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A novel approach to decrease friction of graphene

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ABSTRACT

Graphene as a well-known solid lubricant is widely used in micro- and nano-scale mechanical devices, decreasing the friction of graphene as far as possible is a perpetual task to improve the performance of these devices. A novel approach was proposed to decrease the friction of graphene against atomic force microscopy (AFM) tip by plasma treatment of the substrate. The plasma treatment of the substrate enhances the adhesive attraction between graphene and SiO_2 substrate by generating stronger van der Waals attraction. Enhancing the adhesive attraction can indeed decrease the friction of graphene, regardless of the thickness of graphene and the kinds of AFM tip. Longer time of plasma treatment results in stronger adhesive attraction, leads to smaller friction. The decreased friction is mainly due to the combined action of the suppressed puckering of graphene and the reduced ability of graphene to adjust its atomic configuration. This novel approach will promote the engineering application of graphene and other related 2D materials as lubricants in MEMS/NEMS.

1. Introduction

Micro- and nanoelectromechanical systems (MEMS/NEMS), such as accelerometers in air bags, ink pumps in inkjet printers and micro-mirror arrays in computer projectors, have a major impact on the manufacturing industry [1]. However, the effects of adhesion and friction are challenging the development and commercialization of MEMS/NEMS devices [2]. For example, a MEMS actuator (electrostatic lateral output motor) operated in vacuum fails very quickly due to the catastrophic wear of device components (micro-dimples) [3]. Graphene, as a building unit for graphite, is an ideal candidate for solid lubricants that can be used to reduce the adhesion and friction between contact surfaces in MEMS/NEMS devices while protecting the coated surface [4–6]. Considering that anti-friction and wear-resistance is an eternal subject for promoting the engineering application of graphene in MEMS/NEMS devices, more new and practical approaches are needed to decrease the friction of graphene.

In previous studies, Lee et al. found the reduced friction can be achieved by increasing the number of graphene layers on SiO_2 substrates [7]. Meanwhile, this good frictional performance was also obtained on graphene deposited on mica, where the graphene was strongly bound to the substrate [7]. Wang et al. studied the tribology of reduced graphene oxide sheets covalently assembled onto silicon wafers, and obtained the good friction reduction and antiwear ability, which was ascribed to the covalent bonding to the substrate [8]. Analogously, the covalent bonding between graphene and substrate interface decreasing the friction of graphene was also discovered by Paolicelli et al. They found the shear strength and work of adhesion on graphene-Ni(111) interface were always smaller than that on graphene-SiO_2 interface, which resulted form the covalent bonding in graphene-Ni(111) interface [9]. However, by increasing the number of graphene layers to decrease the friction can not meet the requirements of ultrathin lubricating layer in nano-scale mechanical devices. Forming the covalent bonding is not applicable to most of the interfaces in engineering application. But these previous studies imply that the stronger interaction between graphene and underlying substrates enables superior tribological performance.

Since graphene was discovered on SiO_2 surfaces by optical measurement, SiO_2 substrates became the first choice to design and conduct various experiments on graphene, including the measurement of fundamental properties and device fabrication [10]. Meanwhile, NEMS/MEMS were usually fabricated from single- and multilayer graphene sheets by mechanically exfoliating thin sheets from graphite over trenches in silicon oxide [11]. Silicon and silicon oxide are extremely important substrate materials for NEMS/MEMS applications [12]. But it has been experimentally established that graphene is weakly bound to SiO_2 substrates through van der Waals and/or capillary forces, which suggests the interfacial adhesion

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between graphene and SiO_2 is much weak compared with covalent bonds [13,14]. This weak interfacial adhesion will increase friction force and prevent the practical applications of graphene in NEMS/MEMS devices. How to enhance the adhesive attraction between graphene and underlying SiO_2 substrate in a practical and universal way is of great significance.

Plasma treatment has proven to be a relatively simple but effective technique for introducing some certain of chemical groups on the surface so as to improve the surface adhesion [15,16]. Furthermore, this technique can offer a wide range of surface modifications by means of altering the discharge parameters. Given this, the interfacial adhesion between graphene and SiO_2 substrate can be enhanced by plasma treating the SiO_2 surface.

Here, a novel and universal approach was proposed to decrease the friction of mechanical exfoliated graphene by plasma treatment of the substrate. The interfacial adhesion between graphene and SiO_2 substrate was enhanced to varying extents with different time of plasma treatment. The friction of graphene was investigated by atomic force microscopy (AFM). Plasma treatment of the substrate enhances the adhesive attraction between graphene and SiO_2 substrate. The enhanced adhesive attraction between graphene and SiO_2 substrate decreases the friction force due to the combined actions of two aspects.

2. Experimental

N-doped Si covered with dry oxidation generated 300 nm-thick SiO_2 was used to prepare the substrates (called SiO_2 substrate in this article). The SiO_2 substrates were sonicated in acetone solution, ethanol solution and deionized water successively for 10 min, and then dried with nitrogen. The surface roughness (Ra) of the substrates was measured by AFM (MFP-3D, Asylum Research) topographies with 1 μm × 1 μm areas to ensure they were cleaned up. Each value of Ra was the average of five measurements on adjacent regions. Direct voltage glow-discharge plasma treatment was performed on these cleaned SiO_2 substrates in the plasma cleaner (PDC-32G-2, Harrick Plasma, USA). After the plasma cleaner chamber had being vacuumized, the power for plasma treatment was set to 10.5 W, and the treated time was set to 1 min, 3 min and 10 min respectively for different substrates. The surface wettability of the treated substrates was measured in 2 min after they were taken out from the vacuum chamber by determining the contact angle (CA) with a deionized water droplet of volume 3 μl and a glycerol droplet of volume 3 μl via contact angle meter (OCA15EC). The values were taken the average of three repeat measurements, and the error was below 3°.

Graphene was prepared by mechanically exfoliating from the Highly Oriented Pyrolytic Graphite (HOPG) and deposited onto the cleaned SiO_2 substrates in 1 min after the substrates were taken out from the vacuum chamber [17]. The identification of the prepared graphene on the substrates was realized by Raman spectroscopy (inVia Reflex) using a 533 nm laser wavelength. The thickness and location of graphene on the substrates were determined by optical microscopy (Motic/PSM1000) and AFM. The topographies of graphene were also obtained by AFM at tapping mode using silicon probes with a nominal normal spring constant of 3 N/m and tip radius less than 10 nm (Multi75Al-G, Budget Sensors). SEM (HITACHI S-4800) was applied to measure the tip radius and to determine whether it wears or not.

Nanotribological properties of graphene were studied by measuring the friction force as a function of normal force in ambient conditions (20–30 °C and 30%–40% R.H). Three kinds of different probes, whose parameters were presented in Table S1, were used for the friction test. Note that the probe used in the article for friction test was the PPP-LFMR (Nanosensors). For quantitative force measurement, normal and lateral force calibrations of AFM tips were performed prior to friction test via noncontact method [18]. The adhesion force was determined by measuring the pull-off force which was the maximum force to pull the AFM tip out of contact with the surface. The normal force used for adhesion force measurement was 5 nN, and the loading rate was 1 Hz. The error of the adhesion force was calculated as the standard deviation of five measurements recorded on different regions of the surface. Before and after friction test, the adhesion force between the AFM tip and graphene was also measured to exclude the influence of the AFM tip wear on the experimental results. Friction tests were performed by obtaining the friction loops in the areas of 300 nm × 300 nm with the scanning speed of 600 nm/s. Each friction loop corresponds to a complete trace and retrace scan over the same line, and the friction force equals to the half difference between the lateral forces obtained through trace and retrace scanning. The quantitative friction force was based on the average of the values measured through repeating the friction test 3 times. Matlab software (MathWorks, USA, version 7.14) was applied to fit the friction force relative to normal force curves based on the general equation.

3. Results and discussion

3.1. The decrease of friction of graphene with different thicknesses

Before AFM experiments, optical microscopy and Raman spectroscopy are applied to confirm the graphene is successfully deposited on SiO_2 substrates (see Supplementary Section A and B). Based on the color contrast in optical microscopy image (Fig. S1) and Raman characteristic peaks of graphene, G peak (1580 cm^{-1}) and 2D peak (2680 cm^{-1}), in Raman spectra (Fig. S2), it can be considered that the graphene is well prepared on the substrates.

The thickness of graphene is an important factor in friction because the friction force of graphene depends on the thickness of graphene layers [19]. The thickness of graphene is generally determined by AFM and Raman spectra [20,21]. AFM topographic image of graphene on untreated SiO_2 substrate is shown in Fig. 1(a), along with cross-sectional height profiles. The areas used for friction test are marked by number one, two and three, whose thicknesses are about 0.8 nm, 1.5 nm and 2.5 nm respectively. The theoretical thickness of a single-layer graphene is reported to be 0.35 ± 0.01 nm [22]. However, the measured thickness by AFM may be larger than the theoretical value due to the instrumental offset that is caused by the different surface interactions between the substrate and graphene [21–23]. Generally, the thickness of a single-layer graphene on SiO_2 substrate appears to be 0.6–1.2 nm. The three areas of graphene on untreated SiO_2 substrate are also characterized by Raman spectra (see Supplementary Section C). Based on the Lorenz multi-peaks fitting of 2D peaks, the numbers of sub-2D peaks of the corresponding graphene are 1, 6 and 2 respectively, which means the numbers of graphene layers are 1 layer, 3 layers and greater than 5 layers respectively [20]. Combining the thickness acquired from AFM topographic images with the Raman spectra, it can be concluded that the thicknesses of 0.8 nm, 1.5 nm and 2.5 nm correspond to the number of graphene layers are 1 layer, 3 layers and 6 layers respectively. In order to eliminate the influence of the thickness on friction, the thicknesses of graphene, whose underlying SiO_2 substrates treated by plasma for different time, are selected in the same level with above three thicknesses.

Fig. 1(c) shows the friction image of graphene on untreated SiO_2 substrate and corresponding cross-sectional profile. Some damages occur at the thin edges of graphene after the continuous contact scan by AFM tip as the white solid oval shown. Owing to this