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Nanoscale wear of graphene and wear protection by graphene

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ABSTRACT

Mechanical stability and wear resistivity of graphene are prerequisite for its applications in nano-mechanical devices. We employ atomic force microscopy based scratching in order to explore the wear of graphene at nanoscale, and the efficiency of graphene for the wear protection of an underlying substrate. We show that the wear of graphene consists of two processes: 1. the plastic deformation for lower normal loads, followed by 2. a sudden tearing of graphene for high enough normal load, with subsequent graphene peeling off from the substrate. The complete progress of the friction during these processes is measured and explained: the friction starts from low values on plastically deformed graphene, then strongly increases for a short time during graphene tearing, and ends up at lower value on uncovered substrate after graphene peeling. Finally, we demonstrate that around 5 nm thick (over ten layers) graphene flakes provide wear protection of the underlying substrate, while thin graphene flakes, around 1 nm thick (single and bilayer), can only enhance the mechanical capacity of the underlying substrate.

1. Introduction

Graphene is atomically thin and flexible conductor [1], with very large stiffness and strength [2], and with good lubricating properties [3]. Therefore, graphene is a promising material for future nano-electromechanical devices such as nano-electromechanical resonators [4,5], piezoresistive sensors [6–9], and nano-electromechanical switches [10,11]. Graphene, as a very stiff material with a low friction, is an excellent choice for the mechanical protection of underlying substrates and nano-objects, including the wear protection and friction reduction [12,13], as well as van der Waals screening [14]. At the same time, graphene is impermeable to standard gases [15], chemically inert and stable, thus allowing protection against oxidation [16] and corrosion [17,18]. Prerequisite for all these graphene applications is a good understanding of its mechanical stability and wear resistivity at nanoscale.

Wear of graphene as well as wear protection by graphene was mainly studied on micro- and macro-scale, on large graphene sheets obtained by the solution processing [13,19], the epitaxial growth on SiC [20,21], or the chemical vapour deposition (CVD) on copper [22]. Although highly relevant for practical applications, these studies did not consider *nanoscale* wear mechanism of monocrystalline graphene. Graphene fracture at nanoscale was investigated using atomic force microscopy (AFM) based nano-indentation experiments in the context of graphene elastic properties [2,23–25], but without considering the graphene wear during sliding. Some of the first insights into nanoscale wear properties of graphene were gained indirectly, as side results of AFM based scratching experiments used for graphene patterning [26–28]. AFM scratching was used to study graphene wear properties by plowing parallel trenches, but only in the regime of graphene plastic deformation, without graphene fracture [29]. Similar methods were employed to explore the influence of wrinkles on wear of CVD graphene [30] and wear initiated from graphene edges [31,32]. Simultaneously, nanoscale wear of graphene was investigated by numerical simulations as well [12,33–37].

So far, the wear protection of underlying substrate was experimentally demonstrated by the solution processed graphene [13,19], where it was shown that wear tracks were more narrow on the graphene protected steel surface. Wear protection by graphene has been already applied for increased endurance and durability of graphene coated AFM probes [38,39] and enhanced mechanical stability of graphene covered macromolecules [40,41]. Meantime,

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numerical simulations showed that single layer graphene enhanced the load carrying capacity of the surface during nanoindentation experiments [12], while the wear protection under sliding conditions could be provided by at least two graphene layers [35].

Low shear strength of graphene makes it an excellent ultra-thin solid lubricant [42]. Nanoscale friction of graphene was widely studied on pristine [3,12,43–46], fluorinated [47–50], hydrogenated and oxidized graphene [49], as well as on graphene-oxide [51,52]. It was shown that graphene enables friction reduction compared to surrounding substrate, while the friction can be efficiently controlled either by a proper functionalization or by controlling the number of graphene layers. Still, the friction progress during the contact sliding, during the plastic deformation and especially at the onset of graphene fracture was much less studied. Only an increase of the friction during graphene rupturing has been demonstrated so far [12,19]. Still, many questions regarding graphene wear properties at nanoscale, friction changes during graphene tearing, and graphene efficiency for wear protection have remained open.

We study wear properties of graphene at nanoscale using AFM based scratching and observe two different processes depending on the applied load: 1. plastic deformation of graphene and underlying substrate at lower normal loads, and 2. graphene tearing and subsequent peeling off from the substrate at higher normal loads. The friction between AFM tip and graphene is low on plastically deformed graphene, then it suddenly increases during the tearing, and thereafter it falls down resembling the friction of bare substrate. Finally, we show that the complete wear protection of the underlying substrate is achieved with 4–5 nm thick graphene layers. On the other hand, thin graphene layers, around 1 nm thick, can only increase the mechanical capacity of the underlying substrate, but cannot protect it from wear.

2. Experimental

Graphene samples were produced by the micromechanical exfoliation on silicon wafers with a thin layer of silicon-oxide on top (around 80 nm thick). AFM measurements were done using NT-MDT system NTEGRA Prima. Topographic imaging of graphene flakes before and after AFM based scratching was done in tapping mode. The phase lag of the AFM cantilever oscillations was recorded simultaneously in order to detect changes in a material contrast of investigated samples before and after the scratching.

AFM based scratching experiments were carried out in contact mode with increased normal load necessary to produce desired changes - deformation of graphene and its tearing. Graphene was scratched only once, both in the case of line scratching as well as in the case of scratching of square domains. The scanning velocity during the scratching was the following: 0.3–0.5 μm/*s* in the case of line scratching, and 1.5 μm/*s* in the case of square domain scratching. We did not observe an influence of the scratching velocity in the range 0.4 μm/*s*–3.5 μm/*s* on resulting graphene deformation and tearing as shown in the Supplementary material in Fig. S1. After scratchings, AFM topographic images were recorded in the tapping mode. Both imaging and AFM scratching were performed using diamond coated DCP20 probes from NT-MDT with a typical force constant of 48 N/m and with a typical tip curvature radius of 50–70 nm. These stiff cantilevers with very robust probes enabled both the AFM scratching with high normal loads up to around 20 μN as well as subsequent imaging without probe replacement. Still, in some case when diamond probes could not give clear images due to their wear and/or attached adsorbates, the imaging was performed using NSG01 probes from NT-MDT with much smaller tip curvature radius, typically around 10 nm. All AFM measurements were done at ambient conditions.

The lateral deflection of AFM cantilevers was recorded during AFM based scratching experiments in order to get information about friction between AFM tip and sample. The friction signal was calculated as the average of the difference between the lateral force signal in the forward and backward direction. Opposite to the topographic images recorded after the corresponding scratching, the presented friction maps were measured during the scratching.

Calibration of the normal force was done by force-distance measurements on hard substrate such as bare SiO_2. The normal force was then calculated as $F_N = kd$, where k is the force constant of employed DCP20 probes, and d is the displacement of the piezo-scanner for the given set-point. Calibration of the lateral force was done using the simple procedure given in Ref. [53].

For studies on wear protection by graphene films, AFM scratching both on bare and graphene covered SiO_2 substrate was done with the same normal load in order to enable straightforward comparison between these two cases. Here we considered the protection of SiO_2 since it allows a straightforward visualization of the flakes, and does not require any additional transfer steps after the exfoliation. Still, the employed method and obtained results can be applied for technologically more relevant materials on which graphene can be either directly grown or transferred, although in that case, grain boundaries and wrinkles in graphene influence its wear properties [30]. Two different cases were explored in the context of wear protection by graphene: 1. the protection by thin graphene layers, with the thickness of around 1 nm corresponding to single or bilayer graphene, and 2. the protection by thicker graphene films, with the thickness of several nanometers, between 3 nm and 5 nm, corresponding to around 10–15 graphene layers.

Raman imaging of graphene was carried out on NTEGRA Spectra confocal Raman system (NA 0.7) with approximately 1 μm spatial resolution. The excitation source was a green laser ($\lambda = 532$ nm).

3. Wear of graphene during AFM scratching

The study on wear properties of graphene we start with AFM scratching of parallel trenches in graphene/SiO_2 substrate. Corresponding topography and phase contrast images obtained with increasing normal load F_N (from 1.41 μN to 17.48 μN) are shown in Fig. 1 (a) and 1(b), respectively. Two selected cross sections are depicted in Fig. 1(c), and the change of the trench depth is given in Fig. 1(d). The trench depth increases with F_N, but there are two distinct processes. In the first one, for the normal loads below approximately 10 μN, graphene is only strained and plastically deformed. In the topographic image, plowed trenches from 1 to 8 are only slightly darker, but without any bumps and cracks. At the same time, the corresponding phase signal is similar to surrounding flat graphene implying there is no material contrast between them. On the other hand, for the normal loads above approximately 11 μN, graphene is cut and torn in an uncontrolled manner, leaving large bumps (bright spots in Fig. 1(a)) near trenches from 9 to 12. In the phase image in Fig. 1(b), trenches 9–12 are dark, with the same contrast as neighboring SiO_2 substrate, confirming that graphene is peeled off, leaving bare and scratched SiO_2 substrate. Typical plateau with uncovered SiO_2 substrate left after the tearing and peeling of graphene is more emphasized with encircled area in enlarged image of trench 12 in Fig. 1(e), as well as in the corresponding cross section along dotted line (SiO_2 plateau is represented with the drop in the height profile on the left side, between the graphene and the trench).

Further insights into graphene wear properties are obtained by AFM scratching of finite domains, not only along single line. Fig. 2 depicts the results for such an example where six square domains (with size 1.5×1.5 μm^2) were plowed for increasing normal load F_N