Raman Spectral Band Oscillations in Large Graphene Bubbles

Yuan Huang,[1,†] Xiao Wang,[1,†] Xu Zhang,[1] Xianjue Chen,[1] Baowen Li,[1] Bin Wang,[1] Ming Huang,[1,3] Chongyang Zhu,[1] Xuewei Zhang,[1,5] Wolfgang S. Bacsa,[4] Feng Ding,[1,3] and Rodney S. Ruoff[1,2,3,*]

[1]*Center for Multidimensional Carbon Materials (CMCM), Institute for Basic Science (IBS), Ulsan 44919, Republic of Korea*
[2]*Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea*
[3]*School of Materials Science and Engineering, Ulsan National Institute of Science and Technology, Ulsan 44919, Republic of Korea*
[4]*CEMES-CNRS and University of Toulouse, 29 rue Jeanne Marvig, 31055 Toulouse, France*
[5]*Institute of Applied Mechanics and Key Laboratory of Soft Machines and Smart Devices of Zhejiang Province, Zhejiang University, Hangzhou 310012, People's Republic of China*

(Received 16 July 2017; revised manuscript received 21 December 2017; published 3 May 2018)

Raman spectra of large graphene bubbles showed size-dependent oscillations in spectral intensity and frequency, which originate from optical standing waves formed in the vicinity of the graphene surface. At a high laser power, local heating can lead to oscillations in the Raman frequency and also create a temperature gradient in the bubble. Based on Raman data, the temperature distribution within the graphene bubble was calculated, and it is shown that the heating effect of the laser is reduced when moving from the center of a bubble to its edge. By studying graphene bubbles, both the thermal conductivity and chemical reactivity of graphene were assessed. When exposed to hydrogen plasma, areas with bubbles are found to be more reactive than flat graphene.

DOI: 10.1103/PhysRevLett.120.186104

The electronic and mechanical properties of graphene can be tuned by reducing the lateral size, applying strain, or introducing curvature [1–3]. Because of the impermeability, exceptional flexibility, and excellent mechanical strength of the graphene sheet, bubbles can be formed on graphene [4–7]. Theoretical studies have shown that the radius and height of a bubble are determined by the energy balance between the strain energy of graphene, the potential energy of the gas inside the bubble, and the interfacial energy of the graphene layer with the substrate [8]. Thus, by measuring the bubble size, intrinsic properties such as the adhesion energy of graphene to the substrate can be determined [9], and this method can be extended to other 2D materials [10,11].

Raman spectroscopy is a versatile tool to identify the number of graphene layers, stacking and defect types, as well as strain [12–15]. In graphene, both the G and 2D bands are sensitive to strain; this strain dependence has been used to study the properties of graphene under uniaxial or biaxial stress [16–20]. Because of static effects on bond lengths and nonadiabatic electron-phonon coupling [21], both bands are also affected by doping, achieved either by applying an electrical field [22,23] or by chemical substitution [24–26]. Raman spectroscopy has also been used to investigate the biaxial strain distribution in graphene [15,16]. Thus, Raman spectroscopy of graphene bubbles can provide valuable information on the physical properties as well as on the chemical reactivity of graphene.

Graphene flakes were prepared by mechanical exfoliation from natural graphite and transferred onto a SiO_2/Si wafer (Fig. S1) [27,28]. A schematic of the preparation procedure is shown in Fig. 1(a). The formation of bubbles is due to the presence of adsorbed molecules on the polar SiO_2 surface that evaporate when heated, forming graphene bubbles [Fig. 1(a)]. Figure 1(b) shows the optical microscopy image of a circular graphene bubble where Newton rings caused by optical interference are clearly seen [7]. More detailed discussions about the sample preparation are presented in Supplemental Material [29].

Figure S2(a) shows the AFM image of a circular bubble on the graphene surface. The radius R of this bubble is 4.7 μm, and the maximum height h_{max} is 0.5 μm [Fig. S2(b) [29]], yielding an aspect ratio of $h_{max}/R \approx 11\%$, which is similar to that previously measured for graphene bubbles on a SiO_2/Si substrate (11%) [7]. More AFM images of graphene bubbles are shown in Fig. S3 [29]. Figure S2(c) shows Raman spectra measured on a graphene flake with bubbles. The four spectra shown in Fig. S2(c) were collected at different locations in the sample numbered 1–4 (Fig. S4 [29]). For regions 1 (2)

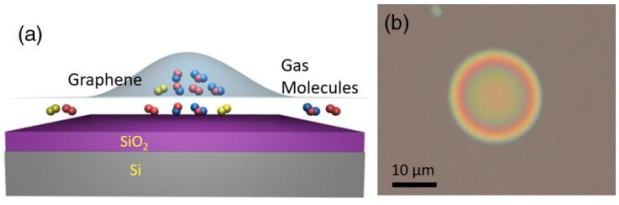

FIG. 1. (a) Schematic of a graphene bubble and trapped molecules between the SiO_2 surface and graphene. (b) Optical microscopy image of a graphene bubble (size 20 μm) on a 100 nm SiO_2/Si substrate showing Newton rings.

