Adsorption and Thermal Stability of Hydrogen Termination on Diamond Surface：A first-principles study

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Abstract. In this paper, we systematically investigated the adsorption characteristics, electronic structure(DOS), band structure and thermal stability of diamond surface with Hydrogen terminals. We found that the most stable adsorption performance may occur on (100) surface. The adsorption stability of hydrogen atom on plane (110) is the second, and the worst on plane (111). A very shallow acceptor level is introduced through Hydrogen termination, explaining the ideal p-type diamond characteristics. The stability of the hydrogen terminal structure decreases as temperature rises. This structure has deteriorated significantly since 400K, and the instability of the hydrogen-terminated structure on the surface is the root cause of the decrease in the hole concentration of hydrogen-terminated diamond at high temperature.

Keywords: Hydrogen termination, Thermal Stability, Surface Adsorption

1 Introduction

Diamond has been extensively studied due to its outstanding properties since the end of the last century [1-3]. Diamond is not only a superhard material for mechanical cutting, but also a semiconductor material with full potential, and it is even expected to become the ultimate semiconductor material. Diamond performs extremely well in power capability and thermal conductivity, far exceeding the related properties of SiC [4-7].

Doping is a key problem in diamond at present. The performance of bulk doped diamond has not been ideal at present, whether it is single doping (B/P/N/O/S) [8-13] or co-doping (B-S/Li-N/B-O/B-P/B-N) [14-18]is difficult to achieve shallow doping in diamond. The low carrier concentration of diamond at room temperature hinders its wide application [19]. Hydrogen-terminated diamond can form a sufficiently high concentration of holes on the surface, which is an important method to realize p-type diamond [20]. At present, hydrogen surface termination can realize the accumulation of holes on the diamond surface, and the concentration can reach ~10^{13} cm^{-2} at room temperature, which is enough to be applied to realize devices such as transistors [21-22].

The concentration of holes accumulated on the H-terminated diamond surface will decrease drastically due to high temperature [23-24], which shows that this p-type doping method has the defect of high temperature instability. The reason for this phenomenon

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is still controversial.There are currently a series of works to increase the thermal stability of H-terminated diamond, mainly through layer deposition at the hydrogen terminal interface. Kueck et al [25] deposited an AlN thin film by atomic layer deposition (ALD) at 370°C to maintain 65% of the initial current level. Kasu et al [26] kept the concentration and mobility of H-terminated p-type channel at 230°C through Al_2O_3 deposition. According to our calculations in this paper, the hydrogen-terminated structure will be structurally unstable at high temperatures(>400K), which may be the key reason why the surface hole concentration of hydrogen-terminated diamonds decreases at high temperatures. In addition, we further calculated the critical temperature of the hydrogen-terminated stable structure.

2 Calculation Methods

The geometric characteristics of hydrogen-terminated diamond surfaces have been studied through periodic slab using density functional theory (DFT). We adopted the Perdew-Burke-Ernzerhof (PBE) form of the generalized gradient approximation (GGA) through VASP[27-28], consistent with the setting of our previous work[14-15]. For calculations, the 64-atom supercell of diamond (2×2×2) and the Monkhorst-Pack grid of KPOINTS (9×9×1) are employed. The cut-off energy of the plane wave is set to 500 eV. the convergence criterion of the interatomic force is adjusted to 1×10^{-4} eV after the convergence verification [29].

3 Results and discussion

3.1 Adsorption properties of hydrogen atoms on diamond surface

Surface adsorption characteristics are an important way to describe the stable structure of hydrogen terminal on the diamond surface[30]. We calculated the surface energy and desorption activation energy of hydrogen atoms at (100), (110) and (111) diamond surfaces. Different crystal planes are achieved by setting different slab directions.
The diamond surfaces were calculated through symmetrically terminated slabs, hence, including two interfaces. Since the surfaces with suspension keys are very active, hydrogen passivation is performed on both such interfaces to ensure the accuracy of the calculation results.
The surface energy per area is calculated using the following expression[31]:

$$\gamma = \frac{E_{slab} - E_{bulk}}{2A}$$

where E_{slab} is the total energy of the whole slab containing all Hydrogen atoms and Carbon atoms, E_{bulk} is the bulk energy, which here refers to the energy of pure diamond structure, and A is the surface area. Given that there are two interfaces in a slab, the factor of two in the denominator must be included.

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Hydrogen desorption activation energy is defined as[32]

$$E_{desorp} = (E_{bulk} + N_H \cdot \mu_H) - E_{slab}$$

where E_{bulk} is the total energy of the bare diamond surface, E_{slab} is the total energy of the system containing hydrogen atoms, N_H is the number of H atoms on the surfaces, and μ_H is the chemical potential of hydrogen, which is calculated by the total energy of H_2 molecule.

Table 1 Surface energy and desorption activation energy of hydrogen terminals on different surfaces

Surface type	Surface energy(eV/A^2)	Desorption activation energy(eV)
(100)	-0.23	9.99
(110)	-0.19	9.59
(111)	-0.11	6.96

In general, the lower the surface energy, the higher the desorption activation energy, indicating that hydrogen atoms adsorbed more firmly on the surface. Combined with the calculation results, hydrogen atom has the lowest surface energy and the highest desorption activation energy on plane (100), which is the most stable adsorption. The adsorption stability of hydrogen atom on plane (110) is the second, and the worst on plane (111). Therefore, from the point of view of surface adsorption stability, h-terminated diamond should be selected (100), which is consistent with the results of current experiments in which (100) h-terminated diamond is used to prepare devices.

3.2 Electronic structure and Band Structure

We have calculated the band structure and total density of states of H-terminated diamond. Credible p-type characteristic is achieved through hydrogen terminal structures, consistent with experiments results.

It can be seen from the calculation results that there is a very close acceptor energy level near the top of the valence band, which we believe is the introduction of an intermediate energy level due to the introduction of the hydrogen terminal structure. The gap between this intermediate energy level and the valence band maximum (VBM) is so small that a shallow acceptor energy level can be seen, which explains why the hydrogen-terminated structure can realize a ideal p-type diamond.

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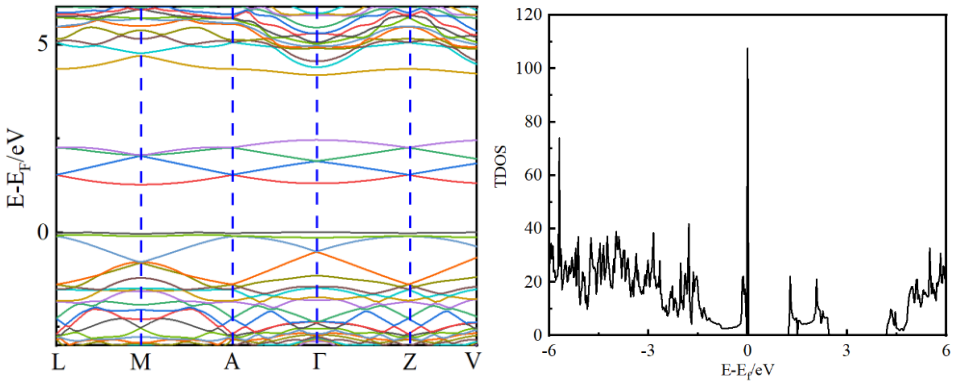
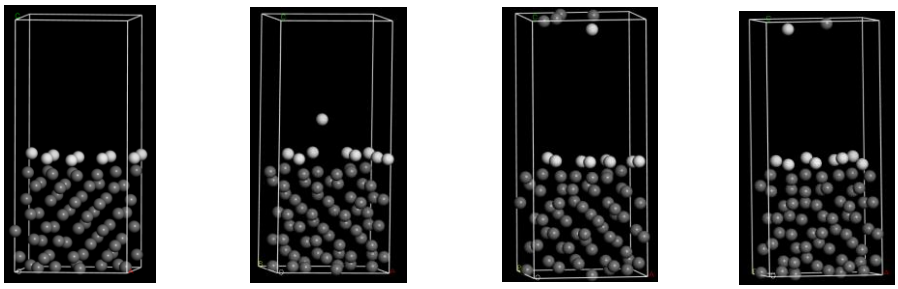


Fig. 1 Band structure of hydrogen-terminated diamond(a); Total density of states(TDOS) of hydrogen-terminated diamond(b)

3.3 Thermal stability of hydrogen atoms on diamond surface

Poor thermal stability is a key factor hindering the continued development of H-terminated diamond. It has been found in experiments that the concentration of holes on the surface of H-terminated diamond will decrease at high temperature. The reason for this phenomenon is still controversial. We applied ab initio molecular dynamics methods to calculate the structural changes of hydrogen atoms adsorbed on the surface of (100) diamond at different temperatures (0K-1000K).



(a) 300K (b) 400K (c) 500K (d) 1000K

Fig. 2 Hydrogen termination structure on diamond surface at different temperatures; (a) at 300K; (b) at 400K; (c) at 500K; (d) at 1000K

Based on our calculation results, the stability of hydrogen terminal structure deteriorates with the increase of temperature. Below 300K, the hydrogen terminal can always be stably adsorbed on the diamond surface. At 400K, the surface structure begins to change, and individual atoms emerge from the diamond surface. Considering the limited duration of molecular dynamics simulation (ps level), this temperature is sufficient to completely change the morphology of hydrogen terminal on diamond surface in practical experiments. At 500K, the surface structure of hydrogen terminal is no longer

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stable, and hydrogen atoms have been completely excited out. When the temperature increased further (over 1000K), the structure of hydrogen terminal on the surface became more chaotic, and the overall flatness and interatomic distance changed greatly. The change of hydrogen terminal surface structure directly affects the cavity concentration of the whole structure surface. In the high temperature environment, the terminal structure of hydrogen is no longer stable, and even completely excited ionization occurs, so the concentration of p-type carrier decreases inevitably.
Our calculations validated the poor thermal stability of hydrogen terminations on the diamond surface. This deficiency is unfavorable for its application in high-temperature and high-power applications, and technical means such as surface passivation are very critical for the application of hydrogen terminals on the diamond surface.

4 Conclusions

In conclusion, H-teminated diamond is currently a p-type diamond implementation method with better performance. The core is to realize the accumulation of holes through the hydrogen terminal on the surface. According to the calculation of surface energy and desorption activation energy, we believe that the hydrogen terminal has the best adsorption characteristics on the (100) surface, followed by the (110) surface, and the worst adsorption characteristics on the (111) surface. The hydrogen-terminated structure introduces an intermediate energy level very close to the top of the valence band, which makes hydrogen-terminated diamonds have shallow acceptor characteristics and can achieve good P-type diamonds. The hydrogen terminal structure remains stable and complete below 300K; at 400K, individual hydrogen atoms dissociate from the surface; above 500K, the stability of the hydrogen terminal structure decreases significantly, and complete excitation and dissociation occurs. The instability of the hydrogen-terminated structure at high temperature may be the fundamental reason for the decrease of the hole concentration on the surface of hydrogen-terminated diamond at high temperature. In order to realize the good performance of p-type doping of diamond at high temperature, it is worth paying attention to the research on improving the stability of hydrogen terminal or bulk doping. Our calculation results still need to be verified by future experimental results.

References

1. Pezzagna S, Meijer J. Quantum computer based on color centers in diamond[J]. Applied Physics Reviews, 2021, 8(1): 011308.
2. Arnault J C, Saada S, Ralchenko V. Chemical vapor deposition single-crystal diamond: a review[J]. physica status solidi (RRL)–Rapid Research Letters, 2022, 16(1): 2100354.
3. Bauch E, Singh S, Lee J, et al. Decoherence of ensembles of nitrogen-vacancy centers in diamond[J]. Physical Review B, 2020, 102(13): 134210.
4. Shen S , Shen W , Liu S , et al. First-principles calculations of co-doping impurities in diamond[J]. Materials Today Communications, 2019, 23:100847.

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5. Li Y , Liao X , Guo X , et al. Improving thermal conductivity of epoxy-based composites by diamond-graphene binary fillers[J]. Diamond and Related Materials, 2022(126-):126.
6. Zhang Z , Lin C , Yang X , et al. Solar-blind imaging based on 2-inch polycrystalline diamond photodetector linear array[J]. Carbon, 2021, 173(42):427-432.
7. Liu X , Chen X , Singh D J , et al. Boron–oxygen complex yields n-type surface layer in semiconducting diamond[J]. Proceedings of the National Academy of Sciences, 2019.
8. Czelej K , Piewak P , Kurzydowski K J . Electronic Structure and N-Type Doping in Diamond from First Principles[J]. Mrs Advances, 2016, 1(16):1093-1098.
9. Shah Z M , Mainwood A . A theoretical study of the effect of nitrogen, boron and phosphorus impurities on the growth and morphology of diamond surfaces[J]. Diamond & Related Materials, 2008, 17(7-10):1307-1310.
10. B, Hiromitsu Kato A , et al.Diamond bipolar junction transistor device with phosphorus-doped diamond base layer[J]. Diamond and Related Materials, 2012, s 27–28:19-22.
11. Sque S J , Jones R , Goss J P , et al. Shallow donors in diamond: chalcogens, pnictogens, and their hydrogen complexes.[J]. Physical Review Letters, 2004, 92(1):017402.
12. Prins J F . n-type semiconducting diamond by means of oxygen-ion implantation[J]. Physical Review B, 2000, 61(11):7191-7194.
13. Kato H , Makino T , Yamasaki S , et al. n-type diamond growth by phosphorus doping on (001)-oriented surface[J]. Mrs Proceedings, 2007, 1039(40):6189.
14. D Zhou, Tang L , Geng Y , et al. First-principles calculation to N-type Li N Co-doping and Li doping in diamond[J]. Diamond and Related Materials, 2020, 110:108070.
15. Tang, Lin, Yue, et al. N-type B-S co-doping and S doping in diamond from first principles[J]. Carbon: An International Journal Sponsored by the American Carbon Society, 2018, 130:458-465.
16. Shao Q Y , Wang G W , Zhang J , et al. First principles calculation of lithium-phosphorus co-doped diamond[J]:Condensed Matter Physics, 2013, Vol. 16, No 1, 13702: 1–1
17. Zhou D , Tang L , Zhang J , et al. n-type B-N Co-doping and N Doping in Diamond from First Principles[C]// International Conference on Computational Science. Springer, Cham, 2022.
18. Sun S , Jia X , Zhang Z , et al. HPHT synthesis of boron and nitrogen co-doped strip-shaped diamond using powder catalyst with additive h-BN[J]. Journal of Crystal Growth, 2013, 377(aug.15):22–27.
19. Yu C, Zhou C J, Guo J C, et al. 650 mW/mm output power density of H-terminated polycrystalline diamond MISFET at 10 GHz[J]. Electronics Letters, 2020, 56(7): 334-335.
20. Nebel C E, Rezek B, Shin D, et al. Surface electronic properties of H-terminated diamond in contact with adsorbates and electrolytes[J]. physica status solidi (a), 2006, 203(13): 3273-3298.
21. Verona C, Ciccognani W, Colangeli S, et al. V 2 O 5 MISFETs on H-terminated diamond[J]. IEEE Transactions on Electron Devices, 2016, 63(12): 4647-4653.
22. Kubovic M, Janischowsky K, Kohn E. Surface channel MESFETs on nanocrystalline diamond[J]. Diamond and related materials, 2005, 14(3-7): 514-517.
23. Ye H, Kasu M, Ueda K, et al. Temperature dependent DC and RF performance of diamond MESFET[J]. Diamond and related materials, 2006, 15(4-8): 787-791.
24. De Santi C, Pavanello L, Nardo A, et al. Degradation effects and origin in H-terminated diamond MESFETs[C]//Terahertz, RF, Millimeter, and Submillimeter-Wave Technology and Applications XIII. SPIE, 2020, 11279: 230-236.
25. Kueck D, Leber P, Schmidt A, et al. AlN as passivation for surface channel FETs on H-terminated diamond[J]. Diamond and related materials, 2010, 19(7-9): 932-935.

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26. Kasu M, Saha N C, Oishi T, et al. Fabrication of diamond modulation-doped FETs by NO2 delta doping in an Al2O3 gate layer[J]. Applied Physics Express, 2021, 14(5): 051004.
27. JC SanchogarcíA, JL Brédas, Cornil J . Assessment of the reliability of the Perdew–Burke–Ernzerhof functionals in the determination of torsional potentials in π-conjugated molecules[J]. Chemical Physics Letters, 2003, 377(1):63-68.
28. Monkhorst, H. J , and J. D. Pack . "Special Points for Brillouin-zone Integrations. " *Physical review. B, Condensed matter* 13.12(1976):5188-5192.
29. Jones R , Goss J P , Briddon P R . Acceptor level of nitrogen in diamond and the 270-nm absorption band[J]. Physical Review B Condensed Matter, 2009, 80(3):1132-1136.
30. Rivero P, Shelton W, Meunier V. Surface properties of hydrogenated diamond in the presence of adsorbates: A hybrid functional DFT study[J]. Carbon, 2016, 110: 469-479.
31. Ostrovskaya L, Perevertailo V, Ralchenko V, et al. Wettability and surface energy of oxidized and hydrogen plasma-treated diamond films[J]. Diamond and Related Materials, 2002, 11(3-6): 845-850.
32. Carter G. Thermal resolution of desorption energy spectra[J]. Vacuum, 1962, 12(5): 245-254.

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