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Minimal graphene thickness for wear protection of diamond

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We show, by means of molecular dynamics simulations, that the transformation from diamond to amorphous carbon occurring while sliding under pressure can be prevented by having at least two graphene layers between the diamond slabs. The resulting reduction of wear makes this combination of materials suitable for new coatings and micro- and nanoelectromechanical devices. Grain boundaries, vacancies and steps on the diamond surface do not change this prediction. We attribute this behavior to the bonding in layered materials like graphene. The strong in-plane bonding and the weak interlayer interaction that evolves to a strong interlayer repulsion under pressure prevent the transition to amorphous carbon when more than one layer is present. © *2015 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution 3.0 Unported License.* [http://dx.doi.org/10.1063/1.4905942]

Control of friction and wear is one of the key challenges for the design of micro- and nano-electromechanical systems (MEMS/NEMS).[1] There is an ongoing quest to make these devices reliable, robust and able to resist demanding environments, under high stress and with sliding surfaces in contact. To avoid undesirable effects associated with viscosity,[2] squeeze out,[3] and stiction,[4] lubrication has to be based on dry solid coatings rather than on liquids.

The present MEMS/NEMS technology is based on silicon,[5,6] but its poor mechanical, chemical and tribological properties make alternatives desirable and actively sought after.[7,8] In particular at the nanoscale, wear is a limiting factor as it drastically shortens their lifetime.[4] Diamond is a promising material in view of its hardness and chemical inertness. Perfectly crystalline diamond is difficult to grow, but nanocrystalline diamond (grain sizes of 10-200 nm) shares many of its properties and is attainable by chemical vapor deposition (CVD).[5]

Although diamond is very hard, it is not resistant to wear and it can be polished. The polishing rate has been shown to depend on the surface orientation and sliding direction.[9] The amorphous layer which develops at the sliding interface is easily removed leading to wear of the surface. This amorphous layer also leads to a high friction coefficient because it has many bonds at the interface. Fortunately, lowering of the friction coefficient after some time, also called running-in, is observed for sliding amorphous carbon.[10,11] The microscopic mechanisms for this behavior are still a matter of debate. Molecular dynamics based on a modified version of the reactive empirical bond order (REBO) potential[12] reports the formation of a graphene-like layer[13] during sliding under pressure that would inhibit the further growth of an amorphous layer at the interface. Recent ab-initio calculations, instead, attribute the reduction of friction after the initial phase (running in) to passivation of the dangling bonds by water or, preferably, by hydrogen.[14–16] For the latter case, a minimum humidity or hydrogen gas pressure is necessary and the contact pressure needs to be below a critical value[14] for passivation. These results suggest that operation in vacuum or high-pressure environments would be difficult.

An approach to reduce wear is to look for suitable coatings, effective at the nanoscale. Moreover, it is desirable to have a very thin coating. Graphene is a natural candidate for this purpose in view of its exceptional mechanical properties.[17] The frictional properties of (few-layer) graphene have been recently intensively studied[18,19] showing an increase of friction with decreasing number

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of layers. Coating of sliding steel surfaces with few layer graphene reduced drastically the friction and wear during sliding.[20] Also on a smaller scale, coating of an atomic force microscopy (AFM) tip with graphene improved the resistance to wear.[21] Moreover it has been recently shown that graphene withstands without damage much higher loads than diamond-like carbon,[22] making graphene suitable for high-pressure conditions.

Here we suggest combining the properties of diamond and graphene to form a hard but smoothly sliding structure for new MEMS/NEMS technologies.

We perform atomistic simulations to describe the wear of diamond surfaces during sliding under pressure when the surfaces are either bare or separated by one or two layers of graphene. We find that at least two layers of graphene are needed to form a contact that drastically reduces friction and wear.

The interatomic interactions are given by the long-range carbon bond order potential (LCBOP)[23] as implemented in the molecular dynamics code LAMMPS.[24] This bond-order potential includes dispersive interactions and can accurately describe different phases of carbon,[25] the transformations between them and the elastic constants of diamond and graphite. It can also describe the interaction of carbon adatoms with the diamond surfaces and graphene.

In Fig. 1 we show a sketch of our model. Our initial sample consists of two slabs of diamond with (100) surfaces, which are pressed against each other. The (100) surface has a square unit cell given by one face of the cubic lattice with lattice parameter 3.5668 Å. Periodic boundary conditions
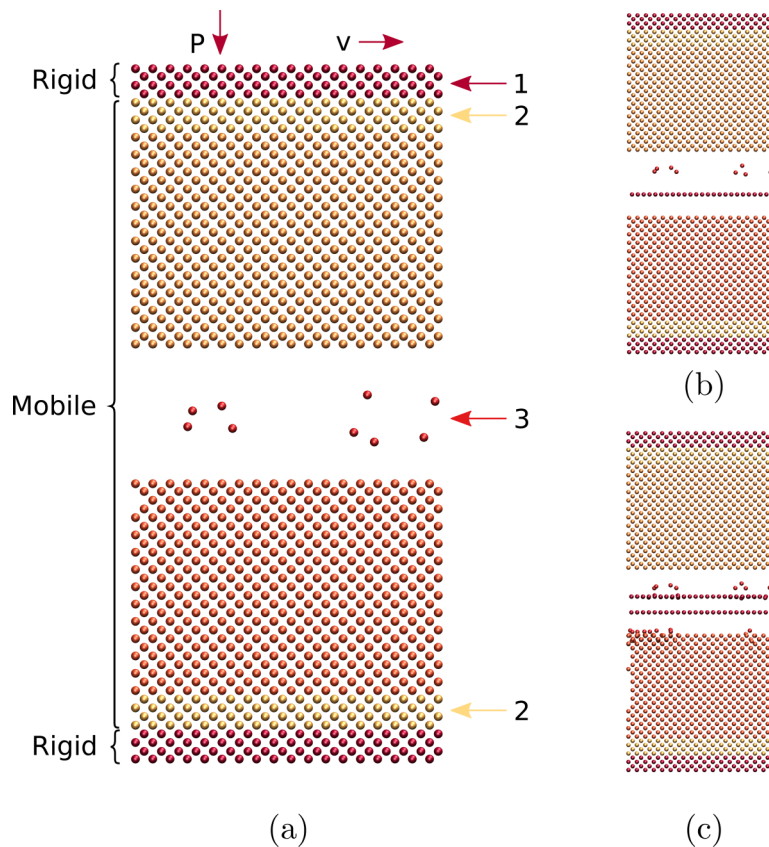

FIG. 1. (a) Model of the simulated system, consisting of two diamond slabs, each formed by 3564 atoms (108 per atomic layer) with periodic boundary conditions in the in-plane x and y direction. The top and bottom 4 atomic layers (red, 1) are kept rigid. The top rigid part moves with a constant velocity in the x direction and can move in the z direction as a consequence of the applied pressure and interactions with the mobile atoms. The temperature is controlled by a Langevin thermostat applied to four atomic layers adjacent to the rigid parts (yellow, 2). A few randomly placed atoms (3) prevent cold welding of the slabs. (b) Initial configuration with one layer of graphene of 260 atoms between the sliding diamond surfaces. (c) Initial configuration with two layers of graphene.

are imposed in the in-plane x and y directions. Each diamond slab is made of $9 \times 6 \times 8$ unit cells. This size is chosen to avoid strain and match the periodic boundary conditions when one or two graphene layers, each made of 260 atoms, are placed between the diamond slabs as shown in Fig. 1(b) and 1(c). The top and bottom 4 atomic layers are kept rigid. The bottom rigid part is kept still, whereas the top rigid part moves in the x direction ($\langle 100 \rangle$ direction) at a fixed velocity v=30 m/s. The top rigid part can also move as a whole in the z direction under the influence of a constant force on each atom, which results in a pressure of 10 GPa. The temperature is controlled by a Langevin thermostat with damping constant γ^{-1}=0.1 ps applied to the 4 atomic layers adjacent to the top and bottom rigid layers. All simulations are performed at room temperature (300 K).

For the case of bare diamond slabs, following Ref. 9 we randomly place a few carbon atoms between them to prevent cold welding, that is the joining of the two slabs. When the slabs are separated by one or two graphene layers, we use these atoms to mimic possible imperfections of the surfaces or the presence of reactive adsorbates.

It has been shown[9] that when two diamond slabs slide against each other, the crystalline structure at the interface is damaged, leading to an amorphous structure with a rate of amorphization which depends on the surface and on the sliding direction.

We consider (100) diamond surfaces sliding in the $\langle 100 \rangle$ direction, which is a fairly soft direction. As shown in Fig. 2(a) we find that the bare contact area transforms to amorphous carbon with $\sim 90\ \%$ sp^2 bonds. The precise percentage of bonding type in disordered, liquid or amorphous, phases may depend on the used potential.[11,26]

A single graphene layer between the two surfaces leads to the same result, namely the graphene layer is destroyed within tens of picoseconds and the contact area becomes amorphous. This situation changes dramatically for a bilayer graphene (Fig. 2(c)). Sliding occurs in this case preserving the structure of the diamond surface as well as that of the bilayer graphene. In Fig. 3 we show that also the velocity and temperature profiles along the sample height are very different. While the samples which degrade to amorphous carbon show a gradual change in velocity, the sample with two layers of graphene shows a sharp transition where the two slabs slide over each other. In this case, the temperature remains constant at 300 K while for the amorphous contact area it raises to 600 K at the interface.

To understand the reason for the marked difference between one- and two-layer graphene coating of the diamond surface we have considered all the systems sketched in Fig. 4. We have divided them into those that do not present wear within the 2 ns duration of our simulations and those that do. We see that, for a single layer, wear occurs in all cases apart from that of ideally planar, clean surfaces (panel NW1). Adatoms in between the diamond surfaces and graphene lead to the formation of bonds as shown in Fig. 5, pulling graphene out of planarity. The consequences are very different for one or two layers. For one layer, once a bond is formed with the upper diamond surface, the deviations from planarity facilitate bonding of a neighboring atom with the lower diamond surface. Bonds with upper and lower diamond surface become sp^3-like and propagate, leading to an
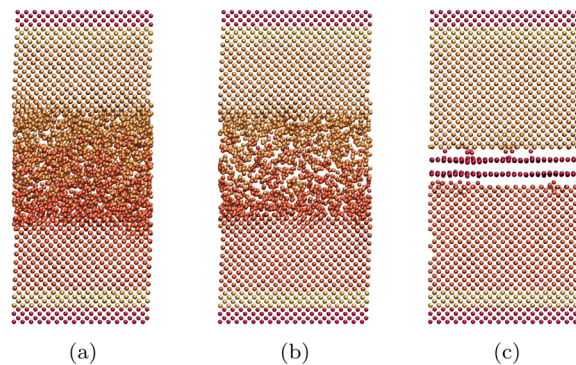

FIG. 2. Structure of the samples of Fig. 1 after 2 ns of sliding: bare surfaces (a), with one layer of graphene (b) and with two layers of graphene (c). Notice that two layers of graphene prevent amorphization.
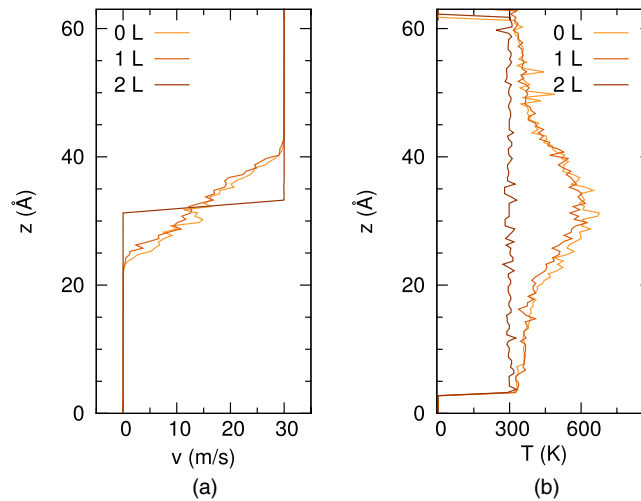
FIG. 3. (a) Velocity in the sliding direction along the height of the sample after 2 ns for the samples of Fig. 1 with zero (0 L), one (1 L) or two (2 L) graphene layers. For two graphene layers, a sharp transition is visible between the two slabs whereas the velocity gradually changes in for 0 L and 1 L due to the amorphous layer. (b) Temperature along the height of the sample after 2 ns for samples with zero (0 L), one (1 L) or two (2 L) layers. The temperature is higher in the amorphous part.

amorphous structure as in Fig. 2(b). If instead there is a second layer of graphene, as in Fig. 5(b), bonding between the two graphene layers does not occur for the following reason. Two atoms form a bond when they come closer than 2.2 Å, the cut-off radius for covalent interactions. For atoms belonging to different graphene layers, approaching to such a distance is prevented by the high energy barrier due to interlayer repulsion[23,27] and by the large bending constant of graphene.[28] A similar difference between one and two layers is also found for surfaces with steps. We have simulated the effect of steps on the diamond surface. We doubled the size of the sample in the sliding direction to 18 diamond unit cells. For 9 unit cells in the top diamond slab we have removed the lowest two atomic layers, resulting in two steps as shown in Fig. 6(a) and 6(b). We find that a single layer graphene between clean surfaces (no adatoms) leads to wear (Fig. 6(c)) whereas two graphene layers protect the diamond slab from wear even in presence of steps and adatoms (Fig. 6(d)). All these results show that for a single layer graphene any imperfection of the surface (edges, steps, adatoms) forms a source of wear that propagates quickly throughout. For two graphene layers the only situation where wear occurs is when we place single carbon atoms also between the graphene
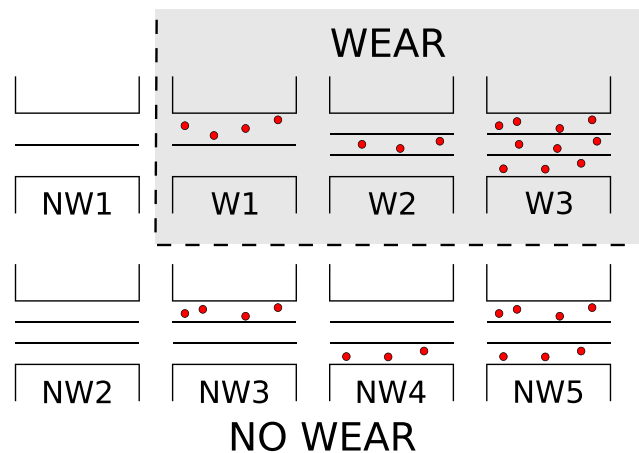

FIG. 4. Sketch of the simulated structures indicating the graphene layers between the diamond surfaces and the presence of single carbon atoms. The shading indicates the structures that present wear after 2 ns.
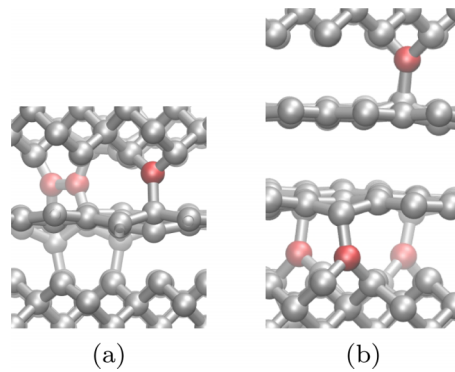
FIG. 5. Snapshots after a few picoseconds of the structure with one or two graphene layers. (a) For the single graphene layer bonds form on both sides and lead eventually to amorphization and wear. (b) For the two graphene layers, instead, the adatoms cannot induce bonds between the two graphene layers.

layers. This situation is however rather extreme because single carbon atoms, having valency four, are much more reactive than typical adsorbates.

Next, we consider the effect of the most common defects in graphene, namely grain boundaries and vacancies. In the equilibrium structure[29] of the grain boundary shown in Fig. 7(a) the bonds form pentagons and heptagons which are more prone to rearrangement than the ideal hexagonal structure. The vacancies in Fig. 7(b) lead to unsaturated bonds. Also for these cases, we have found the drastic difference between one and two layers discussed previously. For the sample with vacancies, we find that they remain intact and smooth when one percent or three percent of the atoms is missing. If we further increase the ratio of deleted atoms to five percent, the graphene layers degrade to amorphous carbon. Since the growth of perfect graphene is still a technological challenge, it is encouraging that the graphene layers do not need to be perfect in order to inhibit wear.

Up to now, we have considered AB stacking of the two layers of graphene. This commensurate orientation results in much higher friction than incommensurate orientations.[30,31] As high friction is generally associated with wear, we expect that other orientations will not lead to wear either. We have simulated a case where one graphene layer was rotated by 30° with respect to the other layer and this indeed resulted in sliding without wear.

In summary, we have shown that two layers of graphene between diamond slabs may provide a strong wear-resistant layer. While clean diamond surfaces or diamond surfaces separated by only one layer of graphene transform to amorphous carbon during sliding under pressure, two layers of graphene preserve their structure and protect the diamond from wear. This result holds also when the diamond surface is not perfectly flat or when the graphene layers present defects such as grain
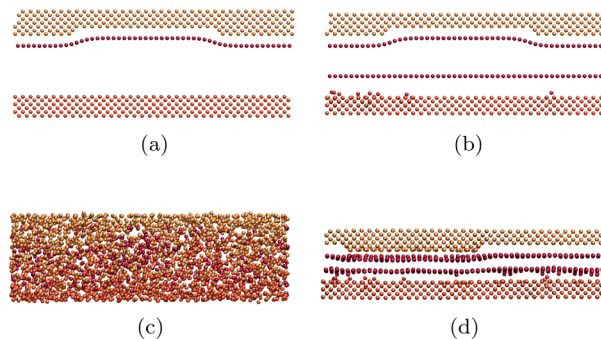

FIG. 6. (a) Interface of the starting configuration with steps and one graphene layer. (a) Interface with steps and one graphene layer after 2 ns of sliding. (c) Interface of the starting configuration with steps and two graphene layers. (d) Interface with steps and two graphene layers after 2 ns of sliding.
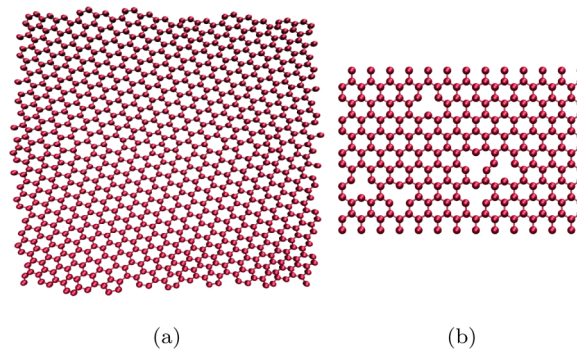
FIG. 7. (a) Graphene layer with a $\Sigma = 39$ grain boundary.[29] (b) Porous layer with vacancies obtained by randomly removing 3 % of carbon atoms.

boundaries or vacancies. We believe that our findings can be relevant for the development of fully carbon based MEMS/NEMS.

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