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The diffusion of vacancies near a diamond (001) surface

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Abstract

The diffusion process of the vacancy near diamond (001) surface at different temperatures was investigated by molecular dynamics simulation. The vacancy in the second layer begins to diffuse towards the surface at about 1000 K, and it can migrate to the surface in the temperature range of 1400–2000 K. In the 1400–1800 K temperature range, two migration stages, which correspond to two maxima in the mean square displacement curves, are observed in the vacancy diffusion process. In addition, the vacancy diffusion path is obtained without any constraints imposed on the atoms, and the calculated diffusion barrier of the vacancy near diamond (001) surface is about 0.42 eV. © 2002 Published by Elsevier Science Ltd.

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1. Introduction

As a very important defect in diamond, a vacancy can strongly affect the diamond growth as well as its electronic and optical properties. Bar-Yam and Moustakas [1] proposed a quasi-thermodynamic model, in which high vacancy concentrations were present near the growth face of the diamond film. The formation energy of vacancy in diamond is smaller than in graphite, so that large vacancy concentrations can raise the formation energy of graphite above diamond, permitting nucleation and stable growth of diamond. This model predicted that the growth of diamond film with low vacancy concentration would be difficult. Mainwood [2] suggested that the vacancies were mobile at temperatures at which the growth proceeded, and they could migrate to the surface or combine with each other. Obviously, what effect the temperature can cause on the vacancy movement is an important question in the study of diamond growth. However, to our knowledge, there is no systematical investigation of the temperature effects on vacancy diffusion process, such as vacancy diffusion path and its diffusion barrier. Halicioglu [3] investigated the vacancy formation in diamond surface and found that the diffusion of a single vacancy from the top surface to the second layer was not favored in energy. Breuer and Briddon [4] studied the vacancy diffusion and its diffusion barrier in bulk diamond using ab inito method, and they obtained vacancy diffusion path using quasi-dynamics method. However, they used a small cluster $C_{44}H_{42}$, which may limit the calculation accuracy. In experiment, the vacancy was investigated by optical and electrical methods, and the results gave the average properties as a result of various effects on it, from which the effects of specific factor on the vacancy movement could not be identified easily [5].

In present work, we use molecular dynamics (MD) method via Tersoff many-body potential [6] to investigate the temperature effects on the vacancy diffusion near diamond (001) surface. Also, the vacancy diffusion path is achieved without any constraints imposed on the atoms, and the diffusion barrier energy is calculated.

2. Calculation method

A $5a \times 5a \times 5a$ (a is lattice constant of diamond) supercell was used and it consisted of 20 layers of 50 carbon atoms each, totally 1000 atoms. The z-axis was directed along the [001] direction, perpendicular to the diamond (001) surface, whereas the x- and y-axes lie on the surface plane. To get (001) surface, the atoms of bottommost two layers were held fixed and two-dimensional periodic boundary condition was applied to the system along x- and y-axes.

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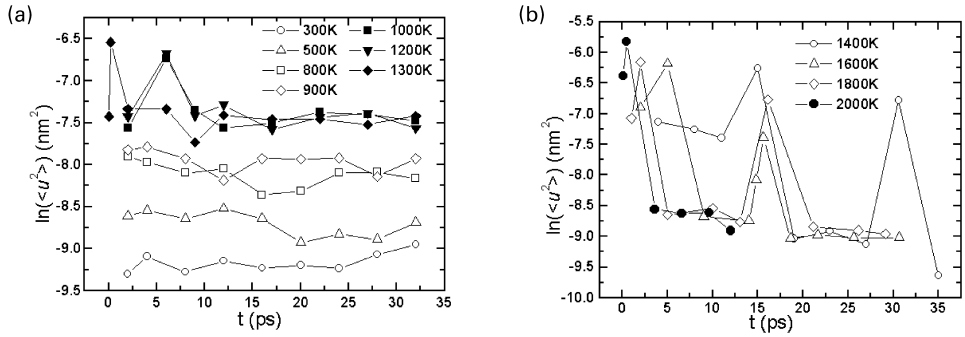

Fig. 1. MSD curves of the vacancy's nearest neighbor atom in the surface in the 300–2000 K. (a) 300–1300 K; (b) 1400–2000 K.

The atomic interaction was described by Tersoff many-body potential [6]. The Newton equations of motion for atoms were integrated using the velocity Verlet algorithm [7] with a time step of 1 fs, and the rescaling velocity method [8] kept the system at a certain temperature. The considered temperature was varied from 300 to 2000 K. The initial atomic coordinates were chosen from a diamond lattice at 0 K. After the system was relaxed at 300 K for 5 ps, an atom in the second layer was removed. Then, the system with a vacancy was relaxed for another 5 ps at 300 K, and the atomic configuration at the end of the relaxation was taken as the starting point of subsequent MD run at given temperature. The total run time lasted from 12 to 35 ps depending on the temperature, and the atom's position was recorded at every time step during the calculation.

Diffusion coefficient of vacancy was calculated according to Einstein relation:

$$D = \frac{\left\langle u_\alpha^2 \right\rangle}{2N_\mathrm{d}t}, \tag{1}$$

where D is diffusion coefficient, $\langle u_\alpha^2 \rangle$ mean square displacement (MSD) of the atom, t time, and N_d dimensionality of the space in which the process is taking place ($N_\mathrm{d} = 3$ for the bulk simulation, $N_\mathrm{d} = 2$ for the surface simulation). The atom's MSD is a useful quantity to express the atom diffusion in solid [9,10], as a vacancy can diffuse via its neighbor atoms by exchanging their positions [11], we choose the MSD of vacancy's nearest neighbor atom in the surface to quantitatively describe the vacancy diffusion. It is evaluated by:

$$\left\langle u_\alpha^2 \right\rangle = \left\langle r_\alpha^2 \right\rangle - \langle r_\alpha \rangle^2 \qquad (\alpha = \{x, y, z\}), \tag{2}$$

where r_α is the atom's position in the x, y, z direction, and the angle brackets denote an average over time. The time average in Eq. (2) is carried out during different period of time, the length of which is chosen according to the atom's trajectory. The diffusion barrier is calculated by Arrhenius equation:

$$D = D_0 \exp\left[\frac{-E_\mathrm{m}}{k_\mathrm{B}T}\right], \tag{3}$$

where D_0 is a prefactor, E_m diffusion barrier, k_B Boltzmann constant, and T temperature.

3. Results and discussion

Fig. 1 presents the MSD curves of vacancy's nearest neighbor atom in the temperature range of 300–2000 K. From Fig. 1(a), in the 300–900 K temperature range, there is no obvious maximum found in the MSD curves, which implies that the atom only relaxes at a certain distance away from the surface without long distance migration. When the temperature increases to 1000 K, we can clearly detect a sharp maximum at about 5 ps in the corresponding MSD curve. This maximum indicates that the atom has migrated for a long distance. Checking its trajectory, we find that the atom moves towards the site of the vacancy and it reaches an intermediate position, which is closer to its original site than to the vacancy site. After that time, the atom relaxes at this position until the end of the simulation. When the temperature increases to the range of 1400–1800 K (Fig. 1(b)), there are two maxima in the MSD curves, implying that the atom migrates twice during its diffusion process. In fact, the atom first moves towards the vacancy site and it reaches an intermediate position. Then, the atom relaxes at the position for a period of simulation time. Next, it again migrates towards the vacancy site and finally reaches the site. To the best of our knowledge, it is the first time to observe the phenomenon, where, the atom migrates two times in its diffusion process. However, at 2000 K, there is only one maximum in the MSD curve, which means that the atom can arrive at the site by migrating once.

Mainwood [2] suggested that when the temperature was in the range of 1073–1373 K, the vacancy was mobile and could move to the surface of diamond. Also, the experimental results of Davies et al. [12] showed that when Type II a diamond was annealed at 973–1023 K, its vacancy

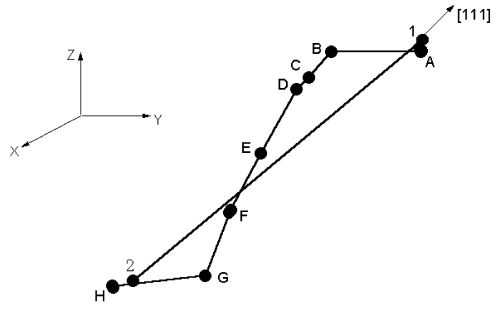

Fig. 2. Dynamic diffusion path of vacancy at 1800 K. Diffusion path is the connection line ABCDEFGH, and the connection line between 1 and 2 represents [111] direction.

concentration decreased greatly, indicating the mobility of vacancy at 973–1023 K. Usually, diamond deposition temperature is in the range of 973–1073 K in experiment [13–16]. In our simulation, from Fig. 1(a), the maximum appears only when the temperature comes to about 1000 K. It indicates that in the range of 1000–1300 K the vacancy is mobile though it cannot reach the surface within the simulation time. In addition, the vacancy shows a complete migration at 1400–2000 K, which is higher than the experimental temperature. However, in experiment, the diamond growth temperature usually refers to the substrate temperature. The temperature of the surface of the diamond film must be higher than that of the substrate because of the continuous energetic particle bombardment. All kinds of surface reactions, including adatom diffusion and vacancy diffusion, take place under this high temperature. From this point, our simulation result is reasonable and shows that diamond growth may relate to the movement ability of vacancy. Moreover, if the model of Bar-Yam and Moustakas [1] is valid, we can predict that diamond growth relates not only to the existed vacancy concentration but also to its migration ability. In addition, comparing Fig. 1(a) with Fig. 1(b), we find that the first maximum of the atom's MSD appears earlier and its value increases with increasing temperature. This phenomenon denotes that the velocity of the vacancy diffusion increases with increasing temperature. In addition, when the temperature is at and above 1400 K and the value of the first maximum of MSD reaches 1.91×10^{-3} nm^2, the atom can have the chance to completely move to the vacancy site.

To understand better the observed two migration stages in the vacancy diffusion process in the temperature range of 1400–1800 K, we studied the vacancy diffusion path shown in Fig. 2, which presents a diffusion path at 1800 K. Using quasi-dynamics method, Breuer and Briddon [4] investigated the vacancy diffusion path via its neatest neighbor atoms' trajectories. They moved the atom stepwise along the [111] direction, and let it relax in the plane perpendicular to the [111] direction. Finally, the diffusion path of the vacancy can be obtained. In our simulation, there are no constraints imposed upon the atoms. From Fig. 2, it is found that the two migration stages in the diffusion process of 1800 K correspond to path BCD and EFGH, respectively. At the same time, it is obvious that the two distances, between B and C as well as C and D, are smaller than those between E and F as well as F and G. Jiang and Brown [17] suggested that the atom had to break C–C bond before it was able to form a new bridging configuration with other carbon atoms. Breaking a bond is more difficult than forming a bond, so that the atom's position changes a little before the bond breaking in the same time interval. Consequently, the atom's positions of B, C, and D is close to each other in Fig. 2. While formation of a bond is a process in which energy continuously reduces, the atom moves more quickly relative to that in the process of breaking a bond, and the distance between E and F as well as that between F and G become bigger in the same time interval. Also, some researchers fixed the saddle point at the middle of the connection line between the beginning and the end position of the vacancy diffusion path [4,18]. In our simulation, if the atom's MSD does not exceed 1.91×10^{-3} nm^2, it may be difficult for the atom to move to the site of the vacancy. Therefore, the atom site corresponding to the atom's MSD 1.91×10^{-3} nm^2 should be considered as a saddle point. It is point C in Fig. 2 and is not the middle point of diffusion path ABCDEFGH. Obviously, the vacancy diffusion path is not symmetric about the saddle point, which also may be caused by the configuration difference between the surface and bulk of diamond. From Fig. 2, the atom rotates around the [111] direction, which makes the number of breaking bond smallest and the atom diffusion favorable in energy [4]. In addition, the system energy decreases after the vacancy migrates to the surface. At 1800 K, the energy decreases by 3.4 eV. Moreover, we do not find any vacancy in the third layer to move to the second layer.

The diffusion coefficient is calculated according to Eq. (1) and its Arrhenius plot for the vacancy diffusion is shown in Fig. 3. From Fig. 3, the prefactor $D_0 = 3.69 \times 10^{-6}$ cm^2/s and diffusion barrier $E_m = 0.42$ eV are obtained by linear fit. Mainwood [2] obtained the vacancy migration energy 2.3 eV in natural diamond. Breuer and Briddon [4] found that the vacancy diffusion barrier was 2.8 eV. Also, the vacancy migration energy calculated by Bernhole et al. [18] was 1.7–1.9 eV. However, all these values are calculated in bulk diamond. Vacancy diffusion near the surface has a lower diffusion barrier than that in the bulk [11], which indicates that the vacancy indeed more easily diffuses near diamond surface than in bulk diamond. It is helpful to the diamond growth and supports the model of Bar-Yam and Moustakas [1] from another aspect.

4. Conclusions

The effects of temperature on the vacancy diffusion near diamond (001) surface were investigated by MD simulation

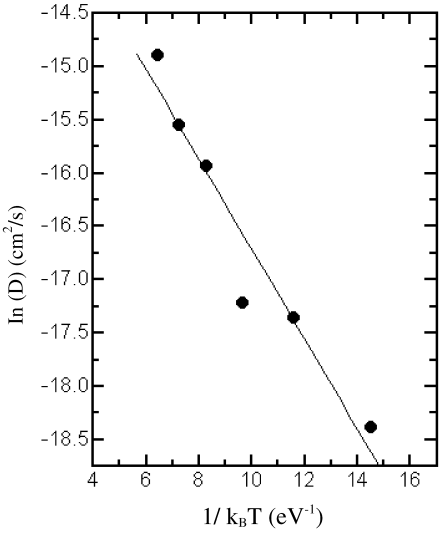

Fig. 3. Arrhenius plot for the vacancy diffusion.

using the Tersoff many-body potential. The MSD of vacancy's nearest neighbor atom was used to quantitatively characterize the vacancy diffusion. The vacancy dynamic diffusion path was obtained without any constraints imposed on the atoms.

At about 1000 K, the vacancy in the second layer begins to diffuse towards the surface. In the temperature range of 1400–2000 K, the vacancy can migrate to the surface. This result predicts that diamond growth relates not only to the vacancy concentration but also to its migration ability. Specially, in the temperature range of 1400–1800 K, two migration stages, which correspond to two maxima in the MSD curves, are observed in the vacancy diffusion process. In addition, the saddle point of the vacancy diffusion near diamond (001) surface is not in the middle of the diffusion path. The calculated diffusion barrier of the vacancy near diamond (001) surface is 0.42 eV.

Acknowledgements

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References

[1] Y. Bar-Yam, T.D. Moustakas, Nature 342 (1989) 786.
[2] A. Mainwood, Phys. Status Solidi. (A) 172 (1999) 25.
[3] T. Halicioglu, Thin Solid Films 228 (1993) 293.
[4] S.J. Breuer, P.R. Briddon, Phys. Rev. B 51 (1995) 6984.
[5] I. Rosenblum, J. Adler, S. Brandon, Compos. Mater. Sci. 12 (1998) 9.
[6] J. Tersoff, Phys. Rev. B 39 (1989) 5566.
[7] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 1987, p. 7 pp. 79.
[8] M.P. Allen, D.J. Tildesley, Computer Simulation of Liquids, Clarendon Press, Oxford, 1987, p. 7 pp. 231.
[9] G.C. Kallinteris, G.A. Evangelakis, N.I. Papanicolaou, Surf. Sci. 369 (1996) 185.
[10] V.P. Sokhan, D. Nicholson, N. Quirke, J. Chem. Phys. 113 (2001) 2007.
[11] X.M. Duan, D.Y. Sun, X.G. Gong, Compos. Mater. Sci. 20 (2001) 151.
[12] G. Davies, S.C. Lawson, A.T. Collins, A. Mainwood, S.J. Sharp, Phys. Rev. B 46 (1992) 13137.
[13] D. Takeuchi, S. Yamanaka, H. Watanabe, S. Sawada, H. Ichinese, H. Okushi, K. Kajimara, Diamond Relat. Mater. 8 (1999) 1046.
[14] C. Wang, M. Irie, T. Ito, Diamond Relat. Mater. 9 (2000) 1650.
[15] N. Ishigaki, S. Yugo, Diamond Relat. Mater. 9 (2000) 1646.
[16] J. Kang, C.Y. Xiao, Y.Y. Xiong, Y.G. Wang, Q.B. Meng, Z.D. Lin, K.-A. Feng, Diamond Relat. Mater. 9 (2000) 1691.
[17] Z. Jiang, R.A. Brown, Phys. Rev. Lett. 74 (1995) 2046.
[18] J. Bernhole, A. Antonelli, T.M. Del Sole, Phys. Rev. Lett. 61 (1988) 2689.