Domain-boundary independency of Raman spectra for strained graphene at strong interfaces

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ABSTRACT

Strains in graphene play a significant role in graphene-based flexible devices, but many aspects of the domain boundary effects in strained graphene remain unclear, such as the evolution of Raman spectra. Here we present a systematic investigation on the domain boundary effects on the Raman spectra of strained graphene, using a designed strong interface formed by formvar resins. We achieve in single-crystal graphene by far the largest strain up to 2%, significantly improved from the previous highest value of 1.3%, as well as the redshift and splitting for its G and 2D peaks. More importantly, the Raman spectra of strained bi-crystal graphene with a domain boundary show that the spectral evolution follows the same trend as the single crystal, and this trend was also confirmed by the result in polycrystalline graphene, demonstrating that the straining effect on the G and 2D peaks of graphene at strong interfaces is actually independent of its domain boundaries, different from the previous report of graphene deposited on weak interfaces. We attribute it to the efficient interfacial stress transfer at the formvar interfaces, and believe they can provide new insights into the understanding of graphene mechanical behaviors and valuable guidance for graphene-based flexible electronics.

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1. Introduction

The outstanding electrical and mechanical properties of graphene (GR) have attracted broad interests in the next-generation electronics including high-performance semiconductor technologies and flexible applications [1]. In particular, flexible electronics stands to greatly benefit from the development of GR synthesis techniques for the access of patterning and fabricating multifunctional devices on polymer substrates [2–5]. Therefore, the study on the mechanical behaviors of GR on its supporting polymer substrates has attracted more and more research interests, including the sliding, buckling and inhomogeneous strain fields in GR that can directly influence the performance and reliability of the devices

[6,7]. Based on the well-established relation between the phonon dispersion and the strain in GR [8], Raman spectroscopy has been intensely used to quantitatively assess its mechanical behaviors owing to the high sensitivity in detecting the phonon energy variations (peak shift) of featured peaks in strained graphene (SGR) [7–22]. However, most of these previous Raman studies focus on the single-crystal GR that is obtained from the mechanical cleavage of highly oriented pyrolytic graphite (HOPG) [7–19], but the fabrication of GR flexible devices always require large-area and low-cost films that by far can only be obtained from the chemical vapor deposition (CVD) method [23], whose strain-related Raman spectra on the underlying polymer substrates can show anomalies due to the presence of domain boundaries (DBs), for instance, the inversed G peak shift as a function of the applied strain [22], leading to the puzzlement for the investigation of SGR using Raman spectroscopy: Should we only use the Raman 2D peak to determine the GR strain or all the featured Raman peaks are applicable? To solve this question, designing a reliable interface that allows an efficient stress transfer to study the DB effects on Raman spectra of SGR

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becomes an essential prerequisite.

Here we present a systematic investigation on the DB effects on Raman spectra of SGR at a designed strong interface formed by formvar resins, using CVD-synthesized single crystal (*sc*-), bi-crystal (*bc*-) and polycrystalline (*p*-) GR samples. At this interface, we achieved in SGR by far the largest strain up to 2% and 2D peak shift of 124.5 cm^{-1} for *sc*-GR, as well as apparent redshift and splitting for both G and 2D peaks. More importantly, the Raman spectra of *bc*-SGR with a DB shows that the evolution of its featured Raman peaks under strain follows the same trend as *sc*-GR, and this trend was also confirmed by the results in *p*-GR films, demonstrating that the straining effect on the Raman spectra of GR is actually independent of its DBs when it is deposited at a strong interface.

2. Experimental section

GR synthesis. Commercially available Cu foils (25-µm-thick, #46365, Alfa Aesar China Chemical Co., Ltd.) were adopted for the CVD growth of both *sc*-GR and *p*-GR. For *sc*-GR, Cu foil was heated at 230 °C in air by a hot plate for 15 min to create a layer of metal oxide before it was loaded into a CVD quartz chamber, and an atmospheric pressure CVD process was used for the growth using 20 sccm diluted CH$_4$ (0.05% in Ar), 10 sccm H$_2$ and 300 sccm Ar [24]. The typical size of *sc*-GR used in this work was ~100 µm. After visualizing the GR domains on Cu by mild oxidization [25], coalesced *sc*-GR was carefully selected for the preparation of *bc*-GR samples. *p*-GR was prepared by the low pressure CVD process using 1 sccm CH$_4$ and 10 sccm H$_2$ [23].

GR transfer. After the GR synthesis, it was transferred and prepared as the SGR samples. A thin layer (~0.5 µm) of formvar (1 wt% in chloroform) was dip-coated and cured on top of GR, then brought into contact with the polydimethylsiloxane (PDMS, 0.7 mm thick, Sylgard 184 elastomer Kit, Dow Corning, USA) before dissolving the Cu substrate using aqueous 1 M FeCl$_3$. The prepared GR/formvar/PDMS sample was then rinsed and cut into a 16 mm (effective length 8 mm) × 5 mm piece for strain loading.

Raman measurements. The straining experiments were conducted using a home-made tensile testing machine modified from a micrometer-equipped multi-axis stage (MAX313D, ThorLabs, Inc.) at 1.5 µm s^{-1}, corresponding to a tensile strain rate of 0.0175%·s^{-1} along the stretching direction (Fig. S1, Supplementary Data). The Raman spectra were carried out with a micro-Raman spectroscopy (LabRAM HR Evolution, Horiba Co., Ltd.) using a laser excitation wavelength of 532 nm with a power of 12.5 mW. A long-focal-depth 50 × objective lens with NA = 0.95 and a standard grating (1800 g/mm) were used and the laser spot size was estimated to be ~1 µm. The polarization of the incident light was kept perpendicular to the applied strain direction. The obtained Raman spectra had a resolution of <0.5 cm^{-1} and the data were analyzed using LabSpec6 and Fityk software.

3. Results and discussion

The strong interfaces for GR and the underlying PDMS substrates were achieved by adding a thin layer of formvar resins—a group of polymers with polyvinyl formals—between them. The sandwiched structure of GR/formvar/PDMS stack is illustrated in Fig. 1a. For *sc*-GR samples used in the experiments, they exhibit a well-defined hexagonal shape with zigzag (ZZ) edge orientations [24] and can be directly visualized on Cu by mild oxidization in air [25] (Fig. S2, Supplementary Data), which helps manipulate the strain loading along the required crystallographic orientation, as shown by the optical microscopy (OM) image in Fig. 1b. As to the Raman spectrum, for monolayer GR, it shows two featured peaks of

G-band (~1580 cm^{-1}) and 2D-band (~2680 cm^{-1}), originated from the first order Raman scattering process of doubly degenerate TO and LO phonon at the center of the Brillouin zone (BZ) and the second-order double-resonant process between the K and K′ points in the BZ involving two TO phonons, respectively [26], and both peaks can be well fitted with Lorentzian lineshapes and the intensity ratio between the 2D-band to G-band is usually larger than 1.5 [26]. The use of formvar as the buffering layer helps form a conformal contact between GR and PDMS, which allows larger contact area at their interface to transfer stress. The Poisson's ratio of the formvar/PDMS substrate is ~0.2, calculated from the variations of several pairs of distant dots (indicated by red arrows in Fig. 1b) on formvar during the stretching. This Poisson's ratio is close to that of GR's (~0.18), ensuring that no buckling and detaching occur for GR when it is compressed along the direction perpendicular to the applied strain, which also helps maintain the stress transfer from the substrate to the GR sample. Moreover, the formvar/PDMS substrates serve as a suitable platform for detecting both the GR Raman G- and 2D-band peaks (Fig. S3 in Supplementary Data), significantly improved from other widely used stretchable substrates such as polyethylene terephthalate (PET), which has a strong noisy peak at ~1620 cm-1 to overlap the GR G-band peak, leaving only 2D-band peak detectable for the strain measurements [9,16]. Fig. 1c shows the spectral evolution of the Raman G and 2D peaks as a function of applied strain along the ZZ and armchair (AC) directions of *sc*-GR. Both of them exhibit significant redshift and peak splitting in the G and 2D peaks with increased applied strain, due to the symmetry breaking in SGR and the resultant anisotropy of the electronic and phonon bands [10,14,15]. The maximum strain values applied to the ZZ and AC samples without sliding are 2% and 1.8%, respectively, and the maximum 2% strain is by far the highest value for GR straining using flexible substrates and >50% higher than the previous report (1.3%) [8]. During the evolution of the GR Raman spectra from 0% to the maximum strain, apparent splitting occurs to both the G and 2D peaks, and the decomposed subpeaks can be well fitted with Lorentzian lineshapes indicated by G$^+$, G$^-$ and 2D$^+$, 2D$^-$, respectively, referring to the polarizations parallel (−) and perpendicular (+) to the applied strain [8], as illustrated in the right panel of Fig. 1c.

The fitted peak positions of subpeaks for the ZZ and AC samples are plotted and fitted as a function of applied strain in Fig. 2 for (a) 2D peak of ZZ (b) G peak of ZZ (c) 2D peak of AC and (d) G peak of AC. All of them follow linear dependencies on the applied strain up to the maximum values, proving an efficient shear stress transfer from formvar/PDMS to GR [20]. For GR sample strained along the ZZ direction, the maximum peak shifts for G$^+$, G$^-$, 2D$^+$ and 2D$^-$ are 30.5, 64.8, 65.5 and 124.5 cm^{-1}, respectively, which are also by far the highest values derived for SGR. Fitted Raman slopes (shifting rates) of $\partial\omega_{G+}/\partial\varepsilon \sim -16.6$, $\partial\omega_{G-}/\partial\varepsilon \sim -35.2$, $\partial\omega_{2D+}/\partial\varepsilon \sim -32.7$, $\partial\omega_{2D-}/\partial\varepsilon \sim -62.2$ cm^{-1}/% are derived when GR is strained along the ZZ direction, and $\partial\omega_{G+}/\partial\varepsilon \sim -16.2$, $\partial\omega_{G-}/\partial\varepsilon \sim -35.2$, $\partial\omega_{2D+}/\partial\varepsilon \sim -28$, $\partial\omega_{2D-}/\partial\varepsilon \sim -56.7$ cm^{-1}/% for the AC direction. The two subpeaks of the G-band exhibit similar shifting rates along the ZZ and AC directions, whereas those of the 2D subpeaks along the AC direction are smaller. A possible reason for this is the slight difference of the modified electronic and phonon bands for the doubly resonant TO phonons in SGR along the two directions [15]. Moreover, no apparent broadening in full-width-at-half-maximum (FWHM) was observed for all the G$^+$ and G$^-$ subpeaks during the strain loading, demonstrating the high structural stability of GR even with a relatively high strain value.

Scanning Raman maps for *sc*-GR during the strain loading were collected in large scale and shown in Fig. 3. The maps were collected at ε = 0.39% and 0.8% for the ZZ-strained sample and ε = 0.45% and 0.95% for the AC-strained one. We chose the position