Multiscale Modeling of Polycrystalline Diamond

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ABSTRACT

Two modeling techniques used to characterize fracture behavior of polycrystalline diamond films are discussed. The first technique is a multiscale modeling method in which atomic level calculations on selected structures are combined with an analytic mesoscale model to obtain cleavage 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 load. 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.

INTRODUCTION

Chemical vapor deposited (CVD) diamond is now commercially available for a variety of applications ranging from wear resistance coatings for machine parts to micro- and optoelectronic devices [1]. Because CVD diamond is usually polycrystalline, its strength may be affected by grain boundary structure. 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 <001> and <011> misorientation axes studied in the present paper are of practical interest because CVD diamond films are usually well textured with primarily <011> or <001> orientations.

We discuss two atomistic modeling techniques to characterize defect energies and fracture behavior of polycrystalline diamond. The first technique combines atomic level calculations on selected structures with a continuum model to obtain grain boundary and cleavage fracture energies for <001> and <011> tilt grain boundaries 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 <001> and <011> misorientation axes. 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 selected <001> tilt GBs, including a two-phase GB model [8], are calculated with a tight-binding Hamiltonian.

METHODS

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. 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 30Å 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 80x180x20 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 [9]. 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[10].

RESULTS AND DISCUSSION

Grain Boundary Cohesion and Strength

The energy required to cleave a brittle material along a GB plane without plastic deformation is defined as a difference between energies of the two unreconstructed surfaces, created due to cleavage, and the GB energy. Plotted in Figure 1 are GB cohesive energies for <001> symmetrical tilt GBs calculated from first-principles density functional theory within the local density approximation (DFT/LDA) 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, which are necessary for calculating GB cleavage energies, were evaluated in the entire misorientation range with a disclination structural units model using as input energies of a few key structures calculated with DFT/LDA. Details

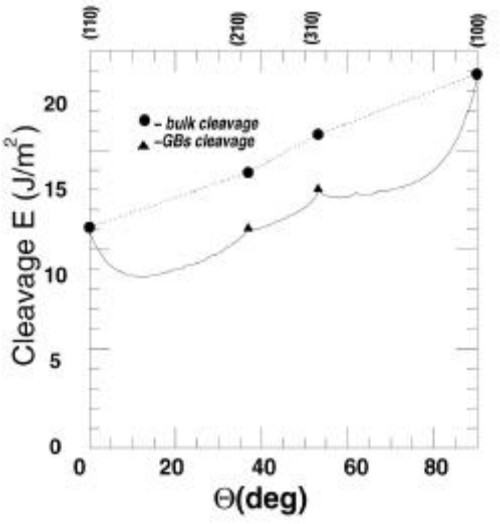

Fig.1 Cleavage energies of <001> tilt GBs calculated from first principles DFT/LDA.

Table I. Grain boundary strength properties, calculated from molecular dynamic simulations using the bond order potential. σ_{cr} is critical stress of crack propagation (30 A length)

Θ degrees	Σ	boundary plane	Young's modulus (GPa)	Maximum Stress (GPa)	Maximum Strain (%)	Relative Work for Fracture (W_{gb}/W_{11})	Cohesive Energy (J/m^2)	σ_{cr} (GPa)
		(111)	1100	96	15.6	1.0	10.8	44
			<001> STGB:					
0.0	1	(110)	1000	115	19.5	1.40	6.7	46
12.68	41	(450)	900	52	8.7	0.29	4.7	27
20.01	149	(7 10 0)	830	53	7.5	0.26	5.2	
36.87	5	(120)	810	62	10.5	0.42	8.6	46
53.13	5	(130)S	800	73	14.8	0.67	11.0	54
		(130)Z	800	69	13.7	0.57	11.2	36
73.74	25	(170)	730	46	8.3	0.23	13.2	38
90.0	1	(100)	850	90	24.0	1.60	22.0	51
			<011> STGB:					
13.44	73	(166)	860	50	7.6	0.23	4.1	
31.59	27	(255)	910	58	8.8	0.34	7.8	32
38.94	9	(122)	940	62	9.2	0.37	9.1	38

of the calculations are given elsewhere [3].

As can be seen from Fig.1, cleavage energies for GBs with <001> tilt axes increase with misorientation angle so that from this analysis higher strengths are expected for GBs with misorientation angles close to 90°. Also apparent are relative peaks in the cleavage energy curve in the vicinity of special Σ=5 GBs. The term 'special' is applied to GBs with minimum periods for the given tilt axis, from which all other GBs in the nearby misorientation range can be constructed. For <001> tilt axis these are two Σ=5 GBs. Cleavage energies of most <001> tilt GBs are about 60-75% of those for the ideal bulk crystals with the same orientation. Cohesive energies of some <001> and <011> tilt GBs calculated with the analytic bond-order potential are given in Table I.

Strength properties of different GBs with <001> and <011> misorientation axes calculated from the dynamic simulations using the bond-order potential are summarized in Table 1. 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 <111> 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 Σ=5 special GBs possess about a 30% higher critical stress and a 30% higher work for fracture than GBs in the nearby misorientation range.

Crack Propagation in Diamond Samples Containing GBs

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 Fig.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.

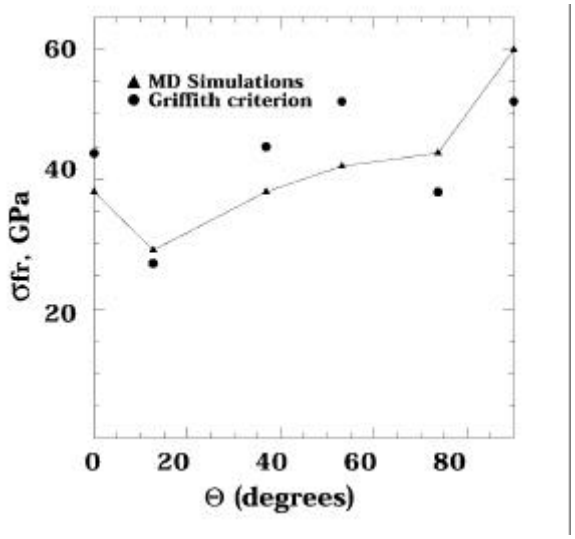

Fig.2 Critical stresses of a crack propagation within <001> tilt GBs.

Critical stresses for crack propagation within GBs are about 30-40% lower than those for an ideal crystal, except for the Σ=5(012) and Σ=5(013) 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 [11]. 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 [12]. Our molecular dynamics simulation results for both <001> and <011> tilt GBs indicate predominantly a transgranular mode of fracture in polycrystalline diamond [12].

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 [13].

Electronic Properties of GBs in Diamond

Electronic structure associated with GBs were calculated using a tight-binding Hamiltonian developed by Xu et al.[14] . 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. [15] 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.

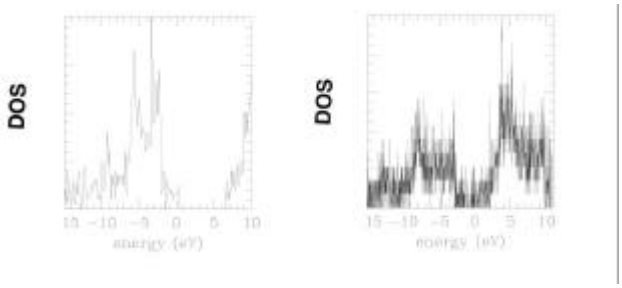

Fig.3 Comparison of the total electronic density of states for Σ=17(350) GB models with all four-fold coordinated atoms (left) and a two-phase structure (right).

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 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 background observed between the two graphite peaks 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.

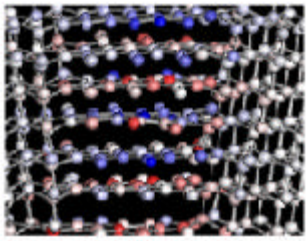

Fig.4 Illustration of graphitic regions at a GB in diamond. Defects such as these may enhance electron emission from diamond films.

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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