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Indentation behavior of the stiffest membrane mounted on a very compliant substrate: Graphene on PDMS

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ABSTRACT

Graphene is the stiffest membrane and PDMS is one of the very compliant materials. The indentation response of a graphene monolayer mounted on a PDMS substrate (graphene/PDMS) is studied by both experimental and computational investigations. Due to the huge elastic modulus ratio between membrane and substrate (~10^6) and the very large ratio of indentation depth to membrane thickness (~10^3), the indentation deformation of graphene in the graphene/PDMS structure is analogous to that of free-standing (F-S) graphene but just with a relatively smaller indentation depth (i.e., the graphene deformation is insensitive to the appearance of PDMS substrate); the graphene can create a screening effect, which causes the PDMS substrate deformation to be insensitive to the tip geometry. In addition, with the aid of finite element method (FEM), the elastic modulus of graphene monolayer can be accurately determined from the overall indentation response of graphene/PDMS using an inverse analysis, which is determined as 0.982 TPa (very close to previously reported values). The present approach can be also extended to other 2D materials.

1. Introduction

Due to their particular electrical, thermal, chemical and mechanical properties, two-dimensional (2D) materials/structures (e.g., graphene) have attracted extensive research investigations (Geim and Novoselov, 2007; Novoselov et al., 2005; Stankovich et al., 2006; Eda et al., 2008; Xu et al., 2013). Due to a very small thickness of 2D materials (~a couple nanometers), their elastic moduli are typically measured by indentation tests. There are two types of indentation tests: (I) free standing indentation (FSI) tests performed by atomic force microscopy (AFM) (Lee et al., 2008; Frank et al., 2007; Lee et al., 2013; Bertolazzi et al., 2011; Castellanos-Gomez et al., 2012), in which graphene is mounted on the substrate with cylindrical holes, in other words, there is no substrate beneath the part of graphene indented; (II) conventional indentation (CI) tests based on commercial nanoindentor (Zhang and Pan, 2012; Chen et al., 2013a), in which graphene is mounted on the common substrate, e.g., SiO_2 or poly(ethylene terephthalate) (PET).

In FSI tests, the elastic modulus of 2D-material is obtained by fitting the measured indentation force-displacement (P-δ) relationship as the following model: (Lee et al., 2008)

$$P = \sigma_0(\pi a)\left(\frac{\delta}{a}\right) + E_g\left(q^3 a\right)\left(\frac{\delta}{a}\right)^3 \tag{1}$$

where E_g and σ_0 are the elastic modulus and the pre-stress of 2D-material, a is the radius of the cylindrical substrate hole, δ is the indentation displacement of AFM tip and q is the constant related to the Poisson's ratio ν of 2D-material. For example, E_g is determined as ~1.015 TPa for monolayer graphene from FSI tests (Lee et al., 2008). In CI tests, the overall reduced modulus (E') of 2D-material with a substrate can be determined from the measured P-δ relationship on the basis of the Oliver–Pharr method (Oliver and Pharr, 2004), and then, E_g is estimated from E' after decoupling the contribution of substrate based on the following model: (Chen et al., 2005)

$$\frac{1}{E'} = \frac{1-\nu_g^2}{E_g}\left(1 - e^{-\zeta h A^{-0.5}}\right) + \frac{1-\nu_s^2}{E_s} e^{-\zeta h A^{-0.5}} \tag{2}$$

where E_s is the elastic modulus of substrate, ν_f and ν_s are the Poisson's ratios of 2D-material and substrate, respectively, A is the contact area, h is the thickness of 2D-material and ζ is

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the commercial indenter tip geometric factor ($\zeta = 1.3$). Based on Eq. (2), E_g is then identified as 0.89 TPa for monolayer graphene (Zhang and Pan, 2012), which is about 10% lower than that determined from the FSI tests (Lee et al., 2008).

In important applications, e.g., nano-electro-mechanical devices or graphene reinforced polymers, 2D-materials are always attached with their substrates by the van der Waals (vdW) interaction, which might change the mechanical behavior of 2D-materials. For example, the vdW interaction between 2D-materials and substrate will eliminate the effect of the vdW interaction between AFM tip and 2D-materials (Zhou et al., 2013a, b; Cao, 2014) as well as the local out-of-plane curvature of 2D-materials, which will change the stress distribution induced by AFM tip, as reported by Song et al. (2015). Thus, studying the mechanical behavior of the 2D-materials mounted on substrate is more effective to provide a useful guideline for developing the applications based on 2D-materials. However, the overall P-δ relationship obtained in CI tests might be not good to accurately determine the elastic moduli of 2D-materials since the contribution of 2D-materials to the overall indentation modulus is very small. Consequently, the measured results are highly scattered, e.g., the E' of graphene/PET is reported as ~4.3 GPa, which is only about 16% higher than that of PET (~3.7 GPa) (Chen et al., 2013a); whereas the E' of graphene/SiO_2 (~0.305 TPa) is reported to be about four times more than that of SiO_2 (~70 GPa) (Zhang and Pan, 2012). These results obviously conflict to our common knowledge because the elastic modulus of SiO_2 is about 20 times higher than that of PET. Reducing the substrate stiffness is the most effective way to increase the contribution of 2D-materials to the overall indentation stiffness, and by doing so, the E_g of 2D-materials might be effectively determined from CI tests.

In the present work, the indentation response of a graphene monolayer (the stiffest membrane) mounted on a PDMS substrate (very-compliant matter) is measured using AFM, and the deformation mechanism of graphene/PDMS in AFM indentation is also investigated using FEM. The present work can give us a more effective understanding about the mechanical behavior of 2D-materials after incorporating the substrate effect, and thus, it provides a great help for developing the important applications based on 2D-materials.

2. Methods

2.1. Experimental method

In the present work, the sample is made by a graphene monolayer covered with a very-compliant substrate (PDMS) ($10 \times 10 \times 2$ mm, where the thickness is 2 mm), as shown in Fig. 1. As to our best knowledge, this is the first time to investigate the indentation response of the stiffest membrane on the very compliant substrate.

A two-component PDMS from Dow Corning (Sylgard^R 184) is selected. The mixing ratio of PDMS base to curing agent is 10:1 and the curing condition is 85 °C for 4 h. The monolayer graphene on copper foil grown by chemical vapor deposition (CVD) (ACS Materials, USA) is used. Graphene is transferred to the PDMS substrate following the common procedure reported by Chen et al. (2013b). The graphene grown on copper foil is first flattened between two glass slides under a gentle pressure, and then attached to the PDMS substrate. A small pressure (~0.05 MPa) is applied on the foil by glass slide for 1 h to make sure the foil fully adhere to the substrate. The upper graphene layer covered on the top of copper foil is removed by oxygen plasma (100 w for 3 min), and then the underlying copper foil is etched in ammonium persulfate solution (1 M) for 1 h. The deionized water is used to rinse the sample to remove residual etchant and then the sample is dried with N_2.

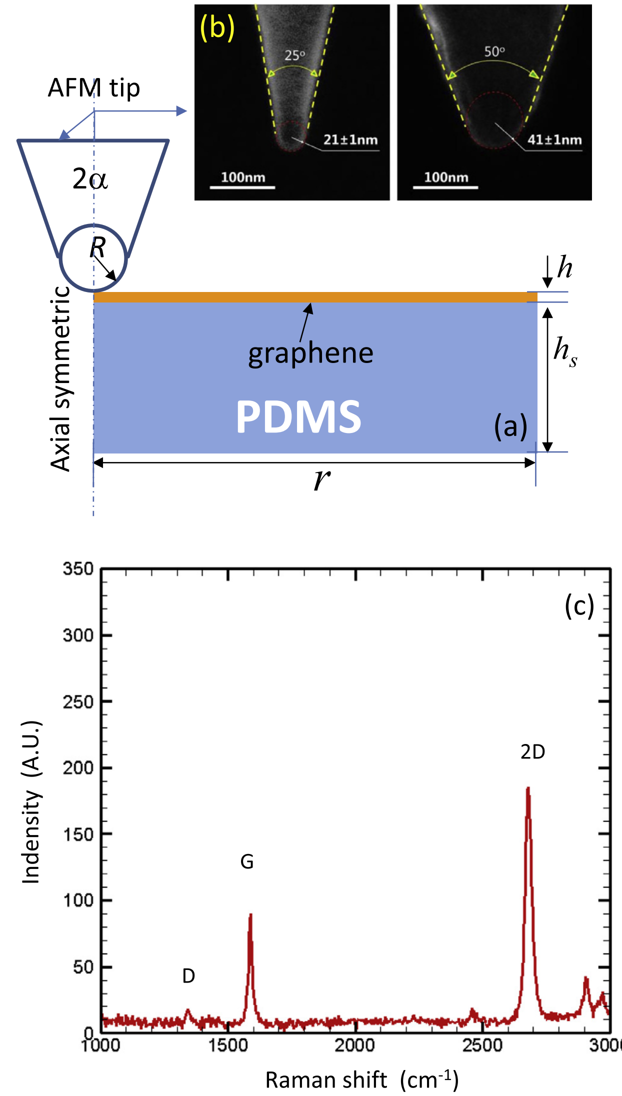

Fig. 1. Images of the indentation of graphene/PDMS. (a) Schematic of nanoindentation of graphene/PDMS; (b) SEM images of AFM tips; (c) Raman spectroscopy of graphene/PDMS at 532 nm.

The monolayer graphene on PDMS is confirmed by Raman spectroscopy (see Fig. 1(d)). The indentation response of graphene/PDMS is measured by AFM (NanoWizard 3, JPK), as illustrated in Fig. 1(a). Two different diamond AFM tips (APPNANO) are selected in the present work. Since the top-part of AFM tip (typically in pyramidal shape) is commonly approximated to be spherical in the indentation tests, the tip size is characterized by an equivalent radius (Lee et al., 2008, 2013; Bertolazzi et al., 2011). The tip sizes are characterized as: $R = 21$, 41 nm (see Fig. 1(b)).

Overall, there are five samples tested; 60 P–δ curves were measured. The measured P–δ curves are highly repeatable; the results obtained from different samples are statistically indistinguishable.

2.2. Finite element modeling method

All FEM simulations are carried out using ABAQUS v6.10. In FEM, both the sample and the AFM tip are simplified to be axial symmetric, e.g., AFM tip is considered to be spherical and the sample is modeled as a circular membrane mounted on a cylindrical substrate. Since the thickness of graphene is at atomic level and its bending stiffness is very small (Wei et al., 2013), graphene can be modeled using the membrane elements. The AFM tip is consid-