# Meta-stable Sites in Amorphous Carbon Lattice Generated by Rapid Quenching of Liquid Diamond

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## ABSTRACT

Formation of amorphous structure of carbon by rapid quenching of the liquid phase was investigated by molecular dynamic (MD) simulation using Tersoff's empirical potential. Physical properties of crystalline diamond, such as lattice parameter, surface energy and elastic constants were well described by the present calculations. The amorphous structure was generated by rapid quenching the melted diamond lattice from 10,000K at various cooling rate from $1.25x10^{15}$K/s to $6.25x10^{15}$K/s. In the amorphous carbon lattice, only first and second nearest order were observed at 1.52 and 2.52 Å, respectively. However, when the cooling rate was larger than $6x10^{15}$K/s, it was observed that significant number of atoms exist at a meta-stable site at about 2.2 Å. This site was commonly observed regardless to the preparation method. Relaxation behavior was investigated by annealing of the quenched sample at elevated temperatures. It was observed that the relaxation was governed by Arrhenius type reaction with the activation barrier of $4.8x10^{-14}$ erg/atom.

***Keywords***: Amorphous carbon, Atomic bond structure, Classical MD simulation, Meta-stable sites, Activation barrier

## 1 INTRODUCTION

There is considerable interest in the formation and characterization of amorphous carbon films of high content of $sp^3$ hybridization bond. One of the most important materials would be tetrahedral amorphous carbon (ta-C) film deposited by the bombardment of carbon ions of high kinetic energy and flux. Because of high hardness and wear resistance with optical transparency, the film has been investigated for various applications such as protective coating for optical fibers, IR optics or MEMS (micro electromechanical system) devices [1-3].

Since the ta-C films are deposited by severe ion bombardment, the atomic bond structure of the film is strikingly disordered, showing a mixture of $sp^1$, $sp^2$ and $sp^3$ bonds. The diamond-like properties of ta-C films are intimately related with the content of $sp^3$ bonds that would increase three-dimensional interlinks of the carbon atoms. In order to understand the variation of the physical and chemical properties, it is thus required to investigate the atomic bond structure of amorphous carbon in a quantitative manner.

Atomic scale simulation based on the dynamics of carbon atoms including ion bombardment would be significant to understand the structural variation in ta-C films. We have investigated the formation of amorphous carbon films by molecular dynamic (MD) simulation using a realistic many-body potential [4]. Amorphous structure of carbon was generated by various methods such as rapid quenching of liquid carbon, interstitial addition of carbon atom in diamond or high-energy carbon ion bombardment. In the present paper, we report the characteristics of meta-stable sites in amorphous carbon materials observed when liquid carbon was rapidly quenched. Carbon atoms being placed at the meta-stable sites were readily relaxed by high temperature annealing. The relaxation process was governed by Arrhenius type reaction.

## 2 CALCULATIONS

Table 1. Calculated and Experimental Values of the Properties of Crystalline Diamond

| Properties | | Experimental | Calculated |
|---|---|---|---|
| Lattice Parameter @ 300°K (nm) | | 0.3562 | 0.3565 |
| Elastic Constants (Gpa) | C11 | 10.8 | 10.58 |
| | C12 | 1.3 | 1.3 |
| Surface Energy ($Jm^{-2}$) | (100) | 9.25 | 7.67 |
| | (110) | 6.54 | 5.03 |
| | (111) | 5.34 | 4.11 |

Crystalline diamond of 512 carbon atoms was used as a starting material for the simulation of amorphous carbon.

Periodic boundary condition was applied in all x, y and z directions, which enables one to treat bulk materials. In all simulations, the carbon-carbon interactions are described via the empirical classical many-body potential proposed by Tersoff [4]. XMD 2.5.29 was used in the present calculation [5]. Time step for calculation was $0.8 \times 10^{-13}$ sec.

The calculated physical properties of crystalline diamond and the measured values are summarized in Table. 1. The lattice parameter and elastic constants of diamond are well described. Calculated surface energies were slightly smaller than the experiments. However, the orientation dependence of the surface energy compares well with the measured values. It can be thus said that Tersoff's potential gives a rather satisfactory overall description of diamond. The potential is expected to be reasonably accurate in the simulation of amorphous carbon materials.

The amorphous structure was generated by rapid quenching the melted diamond lattice from 10,000K at various cooling rate from $1.25 \times 10^{15}$K/s to $6.25 \times 10^{15}$K/s. Instantaneous freezing to 0K was also used to investigate the extreme case. The lattice structure of the liquid and amorphous phase was characterized by radial distribution function (RDF).

## 3 RESULTS AND DISCUSSION

### 3.1 Melting of Diamond

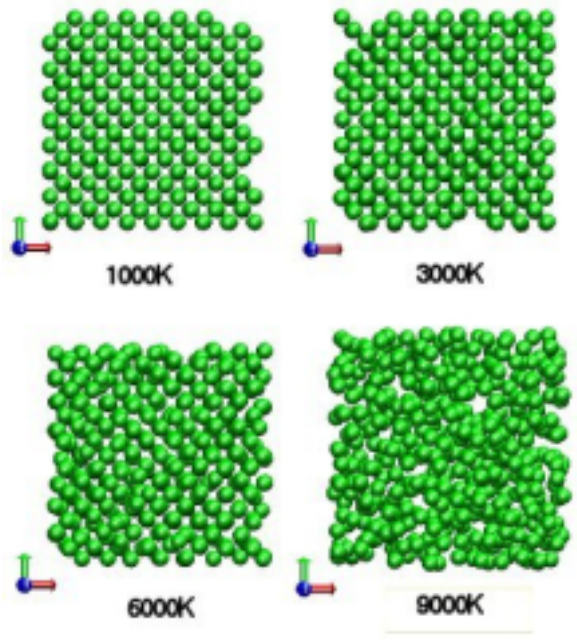


Fig.1. Snapshot of diamond lattice at various temperatures.

Fig. 1 shows the changes in diamond lattice during heating the sample. While ordered crystalline lattice was maintained up to 6,000 K, sudden decrease in the lattice order and the lattice expansion were observed above 7,000K. RDF showed that the long range order disappeared at about 6,000 or 7,000 K. Changes in energy and atomic number density of Fig. 2 definitely show that the melting of diamond lattice occurred between 7,000 and 8,000K.

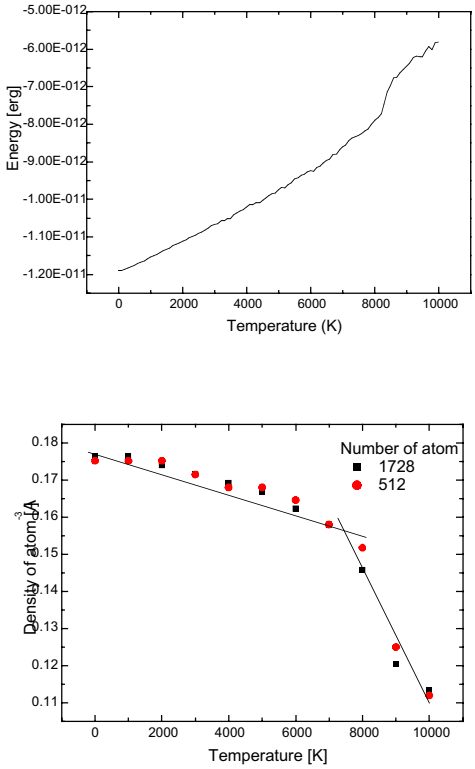


Fig. 2. Changes in total energy and atomic number density of diamond lattice during heating

Dynamic simulation hardly suggests the well-defined melting temperature of bulk materials. However, the results were sufficient for the present purpose, showing that the samples are to be melted at 10,000K in order to obtain sufficiently disordered structure.

### 3.2 Structure of Amorphous Solid Carbon

Melted diamond was quenched to 0K at various cooling rates. During the quenching process, shrinkage of the lattice occurred in all cases of the cooling rate. In contrast to liquid diamond at 10,000K, short-range order could be observed in solid amorphous carbon. Fig. 3 shows the radial distribution function (RDF) for various cooling rates. First and second nearest order peaks were observed at 1.52 and 2.52 Å, respectively. However, when the cooling rate was larger than $6 \times 10^{15}$ K/s, significant number of atoms was placed at a meta-stable site at about 2.2 Å (indicated by an arrow in Fig. 3). The number of atoms in the meta-stable

site increased with increasing cooling rate. Total energy of the sample was also dependent on the quenching rate. At higher quenching rate, the sample had higher total energy mainly due to the increase in potential energy.

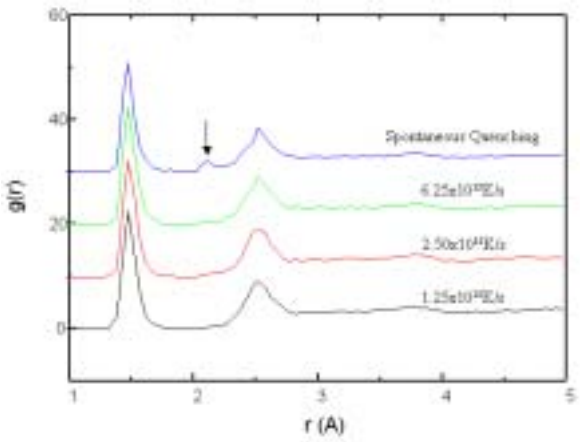


Fig. 3. Radial distribution functions of amorphous carbon generated by quenching from liquid carbon at 10,000K at various cooling rates

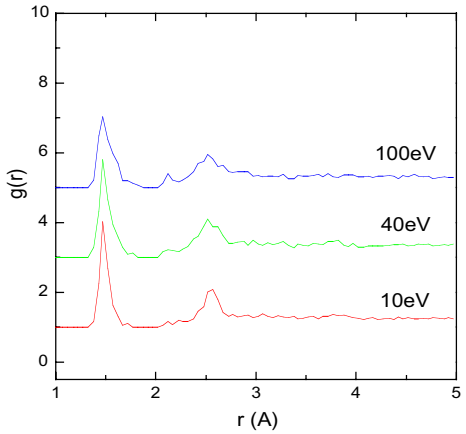


Fig. 4. . Radial distribution function of amorphous carbon materials generated by high-energy carbon bombardment on diamond.

Fig. 4 shows radial distribution functions of amorphous surface layer when neutral carbon atoms of various kinetic energies bombarded the diamond lattice [6-7]. The formation of meta-stable site became significant as the kinetic energy increased. The similarity in the atomic arrangement between high-energy atom bombardment and rapid quenching from liquid supports the thermal spike model of dense amorphous carbon phase formation [8-11]. High-energy bombardment also resulted in more smeared peaks showing higher degree of disorder. The changes in atomic bond character and physical properties will be reported later.

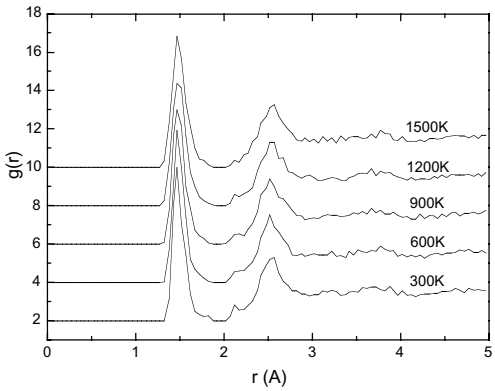


Fig. 5. Changes in radial distribution function after heating the quenched sample to the specified temperatures.

The atoms in meta-stable site were readily relaxed by annealing at an elevated temperature. Fig. 5 shows the changes in RDF occurred by rapid heating to the specified temperatures within $2.4x10^{-12}$sec. As the annealing temperature increased, the meta-stable peak at 2.2 Å significantly decreased, which implies that the atoms placed at the meta-stable site were relaxed by thermally activated process. Fig. 6 shows the changes in energy during heat-up to 1,200 K and holding at the temperature for $4x10^{-12}$ sec. In the initial stage of heat-up, only kinetic energy increased in the sample. However, at about 400 K, potential energy started to decrease presumably due to the atomic rearrangement. In this stage, total energy was kept approximately constant showing that the increase in kinetic energy by increasing temperature was cancelled by decreasing potential energy. When holding at 1,200K, both total energy and potential energy decreased as the relaxation process continued.

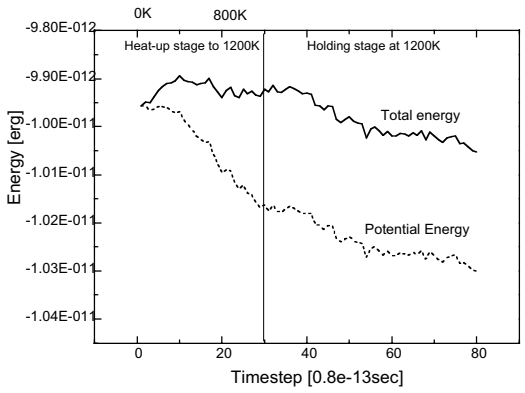


Fig. 6. Energy change during heat-up of quenched samples

The relaxation rate was characterized by decrease in the peak intensity at 2.2 Å as a function of holding time. Fig. 7 shows a linear dependence of logarithm of relaxation rate on the inverse of annealing temperature. The relaxation kinetics was thus governed by Arrhenius type reaction, which enables us to calculate the activation barrier of the meta-stable site. The activation energy was estimated to be $4.8 \times 10^{-14}$ erg/atom. This meta-stable site would play an important role in understanding the phenomena in dense amorphous carbon film deposition. The behavior will be compared with those of the amorphous carbon materials prepared by different methods such as ion impingement.

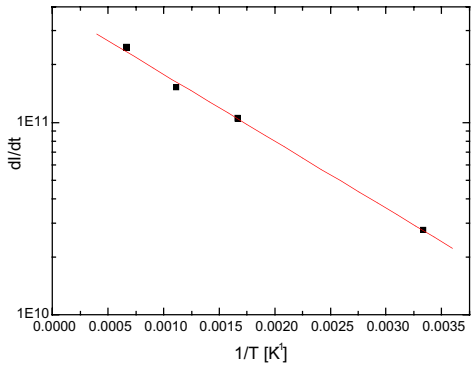


Fig. 7. Arrhenius plot of the relaxation kinetics

## 4 CONCLUSIONS

Structure of amorphous carbon prepared by rapid quenching the liquid was investigated by MD simulation. We observed that a meta-stable site exists at 2.2 Å, and the atomic population of the site increased as the quenching rate increased. The activation barrier of the site was $4.8 \times 10^{-14}$ erg/atom. Similar meta-stable sites were also observed when carbon atoms of high kinetic energy bombarded the diamond lattice. This meta-stable site would play a role in understanding the deposition behavior of dense amorphous carbon. More investigation is in progress to compare the structural variation with those in amorphous carbon prepared by different methods.

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