



Dangling bond induced cross-linking model in nanoscratched graphene layers

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ABSTRACT

Dangling bond induced cross-linking in an interlayer graphene during nanoscratch is simulated by molecular dynamics method. The normal stress over 74 GPa leads to a broken hexagonal ring of the intralayer graphene, producing unstable dangling bonds which easily make up sp^2 or sp^3 between neighbor layers. The cross-linking density increases with increasing scratching depth, causing higher scratch hardness. The maximum scratch hardness is 90 GPa. The cross-linking is reversible after scratch when the normal stress is less than 90 GPa, beyond which the atoms from different graphene layers will be mixed together forming amorphous structure, making the scratch hardness decrease sharply. These results provide insights into the structural and mechanical properties of graphene based materials.

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1. Introduction

Various new functional carbon films present super hard property, such as tetrahedral amorphous carbon films [1,2], fullerene-like carbon nitrogen (CN) films [3–5], and carbon nano-crystallite films [6,7]. These hard carbon films have been developed by mainly two guiding principles. One is to increase sp^3 bonding component as much as possible, for example the tetrahedral amorphous carbon films exhibiting more than 80% sp^3 bonding. The other is to increase the cross-linking structure of graphene basal planes, both fullerene-like CN films and carbon nano-crystallite film showing highly tangled cross-linking structure. Lars Hultman et al. reported that a fullerene-like material consisting of C and N cross-linked curved basal planes synthesized by reactive magnetron sputtering shows high resilience with hardness of 7 GPa and Young's modulus of 37 GPa [3]. By testing the scratch hardness, Hirano et al. found that the hardness of a unique carbon film which they developed by ion irradiation is comparable to diamonds, but the electrical conductivity is 19 orders larger than diamonds, and this is attributed to the bond connection between the parallel and curved graphene sheets of the sp^2 nanocrystallites [6]. B. Peng et al. carried out both in situ transmission electron microscopy test and molecular mechanics calculations to demonstrate that electron irradiation-induced cross-linking of multiwalled carbon nanotubes can yield dramatic increase in sustainable loads [8].

There are many previous studies which reported that cross-linking can be formed under the process of chemical modification (such as nitrogen element mixing, nitrene reaction or 1,2,3,4-Butanetetra-carboxylic acid dealing and so on) [3–5,9,10], ion or electron irradiation [6–8,11], and externally applied mechanical forces such as nanoindentation [12]. Unfortunately, they did not explore the essential reason of cross-linking formation, and how does it process. Until now, the intrinsic transformation mechanism of the bond connections between parallel and curved graphene basal planes is not well understood. Therefore, in order to clarify the mechanism of the cross-linking structure formation of graphene basal planes, we carried out nanoscratching to employ externally applied forces on a four-layer graphene, using molecular dynamics calculation with second-generation reactive empirical bond order (REBO) potential [13]. In addition, the effects of cross-linking on the graphene layers' scratch hardness are studied.

2. Methods and calculation

To compute the scratching behavior of graphene, a hemispherical diamond tip with 2.5 nm radius is initially indented for the four-layer graphene at a certain depth. After a 50,000 step relaxation, the tip scratches graphene with a speed of 5 m/s. Each graphene layer contains 3200 atoms with the size of 9.8 nm × 9.8 nm. The two boundary atoms around each graphene layer are kept fixed at a constant temperature of 300 K controlled by the Berendsen thermostat method [14].

In the simulation, REBO potential [13] was adopted to describe the intralayer graphene interactions as well as the interactions of the diamond tip. It has been demonstrated that REBO potential can accurately characterize the bond transformation with changes in atomic

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hybridization between carbon atoms [12,15], because a bond order function is used to describe many-body effects. The interaction is in the form

$$U = \sum_i \sum_{j(>i)} \left[V^R(r_{ij}) - b_{ij} V^A(r_{ij}) \right] \quad (1)$$

where $V^R(r)$ is the function of all interatomic repulsive interactions while $V^A(r_{ij})$ represents the attractive interactions. r_{ij} is the distance between pairs of nearest-neighbor atoms i and j . Moreover, b_{ij} is a bond order function between atoms i and j . The forces between the tip and graphene atoms are determined by the Lennard-Jones (LJ) potential [16], in which the equilibrium distance is 0.34 nm [17].

3. Results and discussions

Fig. 1 shows the atomic structure changes of graphene during the scratching process under different scratching depths. According to the calculation results, when the distance between the bottom of the diamond tip and the top surface of graphene is 0.34 nm, the atoms in the diamond tip begin to enter the repulsive force field of graphene. At this time the scratching depth is defined as zero. Then the diamond tip is fixed at different depths, and the system is in relaxation with 50,000 steps at 300 K, after that the nanoscratching simulations are proceeded respectively. When the scratching depth is 0.448 nm, the graphene atoms around the tip are depressed, the maximum deformation occurs at the top layer of graphene, and the deformation decreases downwards. In order to keep consistent with the following content, we described the condition of graphene under 0.448 scratching depth because it is one of the critical values to the scratch hardness. By this time, the bond lengths between the intralayer atoms become longer and the bond angles are deflected due to the depression deformation. After the tip sliding away, the hollow of the original area disappears, and the deformation elastically recovers instantaneously. The depression increases with the increasing scratching depth, leading to smaller spacing between the adjacent graphene layers just beneath the tip, especially the top layer and the second layer. When the spacing reaches the C–C bond range (<0.17 nm), new bonds arise in the interlayer graphene, which are defined as “cross-linking” (shown in Fig. 1(b)). The cross-linking first occurs between the top and second graphene layers when the scratching depth is 0.5 nm. As shown in Fig. 1(b), under the scratching depth of 0.53 nm, more interlayer bonds are produced when the scratching distance is zero, illustrating that the density of cross-linking increases with the increasing scratching depth. It is also found that the original cross-linking vanishes after a scratching distance of 1.2 nm, and new cross-linking is generated around the diamond tip. Further increases in the scratching depth (the scratching depth is 0.58 nm, shown in

Fig. 1(c)) induce sharp increment of cross-linking density. Finally, the area scratched by the diamond tip turns into a mass of disordered carbon atom stacking, which cannot recover. Meanwhile, after a 1.2 nm scratching distance, a part of carbon atoms in the top and second graphene layers nearby the tip mix together to form a one layer amorphous structure. In this way, the cross-linking disappears. Besides, the right part of graphene performs bump due to the squeezing of the tip.

By tracking the trajectory of graphene atoms, the formation principle of the cross-linking is obtained when the scratching depth increases to a certain value. Fig. 2 shows this process from some atoms of the graphene when the scratching depth is 0.53 nm. One intact hexagonal carbon atom ring of the top layer graphene is marked by blue color, the second layer is pink, and the third layer is white. Because the bottom layer is rigid and does not have obvious changes, we do not display it in Fig. 2. When the diamond tip scratches, the sp^2 bond between the neighbor atoms T_1 and T_2 in the top layer is broken, and both T_1 and T_2 produce a dangling bond respectively as shown in Fig. 2(b).

The dangling bonds are extraordinarily unstable and swaying in the space. Meanwhile, the dangling bonds are induced by the fracture of sp^2 bond between the adjacent carbon atoms S_1 and S_2 in the second graphene layer. Once the swaying dangling bonds from the atoms T_1 and S_1 meet in the space, a new sp^2 bond is generated between the first and second graphene layers, and this is the first form of cross-linking. It can be seen that the third graphene layer does not have any bond fracture, and the dangling bond of the other atom S_2 in the second layer links with that of the corresponding atom in the third layer, then the π bond turns into σ bond, so the other cross-linking is formed by sp^3 . Cross-linking has great influence on the mechanical properties of graphene, especially the hardness.

The variation of scratch hardness of graphene with the increasing scratching depth is shown in the plot line of Fig. 3. This scratch hardness is defined as the average value of the vertical load divided by the contact area during one nanoscratching process, which is analogous with the indentation hardness [18]. With the increasing of the scratching depth, graphene experiences progress from soft to hard phase transition, which is similar to that in the nanoindentation process [12]. In the soft phase region when the scratching depth is smaller than 0.448 nm, the hardness increases slowly with the increasing scratching depth by the following two reasons. Firstly, the residual stress in the intralayer graphene increases because of the increasing bond length and the bond angle deflection in the six member rings by the press of the tip. Secondly, the decreasing distance between the interlayer graphene causes the increasing of the Van der Waals forces. In the hard phase region when the scratching depth is in the range between 0.448 nm and 0.54 nm, the slope rate of vertical average stress sharply becomes very large. The Van der Waals forces of the interlayer graphene enter a dramatic increase period due to the further closing distance with

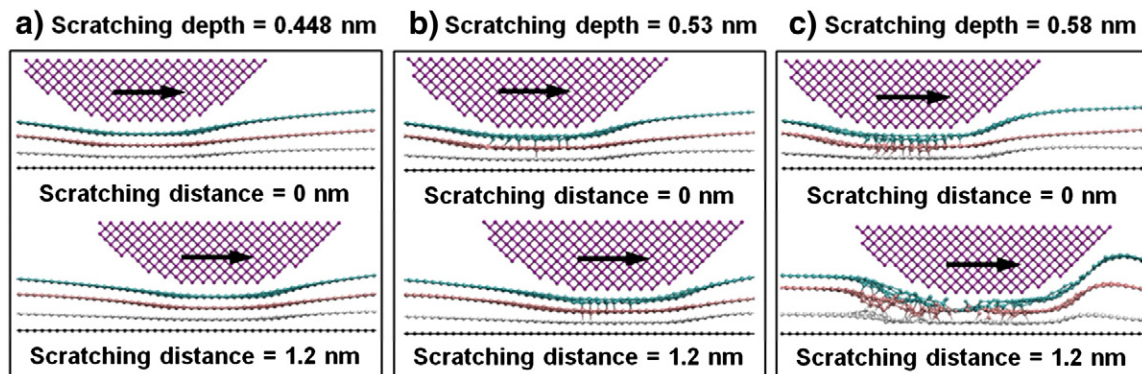


Fig. 1. The simulation results of the front views at scratching distances of 0 nm and 1.2 nm with various scratching depths. (a), (b) and (c) correspond to scratching depths of 0.448 nm, 0.53 nm and 0.58 nm, respectively.

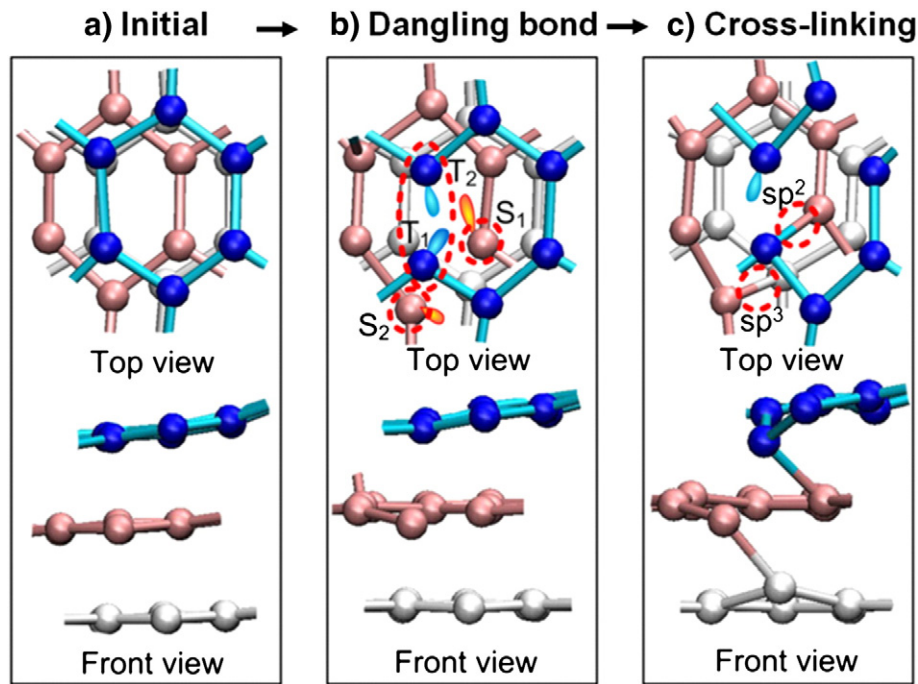


Fig. 2. Evolution of cross-linking in the interlayer graphene when the scratching depth is 0.53 nm. (a) The initial statue of one location of the graphene. (b) The dangling bonds generated from neighbor atoms T₁, T₂ in the top layer (blue atoms) and S₁, S₂ in the second layer (red atoms) by the stress of the diamond tip, and then the cross-linking is formed over the course of the simulation, as can be seen from image (c).

the scratching depth ranging from 0.448 nm to 0.5 nm. Remarkably, according to an amount of calculation, it is found that when the depth is under 0.5 nm, the intralayer hexagonal lattices keep intact during the scratching process, only with a little deformation, and as described before, no cross-linking occurs in the interlayer graphene.

However, when the scratching depth is over 0.5 nm, the cross-linking begins to come out, and this new phase strengthens graphene's compressive resistance obviously. The scratch hardness is 74 GPa at the depth of 0.5 nm compared to 42 GPa at the depth of 0.49 nm. The increasing density of cross-linking with the increasing scratching depth, can afford higher pressure up to the maximum value of 90 GPa (the scratching depth is 0.54 nm). We also observed the dynamic alternation of the intralayer atomic structure when the scratching depth is between 0.5 nm and 0.54 nm. Accompanied by the formation of cross-linking, the intralayer hexagonal crystal structure below the tip will be disordered in varying degrees under different scratching depths. However, after the tip sliding away, the cross-linking disappears and the deformations of intralayer graphene soon recover. In this way, both the cross-linking and the strong sp² bonds in the intralayer graphene can bear the tensile stress, leading to the increasing scratching hardness. Under the

depth of 0.52 nm the defect in the intralayer is more serious than that when the depth is 0.51 nm, while the cross-linking densities are the same, which is why the hardness suddenly drops as the depth increases to 0.52 nm. When the scratching depth is over 0.54 nm, although more cross-linking is produced, most depressed atoms from different layers are mixed together. After scratching, the deformation permanently exists, and the disordered amorphous carbon structure is created (shown in Fig. 5), which will definitely reduce the compressive resistance of graphene, and decrease the scratch hardness remarkably.

The ratio of nanoindentation hardness (H_i) to nanoscratch hardness (H_s) varying with scratching depth is presented in Fig. 4. When the scratching depth is lower than 0.33 nm, H_i/H_s is 0.96 for average. The ratio is about 1.1 with the depth in the range from 0.33 nm to 0.47 nm. As a result, the scratching hardness will be in good agreement with the nanoindentation hardness if the scratching depth is in the certain range (0 nm–0.47 nm). For graphene with small thickness about several angstroms, because of the limitation of precision, it is difficult to measure the hardness using a nanoindentation tester. However, we can take advantage of nanoscratching method, which can lead to higher accuracy. When the depth is over 0.53 nm, the deeper depths cause a

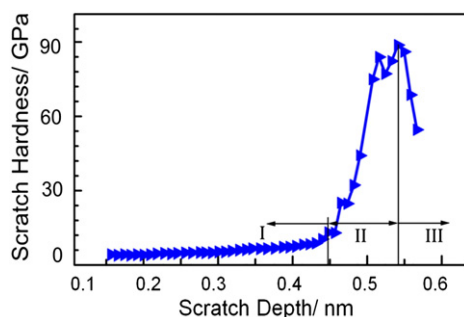


Fig. 3. Scratch hardness curve of four layer graphene with three different regions with scratching depth: soft region I, hard region II, and decrease region III.

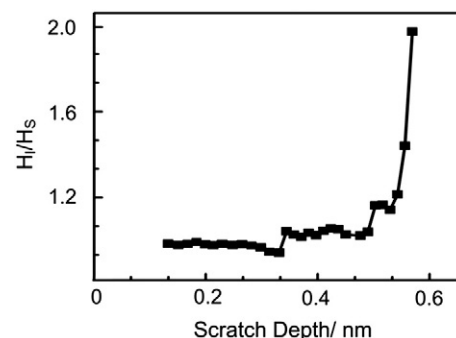


Fig. 4. The variation of the ratio of nanoindentation hardness (H_i) to nanoscratch hardness (H_s) with scratching depth.

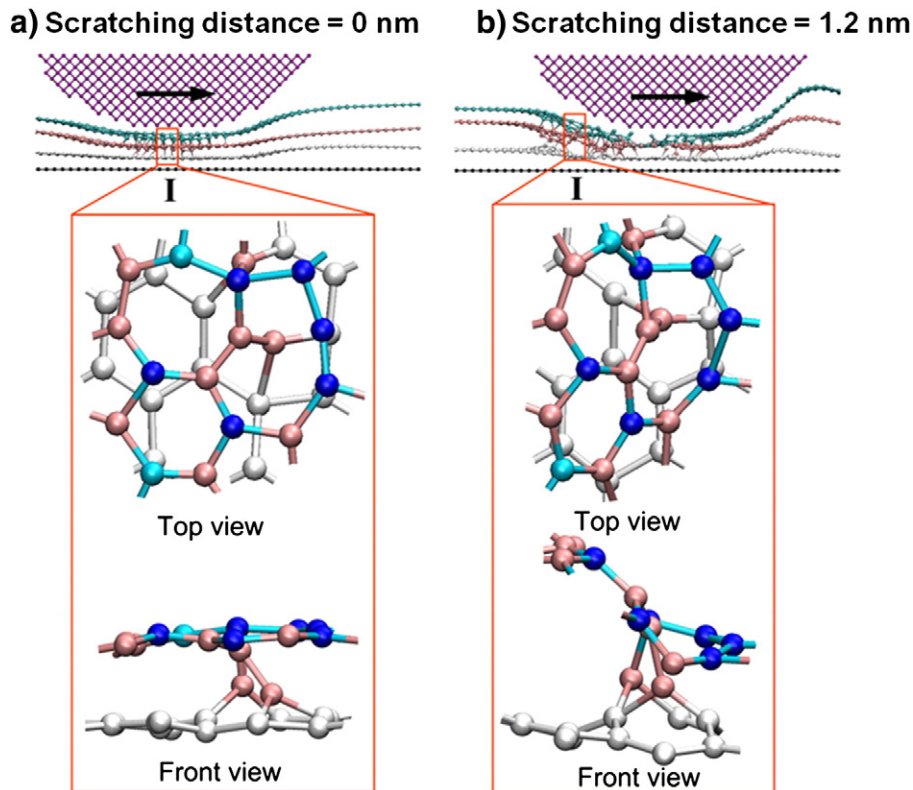


Fig. 5. The bonding conditions of region I (marked by the red box) of the sample during and after the diamond tip scratching with the scratching depth of 0.58 nm, where the blue atoms are from the first layer and the red ones are from the second layer, and the six dark blue atoms initially made up a hexagonal ring. (a) and (b) are the top view and the front view of the atomic structure when the tip is directly over region I and slides by 1.2 nm.

dramatic increase in H_t/H_s , and the hardness of nanoindentation is 1.95 times larger than scratching hardness.

4. Conclusion

Graphene exhibits three distinct structural changing principles as follows. When the scratching depth is smaller than 0.5 nm, no cross-linking between the interlayer is created, and the intralayer graphene keeps intact during the whole scratching processes. When the depth is in the range from 0.5 nm to 0.54 nm, cross-linking occurs and the intralayer graphene lattice under the tip was destroyed. Yet all these phase transitions are recovered after the diamond tip passed by. As the depth increases more than 0.54 nm, the phase transition exists permanently. The formation principle of cross-linking is proposed, which is in the form of sp^2 or sp^3 . Cross-linking leads to the changes of scratching hardness, and graphene can afford the maximum pressure of 90 GPa. The nanoindentation hardness and nanoscratching hardness are almost the same when the scratching depth is less than 0.54 nm. However, the difference between the hardness obtained by the two methods is growing and the scratching hardness decreased sharply once scratching depth is over 0.54 nm. That is because during the scratching process with a large scratching depth, the graphene lattice is destroyed. Especially the top layer and second layer graphene are mixed together forming an amorphous carbon film. In this way, cross-linking is disappeared. This study helps in understanding the processes occurring in nanoscratches of graphene layers and provides guidance to the applications of graphene.

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