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Relationships between the optical and Raman behavior of van Hove singularity in twisted bi- and fewlayer graphenes and environmental effects

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ABSTRACT

Twisted bilayer graphene (tBLG) provides an opportunity to control the optoelectronic properties of graphene owing to the relative orientation (θ)-induced van Hove singularities (vHs). However, how different environments affect vHs behaviors of various tBLGs and their Raman resonance window is not clear. A study of the optical vHs properties of tBLGs on a quartz substrate, prepared by chemical vapor deposition, was carried out using simultaneous reflection and Raman imaging techniques according to the presence of ubiquitous residual amorphous carbon (RAC). The results show that the presence of RAC exhibits a narrower vHs peak width and resonance Raman windows of tBLG as compared to that without RAC, due to the absence of charge-inhomogeneous interactions from bare substrate. In addition, the background-subtracted vHs peak reflectances from various θ values at a specific laser energy are proportional to the measured G-band enhancement factor (GEF). The comparison reveals the detailed optical and Raman resonance windows of various tBLGs in both environments. Extension of the approach to twisted fewlayer graphenes reveals the different vHs peak behaviors including broadening, intensification, and splitting governed by θ-, along with layer number-dependent band structure hybridization.

1. Introduction

Few atom thick two dimensional (2D) materials have drawn enormous attention recently owing to their excellent optoelectronic and mechanical properties, which make them useful in next generation applications [1–4]. The hybrid structures of these materials, associated with either vertically stacked or laterally-junctional configurations enable a fine control of their properties [5]. However, knowledge leading to a fundamental understanding of how these structural features govern the properties of the 2D materials is needed. Especially interesting in this regard are vertical hetero- and homo-structures and the resulting superlattice interference which offer a venue to test new phenomena such as Hofstadter's Butterfly [6] and chiral 2D materials [7]. Among various 2D materials, twisted bilayer graphene (tBLG), a two atom thick flat honeycomb lattice sheet, should be an ideal system to probe the relationships between hybrid structures and properties because it has a small interlayer distance and enhanced electronic band structure coupling.

tBLG is formed when two single layer graphenes (SLGs) are stacked with a relative rotation angle θ (inset of Fig. 1A) other than with Bernal and, less commonly, rhombohedral stacking. tBLG having superlattices with a moiré interference pattern [6,8,9] possesses θ-dependent van Hove singularity (vHs, Fig. 1C) [10–12] on top of joint density of state (JDOS) from Bernal-stacked BLG [11,13], caused by electronic band anticrossing of saddle point M in the Brillouin zone (Fig. 1B) [14,15]. The vHs and resulting interference is a signature to identify θ by using scanning tunneling spectroscopy [8,16–18], transmission electron microscopy (TEM) [11,19–21], reflection and optical spectroscopies [10,12,19,20,22], Raman spectroscopy [21–27], and other techniques [28–30].

Among various analytical tools, Raman spectroscopy is the most versatile for probing tBLG [11,23–26,31] because it can be employed to observe interesting vibrational properties such as G band (high-frequency E_{2g} phonon) enhancements [11,14,24–26,32], rotational (R) bands [21,23], and low-frequency layer breathing modes [22,26,27]. Especially, G-band enhancements of up to several orders of magnitude are observed when the vHs peak energy (E_{vHs}) matches the Raman excitation laser energy

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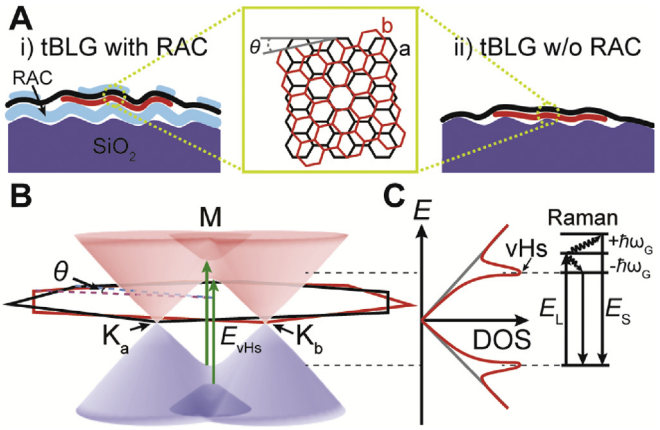

Fig. 1. (A) tBLG in the presence (left) or absence (right) of RAC on a quartz substrate. Inset: tBLG with θ illustrating a superlattice-induced moiré pattern. (B) Saddle point M between K_a and K_b points, separated by θ in reciprocal lattices of tBLG. (C) The resulting JDOS of tBLG having vHs (red), as compared to that of Bernal-stacked BLG (grey), and the related G-band phonons near the vHs. E_s: Scattered energy. (A colour version of this figure can be viewed online.)

(E_L) [24]. G and R band enhancements of tBLG result from resonance Raman scattering associated with optical vHs transitions [19,32]. Importantly, the ability to probe optical properties of spatially-distributed tBLG is necessary in order to acquire a fundamental understanding of stacking configurations and to be able to tune optoelectronic properties to fit novel applications [7]. In this aspect, imaging techniques are appropriate since graphene have various spatial inhomogeneities induced by complexation with substrate [33–35]. However, despite their importance, comprehensive relationships between optical properties of vHs and Raman behavior have not yet been experimentally determined.

In this regard, globally illuminated reflection [19] and Raman [36,37] methods can be utilized to probe spatial inhomogeneity in a high throughput manner and with sub-micrometer resolution. In contrast to absorption method, contrast measurement can be performed on any substrate with better spatial resolution [38] and it does not require the use of suspended samples. Consequently, by employing a combination of these types of optical methods, one can gain a comprehensive understanding of the linkage between optical and Raman behavior of tBLG including those that are a result of spatially-varying substrate-induced effects.

Moreover, chemical vapor deposition (CVD)-grown graphene inevitably contains residual amorphous carbon (RAC), as a mixture of sp^2 and sp^3 hybridized forms, as a result of polymer-assisted transfer and subsequent annealing steps [11,12,37,39–42]. Although RAC as well as residual polymeric materials are known to affect the electrical performances of graphene [41], little is known about the influence of these substances on optical properties [37]. This is mainly caused by flat absorption of graphene having a fine structure constant (*i.e.* $\pi\alpha = 2.3\%$) [43] where α is a fine structure constant defined by $e^2/\hbar c$ ($\hbar$ is a reduced Plank's constant (1.05×10^{-34} J s), e the electron charge (1.6×10^{-19} C), and c a speed of light (3×10^8 m/s)). Consequently, optical vHs peaks and associated Raman properties of tBLG provide useful information to understand the aforementioned environmental effects.

In the effort described below, we carried out a systematic study of the relationships between and environmental effects on the optical and Raman behavior of vHs peaks of tBLGs on a quartz substrate employing a combination of imaging spectroscopies. For this purpose, we utilized low-pressure CVD (LPCVD) to prepare twisted fewlayer graphenes (tFLGs) which contain localized RAC formed by poly (methyl methacrylate) (PMMA) annealing step. Reflection imaging spectroscopy was used to obtain spatio-spectral information about the tFLGs, and widefield Raman spectroscopy was employed to generate correlated Raman G and R bands. vHs peaks of tBLG containing RAC have slightly narrow peak width. Moreover, the net reflection trends of various vHs peaks at E_L are proportional to that arising from experimental G-band enhancement factors (GEFs) which increase up to 36 times. Two trends are simulated by GEFs calculated using Raman Stokes theory. On the other hand, tBLG on a bare substrate display substantial vHs peak broadening and GEFs that are decreased by one-half as a consequence of charge inhomogeneity induced by substrate. The optical measurements were also used to probe the behavior of vHs peaks of tBLG with additional layer having different θ values and layer numbers. These vHs peaks display various phenomena including broadening, intensification, and splitting, all of which stem from θ-dependent non-degenerate multiple transitions of the hybridized band structure.

2. Experimental

2.1. Materials and methods

Copper foil (purity > 99.96%, Cat. No.: Cu-113213) was purchased from Nilaco (Japan). Acetic acid (99.5%) and isopropyl alcohol (99.5%) were obtained from Samchun chemical. All gases including N_2 (purity over 99.99%), H_2 (purity over 99.9999%), and CH_4 (purity over 99.95%) were purchased from Donga Gas (Korea). PMMA (molecular weight: 950 kDa, 2% dilution) as a protective layer for transferring graphene to a desired substrate was obtained from Micro Chem. Millipore quality deionized water with a resistivity greater than 18 MΩ was used to wash graphene samples. A quartz substrate (ST-cut quartz, cutting angle: 42° 45′) was obtained from Hoffman Materials LLC. All optical elements were purchased from Thorlabs unless otherwise noted. Scanning electron microscopy (SEM) image was acquired by JSM-7001F (JEOL Ltd.) with 3 kV acceleration. Atomic force microscopy (AFM) images were acquired by using Nanowizard I (JPK Instrument). A tapping mode by using a silicon cantilever (force constant (norminal): 37 N/m, ACTA-20, App Nano) resonated at 361.96 kHz was used to acquire height topography. AFM image has 1024 × 1024 pixels, and was flattened by using polynomial routine. PMMA annealing experiments were conducted in the CVD setup which will be mentioned below under air atmosphere at 350 °C at different annealing time (2 and 3 h). The samples were prepared by spin-coating the PMMA solution onto quartz substrates for 60 s at 3000 rpm.

2.2. LPCVD growth of tFLG

Synthesis of hexagonal fewlayer graphene (FLG) containing tFLG was carried out by using our previously described method [37]. Native oxide layer of the Cu foil was removed by dipping the foil in acetic acid solution for 10 min. The treated foil was rinsed with isopropyl alcohol several times, and dried under a N_2 stream. The purified Cu foil was placed into a hotzone of a one inch diameter quartz tube placed in a tube furnace (max. temperature: 1100 °C, Cat. No.: TF55030C-1, Lindberg Blue/M Mini-Mite, Thermo Scientific) equipped with an oil-free scroll pump (maximum vacuum pressure: 10^{-3} torr, XDS10, Edwards). The oven temperature was adjusted to 1000 °C with 60 standard cubic centimeter per min (sccm) H_2 flow which continued until a cooling step after the growth reaches at 230 °C. Once the furnace temperature reaches to 1000 °C, additional 1 sccm of CH_4 was fed into the tube for 1 h. After graphene growth, the flow of methane gas was stopped and the sample was cooled to 230 °C. After this, the lid of the tube furnace