別紙様式８

研　究　主　論　文　抄　録

論文題目

Decomposition Reaction of Hydrocarbons and Graphene Formation on Nickel (111) Surface from *ab initio* Calculation

(第一原理計算に基づくニッケル(111)表面における炭化水素の解離及びグラフェン形成過程)

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主論文要旨

Many experimental and theoretical researches have been carried out to study the graphene growth using various methods. The goal of their studies is addressed to achieve the mass production of high quality graphene material that can be easily transferred to any desired substrate. The CVD method is one of the successful methods for this purpose. It has been well agreed that the one of the most important key-points to control the graphene growth process is to understand the complete mechanism of the growth. The comprehensive experimental and theoretical studies in any levels, *i.e.* from macroscopic to microscopic, are absolutely required. This reason motivates us to take part in a microscopic investigation of graphene growth using a theoretical method. The purpose of this study is to clarify the microscopic mechanism of graphene growth on the nickel (111) surface using a sophisticated method, so-called *ab initio* molecular dynamics (AIMD) simulation, which can describe the bonding between atoms accurately and the dynamics of the reactions at the finite temperature are able to be investigated as well.

In the initial stage of graphene growth process on the nickel (111) substrate via CVD technique, the carbon precursor molecules are dissociated into carbon atoms. In this research, we studied the dehydrogenation of two species hydrocarbon molecules, *i.e.* methane and ethylene molecules. The process is continued by the carbon and hydrogen cleavage on the nickel (111) surface.

From our AIMD simulation, we proposed the following mechanism of dehydrogenation of methane molecule on the nickel (111) surface (*i*) $CH_4 \rightarrow CH_3 + H$, (*ii*) $CH_3 \rightarrow CH + 2H$, and (*iii*) $CH \rightarrow C + H$. We also clarify that the spontaneous

dissociation of two hydrogen atoms from CH_3 molecules is due to the low energy barrier of the second hydrogen dissociation, that is $CH_2 + H \rightarrow CH + 2H$. The effect of temperature on the dissociation processes is also evaluated. In the cases of methane (CH_4) and methylene (CH_2) dissociations, the effects of temperature are barely visible that differ from the methylidine (CH) dissociation where the temperature largely lowers the energy barrier.

The three reaction mechanisms are proposed in the ethylene dehydrogenation on the nickel (111) surface. We obtained C=CH and C-CH_3 in the final product of the reaction (for 3.63 ps of AIMD simulation at 1500 K). An additional AIMD simulation is carried out for 1.21 ps to investigate the behavior of diatomic carbon (C_2) on the nickel (111) surface. Until the AIMD simulation finish, some diatomic carbons maintain their bonding while some others are dissociated into monatomic carbon (C) atoms. The diatomic carbons prefer to stay on the nickel (111) surface, while the monoatomic carbon atoms diffuse into the nickel subsurface.

In our study of graphene growth on the nickel (111) surface, we first examine the segregation of the carbon atoms from the nickel (111) surface at 1000 K. We observe that several carbon atoms stay on the nickel surface until 5 ps of AIMD simulation, while some of them form diatomic- and triatomic-carbon chains which segregate to the nickel surface. This result proposed the mechanism of graphene growth by that the carbons segregate to the nickel (111) surface in the form of diatomic- or higher membered carbons. We also investigate the graphitization process of carbon atoms on the nickel (111) surface by employing different concentration of carbon atoms and various quenching temperature. We obtained that the optimum temperature for the graphene growth is about 1000 K. We also found that the graphene can be grown in 800 K, with the similar condition as the growth in 1000 K, with the sufficient number of carbon atoms which are in agreement with the experimental result.