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FIRST-PRINCIPLES STUDY OF π-BONDED (100) PLANAR DEFECTS IN DIAMOND

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ABSTRACT

A periodic density functional study of the high-energy π-bonded (100) stacking fault in diamond that can serve as a prototype of a twist grain boundary has been carried out. Information on formation energies, geometries and the electronic structure has been obtained. A single point electronic structure calculation of a Σ5 twist grain boundary based on the geometry taken from a molecular dynamics simulation has also been performed.

INTRODUCTION

Recent successes in growth of nanocrystalline diamond from hydrogen poor plasmas\(^1\) has attracted attention due to a number of highly desirable mechanical and electronic properties of the new materials. It also raised an interest in effect of the grain boundaries on diamond properties. Indeed, for a typical grain size in the synthesized materials of 3-10 nm, a significant portion of diamond atoms (several percent) is located in the grain boundaries. Therefore, grain boundaries effectively control many properties. Understanding grain boundary formation and structure in the nanocrystalline diamond can help in tailoring new diamond materials in a systematic fashion. A number of molecular dynamics studies have investigated the energetics and structures of grain boundaries.\(^2\) It was found that twist (100) grain boundaries are usually high-energy structures having a large portion of sp\(^2\)–bonded atoms in the interface region which is corroborated by TEM studies.\(^3\) It should be noted that the (100) surface can be considered to represent a general diamond surface because atoms on this surface have two broken bonds which is a general situation with only exceptions for two special surfaces, namely (111) and (110) surfaces. Therefore, we concentrate our attention on (100) interfaces.

First-principles calculations give reliable results for atomic structure and chemical bonding. However, their use in grain boundary studies in diamond is limited due to the low symmetry and a large size of such systems. We performed a periodic density functional study of a stacking fault in diamond. This system is characterized by π-bonded dicarbon moieties in the interface region and a high formation energy, similar to the twist grain boundaries. In addition, we considered more complicated structure that could occur in the nanocrystalline diamond such as graphite-like planar structures that interconnect two diamond grains. In principle it is desirable to calculate a more realistic grain boundary structure at \textit{ab initio} level but the size of the problem, disordered geometry and a large number of possible metastable states makes it computationally intractable. Instead we have used the equilibrium geometry of a Σ5 twist grain boundary geometry obtained in tight-binding molecular dynamics calculation for a single-point density functional calculations.

THEORETICAL METHOD

The periodic density functional method implemented in CRYSTAL\(^9\)\(^5\)\(^\text{\textdagger}\) was used to calculate the properties of a model for the grain boundary in nanocrystalline diamond. Crystalline orbitals in this approach are constructed from the localized atomic orbitals, which are linear combinations of Gaussian orbitals. Becke exchange\(^5\) and Perdew-Wang correlation\(^6\) functionals were employed in this study. The standard 6-31G* basis set for carbon was modified by using a
scaling factor of 1.1 for outer sp and d functions to account for less diffuse atomic orbitals in the crystalline environment. A large number of k-points in the irreducible part of Brillouin Zone (approximately 600) was used for reciprocal space integrations. Optimized lattice constants for diamond (3.58 Å) and graphite (a = 2.47 Å and c = 6.71 Å) are in a very good agreement with experimental data (3.57 Å for diamond and a = 2.46 Å and c = 6.7 Å for graphite). We have calculated the difference in total energies between diamond and graphite to be 0.9 kcal/mol per one carbon atom. As far as the electronic structure is concerned, we have obtained a value of 4.1 eV for the indirect forbidden energy gap width of diamond as compared to the experimental result of 5.45 eV. The position of the conduction band minimum is in the Γ-X direction about ¼ of the way to the X point. For graphite, our calculations produce a zero width band gap at the K point in agreement with other studies.

STACKING FAULT RESULTS

The model for the diamond stacking fault comprises a 6-layer slab periodically repeated in the z-direction. The two innermost layers of the slab represent a (100) stacking fault, which is separated by 4 layers of diamond from the next equivalent defect. The geometry of the system is shown in Fig. 1. There are 12 atoms in the unit cell, only 3 of which are symmetry unique. The positions of atoms in the xy-plane were restricted to be those in bulk diamond, leaving three interplanar spacing parameters to be optimized: the distances between the two interface planes (d₁ in Fig. 1), between the surface plane and the second diamond plane (d₂ in Fig. 1), and between the second and third diamond planes (d₃ in Fig. 1). The remaining interplanar spacing, d₄, was fixed at the bulk diamond value of 0.895 Å. The optimized values of these parameters are 1.34 Å, 0.828 Å and 0.918 Å. The distance between interface atoms is smaller than that in graphite rings (1.42 Å) and the interlayer distances between diamond layers are slightly different from the defect-free diamond interplanar spacing of 0.895 Å. The volume increase per unit surface area is 0.1 a. As far as the system energetics is concerned, the formation energy per one interface atom is 0.84 eV. This translates into a defect energy per surface area of 4.2 J/m².

Figure 1. Geometry of a periodic planar defect in the diamond structure. Inequivalent distances between interface layers (d₁), interface layer and second layer (d₂), as well as between the next two diamond layers (d₃ and d₄) are shown.
The density of states (DOS) plot for diamond with stacking faults is compared to diamond and graphite DOS plots in Fig.2. Peaks that are similar to graphite π-states appear in the band gap of the diamond as a result of the presence of sp²-bonded atoms. The height of the peaks is strongly dependent on the concentration of planar defects. Since our model has too high a defect concentration (one interface atom per two bulk atoms), it is expected that the density of states in the energy gap of real nanocrystalline material should be several times lower. The three most prominent peaks are at –0.1 eV, 1.1 eV and 2.1 eV with respect to the Fermi level. The appearance of defect states in the fundamental gap of diamond is attributed to the electronic states of atoms in the interfacial layer. The DOS projected on the orbitals of atoms in the interface (first) layer and other layers are shown in Fig.3. It is evident that electronic states in the gap are localized in the interface layer of the stacking fault. Further analysis reveals that the states in the gap are π-states formed by p-orbitals lying in the y-direction in the defect plane. These states might play a role in grain boundary electric conductivity.
Since sp²-bonded carbons do not form a continuous network in the system, some additional explanations are required for mechanism of grain boundary conductivity. A hopping mechanism for grain boundary conductivity was recently suggested⁷. On the other hand, the highest occupied states in the valence band belonging to four-coordinated diamond atoms are very close in energy to the unoccupied states of sp²-bonded atoms. This leads to another possible mechanism for grain boundary conductivity involving atoms in the interfacial layer and the next diamond layer that together form a continuous path along the interface.

**Σ5 TWIST GRAIN BOUNDARY**

Real grain boundaries are expected to have disordered structures in the interface layers in contrast to our model calculation of the stacking fault. Nevertheless, they still have predominantly three-coordinated carbon atoms in the interface layers and almost perfect diamond structure throughout the rest of the crystal. Indeed, molecular dynamics calculations of Σ29 twist grain boundary found that 80% of atoms in the grain boundary are three coordinated². Therefore, we expect our conclusions from the stacking fault study to remain valid in the case of more complicated grain boundaries. As a next step in first-principles calculations of grain boundaries, we have studied the electronic structure of a Σ5 twist grain boundary, which has the smallest possible planar unit cell with five carbon atoms in each layer. We have performed a single-point calculation taking the equilibrium geometry from the tight-binding molecular dynamics calculations of Cleri⁸. We have reduced the 24-layer 120-atom unit cell that has two Σ5's in it to a smaller unit cell of 40 atoms as illustrated in Fig. 4. The latter structure comprises two diamond-like layers and two interface layers periodically repeating in z-direction. Coordinates of the atoms in the unit cell were taken from molecular dynamics without changes. The average distance between two interface layers is 1.26 Å. A smaller STO-3G basis set was used in this calculation and 36 k-points in the first Brillouin Zone were used in reciprocal space integration. The formation energy of the grain boundary was calculated to be 1.4 eV/atom, which translates into 6.5 J/m². It is a higher value compared to our stacking fault results but geometry optimization using density functional method would bring it down somewhat.

Figure 4. Geometry of Σ5 (100) twist grain boundary used in density functional calculations. Atoms in the interface layers are shown in black, atoms in the diamond-like layers are shown in white.
The calculated density of states plot for the Σ5 grain boundary is shown in Fig. 5. The main peaks in the diamond band gap region are attributed to π-like states on $sp^2$ atoms and have energies 0.1 eV, 1.1 eV and 3 eV with respect to the Fermi level. A large number of smaller peaks is explained by structural disorder in the grain boundary region. The incomplete convergence of DOS calculation also introduces some spurious features. Thus, the presence of electronic states in the diamond band gap caused by three-coordinated atoms in the interface is a common feature for both high-energy twist grain boundaries as well as stacking faults.

CONCLUSIONS

Periodic density functional calculations of high-energy planar defects in diamond adequately reproduce properties of (100) twist grain boundaries. The formation energy of a π-bonded stacking fault is 4.2 J/m². The defect region is very thin, having a thickness of one-two atomic layers. The electronic structure of both the stacking fault and the Σ5 grain boundary is characterized by the presence of π-states in the forbidden gap localized on the interfacial atoms of diamond with defects. These states produce several broad peaks in the gap and might play a key role in both grain boundary conductivity and mechanical properties. These results have also shown that single point density functional calculations using molecular dynamics geometry can be useful in studying the electronic structure of the grain boundaries.

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