Advanced Materials '93, I / B: Magnetic, Fullerene, Dielectric, Ferroelectric,
Diamond and Related Materials, edited by M. Homma et al.
Trans. Mat. Res. Soc. Jpn., Volume 14B

MOLECULAR ORBITAL CALCULATIONS OF DIAMOND (001) SURFACES

K.Tsugawa and H.Kawarada

Department of Electronics and Communication Engineering, School of Science and Engineering,
Waseda University, 3-4-1 Ohkubo, Shinjyuku-ku, Tokyo 165, JAPAN.

Many experiments and semiempirical calculations on the diamond (001) surfaces have been achieved to determine the 2×1 reconstructed structure. However,*ab initio* calculations have been carried out in only a few cases, and consequently, the stablest structure of the diamond (001) surfaces has never been defined theoretically. Thus this study defines the stablest model structure of the (001) surfaces of diamond synthesized by chemical vapor deposition by cluster calculations using*ab initio* molecular orbital methods. The monohydride dimer model of the 2×1 reconstructed structure results in the stablest structure of the diamond (001) surfaces.

1. INTRODUCTION

Exact understanding on diamond (001) surfaces is important to clarify the mechanizm of diamond growth by chemical vapor deposition (CVD). The (001) surfaces of diamond synthesized by CVD are reconstructed to the 2×1 structure. The 2×1 reconstruction of the CVD diamond (001) surfaces has been observed using several diagnostic techniques such as reflection high-energy electron diffraction (RHEED) or scanning tunneling microscopy (STM)[1-3]. Otherwise, many theoretical approaches to the 2×1 reconstruction of the CVD diamond (001) surfaces have been developed using semiempirical calculations[4-6]. However, *ab initio* calculations have been carried out in only a few cases[7]. Thus this study adopts the *ab initio* MO methods in the cluster calculations to define the stablest structure of the CVD diamond (001) surfaces.

2. CALCULATION PROCEDURES

This study proposes six types of 4-layer atomic clusters for the calculations of the CVD diamond (001) surfaces (Fig.1). In Fig.1, the grey circles are removed to form the cluster models, and the open circles are replaced with H atoms to saturate the dangling bonds of the clusters.

The cluster models comprise nine C atoms in common: a single surface pair and a substructure of the 2nd-, 3rd- and 4th-layer C atoms with bond-saturating H atoms (Fig.2). They are a spin singlet C_9H_{12}, a doublet C_9H_{13}, a singlet C_9H_{14}, a doublet C_9H_{15}, and a singlet C_9H_{16} cluster model. All the cluster models are constructed on the basis of the C_9H_{12} cluster.

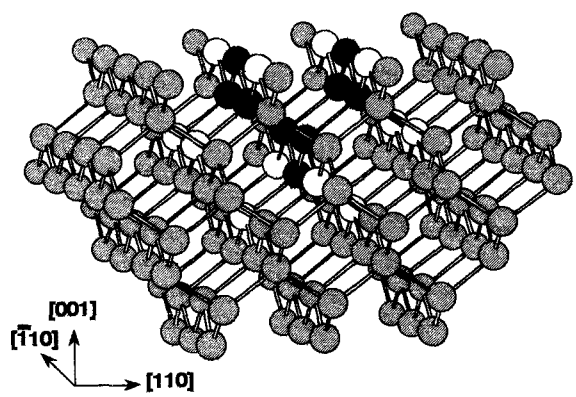


Fig.1. Unreconstructed diamond (001) surface.

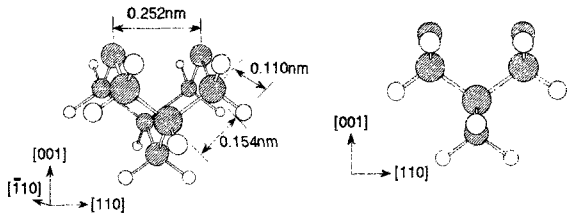


Fig.2. C_9H_{12} cluster model constructed from Fig.1. The solid and open circles denote C and H atoms, respectively.

The two C_9H_{12} cluster models in the spin singlet state and the spin triplet state represent the symmetric dimer structures of clean CVD diamond (001) 2×1 surfaces. Diamond grows in the ambient of atomic hydrogen during CVD growth, and consequently surfaces of the CVD diamond are consider to be hydrogenated. Thus this study proposes 4 types of cluster models of the H-terminated CVD diamond (001) surfaces. The C_9H_{13} in the doublet state represents an asymmetric dimer structure with an H atom bonded to one of the dimer C atoms. The C_9H_{14} in the singlet state represents the monohydride symmetric dimer structure. The C_9H_{15} in the doublet state represents another asymmetric dimer structure with two H atoms bonded to one dimer C atom and one H atom bonded to the other dimer C atom. The C_9H_{16} in the singlet state represents the dihydride 1×1 structure.

The optimized geometry and the total energy of each cluster model are calculated using *ab initio* MO methods[8] to define the stablest structure of the CVD diamond (001) surfaces. The geometry of each cluster model is optimized at the Hartree-Fock (HF)[8] level, while the two topmost C atoms and their additional H atoms in each cluster model, except the C_9H_{16}, are allowed to move freely while the substructure is kept fixed in an ideal bulk position. In the C_9H_{16} cluster model, the two topmost C atoms and the four additional H atoms bonded to them move while maintaining the 1×1 structure.

The total energy of each geometry-optimized cluster model is calculated using the 2nd-order Mφller-Plesset perturbation theory (MP2)[8]. The 3-21G basis set is applied to all the atoms of the cluster models in all the calculations.

3. RESULTS AND DISCUSSION

The optimized structures of the proposed cluster models are shown in Fig.3. Two different types of optimized structures are obtained for the C_9H_{16} cluster model, and one type for each of the other cluster models.

The total energy differences between the optimized structures are shown in Fig.4. Since each cluster model includes a different number of H atoms, each total energy is compared with that of C_9H_{12}(singlet)+nH2 where the number of H atoms is equalized with that of each cluster model. Thus the total energy difference between each cluster model and C_9H_{12}(singlet) means the energy gain by hydrogenating the surface. In Fig.4, the total energy of unreconstructed C_9H_{12} in the triplet state, the lowest total energy state, with all C atoms in ideal bulk positions is also shown. It was calculated as a reference of the unreconstructed clean diamond (001) surfaces.

In Fig.4, the C_9H_{14} monohydride symmetric dimer model is the stablest of all the proposed cluster models. On clean diamond (001) surfaces without hydrogen, the spin singlet symmetric dimer model, the singlet C_9H_{12}, is the stablest. The total energy of the monohydride symmetric dimer model is lower than that of the singlet symmetric dimer model by 4.30eV. Since CVD diamond grows in the ambient of atomic hydrogen, it is expected that the CVD diamond (001) surfaces are terminated by hydrogen.

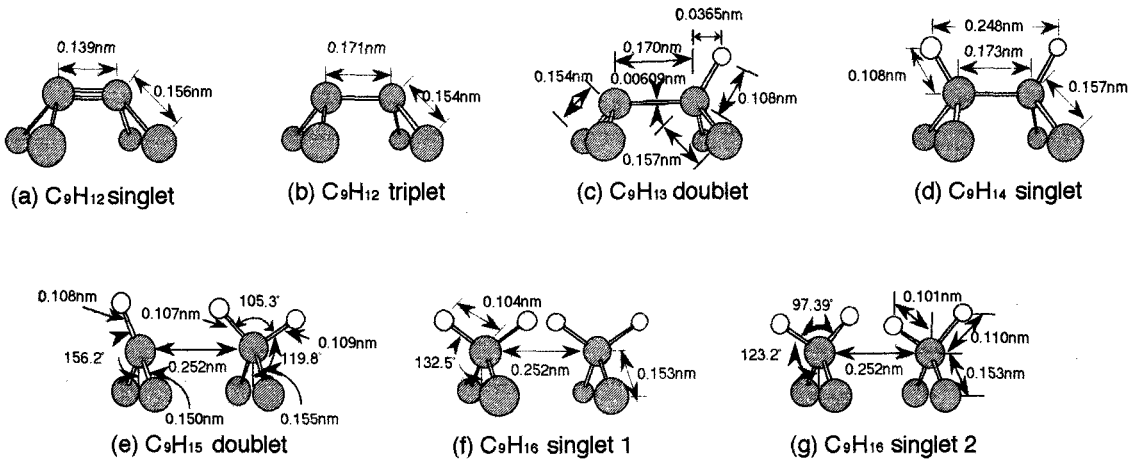


Fig.3. Optimized structures of the proposed cluster models. The surface atoms and the 2nd layer atoms are shown.

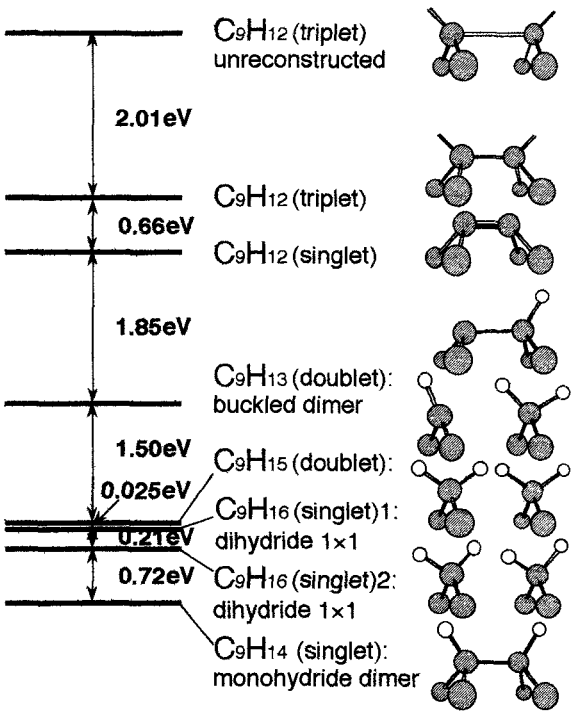


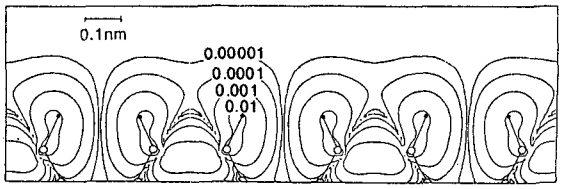
Fig.4. Total energy differences between the clusters

Judging from these findings, the monohydride symmetric dimer structure is the most probable candidate for the 2×1 reconstructed structure on the CVD diamond (001) surfaces. However, the total energy difference between the C9H14 monohydride symmetric dimer model and the C9H16 dihydride 1×1 structure model is only 0.93eV. This relatively small difference implies that both the monohydride 2×1 and the dihydride 1×1 structure may coexist on the CVD diamond (001) surfaces. The coexistence of the 1×1 and the 2×1 structure is observed by STM [3].

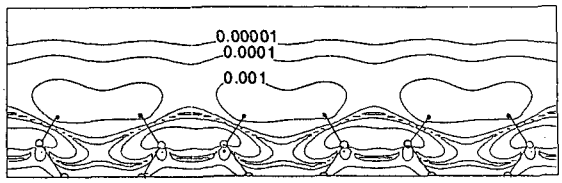
Contour plots of the electron density distribution of the monohydride diamond (001)2×1 surface constructed from the four C9H14 cluster models are shown in Fig.4. The highest occupied molecular orbital (HOMO), corresponding to the valence band maxima, and the lowest unoccupied molecular orbital (LUMO), corresponding to the conduction band minima are shown. These contour plots can be compared with atomically resolved STM images in the near futur.

4. CONCLUSIONS

The optimized structures and the total energy of the proposed cluster models are calculated using



(a) HOMO



(b) LUMO

Fig.4. Contour plots of the electron density distribution of the HOMO (a) and the LUMO (b) of the monohydride dimers on the diamond (001) surface, in units of e/Bohr^3. The open circles denote C atoms and

ab initio MO methods. The optimized structures are calculated at the HF level, and seven types of optimized structures are obtained: two types for the C_9H_{16} and one type for each of the other cluster models. The total energy of each geometry-optimized cluster model is calculated using the MP2 perturbation theory.

The monohydride symmetric dimer model, C_9H_{14}, is the stablest of all the proposed cluster models of the CVD diamond (001) surfaces.

5. ACKNOWLEDGEMENTS

The authors thank Prof. I.Ohdomari, Mr. T.Hoshino, Mr. S.Mabuchi, and Mr. H.Sasaki at Waseda University for their warmful support and imformative suggestions. The authors also thank the Computer Center, Institute for Molecular Science, Okazaki National Research Institute for the use of the HITAC M-680H/S-820 computer system and Library Program *GAUSSIAN86*[8]. The calculations were partly carried out using *GAUSSIAN90*[9] program as Specific Study at the Center for Informatics of Waseda University. The contour plots are drawn at the Computer Center of Chiba University.

REFERENCES

1. T.Tsuno, T.Imai, Y.Nishibayashi, K.Hamada and N.Fujimori, Jpn.J.App.Phys., 30 (1991) 1063.
2. H.Sasaki, M.Aoki and H.Kawarada, Diamond and Related Materials, 2 (1993) 1271.
3. H.Sasaki and H.Kawarada, J.Vac.Sci.and Technol., to be published.
4. W.S.Verwoerd: Surf.Sci., 103 (1981) 404.
5. F.Bechstedt and D.Reichardt, Surf.Sci., 202 (1988) 58.
6. F.Bechstedt and D.Reichardt, Surf.Sci., 202 (1988) 83.
7. S.H.Yang, D.A.Drabold, and J.B.Admas, Phys.Rev., B 48(1993)5261
8. A.Szabo and N.S.Ostlund, Modern Quantum Chemistry, Macmillan (1982).
9. M.J.Frisch, J.S.Binkley, H.B.Schlegel, K.Raghavachari, C.F.Melius, R.L.Martin, J.J.P.Stewart, F.W.Bobrowicz, C.M.Rohlfing, L.R.Kahn, D.J.Defrees, R.Seeger, R.A.Whiteside, D.J.Fox, E.M.Fluder and J.A.Pople, *'Gaussian 86*," Gaussian, Inc., Pittsburgh, PA, 15213
10. *Gaussian90*, M.J.Frisch, M.Head-Gordon, G.W.Trucks, J.B.Foresman, H.B.Schlegel, K.Raghavachari, M.A.Robb, J.S.Binkley, C.Gonzalez, D.J.Defrees, D.J.Fox, R.A.Whiteside, R.Seeger, C.F.Melius, J.Baker, R.L.Martin, L.R.Kahn, J.J.P.Stewart, S.Topiol and J.A.Pople, Gaussian, Inc., Pittsburgh, PA, 1990