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Direct measurement of graphene adhesion on silicon surface by intercalation of nanoparticles

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We report a technique to characterize adhesion of monolayered/multilayered graphene sheets on silicon wafer. Nanoparticles trapped at graphene-silicon interface act as point wedges to support axisymmetric blisters. Local adhesion strength is found by measuring the particle height and blister radius using a scanning electron microscope. Adhesion energy of the typical graphene-silicon interface is measured to be 151 ± 28 mJ/m^2. The proposed method and our measurements provide insights in fabrication and reliability of microelectromechanical/nanoelectromechanical systems.
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Graphene, the monolayer of carbon atoms packed into a two-dimensional honeycomb lattice, has attracted much attention in the scientific community because of its ultrahigh mechanical strength, conductivity with high electron mobility, and optical transparency. Whether graphene is a promising material for transparent or stretchable electronics[1–4] depends predominantly on the nanostructure's mechanical integrity and ability to integrate or to adhere to electronic substrates. There is, therefore, an urgent need for experimental methods to characterize the mechanical properties and adhesion behavior. However, viable techniques remain scarce despite the voluminous literature on theoretical and molecular dynamics simulations. Recently, direct force measurements using atomic force microscope (AFM) indentations were performed on graphene beams clamped at opposite ends,[5] and also on freestanding graphene sheets suspended over lithographically etched holes.[6] The measured changes in indenter displacement as a function of the applied load allowed researchers to find the elastic modulus in the range of 0.5–1.0 TPa and an ultimate strength of 130 GPa.[5,6] These results are consistent with theoretical computation.[7] On the other hand, measuring graphene adhesion on dissimilar substrates is difficult since the extremely thin sheet is hard to handle and prone to damage by clamps and fixtures as in the conventional peel test. In this paper, we describe a simple method to quantitatively measure local graphene adhesion on silicon surface, and report the value of adhesion energy of the dissimilar interface.

Silicon wafer (100) with a 280-nm-thick oxide layer was chosen as the substrate.[8,9] The wafer was diced into 1×1 cm^2 square pieces, cleaned with alcohol, and dried with nitrogen. Gold nanoparticles (from BBInternational Ltd., Cardiff, UK) in diameter $2R \approx 50$ nm in an aqueous colloidal suspension with concentration of 4.5×10^{10} particles/ml or silver particles with diameter $2R \approx 80$ nm and 1.1×10^9 particles/ml were used in the experiments. They were spread as randomly and evenly as possible on the silicon substrate and then left to completely dry out under ambient conditions. Clustering of the particles was inevitable among the isolated ones. Graphene sheets were mechanically cleaved from the surface of highly oriented pyrolytic graphite (HOPG) (ZYH grade from NT-MDT Co., Moscow, Russia. Note that the ZYH grade is a common standard grade that notifies the perfection of the HOPG samples.), using the celebrated method of Scotch tape peeling.[10,11] The tape attached with small flakes of graphite was then brought into contact with the Si substrate in dry condition, trapping a number of prespread particles at the graphene-silicon interface. The thick silicon substrate suffered negligible deformation and was taken to be rigid, while the thin graphene sheet constituted most of the elastic deformation. Attractive intersurface forces (e.g., van der Waals) pulled the graphene sheets into intimate contact with the substrate. Mechanical equilibrium was reached when the planar graphene-silicon "surface tension" contracted to an axisymmetric blister around the wedging particle in the center. The interfacial strength and adhesion energy was found by measuring the particle height and the blister radius. For fixed particle dimension, the larger the blister, the lower the adhesion strength. Mean value of the stochastic adhesion energy across a large interface can therefore be found. AFM (Agilent 5500, Agilent Technologies Inc., Palo Alto, CA) topology scanning showed the average graphene samples to be below 2-nm-thick (~5 layers of graphene) using the *non*contact mode.

Distribution and number of blisters depend on the dimension of the graphene samples and particles concentration. Figures 1(a) and 1(b) shows a scanning electron micrograph (SEM) of a typical sample (Surpa 25, Carl Zeiss SMT Inc., Peabody, MA). Since gold has much higher atomic number than carbon, and the graphene sheets are ultrathin and virtually "transparent" to SEM electronic beam, the embedded nanoparticles appear bright and are easily detected in the SEM micrograph. Various blister geometries were observed. Isolated particles being trapped at the graphene-silicon interface and distant from the adjacent particles gave

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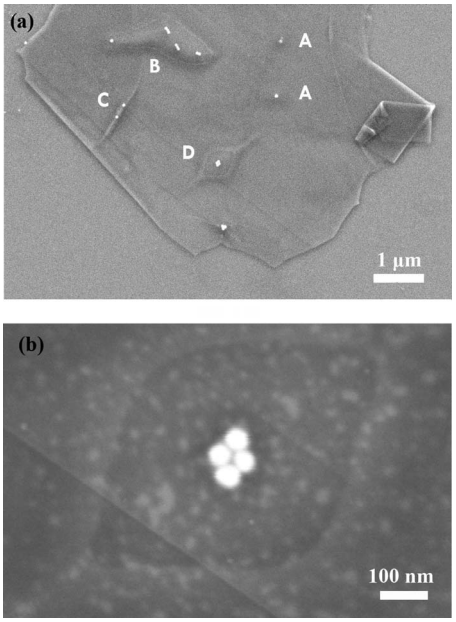

FIG. 1. SEM showing a typical graphene-silicon sample with a distribution of blisters wedged open by gold nanoparticles. (a) A number of distinct geometries are observed (scale bar=1 μm): (A) circular blister wedged open by a single particle; (B) irregular blister as a result of adjacent blisters interacting with one another; (C) elongated blister as two particles are trapped at the crystallographic ledge (note the thin layer on the right contrasting the thick multilayer on the left that appears more opaque); (D) trapezoidal blister wedged open by a particle cluster is interacting with a longitudinal buckle. (b) The trapezoidal blister (D) with the four wedging nanoparticles is magnified (scale bar=100 nm).

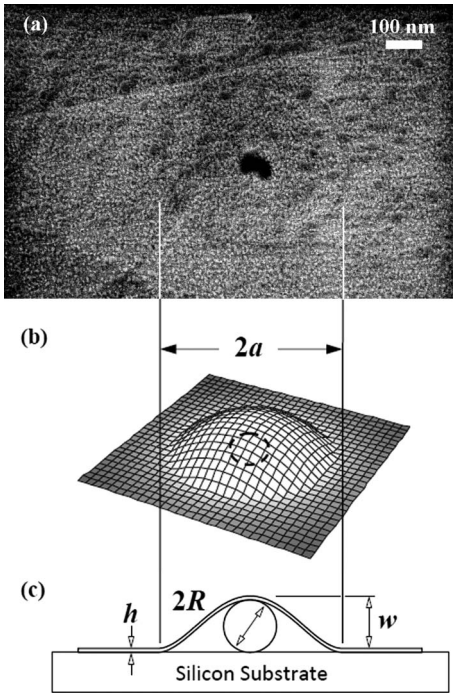

FIG. 2. A typical circular blister trapping two nanoparticles at the interface. (a) A SEM image. The contrast is inverted to highlight the blister periphery so the two trapped particles appear dark (scale bar=100 nm). (b) A 3D representation. (c) Sketch of blister for theoretical modeling.

rise to ideal circular blisters. Irregular geometry was observed when adjacent particles were in close proximity such that the circular blisters interacted and coalesced with one another. Other irregular blisters were caused by particles being trapped at the crystallographic ledges, steps, or other forms of defects since there were inevitably regions of multilayers of graphene in a sample sheet. Another distinct geometry that occurred was local buckling of the manually laid sheet that distorted the circular blister geometry on the substrate. Figure 2 shows a typical circular blister. A mechanical model can be derived based on the thermodynamic energy balance of the elastic energy stored in graphene with the interfacial adhesion energy to heal open surfaces. Ignoring the molecular structure, the graphene sheet is here taken to be a continuous linear elastic membrane with elastic modulus $E=0.5$ TPa (Ref. 5) and thickness $h=1.7$ nm (roughly five layers of graphene with the 0.34 nm monolayer thickness), being supported by the central particle to create a central blister displacement, $w=2R$. The governing equation is analogous to that of a thin membrane clamped at the periphery and being transversely loaded at the center.[12] At equilibrium, the blister contracts to a radius a and the adhesion energy is given by

$$\gamma = \lambda Eh\left(\frac{w}{a}\right)^4, \tag{1}$$

with a geometrical factor $\lambda = 1/16$. For a specific interface with fixed adhesion energy, the blister radius increases linearly with the particle size. Equation (1) is derived based on several assumptions.

(i) Graphene behaves as a flexible membrane with negligible flexural rigidity because $w \gg h$ and $a \gg h$. Membrane stretching is thus the dominant deformation mode. The classical penny crack under plate bending with $w \ll h$ requires $\gamma = [2Eh^3/3(1-\upsilon^2)](w/a^2)^2$ according to Ref. 13, which is distinctly different from Eq. (1) and inapplicable here. It is worthwhile to note that Eq. (1) predicts a linear relationship $w \propto a$ for fixed γ, while the classical penny crack requires $w \propto a^2$.

(ii) The intersurface potential is herein assumed to be effective only at intimate contact or closed interface, in that attraction vanishes once the adhering surfaces separate at the contact edge. In reality, van der Waals, electrostatic, and meniscus forces possess finite range, and a cohesive zone model is needed to better model the blister.

(iii) The substrate is taken to be rigid with negligible deformation, which is justified because of the ultrathin graphene. The wedging particle is also assumed rigid and does not exert any surface forces even though it is in direct contact with the graphene sheet. Since the particle only acts as a wedge, as long as it can support the load and does not mechanically collapse, the minor correction to Eq. (1) is negligible.

Figure 2(a) shows a SEM image of a typical circular blister with $\gamma = 124$ mJ/m^2. Despite the relatively poor contrast due to the ultrathin sheet, the periphery of the blister is distinctly identifiable to be the contact edge. An average blis-

ter possesses diameter in the range of 500–600 nm for a 50–70 nm particle. The average adhesion energy in the high vacuum SEM chamber is found to be $\gamma = 151 \pm 28$ mJ/m^2. Note that the SEM vacuum chamber might cause the air trapped in the blister void to expand and thus applies additional load on the graphene. Moreover, should the specimen be exposed to an environment such as high relative humidity, water molecules might be able to diffuse into the blister via the graphene-silicon interface, lower the adhesion strength, and cause the blister to grow. Though the literature does not give a value we can weigh against, our measurements compare favorably with relevant data to a good extent. A recent[14] paper used contact angle method to measure surface free energy of graphene sheets and reported $\gamma = 46.7$ mJ/m^2 and that of natural graphite flake to be $\gamma_{\text{graphite}} = 54.8$ mJ/m^2. Various researchers[15] adopted other experimental techniques and reported $\gamma_{\text{graphite}} = 150-200$ mJ/m^2.

The proposed method of adhesion measurement possesses several major advantages over other methods: (i) The axisymmetric geometry is free from any edge effects that are inevitable in a standard peel test. When a rectangular membrane with finite width is peeled from a substrate, the delamination front is usually curved and the uncertainty in determining the crack length and therefore adhesion energy is large. (ii) Local adhesion can be mapped over large sample surface provided the particles spread out evenly over the region of interest. (iii) Any particle can be used as wedge as long as it has suitable dimensions and is structurally rigid to support the adhering membrane. (iv) The method is applicable to any rigid or flexible substrates, though the governing Eq. (1) will have to be modified accordingly to account for substrate deformation. There is one minor shortcoming of the present method. Since γ depends on $(w/a)^4$, a small deviation in measuring w or a will lead to a significant amplification of the uncertainty in γ. However, in surrogate tests where similar interfaces (e.g., graphene adhered to silicon surface with different crystallographic orientations, amorphous silicon, silicon nitride) are compared, mere measurement of the blister radii indicates the relative adhesion strength, provided the same batch of wedging particles are used.

In conclusion, a simple and convenient particle intercalation method is reported to characterize graphene adhesion, which is essential in designing graphene based electronic devices and in gauging their reliability. Adhesion energy at graphene-silicon interface is found to be $\gamma = 151 \pm 28$ mJ/m^2.

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