

§9. Study on Bond Orientation of Amorphous Carbon Materials

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In general, diamond-like carbon is classified depending on the sp^2 , sp^3 contents and hydrogen content as known as ternary phase diagrams of amorphous carbons. We discuss the structure of amorphous carbon materials formed in deposition and annealing processes by molecular dynamics simulation^{1, 2)} with Brenner's potential³⁾. It has been found that there is some structural difference even though the amorphous carbons are located at the same point on the ternary phase diagram.

The simulation of carbon deposition onto the (111) surface of a diamond substrate is executed. The size of diamond substrate is $20.19 \text{ \AA} \times 20.86 \text{ \AA} \times 8.24 \text{ \AA}$. Langevin thermostat is attached to the diamond substrate to keep the temperature at 600 K. Periodic boundary conditions are used in the x and y directions. The size of the simulation box in the x and y directions cannot be set arbitrarily because of the periodic boundary conditions. Therefore, the size of the simulation box in the x and y directions is determined as the lengths of the unit cells of integer pieces. Incident carbon atoms are injected from 100 \AA above the surface of the diamond substrate with the incident energy of 1 eV and the flux of $2.37 \times 10^{30} \text{ m}^{-2}\text{s}^{-1}$, where the z components of momentum of the injected atoms are negative. The injection position of x and y coordinates are set at random.

From the result of the simulation of deposition, it is found that the average density of the carbon materials is 2.44 g cm^{-3} under the deposition condition we executed. Therefore we prepare the carbon materials with the density of 2.44 g cm^{-3} by annealing the carbon atoms which placed randomly. To adjust the density to 2.44 g cm^{-3} , 1033 carbon atoms are placed randomly in a simulation box whose size is $20.19 \text{ \AA} \times 20.86 \text{ \AA} \times 20.00 \text{ \AA}$. Periodic boundary conditions are used in the x , y and also z directions. The carbon atoms are annealed for 100 ps at 2400 K by attaching the Langevin thermostat.

Let us use symbols a-C_{dep} and a-C_{ann} for the materials formed by the simulation models of deposition and annealing, respectively. To compare the properties of a-C_{dep} and a-C_{ann}, sixteen samples of amorphous carbon materials are prepared by each model. Table I shows the ratios of sp , sp^2 and sp^3 carbons and the densities in a-C_{dep} and a-C_{ann}. The ratios and the densities are averaged through the sixteen samples. It is interesting that the ratios of sp , sp^2 and sp^3 carbons of a-C_{dep} and a-C_{ann} are almost the same.

Table I. The ratios of sp , sp^2 and sp^3 carbons in a-C_{dep} and a-C_{ann}.

	sp	sp^2	sp^3
a-C _{ann}	$3.8 \pm 0.3\%$	$79.1 \pm 0.4\%$	$17.0 \pm 0.2\%$
a-C _{dep}	$3.2 \pm 0.4\%$	$79.1 \pm 0.6\%$	$17.7 \pm 0.3\%$

From the aspects of sp^2 , sp^3 contents, the densities and radial distribution functions, it is difficult to distinguish a-C_{dep} and a-C_{ann}. However it is found that there is difference between orientations of bonds of a-C_{dep} and a-C_{ann}. For the investigation of the bond orientations in our simulation, let us introduce a value σ defined by

$$\sigma(\theta, \varphi) \equiv \frac{1}{N} \sum_i^{\vec{r}_i \in V} \sum_j^{|\vec{r}_{ij}| < r_c} \left(\vec{a}(\theta, \varphi) \cdot \frac{\vec{r}_{ij}}{|\vec{r}_{ij}|} \right)^2, \quad N \equiv \sum_i^{\vec{r}_i \in V} \sum_j^{|\vec{r}_{ij}| < r_c} 1,$$

where, $\vec{a}(\theta, \varphi) = (\sin \theta \cos \varphi, \sin \theta \sin \varphi, \cos \theta)$ is a unit vector which directs the direction where orientation is examined. $\sigma(\theta, \varphi)$ is a function of the polar angle θ and the azimuthal angle φ of the vector \vec{a} . \vec{r}_i is the position of i -th carbon atom and $\vec{r}_{ij} \equiv \vec{r}_i - \vec{r}_j$. N is the total count of the summation. r_c is a cut off length of a bond. r_c is set to 1.85 \AA that is the distance which gives the half value of the cutoff function of Brenner's potential. All the atoms located in a distance of r_c from i -th atom are regarded as having chemical bonds to i -th atom. V is a set of the positions of all carbon atoms in a box.

Figure 1 shows the contour plots of σ of a-C_{dep} and a-C_{ann}. The $\sigma(\theta, \varphi)$ is averaged through the sixteen samples. It is clearly seen that these two contour plots are completely different. The contour plot of a-C_{dep} has peak at $\theta = \pi/2$ which is parallel to the surface of substrate, although a-C_{ann} is isotropic.

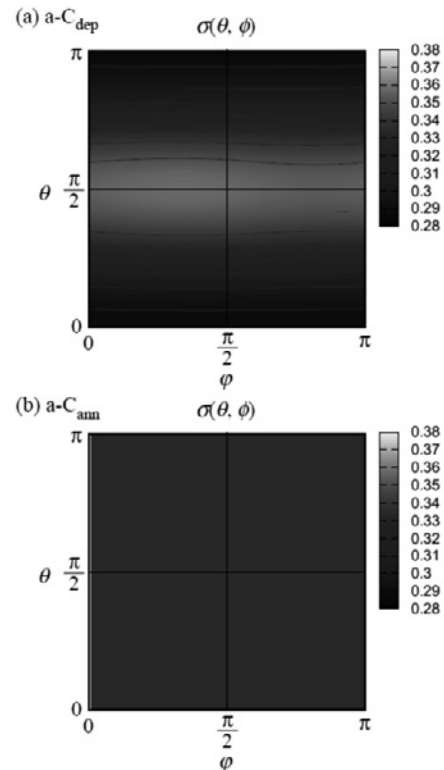


Fig. 1. The contour plot of $\sigma(\theta, \varphi)$ of (a) a-C_{dep} and (b) a-C_{ann}.¹⁾

- 1) S. Saito, A. M. Ito, A. Takayama, and H. Nakamura: Jpn. J. Appl. Phys., **51** (2012) 01AC05.
- 2) S. Saito, A. M. Ito, and H. Nakamura: J. Appl. Phys. **110** (2011) 084320.
- 3) D. W. Brenner, O. A. Shenderova, J. A. Harrison, S. J. Stuart, B. Ni, and S. B. Sinnott: J. Phys. Condens. Matter **14** (2002) 783-802.