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Missing-atom structure of diamond $\Sigma 5$ (001) twist grain boundaryPeter Steneteg,^{1,*} Valeriu Chirita,¹ Natalia Dubrovinskaia,² Leonid Dubrovinsky,³ and Igor A. Abrikosov¹¹*Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden*²*Materialphysik und Technologie, Lehrstuhl für Kristallographie, Physikalisches Institut, Universität Bayreuth, D-95440 Bayreuth, Germany*³*Bayerisches Geoinstitut, Universität Bayreuth, Universitätsstrasse 30, 95440 Bayreuth, Germany*

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We carried out a combined experimental and theoretical study of grain boundaries in polycrystalline diamond, aimed at achieving the conditions in which grain boundaries are equilibrated. Raman spectra of compacted at high-pressure and high-temperature diamond powders allow us to identify signals from sp^2 -bonded atoms, in addition to a strong peak at 1332 cm^{-1} , corresponding to sp^3 -bonded carbon. To verify our interpretation of the experiment, $\Sigma 5$ (001) twist grain boundaries of polycrystalline diamond were studied by means of molecular dynamics simulations using the technique proposed by von Alftan *et al.* [*Phys. Rev. Lett.* **96**, 055505 (2006)]. We find that grain-boundary (GB) configurations, from which one atom is removed, have significantly lower energy compared to those obtained with conventional techniques. These calculated GBs are highly ordered, a few monolayers thick, in agreement with experimental observations, and are primarily sp^2 bonded. This paper underlines the importance of varying the number of atoms within GBs in molecular dynamics simulations to correctly predict the GB ground-state structure.

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I. INTRODUCTION

Diamond, with its many interesting properties, has always attracted significant attention. During the past decades, when the technology to produce artificial diamonds became available, the interest in studies of this material has grown rapidly. In particular, there is much work devoted to the production of high-quality smooth diamond films on metallic and ceramic substrates for use in a variety of engineering applications.¹ Moreover, in the past few years, it has been possible to produce materials with very small diamond crystals, with particle sizes in the order of a few nm.² Indeed, the synthesis of nanocrystalline films of diamondlike carbon, polycrystalline cubic diamond, and aggregated diamond nanorods has been reported in literature^{3–9} Importantly, polycrystalline diamond, reported to consist of very fine granular crystals, was found to be as hard or even harder than single-crystal diamond, with constant hardness throughout the sample.³ The aggregated diamond nanorods, and mesoporous diamond composed of interconnected nanocrystals, were found to be the densest among all carbon materials and had the lowest experimentally determined compressibility.⁸

In such polycrystalline aggregates, the amount of substance located in between the crystallites, i.e., in the grain boundary (GB), becomes considerably larger and hence very important for the material properties. Diamond GBs have therefore been studied extensively, both experimentally² and theoretically,^{10–12} with substantial attention given to the determination of their chemical bonding. Nevertheless, the great versatility of carbon materials arises from the strong dependence of their physical properties on the ratio of sp^2 (graphene-like) and sp^3 (diamondlike) bonds.¹³ In particular, several experimental studies suggested that polycrystalline diamond thin films consist of grains of pure sp^3 -bonded carbon separated by relatively thin GBs with sp^2 -bonded carbon.^{1,14,15} However, there is no consensus on the exact interpretation of the signal coming from sp^2 -bonded carbon, as it may originate from amorphous or graphitic phases. For

instance, in ultrananocrystalline diamond thin films grown by microwave plasma-enhanced chemical vapor deposition (MPECVD), a disordered mixture of sp^2 - and sp^3 -bonded carbon was suggested to be present at the GBs.^{14,15} On the other hand, for nanocrystalline diamond thin films deposited by hot filament CVD on monocrystal silicon, the interpretation of experimental data on elastic properties was most consistent with a model film microstructure consisting of sp^3 -diamond grains and monocrystal graphitic phases (sp^2 -bonded carbons) at GBs.¹⁶ Most importantly, to the best of our knowledge, all earlier experimental studies of bonding in diamond GBs were carried out for thin films, and therefore unlikely to correspond to an equilibrium situation. Consequently, studies of bonding carried out for bulk polycrystalline diamonds are highly desirable.

In time, computer simulations have become increasingly important for determining GBs structure. One type of GB which has been studied extensively is the so-called twist GB. These are generally high-energy GBs and are seen as representative for many relevant GBs in nanocrystalline diamond. Simulations have shown these structures to have a very high amount of sp^2 -bonded atoms, up to 80%.¹⁰ Their boundaries often show high structural order at the expense of coordination disorder. The widths of these boundaries are very narrow, usually in the range of one or two lattice constants.¹⁰

Note that the problem of finding the structure of a GB theoretically is generally very difficult, since the configurational phase space is very large for an arbitrary GB, severely limiting the time and space scales computational methods apply to. Most attempts to find the ground-state structure of a twist boundary were based on creating a supercell representing the GB, subjecting it to simulated annealing at high temperature, and thereafter cooling it to 0 K.^{10,11} However, recently von Alftan *et al.*¹⁷ successfully introduced a method to create initial configurations by varying the number of atoms in GBs. An application of this method in studies of silicon GBs resulted in large differences compared to previous traditional

simulations. Clearly, there is an obvious need to reexamine earlier theoretical results obtained for GBs in diamond.

In this paper we report an experimental study of GBs of compacted at high-pressure–high-temperature diamond powders, followed by theoretical molecular dynamics (MD) simulations to determine the lowest-energy structure of diamond GBs. The aim is to achieve the conditions at which the GBs are equilibrated, experimentally, as well as theoretically. Nevertheless, GBs in nanocrystalline films of diamondlike carbon, polycrystalline cubic diamond, or aggregated diamond nanorods should not be in an equilibrium state. However, a study of equilibrium GBs is an important first step on the path to understanding the superior properties of nanocrystalline diamonds. Our experimental observations on nanodiamond compacts support the picture that, even in the bulk phase, polycrystalline diamond consists of sp^3 -bonded carbon grains separated by sp^2 -bonded GBs. Using the technique of Ref. 17, we find new GB configurations with considerably lower energy, up to 20%, and a higher degree of order, compared to those found using conventional methods. We demonstrate that, in agreement with experiment, the lowest-energy GB has predominantly sp^2 bonds, but since the GB is relatively narrow, the total fraction of sp^2 bonds in the material is very small.

II. EXPERIMENT

It is well known¹⁸ that Raman spectroscopy is very sensitive to the electronic state of carbon, and in pure carbon, phase peaks at 1330 cm^{-1} (D band) and at 1600 cm^{-1} (G band) are often used to recognize the presence of sp^3 - and sp^2 -bonded carbon atoms, respectively.¹⁹ We prepared the sample of sintered polycrystalline diamond by sintering diamond powder with an average $0.1\text{ }\mu\text{m}$ particles (Alfa Inc., purity 99.999%). The material was loaded in a Ta capsule, compressed to 14(1) GPa, and heated at 2000 K for 3 h in a multianvil apparatus (for details of the experimental procedure, see Ref. 8). X-ray powder diffraction shows that the lattice parameter [$3.5679(1)\text{ \AA}$] of the starting and sintered materials are not distinguishable. The measured density of the sintered sample is $3.50(1)\text{ g/cm}^3$, which is within the precision of measurements, and coincides with the density of bulk crystalline diamond, confirming the quality of the sintering process. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) analyses confirmed the chemical purity of the sintered material. High hardness [$H_V = 110(15)$ GPa, measured in an asymptotic high-load (2 N) limit²⁰] comparable with the hardness of single-crystal diamonds also suggests that the GBs are equilibrated.

The Raman spectra of diamond powder compressed to 14(1) GPa and decompressed to ambient conditions demonstrate only one peak of the A_g (1332 cm^{-1}) vibration mode (Fig. 1). The Raman spectra of sintered materials collected with 632-nm (LabRam, Hariba Scientific, Inc.) or 514-nm (Dilor XY) excitation lasers show very high fluorescence (Fig. 1), probably due to light scatter in numerous defected GBs (similar to the phenomena observed in nanocrystalline diamonds⁷). Spectra collected using an UV 244-nm laser (LabRam, Hariba Scientific, Inc.) is dominated by a strong peak at 1332 cm^{-1} (sp^3 -bonded carbon). Moreover, there is a weak but very clear (see the insert in Fig. 1) signal at

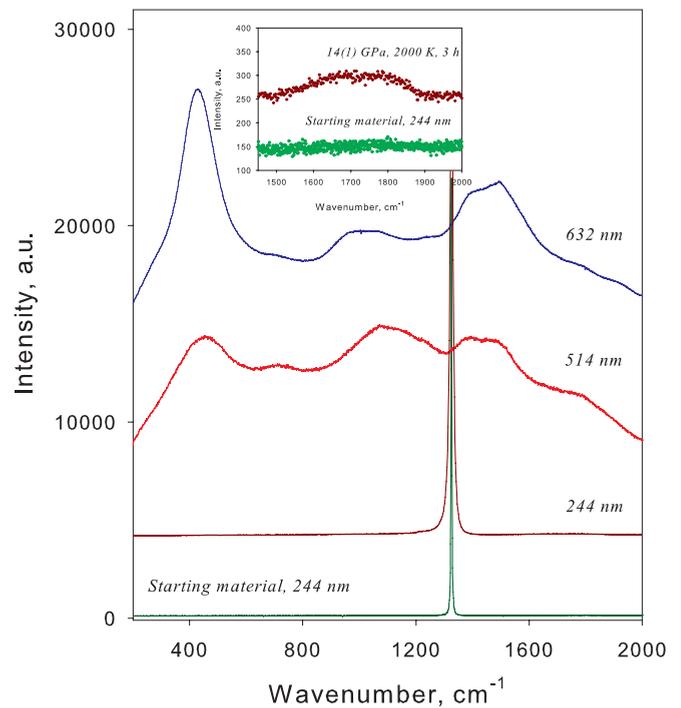


FIG. 1. (Color online) Raman spectra of diamond powder compressed to 14(1) GPa (starting material) and sintered at 14(1) GPa and 2000 K in a multianvil press for 3 h. Spectra collected at ambient conditions (on recovered materials) using different excitation lasers.

$1600\text{--}1800\text{ cm}^{-1}$, which we can interpret as due to the presence in the sample of sp^2 -bonded carbon atoms. We therefore demonstrate that, similar to a situation in thin films, the GBs of compacted at high- P, T diamond powders can have predominantly sp^2 bonding.

III. THEORETICAL SIMULATIONS

In order to confirm this experimental observation, we study equilibrium GBs in diamond by means of molecular dynamics simulations. The starting configuration for the simulation of a twist GB is generated by cutting a block of atoms along a certain plane, usually (001), (011), or (111), and rotating one of the resulting slabs around the axis perpendicular to the cut. In the case of molecular dynamics simulations, periodic boundary conditions are required at least in the plane of the cut. To fulfill these conditions with a limited amount of atoms, only a few angles of rotation are available. These special cases are called Σ GB and are indexed by how many times larger they are than the original unit cell. The smallest GB in the (001) direction is called $\Sigma 5$ and has a unit cell that is five times larger than the ordinary diamond unit cell, with an angle of rotation of 36.87° .

To better explore the phase space of possible GB configurations and find the ground-state structure of the boundary, we use the scheme proposed in Ref. 17 to remove a number of atoms from the GBs, ΔN , before performing the relaxation. In our study the $\Sigma 5$ twist GB unit cell consists of four monolayers parallel to the GB, just as the conventional diamond unit cell, but each monolayer has five atoms instead of two. Initial simulations cells of 2×2 $\Sigma 5$ unit cells in the GB plane,

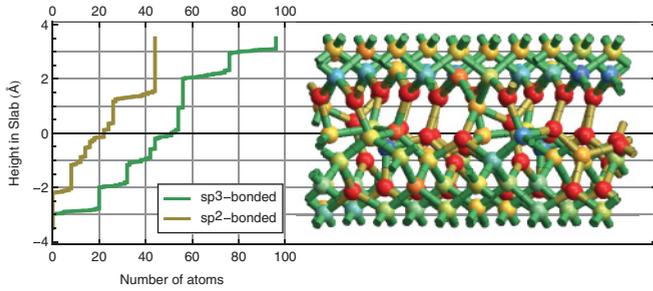


FIG. 2. (Color) Side view of the lowest-energy GB, $\Sigma 5$ (2×2), $\Delta N = 0$. Green bonds represent sp^3 -bonded atoms and yellow bonds represent sp^2 -bonded atoms. The color of the atoms is proportional to the “energy” of the atom in the Tersoff potential, with green the lowest and red the highest. The left-hand plot shows the corresponding accumulated number of sp^2 - and sp^3 -bonded atoms (only the central layers are shown for clarity).

and 32 monolayers in the direction perpendicular to the GB, 640 atoms in total, were used for all calculations. Periodic boundary conditions were used in the GB plane, while in the perpendicular direction the system was truncated with a free surface. We allow for a sufficient number of bulk layers to eliminate any influence of the free surfaces on the GB. The symmetry of the unit cell implies that if two full monolayers are removed from the unit cell, and a small translation is performed, the initial GB configuration is obtained. Hence, the removal of two monolayers is sufficient to fully explore the phase space of possible GB configurations. In the $\Sigma 5$ case, this translates into removing between zero and nine atoms from the initial configuration. For each number $0 \leq \Delta N \leq 9$, a set of ten configurations is generated by randomly selecting ΔN atoms and removing them from the GB. On each configuration we perform a simulated annealing process, in which the sample is heated to near its melting point, and then slowly cooled. We keep the GB close to melting for 10^6 time steps of 0.1 fs, then cool the system for 4×10^6 additional steps, during which all atoms in the simulation cell are allowed to move. Upon cooling, several quenches to 0 K are performed using the steepest descent energy minimization method²¹ to find the lowest-energy configuration. All simulations are performed using standard molecular dynamics algorithm implemented by Steneteg²² and the well-known Tersoff potential.²³ Although transferability of potentials is always of concern for MD studies,²⁴ this particular interaction potential is known to be well suited for the simulation of C, as it can reproduce the features of both sp^2 - and sp^3 -bonded atoms.^{10,25,26}

The structure of the GB obtained in simulations with $\Delta N = 0$ is presented in Fig. 2. In this case no atoms are removed from the original supercell before relaxation, and therefore it corresponds to a conventional simulation approach.

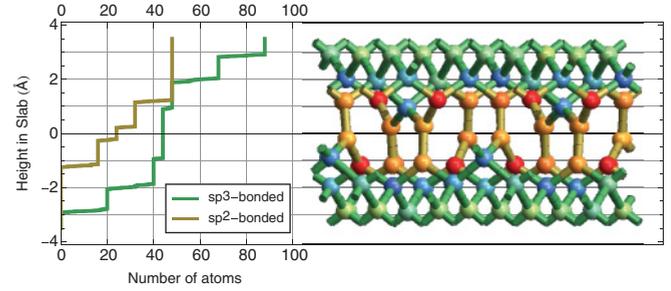


FIG. 3. (Color) Side view of the lowest-energy GB, $\Sigma 5$ (2×2), $\Delta N = 1$. Colors and notations are the same as in Fig. 2.

The obtained GB structure is quite disordered, and its energy is rather high, 4.96 J/m^2 . Still, the energy is somewhat lower than that obtained for $\Sigma 5$ GB in conventional MD simulations with the same phase field reported in Ref. 26. This may indicate that even for $\Delta N = 0$ we obtained a more stable structure. The boundary has a mixture of sp^2 - and sp^3 -bonded atoms over the entire width of the boundary, as can be seen in Fig. 2.

Next, we carried out simulations with an increasing number of atoms ΔN removed from the original supercell. The lowest GB energies found for each ΔN are summarized in Table I. The smallest energy is found for the case of $\Delta N = 1$. It is $\sim 20\%$ lower than the energy for the configuration with $\Delta N = 0$, described above. We also note that the GB with $\Delta N = 9$ has substantially lower energy compared to the $\Delta N = 0$ case. Watanabe *et al.*²⁶ reported on the calculation of thermal conductivity in diamond GB and did not find any structures with lower energy when using the method of Ref. 17 for the $\Sigma 21$ GB. However, we clearly see the importance of the technique used here, at least in the case of $\Sigma 5$ GB.

The structure with the lowest-energy GB, corresponding to $\Delta N = 1$, is presented in Fig. 3. A simple visual comparison with the $\Delta N = 0$ case (Fig. 2) shows that for $\Delta N = 1$ a higher degree of order is obtained in the GB. On the right-hand side of Fig. 3, the distribution and total number of sp^2 - and sp^3 -bonded atoms in the GB are shown. In the central region of the GB more than 85% of the atoms are sp^2 bonded. The GB width measured between the two fully sp^3 -bonded monolayers closest to the GB would only be slightly larger than in the perfect crystal, ~ 1.12 lattice constants. The steplike distribution of the number of sp^2 - and sp^3 -bonded atoms presented in the left-hand panel of Fig. 3 clearly reveals an ordered structure, as compared to the smoother distribution in Fig. 2. All sp^2 -bonded atoms are located in a region that is close to 2.5 \AA wide. By comparison, for the $\Delta N = 0$ GB, the sp^2 -bonded atoms are spread out over a larger region that is almost 4 \AA wide. In Table I we also present the excess volume of the GB compared to bulk diamond per unit area of the GB as a fraction of the lattice constant

TABLE I. The minimal GB energy E_{GB} (J/m^2) found for all different numbers of removed atoms ΔN . ΔV is the GB volume increase per unit area as a fraction of the lattice constant.

ΔN	0	1	2	3	4	5	6	7	8	9
ΔV (%)	16	16	21	22	38	18	23	31	27	48
E_{GB}	4.96	3.93	4.75	5.00	5.13	5.38	5.09	4.93	5.69	4.35

$\Delta V = (V_{\text{GB}} - V * N_{\text{GB}})/(A_{\text{GB}} * a)$, where V_{GB} is the volume of the GB region, V is the bulk volume per atom, N_{GB} is the total number of atoms within V_{GB} , A_{GB} is the area of the GB, and a is the bulk lattice constant. As expected, these results show that, compared to the pure phase, equilibrium GBs are less dense. However, we note that the lowest-energy GB $\Delta N = 1$ is as dense as the $\Delta N = 0$ case, despite the fact that it has one atom less. This demonstrates that bonds are optimized in such a manner as to compensate for atom removal.

IV. CONCLUSIONS

In summary, we demonstrate experimentally that Raman spectra of equilibrated bulk polycrystalline diamond is dominated by a peak corresponding to sp^3 -bonded carbon, but a very clear signal, which can be associated with the presence of sp^2 -bonded carbon, is observed as well. In theoretical simulations, a new configuration of $\Sigma 5$ GB in diamond with one atom removed from the boundary is found to have energy $\sim 20\%$ lower compared to the standard configuration used

in calculations. This lowest-energy configuration is narrow, has a higher degree of order, and is predominantly sp^2 bonding between the atoms in the GB. This theoretical model of equilibrium GBs in diamond aggregates provides strong support for our interpretation of the experimental results. Moreover, this paper demonstrates the importance of a protocol which allows for the variation of the number of atoms in GBs in MD simulations. Our findings suggest that the earlier results obtained with conventional methodologies may need to be revisited.

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