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Ultraviolet Raman spectra of double-resonant modes of graphene

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ABSTRACT

Ultraviolet (UV) Raman spectroscopy is a powerful technique for applications in fundamental and applied sciences of condensed matter and material science. To investigate double-resonant Raman scattering processes of graphene, we study the characteristic 2D Raman mode profiles of 1–4 layer graphene (supported and suspended) and graphite using both UV and visible excitation lasers at room temperature. At UV excitation energy of 3.81 eV, we observe that three scattering processes contribute dominantly to 2D mode profiles, which is a general feature for all graphene samples, showing the intensity diminishing of other scattering processes as theoretically predicted. We also find the asymmetric G^* double resonant mode is sensitive to the high incident laser energy, and I(G)/I(2D) of monolayer graphene is most sensitive to UV laser energy due to near off resonant behavior of 2D modes at high excitation energy. Our results provide direct experimental evidences to further understand double-resonance scattering mechanism of few layer graphene.

Graphene, one of the most prominent representatives in two-dimensional material family, possesses many interesting aspects such as superior mechanical strength, thermal conductivity, optical transparency, high carrier mobility and valley degeneracy [1–3]. These distinct features inspired intense investigation of graphene in various directions like transport, opto-electronics, valleytronics and recently graphene based heterostructures [4–10], among which Raman scatting technique was found to be a versatile tool to probe graphene as a convenient and non-destructive approach [11]. Particularly, double resonant 2D Raman modes, can be used not only to characterize properties such as layer number, defects, disorder, doping and strain, but also to investigate fundamental electronic and vibrational structures.

Due to the splitting of electronic bands of few layer graphene, the multiple scattering processes of 2D Raman mode initiated many experimental and theoretical works [12–19]. It was generally believed that one single scattering process is sufficient to describe monolayer graphene 2D mode and four processes for two-layer graphene, which offers an effective method to identify graphene layer number [20]. Recently, a first-principles simulation of bilayer graphene argued that three dominant processes (P_{11}^{44}, degenerate P_{12}^{43}/P_{21}^{34}, inner P_{22}^{33}) and one weak process (outer P_{22}^{33}) contribute to the 2D mode profile, and the weak P_{22}^{33} process will diminish at high incident energy. Thus three peaks were sufficient to fit 2D mode spectrum of a freestanding bilayer graphene measured by 2.54 eV excitation laser [12], which was in contradiction with numerous reports of four-peak structure of 2D modes, despite influences from factors like strain, doping and disorder may exist [14–19]. To our best knowledge, most experiments were performed using excitation laser energies up to visible 2.71 eV [17]. Only in very few works, UV lasers were utilized, but the main focuses were the 2D mode center frequencies [21–23] and the submode frequency shifts [24] rather than submode intensity evolution by varying the incident laser energy. Due to its weak signal intensity at off-resonant conditions, no 2D mode was observed at UV excitation energy of 266 nm (4.66 eV) in a recent paper [22]. Considering the importance to understand 2D Raman mode scattering processes, we believe one simple way to clarify the present situation is to use proper excitation energy lasers to investigate graphene 2D mode

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thoroughly as presented below.

In this report, we investigate mechanically exfoliated few layer graphene using visible 514 nm (2.41 eV), 633 nm (1.96 eV) and UV 325 nm (3.81 eV) lasers. 2D Raman modes of bulk graphite as well as 1–4 layer (1L–4L) supported and suspended graphene are recorded and fitted with multiple Lorentzian functions. For all graphene samples under high excitation energy 3.81 eV, we observe strong suppression of 2D mode intensities and thus larger I(G)/I(2D) values. Compared with spectra at visible excitation energy, line shapes of 2D mode peaks show an intensity decrease at the higher energy side and an intensity increase for the lower energy side. Interestingly, the UV 2D mode profile fitting needs three Lorentzian peaks, even for the monolayer graphene, and peak positions are almost the same for both suspended and supported samples. Our detailed Raman spectra thus provide important experimental observation for understanding multiple phonon Raman resonant scattering processes at high energy UV region.

To fabricate few layer graphene samples, we use the typical mechanical exfoliation method, i.e. scraping the high quality graphite on the SiO_2 (300 nm)/Si substrate. Graphene samples can be first identified under microscope due to their layer dependent color interference effect. As shown in Fig. 1(a), one piece of the sample containing consecutive 1–3L graphene is presented, the size of every layer is tens of microns and their layer numbers are identified by Raman spectroscopy. To get suspended few layer graphene samples, we fabricate trenches with depth of 150 nm and width of 2 microns in the 300 nm SiO_2 covering layer above the Si substrate using the ultraviolet photolithography approach. Then the same mechanical exfoliation method was used to get the suspended few layer graphene samples. In Fig. 1(b–d), 1-3 layer suspended graphene samples are shown, where layer numbers are also identified by Raman features of their supported parts.

To investigate the UV Raman features of few layer graphene, a Horiba-JY T64000 system was used to record all Raman spectra at ambient conditions in the backscattering geometry with incident lasers of three wavelengths 633 nm, 514 nm and 325 nm. The laser spot size is of 1.0 μm in diameter when adopting a 100× objective lens, thus suitable for suspended graphene measurements. For every spectrum, the incident laser power is kept as low as 0.5 mW to minimize the laser heating effect, the typical spectrum collection time was 60 s for visible lasers and 900 s for the UV laser due to its weak 2D mode intensity being proportional to E_L^{-3} [17].

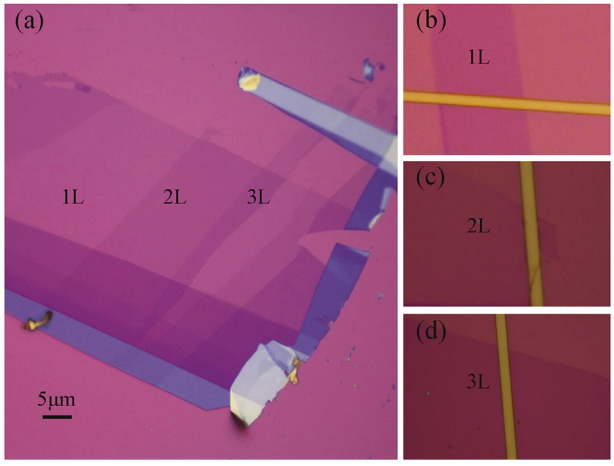

Fig. 1. Optical images of graphene samples on *Si* with 300 nm SiO_2 cover layer: (a) 1–3 layer supported graphene, labeled as 1L, 2L and 3L respectively. (b)–(d) suspended 1–3 layer graphene above trenches (yellow color) with depth of 150 nm and width of 2 microns. (A color version of this figure can be viewed online.)

In Fig. 2, UV Raman spectra from the excitation of 3.81 eV are shown for 1–4L graphene and graphite. The strong G mode at 1582 cm^{-1} is non-dispersive as the first order Raman scattering process at Γ point of Brillouin zone center. The absence of disorder-related D modes is also observed by visible lasers, whose values should be around 1425 cm^{-1} as half of 2D modes, which indicates high quality of graphene samples and no laser induced damage during measurements. Here we observed the broad asymmetric G^* mode around 2330 cm^{-1} as the double resonance of $D + D''$ modes for the first time, where D'' mode is the weak defect induced one phonon process around 1100 cm^{-1} for visual lasers [14]. The inner scattering process contributes dominantly to G^* mode intensity with associated phonon along $K\Gamma$ direction of Brillouin zone. The asymmetric G^* line shape at higher frequency side is from the weak phonon scattering at angles deviating from $K\Gamma$ line [25]. In previous visible laser measurements of 1.96 eV–2.8 eV, G^* modes have a negligible shift rate around 2 eV [26,25,11], which is also confirmed here in our measurements by using 1.96 eV and 2.41 eV lasers. At 2.8 eV, the peak value of G^* mode is around 2425 cm^{-1} [26], suggesting a large shift rate of −100 cm^{-1}/eV to 3.81 eV. Taken into account that the D mode has a shift rate about 50 cm^{-1}/eV up to 3.81 eV [24], D'' mode should have a surprisingly large shift rate of −150 cm^{-1}/eV. This trend is in good agreement with D'' phonon dispersion relation from calculation in Ref. [14], while the high sensitivity of G^* and D'' modes to excitation energy at high energy range has never been observed until our present experiment.

In Fig. 2 insets (a) and (b), four scattering processes of the double resonant 2D Raman mode are schematically shown for a Bernal stacked 2LG along the Γ-*K*-*M*-*K*′-Γ high-symmetry direction [12], where symmetric (antisymmetric) scattering processes happen between equivalent (inequivalent) electronic bands of *K* and *K*′ points. The inner (P_{22}^{33} and P_{21}^{34}) and outer (P_{11}^{44} and P_{12}^{43}) processes involve two transverse optical modes with wave vectors in the sector range ±30° next to the *K*Γ and *KM* directions separately [12]. In Fig. 3, we present and compare 2D Raman spectra of 1L–3L graphene measured by three excitation energies. Raw data and Lorentzian fitting are shown as black and red lines, whose multiple Lorentzian splittings are lines in blue, cyan, green and magenta with discrete Raman frequencies plotted in Fig. 4 (a) with respect to graphene layer number. To our best knowledge, we get the clear line profiles of 2D mode for the first time at 3.81 eV with only *three*

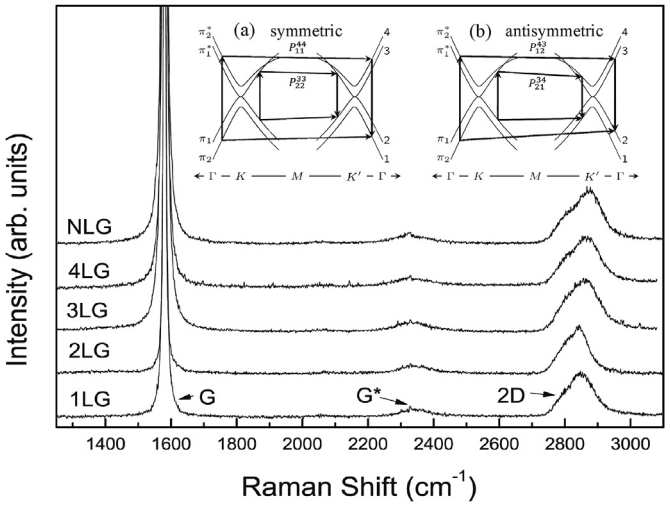

Fig. 2. Raman spectra of supported 1–4L graphene and graphite measured by 325 nm (3.81 eV) excitation energy at room temperature. G, G^* and 2D modes are around 1582 cm^{-1}, 2330 cm^{-1} and 2850 cm^{-1} respectively. Insets (a) and (b) are schematic illustration of symmetric and antisymmetric 2D double resonant processes for a Bernal stacked 2LG.