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Adhesion energy of few layer graphene characterized by atomic force microscope

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ABSTRACT

This paper presents a generic approach to characterize and analyze the adhesion energy between graphene and different materials using nanoindentation of an atomic force microscope (AFM), which is extremely essential and critical for variety of graphene based micro- and nano-devices. AFM was used to press a free-standing graphene beam down to a substrate. During the retraction, the adhesion force (named as the secondary pull-off force) was measured to analyze the adhesion energy between the graphene beam and the substrate. This approach is easy for manipulation and it can detect the adhesion energy after the device fabrication. According to our measurement, the graphene/SiO_2, graphene/gold, and graphene/graphene adhesion energies per area are approximately 270 mJ/m^2, 255 mJ/m^2, and 307 mJ/m^2, respectively. This result was used to predict the performances and guide the design of graphene M/NEMS devices.

1. Introduction

Graphene, initially generated by Novoselov et al. [1], is an attractive material due to its unique electrical and mechanical properties. The ultra-high carrier mobility (200,000 cm^3/V s [2]) makes it an ideal candidate for future microelectronic applications [3–11]. Its thermal conductivity is 5000 W/mK [12], and its Young's modulus is about 1 TPa [13], making it an excellent material for micro- and nano-electromechanical systems (M/NEMS) [14–19]. As the geometry of mechanical structures is downscaled, the adhesion force plays a more and more crucial role. Quite a few papers reported that the adhesion force significantly influences the mechanical behavior of graphene and the performance of graphene M/NEMS devices [16,19–24]. It is responsible for the hysteresis effect of graphene MEMS switches [16], and it can clamp the graphene beam to substrate and causes failure [19]. In order to have a better understanding of bonding mechanism and better control of the mechanical release of the graphene from the substrates in graphene M/NEMS devices, it is highly important to fundamentally investigate 2-dimensional material's surface energy of graphene. To measure the adhesion energy, Koenig et al. [25] transferred graphene flakes on top of SiO_2 with numerous cavities, and experimentally peeled the graphene off through a pressure difference. Yoon et al. [26] grew graphene on copper foil by chemical vapor deposition, and mechanically peeled graphene off from copper substrate. Vahdat et al. [27] used vibrational spectroscopy to investigate the adhesion force between graphene and SiO_2. All of the above approaches are only suitable to measure adhesion energy between graphene and one type of substrate (without a device construction). Therefore, a generic approach is highly necessary. In this paper, we present an easy manipulation approach which can directly detect the adhesion energy between graphene and many different substrate materials. Moreover, our method allows us to measure the adhesion energy after device fabrication. This is very critical because the surface energy may change due to the fabrication process, such as lithography, etching, or even surface modification processes.

2. Experimental details, results and discussion

2.1. Secondary pull-off force

The sample preparation started with transferring a few layers of mechanically exfoliated graphene on a Si substrate with SiO_2 300 nm thick on top, and etching randomly shaped graphene

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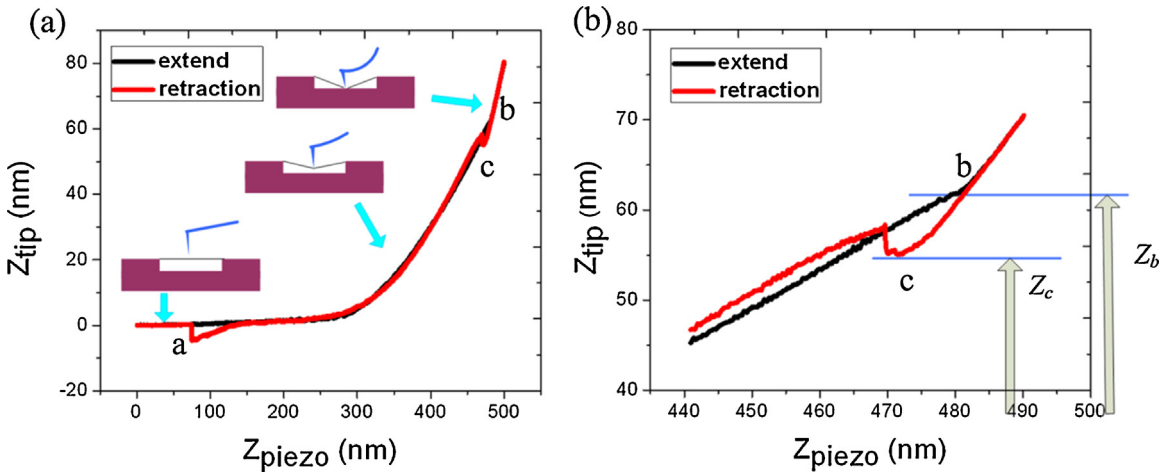

Fig. 1. Secondary pull-off force (SPF) measurement. (a) Z_{tip} vs Z_{piezo} indentation curve (extend and retraction curve). (b) Zoom in of SPF part in a. The SPF can be easily derived from the AFM cantilever deflection difference multiplies AFM spring constant K.

flakes into rectangular beams by O_2 plasma. The thinnest graphene flake that we chose was bi-layer because monolayer graphene is very easy to degrade and break down during operation as an NEMS device (NEMS switch) [21], while a few layers of graphene usually perform much better. The electrode fabrication involves photolithography, Cr (10 nm)/Au (100 nm) electron-beam evaporation, and metal lift-off. Buffered oxidize etchant (BOE) was applied to etch SiO_2 beneath graphene, and release the free-standing structures, followed by critical point drying to avoid stiction. We fabricated graphene beams with different lengths. The width of the beam is 1–3 μm, and the gap between SCG and substrate is 300 nm. The adhesion force between graphene and substrate was measured by AFM indentation, since AFM is sensitive enough to detect small surface forces at nanoscale [28,29]. Before measurement, samples were annealed in 5% H_2/95% N_2 at 300 °C for 1 h to clean the graphene surface (remove the contaminants from the tape during the graphene transferring process and photoresist residual from the photolithography). All the AFM measurements described in this paper were implemented in a chamber filled with dry N_2 instead of ambient environment to minimize water vapor. Dynamic mode AFM instead of contact mode was chosen for high-resolution topographic imaging (Fig. 2a), to minimize the tip's shear interaction with the delicate graphene beam to avoid damage. The driving parameters of an AFM cantilever were chosen to place the oscillator in the net attractive regime during dynamic mode imaging, as monitored via the phase signal. When the AFM was located above the graphene beam, the AFM tip and the graphene beam were brought together so that the vertical oscillation of the AFM cantilever reduced to zero and a contact was achieved. The relationship among the graphene beam displacement, Z_{beam}, the piezo stage movement (here beneath sample), Z_{piezo}, and the AFM cantilever deflection, Z_{tip}, is

$$Z_{beam} = Z_{piezo} - Z_{tip} \tag{1}$$

Fig. 1a is the indentation curve demonstrating the relationship between Z_{tip} and Z_{piezo}. A larger slope indicates a higher local stiffness. During extension, a sudden slope increase took place at position b (Fig. 1b), indicating that the graphene was pressed down and started to be in contact with the stiff substrate. A very weak "jump-to-contact" phenomenon was observed. The AFM tip and the contact part of a graphene beam moved together during indentation without separation due to the elastic force from graphene. Two forces were applied on them at position b: elastic force from the AFM cantilever, F_{afmb}, and the elastic force from the graphene beam, F_{grb}. Due to a state of equilibrium, the relationship between the two forces is given by:

$$F_{afmb} + F_{grb} = 0 \tag{2}$$

During retraction an abrupt separation took place between the graphene beam and the substrate at position c instead of b, where a kink slope and a sudden slope were observed, because of the adhesion force. Three forces were considered at position c: the elastic force from the graphene beam, F_{grc}, the elastic force from AFM cantilever, F_{afmc}, and the adhesion force between the graphene beam and substrate, F_{spf}, named as secondary pull-off force (SPF). Because they were in a state of equilibrium, the relationship is the following:

$$F_{grc} + F_{afmc} + F_{spf} = 0 \tag{3}$$

From b to c, the deformation of graphene beam kept constant because the AFM tip was still in contact with the substrate. Therefore, the elastic force of the graphene beam at position b should be equal to that at position c:

$$F_{grb} = F_{grc} \tag{4}$$

The SPF can be derived by Hooke's law:

$$F_{spf} = -F_{grc} - F_{afmc} = F_{afmb} - F_{afmc} = K(Z_b - Z_c) \tag{5}$$

where K is the spring constant of AFM cantilever, Z_b and Z_c are the deflection of AFM cantilever at b and c, respectively. Therefore, the SPF can be easily derived from the AFM cantilever deflection difference multiplies AFM spring constant K.

We measured SPF at 3 different positions described in Fig. 2a using one AFM tip. Although the slopes of the 3 indentation curves are different, the SPF values are identical (Fig. 2b), demonstrating that SPF does not strongly depend on the indentation position. It is mainly relevant to the shape of AFM tip, AFM cantilever spring constant, and contact materials. After 9 times of indentation, the graphene beam was still in good shape (Fig. 2c), proving that this approach is unlikely to cause damage on graphene devices if the force applied is well controlled. The Raman spectra pre and post measurements (Fig. 2d) show that the graphene beam has very small D peak around 1350 cm^{-1}, indicating negligibly small defect (or damage) and further proving that the SPF method is unlikely to damage the graphene devices.

2.2. AFM calibration

Before SPF measurement, we calibrated the AFM. The "reversal imaging" technique was used to measure the AFM tip radius,