Graphene, the two dimensional carbon, is one of the most actively studied nanomaterials due to its many fascinating properties and potential technological applications. Raman spectroscopy and imaging has become a simple yet powerful, non-invasive method to characterize graphene and a wide range of other nanomaterials. This paper will review examples of using Raman spectroscopy and imaging to study a broad range of structural, phononic, electronic, and thermal properties of graphene, drawing mostly from work in my laboratory on both exfoliated graphene and synthetic graphene grown by chemical vapor deposition. Combining electronic transport and gating with Raman measurements also gives a powerful technique to characterize electron-phonon coupling. Similar experimental techniques can be applied to many other “beyond-graphene” 2D materials and their Van der Waals (VdW) coupled heterostructures.

Introduction

Graphene is the Two-Dimensional (2D) form of carbon with planar sp² bonding in a honeycomb lattice (Figure 1a). Only about 0.5 nm thick, graphene represents a single atomic layer of graphite and is also the building block for many carbon nanomaterials including carbon nanotubes (which are graphene sheets wrapped into cylinders). In the past decade, graphene has received tremendous interests and become one of the most studied and talked about nanomaterials due to a large number of fascinating properties and exciting potential applications. For example, graphene claims one of the highest electrical conductivity, current carrying capability, thermal conductivity, and mechanical strength among all materials, while at the same time is highly transparent, flexible and impermeable. Potential applications where graphene can play major roles include high speed and high frequency electronics and communications, flexible electronics and transparent conductors (e.g. for touch screens and solar cells), and protective coating for chemical or biological samples, etc. My group has been working on graphene since 2007 on its fabrication and growth, fundamental properties as well as device applications. We produce graphene using both the (top down) “scotch tape” based exfoliation from graphite, as well as (bottom up) synthesis from hydrocarbon (e.g., CH₄) using Chemical Vapor Deposition (CVD) on various substrates. Figure 1b-f shows various images of graphene (ranging from microns to centimeters in size) from our work.

Raman spectroscopy is a commonly used method, based on inelastic light scattering, to characterize excitations (that give the measured energy or frequency difference, known as the “Raman shift”, between the incident and scattered
light) in diverse systems ranging from molecules to solids and nanomaterials (including graphene\[^{7,8}\]). In our lab, we have a confocal Raman microscope (HORIBA XploRA), to which we have further added a stage to scan the sample for imaging/mapping of spectral features (“Raman imaging”), and another two optical cryostats with electrical feedthroughs to control the temperature (from 4 K to >800 K) and pressure of the sample and allow electrical connection/gating for simultaneous Raman/optical and electrical measurements (see Figure 2). This system has become an indispensable tool routinely used in our graphene research, and a powerful tabletop laboratory and workforce that have supported or enabled many other projects in our lab. As we will demonstrate with various examples below, Raman spectroscopy and imaging offers a noninvasive and efficient technique to characterize and study a broad range of properties of graphene, including (but not limited to) the thickness (number of layers), doping (carrier density/chemical potential), stacking order (between layers in multilayers), defects, edges, grain boundaries, thermal conductivity, and electron-phonon coupling. The measurement methods and techniques we used and developed can be applied to many other nanomaterials, particularly “beyond-graphene” 2D materials that are currently attracting intense interests due to their novel properties and exciting application potentials, and are among a major thrust also in our current and future research.

\*1: See for example, http://www.physics.purdue.edu/quantum/publications.php

Raman Spectra of Vibration/Phonon Modes of Graphene and its Multilayers.

The excitations responsible to the Raman shift measured in the Raman spectroscopy on graphene are typically various lattice vibration modes (or phonon modes) of graphene\[^{7,8}\]. Figure 3a shows a typical Raman spectrum of graphene (middle trace, note in this paper “graphene” means a single layer graphene unless otherwise specified), along with the spectra for a 2-layer graphene (lower trace) with “AB” (or “Bernal”) stacking (similar to the stacking in graphite) and a more disordered graphene (upper trace) where we have used e-beam irradiation to create (a controllable amount of) artificial defects. The right and left insets depict the lattice vibration patterns (optical phonon modes) for two particularly important Raman peaks we study: the “G” peak (~1580 cm\(^{-1}\), seen in all 3 spectra), which is a “(Brillouin) zone-center” (Γ) phonon, and the...
“D” peak (~1350 cm⁻¹), which is a “zone-edge” (K) phonon and is only activated in the presence of (short-range) defects. The “2D” peak (~2700 cm⁻¹, at 2nd harmonic of “D”) comes from a double resonance process and requires no defects. The Raman spectrum systematically changes with the number of graphene layers (thickness, and the spectrum for thick multi-layers approaches that of graphite). For example, the intensity ratio between the G and 2D peaks and the shape of the 2D peak can be used (and even mapped) to identify single layer graphene and 2D peaks and the shape of the 2D peak can be used to create artificially disordered graphene with tunable amount of disorder and defect density, and performed systematic Raman studies of how Raman spectra evolve for graphene with variable levels of disorder (complemented by electronic transport measurements). We have discovered that the empirical relation used in the past 30+ years to extract defect density (or correlation length or “domain size”) from the D peak over G peak intensity ratio has several fundamental problems and are in fact not complete. This line of work could lead to new methods of extract defect information and length scale from Raman spectra, and also demonstrated that such e-bema or plasma irradiations can be used to create an artificial, tunable disorder in graphene to study disorder physics and defect chemistry in graphene and other nanomaterials in general.

**Studies of Graphene Single Crystals and Grain Boundaries**

The macroscopic large-scale graphene films such as those grown by CVD are typically polycrystalline (formed by many graphene single crystals merged together, while the synthesis of large single crystal graphene is an important next frontier). We have performed a comprehensive study of CVD graphene single crystals and grain boundaries (between merged single crystals). We demonstrated synthetic hexagonal shaped graphene single crystals (an example shown in Figure 1c), and such crystals can even be controllably synthesized in ordered arrays using seeded growth with well-defined (zigzag) oriented edges. In particular, we showed that Raman imaging (of Raman D peak intensity) provides a quick and powerful method to visualize nucleation centers (within single crystals) and grain boundaries that are difficult to see in optical image or even other microscopy such as atomic force microscopy. (Figure 4)

**Raman Studies of Defects in Graphene**

Raman “D” peak (~1350 cm⁻¹) in graphitic materials has been widely used as a measure of the amount of disorder (density of lattice defects) in graphene. For example we have used mapping (imaging) of the D peak intensity to assess the quality of the CVD-grown large scale graphene. We also developed two experimental methods --- using electron beam irradiation and oxygen plasma etching -- to create artificially disordered graphene with tunable amount of disorder and defect density, and performed systematic Raman studies of how Raman spectra evolve for graphene with variable levels of disorder (complemented by electronic transport measurements). We have discovered that the empirical relation used in the past 30+ years to extract defect density (or correlation length or “domain size”) from the D peak over G peak intensity ratio has several fundamental problems and are in fact not complete. This line of work could lead to new methods of extract defect information and length scale from Raman spectra, and also demonstrated that such e-bema or plasma irradiations can be used to create an artificial, tunable disorder in graphene to study disorder physics and defect chemistry in graphene and other nanomaterials in general.

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*2: The spectra in Figure 3b were measured using a low energy Raman setup in collaborator R. He’s lab that can access such low Raman shift.

*3: For example, AB-stacked multilayer graphene has a “shear mode” (P. H. Tan et al., Nature Materials, 11, 294 (2012)) that is highly sensitive to the thickness (number of layers).
Electro-Raman Measurements of Thermal Conductivity of Graphene

Graphene has one of the highest thermal conductivity among all materials known\(^{25}\), however the precise value of its thermal conductivity has been somewhat debated. We have developed an “electro-Raman” technique (Figure 5)\(^{26}\) to measure the thermal conductivity of combining electrical transport (using a current to induce Joule heating in a suspended graphene) and Raman spectroscopy (using the temperature dependent Raman spectral peak of graphene as a thermometry), and measured the thermal conductivity of both CVD and exfoliated graphene to be \(\approx 2000 \text{ W/mK}\). Such a method can be generalized to measure thermal conductivity of other nanomaterials (2D materials and nanowires) and also to study energy dissipation of nanomaterial based electronic devices.

Gate-tunable Raman Spectrum and Electron-phonon Coupling

The Raman spectrum of graphene is known to depend on the doping or carrier density,\(^{27,28}\) which can be conveniently varied by electrostatic gating in a graphene Field Effect Transistor (FET) device. This reflects the coupling of phonons with the electronic charge carriers in graphene. For example, the G peak will blue-shift and become narrower with increasing carrier density of either n (electrons) or p (holes) type (Figure 6a-6c), a behavior related to such interesting physics as the “Kohn-anomaly”\(^{27}\) as well as the breakdown of the Born-Oppenheimer approximation (due to the absence of electronic bandgap in the Dirac cone band structure).\(^{28}\) This dependence can be used to directly extract the Electron-Phonon Coupling (EPC) constant in graphene (\(-1.4\times10^{11} \text{ eV/m}\))\(^{27,17,30}\). Combining Raman spectroscopy and electrostatic gating in a graphene FET device (both with conventional dielectric back-gating, and with ionic liquid gating), we have performed gate-dependent Raman spectroscopy studies also on disordered graphene (defects created by e-beam irradiation) and twisted bilayer graphene and measured systematically the evolution of Raman spectra (esp. D peak in disordered graphene, and G peak resonantly enhanced by van Hove singularity in tBLG) when the carrier density (chemical potential) in graphene is tuned by the gate.\(^{17,30}\) This has allowed us to perform the first measurement of EPC parameters (important for understanding electronic, thermal, and thermoelectric transport and device operations) in disordered graphene and tBLG, and also observation of novel features such as electric field induced quenching and splitting of resonantly enhanced G peak in tBLG. (Figure 6d) This powerful technique can be applied to study electron-phonon or electron-vibron coupling in other nano/molecular materials.

Figure 5     (a) Schematic of measuring thermal conductivity of graphene by combining electrical current Joule heating with Raman spectroscopy. Graphene is suspended over a trench. (b) Raman spectra of graphene near “G” phonon peak without and with 20 mA heating current. The red shift of G peak is used to measure the temperature rise in graphene. Data adapted from Ref. [26]

Figure 6     (a) Evolution of graphene Raman spectrum near “G” peak with gate voltage (V, applied to the SiO\(_2\)/Si backgate and ranging from -60 V to 60 V relative to the Dirac point voltage \(V_D\)) that tunes the graphene carrier density.\(^{17}\) The G peak frequency (b) and width (c) as functions of \(V-V_D\) (bottom axis) and carrier density (top axis, positive for electrons, negative for holes). (d) Evolution of Raman spectrum in a tBLG (left inset) when its carrier density is tuned by an ionic gate. Right inset is a model of gate-modulated electronic band structure to explain the splitting and quenching of resonantly enhanced Raman G peak.\(^{30}\)
Future Directions

There are many interesting further questions one can study with Raman measurements on graphene-based materials (including chemically functionalized graphene and hybrid materials mixing graphene with other (nano) materials). The measurements and techniques developed for graphene can also be extended to study other nanomaterials, particularly a wide range of so called “graphene-like or “beyond graphene” 2D materials --- Van der Waals coupled layered materials that can be reduced to one or few atomic layers, ranging from insulators such as h-BN, semiconductors such as silicene, phosphorene, MoS$_2$, topological insulators and thermoelectric materials such as Bi$_2$Te$_3$, superconductors such as FeSe, and some complex oxides etc. Many Raman-based measurements described above (such as thermal conductivity, electron-phonon coupling in gate-tuned Raman, low energy interlayer Raman modes) have just started to be performed on these 2D materials and this would be a very fertile area of future research. The same experimental setup used for Raman (Figure 2) can also be conveniently used to measure Photoluminescence (PL) and photoconductivity. In addition, by stacking different 2D materials, we can make novel “Van der Waals” stacked heterostructures (such as MoS$_2$/graphene as an example) and superlattices that have never existed or been studied before, and we plan to apply our techniques (such as interlayer Raman modes) to study these hetero-structures. Such 2D materials and heterostructures have exciting potentials both in terms of fundamental science (new materials with novel properties due to 2D nature or proximity/hybrid-heterostructures) and potential technological applications in electronics/ optoelectronics, flexible devices, energy (thermoelectrics, solar cells, and measurements of electron phonon coupling in 2D materials for example will give key insights to the processes involved in such energy conversions).

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