

# 第一原理分子動力学シミュレーションによる不規則炭素系の研究

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Carbon has various forms such as diamond, graphite, many types of fullerenes and carbon nanotubes which show interesting properties. These properties of carbon systems mainly come from the various bonding states with  $sp$ -,  $sp^2$ - and  $sp^3$ - hybrid orbitals. While the crystalline phases of carbon are well known, disordered carbon systems such as liquid carbon and amorphous-like carbon are little known. These disordered carbon systems have structures in which the  $sp$ -,  $sp^2$ - and  $sp^3$ -bonding states coexist.

Recently, diamond/liquid melting curve has been investigated theoretically and it has been reported that the slope of the melting curve changes from positive to negative value. However, the structural and electronic properties of liquid carbon at high pressures remain unclear because of the difficulty of carrying out experiments at the extremely high temperatures and pressures. It is also interesting to investigate the systematic structural change of the liquid state of group 14, carbon, silicon, germanium, tin and lead, since carbon is the lightest element of group 14.

The amorphous-like carbon produced by mechanical milling of graphite, which is called "*nanostructured graphite*", is important

for the application fields as well as for the academic interest. For example, it is reported that the nanostructured graphite prepared by mechanical milling under a hydrogen atmosphere has the hydrogen storage capacity of 7.4 wt.% ( $\text{CH}_{0.95}$ ). The adsorbed hydrogen atoms are desorbed with increasing temperature, and two desorption peaks at about 750 and 1000 K have been observed from experiments. From x-ray diffraction measurements, it is suggested that the desorption peak at about 1000 K is given by the desorption of hydrogen atoms bonding chemically with carbon atoms and is related to a recrystallization of the nanostructured graphite. However, microscopic mechanisms of the desorption of hydrogen atoms has not been clarified yet.

*Ab initio* molecular-dynamics (MD) simulation based on the density-functional theory (DFT) can describe various types of bonding states accurately. Therefore the *ab initio* MD method plays a fundamental role for studying the disordered carbon systems including the  $sp$ -,  $sp^2$ - and  $sp^3$ - bonding states. In this thesis, we concern ourselves with the structural and electronic properties of disordered carbon systems, especially the liquid carbon and the nanostructured graphite with adsorbed hydrogen atoms.

The purposes of this thesis are

1. to investigate the structures and bonding characters of liquid carbon using the *ab initio* MD simulations at various densities. We are particularly concerned with the pressure-induced structural change of liquid carbon and the systematic trend of the structural change in group 14 liquid;
2. to investigate the bonding states of hydrogen atoms adsorbed in the nanostructured graphite using the *ab initio* MD simulations. We also investigate the effects of recrystallization of the nanostructured graphite on the bonding states of the hydrogen atoms, and a desorption mechanism of the hydrogen atoms adsorbed on a graphite layer.

Our results are as follows:

We have applied the *ab initio* MD simulations to liquid carbon at densities of 2.9, 5.8, 8.7, and 11.6 g/cm<sup>3</sup> at a constant temperature of 9000 K. The calculated pressures for each density are 16, 300, 1000 and 2000 GPa, respectively. We have shown that the structure of liquid carbon changes drastically with increasing density or pressure.

- The structure factor,  $S(k)$  changes its shape qualitatively and, at 11.6 g/cm<sup>3</sup>, becomes similar to that of liquid Si and Ge at ambient pressure, which is characterized by a shoulder of  $S(k)$ .
- The average coordination numbers increase from three to eight with increasing density (pressure). Since the region we have investigated in this thesis corresponds to the diamond phase with the coordination number of four for

solid state, these results predict that the slope of the diamond/liquid melting curve changes from positive to negative value at about 300 GPa from the Clausius-Clapeyron equation.

- From the electronic density distributions and the population analysis it is shown that there are  $sp$ - and  $sp^2$ - covalent bonds between carbon atoms at 2.9 g/cm<sup>3</sup>. At 5.8 g/cm<sup>3</sup>, the  $sp^3$ -bonds increase. As a result of further compression, the electron density distribute over the whole system. We have shown that, with increasing density, the bonding character changes from covalent bonding to metallic bonding.

We have applied the *ab initio* MD simulations to the model systems of hydrogen-adsorbed nanostructured graphite.

- The recrystallization of the nanostructured graphite is successfully simulated at 1000 K. As a result of the recrystallization, the hydrogen atoms adsorbed at edge of graphite are pushed out both sides of the graphite layer and the bonding state of the carbon atoms bond with the hydrogen atoms changes from threefold coordinate to fourfold-like coordinate.
- We have found for the first time that two hydrogen atoms desorb from the graphite layer and form a hydrogen dimer at 2000 K. The dimer is stable, though the H-H bond length is slightly longer than that of the isolated dimer, and moves almost freely between the graphite layers.
- From the population analysis, we have clarified that the dimerization occurs

through the intermediate 'bridge' state, -C-H-H-C-, in which the strength of the C-H, H-H and H-C covalent bonds is almost same. We conclude that the desorption of the hydrogen atoms from the nanostructured graphite found in this study is one of the possible

mechanisms of the experimentally observed hydrogen desorption from the nanostructured graphite.

**keyword:**

carbon, disorder phases, liquid, graphite, ab initio molecular-dynamics simulation