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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（総合化学）

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学 位 論 文 題 名

Synthesis, Characterization and Materials Design of Molecule-Incorporated Carbon-Based Materials
(分子状構造を含んだ炭素系材料の合成、評価および物質設計に関する研究)

Carbon solids can exhibit various properties ranging from insulators to metals. It is well established that the network structure of carbon atoms are responsible for the variation in the physical properties. However, it is very difficult to synthesize carbon solids with designed network of carbon atoms. In this study, a concept of incorporating molecules into carbon and boron nitride networks was pursued in experimental and theoretical viewpoints.

The first part is the experimental study of incorporating π -conjugated molecules in diamond-like carbon (DLC). A new equipment (Fig.1) was developed to co-deposit π -conjugated organic semiconductor molecules with DLC during plasma-assisted chemical vapor deposition (PACVD) using methane gas source. Three molecules - copper phthalocyanine (CuPc), perylene tetracarboxylic dianhydride (PTCDA) and C_{60} were examined. Optical absorption and Raman spectroscopy revealed that the main structure of

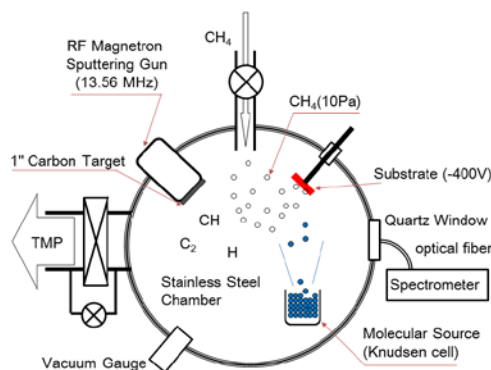


Fig.1 PACVD with molecular source

CuPc remained in DLC, whereas the moieties other than carboxylic dianhydride were destroyed.

A distinct feature was observed in C_{60} -incorporated DLC. It was transparent just after the deposition, but strong iridescence (interference color) appeared within a few minutes after the sample was exposed to the air. The environment to expose the sample after the deposition was changed, and it was found that water vapor was responsible for the appearance of iridescence. The optical property was quantitatively examined by angle-resolved ellipsometry and it was found that the iridescence was partly due to the high refractive index (3.6 at 650 nm) with relatively low extinction coefficient. The structural analysis by SEM and TEM showed that the film thickness expanded more than twice

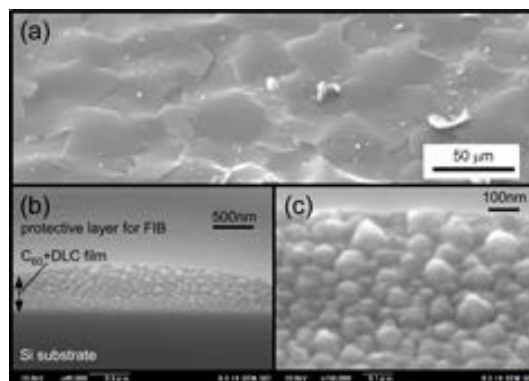


Fig.2 SEM of C_{60} +DLC after the reaction with H_2O vapor

and grain-like structures ranging from 10-100nm appeared with the iridescence. The reaction with water is confirmed by FTIR analysis using D_2O exposure. -OH bonds were formed on carbon and the surface became hydrophilic. The detail of the reaction was further investigated by DFT calculation. After the optimization of the model fragment of C_{60} connected with DLC network, H_2O molecules were put close to the

fragment and the structure was further optimized. It was observed that H_2O molecules reacted with the model fragment to make $-\text{OH}$ bonds and the cage was cracked open. It is suggested that the formation of the nanostructure is due to the strong internal stress in the carbon network which is released by the reaction with water. This result provides a new strategy to modify DLC and other carbon solids by incorporating reaction center such as C_{60} .

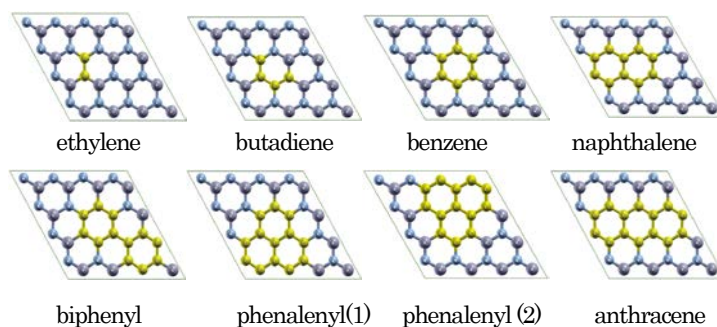


Fig.3 Some of the structures of examined C-doped h-BN

The second part is about the materials design of carbon doping in hexagonal boron nitride (h-BN) by DFT. Tuning the band gap of carbon based solids are very important for the application in solar cells and so on. In literatures, it is reported that making a hybrid layer of graphene and h-BN has become possible, but theoretical prediction of the relationship between the physical properties and the atomic scale structure is very limited. The theoretical study of incorporating carbon atoms in h-BN has therefore been pursued in this study using DFT calculations. It was found that carbon atoms segregate with each other to make “molecules” embedded in h-BN in the most stable structures. The band gap of monolayers can be tuned by the carbon ratio doped in h-BN, but the topology, i.e., the structure of the “molecule” is also important. By replacing an odd number of atoms h-BN to carbon atoms, it is possible to make metallic electronic structures with the Fermi level residing in HOMO or LUMO bands. The work function is much different between materials, the bilayer stacks of those odd-number C-replaced h-BN were examined. Just by examining the bilayer with a

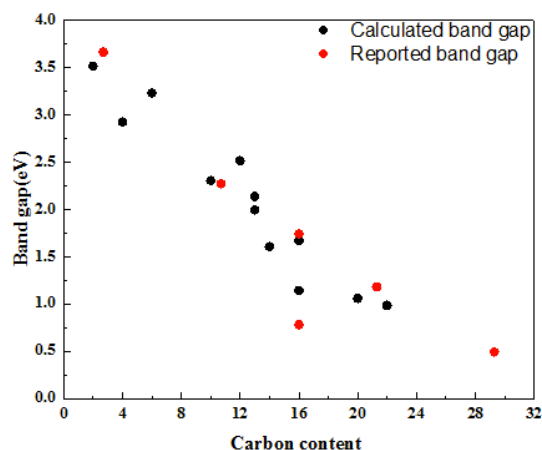


Fig.4 Band gap values as a function of C content in $\text{h}-(\text{BN})_{18}$

C-atom replacing B-atom in one layer and a C-atom replacing N-atom in another layer, it was found that the interatomic distance between C atoms are very important. In one case, C atoms are directly bonded to make s-bond between layers. In another case, a charge transfer complex was formed. In another case, interlayer B-C bond was formed and the band structure became metallic. It is concluded that there is a rich chemistry in the C-doped h-BN and it is now understood that this is the reason why reported physical properties of C-B-N system deviates. It is currently impossible to precisely control which atoms are replaced by carbon, but by using plasma CVD technique with bias voltages as in the first part of this thesis, it might be possible to make a first step to it.

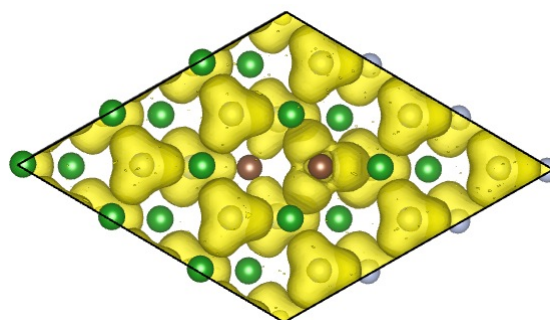


Fig.5 Electron localization function of a bilayer resembling a charge transfer complex.