J. Phys. D: Appl. Phys. 44 (2011) 405401 (10pp)

# Strength of ultrananocrystalline diamond controlled by friction of buried interfaces

### Yifei Mo<sup>1,2</sup>, Donald Stone<sup>1,3</sup> and Izabela Szlufarska<sup>1,3</sup>

<sup>1</sup> Materials Science Program, University of Wisconsin, Madison, WI 53706, USA

<sup>2</sup> Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA,

02139, USA

<sup>3</sup> Department of Materials Science and Engineering, University of Wisconsin, Madison, WI 53706, USA

E-mail: yfmo@mit.edu and szlufarska@wisc.edu

Received 23 June 2011, in final form 2 August 2011 Published 14 September 2011 Online at stacks.iop.org/JPhysD/44/405401

#### Abstract

Grain boundary (GB) plasticity plays a critical role in deformation of nanocrystalline (NC) materials. However, it has been unclear how strength of these materials depends on GB properties. We use ultrananocrystalline diamond (UNCD) as a model material in which the plastic deformation is mainly located at the GBs and the dislocation processes are not active. We discover that hardness and yield stress have a simple functional dependence on the stress required for GB sliding. Our results on hydrogenated UNCD demonstrate that phenomena from the field of nanoscale friction can be utilized to understand the deformation of NC materials.

(Some figures in this article are in colour only in the electronic version)

#### 1. Introduction

Materials with grain size refined to the nanometre scale hold great potential for mechanical applications that range from microelectromechanical systems (MEMS) to macroscopic abrasive coatings and cutting tools used in industrial applications [1-9]. Superior mechanical properties of nanocrystalline (NC) materials include high hardness, outstanding wear resistance, and improved fracture toughness and ductility [1, 4, 5, 7]. When the grain diameter is reduced to  $\sim 10$  nm or less, it is expected that mechanical response will be dominated by grain boundary (GB) sliding [10-20]. It is therefore not surprising that many studies have been dedicated to investigating GB phenomena in deformation, which include atomistic mechanisms and dynamics of GB sliding, nucleation and annihilation of dislocations at GBs, and the coupling between GB sliding and GB migration [16, 21-29]. Important insights into GB sliding have been also brought by studies of coarse-grained materials. In particular, it has been shown that when the accommodation mechanism for GB sliding is entirely elastic, resistance to sliding can be interpreted as internal friction [30-32]. In the plastic regime, GB sliding has been extensively studied in the context of time-dependent phenomena (e.g. creep), where GB friction acts as an energy dissipation mechanism during deformation. In coarse-grained materials GB sliding is usually controlled by accommodation mechanisms. Specifically, accommodation mechanisms exert a back stress on the sliding GB and thereby they control the amount of deformation [30, 32]. In NC materials GB sliding occurs on much smaller length scales (on the order of a few Å) [10–20] and therefore it is possible that it can be entirely accommodated by the free volume [30, 32] at GBs so that accommodation mechanisms do not provide any back stress on the GB. In this regime GB shear strength is expected to play an important role in deformation, but it remains an open question how it affects the overall strength of NC materials. In dislocation plasticity the yield strength Y of the material is proportional to the critical shear strength for dislocation motion  $\tau_{dis}$ . An equivalent relationship for GB controlled deformation has not been established.

To address the above questions we employ large-scale molecular dynamics (MD) simulations and we investigate plastic deformation of ultrananocrystalline diamond (UNCD). We chose this material for a few different reasons. First of all, UNCD is a promising material for tribological applications because of its superior mechanical properties [2, 6, 9, 33–42]. For example, hardness of UNCD can be as high as 98 GPa [38]. Although it is expected that deformation of UNCD is localized at GBs, so far specific mechanisms of plasticity in this material have not been identified. UNCD serves also as an excellent model material to quantify the effect of GBs on a mechanical response because the extremely high value of  $\tau_{dis}$ 

in diamond ( $\sim$ 90 GPa, see section 3) makes the nucleation of dislocations unlikely during mechanical deformation [2, 33– 35, 38]. Understanding gained in the studies of UNCD will provide insights into deformation mechanisms of other NC materials (and NC ceramics in particular) in the regime where dislocation activity is known to be suppressed [18, 19]. Another advantage of modelling UNCD is that numerous experimental studies have been reported on the dependence of mechanical properties of UNCD on GB properties, and more specifically on the concentration of H atoms at the GBs of this material [36, 39, 41, 43–48]. It was shown that both hardness and elastic modulus of UNCD decrease with increasing amount of hydrogen atoms in GBs [36, 39, 46], although specific mechanisms responsible for these trends have not been established. We take advantage of the published experimental data to validate our modelling predictions.

#### 2. Modeling methods

We perform large-scale MD simulations of nanoindentation and of compressive uniaxial test on UNCD. All MD simulations are performed using our in-house codes and the second generation reactive empirical bond-order (REBO) potential [49]. The REBO potential accurately captures the complex chemistry of hydrocarbon systems and the elastic modulus of various solid forms of carbon.

UNCD samples are generated using the Voronoi construction method [50]. Each sample consists of 2048 grains with the average grain diameter of 4 nm. The dimensions of each sample are  $40 \text{ nm} \times 40 \text{ nm} \times 40 \text{ nm}$ . First, the UNCD structure is relaxed in a high-temperature sintering process with periodic boundary conditions applied in all three spatial directions. The sample is first sintered at 1800 K for 100 ps and then equilibrated at 300 K with no external pressure.

Both experimental studies and simulations have confirmed that hydrogen atoms introduced during processing of UNCD become incorporated at GBs of this material [36, 39, 44, 45]. The concentration of H in UNCD samples can be as high as 8% [39]. In order to discover the effect of H concentration on mechanical properties of UNCD, hydrogen-doped UNCD samples are generated by replacing a certain fraction of carbon atoms in the GBs with H atoms. The GB atoms have to be identified as the first step. Since the carbon atoms near the GB still preserve their local diamond environments, these atoms have the cohesive energy very close to the cohesive energy of diamond, which is -7.36 eV. In contrast, atoms in GBs have local bond geometries and/or hybridization different from the perfect crystal, these atoms will therefore have a higher energy (less negative) than those in the crystalline grains. An atom is identified as belonging to a GB if its atomic energy is higher than the cut-off value of -6.63 eV, which is 90% of the cohesive energy of diamond. This energy criterion gives the fraction of GB atoms equal to 12.23% and the thickness of GB is approximately two to three atomic layers (2 Å to 4 Å in width), which is consistent with the experimental measurements of GB width [36]. Additionally, [46] reports the fraction of GB atoms to be 8.1% in the UNCD sample with average grain diameter of 7 nm. Since the fraction of GB atoms scales approximately



Figure 1. Fractions of carbon atoms with  $sp^2$  (circles) and  $sp^3$  (squares) hybridization in the UNCD sample with different H content.

linearly with the grain diameter d [46], the fraction of GB atoms in samples with average grain size of d = 4 nm (as in our models) is estimated to be 14.3%. This estimate is consistent with the 12.23% calculated directly for our samples using the energy criterion.

After identifying the atoms in GBs, we constructed hydrogen-incorporated UNCD samples by replacing a certain fraction of carbon atoms in the GBs with H atoms. The hydrogenated UNCD samples have hydrogen concentrations equal to 0%, 2.45%, 4.89%, 7.33%, 9.78% and 12.23%. These samples are annealed further at 1200 K for 100 ps and then equilibrated at 300 K. After annealing we confirmed that the H atoms remained in the GB regions. Since all hydrogenated samples are prepared starting from the same H-free UNCD structure, all samples are characterized by the same GB network and grain misorientations. The main difference among the samples is H concentration in GBs. Our analysis of computer generated UNCD samples shows that the fraction of sp<sup>3</sup>-bonded atoms is 93.3% for the non-hydrogenated sample (see figure 1). The fraction of  $sp^2$  atoms is 6.7%, which is close to 2–5% reported in experiments [37, 38, 40, 42]. While it is generally agreed upon that the fraction of  $sp^2$  atoms depends on the H content in UNCD, both a decrease [44, 47, 48] and an increase [39] of sp<sup>2</sup> fraction with an increasing H content have been reported. The cause of the discrepancy is not clear yet. The relationship between H content and carbon hybridization is complicated by the fact that incorporation of H during the growth affects the grain size of UNCD, which results in a different volume fraction of GBs [41, 42]. In this study, we focus on the dependence of mechanical properties of UNCD on GB chemistry alone, while the grain size is kept constant. Therefore, we are comparing our simulation results with the experiments by Xiao et al [39], where the grain size of UNCD was kept relatively constant while H concentration was increased. In Xiao et al 's experiments [39], the fraction of sp<sup>2</sup>-bonded atoms increases with the H content in UNCD. As shown in figure 1, the same trend is observed in our MD simulations.

We also found that the presence of H affects the magnitude of the compressive residual stresses in the GBs, which is consistent with finding from *ab initio* calculations of Qi *et al* [46]. In our samples, the magnitude of residual stresses is always smaller than  $\sim 200$  MPa, which is comparable to experimentally reported values [39]. Since the magnitude of the residual stress is insignificant as compared with the elastic modulus of UNCD (hundreds of GPa), therefore these GB stresses will have a negligible effect on the deformation mechanisms of UNCD.

In the nanoindentation simulations, the indenter is made of diamond-like carbon and its surface is not passivated. With the exception of the surface passivation, the indenter is prepared using exactly the same schedule as described in [51]. The radius of curvature of the indenter is 20 nm. During the indentation, the indenter is held rigid, i.e., none of the atoms of the indenter are allowed to move. This approach allows us to explore deformation in UNCD without having to take into account material properties of the indenter. The power-12 repulsive term of the Lennard–Jones (LJ) potential is superimposed on the REBO potential to increase the strength of the interfacial repulsion and to prevent sample atoms from sticking to the indenter. The parameters of LJ are the same as in [51], except that the value of  $\sigma$  is multiplied by 10.

The simulations of nanoindentation are displacementcontrolled and are performed using a push-hold schedule. In each step the indenter is displaced by 1 Å (corresponds to 0.2% of equivalent strain) and then it is held in place allowing for transient forces to decay. The duration of the pushing and holding phases are 1 ps and 10 ps, respectively. The load is measured as the total normal force acting on the indenter atoms and we report the value of load averaged over the last 3 ps of the holding phase. Compression simulations are performed using a similar push-hold schedule as in nanoindentation simulations. In each step a 0.5% uniaxial strain is applied for a period of 1 ps and then the sample is held at the constant strain for 10 ps. The sample is allowed to deform in both directions perpendicular to the loading axis so that the corresponding stress components are zero. The maximum strain in both nanoindentation and compression simulation is  $\sim 8\%$ .

#### 3. Results and discussion

#### 3.1. Elasto-plastic properties of UNCD

The load (*P*) versus displacement (*h*) curves of our nanoindentation simulations are shown in figure 2(a). The *P*-*h* curve is continuous and shows no signs of discrete events. We fit the load–displacement curve to the relationship predicted by Hertz model [56],

$$P = 4/3E^*R^{1/2}(h - h_0)^{3/2},$$
(1)

where R = 20 nm is the curvature radius of the indenter,  $h_0$  is a fitting parameter that corresponds to zero displacement, and

$$E^* = \left(\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}\right)^{-1} \tag{2}$$

is the effective modulus of the contact,  $E_1$  and  $E_2$  are the tip and the sample Young's moduli, and  $v_1$  and  $v_2$  are Poisson's ratios of the tip and the sample, respectively. Only data



Figure 2. (a) Load-displacement curves for UNCD samples with varying H concentration. (b) Instantaneous hardness of UNCD samples calculated as a function of indenter displacement h.

points at displacements lower than 6 Å are fitted because in this regime the deformation is purely elastic. The effective elastic modulus  $E^*$  of a given sample is obtained as a fitting parameter. The fitting quality is  $R^2 = 0.999$  for all samples. As shown in figure 3(a), the elastic modulus obtained from fitting simulation data to Hertz model (filled squares) is in very good agreement with values obtained from compressive simulations (crosses) and is within the range of experimental data (blue symbols). For example, experimentally measured values of the modulus are in the range 790 to 950 GPa, for low hydrogen content (less than a few per cent) [2, 52-55] while our simulations for 0% H sample gave the value of 791 GPa. Our simulations show that elastic modulus decreases from 791 GPa for 0% H to 417 GPa for 12.23% H, consistent with experimental trends reported in [39]. The experimental values on samples with an average grain size of d = 7 nm[39] is also shown in figure 3(a). The deviation may be due to the fact that our simulations are preformed on UNCD with a smaller grain size (d = 4 nm). An increase in elastic modulus with increasing grain size for UNCD has been previously demonstrated by computer modelling [55] and experiments [41].

The change in hardness as a function of indenter displacement h is plotted in figure 2(b). Instantaneous values of hardness are calculated by dividing the normal load by



**Figure 3.** (*a*) Elastic modulus and (*b*) hardness of UNCD samples as a function of H content. The reported hardness is averaged over instantaneous values measured in the plastic regime. Error bar (standard deviation from this average) is comparable to the symbol size. We also plot points corresponding to published data, i.e. expt 1 from [39], expt 2 from [2], expt 3 from [52], expt 4 from [53], expt 5 from [54]. Model 1 from [55]. Corresponding grain diameters are listed in the figure legends.

the contact area. The contact area is calculated as the area enclosed by the edge of the contact zone of the indenter and the sample (details provided in [57]). It is shown in figure 2(b) that the instantaneous values of hardness reaches an asympototic value at displacements  $h \ge 20$  Å. The indentation hardness of each sample is calculated as the average over four indentation steps in the regime of constant hardness value, that is within the range of displacements from 20 to 24 Å. We find that hardness in our simulations agrees with experimental values reported in the literature. Specifically, the hardness of simulated UNCD with 0% H was found to be 92 GPa, which is comparable to the experimentally measured values between 88 to 98 GPa [2, 38, 54]. As shown in figure 3(b), calculated hardness (filled squares) decreases from 92 GPa for 0% H to 51 GPa for 12.23%H, and this decrease is consistent with the experimentally observed trend in hardness (open symbols). The very good agreement of elasto-plastic properties between the model UNCD and experimental data indicates that our computational model captures correctly the relevant physics of UNCD's deformation.

The yield strength of UNCD samples was measured in the uniaxial compression simulations. Typically yield strength is defined as a stress corresponding to a pre-defined value of a permanent (plastic) strain. In our study, the yield strength of each sample is measured as the flow stress at the strain of 7.5%. This strain level is selected because it corresponds to the equivalent strain in the nanoindentation simulations where the hardness is measured. The equivalent strain in nanoindentation with a spherical indenter is defined as 0.2a/R [58], where R = 20 nm is the radius of the indenter and a is the radius of the contact area. The equivalent strain of 7.5% corresponds to the nanoindentation at the displacement h = 22 Å.

#### 3.2. Effect of GB sliding on yield stress and hardness

Having shown that our models reproduce correctly mechanical properties of UNCD samples, we now investigate the fundamental mechanisms underlying the deformation. No dislocation activity is observed in UNCD, which is consistent with in situ transmission electron microscope studies performed during nanoindentation experiments [2]. At present, there is still lack of experimental room-temperature measurements of the critical shear stress  $\tau_{dis}$  for dislocation glide in a single crystal diamond. However, one can extrapolate this value from measurements carried out at higher temperatures. The authors of [59] provide a universal relationship between the critical shear stress in materials with diamond-like lattice (e.g. Si, Ge, SiC and diamond) and the parameter  $kBT/Gb^3$ , where kB is the Boltzmann constant, T is the temperature, G is the shear modulus and b is the length of the Burgers vector. The critical shear stress for diamond has been measured at 2073 K by Evans and Wild [60] and was found to be 0.5 GPa. Using the values of G = 510 GPa and b = 2.52 Å, we extrapolated the critical shear stress to 300 K and we estimated it to be 127 GPa. The theoretical shear strength calculated using the REBO potential is 96 GPa [61], which is lower than the extrapolated value, but still much higher than the maximum shear stress ( $\sim$ 50 GPa) observed in our samples during nanoindentation. Therefore, although REBO potential is not capable of modelling dislocation structures of diamond correctly, based on the shear stresses reached in the samples it is reasonable to assume that no dislocations will be nucleated within the diamond grains.

We found that the dominant mechanism of plasticity in UNCD is GB sliding. To visualize the GB sliding we colour the samples into stripes and monitor the motion of the stripes during the deformation. Assignment of atoms into stripes is based on the position of these atoms along the loading direction before the deformation. An example of a colour-coded sample before any deformation is shown in figure 4(a). After the deformation atoms are visualized with the initially assigned colors (figures 4(b)-(d)) so that the motion of the stripes can be monitored. Figure 4 shows one example of a GB that slides during the deformation of UNCD and it is clear that GB sliding is more pronounced for samples with higher H content. It is important to point out that although the figure shows one example of a GB, the increase in a sliding distance with increasing H content is typical among GBs that slide during deformation. The sliding distance depends on both the H content and the orientation of the GB with respect to the

J. Phys. D: Appl. Phys. 44 (2011) 405401



**Figure 4.** The snapshot of the system (*a*) before and (*b*)–(*d*) after nanoindentation of UNCD samples with H concentration of (*a*) 7.33%, (*b*) 2.45%, (*c*) 7.33%, and (*d*) 12.23%. Both C and H atoms are visualized, with H atoms having a smaller diameter. GB sliding is demonstrated by a relative shift of the coloured stripes, which are marked before the deformation in (*a*) and are then visualized after deformation (*b*)–(*d*). Only the sample with 7.33% H is shown before nanoindentation, because the coloured stripes look the same before deformation. Black lines mark the GB plane. The arrows are added to guide the eye and they indicate shifts of the colour stripes, i.e. the magnitude of GB sliding.

loading axis. Typical sliding distance was found to be on the order of 0.5–3.5 Å.

How to quantify the increase in the GB sliding distance due to the higher H content? We propose that this trend can be analysed by viewing the GB sliding resistance as an interfacial friction of these buried interfaces. The key parameter that characterizes a frictional resistance of a sliding interface is the interfacial shear strength  $\tau_{GB}$ . We measure the shear strength for those GBs that were observed to slide during nanoindentation and/or compression. To determine  $\tau_{GB}$  we first calculate a stress tensor for a 10–15 Å thick slab that contains the GB itself and parts of the two adjacent grains. The GB shear strength  $\tau_{GB}$  is then calculated as the shear stress resolved on the plane of the GB.

We found that hardness scales linearly with the shear strength  $\tau_{GB}$  of those GBs that slide during deformation. As shown in figure 5(*a*), the ratio of a hardness over  $\tau_{GB}$  varies among different GBs and ranges from 2.87 to 5.32. This ratio is a geometric factor that relates the local stress to the orientation of a GB plane with respect to the applied stress and this ratio is also dependent on the atomic structures of the GB.

To exclude the effect of a non-uniform stress distribution under the indenter on GB deformation, the yield strength was calculated in uniaxial compression test. We find that the yield strength *Y* is also linearly dependent on the GB shear strength  $\tau_{\text{GB}}$  (figure 5(*b*)). The average ratio of *Y* 



**Figure 5.** GB shear strength  $\tau_{GB}$  as a function of (*a*) hardness, (*b*) yield strength and (*c*) H content. Each symbol represents a distinct GB and the lines are linear fits to the data. Error bars are defined as the standard deviations from the average value calculated over four indentation steps. Error bars are comparable to the symbol size. In (*b*) and (*c*) yield strength and GB shear strength are averaged over 3 ps of compression simulations. Similar magnitude of error bars is expected as in (*a*).

to  $\tau_{\rm GB}$  is calculated to be 2.00  $\pm$  0.28. It is analogous to the Taylor's factor  $Y/\tau_{\rm dis}$  calculated for materials exhibiting dislocation-based plasticity, where typically the value of the factor is measured to be between 2 and 3 [62]. We have also quantified the dependence of the GB shear strength on H



**Figure 6.** Shear stress resolved on GB planes (*a*) for an event of a single GB sliding (the plotted stress is for GB i from figures 5(a)) and (*b*) an event of two GBs sliding together (double sliding event). The ends of the horizontal axes coincide with the locations of GB junctions. The stress is measured at the equivalent strain of 7.5%.

content in the GBs (figure 5(*c*)). We conclude that GB sliding is the dominant plastic deformation mechanism in UNCD and that shear strength of GBs,  $\tau_{GB}$ , controls hardness and yield strength of this material. The GB shear strength  $\tau_{GB}$  is a fundamental parameter equivalent to  $\tau_{dis}$  in dislocation-based plasticity. In addition, the decrease in  $\tau_{GB}$  with increasing H content (figure 5(*c*)) is responsible for the observed decrease in hardness in hydrogenated samples (figure 3).

#### 3.3. Accommodation mechanisms

It remains to be addressed what mechanisms accommodate GB sliding during deformation of UNCD. To shed light on the coupling between GB sliding and accommodation processes, we plot the resolved shear stress on a sliding GB as a function of the position along the GB. Figure 6(a) shows the stress distribution along one such GB in the sample with 12.23% H. This profile is typical of stresses measured for the sliding GBs listed in figure 5(a). It is characteristic that although the stress fluctuates along the GBs, there is no stress accumulation at any of the ends (junctions) of the GB. The lack of stress accumulation suggests that GB sliding is accommodated by a plastic deformation and that the back stress from the elastic accommodation is negligible [30, 32, 63]. As we will show later, the fundamental mechanism underlying plastic accommodation in this case is the reduction of free volume (densification) in the GB network.

The lack of stress build-up combined with the short GB sliding distances (~0.5–3.5 Å) further supports the interpretation that the measured shear stress  $\tau_{GB}$  is the inherent frictional resistance of a GB to slide. We have also observed that in the regime where hardness no longer changes with

the applied strain (for strains >6%),  $\tau_{GB}$  on each sliding GB also remains constant, which means that the stress required to sustain GB sliding is related to the properties of GB itself rather than to the accommodation mechanism. This analysis confirms that GB sliding at the nanoscale is distinct from the macroscopic GB sliding observed in coarse-grained materials, where sliding of an isolated GB is typically accommodation limited.

Interestingly, we found a number of cases where accommodation does play a role in the GB sliding in UNCD. Specifically, when two adjacent GBs slide simultaneously towards a common GB junction, there is a stress accumulation at the GB junction as shown in figure 6(b) due to the elastic deformation of the surrounding material. In contrast to the single GB sliding event, the stress accumulation indicates that a simultaneous sliding of two GBs cannot be adequately accommodated by the free volume of GB junctions and the elastic accommodation becomes active. Such double sliding events have been found only in the nanoindentation simulations, where by the nature of the test the deformation is highly localized. The pile-up of GB sliding events and associated hardening are analogous to phenomena resulting from dislocation intersections. Dislocations can glide in response to the resolved shear stress  $\tau_{dis}$ . However, if two dislocations intersect, they can interact and impede further glide. In the case of simultaneous sliding of adjacent GBs the shear stress measured on the GB does not correspond to the intrinsic frictional strength of GBs but it also includes a contribution from a back stress. We also find that in the case of simultaneous GB sliding the dependence of the GB resolved shear stress on H content is less pronounced than was found for isolated sliding events (shown in figure 6(a)).

It is instructive to discuss the details of the plastic accommodation mechanism, which is the reduction of free volume in the GB network. Figure 7 shows such volume reduction in a GB that is aligned perpendicularly to the loading direction. Volume reduction is induced by a movement of two grains towards each other and this process is accompanied by bond breaking and forming within the GB. This process of bond reforming starts at approximately  $h \sim 10-11$  Å. During the indentation displacement from h = 12.5 to 13.5 Å, the two grains shown in figure 7 are moved closer to each other by 0.4 Å in the direction normal to the GB plane. No sliding is observed in this particular GB.

We found that in addition to densification of GBs, GB sliding is also accommodated by a limited amount of local amorphization within the crystalline grains near the GB junctions. However, the occurrence of this mechanism is rare. The maximum strain considered in our study is  $\sim 8\%$ . For larger strain, other accommodation mechanisms mentioned above will become more active. However, given the large hardness of UNCD, it would be challenge to achieve a strain that is much larger than what we investigated.

## 3.4. Relationship between atomic scale friction and GB sliding

We have shown that a decrease in GB shear strength  $\tau_{GB}$  leads to a decrease in Y and hardness. The decrease of  $\tau_{GB}$ 



**Figure 7.** Bond reforming during GB yielding. The snap shots are taken at displacements of (a) 12.5 Å(before sliding) and (b) 13.5 Å(after sliding) for the sample with 0% H. All spheres represent carbon atoms. Blue colour corresponds to atoms that reform bonds during this indentation step. Yellow atoms are the atoms that do not change their local bonding. The black circles show the newly formed bonds.

with increasing H content can be understood by viewing GBs as frictional interfaces. It is well established in the field of nanotribology that friction and the interfacial shear strength are dramatically reduced when diamond surfaces are passivated with H [37, 64–67]. It is because H passivation leads to a replacement of strong interfacial C-C bonds with weaker C-H bonds and thus it lowers the resistance to sliding. The same mechanism explains the reduction of GB shear strength  $\tau_{GB}$  with increasing H content observed in our simulations (figure 5(c)). This analysis exemplifies how understanding of mechanisms that govern atomic scale friction provides a connection between plastic properties of NC materials and the atomic structure of GBs. It is worth pointing out that while H decreases the interfacial shear strength, other dopants may increase the resistance to GB sliding and they can therefore enhance the yield strength of materials. For instance, it has been shown that creep resistance of polycrystalline alumina is enhanced by the presence of rare earth impurities (e.g. yttrium) segregated to GBs [68]. Guidance as to whether particular impurities will enhance or retard GB sliding in a material can be brought in from studies of interfacial shear strength between a relevant pair of materials.



**Figure 8.** The percentage increase of the  $sp^3$ -bonded atoms as a function of indentation displacement. Only C atoms are included in this analysis. The percentage increase is calculated relatively to the number of  $sp^3$  atoms calculated for the same sample before indentation. Symbols correspond to UNCD samples with different H contents as explained in the legend.

#### 3.5. Effect of rehybridization

We find that atoms can change their hybridization during deformation. The hybridization state of carbon atoms is determined by the number of nearest neighbours, which is defined by the coordination number provided in the REBO potential. Specifically, figure 8 shows that the number of sp<sup>3</sup> carbon atoms increases in the sample during indentation. Since most carbon atoms are  $sp^2$  and  $sp^3$  hybridized, this change (increase) in the number of sp<sup>3</sup> atoms is approximately equal to the change (decrease) in the number of  $sp^2$  atoms. Consequently, the chemical changes that we observe during plastic deformation correspond to a transition from sp<sup>2</sup> to sp<sup>3</sup> hybridization and the change to other hybridization states is negligible. Since most of the bond reforming takes place in the GB regions, we conclude that GB yielding is accompanied by an increase in the sp<sup>3</sup> hybridization in GBs. The increase of sp<sup>3</sup> is consistent with the fact that high pressure will stabilize the diamond phase over graphite at room temperature. The rehybrization has a negligible effect on our conclusions. As shown in figure 8, the rehybridization only accounts for approximately 1% of all sp<sup>3</sup> atoms. In addition, no aggregation of the  $sp^2$  hybridized atoms, i.e. the formation of graphite flakes, is observed. The shear strength of GB is averaged over the last four indentation steps. During these steps, the shear strength of GB is constant while the number of rehyrbridized atoms increases by a factor of two. This observation suggests that there is negligible effect of rehybridization on the shear strength of GB.

#### 3.6. Applicability of phenomenological models to UNCD

We have shown that dislocation plasticity is inactive in UNCD and that plastic deformation is controlled by GB sliding. It is instructive to ask whether quantitative relationships between indentation hardness and yield strength Y that are predicted by phenomenological indentation theories



**Figure 9.** The ratio of hardness over yield strength *Y* as a function of non-dimensional strain  $E^*a/YR$ . Experimental data shown in light grey [69] and dark grey [70]. Predictions of the cavity model [56] are shown for a cone indenter (dashed line) and for a spherical indenter (solid line). Data for UNCD are shown as red diamonds.

apply when deformation is controlled by GB sliding. For polycrystalline metals, Tabor [58] proposed that the indentation hardness equals three times the yield strength Y. More complex models have been developed to describe the correlation between hardness and Y as a function of other material properties, such as Young's modulus and Poisson's ratio [56, 69, 70]. Specifically it has been shown that the ratio of hardness to Y depends on a non-dimensional strain  $E^*a/YR$  (see figure 9), where a is the radius of the contact area, R is the indenter radius of curvature and  $E^*$  is the effective modulus of the interface [56, 58]. These theories have been developed and validated for polycrystalline materials that exhibit dislocation plasticity and for amorphous materials. We test the applicability of the above phenomenological indentation theories to UNCD. Using the cavity model of Johnson [56] as well as the elastic moduli and the yield strength of UNCD measured in our simulations, we predict that for all our samples the hardness to Y ratio is  $\sim 1.75$  (red symbols in figure 9). The ratio of hardness to Y measured directly from our simulations ranges from 1.68 to 1.84 with the average value of 1.75. The very good agreement between the theory and simulations shows that the phenomenological indentation theories are applicable for both dislocation plasticity and for intergranular plasticity controlled by GB sliding.

#### 4. Concluding remarks

We have demonstrated that friction of buried interfaces controls mechanical properties of NC materials in the regime where dislocation plasticity is inactive. In such cases the yield stress and hardness of the material scale linearly with the interfacial shear strength of GBs. By viewing GB sliding as a frictional phenomenon, we provided understanding of the experimentally observed effect of H incorporation in UNCD on hardness and yield strength of this material. The relationships among yield strength, hardness and interfacial strength are consistent with phenomenological models that had been developed for materials exhibiting dislocation plasticity. Our study demonstrates that the knowledge from the field of nanoscale friction can be utilized to understand the deformation of NC materials.

Conclusions from this study are expected to apply to other NC materials in which intergranular yielding has a lower energy barrier than intragranular yielding and where GB sliding has been observed to be the dominant mechanism of deformation in the early stages of plasticity [11, 12, 14, 18, 20]. Our conclusion may not apply to cases where GB sliding is accommodated by other processes such as GB migration, the emission and annihilation of dislocation from GBs, or GB diffusion creep.

#### Acknowledgments

IS gratefully acknowledges financial support from the Air Force Office of Scientific Research (AFOSR) grant No FA9550-07-1-0126 and from the American Chemical Society grant PRF-47978-G5.

#### References

- Sternitzke M 1997 Structural ceramic nanocomposites J. Eur. Ceram. Soc. 17 1061–82
- [2] Sumant A V *et al* 2000 Fabrication of MEMS components based on ultrananocrystalline diamond thin films and characterization of mechanical properties *Mater. Res. Soc. Symp. Proc.* 657 5
- [3] Kohn E, Ebert W, Adamschik M, Schmid P and Denisenko A 2001 Diamond-based MEMS devices New Diamond Front. Carbon Technol. 11 81–100
- [4] Zhang S, Sun D, Fu Y Q and Du H J 2003 Recent advances of superhard nanocomposite coatings: a review *Surf. Coat. Technol.* 167 113–19
- [5] Zhao Y S, Qian J, Daemen L L, Pantea C, Zhang J Z, Voronin G A and Zerda T W 2004 Enhancement of fracture toughness in nanostructured diamond-sic composites *Appl. Phys. Lett.* 84 1356–8
- [6] Sumant A V, Krauss A R, Gruen D M, Auciello O, Erdemir A, Williams M, Artiles A F and Adams W 2005 Ultrananocrystalline diamond film as a wear-resistant and protective coating for mechanical seal applications *Tribol. Trans.* 48 24–31
- [7] Veprek S, Veprek-Heijman M G J, Karvankova P and Prochazka J 2005 Different approaches to superhard coatings and nanocomposites *Thin Solid Films* 476 1–29
- [8] Erdemir A 2005 Review of engineered tribological interfaces for improved boundary lubrication *Tribol. Int.* 38 249–56
- [9] Heaney P J, Sumant A V, Torres C D, Carpick R W and Pfefferkorn F E 2008 Diamond coatings for micro end mills: enabling the dry machining of aluminum at the micro-scale *Diamond Relat. Mater.* 17 223–33
- [10] Yip S 1998 Nanocrystals—the strongest size Nature 391 532-3
- [11] Schiotz J, Di Tolla F D and Jacobsen K W 1998 Softening of nanocrystalline metals at very small grain sizes *Nature* 391 561–3
- [12] Van Swygenhoven H, Spaczer M, Caro A and Farkas D 1999 Competing plastic deformation mechanisms in nanophase metals *Phys. Rev.* B 60 22–5
- [13] Van Swygenhoven H 2002 Polycrystalline materials—grain boundaries and dislocations *Science* 296 66–7
- [14] Schiotz J and Jacobsen K W 2003 A maximum in the strength of nanocrystalline copper Science 301 1357–9
- [15] Yamakov V, Wolf D, Phillpot S R, Mukherjee A K and Gleiter H 2004 Deformation-mechanism map for nanocrystalline metals by molecular-dynamics simulation 2004 Nature Mater. 3 43–7

- [16] Meyers M A, Mishra A and Benson D J 2006 Mechanical properties of nanocrystalline materials *Prog. Mater. Sci.* 51 427–56
- [17] Vo N Q, Averback R S, Bellon P, Odunuga S and Caro A 2008 Quantitative description of plastic deformation in nanocrystalline Cu: dislocation glide versus grain boundary sliding *Phys. Rev.* B 77 134108
- [18] Szlufarska I, Nakano A and Vashishta P 2005 A crossover in the mechanical response of nanocrystalline ceramics *Science* 309 911–14
- [19] Demkowicz M J, Argon A S, Farkas D and Frary M 2007 Simulation of plasticity in nanocrystalline silicon *Phil. Mag.* 87 4253–71
- [20] Bachurin D V and Gumbsch P 2010 Accommodation processes during deformation of nanocrystalline palladium Acta Mater. 58 5491–5501
- [21] Lee S M and Stone D S 1994 Grain-boundary sliding in as-cast Pb–Sn eutectic Scr. Metall. Mater. 30 1213–18
- [22] Molteni C, Francis G P, Payne M C and Heine V 1996 First principles simulation of grain boundary sliding *Phys. Rev. Lett.* 76 1284–7
- [23] Chandra N and Dang P 1999 Atomistic simulation of grain boundary sliding and migration *J. Mater. Sci.* 34 655–66
- [24] Van Swygenhoven H and Derlet P A 2001 Grain-boundary sliding in nanocrystalline fcc metals *Phys. Rev.* B 64 224105
- [25] Namilae S, Chandra N and Nieh T G 2002 Atomistic simulation of grain boundary sliding in pure and magnesium doped aluminum bicrystals Scr. Mater. 46 49–54
- [26] Noreyan A, Qi Y and Stoilov V 2008 Critical shear stresses at aluminum–silicon interfaces Acta Mater. 56 3461–9
- [27] Ivanov V A and Mishin Y 2008 Dynamics of grain boundary motion coupled to shear deformation: an analytical model and its verification by molecular dynamics *Phys. Rev. B* 78 064106
- [28] Du N N, Qi Y, Krajewski P E and Bower A F 2010 Aluminum sigma 3 grain boundary sliding enhanced by vacancy diffusion Acta Mater. 58 4245–52
- [29] Wan L and Wang S 2010 Shear response of the  $\Sigma 9 \langle 1 1 0 \rangle \{ 2 2 1 \}$  symmetric tilt grain boundary in fcc metals studied by atomistic simulation methods *Phys. Rev.* B **82** 214112
- [30] Raj R and Ashby M F 1971 Grain boundary sliding and diffusional creep Metall. Trans. 2 1113
- [31] Bohn H G, Prieler M, Su C M, Trinkaus H and Schilling W 1994 Internal friction effects due to grain boundary sliding in large- and small-grained aluminium J. Phys. Chem. Solids 55 1157–64
- [32] Sutton A P and Balluffi R W 1995 Interface in Crystalline Materials (Oxford: Oxford University Press)
- [33] Qin L C, Zhou D, Krauss A R and Gruen D M 1998 Tem characterization of nanodiamond thin films *Nanostruct*. *Mater.* 10 649–60
- [34] Zhou D, Gruen D M, Qin L C, McCauley T G and Krauss A R 1998 Control of diamond film microstructure by ar additions to CH<sub>4</sub>/H<sub>2</sub> microwave plasmas *J. Appl. Phys.* 84 1981–9
- [35] Gruen D M 1999 Nanocrystalline diamond films Ann. Rev. Mater. Sci. 29 211–59
- [36] Jiao S, Sumant A, Kirk M A, Gruen D M, Krauss A R and Auciello O 2001 Microstructure of ultrananocrystalline diamond films grown by microwave Ar-CH<sub>4</sub> plasma chemical vapor deposition with or without added H<sub>2</sub> *J. Appl. Phys.* **90** 118–22
- [37] Sumant A V, Grierson D S, Gerbi J E, Birrell J, Lanke U D, Auciello O, Carlisle J A and Carpick R W 2005 Toward the ultimate tribological interface: surface chemistry and nanotribology of ultrananocrystalline diamond *Adv. Mater.* 17 1039–45

- Y Mo et al
- [38] Butler J E and Sumant A V 2008 The cvd of nanodiamond materials *Chem. Vapor Depos.* 14 145–60
- [39] Xiao X, Sheldon B W, Qi Y and Kothari A K 2008 Intrinsic stress evolution in nanocrystalline diamond thin films with deposition temperature *Appl. Phys. Lett.* **92** 131908
- [40] Sumant A V, Auciello O, Carpick R W, Srinivasan S and Butler J E 2010 Ultrananocrystalline and nanocrystalline diamond thin films for MEMS/NEMS applications MRS Bull. 35 281–8
- [41] Williams O A, Kriele A, Hees J, Wolfer M, Müller-Sebert W and Nebel C E 2010 High young's modulus in ultra thin nanocrystalline diamond *Chem. Phys. Lett.* 495 84–9
- [42] Williams O A 2011 Nanocrystalline diamond *Diamond Relat.* Mater. 20 621–40
- [43] Keblinski P, Phillpot S R, Wolf D and Gleiter H 1999 On the nature of grain boundaries in nanocrystalline diamond *Nanostruct. Mater.* 12 339–44
- [44] Zapol P, Sternberg M, Curtiss L A, Frauenheim T and Gruen D M 2001 Tight-binding molecular-dynamics simulation of impurities in ultrananocrystalline diamond grain boundaries *Phys. Rev.* B 65 045403
- [45] Reichart P, Datzmann G, Hauptner A, Hertenberger R, Wild C and Dollinger G 2004 Three-dimensional hydrogen microscopy in diamond *Science* 306 1537–40
- [46] Qi Y, Sheldon B W, Guo H, Xiao X and Kothari A K 2009 Impact of surface chemistry on grain boundary induced intrinsic stress evolution during polycrystalline thin film growth *Phys. Rev. Lett.* **102** 056101
- [47] Michaelson Sh, Ternyak O, Hoffman A, Williams O A and Gruen D M 2007 Hydrogen bonding at grain surfaces and boundaries of nanodiamond films detected by high resolution electron energy loss spectroscopy *Appl. Phys. Lett.* **91** 103104
- [48] Michaelson Sh, Stacey A, Orwa J, Cimmino A, Prawer S, Cowie B C C, Williams O A, Gruen D M and Hoffman A 2010 Bulk and surface thermal stability of ultra nanocrystalline diamond films with 10–30 nm grain size prepared by chemical vapor deposition J. Appl. Phys. 107 093521
- [49] Brenner D W, Shenderova O A, Harrison J A, Stuart S J, Ni B and Sinnott S B 2002 A second-generation reactive empirical bond order (REBO) potential energy expression for hydrocarbons J. Phys.: Condens. Matter 14 783–802
- [50] Voronoi G 1908 Nouvelles applications des paramètres continus à la théorie de formes quadratiques Z. Reine Angew. Math. 134 198–287
- [51] Mo Y F, Turner K T and Szlufarska I 2009 Friction laws at the nanoscale Nature 457 1116–19
- [52] Adiga V P, Sumant A V, Suresh S, Gudeman C, Auciello O, Carlisle J A and Carpick R W 2009 Mechanical stiffness and dissipation in ultrananocrystalline diamond microresonators *Phys. Rev.* B 79 245403
- [53] Sekaric L, Parpia J M, Craighead H G, Feygelson T, Houston B H and Butler J E 2002 Nanomechanical resonant structures in nanocrystalline diamond *Appl. Phys. Lett.* 81 4455–7
- [54] Krauss A R et al 2001 Ultrananocrystalline diamond thin films for MEMS and moving mechanical assembly devices *Diamond Relat. Mater.* 10 1952–61
- [55] Remediakis I N, Kopidakis G and Kelires P C 2008 Softening of ultra-nanocrystalline diamond at low grain sizes Acta Mater. 56 5340–4
- [56] Johnson K L 1987 Contact Mechanics (Cambridge: Cambridge University Press)
- [57] Mo Y and Szlufarska I 2010 Roughness picture of friction in dry nanoscale contacts *Phys. Rev. B* 81 035405
- [58] Tabor D 1948 A simple theory of static and dynamic hardness Proc. R. Soc. Lond. A 192 247

- [59] Suzuki T, Yonenaga I and Kirchner H O K 1995 Yield strength of diamond Phys. Rev. Lett. 75 3470
- [60] Evans T and Wild R K 1965 Plastic bending of diamond plates *Phil. Mag.* 12 479
- [61] Shenderova O A, Brenner D W, Omeltchenko A, Su X and Yang L H 2000 Atomistic modelling of the fracture of polycrystalline diamond *Phys. Rev.* B 61 3877
- [62] Taylor G I 1938 Plastic strain in metals J. Inst. Met. 62 307-24
- [63] Ovid'ko I A and Sheinerman A G 2007 Generation of cracks at triple junctions of grain boundaries in mechanically loaded polysilicon *Phil. Mag.* 87 4181–95
- [64] van den Oetelaar R J A and Flipse C F J 1997 Atomic-scale friction on diamond(111) studied by ultra-high vacuum atomic force microscopy Surf. Sci. 384 L828–35
- [65] Gao G T, Mikulski P T and Harrison J A 2002 Molecular-scale tribology of amorphous carbon coatings: effects of film

thickness, adhesion and long-range interactions 2002 J. Am. Chem. Soc. **124** 7202–9

- [66] Sumant A V, Grierson D S, Gerbi J E, Carlisle J A, Auciello O and Carpick R W 2007 Surface chemistry and bonding configuration of ultrananocrystalline diamond surfaces and their effects on nanotribological properties *Phys. Rev. B* 76 235429
- [67] Mo Y, Müser M H and Szlufarska I 2009 Origin of the isotope effect on solid friction Phys. Rev. B 80 155438
- [68] Buban J P, Matsunaga K, Chen J, Shibata N, Ching W Y, Yamamoto T and Ikuhara Y 2006 Grain boundary strengthening in alumina by rare earth impurities *Science* 311 212–15
- [69] Tabor D 1951 Hardness of Metals (Oxford: Oxford University Press)
- [70] Marsh D M 1964 Plastic flow in glass Proc. R. Soc. A 274 420