



Liquid-assisted, etching-free, mechanical peeling of 2D materials



Yue Zhang, Qingchang Liu, Baoxing Xu*

Department of Mechanical and Aerospace Engineering, University of Virginia, Charlottesville, VA 22904, USA

ARTICLE INFO

Article history:

Received 5 August 2017

Received in revised form 24 August 2017

Accepted 24 August 2017

Available online 6 September 2017

Keywords:

2D materials
Mechanical peeling
Surface wettability
Liquid environment
Theory

ABSTRACT

Mechanical peeling is a well-known route to transfer a single piece of two-dimensional (2D) materials from one substrate to another one, yet heavily relies on trial and error methods. In this work, we propose a liquid-assisted, etching-free, mechanical peeling technique of 2D materials and systemically conduct a theoretical study of the peeling mechanics for various 2D materials and substrates in a liquid environment. The surface wettability of 2D materials and substrates and surface tension of liquids have been incorporated into the peeling theory to predict the peel-off force. The theoretical model shows that the peel-off force can be significantly affected by liquid solvents in comparison with that in dry conditions. Moreover, our analysis reveals that the mechanical peeling-induced selective interface delamination in multilayered 2D materials can be achieved by employing a liquid environment. These theoretical results and demonstrations have been extensively confirmed by comprehensive molecular dynamics simulations and good agreement is obtained between them. The present work in theory provides a new approach of peeling 2D materials from substrates and can also be extended for peeling thin films and membranes.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Atomically thin two-dimensional (2D) materials, also referred to as monolayer materials, have attracted extraordinary attention since the discovery of graphene [1]. The continuous interest of 2D materials is largely motivated by application spaces ranging from flexible electronics [2] to high-efficiency water purification, [3] from transparent films [4] to anti-corrosion coatings, [5] and from highly sensitive gas sensors [6] to drug delivery systems, [7] because of their superlative properties including strength, conductivity, flexibility and transparency which are beyond their bulk counterparts. To realize the myriad of these applications, the transfer of 2D materials from their growth/processed substrate to target substrate with a clean surface in a low-cost and high-yield manner is very critical.

Numbers of transfer methods have been developed over the last decades from the earliest mechanically peeling of graphene from graphite by scotch tape [8]. For instance, to isolate a single layer film from their bulk materials, through the balance of the solvent-2D material interaction in different solvents, liquid-phase mechanical exfoliation has been used to produce graphene, [9] hexagonal boron nitride, [10] transition metal dichalcogenides, [11] and layered metal oxides [12]. To transfer graphene CVD-grown on metal substrates (e.g. Fe, Ru, Co, Ni, and Cu), chemical etching of the seed metals by their etchants or electrochemical delamination

of graphene and substrates have been proposed [4,13,14]. In the transfer of MoS₂, ultrasonication-induced microbubble in a liquid environment is developed to help delaminate the MoS₂ layers from substrate, [15] and this similar mechanical technique is also applied to roll-to-roll technique in the transfer of large-area 2D materials [16].

From the mechanical exfoliation to environment-assisted transfer, most transfers involve the use of chemicals, sometimes with the employment of scarifying layers, in particular, in the transfer of CVD-grown 2D materials onto target substrates. In principle, the successful transfer of a film is to apply a peel-off force that leads to an energy release rate at the interface beyond the critical one, and the presence of chemicals generally decreases the critical energy release rate, thus promoting the transfer. These transfer processes inevitably lead to degradation and damage (e.g. failure or contamination) of 2D materials, [17,18] and consumption of the substrates [19]. Generally, the adhesive interactions between most 2D materials and substrates are van der Waals force [20–22]. In comparison with a direct chemical degradation to substrates, the presence of liquid molecules will affect physical interactions at the interfaces between film and substrate and can be utilized to regulate their interfacial energy without the need of chemical etching.

In the present study, we will introduce in theory an alternative approach of transferring 2D materials in a liquid environment. This approach relies on the surface wettability of both 2D materials and substrates to liquid environments and is free of chemical reaction. A mechanics theory is proposed to quantitatively probe the effect

* Corresponding author.

E-mail address: bx4c@virginia.edu (B. Xu).

$$\left(\frac{F}{b}\right)_{\min} = \begin{cases} \frac{-1 + \sqrt{2\left(\frac{1}{t_1 E_1} + \frac{1}{t_2 E_2} + \dots + \frac{1}{t_n E_n}\right)[G_{m-t_{n+1}} - \gamma_l(\cos\theta_{tl_n} + \cos\theta_{tl_{n+1}})]}}{\frac{1}{t_1 E_1} + \frac{1}{t_2 E_2} + \dots + \frac{1}{t_n E_n}}, & 0^\circ \leq \alpha < 90^\circ \\ - (1 - \cos\alpha) + \sqrt{(1 - \cos\alpha)^2 + 2\left(\frac{1}{t_1 E_1} + \frac{1}{t_2 E_2} + \dots + \frac{1}{t_n E_n}\right)[G_{m-t_{n+1}} - \gamma_l(\cos\theta_{tl_n} + \cos\theta_{tl_{n+1}})]}}{\frac{1}{t_1 E_1} + \frac{1}{t_2 E_2} + \dots + \frac{1}{t_n E_n}}, & 90^\circ \leq \alpha \leq 180^\circ \end{cases} \quad \text{at } 1 \leq n \leq N-1 \quad (5)$$

Box I.

of liquid on peel-off process by integrating the surface wettability with classic peel-off theory and is validated by extensive molecular dynamics (MD) simulations. The peeling-induced sliding of 2D materials at the interface is also discussed. Applications in the transfer of monolayer and layered graphene-hexagonal boron nitride (h-BN) heterostructures on various substrates are demonstrated, and remarkable agreement between theoretical predictions and MD simulations is obtained.

2. Mechanics model of liquid-assisted mechanical peeling

2.1. Peeling of a monolayer 2D material

Given the weak van der Waals interaction between 2D materials and substrates, in addition to the vertical peeling from the substrates, a lateral sliding of 2D materials along the substrates may happen during the peeling process [23]. Without loss of generality, assume there is a sliding distance Δd and peeling length of Δl when a monolayer 2D material with width of b is peeled off from a substrate by a peel-off force F at the peel-off angle of α in a liquid environment, as illustrated in Fig. 1a. Consider this peeling process is quasi-static, the energy balance among the work done by peel-off force W^F , elastic deformation of the 2D material $E_{\text{deformation}}$, and surface energy between solid and liquid E_{surface} will lead to [24,25]

$$W^F + E_{\text{deformation}} = E_{\text{surface}} \quad (1)$$

where $W^F = F(1 - \cos\alpha)\Delta l + F\cos\alpha\Delta d$, and $E_{\text{deformation}} = \frac{F^2(\Delta l + \Delta d + |\Delta l - \Delta d|)}{4bEt}$, where $\frac{\Delta l + \Delta d + |\Delta l - \Delta d|}{2}$ represents the length of unadhered thin film, E and t are the Young's modulus and thickness of the monolayer 2D material, respectively. Due to the presence of liquid, we have $E_{\text{surface}} = (\gamma_{tl} + \gamma_{sl} - \gamma_{ts})b\frac{\Delta l + \Delta d + |\Delta l - \Delta d|}{2}$, and with the help of the Young's equation $\gamma_{tl} = \gamma_t - \gamma_l\cos\theta_{tl}$, $\gamma_{sl} = \gamma_s - \gamma_l\cos\theta_{sl}$, we have $E_{\text{surface}} = [(\gamma_t + \gamma_s - \gamma_{ts}) - \gamma_l(\cos\theta_{tl} + \cos\theta_{sl})]b\frac{\Delta l + \Delta d + |\Delta l - \Delta d|}{2}$, where γ_t , γ_s and γ_l are the surface tension of 2D material, substrate and liquid, respectively. γ_{ts} , γ_{tl} and γ_{sl} are the interface tension between 2D material and substrate, 2D material and liquid, and substrate and liquid, respectively. θ_{tl} and θ_{sl} are the contact angle between 2D material and liquid, and substrate and liquid at the equilibrium, respectively, and are employed to characterize the surface wettability of 2D material and substrate, respectively. The parameter λ is the sliding factor and is defined as $\lambda = \frac{\Delta l}{\Delta l + \Delta d}$. At $\lambda = 1$, there is no lateral sliding and only a vertical peeling of 2D material occurs; at $\lambda = 0$ there is a purely lateral sliding without vertical peeling. Therefore, the peel-off force per unit width can be written as

$$\frac{F}{b} = \frac{-2(\lambda + \cos\alpha - 2\lambda\cos\alpha)Et}{1 + |2\lambda - 1|} + \sqrt{\frac{4(Et)^2(\lambda + \cos\alpha - 2\lambda\cos\alpha)^2}{(1 + |2\lambda - 1|)^2} + 2Et[G_{ts} - \gamma_l(\cos\theta_{sl} + \cos\theta_{tl})]} \quad (2)$$

where $G_{ts} = \gamma_t + \gamma_s - \gamma_{ts}$ is the interface adhesion energy between the 2D material and substrate in dry conditions.

Generally, the elastic deformation is very small during the peeling of most 2D materials such as graphene due to ultrahigh

in-plane stiffness, [26,27] and the effect of $E_{\text{deformation}}$ on the peel-off force can be neglected (see Supplementary Figure S1a and b). Note that when the 2D materials possesses a low in-plane stiffness such as phosphorene, [28–30] the elastic deformation effect may become obvious (see Supplementary Figure S1c and d). For simplification, with the neglectful elastic deformation, Eq. (2) can be written as

$$\frac{F}{b} = \frac{1 + |2\lambda - 1|}{2(\lambda + \cos\alpha - 2\lambda\cos\alpha)} [G_{ts} - \gamma_l(\cos\theta_{sl} + \cos\theta_{tl})]. \quad (3)$$

Eq. (3) shows that there is a minimum peel-off force F/b at $\alpha = 0^\circ$, where the peeling distance Δl is zero, i.e. $\lambda = 0$, and only lateral sliding of 2D materials along the interface occurs. Besides, when the peeling angle $0 < \alpha < 90^\circ$, the peel-off force reaches a minimum value at $\lambda = 0.5$, where there is an equal contribution of vertical peeling and lateral sliding in the peeling of 2D materials from substrate. When the peeling angle $\alpha \geq 90^\circ$, the peel-off force has the minimum value at $\lambda = 1$, where there is only vertical peeling and the lateral sliding will not happen. Under this circumstance, the minimum peel-off force F/b can be summarized to

$$\left(\frac{F}{b}\right)_{\min} = \begin{cases} G_{ts} - \gamma_l(\cos\theta_{sl} + \cos\theta_{tl}), & 0^\circ \leq \alpha < 90^\circ \\ \frac{1}{1 - \cos\alpha} [G_{ts} - \gamma_l(\cos\theta_{sl} + \cos\theta_{tl})], & 90^\circ \leq \alpha \leq 180^\circ. \end{cases} \quad (4)$$

Fig. 1b shows the variation of peel-off force F/b with the peeling angle α at $\theta_{tl} = 30.4^\circ$. It is shown that there exists a lowest bound for the peel-off force with the variation of λ at any given peeling angle, which is consistent with $(F/b)_{\min}$ in Eq. (4). The similar results are obtained for $\theta_{tl} = 92.5^\circ$ and $\theta_{tl} = 151.2^\circ$ (Supplementary Figure S2). We should note that when the peeling is conducted in dry conditions, and the lateral sliding is not considered (i.e. $\lambda = 1$), Eq. (3) will reduce to the classical Kendall's peeling model with the peel-off force of $\frac{F_d}{b} = \frac{G_{ts}}{1 - \cos\alpha}$ [24].

2.2. Peeling of multilayered 2D materials

When there are multilayered 2D materials on a substrate, the peel-off force required to peel a certain number of layers can also be obtained by following a similar procedure with that of a monolayer in Section 2.1. Because the minimum peel-off force is desirable in practical experiments, the minimum peel-off force in this section will be focused. Assume n layers ($1 \leq n \leq N$, N is the total number of layers on substrate) need to be peeled off, the n layers can be considered an integrated one and the rest layers and substrate is deemed a new substrate. Under this assumption, similar to Eqs. (2) and (4), the minimum peel-off force can be obtained via (see equation given in Box I)

and when $n = N$, all layers will be considered an integrated one and the separation will occur at the interface between the bottommost layer and substrate, and the minimum peel-off force will be (see equation given in Box II)

where t_n and E_n ($n = 1, 2, \dots, N$) are thickness and Young's modulus of the n th layer, respectively. $G_{m-t_{n+1}}$ and $G_{t_{N-s}}$ represent the adhesion energy between n th layer and $(n+1)$ th layer, between

Download English Version:

<https://daneshyari.com/en/article/5014443>

Download Persian Version:

<https://daneshyari.com/article/5014443>

[Daneshyari.com](https://daneshyari.com)