Chemically induced graphene to diamond transition: a DFT study

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ABSTRACT

The conversion of graphene into diamond is a new way for preparing ultrathin diamond film without pressure. Herein, we investigated the transformation mechanism of surface-hydrogenated bilayer graphene (SHBG) into surface-hydrogenated single-layer diamond (SHSLD) crystal, inserting fifteen kinds of single metal atoms without any pressure, by using the systematical first-principles calculations. Compared with the configuration without metal atom, SHBG can be transformed into SHSLD spontaneously in thermodynamics under the action of single metal atom, and its formation energy can even decrease from 0.82 eV to -5.79 eV under the action of Hf atom. According to our results, the outer electron orbits and atomic radius of metal atom are two important factors that affect the conversion. For the phase transition to occur, the metal atom needs to have enough empty d orbitals, and the radius of the metal atom is in the range of 0.136-0.159 nm. Through further analysis, we find that the p orbitals of carbon atoms and d orbital of metal atom in SHBG will be strongly hybridized, thereby promoting the conversion. The results supply important significance to experimentally prepare diamond without pressure through hydrogenated graphene.

KEYWORDS:

INTRODUCTION

It is well known that diamond is an important material in the application of electronic devices\textsuperscript{1,2}, quantum technologies\textsuperscript{3}, bipolar junction transistors\textsuperscript{4}, energy conversion devices\textsuperscript{5,6} and nanoscale sensors\textsuperscript{7,8}. Natural diamond is expensive and scarce for industrial applications or large-area requirements\textsuperscript{9}. Therefore, as an alternative, synthetic diamond was widely extended to the application in various fields\textsuperscript{10,11}. The conventional synthetic diamonds can be produced by high pressure and high temperature method\textsuperscript{12–14}. However, it is difficult to prepare large-area of single crystal diamond even with extremely high cost by this method. Thus, fabrication of the high-quality diamond crystal under milder conditions becomes a long-term goal\textsuperscript{15}. In recent years, a nanometer
thin quasi-two-dimensional diamond film was proposed\textsuperscript{16}, namely, diamane\textsuperscript{17,18}. The growing interest to this material is reflected in a large number of theoretical and experimental studies of multilayer graphene diamondization without pressure\textsuperscript{16,18–20}. For instance, previous theoretical results indicated that full hydrogenation on both sides of graphene can form thermodynamically stable $sp^3$ carbon without pressure, and the following experiment work has also confirmed it\textsuperscript{21,22}. In addition, the rapid development of growth of bilayer graphene through multilayer graphenes\textsuperscript{23,24} and development of large-area graphene\textsuperscript{25–27} have made it possible to prepare large-area diamond by few-layer graphene. Unfortunately, bilayer graphene needs to be hydrogenated on both top and bottom surfaces to convert into diamond, and it is difficult to control the ratio of hydrogenation experimentally\textsuperscript{16,28}. Previous studies have made some progress in using metal surface (Co, Pt, and CuNi) to convert partially hydrogenated bilayer graphene into diamond without any pressure\textsuperscript{15,20,29}. Compared with metal surface, single metal atom has higher atomic efficiency, higher selectivity, and atomic activity\textsuperscript{30}, which will bring novel effects on the phase transition. Besides, uniform single metal atom can be obtained by co-precipitation\textsuperscript{31}. That is, it is feasible to achieve this conversion by using single metal atom to replace the hydrogen atoms on the bottom surface of bilayer graphene. Thus, it is very important to find what kind of metal atom will play this important role in the ordinary-pressure phase transition. However, to the best of our knowledge, there are not related report about this aspect.

Here, we systematically studied the role of fifteen kinds of metal atoms (K, Rb, Ca, Ba, Ti, Zr, Hf, Ta, W, Re, Co, Ir, Pt, Ag, and Au, respectively) on the conversion of surface-hydrogenated bilayer graphene (SHBG) transforming into ultra-thin surface-hydrogenated single-layer diamond (SHSLD). The results show that, single metal atom can greatly reduce the formation energy of SHBG transforming into SHSLD compared with no metal atom. This shows the possibility of using single metal atom to convert SHBG into ultra-thin SHSLD.
We also performed a computational investigation on the electronic properties of the diamond/graphene interface configuration with single metal atom to explore the role of metal atom in this conversion and found that there is electron transfer between single metal atom and SHBG in this conversion. Besides, to better understand the underlying electronic origin of the SHBG into SHSLD, we calculated the electronic band structure and partial density of states (DOS) of the configuration with metal atom. And there will be hybrid bonds between the $d$ orbitals of metal atom and the $p$ orbitals of SHBG. The current results provide important guidance for the experiment to prepare diamond without pressure.

**Method**

The generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange correlation functional was used to calculate all structural relaxation and electronic structure calculations, as implemented in the Vienna *Ab initio* Simulation Package (VASP, version 5.4.4)\textsuperscript{32} containing the projector augmented wave (PAW) pseudo-potential method\textsuperscript{33}. The cutoff energy was set to 520 eV with an energy precision of $10^{-4}$ eV\textsuperscript{34}, and a $4 \times 4 \times 1$ Monkhorst-Pack $k$-points grid for calculations were used to give a sufficient convergence of the total energies during the structural relaxation. We also used GGA+$U$ method to illustrate the strong correlation of an unfilled $d$ orbital of single Co atom\textsuperscript{35}. And we performed all calculations related to single Co atom with an effective $U$ value of 3.32 eV\textsuperscript{36}. Meanwhile, the partial DOS with denser $k$ meshes of $9 \times 9 \times 1$ was performed by using PBE exchange-correlation potential after structures reaching the required accuracy. And we ensured that the vacuum space was at least 25 Å in all calculations, in order to minimize the interaction caused by periodic boundary conditions between the neighboring layers. During the structural relaxation, the atoms in the bottom five layers of the hydrogenated diamond substrate were fixed while relaxing the remaining atoms. We calculated the formation energy of SHBG transforming into SHSLD with metal atom by using the climbing-image nudged elastic band (CI-NEB)
method\textsuperscript{37}. The geometry and energy of the six intermediate configurations of SHBG into SHSLD with a metal atom were optimized until the total energy is less than $10^{-4}$ eV.

**Results and discussion**

Figure 1a-d shows the process of SHBG transforming into SHSLD on hydrogenated diamond with a metal atom. The two layers of graphene are close to each other, changing from $sp^2$ carbon bonding to $sp^3$, while the hydrogenated diamond substrate is stable. We investigated the role of fifteen metal atoms, including K, Rb, Ca, Ba, Ti, Zr, Hf, Ta, W, Re, Co, Ir, Pt, Ag, and Au, in this process for a more comprehensive and systematic study. We used the chair-like configuration\textsuperscript{38,39} that the C-H bonds are equally spaced for calculations, because Dorj et al.\textsuperscript{15} found that only the chair-like SHBG can induce full-carbon $sp^3$ hybridization in the carbon atoms. Table S1 lists the structural properties of SHSLD with and without a metal atom on hydrogenated diamond. Compared to structural properties of diamond and graphite, bond lengths and bond angles in these configurations show obvious characteristics of $sp^3$ carbon (diamond-like) bond. The calculated intralayer C-C bond lengths are range from 1.53-1.54 Å at PBE (+$U$) level, which are fully close to the $sp^3$ bond length in bulk diamond (1.54 Å). And the interlayer C-C bond lengths are in the range of 1.56-1.69 Å, which are significantly lower than the interlayer distance of graphite (3.18 Å). Additionally, the tetrahedral angles of the C-C-C bond within the layer $\alpha$ and formed by interlayer C-C bond $\beta$ are range from 110.3-112.0° and 107.1-110.1°, respectively. It should be pointed out that compared with the system without metal atom, the SHSLD structures formed under the action of single metal atom are closer to bulk diamond, especially the transition metal atoms of Group IVB to VIIB.
Figure 1 | The side view and top view of (a) initial (b-c) transition state (d) final structure of surface-hydrogenated bilayer graphene converted to diamond on hydrogenated diamond and single metal atom. The green, red, and blue spheres represent metal, carbon and hydrogen atoms, respectively.

We first investigated the formation energy of the SHBG converted to SHSLD by CI-NEB method on hydrogenated diamond with and without single metal atom, as shown in Figure 2. The formation energy of the system without single metal atom is about 0.82 eV (see Figure 2a), which means that there is an activation barrier in the conversion. As a result, SHBG is difficult to convert into SHSLD if no additional energy is provided thermodynamically. However, when SHBG with a metal atom is positioned on hydrogenated diamond, the energetics for conversion to SHSLD are significantly different than without a metal atom. In Figure 2a-c, obviously, the formation energies of SHBG converted into SHSLD can be greatly reduced after adding single metal atom. We divide them into three groups according to formation energy: (1) K, Rb, Ca, and Ba atoms have an energy barrier of less than 0.25 eV (0 eV < energy < 0.25 eV), as shown in Figure 2a. (2) Co, Pt, Ag, and Au atoms have negative
formation energy (-3.2 eV < energy < -1.4 eV), as shown in Figure 2b. (3) Ti, Zr, Hf, Ta, W, Re, and Ir transition metal atoms also have negative formation energy (-5.8 eV < energy < -4.5 eV), especially Hf, Ta, Ti atoms are stand out in this configuration (lower than -5.0 eV), as shown in Figure 2c. Be aware of the strong correlation effects between Co atom and the configuration\textsuperscript{35,40}, we also adopted the DFT+\textit{U} method (U=3.32 eV)\textsuperscript{36} to calculate the formation energy of SHBG converted into SHSLD with single Co atom, as shown in Figure 2b. And the formation energy calculated by DFT+\textit{U} method (-2.36 eV) is lower than the results (about -1.34 eV) by Dorj \textit{et al.}\textsuperscript{15} who considered same conversion of bilayer graphene on the (0001) surface of Co. Obviously, single Co atom is more active and unstable than the (0001) surface of Co, thus single Co atom is more likely to form bonds with carbon atoms in the bilayer graphene. We speculate that there are two reasons for the different formation energies that effected by different metal atoms. One is the size of the metal atomic radius. There is a Coulomb interaction force between SHBG and metal atom. Thus the larger metal atomic radius, the stronger the Coulomb repulsive force. Another reason is the outer electron orbits of metal atoms. We speculate that metal atom and carbon atoms in bilayer graphene will hybridize to form bonds, making the formation energy of this process greatly reduced. As a result, a bubble diagram of energy barrier, radius, and outer orbit is shown in Figure 2d. The group one, K, Rb, Ca and Ba with energy barrier in the range of 0-0.25 eV, not shown in Figure 2d for its positive value, have a radius larger than 0.2 nm. This obviously revealed that too big atom radius go against to this conversion.
Figure 2 | (a-c) The formation energy of SHBG converted to SHSLD on hydrogenated diamond substrate with and without single metal atom. (d) The dependence of the formation energy of transition metal atoms with atomic radius and valence electron of (i) suitable atomic radius but unsuited electron orbit, (ii) small atomic radius but proper electron orbit, and (iii) suitable atomic radius and electron orbit. Elements of the same subgroup and group VIII use the same color to represent the formation energy. The lower the formation energy, the larger the circle radius. Value in parentheses is calculated by DFT+U method.

Based on the above two reasons, metal atoms in group two and group three are divided into three categories, area i, ii and iii, according to the atomic radius and outer electron arrangement due to their contribution to the negative formation energy of SHBG to SHSLD, as shown in Figure 2d. For atoms in area i, the outer electron orbits of Pt, Ag, and Au atoms are almost occupied by electrons, which are very stable and difficult to form bonds with carbon atoms in bilayer graphene. Therefore, adding Pt, Ag, Au metal atoms to the configuration to reduce the formation energy of SHBG into SHSLD is far less
effective than atoms in area iii which have close radius. Although the outer electron orbit of Co atom is consistent with Ir atom, the atomic radius of Co atom is too small, making the formation energy of SHBG with single Co atom converted into diamond not as low as Ir atom. Similarly, even if Zr, Ti, and Hf atoms all belong to the IVB group, the atomic radius of Zr atom is too large, so that its corresponding formation energy is not as low as Ti and Hf atom. In addition, the atomic radius of some metal atoms are close and their outer electron orbits are similar or even consistent, for instance, Ag and Au atom, Re and W atom, Ta and Ti atom, and their corresponding formation energies are also similar, which shows that the atomic radius and outer electron orbits will affect the formation energy of the conversion.

To further explore the role of metal atoms in the conversion of SHBG to SHS LD, we investigated the electronic properties of the configurations with Ag, Co, Ir, and Hf atom, respectively. First of all, we calculated the charge density difference $\Delta \rho$ of initial and final structures of SHBG transforming into SHS LD with Ag, Co, Ir, and Hf atom, respectively, to investigate whether charge transfer occurs between SHBG and metal atom (Ag, Co, Ir, and Hf atom) on the hydrogenated diamond surface, as shown in Figure 3a-d. The following equation is used to calculate the charge density difference:

$$\Delta \rho = \rho_{\text{surf+metal+SHBG/SHS LD}} - \rho_{\text{surf}} - \rho_{\text{metal}} - \rho_{\text{SHBG/SHS LD}}$$

where $\rho_{\text{surf+metal+SHBG/SHS LD}}$ is the charge density of the hydrogenated diamond surface with single metal atom and SHBG/SHS LD, $\rho_{\text{surf}}$ is the charge density of the pristine hydrogen-terminated diamond surface, $\rho_{\text{metal}}$ is the charge density of the single metal atom, and $\rho_{\text{SHBG/SHS LD}}$ is the charge density of SHBG or SHS LD, respectively. No matter in the initial or final structure, it is obvious that main strong electron accumulation is between the Ag atom and hydrogenated diamond surface, while main electron accumulation is between metal atoms and SHBG/SHS LD for other three metal atoms. Therefore, Ag atom is more inclined to adsorb on the surface of hydrogenated diamond, whereas the other
three atoms are more likely to form bonds with SHBG/SHSLD. In addition, we also calculated the charge density difference $\Delta \rho$ of initial and final structures of SHBG transforming into SHSLD with Co atom by DFT+$U$ method, as shown in Figure S1. Interestingly, in Figure 3b and Figure S1, the electron cloud of the top-view of final structure of the configuration with Co atom presents an approximate triangular shape. As the atomic radius of metal atom increases, the electron cloud of final structure of the configuration with Ir atom resembles three petals, while the electron cloud of the configuration with Hf atom presents three spherical shape. This confirms that the atomic radius of the metal atom mentioned above will affect the formation energy of SHBG into SHSLD, and the atomic radius of Hf atom is more conducive to the conversion of SHBG to SHSLD. Compared with other metal atoms, the electron transfer between the Hf atom and the the six-membered graphene ring directly above Hf atom is more balanced. In other words, Hf atom has the same degree of charge transfer as every carbon atom in the six-membered ring of graphene. In order to quantify the amount of charge transferred between metal atom and SHBG/SHSLD, we also calculated the Bader charge for the configurations. The results are listed in Table S2. It can be clearly seen that almost all the electrons obtained by single metal atom are taken from SHBG/SHSLD, and the number of electrons lost and gained in the diamond substrate is small, indicating that the substrate is stable. In most cases, the metal atoms of the final structure get more electrons from the SHBG/SHSLD than the initial structure, indicating that during this conversion, the SHBG/SHSLD is transferring electrons to the single metal atom. This may be an important reason for the conversion of SHBG into SHSLD without activation barrier. Meanwhile, we calculated separately the electron localization function (ELF) of initial and final structures of SHBG transforming into SHSLD with single metal atom (Ag, Co, Ir, and Hf atoms), as shown in Figure S2. Obviously, there are ionic bonds between the metal atom and the configuration, and the bond between Ag atom and SHBG/SHSLD is weaker than other metal atoms.
Figure 3 | The side-view and top-view of charge density differences of initial and final structures of SHBG transforming into SHSLD with (a) Ag, (b) Co, (c) Ir, and (d) Hf atom, respectively. The yellow and light blue regions represent the electron accumulation and depletion, respectively. The isosurface values are 0.004 e/Å³.

Next, we calculated the electronic band structure and partial density of states (DOS) of initial and final structures of SHBG transforming into SHSLD with and without single metal atom by using the PBE functional, in order to understand the underlying electronic origin of this conversion. As the conversion occurs, the configuration with metal atom changes from a conductor to a semiconductor, which can be reflected from the energy bands of initial and final structures, see band structure in Figure 4 and Figure S3-S6. What’s more, the characteristics of the delocalized π electronic states of SHBG largely disappear with the conversion from $sp^2$ to $sp^3$ bonding, and replaced by a hybrid bond between metal atom and carbon atom in SHBG. It is found that the energy bands near the Fermi level are mainly contributed by the $p_z$ orbital of carbon atom before the conversion, but after the conversion, a hybridization occur between the $p_z$ of carbon and the $d$ orbit of the metal atom. This means that the $d$ orbital of metal atom need to participate in the process of $sp^2$ to $sp^3$ bonding. Detailed projected DOS analysis near the Fermi level of initial structure indicates that the $d_{xy}$, $d_{yz}$, $d_{xz}$, and $d_{xz}$ orbitals of Co (calculated by DFT+U
method) and Ir atoms have more prominent contributions, even five $d$ orbits of Hf, whereas all $d$ orbits of Ag atom give only a small contribution, see Figure S3. And this also confirms the idea that the outer electron orbit of the metal atom is one of the influencing factors of the formation energy of the conversion. Meanwhile, projected DOS of final structure reveals that the only $d_{zz}$ orbit of Ag, Co (calculated by DFT+$U$ method), Ir and Hf atoms give a small contribution to the metallic behavior. It is worth mentioning that in Figures 4a and 4c, although the $p$ orbitals of Hf and Ir atoms contribute at the Fermi level, the absolute value of the abscissa of the $p$ orbital is very small compared to that of the $d$ orbitals. In other words, the conversion of $sp^2$ to $sp^3$ bonding is mainly participated by the $d$ orbitals of metal atom. Besides, the $d$ orbitals of K, Rb, Ca, and Ba atoms all give small contribution to energy bands near the Fermi level, which also explains that the positive formation energies of SHBG with K, Rb, Ca, and Ba atoms converted to SHSLD, as shown in Figure S4. As a result, we speculate that the C atoms in SHBG and metal atom will be hybridized with $p$ and $d$ orbitals to promote $sp^2$ to $sp^3$ bonding.

Figure 4 | The electronic band structure and partial density of states (DOS) of initial and final structures of SHBG transforming into SHSLD with (a-b) Ir, and (c-d) Hf atom, respectively. The Fermi level is set as 0 eV. The value range of the abscissa of partial DOS is relative.
Conclusions

In summary, we have systematically investigated the conversion of SHBG into SHSLD under the action of 15 metal atoms on a hydrogenated diamond substrate by first-principles computation. Our results show that single metal atom can greatly reduce the formation energy of this conversion, for instance, Hf atom (-5.79 eV), Ta atom (-5.39 eV), and Ti atom (-5.01 eV), while the energy barrier for the conversion of SHBG into SHSLD without metal atom is 0.82 eV. The results reveal that the main factors affecting the formation energy of the conversion are outer electron orbits and atomic radius of metal atoms. K, Rb, Ca, and Ba atoms have a strong Coulomb interaction force with SHBG due to their large atomic radius, and the outer d orbitals of Pt, Ag, and Au atoms have been occupied by most of the electrons. As a result, these five metal atoms are not as effective as the other eleven metal atoms in reducing the formation energy of the conversion. During the conversion, the carbon atoms in SHBG will hybridize with the metal atom to form bonds, and the p$_z$ orbitals of the carbon atoms and the d orbital of the metal atom strongly hybridize to make the $sp^2$ to $sp^3$ bonding easier. Our results provide a theoretical basis for the experimental preparation of diamond using graphene without pressure.

Conflicts of interest

There are no conflicts to declare.
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