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A tunable Raman system based on ultrafast laser for Raman excitation profile measurement

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ABSTRACT

The measurement of the Raman excitation profile (REP) is of great importance to obtain the energies of van Hove singularities and the lifetime of the excited state involved in the Raman process of semiconductors. In this Note, we develop a simple tunable Raman system based on an ultrafast laser and tunable Raman filters for REP measurement. The system is testified by measuring REP of twisted bilayer graphene, and the corresponding energy of van Hove singularity is determined.

Raman spectroscopy has been proven to be a powerful characterization tool to study fundamental element excitations in solids.[1,2] In Raman measurement, when the excitation energy (E_{ex}) is chosen to match or approach optically allowed transition energy of a material, Raman intensity can be enhanced by orders of magnitude and resonant Raman scattering (RRS) occurs. The plot of Raman intensity vs E_{ex} gives the Raman excitation profile (REP).[3] From the resonance peaks in the REP, one can estimate the corresponding energies of optically allowed electronic transitions of a material, which provides an additional method to probe the electronic band structures.[4] In addition, the broadening factor for the Raman process can be obtained from the width of resonance window in REP, which is related to the lifetime of photoexcited electrons.[5,6] Therefore, the REP measurement is very crucial to thoroughly understand the material's electronic properties. Despite the diverse analytical application of REP, experiments on the REP measurement are practically restricted by the lack of tunable lasers and a triple-stage Raman spectrometer in a general laboratory. Liu *et al.* developed a tunable Raman system based on the supercontinuum laser, tunable longpass (TLP) filters (VersaChrome Edge^{TM}, Semrock, Inc.), and single-stage spectrometer.[7] However, it is arduous and inefficient to acquire monochromatic excitation sources from a broadband supercontinuum laser covering 400–2400 nm. To realize this purpose, many optical components are used, such as super-cold filters, broadband bandpass filters, transmission grating, and tunable bandpass filters. Due to the relatively low output power of the supercontinuum laser in the visible range and optical loss after dispersion and transmission, the monochromatic excitation source obtained from the supercontinuum laser is left as low as 100–200 μW when it is focused on the sample, much smaller than that from a commercial single-frequency laser. These two aspects limit the wide application of the tunable Raman system based on the supercontinuum laser. With the advent of reliable high-powered mode-locked oscillators and high-quality non-linear crystals, an ultrafast laser has taken the place as a widely tunable laser source for kinds of optical experiments. The characteristics of high power and flexible tunability in a femtosecond laser also make it a potential candidate as a good tunable excitation source for REP measurement to replace the supercontinuum laser used in the above tunable Raman system.

In this Note, we show that the monochromatic excitation source obtained from an ultrafast laser by transmission grating can be an ideal excitation source to realize a high throughput REP measurement. The linewidth of a femtosecond laser can be as narrow as several to tens of nanometers in the visible range. By using transmission grating, the femtosecond laser can be dispersed into monochromatic light with a linewidth of ~1.0 meV and power of tens of milliwatts, which is sufficient as the excitation source for a common Raman measurement. We couple the excitation source and a single-stage spectrometer along with two TLP filters to form a tunable Raman system and demonstrate its performance by the REP measurement of twisted bilayer graphene (tBLG) in a broad excitation range from 1.68 to 2.21 eV.

Figure 1 shows the schematic diagram of the tunable Raman system. The tunable femtosecond laser system is composed of a self-mode locked Ti:sapphire laser (Chameleon Ultra II, Coherent) and an optical parametric oscillator (OPO) (Chameleon Compact OPO, Coherent) pumped by a Ti:sapphire laser. The excitation wavelength in this Note spans in the ranges of 1.68–1.82 eV generated by Ti:sapphire laser and 1.82–2.21 eV generated by second-harmonic generation (SHG) of OPO signals. Figure 1(b) demonstrates the spectrum of the ultrafast laser pulse around 1.85 eV with a full width at half maximum (FWHM) of 13.7 meV, which is equal to 100 cm^{-1} and far too broad for Raman excitation. In order to narrow its linewidth to generate monochromatic excitation source, we utilize one or two transmission gratings (FSTG-XVIS1274-920, Ibsen Photonics) to disperse the ultrafast laser, followed by apertures to select the interested wavelength and reduce the FWHM and beam size of the excitation source. The transmission grating is applicable in the wavelength range of 360–830 nm with a resolution of 1274 lines/mm. As mentioned in Ref. 7, the transmission grating is mounted on the same manually rotatable stage with the corresponding mirror. By adjusting the angle of incidence (AOI) of the transmission grating and the corresponding mirror, the dispersed monochromatic light is selected via two apertures. The resulted FWHM can be reduced as narrow as 0.83 and 0.5 meV at 1.851 eV by one and two transmission gratings, respectively, as illustrated in Figs. 1(c) and 1(d).

Considering that the configuration of one transmission grating is easily performed by common scientists, we use this simple configuration to measure the REP of tBLGs in order to show its possibility of wide application in the standard REP measurement. The resulted monochromatic source is then coupled into a home-made SmartRaman confocal-micro-Raman module and a HORIBA iHR550 spectrometer equipped with a charge-coupled device (CCD) detector. A beam splitter (55% transmission and 45% reflection) is used to reflect the monochromatic source into a 50× objective (numerical aperture = 0.55). The laser power of the monochromatic light at sample can be tens of milliwatts, which is sufficient as excitation for Raman measurement. The laser power used in this Note is attenuated to around 0.5 mW to avoid sample heating. Rayleigh (elastically) signals are then blocked by two TLP filters, while most of the Raman signals are transmitted. The TLP filter exhibits a wide tunable wavelength range, excellent out-of-band blocking (optical density >6), and high transmission of above 90%. Two identical TLP filters are used in tandem to provide better blocking of Rayleigh signals. They are placed in mirror symmetry to compensate the optical path offset caused by refraction. With the AOI of filters increasing from 0° to 60°, the cut-off wavelength of the TLP filter blueshifts, as illustrated in Ref. 7. In this work, we use TLP01-628-25 × 36 and TLP01-704-25 × 36 (VersaChrome Edge, Semrock, Inc.) to cover the whole spectral range of our measurements, whose cut-off edges are tunable in the range of 561–628 nm and 628–704 nm, respectively. Then, the Raman signal is focused into the single-stage spectrometer for measurement. The spectrometer is equipped with a 1200 lines/mm grating and a CCD detector. The entrance slit of the spectrometer is 200 μm.

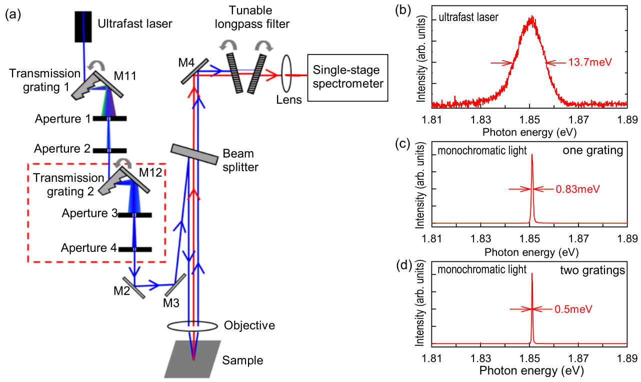

FIG. 1. (a) Schematic diagram of a tunable Raman system including an ultrafast laser, two tunable longpass filters, and one or two transmission gratings, in which the second transmission grating is indicated by a dashed square. (b) Spectrum of the ultrafast laser pulse at 1.85 eV with a full width at half maximum (FWHM) of 13.7 meV. The spectrum of the monochromatic excitation source with a FWHM of (c) 0.83 and (d) 0.5 meV dispersed from ultrafast laser pulse using one and two transmission gratings, respectively.

In order to demonstrate the performance of the tunable Raman system, we apply it to measure the REP of a tBLG. Figure 2(a) shows the optical images of tBLG and single-layer graphene (SLG) samples deposited on the SiO_2/Si substrate with 90 nm SiO_2. SLG and tBLG are identified by Raman spectroscopy at room temperature.[8,9] Figure 2(b) shows the optical contrast of tBLG and bilayer graphene (BLG). An additional absorption peak appears at ~1.84 eV in the optical contrast of tBLG compared with that of BLG, which is associated with van Hove singularities (VHSs) of the joint density of states (JDOS).[4] When E_{ex} (1.96 eV) is close to the VHS energy of tBLG, the G mode intensity I(G) of tBLG is resonantly enhanced by about 40 times compared to that of BLG, as shown in Fig. 2(c). The R mode at ~1525 cm^{-1} is observed, which is the Raman scattering from the moiré phonon[10] in tBLG. According to the relation between the moiré phonon and twist angle in tBLGs,[11] the twist angle θ_t of tBLG can be determined as ~ 9.2°.

Figures 3(a) and 3(b) show Raman spectra of diamond (reference sample) and tBLG excited by 2.14 and 1.85 eV lasers, respectively. Raman peaks of diamond and tBLG show broadened FWHM in comparison with that excited by single-frequency laser due to the broadened FWHM of monochromatic light from ultrafast laser

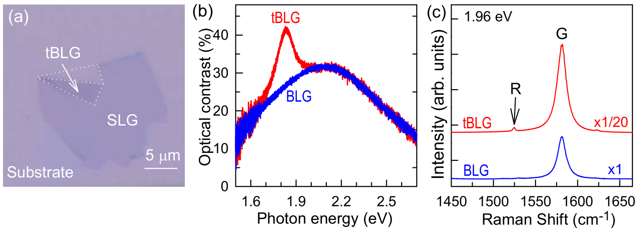

FIG. 2. (a) Optical image of a tBLG sample. (b) Optical contrast of the tBLG (red) and bilayer graphene (BLG) (blue) sample. (c) Raman spectra of tBLG and BLG excited by a 1.96 eV laser.

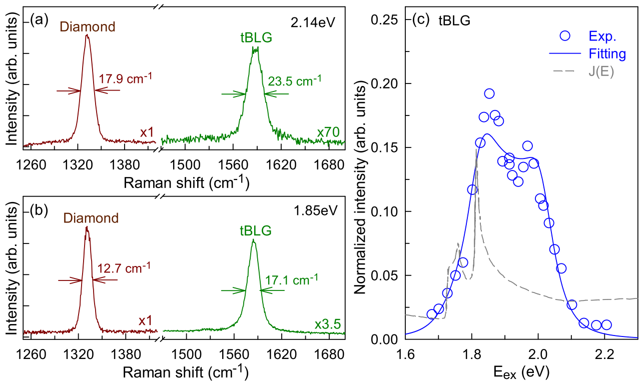

FIG. 3. Raman spectra of diamond and tBLG excited by (a) 2.14 eV and (b) 1.85 eV lasers. (c) The G mode REP of tBLG with θ = 9.2°, where the G mode intensity is normalized by that of diamond at 1332 cm^{-1}. Here, the circles and solid line represent the experimental data and fitting results, respectively. The dashed line represents the renormalized electronic joint density of state [J(E)] of tBLG[12] with θ = 9.43°.

as shown in Fig. 1(c). Figure 3(c) demonstrates the measured REP of tBLG, where the G mode intensity is normalized by that of diamond. The normalized G mode intensity is resonantly enhanced by 20 times at 1.85 eV than that at 2.14 eV. The REP of the G mode, $I(E_{ex})$, can be described by[4]

$$I(E_{ex}) \propto \left| \int \frac{J(E)M(E)}{(E_{ex}-E-i\gamma)(E_{ex}-E_{ph}-E-i\gamma)} dE \right|^2, \qquad (1)$$

where $J(E)$ is the JDOS of tBLG at E and $M(E)$ is a fitting parameter that includes the electron–phonon and electron–photon interaction matrix elements at E. E_{ph} is the phonon energy. The broadening factor (or damping constant) γ gives the energy uncertainty related to the lifetime of the excited states.[5] We simplify $M(E)$ as a constant. Previous result of tBLG shows a similar profile of $J(E)$ in the range of 1.5–2.5 eV around θ_t of 9.43°.[12] Therefore, the theoretical $J(E)$ of tBLG with $\theta = 9.43°$ are scaled in energy by 29.0% to compensate the underestimation of its Fermi velocity due to the absent corrections of electron–electron interactions,[13] as shown by dashed line in Fig. 3(c). The experimental G mode REP in tBLG can be well fitted by Eq. (1) based on the scaled $J(E)$ and γ of 58 meV. The fitted curve is depicted by the solid line in Fig. 3(c). Due to the small γ, both the incoming and outgoing resonances in the G mode REP can be resolved, similar to the previous result.[14] γ was reported to be ~120[11] and 150 meV[4] for tBLGs with a twist angle of 13° and 10.6°, respectively. γ should be dependent on the twist angle of tBLGs because of their twist-angle dependent optical transitions.[13]

In conclusion, we introduce a tunable Raman system based on an ultrafast laser and tunable filters for resonance Raman spectroscopy of solid materials. This Raman system is demonstrated to be reliable and flexible for the REP measurement of tBLG, which suggests its promising applications in resonance Raman scattering and related researches.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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