

Simulation of Material Properties of Amorphous Carbon Nitride with Non-uniform Nitrogen Distribution

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A simulation method is proposed to study the amorphous structure of carbon nitride. The material properties of a non-uniform nitrogen distribution in an amorphous CN matrix can be studied. The cohesive energy of a group of randomly generated atoms can be minimized to find the relative positions of atoms. From the calculated configuration of atoms, many properties of amorphous carbon nitride can be calculated such as bulk modulus, P-V curve, sp^3/sp^2 ratio of carbon, and vibrational spectra. The calculation shows that the cohesive energy of non-uniform nitrogen distribution is lower than that of a uniform distribution. This may suggest that the regular structure of carbon nitride can at most be metastable. It is not easy to incorporate nitrogen atoms into a carbon matrix.

Keywords : Carbon Nitride, Cohesive Energy, Bulk Modulus, Vibrational Spectra

PACS: 61.43.-j, 62.20.-x, 68.35.Bs 73.20.At 81.35.+k

1. INTRODUCTION

Searching for new material with superior properties is a challenge to material research. Theoretical studies can help to provide some orientations besides random search. In the work of searching for high hardness material, Liu and Cohen made a good suggestion upon their theoretical work [1,2]. A new crystal, β - C_3N_4 , was predicted as a hard material, which may have a bulk modulus quite close to that of diamond. Since the prediction in 1989, many researchers have tried to synthesize this hypothesized material with various methods [3-12]. The β - C_3N_4 is expected to be a good alternative of diamond especially in applications at high temperature, where diamond is unstable [13].

Current theoretical work was mostly based on the *ab initio* pseudopotential method with the use of local density approximation [14,15]. This method can be applied to the structures of regular atom distribution from the electron level. It considers the influence of both s and p orbitals. However, for an irregular structure of atoms, the valence band states determination becomes very difficult due to the variation of boundary conditions. It is important to find a method, which can treat the variation of boundary conditions easily without the consideration of electron states. The research on the amorphous carbon nitride structure simulation is still limiting [16,17]. A simple

method is proposed in this paper which has not the difficulty of treating the various boundary conditions.

The main idea of our simulation method is to minimize a group of atoms cohesive energy and find relative positions of atoms. This method can be helpful for the analysis of amorphous structure of carbon nitride, which appears very often in its thin film synthesis. The simulation method is built on the atomic level. This paper discusses mainly the influence of the nitrogen distribution in the amorphous carbon nitride. The difference between uniform and non-uniform nitrogen are compared. The simulation work can build the relation between the material bulk modulus and carbon nitride structure. More detailed studies such as sp^3/sp^2 ratio of carbon and the vibrational spectra of the carbon nitride can be calculated by counting atoms of different types and vibration frequency, respectively. The simulation can give some results, which are measurable in experiments.

2. DETAILS OF MODEL

The simulation starts from randomly initializing the original atom positions in an atom group then minimizes the total cohesive energy. For energy minimization, it is very important to express the interactions between atoms with a good accuracy. The total cohesive energy of the atom group can be expressed as

$$U_{tot} = \sum_{i=1}^N U(R_i). \quad (1)$$

Here, $U(R_i)$ refers to the cohesive energy generated by each atom. The summation covers all the N atoms in the matrix. Several interactions need to be considered in $U(R_i)$. When two atoms are close, a covalent bond can be formed, causing the reduction in the total energy. The covalent bond can be considered as an attraction force. Two adjacent atoms cannot move very close under the attraction force, because of the interactions among the valence electrons of different atoms. This can be considered as a repulsive force. Both forces act on an atom to retain the position in the solid-state matrix. The interactions can be in the form of A/R^n and B/R^m , respectively. To find the values of unknown parameters, two other equations are used.

$$\beta = -V \frac{dP}{dV} = V \frac{d^2 U_{tot}}{dV^2}. \quad (2)$$

$$\frac{\partial U_{tot}}{\partial R_i} = 0. \quad (3)$$

Here, β refers to the bulk modulus. From the known values of average cohesive energy, bulk modulus, and bond length, unknown parameters for the interactions can be calculated.

With the simulated structure of an amorphous matrix, several material parameters can be calculated. Bulk modulus can be calculated by applying a pressure to contract the matrix. Both the P-V curve and the bulk modulus β can be calculated using Eq. (2). The vibrational spectra can also be calculated. Considering vibrations of monoatomic lattices [18], the dispersion relation of the atomic vibration can be expressed as

$$\omega^2 = (2k/M)(1 - \cos Ka), \quad (4)$$

with

$$k = \frac{\partial^2 U(R_i)}{\partial R_i^2}. \quad (5)$$

Here, K , a , and M refer to the wave vector, the lattice constant, and the atomic mass, respectively. If the interactions among four neighbouring atoms are considered, k should be multiplied by a factor of four. The

maximum vibration frequency can be shown as

$$\omega_{max} = 4 \sqrt{\frac{\partial^2 U(R_i) / \partial R_i^2}{M}}. \quad (6)$$

The corresponding wavenumber of the phonon is

$$\frac{1}{\lambda} = \frac{\omega_{max}}{2\pi C} = 2 \sqrt{\frac{\partial^2 U(R_i) / \partial R_i^2}{\pi^2 M C^2}}. \quad (7)$$

C is to the velocity of light. In an amorphous matrix, each atom has its own maximum vibration frequency. Statistical method can be used to count the frequency of each atom and to calculate the density of various vibration modes.

3. RESULTS AND DISCUSSIONS

Cohesive energy $U(R_i)$ of one atom can be expressed according to the previous discussion. Taking diamond as an example, there are four strong bonds forming a tetrahedral configuration. The cohesive energy of one carbon atom in a diamond structure is given as:

$$U_D(R_i) = -\sum_{j=1}^4 \frac{A_D}{R_{ij}^m} + \sum_{j=1}^4 \frac{B_D}{R_{ij}^n} + \sum_{j_1 \neq j_2} \frac{B_D}{R_{j_1 j_2}^n}. \quad (8)$$

In this equation, each j denotes an adjacent atom, which forms a σ bond together with the central atom i . A_D , B_D , m , and n are parameters that should be further determined. R_{ij} represents the bond length between two atoms i and j . Here j_1 and j_2 refer to two different neighboring atoms of the central atom. To study the amorphous structure of carbon and carbon nitride, we need to further determine the cohesive energy of one atom in graphite as:

$$U_G(R_i) = -\sum_{j=1}^3 \frac{A_G}{R_{ij}^m} + \sum_{j=1}^3 \frac{B_G}{R_{ij}^n} + \sum_{j_1 \neq j_2} \frac{B_G}{R_{j_1 j_2}^n}. \quad (9)$$

Here, the π bond energy of the atom in graphite is ignored. Only three neighbouring atoms are considered because the three sp^2 bonds lie in the basal plane of graphite are strong bonds, whereas the Van der Waals-like π bond is comparatively weak [19]. Although the π bond is important for the hexagonal structure of graphite, our simulation is designed only for the amorphous structure of carbon nitride, in which the reduction of energy is the most important concern. Values of A_D , B_D , A_G , B_G , m , and n in above equations can be calculated by applying known results of diamond and

graphite into Eq. (2) and (3). Table 1 lists the calculated results. These values are obtained when the units of cohesive energy, bond length, and bulk modulus are eV, Å, and Gpa, respectively. If both the graphite-like atom and the diamond-like atom are considered in an amorphous structure, the expression of $U(R_i)$ must be determined in the simulation; $U(R_i) = U_G(R_i)$ if $U_G(R_i) < U_D(R_i)$, and $U(R_i) = U_D(R_i)$ if $U_G(R_i) > U_D(R_i)$.

Table 1. Parameters for simulation.

	C-C (Diamond)	C-C (Graphite)	C-N (sp ³ carbon)	C-N (sp ² carbon)	N-N
A	6.54	7.13	3.34	3.97	7.29
B	5.53	6.04	3.72	4.22	5.33

To study the structure of carbon nitride, values of A_{C-N} , A_{N-N} , B_{C-N} , and B_{N-N} are needed for C-N and N-N bonds. These values together with A_D and A_G can cover all types of interactions among carbon and nitrogen atoms. Cohen's prediction [1] gave the values of the bulk modulus and bond length of β -C₃N₄. These values can be used to calculate A_{C-N} and B_{C-N} . The values of A_{N-N} and B_{N-N} can be extrapolated from those of C-C and C-N bonds.

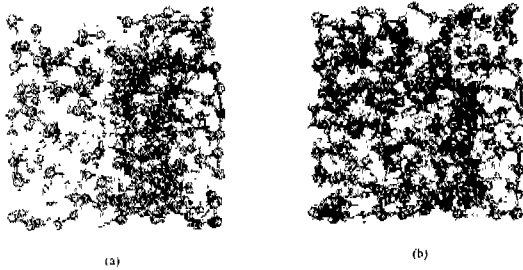


Fig. 1. (a) Example structure of amorphous carbon nitride with $N_{right}/N_{tot} = 0.1$ (b) Example structure of amorphous carbon nitride with $N_{right}/N_{tot} = 0.5$.

Examples of amorphous carbon nitride configurations are illustrated in Fig. 1. Both amorphous matrixes contain 500 nitrogen atoms and 500 carbon atoms. In this paper, the whole matrix is divided into two parts namely the left and the right. Our model can simulate conditions that nitrogen concentrations of two sides have different values. In Fig. 1, nitrogen atoms are represented by light grey spheres and carbon atoms are represented by dark spheres. Bonds connecting atoms are represented by cylinders. N_{tot} is not total nitrogen atom number while N_{right} is the total nitrogen number in the right half. In Fig. 1(a), N_{right}/N_{tot} equals 0.1, while in Fig. 1(b), the value is 0.5. These represent uniform and non-uniform nitrogen distribution conditions when the total nitrogen concentration maintains at 0.5 of total atoms. The total number of atoms

is chosen according to the complexity of calculation. The position of carbon and nitrogen is initialized at random. The type of atoms is decided according to the expected nitrogen distribution. The simulation starts from this initial condition. The total number of the atoms was selected according to the computing capability. The positions of carbon and nitrogen atoms were initialized randomly in a certain range. The type of atom at a position was also decided randomly, so that the condition is closer to a real case. The simulation started from these original atom positions. If the total number of atoms is very low, the fluctuation effect will be very serious. The same percentage of nitrogen atoms after different initialization operation may lead to different simulation results. A large atom number can reduce the fluctuation in the simulation results. However, the time used to minimize the cohesive energy can increase sharply when the atom matrix becomes very large. This can be imagined by considering that the position of one atom affects the positions of the neighboring atoms. In this study, the total number of atoms in a matrix was 1000. In the statistical calculation, the effect of boundary atoms was excluded, that is why only 512 atoms were chosen for statistical operation. From the graph, it is observed that the atoms in the amorphous matrix are not as regular as those in a crystal. The carbon atoms rarely stay at centers of tetrahedral structures of hexagonal structures. The atomic positions show a mixture of both structures. At the boundary, the condition becomes more complicated. Some atoms linked with the internal atoms. Some have dangling bonds. A dangling bond can also happen inside the matrix when one atom is surrounded by atoms, which have already formed strong bonds with other neighboring atoms. A dangling bond can also happen inside the matrix when one atom is surrounded by its neighboring atoms, which has formed strong bonds with other atoms. This case always happens when one atom has a covalent bond with its neighbor forming a long bond length. Both graphs in Fig. 1 show these phenomena.

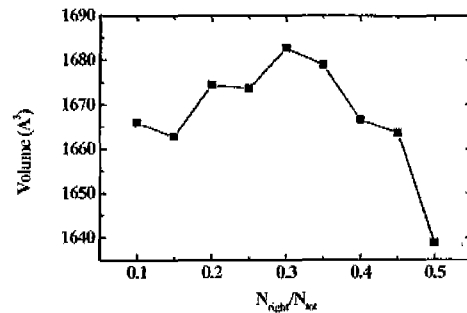


Fig. 2. Simulated total volume of 512 atoms with non-uniform nitrogen concentration.

The total volume of certain number of atoms is an important parameter. It suggests the density of the material of the average bond length of a material. Material tends to have a high hardness when its structure has a higher density. Carbon, which allows structures of diamond and graphite, is a typical example. The π bond of graphite accounts for the low density and large bond length. In Fig. 2, it is found that the volume reaches its lowest value when $N_{\text{right}}/N_{\text{tot}}$ equals 0.5. This means that a uniform structure helps to form enough C-N bonds, which has a very low bond length of 1.47 Å comparing with the 1.54 Å of C-C bond in diamond. The total volume also show a maximum when $N_{\text{right}}/N_{\text{tot}}$ equals 0.3. It indicates that the number of C-N bonds is not the unique factor influencing the volume. The types of carbon bonds also have a very important role. The non-uniform distributed nitrogen atoms can influence that bond type of carbon. This further affects the total volume.

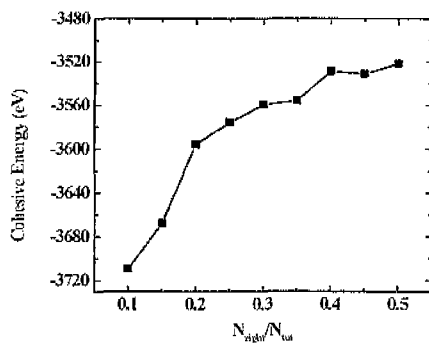


Fig. 3. Simulated total cohesive energy of 52 atoms with uniform and non-uniform nitrogen concentration.

Figure 3 shows the relation of total cohesive energy with the different nitrogen distribution conditions. Cohesive energy per atom is also an important index of material bulk property. Material with low cohesive energy is more fragile compared with those with a high cohesive energy because it needs less energy to break the bond. A surprising phenomenon is that the non-uniform distribution of nitrogen atoms has a lower value of cohesive energy than that of a uniform one. This suggests that non-uniform structure is more stable than a uniform one and the nitrogen atoms in an amorphous matrix may tend to aggregate. It is known that nitrogen triple bond is very strong. This means that amorphous carbon nitride may have the leakage of N_2 due to the movement of nitrogen atoms in the matrix. Carbon and nitrogen can at most form a metastable structure. It also suggests that higher temperature may give enough energy for the leakage of nitrogen. This needs to be avoided in the synthesis of carbon nitride.

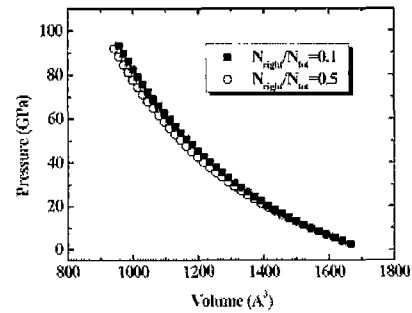


Fig. 4. P-V curve of 512 atoms with uniform and non-uniform nitrogen concentration.

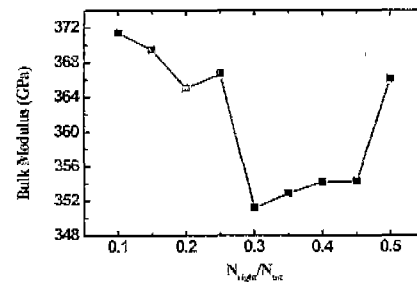


Fig. 5. Calculated bulk modulus of amorphous carbon nitride with non-uniform nitrogen concentration.

P-V curve is used to study the hardness of material because the bulk modulus can be expressed as equation (2). The P-V curve is found by applying a contraction ΔV to the group of atoms and calculating the ΔU_{tot} after deformation. Fig. 4 illustrates examples of this calculation. The curves differ not very much for the uniform and non-uniform nitrogen distribution. From the P-V curve, the bulk modulus with different $N_{\text{right}}/N_{\text{tot}}$ is shown in Fig. 5. This curve has shown that the lowest bulk modulus is achieved when $N_{\text{right}}/N_{\text{tot}}$ equals 0.3. This result is consistent with the volume results in Fig. 2. A surprising phenomenon is that both a uniform and highly non-uniform nitrogen distribution are good for achieving high bulk modulus. This result suggests that the nitrogen distribution affect the bond type of carbon atom and further influence the bulk modulus.

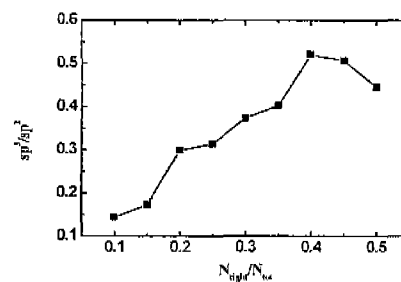


Fig. 6. Ratio of sp^3 hybridized carbon atoms and sp^2 hybridized carbon atoms with non-uniform nitrogen concentration.

Figure 6. studies the hybridization of carbon atoms in the amorphous matrix when nitrogen distribution is non-uniform. Carbon atoms may be in sp^3 or sp^2 hybridization. Either format is adopted depends on the cohesive energy it generates. If the neighboring atoms favor a sp^3 hybridized central carbon, the atom will have a low cohesive energy when it is so configured. If the neighboring atoms favor a sp^2 hybridized central carbon, the atom will have a low cohesive energy when it is configured in that way. One benefit of a simulation method is that the number can be counted. The ratio of sp^3/sp^2 is found by counting each carbon atom. The relation of this ratio with the nitrogen distribution is shown in Fig. 6. The highest ratio is achieved when $N_{\text{right}}/N_{\text{tot}}$ equals 0.4. This suggests that the uniform distribution is not most helpful for the formation of sp^3 hybridization, which is necessary for the hypothesized $\beta\text{-C}_3\text{N}_4$. It is also known that total concentration of nitrogen in an amorphous matrix can also influence sp^3/sp^2 . Therefore the best condition for sp^3 hybridization form needs both the considerations of the nitrogen concentration and the nitrogen distribution

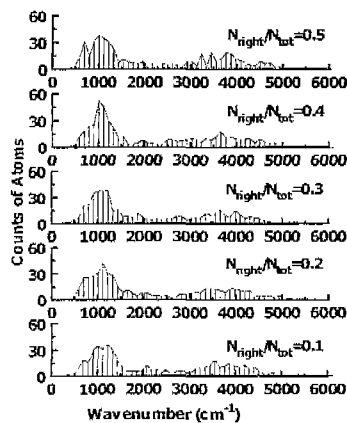


Fig. 7. Calculated atoms vibration density spectra of amorphous carbon nitride with non-uniform nitrogen concentration.

Figure 7. shows the simulated vibration mode density spectra. This is a trial to connect the simulation results with some measurable parameters. It is known that Raman spectra and Fourier Transform Infrared (FTIR) are good analysis methods for the measurement of the vibration mode density of materials. From the simulation, the relative positions of each atom can be found. With the known expression of interactions between atoms, the maximum vibration frequency of one atom and correspondin wavenumber can be expressed as Eq. (6) and (7). The calculated results are illustrated in Fig. 7. The graph shows the number of atoms in a certain wavenumber range from 1550 cm^{-1} and 1650 cm^{-1} , when $N_{\text{right}}/N_{\text{tot}}$ equals 0.1. From the spectra, it is noticed that the spectra consist of two parts. The lower frequency part belongs to carbon while the high frequency part is for nitrogen. It is noticed that the curve differ not very much

when the total nitrogen concentration is maintained at 50%. The result suggests that the spectra are not influenced by the nitrogen distribution significantly when the nitrogen concentration dos not change. In Fig. 7, the spectra show a big full width at half maximum (FWHM) due to the amorphous structure. The estimated value may be used be used for the comparison with the experimental results.

4. CONSLUSION

In this paper, a simulation method is proposed to study the properties of amorphous carbon nitride. Conditions of non-uniform and uniform nitrogen distributions have been discussed. The whole matrix is divided into two parts each with different nitrogen concentration, while the total nitrogen concentration is maintained the same. It is found that the nitrogen distribution influences the total cohesive energy significantly. A uniform distribution has higher cohesive energy. It suggests that nitrogen atoms may segregate in the form of N_2 . The vibration density spectra show no difference when the distribution changes. The bulk modulus is influenced by the distribution of nitrogen atoms. The results deduced from this paper may be used to improve the experiment design. The illustrated phenomena can be compared with experimental results.

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