collisions. The second reason is to consider the temperature effect. The lattice vibration may be significant for atomic migration to build up the NV centers, while it is missing in MC. The third one is to analyze crystallographically the NV center. The identification of a NV center is possible by the PM analysis. Therefore, the highest temperature is set at 1000 K. The highest energy of impact is taken as 200 (eV/atom).

2. METHOD

2.1 MD simulation

The details of the MD simulation for N implantation into a diamond crystal were described in the previous article [6] except for the consideration of the molecular effect due to N2 implantation. Unless a molecule or cluster is so huge and has very high energy, the scaling in terms of the partial energy (=energy/atom) seems to be a probable rule to discuss the molecular effect on each phenomenon. This implies that the molecular effect needs to be examined as the nonlinearity [10]. The molecular effects caused by a cluster beam impact are governed by many factors. For example, they are impact energy E_0 (eV/atom), temperature (T), cluster size, and the kind of phenomena concerned. There are two points that need to be mentioned here.

One is the interaction potentials. If the impact energy is large enough, consideration of the interaction between atoms in the projectile molecule might not be necessary [11]. However, in order to examine the dissociation at the vicinity of surface due to low-energy impact from 100-200 (eV/atom) and trace those atoms, the cohesive interatomic potentials are indispensable. We have derived Morse-type potentials for a N-N and a N-C system based on an ab-inito calculation using the B3LYP method [6]. The bonding energy of a N2 molecule is the second strongest one [12] in nature, thus it is worthwhile to consider those cohesive potentials at low impact energies, as in the present case.

The other point is the lateral range-straggling. The necessary size of the MD box depends on the phenomenon concerned, e.g., our issue demands a large size that includes all total collision cascades. For the previous case of N implantation with energy below 200 eV, the MD volume of $2.1 \times 2.1 \times 2.1$ (nm³) was large enough [6]. The half depth of it agrees with the mean projected range of 200 eV N into carbon, if followed the SRIM prediction. Empirical evidence shows that the ion ranges of X and Xn beams are almost invariant when they have the same partial energy. For example, a few %

of the molecular effect on ion ranges was observed by As^+ and As^{2+} beams implanted into Si at an energy of 3 (keV/atom) [13]. However, collision cascades originated from one molecular ion may share a part of the incident energy in terms of traverse momentums with opposite signs, which means the increase of lateral range straggling as is known in cluster beam sputtering. Thus, for an N_2 beam that has the same partial energy with the previous case, the MD box is expanded laterally by a factor two, i.e., $4.2 \times 4.2 \times 2.1$ (nm³). Depending on the impact point on the crystal surface, the collision events differ. Therefore, a set of one hundred of N_2 molecule implant events are done in order to get a statistical distribution for each condition of (E_0, T). In each event, a newly oriented N_2 molecule was entered a crystal after refreshing the irradiation effect.
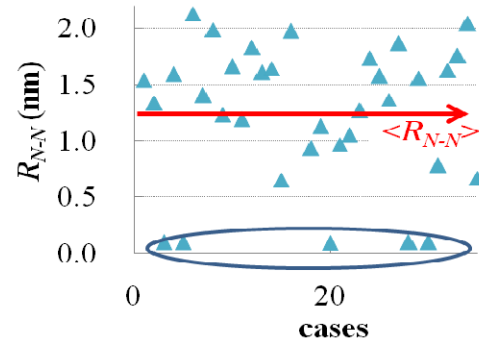

Figure 1. The distribution of R_{N-N} when either N atom forms a NV center produced by N_2 beam with energy of 100 (eV/atom) at 1000 K. The horizontal long arrow shows the mean value $< R_{N-N} >$ of them. Some cases encircled at the bottom show the part of pairs as shown molecule in Table 1.

On the other hand, in order to identify defects in a crystalline target, we have developed the PM method [9] that can also extract various kind of crystallographic information from atomic distributions. It assigns the location of atoms in a cubic crystal not by Cartesian coordinates (x, y, z) with real numbers but by pixel's address. In the case of a diamond [14], the PM method segments one unit cube into $4 \times 4 \times 4$ pixels, each of which is labeled by a set of three integers (l, m, n) as its address. A perfect diamond means that two kinds of pixels are completely occupied: Their address (l, m, n) should satisfy either condition of (i) {MOD(l+ m+ n, 4) =0, where every component of (l, m, n) is even} or (ii) {MOD(l+ m+ n, 4) =3, where every component (l, m, n) is odd}. If one of such a pixel is vacant or occupied by a N atom, it assigns the presence of one V or substitutional N atom, respectively. Note that like a NV center, two adjacent lattice sites belong to different group as (i) and (ii) to each other. This is how we precisely distinguish a NV center along <111> orientation, a NV-N center, a N-N (A center), or even a N-V-N center (H3 center) on the $(1\,1\,0)$ plane, from

the distribution of scattered atoms after (N or N_2) implantation, in connection with a MD simulation.

3. RESULTS

3.1. Distribution of implanted N_2: energy and temperature dependence

The intrapair distance between N atoms (R_{N-N}) in a N_2 molecules is 0.102 nm before implantation, then they are scattered due to atomic collisions with the target

medium. We traced the process for 3 picoseconds, which is long enough to approach quasi-equilibrium with a heat bath. Then, the MD system refreshes the irradiation effect and is ready for a new bombardment.

E_0 (eV/atom) \ T (K)		10 K	100 K	300 K	800 K	1000 K
100 (eV/atom)	$<R_{N-N}>$ (nm)	1.24	1.21	1.30	1.29	1.22
	$R_{N-N,max}$ (nm)	2.90	2.77	2.42	2.46	2.68
	$R_{N-N,min}$ (nm)	0.106	0.103	0.098	0.103	0.0999
	molec. (%)	14 %	12 %	13 %	16 %	17 %
200 (eV/atom)	$<R_{N-N}>$ (nm)	1.94	1.98	1.95	1.59	1.85
	$R_{N-N,max}$ (nm)	4.71	4.43	5.31	4.31	4.35
	$R_{N-N,min}$ (nm)	1.09	0.103	0.104	0.0997	1.00
	molec.(%)	4 %	8 %	5 %	21 %	19 %

Table 1. Intrapair distance between N atoms after ion impact, being independent of the presence of NV centers. R N-N,max and R N-N,min indicate the maximum and minimum value of R N-N, respectively. The latter value is almost same as the initial value of implanted N_2 molecule, whose possibility is added as the rate of "molec.(%)".

As is shown in Table 1, the higher the impact energy, the longer the mean value of R_{N-N} is. This tendency of increase agrees qualitatively with a MC prediction [8]. Nevertheless, some N_2 molecules stick together even after bombardment keeping almost the initial value of $R_{N-N} = 0.102$ nm. The fraction indicated as "molec.(%)" counts the cases of $R_{N-N} < 0.12$ nm in one hundred runs. The lower the temperature and the higher the energy, the lower the fraction of "molec. (%)"1 is. The large bonding energy between N atoms can be the cause of close distance after migration following ion impact. Note that Table 1 lists the data, being independent of whether a N atom forms a NV center or not.

As was shown in Table 1, the temperature effect was not so significant on the value $< R_{N-N} >$. Even with a 100 times higher temperature, 10 K vs. 1000 K, the deviation of the distance R_{N-N} looks not so significant to be compared with that of 10 K.

3.2 NV-N center formation due to N_2 implantation

In order for identification, the presence of a NV center is actually more crucial than the separation between two N atoms (R_{N-N}). The higher the temperature, the more NV centers may be expected. The solid triangles in Fig.1 show the distance R_{N-N}, for cases only when at least one N atom forms NV center. Under the impact energy of 100 (eV/atom) at 1000 K, the mean value $<R_{N-N}>$ of well diverged values is around 1.3 nm, which is lower than the desired value of 2nm for making the NV-N center. Several symbols enclosed at the bottom indicates the cases of $R_{N-N} < 0.12$ nm, which are shown as

molecule in Table 1. This value is much smaller than the first neighbor distance in a diamond, than in the A center, and than that in the H3 center.
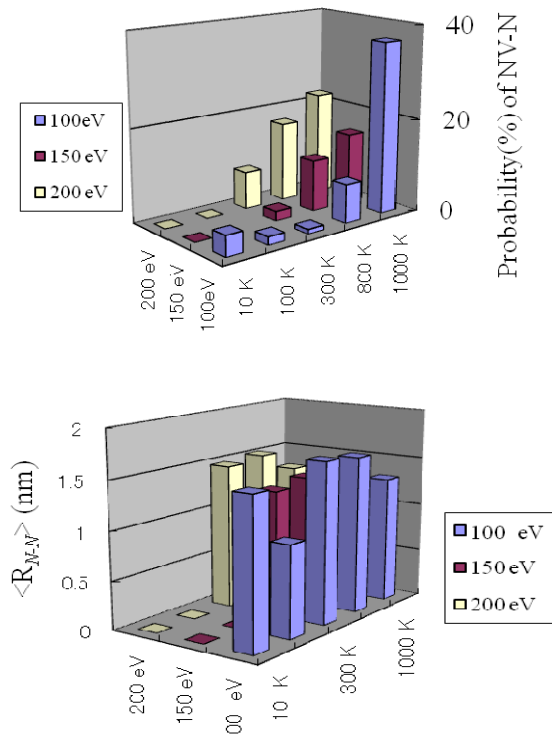

Figure 2.   The energy and temperature dependence on the NV center formation (Fig.2a), where the ordinate indicates the probability (%). The mean values of $<R_{N-N}>$ of them are shown in the second histogram (Fig.2b).

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1 In fact, test runs at much higher energy of 1000 (eV/atom), the mean value of R_{N-N} exceeded 3 nm and no cases of molecular situation as $R_{N-N} < 0.12$ nm was obtained.

The Figure 2 shows the formation probability (ordinate) of NV centers (Fig.2a) and the mean value of $< R_{N-N} >$ when a NV center is formed (Fig.2b) in all conditions of (E_0, T). The formation probability of NV-N centers due to N_2 impact depends strongly on (E_0, T) as is expected. Temperature T (one abscissa) is definitely significant for the formation probability of a NV center as is shown in Fig.2a, whereas the other factor E_0 (another abscissa) is not so evident. Both of them work as compromising factors for the NV-N centers. As far as the condition of $E_0 < 200$ (eV/atom), the mean value $<R_{N-N} >$ is below the ideal value for the NV-N centers.

4. CONCLUSION

In order to study the optimum condition to form a NV-N (nitrogen-vacancy-nitrogen) center in a diamond crystal, we have used a classical molecular dynamics (MD) simulation. The issue was to examine a dimer implantation with very low-energy, where the dimer has very strong cohesive interaction. The desired structure of a NV-N center is supposed to be a substitutional N adjacent to a vacancy, whereas the second one is apart from the first one by the distance of $R_{N-N} \sim 2$ (nm) [5]. The incident energy (E_0) span employed was $E_0 = 100 \sim 200$ (eV/atom) and the temperature span was T = 10 $\sim$ 1000 (K). The value of R_{N-N} increased with E_0 as was predicted by a Monte-Carlo simulation [8], if the presence of the NV center was ignored. As a trend, we can say: The higher the E_0, the longer the distance R_{N-N} is." We need $E_0 > 200$ (eV/atom) $\rightarrow < R_{N-N} > \sim 2$ nm. Evidently, we can say: The higher the temperature (T), the higher probability of a NV center." At T = 1000 K, the probability of NV-N center $\sim$ 20 %. Therefore, the optimum condition can be { $E_0 > 200$ (eV/atom) and T = 1000 (K)} to avoid the surviving molecules and to form ideal NV-N centers, with" $R_{N-N} \sim 2.0$ (nm)".

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