Negative Electron Affinity of Diamond (100) surface induced by Diels-Alder Reaction

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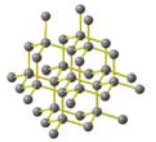


[Introduction]

Important progress in chemical vapor deposition (CVD) of diamond in order to produce (100) and (111) oriented, textured, and p-type films together with the unique property of negative electron affinity (NEA) (Fig. 1), has created a lot of interests in developing NEA diamond-based electronic devices. However, in the past NEA effect was mostly associated with hydrogenated or caesiated diamond surfaces. In this study, we investigated the cycloaddition reaction at CVD diamond (100) surface with 1, 3-butadiene and observed for the first time the NEA feature in this reacted surface. This finding provides us a possible combination of NEA effect with organic functionalization of diamond surfaces and shows potential application in fabricating diamond based molecular electronics devices.

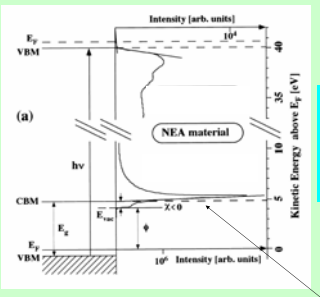


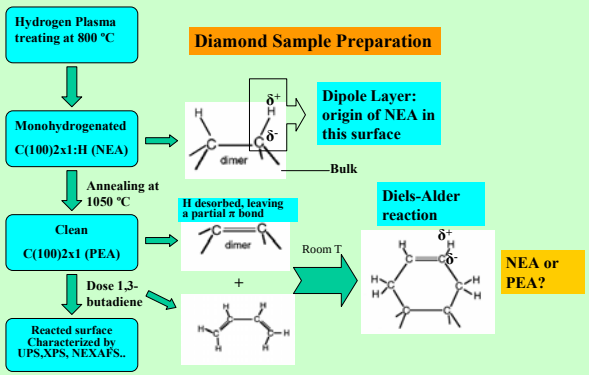
Fig. 1 NEA means the conduction band minimum (CBM) of certain material lies above the vacuum level. So the electrons excited into the conduction band can be thermalized to the CBM and emitted into vacuum without any energy barrier which leads to a very sharp peak at the low electron kinetic energy part in UPS.

NEA Peak

[Experiment]

Experiments were carried out in a UHV chamber with a base pressure of 1×10^{-10} mbar at the ***SINS*** beamline of ***Singapore Synchrotron Light Source***. A type IIb CVD (100) single crystal diamond was used. 1, 3-butadiene gas was introduced to the chamber through a leak valve at room temperature.

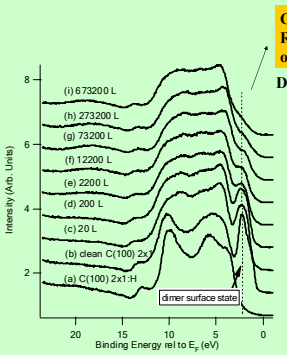
Fig. 2



[Result and Discussion]

In this study we chose 1, 3-butadiene because on one hand 1, 3-butadiene molecules can readily chemisorb on the C(100) 2×1 surface by [4+2] cycloaddition reaction (Diels-Alder reaction)[1,2,3] (Fig. 2). On the other hand because the resulting product on the surface has a monolayer of hydrocarbons with hydrogen facing the vacuum, a dipole layer similar to hydrogenated diamond surface should form, which could lower the vacuum level and induce NEA effect.

A. Valence band spectra of hydrogenated diamond surface, clean diamond surface and diamond surface after chemisorption



Chemical Reaction did occur

Diels-Alder reaction

Fig. 3. Normal emission valence band spectra (Photon Energy 60 eV) of (a) the monohydrogenated C(100)2x1 surface; (b) clean C(100)2x1 surface; (c)-(i) the clean surface exposed to 1,3-butadiene at room temperature with increasing coverage.

The peak near E_F (indicated by dotted line) is due to the surface state originating from π bonds in the dimers. The decreasing height of this peak with the increasing coverage of 1,3-butadiene indicates a chemical reaction occurred on the surface which broke the dimer π bonds to form 6-member-rings as shown in Fig. 2.

B. Electron affinity altered by Diels-Alder reaction

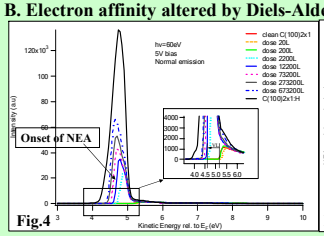


Fig.4

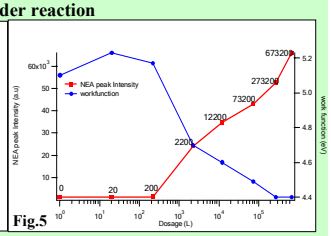


Fig.5

The results clearly show that the surface remained PEA below 200L dosage and then changed to NEA with the NEA peak intensity increasing logarithmically with 1,3-butadiene coverage (Fig. 5). At the same time the lowering of vacuum level indicates that the work function was also decreased accordingly (Blue line in Fig. 5).

C. Near Edge X-ray Absorption Fine Structure (NEXAFS)

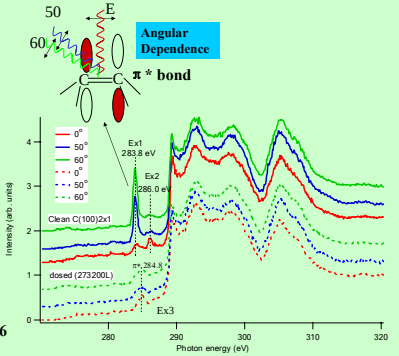
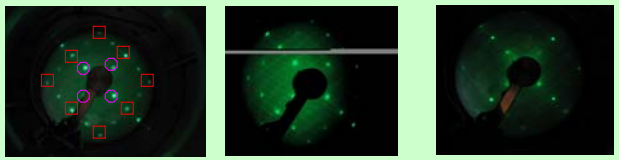


Fig.6

Typical diamond NEXAFS structure, but different pre-edge structures. Peaks Ex1 and Ex2 in the top three spectra were known to be due to surface core resonances associated with π bond of the C-C dimer[4]. Strong angular dependence of Ex1 shows a perpendicular orientation of the π bond relative to surface plane. However, these features were absent in lower three spectra, indicating a chemical reaction. Meanwhile, no angular dependence of Ex3 might suggest no specific orientation of reacted product.

D. Low Energy Electron Diffraction (LEED) images of different surfaces



C(100)2x1:H | C(100)2x1 | Dose 673200L

Bulk termination

Two domains of 2x1 superstructure

Retained 2x1 superstructure after dose! Orderness on the surface.

[Conclusion]

- 1,3 butadiene can readily chemisorb on clean diamond (100)2x1 through Diels-Alder reaction.
- Diels-Alder reaction induced NEA upon certain dosage of 1,3 butadiene.
- Reacted products showed no specific orientation on the surface.
- The 2x1 superstructure could be observed before and after chemisorption.

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