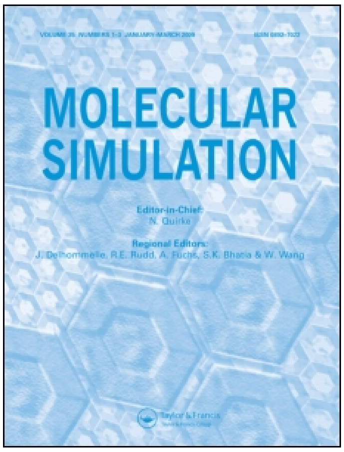

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PROPERTIES OF POLYCRYSTALLINE DIAMOND: MULTISCALE MODELING APPROACH

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Two modeling techniques to characterize fracture behavior of polycrystalline diamond films are discussed. The first technique is a multiscale modeling method in which first-principles local density approximation calculations on selected structures are combined with an analytic mesoscale model to obtain energies and cleavage fracture energies for symmetric ⟨001⟩ tilt grain boundaries (GBs) over the entire misorientation range. The second technique is large-scale atomistic simulation of the dynamics of failure in notched polycrystalline diamond samples under an applied strain. Electronic characteristics of selected ⟨001⟩ symmetrical tilt GBs calculated with a semiempirical tight-binding Hamiltonian are also presented, and the possible role of graphitic defects on field emission from polycrystalline diamond is briefly discussed.

Keywords: Diamond; grain boundaries; fracture properties; electronic properties; simulation; polycrystalline diamond; multiscale modeling approach

INTRODUCTION

The *extreme* properties of diamond, which include the highest known hardness, thermal conductivity five times that of copper, negative electron affinity, high electron/hole mobility, and relatively high melting point make it an ideal candidate for a wide range of applications [1]. These include

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wear and chemical resistant coatings for machine parts, heat spreaders and wide bandgap semiconductors for electronic device applications, and high-current electron emitters for flat-panel displays. While advances in the chemical vapor deposition (CVD) of diamond films have begun to make some of these applications possible, the tendency for diamond to deposit as a polycrystalline film with a high density of grain boundaries (GBs) and related defects degrade many of its desirable properties. Defects in coatings, for example can induce intermediate states in the bandgap, as well as significantly reduce thermal conductivity due to phonon scattering. Mechanical properties of CVD diamond films may also be affected by the presence of GBs and particularly depend on GBs structures. Indeed, it is known that different types of GBs can behave differently under applied load, for example, they may have different resistance to crack propagation [2]. Therefore by studying mechanical properties of different GBs one could, in principle, predict what types of microstructures provide for highest toughness of the film. Tilt GBs with $\langle 001 \rangle$ and $\langle 011 \rangle$ misorientation axes studied in the present paper are of practical interest because CVD diamond films are usually well textured with primarily $\langle 011 \rangle$ or $\langle 001 \rangle$ orientations.

We discuss two atomistic modeling techniques to characterize GB energies and fracture behavior of polycrystalline diamond. The first technique combines atomic level calculations on a few selected structures with a continuum model to obtain cleavage fracture energies for $\langle 001 \rangle$ and $\langle 011 \rangle$ tilt GBs in diamond over the entire misorientation range [3–5]. Atomic level calculations of energies of a few key structures can be done with analytic interatomic potentials or using first-principles calculations [3–5]. The second technique is large-scale atomistic simulation performed to investigate the behavior under load of several symmetrical GBs with $\langle 001 \rangle$ and $\langle 011 \rangle$ misorientation axes with an analytic potential. This technique provides qualitative insight on the dynamics of fracture inittion and propagation. Critical stresses and strains depending on GB type are evaluated and it is found that special short-period GBs possess higher resistance to crack propagation than GBs in the nearby misorientation range. The dynamics of failure in notched polycrystalline diamond samples under an applied strain is also simulated and predominantly transgranular crack propagation is observed.

Electronic properties of polycrystalline diamond films are of practical importance because the potential of diamond as a field emitter has been demonstrated in the past few years [1]. Experimental data indicate enhanced field emission from diamond films with increasing defect concentration [6]. One of the possible mechanisms of enhanced field emission from diamond is subband formation within the intrinsic gap [7] due to the presence of defects, particularly GBs. In the present study electronic characteristics of the $\Sigma = 17\,(350)$ GB, including a two-phase GB model [8], are calculated with a tight-binding (TB) Hamiltonian.

GRAIN BOUNDARY ENERGETIC FROM COMBINED FIRST-PRINCIPLES/MESOSCOPIC MODEL

The central idea of the multiscale modeling technique originated from Refs. [9, 10] is to construct energies of a series of related symmetric tilt GBs from the energies of a few key structures. Both the total number of key structures and their sizes are minimized by using mesoscale models of GBs, either dislocation [9] or disclination description of GBs [10]. This crucial feature facilitates the use of density functional methods to calculate the energy of the key structures, and allows energies over the complete misorientation range to be calculated strictly from first principles [3–5]. Because disclination-structural units model (DSUM) [10] requires fewer calculations of the input structures than dislocation treatment of GBs [9] it has been used for the development of the combined first-principles/mesoscopic approach.

The idea of constructing properties of low-index symmetric tilt GBs from a subset of structures is not new. Sutton and Vitek, for example, proposed a structural units model (on which our technique is based) for tilt GBs in metals over a decade ago [11]. Similarly, a disclination description of GBs was developed by Li in the 1960's [12], and density functional calculations on selected GBs (usually short-period coincident site structures) in covalent materials have been reported by a number of researchers [13]. The combination of these techniques, however, is a unique aspect of our approach which provides a powerful synergy for materials modeling.

According to the Sutton–Vitek structural units model [11], for a given tilt axis there are short-period GB structures consisting of a single type of structural unit from which all related GBs at misorientation angles in the range delimited by these structures can be constructed. The single-structural-unit GBs have short repeat units and stress fields that tend to be more localized than other structures; therefore smaller systems can be used to satisfactorily model these structures at the atomic scale. Structures at intermediate angles, however, have relatively longer repeat cells and less localized stress fields. While calculating energies for these structures is not difficult with analytic potentials, they can be prohibitively large for first-principles calculations.

It is well established in elasticity theory that an edge dislocation can be represented as a dipole consisting of negative and positive wedge disclinations [14]. In this description, a GB consisting of more than one structural unit is treated as a disclination dipole wall, and the energy is given as a weighted sum of the energy of the individual structural units, an elastic energy term, and the energy of the disclination cores. Specific equations for these terms are given elsewhere [3, 10]. With the exception of a single parameter in the disclination core energies, all of the contributions to the energy of a GB are well defined by the bulk elastic properties of the material and the energies of the individual structural units. The disclination core parameter can be evaluated from a single calculation for a tilt angle chosen to minimize, as far as possible, the required system size. This is essential for making efficient use of the results of first-principles calculations. The utility and accuracy of the DSUM for the covalent materials was proved using an analytic potential [3–5]. It was demonstrated an excellent agreement between energies of a variety ⟨001⟩ symmetrical tilt GBs obtained from atomistic calculations using a many-body analytic potential for diamond and values given by the multiscale modeling scheme using as input energies calculated from the analytic potential for four key structures. Energies for these key structures along with bulk elastic properties were then calculated from density functional theory, and these data were used as input into the multiscale model. This provided a completely ‘first principles’ energy estimate for this defect over the entire range of misorientation angle. Details of the density functional approach within the local density approximation (DFT/LDA) used for the GB energies calculations are given elsewhere [3].

The simulation data for GB energies E_{gb} combined with the energies of free surfaces γ allow the evaluation of the energy W required to cleave a brittle material along a GB plane without plastic deformation through the relation $W = 2\gamma - E_{gb}$. Plotted in Figure 1 are GB cleavage energies for ⟨001⟩ symmetrical tilt GBs calculated from DFT/LDA approach over an entire misorientation range. Energies of free surfaces were calculated for several surface orientations and then extrapolated through other misorientation angles. The GB energies were evaluated with a disclination-structural units model using as input energies of a few key structures calculated with DFT/LDA. As can be seen from Figure 1, cleavage energies for GBs with ⟨001⟩ tilt axes increase with misorientation angle. Also apparent are relative peaks in the cleavage energy curve in the vicinity of two single-structural-unit $\Sigma = 5$ (210) and (310) GBs. Cleavage energies of most ⟨001⟩ tilt GBs are about 60–75% of those for the ideal bulk crystals

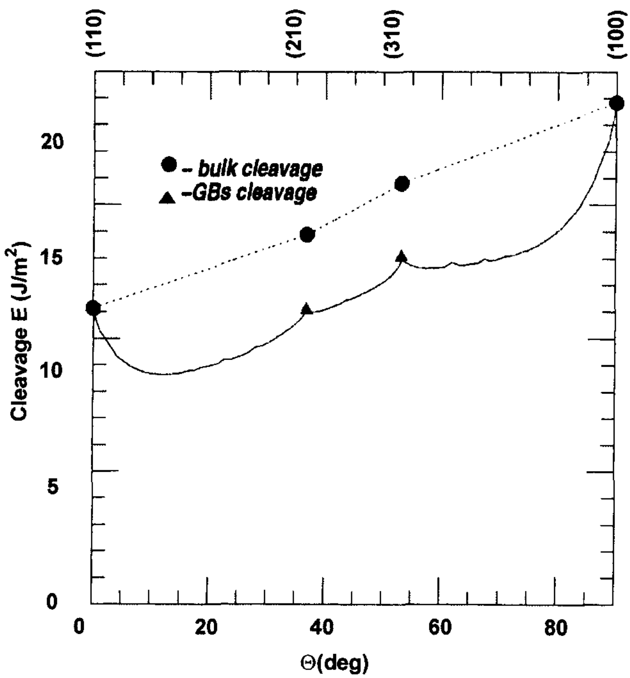

FIGURE 1 Cleavage energies of ⟨001⟩ tilt GBs calculated from DFT/LDA approach.

with the same orientation. Based on the cleavage energy curve, we might expect that GBs with misorientation angles closer to 90 degrees will have higher toughness (which equals $(2WE)^{1/2}$, where E is Young's modulus).

LARGE SCALE MODELING OF FRACTURE OF POLYCRYSTALLINE DIAMOND

Molecular dynamics simulations were carried out to investigate the behavior under load of several symmetrical tilt GBs with ⟨001⟩ and ⟨011⟩ misorientation axes. The lowest-energy grain boundary structures were derived from a coincident-site lattice model in which each atom is four-fold coordinated. To estimate theoretical strengths of individual GBs, bicrystals were stretched in the direction perpendicular to a GB plane at a constant rate. It is proper to call such strength characteristics of GBs theoretical, because the observed strength of a material in a major extend is influenced by flaws present in the sample. The quantities that were considered in this set of simulations were maximum fracture stresses of the GBs compared to the ideal structures, and GB work for fracture defined from the areas under the stress-strain curves.

To model systems with pre-existing flaws, a notch 30 Å long oriented perpendicular to an applied strain was inserted into a sample containing a GB. The applied strain was increased until a crack started to propagate. Simulations have been performed for several $80 \times 180 \times 20$ Å diamond samples, each containing approximately 50,000 atoms. Different GB orientations with respect to the notch were considered; this was to induce either transgranular or intergranular crack propagation.

The interatomic interactions in the simulations were modeled by an analytic many-body bond-order potential [15]. The bond order functional form depends on local coordination and bond angles, as well as terms that empirically account for radicals, conjugation, and dihedral rotation. To better model fracture behavior, the cut-off scheme of the potential was modified to remove an abrupt change in force at a distance between the bulk first and second neighbors. Details of this modification are given elsewhere [16].

Theoretical strength properties of individual GBs with $\langle 001 \rangle$ and $\langle 011 \rangle$ misorientation axes calculated from the dynamic simulations are summarized in Table I. Maximum stresses for samples with GBs are about 30–60% lower than those for the ideal diamond structure. The work for fracture for various types of GBs (W_{GB}) is 40–80% lower than that for the $\langle 111 \rangle$ ideal diamond sample (W_{111}) depending on GB type. It can be concluded that the type of GB determines the relative theoretical strengths of various GBs. Apparent from Table I is that the $\Sigma = 5$ (120) and (130) special GBs possess about a 30% higher critical stress and a 30% higher work for fracture than GBs in the nearby misorientation range.

Because diamond is a brittle material, it is expected that crack propagation will result in atomically flat surfaces, and that critical stresses evaluated from the Griffith criterion using calculated GB cleavage energies will correlate with critical stresses from dynamic simulations.

Critical stresses for intergranular propagation of the initial crack of 30 Å length obtained from molecular dynamic simulations and calculated with the Griffith criterion are illustrated in Figure 2 and summarized in Table I. It is evident from the figure that the dependency of critical stress on misorientation angle is similar for both approaches. The observed agreement between values derived from the Griffith criterion and atomistic simulations is quite reasonable (the difference is about 20%). Thus the results indicate that GB cleavage energy is a major parameter defining GB resistance to crack propagation.

TABLE I Grain boundary strength properties, calculated from molecular dynamic simulations. W_{GB}/W_{111} is relative work for fracture. Cohesive energies are calculated with DFT-LDA approach and using the bond order potential (BOP). Critical stresses of intergranular crack propagation (30 Å length) are obtained from molecular dynamic simulations (σ_{MD}) and calculated from Griffith criterion (σ_{G}) with BOP cleavage energies

θ degrees	*Boundary plane*	*Young's modulus (GPa)*	*Maximum stress (GPa)*	*Maximum strain (%)*	W_{GB}/W_{111}	*Cohesive energy (J/m^2)*		σ_{MD} *(GPa)*	σ_G *(GPa)*
						BOP	*DFT-LDA*		
	(111)	1100	96	15.1	1.0	10.8	13.4	44	49
			⟨001⟩ STGB:						
0.0	(110)	1000	115	19.2	1.30	6.7(10.9*)	11.2	46	38
12.68	(450)	900	52	8.9	0.29	4.7	8.7	27	29
20.01	(7 10 0)	830	53	7.5	0.26	5.2	8.9		29
36.87	(120)	810	62	10.5	0.42	8.6	11.1	46	37
53.13	(130)S*	800	73	14.8	0.67	11.0	12.9	54	42
	(130)Z*	800	69	13.7	0.57	11.2	13.0	36	42
73.74	(170)	730	46	8.3	0.23	13.2	13.2	38	44
90.0	(100)	850	90	24.0	1.60	22.0	18.6	51	61
			⟨011⟩ STGB:						
13.44	(166)	860	50	7.6	0.23	4.1			27
31.59	(255)	910	58	8.8	0.34	7.8		32	38
38.94	(122)	940	62	9.2	0.37	9.1		38	42

* models of $\Sigma = 5(130)$ GB with straight (S) and zig-zag (Z) arrangement of structural units.

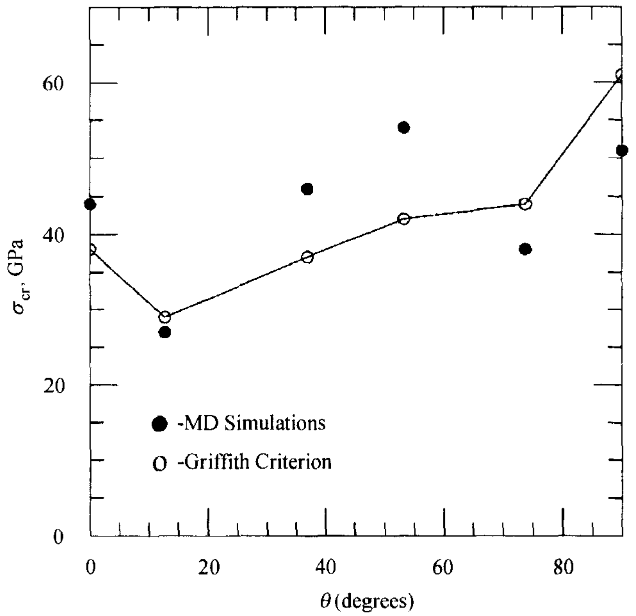

FIGURE 2 Critical stresses of a crack propagation within $\langle 001 \rangle$ tilt GBs.

Critical stresses for crack propagation within GBs are about 30–40% lower than those for an ideal crystal, except for the $\Sigma = 5$ (120) and $\Sigma = 5$ (130) special GBs. For these GBs, maximum stresses for crack propagation exceed those calculated from the Griffith criterion, and are very close to the stresses for crack propagation in ideal samples (Fig. 2).

Crack propagation in a system with different initial orientations between a notch and GB plane was also simulated. In general, when a crack reaches a GB, it can propagate within the GB (intergranular fracture), or penetrate into the second grain (transgranular fracture). Within the second grain, the crack can keep moving in the initial direction of propagation or deviate into an easier cleavage plane. These events depend on the GB cleavage energy, relative bulk cohesive energies of the first and the second grains, and the inclination angle of the GB relative to the initial plane of crack propagation [17]. From the balance of mechanical energy release rate and the relative crack resistance of a GB and grains, it is possible to make rough predictions of the dependence of intergranular *versus* transgranular crack propagation depending on the GB type [18]. Our molecular dynamics simulation results for both $\langle 001 \rangle$ and $\langle 011 \rangle$ tilt GBs indicate predominantly a transgranular mode of fracture in polycrystalline diamond [18].

In summary, critical stresses for crack propagation within a GB obtained from dynamic simulations are consistent with those calculated from the

Griffith criterion. Higher resistance to crack propagation was observed for special GBs. This is in agreement with other studies and experiments on metals and ceramics [2]. In the systems containing GBs with different initial orientation relative to a notch, transgranular crack propagation was observed in most cases. This is consistent with experimental data indicating a predominantly transgranular mode of fracture of CVD diamond films [19].

ELECTRONIC PROPERTIES OF GBs IN DIAMOND

Electronic structure associated with GBs were calculated using a tight-binding Hamiltonian developed by Xu *et al.* [20], which is based on the minimal sp^3 basis set. Of particular interest is the identification of states with energies in the bulk band gap that can contribute to the formation of subbands. Structures of symmetrical tilt GBs with all atoms four-fold coordinated contain no states inside the minimum band gap (Fig. 3, left). The distortion of the atomic structure at the GBs causes boundary-localized states generated at the band edges. Keblinski *et al.* [21] calculated the electronic structure of a (001) twist GB in diamond using a tight-binding model. The calculations predict that the presence of sp^2-bonded dimers and sp^3-hybridized dangling bonds in the GBs can introduce states in the band gap. However, because these sp^2 bonded defects were not spatially connected (or at least their concentration was not high enough), the gap states were localized rather than form a band.

Previously, we have introduced a structural model of two-phase GBs [8] (Fig. 4) where diamond grains are chemically bonded by a graphitic-like region. The graphite planes are oriented so that they are attached to

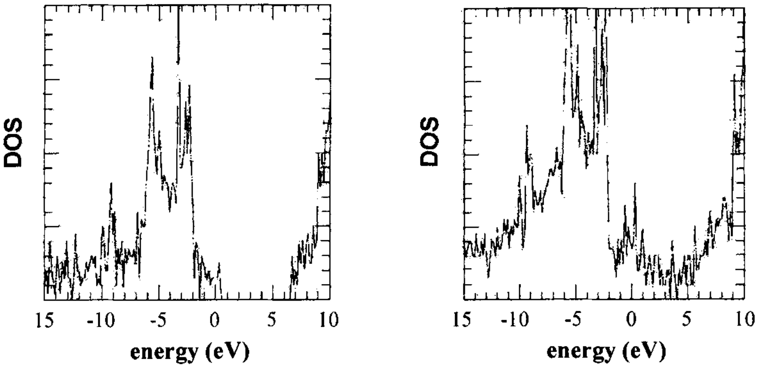

FIGURE 3 Comparison of the total electronic density of states for $\Sigma = 17(350)$ GB models with all four-fold coordinated atoms (left) and a two-phase structure (right).

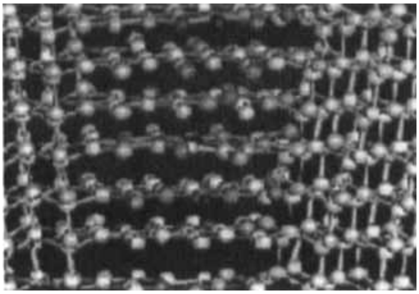

FIGURE 4 Illustration of graphitic regions at a GB in diamond.

diamond (111) planes. It was found that these two-phase GB structures are energetically competitive with conventional four-fold coordinated ⟨001⟩ tilt GBs in diamond in the entire misorientation range [8]. These defected graphite inclusions within GBs can, in principle, contribute to the broad sp^2 related background observed in Raman spectra of CVD diamond films.

Electronic structure calculations of the two-phase GBs show that the graphitic regions introduce energy states within the intrinsic band gap (Fig. 3, right). Furthermore, as the real-space distribution of the local density of states indicates, these states are spatially extended along the GB. The latter yields important information regarding possible conduction channels that enhance field emission, the overlap of these channels with surface states, and the defect densities required for otherwise localized states to interact with one another. Thus our preliminary results suggest that two-phase diamond-graphite GBs are promising structures for contributing to electron emission from polycrystalline diamond.

In general, results of a study focusing on fundamental emission mechanisms for specific defect microstructure might be useful to characterize growth conditions needed to produce films with an optimum field-emission behavior.

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