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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 proportical 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. © 2016 Elsevier Ltd. All rights reserved.

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 sp² and sp³ 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 (*i.e.* $\pi \alpha = 2.3\%$) [43] where α is a fine structure constant (1.05 × 10⁻³⁴ J s), e the electron charge (1.6 × 10⁻¹⁹ C), and c a speed of light (3 × 10⁸ 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 $E_{\rm I}$ 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 N₂ (purity over 99.99%), H₂ (purity over 99.9999%), and CH₄ (purity over 99.95%) were purchased from Donga Gas (Korea). PMMA (molecular weight: 950 kDa, 2% dilution) as a protective laver for transferring graphene to a desired substrate was obtained from Micro Chem. Millipore quality deionized water with a resistivity greater than 18 M Ω 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 spincoating 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 N₂ 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) H₂ 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 CH₄ 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 was opened, and the tube was cooled with a manual convection of a fan.

2.3. Transferring and annealing process of tFLG

According to our previous method [37], after dropcasting PMMA on the graphene-Cu foil mounted on a vacuum chuck, the sample was spin coated for 60 s at 3000 rpm. PMMA-coated graphene-Cu foil was then floated on 0.1 M of ammonium persulfate solution for 3 h to etch the copper from the back. The resulting floating PMMA-graphene film was washed with copious amounts of water by several scooping processes, and was transferred on a 1×1 cm² target substrate which was pre-cleaned by a piranha solution (H₂SO₄: H₂O₂ = 7: 3). PMMA was initially removed by dipping the substrate into an acetone bath for 30 min and subsequent air annealing at 350 °C for 3 h under atmospheric pressure, according to the previous method [44].

2.4. Micro/widefield/line Raman measurements

Micro-, line-, and widefield Raman imaging measurements [45] were conducted by using a custom-made instrument equipped with 532 nm laser (diode-pumped solid state), as reported previously [36,37]. In the case of micro Raman measurements, 1.5 mW laser power was utilized to minimize graphene damage.

2.4.1. Widefield G-band imaging measurements

The beam diameter was adjusted by using an expander (1–8 ×, Cat. No.: 68479, Edmunds), and a 200 mW laser was utilized as in our previous study [37]. A doublet convex lens with a long focal length (AC254-200-A-ML, focal length (f) = 200 mm) was placed in the excitation component, and focused onto a back focal plane of 100 × objective (MPlan, numerical aperture (N.A.) = 0.90, Olympus) mounted in an upright microscope (BX50, Olympus) so that defocused beam illuminates the graphene sample on the substrate. The scattered light was filtered using a bandpass filter (FB580-10, full width at half maximum (FWHM) = 10 nm), and focused by using a tube lens on a Si charge-coupled device (CCD, Cool SNAP MYO, 1940 × 1460 imaging pixels whose size is $4.54 \times 4.54 \ \mu m^2$, Photometrics). Typically, the respective G-band image data were collected for 300 or 500 s.

2.4.2. Line Raman measurements

Accurately-positioned Raman spectra were obtained by line Raman measurement right after G band imaging, according to the method used in our previous report [37]. After removal of the G-band bandpass filter, the emission light was introduced into a monochromator (Triax 320, f = 320 mm, Horiba Jobin-Yvon) with 1800 grooves/mm. The entrance slit was adjusted to 0.3 mm and a Si array CCD (Syncerity, 1024 × 256 pixels whose size is $26 \times 26 \ \mu\text{m}^2$, Horiba Jobin-Yvon) was utilized to collect Raman spectra. The line spectra data were acquired either over *ca*. 30 min or 11 h (for R band measurement), and corrected and normalized with respect to the 520.89 cm⁻¹ Si peak.

2.5. Reflection imaging spectroscope setup and measurements

2.5.1. Reflection imaging spectroscope setup

The reflection imaging spectroscope was constructed by implementing the excitation component of a commercially available fluorescence spectrophotometer (Nanolog[®] 3-211, Horiba Jobin Yvon) which consists of high power Xe arc lamp (220–1000 nm, 450 W, OFR) and a subtractive double mono-chromator. Visible light selected from double monochromator (slit width: 14 nm) was passed through a beam expander consisting of

two bi-convex lenses (LB1811-A (f = 35.0 mm) and LB1761-A (f = 25.4 mm)) to obtain smaller beam size (*ca.* 2 cm). An additional bi-convex lens (LB1676-A, f = 100.0 mm) was used to focus excitation light to the back focal plane over a long working distance 50 × objective (LMPlanFl, numerical aperture (N.A.) = 0.5, Olympus) through an upright microscope (BX41M, Olympus). The reflected light was acquired by using the same CCD used for Raman imaging.

2.5.2. Reflection image stack and spectra acquisition

A series of reflection images were collected with an acquisition rate of 1.1 frames/nm in the range of 440 (2.81) to 650 nm (1.90 eV) (exposure time for each frame: 2 s). An image stack of the bare substrate was also acquired for reflection normalization. The collected image stack was further analyzed by using Image J [46]. Reflection spectra in the specific regions of interest (ROI, 7 × 7 or 10 × 10 pixels) were obtained by using z-axis plot profiling from the normalized image stack.

3. Results and discussion

3.1. Characterization of tFLG growth by CVD

tFLG samples were prepared on a quartz substrate by using LPCVD conditions and a subsequent transfer technique. Graphene was synthesized on a copper foil using our previously reported method (see Experimental for details) [37]. The resulting graphene sheet was transferred to a substrate by using a 75 nm thick PMMA protective layer, and then subject to acetone washing and subsequent air annealing (350 °C for 3 h) [44].

Analysis by using both SEM and AFM revealed that hexagonal FLGs were generated in this manner. Fig. 2A contains a SEM image of the annealed graphene sample on the substrate. The image shows that concentric hexagonal FLGs of up to 10 µm in diameter are distributed over substrate. The progressively darker tone of FLGs toward their center as compared to that for bare substrate (red arrows) is a consequence of increasing layer numbers. Close inspection of the FLG grains shows that multiple hexagonal edges of the FLGs are well-aligned and that number of straight graphene wrinkles exist in thicker tone. The low carbon versus hydrogen feed condition used during the extended growth time period is known to cause the formation of partially grown FLGs because of a reduced nucleation density [47,48]. This result originates from the "pyramid" formation mechanism of FLG growth [47,49]. Figs. 2B and C display AFM height topographies of FLG and SLG regions, respectively. The FLG image shows that ca. 0.5 nm edge steps are present, suggesting that single layer augmentation (0.34 nm) exists in each. Inspection of the zoomed-in image of SLG region (Fig. 2C) shows that height variation is less than 1.5 nm over μ m area, indicating that the graphene has a clean surface without the presence of substantial adsorbates.

Although its surface appears clean, the localized RAC are entrapped between the substrate and graphene. Raman spectra of selected SLG regions are shown in Fig. 2D. The SLG region corresponding to the top Raman spectrum contains strong G and 2D bands at *ca*. 1601 and 2693 cm⁻¹, respectively, with a weaker D band at 1348 cm⁻¹. The G-band is upshifted by 19 cm⁻¹ as compared to that (*i.e.*, 1582 cm⁻¹) of charge-neutral SLG [50], a difference that indicates highly-doped graphene induced by the substrate [35]. The FWHM (numbers in parentheses) of G, 2D, and D bands are 15, 38, 40 cm⁻¹. The intensity ratio of the 2D and G bands (I_{2D}/I_G) is 1.2, indicative of SLG [37,51]. The intensity ratio of the D properties are not changed significantly [37]. In contrast, the SLG region corresponding to the Raman spectrum at the bottom of



Fig. 2. (A) SEM image of CVD-grown hexagonal FLG on a quartz substrate. AFM height topography of (B) FLG and (C) SLG regions. (D) The representative Raman spectra from SLG regions in the absence (top) or presence (bottom) of RAC. The measured (circle) and summated data (red) were offset from Lorentzian components for visual clarity. *E*_L: 2.33 eV. Red, blue, and grey (indicated by asterisk) peaks originate from graphene, RAC, and quartz substrate (see main text for details). Parentheses indicates FWHM. (E and F) Widefield G-band images of tBLG regions (E) without and (F) with RAC. (A colour version of this figure can be viewed online.)

Fig. 2D contains D, G and 2D bands at 1349, 1596 and 2694 cm⁻¹, respectively, with narrowed FWHM values. The G band of SLG is upshifted by 14 cm⁻¹ in comparison to that of charge-neutral SLG. The difference in the position of the G-band indicates that SLGs represented by the top and bottom Raman traces exist in different environments. Especially, drastic differences were observed in the broad underlying peaks. Those broad peaks seem to originate from amorphous carbon [52] and were deconvoluted by using a phenomenological fitting (see Supplementary data (SD) for the fitting details). The fitted peaks (blue) are positioned at 1359, 1509, 1588, 1620, and 2939 cm⁻¹ which corresponds to D, D", G, D' and 2D bands [40,42,53]. The I_D/I_G ratio of RAC (*i.e.*, 1.55) is used to deduce phenomenological average distance between sp³ defects in the sp² matrix (see SD for details) [54,55], which translates into an approximate RAC defect density of *ca*. 1.6 nm, indicating its highly amorphous nature [54].

In order to determine whether these features derive from the protective polymer, annealing experiments of PMMA on a quartz substrate were performed. The Raman spectrum (Fig. S1 of SD) of PMMA immediately after spincoating contains symmetric and asymmetric C–H stretching bands at 2841, 2946, and 3010 cm^{-1} , a carbonyl stretching band at 1730 cm⁻¹, a C=C stretching band at 1618 cm⁻¹, and a C–H rocking band at 1451 cm⁻¹, which are in good agreement with those reported previously [56]. On the other hand, the Raman spectrum of the PMMA layer after 350 °C annealing contains broad bands at 1436, and 1623 cm⁻¹, irrespective of the annealing time (*i.e.*, 2 vs 3 h). This observation shows that carbonyl and C-H stretching bands of PMMA no longer exist, a finding that most of oxygen-related Raman bands vanish during annealing. The slight differences seen in vibrational frequencies of annealed PMMA as compared to the RAC embedded graphene indicate that annealing of residual PMMA in the absence of overlaying graphene produces somewhat different carbonaceous structure. Nonetheless, this result shows that protective PMMA is converted into RAC during the annealing step, a finding that is in line with those described in a recent report [42] that suggest that RAC is derived by heating the protective polymer of graphene.

In Figs. 2E and F are displayed widefield G-band images of regions of tBLG in the absence and presence of RAC, respectively. The images were obtained by using global 532 nm laser illumination of the graphene sample, followed by placement of a bandpass filter in the emission side, according to the previously reported procedure (see Experimental for measurement details) [37]. The G-band image of the sample that does not contain RAC (Fig. 2E) has a silent background, along with several segments that are much brighter than other dark graphene-containing areas. The brighter regions originate from G-band enhancement of tFLGs (see below). A graphene layer number determination was made by using reflection and micro Raman measurements, which yield I_{2D}/I_G value greater (smaller) than unity (Figs. S2A and S2B of SD) that correspond to SLG (BLG) [51]. In the presence of RAC (Fig. 2F), a substantial amount of blurry scattering exist in the background as a consequence of RAC-related broad G band (see above). Variations in the scattering suggest that RAC is present in different thicknesses. In order to determine how the Raman spectroscopic properties vary with the thickness of the RAC layer, an AFM measurement of the SLG region of RAC was made through an unintentional hole to the substrate (Fig. S3A of SD). The results show that the height of the RAC layer is 9.1 nm (Fig. S3B). Analysis of the Raman spectrum (Fig. S3C) of graphene/RAC region indicates that the intensity of the broad Dband arising from RAC is about one fifth of that of G band corresponding to SLG, although the large noise hampers accurate deconvolution and comparison of the peaks. Based on the findings described above, we next determined the optical behavior of tBLG in the presence and absence of RAC using areas that are carefully selected through inspection of prior widefield G-band images.

3.2. Reflection and Raman behaviors of tBLG with RAC

A reflection imaging spectroscope, shown schematically in Fig. 3A (see Experimental), was constructed in order to obtain spatial reflection spectra of tBLG at varying excitation energies (E_{ex}) [19]. Following collection of a sequence images, a normalized reflection image stack was produced by normalizing the reflection image stack of sample (R_s) to that of bare substrate (R) (see Supplementary Movie (Smovie) of SD). Each frame of the stack contains spatial differential reflection (($R_s - R$)/R or $\Delta R/R$) corresponding to a specific E_{ex} . By using this technique, reflection images covering the entire visible spectra range were obtained with a rapid acquisition rate (see Experimental). The image stack provides spatio-spectral reflection information caused by vHs peak of tBLG at once.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.10.001.

In Fig. 3B is displayed a false color composite reflection image whose color represents approximate E_{vHs} (see SD for details) [19]. The image indicates the spatial location of tBLG (yellow-dashed line) and the average few µm sized tBLG (see Fig. S4 for tBLG size distribution). Interestingly, a majority of tBLG boundaries are formed near either border of FLGs or graphene wrinkles. This may originate from graphene slippage during growth and cooling steps of CVD-based tBLG owing to mismatched thermal expansion coefficients between the substrate and graphene [48,57]. The latter case is evident by viewing images in Fig. 3C, showing that different tBLG with different E_{ex} are formed near wrinkles. These imaging

capabilities enable rapid identification of tBLG with various E_{vHs}.

Spatial E_{vHs} variation with sub-µm resolution was observed as well. Fig. 3D, acquired along white arrow in Fig. 3B, illustrates the contour map of the spatial net reflection spectra R_{net} (see SD for details). R_{net} is defined by $\Delta R_{tBLG}/R - \Delta R_{SLG}/R$ and is useful in understanding how the optical characteristics of tBLG deviate from those of SLG [12,19]. While the top region does not show any peak, the middle and bottom sections exhibit peak maximum at *ca.* 2.7 and 2.4 eV without any intermediate spectra, indicating the discreet changes taking place in the tBLG regions. In Fig. 3E are shown representative R_{net} spectra of five different tBLGs. Reflection spectra reveal that tBLG has various E_{vHs} on top of a slightly tilted background reflection with minor variations (*i.e.*, 0.005) which originate from the aforementioned thickness variation of the underlying RAC.

Deconvoluted vHs peak properties are listed in left column of Table 1, which contains E_{vHs} , θ , R_{net} at peak maximum and 2.33 eV, FWHM, area, and the corresponding experimental GEF which will be discussed in the later section. Using the acquired E_{vHs} , we calculate θ using the equation, $E_{vHs} = E_0 \sin (3\theta) [32]$. Here, E_0 is two degenerate energies between M points (*i.e.*, 3.9 eV, designated by two green arrows in Fig. 1B). The calculated θ values range from 10.9 to 15.0° as shown at the top of each spectrum of Fig. 3E.

Based on a thin film approximation owing to graphene thickness $\ll \lambda$ [58], $\Delta R/R$ spectra can be used to obtain absorbance *A* at different *E*_{ex} using eq (1),



Fig. 3. Spatial and spectral identification of tBLG using reflection imaging spectroscopy. (A) Schematics of the reflection imaging spectroscope. Abbreviation: BE: beam expander; CV: convex lens; BS: beam splitter; OL: objective lens; TL: tube lens. (B) False-color composite reflection image of hexagonal FLG. The yellow-dashed lines denote tBLG domains. (C) Different tBLG regions near wrinkles obtained by varying E_{ex} . Scale bar: 5 μ m. (D) Spatial reflection spectra of adjacent tBLGs arrow designated dotted area in (B) with different E_{VHs} . (E) Representative R_{net} spectra from various tBLGs whose vHs peaks span a visible range and the calculated θ values. Note that right axis represents calculated absorbance values. (A colour version of this figure can be viewed online.)

Table 1		
vHs peak parameters of tBLGs with	eft) and without (right) RAC, and the resulting GEF values, obtained from reflection and Raman spectroscopies, respectiv	ely.

With RAC				Without RAC							
Reflection Raman				Reflection					Raman		
$ \begin{bmatrix} E_{\rm vHs} & \theta^{\rm a} [^{\circ}] \\ [eV] \end{bmatrix} $	Background-subtracted		FWHM [eV]	GEF	E _{vHs} [eV]	$\theta^{a}\left[^{\circ}\right]$	Background-subtracted		FWHM [eV]	GEF	
		$R_{\rm net}$ at $E_{\rm vHs}$	R _{net} at 2.33 eV	(area)				$R_{\rm net}$ at $E_{\rm vHs}$	R _{net} at 2.33 eV	(area)	
2.10	10.9	0.038	0.006	0.21 (0.012)	4.5 ± 0.3	2.14	11.1	0.029	0.014	0.27 (0.012)	4.7 ± 0.7
2.21	11.5	0.036	0.016	0.20 (0.011)	35.8 ± 2.1	2.20	11.5	0.024	0.014	0.29 (0.011)	10.3 ± 0.5
2.23	11.6	0.042	0.025	0.21 (0.014)	34.7 ± 1.1	2.28	11.9	0.026	0.023	0.26 (0.011)	7.8 ± 0.7
2.37	12.5	0.042	0.037	0.25 (0.017)	32.7 ± 3.2	2.30	12.0	0.025	0.023	0.22 (0.009)	12.4 ± 0.5
2.43	12.8	0.039	0.020	0.24 (0.015)	23.4 ± 1.3	2.38	12.5	0.025	0.021	0.25 (0.010)	15.4 ± 0.3
2.45	13.0	0.035	0.015	0.20 (0.011)	17.6 ± 1.1	2.51	13.4	0.037	0.019	0.39 (0.023)	12.0 ± 0.7
2.48	13.1	0.033	0.013	0.24 (0.012)	12.3 ± 0.8	2.57	13.7	0.037	0.016	0.42 (0.024)	9.9 ± 0.1
2.61	14.0	0.043	0.005	0.23 (0.015)	3.1 ± 0.4	2.65	14.2	0.035	0.007	0.31 (0.017)	2.1 ± 0.1
2.67	14.4	0.042	0.004	0.20 (0.013)	2.5 ± 0.1	2.66	14.3	0.032	0.006	0.32 (0.016)	3.4 ± 0.4
2.68	14.4	0.035	0.001	0.23 (0.013)	2.6 ± 0.1	2.77	15.1	0.034	0.004	0.34 (0.018)	2.6 ± 0.1
2.68	14.5	0.050	0.007	0.26 (0.021)	2.0 ± 0.07						
2.69	14.5	0.041	0.006	0.28 (0.018)	3.9 ± 1.7						
2.76	15.0	0.040	0.002	0.19 (0.012)	2.6 ± 0.3						
Average 0.039		0.23 ± 0.03				0.031		0.31 ± 0.06			
		±0.005		(0.014 ± 0.003)				±0.005		(0.015 ± 0.006)	

^a Based on deconvoluted $E_{\rm vHs}$.

$$\frac{\Delta R}{R} = \frac{4}{n^2 - 1} A \tag{1}$$

where, n' is the refractive index of the underlying substrate and varies within 1% in our measurement range [59]. A plot of the calculated absorbance *vs.* E_{ex} is parallel with R_{net} spectra, as shown in Fig. 3E. This relation can be further utilized to construct sheet conductivity σ^{s} of tBLG peak (see SD for the calculation and Fig. S5), which is about one sixth of direct A transition of MoS₂, one of 2D materials [60–62].

The contribution of the vHs peak of tBLG was determined to evaluate the deviation from Bernal-stacked BLG. Mean values from background R_{net} of tBLG and R_{net} of the vHs peak-only is *ca*. 0.05 ± 0.01 and 0.039 ± 0.005, respectively. As compared to Bernal-stacked BLG intensity (*i.e.*, $2\pi\alpha$), the maximum vHs peak intensity is *ca*. 39% which is a result of strongly hybridized states between the interlayer, while residual percentage is caused by transitions from other states. The experimental vHs peak intensity is larger by 30% than those recently reported in the literature [20,63], the reason for which will be discussed in a later section. In addition, the optical properties of vHs peak are slightly E_{ex} -dependent. The average FWHM is about 0.23 ± 0.03 eV, and the FWHM displays a roughly inclining pattern by 0.03 eV with increasing E_{vHs} (Fig. S6A). The peak area also slightly increases (Fig. S6B).

Raman analysis of the corresponding tBLG regions was performed to obtain the relationship between resonance Raman behavior and reflection spectroscopic properties. Fig. 4A displays a widefield G-band image of a region containing tBLGs. Several tBLG domains (indicated by dashed enclosure) exist in this region as reflected by differences in G-band intensities as compared to those of the remaining BLG area. This observation suggests that variations occur in tBLG GEFs, defined by intensity ratio of G-band of tBLG to that of SLG (or $I_{G, tBLG}/I_{G, SLG}$) [11,14,24–26,32]. Fig. 4B displays Gband spectra of the tBLG regions with different E_{vHs} (see Table 1). In contrast to factor 2 expected for GEF of Bernal stacked BLG, the GEF value of tBLG was found to vary from 2 to 36 when E_{vHs} matches with E_{L} , a phenomenon that has been observed before [11,14,24–26,32].

Moreover, the R band, whose positions (ω_R) are located in the range of 1481–1502 cm⁻¹, appeared for several tBLGs having larger GEF (inset of Fig. 4B). It is known that R bands are associated with



Fig. 4. tBLG region visualized in G-band and STD reflection images, and subsequent Gband enhancement. (A) Widefield G-band image of tBLG (yellow-dashed line) with $E_L = 2.33$ eV. (B) G-band spectra of tBLGs with different G-band enhancement. Inset: the zoom-in spectra of R-band regions. (C) STD reflection image in the E_{ex} range from 2.14 to 2.52 eV, as compared to a (D) reflection image obtained by using $E_{ex} = 2.33$ eV. (A colour version of this figure can be viewed online.)

intravalley longitudinal-optical (LO) rotation (R' or R_{LO}) and intervalley transverse-optical rotation (R or R_{TO}, see Fig. S7A) created *via* double-resonance process, respectively [23,32,64]. It is also reported that while the R' band is seen when θ is small (<10°) because of a strengthened electron-phonon matrix along the LO phonon branch, the R becomes dominant when θ is large. In the detection range of our measurements, the R band is strong. Since θ is dependent on ω_R (Fig. S7B of SD, obtained from Ref. [23]), the latter value can be used to verify the E_{vHs} -based θ value. The calculated ω_R -based θ values, listed in Table S1, were found to be in agreement with E_{vHs} -based θ values, with a typical difference of less than 0.5°. Moreover, the intensity of R band is about 1% of that of G band, it varies in a proportional manner with the G-band intensity (Table S1 of SD), in accordance with a previous finding [32].

In addition, the spatial locations of tBLG with specific $E_{\rm vHs}$ values

are easily obtained by analysis of a novel standard deviation (STD) reflection image (see SD for details). Fig. 4C displays the corresponding STD reflection image of Fig. 4A in the range of 2.33 \pm 0.19 eV whose width stems from a G-band phonon energy or $\hbar\omega_G$ (*i.e.*, 0.197 eV). The image clearly displays tBLG grains which have strong G-band intensities (Fig. 4A) because of the large difference that exists between the vHs peak value compared to that of its flat BLG reflection. For comparison purposes, it should be noted that the reflection image extracted at 2.33 eV (Fig. 4D), does not show strong reflection from the corresponding tBLG region.

The relationship between the optical properties and resonant Gband behavior at 2.33 eV of various tBLGs was evaluated. For this purpose, plots of the background-subtracted R_{net} and experimental GEF vs. E_{vHs} were first compared (Fig. 5A). Both plots display similar Gaussian peaking at 2.33 eV but they differ in at lower shoulder regions (*i.e.*, 2.2 eV). It is noteworthy that the bare R_{net} and experimental GEF do not match (Fig. S8). This observation suggests that vHs peak is a major GEF contributor. In order to explain the discrepancy seen at energies in the range of 2.2 eV, we utilized resonance Raman theory [45,65] where GEF can be described by Eq (2) [22],

$$GEF = \frac{I_{G,tBLG}}{I_{G,SLG}} = JDOS \times \left| \frac{M_{el-ph}}{(E_L - E_{\nu HS} - i\gamma)(E_L - E_{\nu HS} \pm \hbar\omega_G - i\gamma)} \right|^2$$
(2)

where, $M_{\rm el-ph}$ is a constant that includes matrix elements for electron-phonon interactions by the G-band phonon [66], γ is an experimental peak broadening factor which is half of vHs FWHM, and plus and minus signs in $\hbar\omega_G$ indicate anti- and Stokes processes, respectively. Because JDOS is proportional to the reflection value (or absorbance), the calculated GEF values of individual tBLGs can be obtained using Eq (2), based on $E_{\rm vHs}$ and γ in Table 1. As shown in color-coded curves in Fig. 5B, each tBLG has an individual GEF response. Fig. 5C displays the corresponding calculated GEF trends at 2.33 eV (red) as compared to experimental values (blue). It should be pointed out that the plot of calculated GEF vs. E_{vHs} is asymmetric showing a longer tail at lower energies as a result of Stokes effect. By including Stokes effect, experimental and calculated values display similar GEF patterns. Similarly, a GEF vs. E_{vHs} plot of various tBLG associated with anti-Stokes process (Fig. S9B), extracted from individual GEF (Fig. S9A), was also generated. This plot displays an opposite center position and tailing as compared to its counterpart. Although GEF has been previously observed in tBLG, the earlier observations were based on single tBLG probed by using different Raman laser lines [11,14,24–26,32]. To the best of our knowledge, this is first on/off resonance correlation that has been observed between various optical vHs peaks with GEF values, the two dominant tBLG phenomena.

3.3. Substrate effect on vHs peak and GEF variation

Our attention next turned to evaluating the optical properties of tBLG without RAC. It was suggested that θ of vHs should be largely insensitive to extrinsic factors induced by substrate (i.e., doping and strain) [11]. However, actually vHs properties do significantly depend on the underlying substrate. Fig. 6A shows a comparison of R_{net} spectra of tBLGs in the presence (blue) and absence (red) of RAC. As compared to the case when RAC is present, tBLG without RAC displays a much broader vHs peak with reduced peak height. The corresponding background-subtracted *R*_{net} values of tBLG with and without RAC at 2.33 eV are 0.042 and 0.025, respectively, suggesting that peak broadening occurs due to interaction with the underlying substrate. Moreover, this broadening lowers GEF. Fig. 6B displays the corresponding G-band spectra of respective tBLG grains. The broadening causes reduced GEF (ca. 15) by nearly half as compared to that (ca. 33) with RAC present. As a result, G-band enhancement is more susceptible to bare substrate than is the R_{net} value.

The general behavior of tBLG without RAC was observed by analyzing 10 different grains by reflection spectroscopy (Fig. S10) and Raman measurements (see right column of Table 1 for their peak parameters). Fig. 6C illustrates both background-subtracted R_{net} and GEF vs. E_{vHs} plots of various tBLGs without RAC. Both plots display center positions that deviate from 2.33 eV. Moreover, the widths of the R_{net} and experimental GEF plots (ca. 0.38 and 0.33 eV, respectively) are significantly larger than those (0.19 and 0.27 eV in Fig. 5A) of tBLGs with RAC. These trends originate from the individual peak broadening of tBLG. More specifically, a comparison of average vHs peak properties of tBLGs (left and right columns of Table 1, respectively) reveals that the width (height) of the plot for tBLG in the absence of RAC increases (decreases) by ca. 35 (21)% while the area (i.e., 0.015) remains similar in contrast to those of tBLG with RAC (i.e., 0.014). As a consequence, peak broadening causes weakening of resonance Raman behavior, which is evident in the reduced maximum GEF.

The observed vHs peak broadening seems to originate from inhomogeneity caused by charge puddling and topographic corrugation of the bare SiO₂ substrate existing in SLG [33–35,37]. SLG on a bare substrate exhibits spatial charge puddling induced by ionic impurities such as Na⁺ [34]. Das et al. [50] monitored such doping effect by Raman scattering in an electrochemically topgated graphene transistor which show systematic changes of positions and widths of G and 2D bands according to doping concentrations. This behavior arises from localized charge-induced bond stiffening or softening. Importantly, thermal annealing is known to provide enhanced interactions between the substrate and graphene, which leads to significant irreversible doping [35]. In order to determine the origin of these observations, reflection



Fig. 5. Correlated reflection and GEF behavior of various tBLGs. (A) Comparison of background-subtracted *R*_{net} values at 2.33 eV (green-dotted line) and experimental GEF of tBLGs *vs. E*_{vHs}. Dotted curves were drawn for visual guidance. (B) Calculated individual GEF curves from 13 different tBLGs. (C) Comparison of experimental (blue) and calculated (red) GEF *vs. E*_{vHs} trends. (A colour version of this figure can be viewed online.)



Fig. 6. Comparison of R_{net} and Raman spectra of tBLGs in the presence and absence of RAC. (A) R_{net} spectra of tBLGs with (blue) and without (red) RAC. (B) The corresponding G-band spectra. (C) Background-subtracted R_{net} and experimental GEF vs. E_{vHs} plots of tBLGs without RAC. (A colour version of this figure can be viewed online.)

spectra of tBLG without RAC (Fig. S11) were obtained before and after 350 °C annealing. Clearly, a comparison of these spectra indicates that substantial peak broadening occurs and this phenomenon is caused by enhanced inhomogeneity induced by charge impurities. In addition, the observation of a much narrower vHs peak shape and the aforementioned less-shifted position of the G band position in the spectrum of SLG in the presence of RAC (bottom trace of Fig. 2D) can be ascribed to decoupling of the charge inhomogeneity-causing substrate effect. Also, electrical conductivity of RAC, which is typically ~10⁻⁸ S/cm [67,68] might lead to distributing charge even tBLG onto RAC regions. The ramification of

this broadening is that it would impact lifetime of tBLG. Recently, tBLG on substrate [63] was found to exhibit a longer lifetime (70 ps) compared to than those (sub-ps and ps components [69–71]) of FLG and typical metallic systems. We expect that tBLG on RAC or in suspended geometry would have a longer lifetime than that on substrates.

3.4. Reflection and Raman behavior of tFLG

We extend the approach described above to over 3-layer tFLG. Fig. 7A shows a false-color composite reflection image of adjacent



Fig. 7. Reflection and Raman behavior of tFLGs without RAC. (A) False-color composite reflection image of tFLGs. Dotted box indicates adjacent tFLG regions. (B) Reflection spectra of tFLG with increasing layer number. (C) Widefield G-band image corresponding to the area in (A). (D) G-band spectra from each twisted region. Inset: plot of experimental GEF vs. background-subtracted R_{net} at 2.33 eV. (E to G) Origin of vHs peak broadening of tTLG, as compared to tBLG. (E) Schematics of tTLG on a bare substrate, formed by tBLG with rotated SLG. (F) Energy dispersions of tBLG and tTLG in the Brillouin zone. Green, red, and blue arrows indicate E_{vHs} transitions, constituting vHs peak. tBLG has degenerated E_{vHs} (green) while tTLG has split low (blue) and high E_{vHs} (red). (G) Broadened vHs peak of tTLG due to split E_{vHs} , as compared to that of tBLG. (A colour version of this figure can be viewed online.)

tFLG (in the dotted enclosure) including BLG, TLG, and tetralayer graphene (4LG) without RAC. Fig. 7B displays R_{net} spectra from each of the three tFLG regions. Inspection of the spectra shows that an increase in the layer number leads to vHs peak broadening (from tBLG to t4LG: 0.25, 0.34, and 0.46 eV, see Sample 1 of Table S2) on top of increasing background absorption. Inspection of the R_{net} -dependent GEF (see above), by comparing the G-band image and spectra (Figs. 7C and D) with the reflection spectra also shows that a linear relationship exists (inset of Fig. 7D). This observation suggests that tFLG follows GEF behavior according to R_{net} variation induced by layer stacking and resulting peak broadening.

In order to investigate the stacking orientation on peak behavior, the dependence of θ of tFLG on the layer number was determined. The $E_{\rm VHs}$ -based θ of tBLG is 14.3°. Assuming that tBLG extends to FLG, the R band of t4LG at 1484 cm⁻¹ (Fig. 7D) corresponds to a θ of 13.6°. Unfortunately, the other tFLGs (tBLG and tTLG) do not exhibit R bands, presumably a result of lower G-band enhancement (Fig. 7D). The θ change in tBLG and tFLG appears to result in the observed peak broadening.

This peak behavior can be explained by the occurrence of band anticrossing between tBLG with additional graphene layers [72]. Left and right panels of Fig. 7F illustrate schematics of energy dispersion of tBLG and tTLG, respectively. Upon stacking of tBLG with SLG (Fig. 7E), new lower and higher bands are created by anticrossing of respective band structures near M point. This effect produces two transitions (red and blue arrows in Fig. 7F). In the case of tTLG, consisting of tBLG with Bernal stacked SLG, two bands are nearly equal and produce a minimal transition difference as compared to tBLG. In other cases, on contrast, a rotation angle is present and acts to separate the two bands whose separation would be roughly proportional to θ . As a result, vHs peak of these types of tTLGs produce two separate bands or band broadening (top trace of Fig. 7G), as compared to that of tBLG (bottom). This analysis qualitatively supports the observation of peak broadening of tFLG seen in Fig. 7B which originates from small θ differences between tBLG and t4LG (ca. 1.2°). The peak broadening will be significantly larger for large differences between θ values of tBLG and SLG. It is noteworthy that similar vHs peak broadening of tTLG was observed in an earlier study [22].

In fact, no peak shift is seen with a series of tFLG of similar θ values as the number of layers increases. Figs. S12A and S12B show a false color reflection image and reflection spectra of tFLG regions whose layer numbers range from 2 to 4. The vHs peak positions at *ca.* 2.13 eV (or 11.0° based on E_{vHs}) are similar independent of the layer number, although the background-subtracted R_{net} intensity augments with increasing layer. The corresponding G-band image and spectra (Figs. S12C and S12D, respectively) display that their Gband enhancements of each of tFLG regions (dashed boxes) are roughly proportional to background-subtracted Rnet. The corresponding R bands of tTLG and t4LG (Fig. S12D) are at ca. 1505 and 1507 cm⁻¹ which correspond 11.4 and 11.1°, respectively. These values are in line with the E_{vHs} -based θ of tBLG (*i.e.*, 11.0°). Therefore, tBLG with additional (near) Bernal-stacked SLG displays an increased vHs, yet it has an E_{vHs} which is similar to that of tBLG alone. We also observed an example of the aforementioned vHs peak splitting, as evidenced can be seen in the reflection spectra given in Fig. S13. All of these various optical coupling properties are governed by the difference in θ values of the layers. A more quantitative study of this topic will be carried out in our future research.

4. Conclusions

By using simultaneous imaging methods, we have established that a correlation exists between reflection and G-band enhancement of various substrate governed, twisted graphene structures. The method, utilizing global reflection and Raman imaging spectroscopies, enables identification and characterization of vHs peaks of individual tBLG and tFLG along with RAC with spatial and spectral accuracy. In the presence of RAC, the vHs peak has both a narrower width and larger height. G-band enhancement occurs when E_{vHs} matches the energy of the excitation laser, increasing *ca*. 36 times as compared to SLG. Especially, at the individual level of tBLG, the background-subtracted reflection value at 2.33 eV is nearly proportional to the G-band enhancement effect. The vHs peak of tBLG indicates that, upon thermal annealing, strong coupling takes place with the underlying substrate having charge inhomogeneity, and that this coupling leads to peak broadening. This effect extends to adjacent tFLGs with monotonically increased layer number and leads to vHs peak broadening, strengthening, and splitting according to θ and layer number. The approach developed in this investigation provides a method to correlate the relationship of vHs peak and related Raman behavior of tFLG. This study has led to a comprehensive understanding of vHs peak associated with local dielectric environmental changes, and provides a platform to investigate optical properties of other 2D materials.

Conflict of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2016.10.001.

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Supplementary data for

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

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METHODS

1. Defect density calculation of BLG with RAC

The I_D/I_G ratio can be utilized to deduce the defect density (L_D , in nm⁻¹, average distance between two defects) by using following equation (the modified Tuinstra-Koenig relation) [54, 55]:

$$\frac{I_D}{I_G} = C_A \frac{(r_A^2 - r_S^2)}{(r_A^2 - 2r_S^2)} \left[e^{-\pi r_S^2/L_D^2} - e^{-\pi (r_A^2 - r_S^2)/L_D^2} \right]$$

where C_A is the wavelength-dependent parameter, and r_A and r_S are radius of the area surrounding point defect, and of structurally disordered area, respectively [55]. This curve based on the above equation suggests that defect density can be high or low defect regime according to critical defect density $L_D \sim 5$ nm. In our case, L_D is expected to be positioned below critical defect density and the right term of right equation can be ignored. Considering the excitation-dependent parameter, $C_A = 5.4 \pm 1.6$ at the excitation laser (532 nm), and previously determined r_A and r_S values (*i.e.*, 3.1 and 1 nm) [55], the estimated average distance (L_D) between defects was in the range of 1.4 ~ 1.8 nm.

2. Peak fitting of Raman and reflection spectra

All Raman peaks including graphene, RAC and quartz substrate were deconvoluted by Lorentzian shapes, except *ca.* 1509 cm⁻¹ broad amorphous carbon peak in the bottom spectra of Figure 2D, which was fitted by Gaussian function [52]. Reflection spectra of SLG were subtracted from those of tBLG to produce R_{net} spectra of tBLG. All of reflection spectra were also deconvoluted by Lorentzian fitting, although their backgrounds were divided by two cases: the reflection spectra in most of tBLG (corresponding to Figure 3E, 6A, S10 and S11) were fitted by using the background based on the Bernal-stacked bilayer graphene regions of the normalized image stack. Other spectra from FLG, as shown in Figure 7B, S12B and S13B were considered to have linear background.

3. Data processing of reflection imaging

False color composite image: for false color composite reflection images, RGB color corresponding to excitation wavelength of image frame was overlaid to the original frame by using a plugin K_Time RGB color code (Kota Miura, Centre for Molecular and Cellular Imaging, EMBL Heidelberg, Germany). All image stack were projected in z-axis by using either standard deviation or summing slices function, to produce a combined image. The contrast and brightness of resulting image were adjusted for visual clarity. Optionally, in order to facilitate color distinction of the false color image (*i.e.*, Figure 3B, 7A, S11A, S12A and S13A), the extended image of Bernal-stacked BLG of combined image was subtract from the combined false color image with appropriate factor.

Spatial spectra of tBLG region: wavelength axis of a strip of ROI (1×arbitrary pixels) from the collected image stack from tBLG was converted to x axis in order to obtain spatial reflection spectra (*i.e.*, x axis: wavelength, y axis: distance) by using Montage function of Image J [46]. Similarly, spatial spectra of representative SLG was collected so that R_{net} spatial spectra obtained by subtraction of each spectrum are produced. This image corresponds to Figure 3D.

Sheet conductivity calculation: Absorbance of SLG is 2.3% which corresponding to $\pi\alpha$ [43]. Since α is a unit of conductance divided by c, $\Delta R/R$ value is further converted into σ^s . The relationship between absorbance and σ^s is defined by the following: $\sigma^s = (c/4\pi)A$, where *A* has units of $\pi\alpha$. This σ^s is a product of optical conductivity and thickness (*d*) of thin film. The corresponding sheet conductivity of Figure 3E is also given in Figure S5 as well, in the units of conductance quantum ($G_0 = 2e^2/h$).

STD reflection image: STD reflection image (Figure 4C) was acquired by selecting image stack range, followed by z-axis projection of the image stack with standard deviation function.

4. GEF calculation

In order to compute calculated GEF, reflection parameters listed in Table 1 [*i.e.*, E_{vHs} , θ , R_{net} at peak maximum and 2.33 eV, and the FWHM for γ] were substituted for symbols of eq (2) in the main text. G band $\hbar\omega_{G}$ values (0.197 eV) with negative and positive signs were used for Stokes and anti-Stokes shifts,

respectively. Using eq (2), each tBLG with Stokes scattering process shows color-coded resonance windows displayed in Figure 5B. GEF values at 2.33 eV from various tBLGs are collected and produce the calculated GEF pattern at 2.33 eV excitation, as shown in Figure 5C. Anti-Stokes scattering process with positive $\hbar\omega_G$ value was also computed and the corresponding calculated GEF patterns were shown in Figure S9A and B.



Figure S1. Raman spectra of 75 nm thick PMMA on a quartz substrate with different annealing time under air.



Figure S2. Layer number determination of graphene *via* reflection and micro Raman spectroscopy. (A) False-color composite reflection image, and (B) Raman spectra containing both SLG (red) and BLG (green) without RAC.



Figure S3. AFM image and Raman spectrum of graphene region on RAC with a through hole to substrate. (A) AFM height image of graphene on RAC/quartz substrate. (B) Height profile along dashed line in (A). Raman spectrum of (C) SLG on RAC/quartz substrate region. Red, blue, and gray (indicated by asterisk) peaks originate from graphene, RAC, and quartz substrate. D_{RAC} stands for D peaks originating from RAC.



Figure S4. Size distribution histogram of tBLGs used in this study. Solid line is drawn for visualizing distribution. Counts were obtained by counting number of colored tBLG in the several false color composite images, and their lateral sizes were calculated by taking a square root of the area obtained by using Image J.



Figure S5. The corresponding sheet conductivity spectra calculated from R_{net} spectra (Figure 3E in main text) in the units of conductance quantum G_o .



Figure S6. (A) FWHM and (B) area trends of tBLGs with E_{vHs} . Red lines are linear regression curve.



Figure S7.(A) Schematics of intervalley double resonance scattering of R band in tBLG reciprocal lattice. K and K' are inequivalent Dirac points from a black reciprocal lattice, and q is rotational vector. Q_{inter} is intervalley transition and represents R phonon. (B) Dispersion of R band according to θ , adapted with permission from Ref. [23], Copyright 2011 American Chemical Society.



Figure S8. Comparison of R_{net} trend at 2.33 eV vs. experimental GEF of various tBLGs with RAC.



Figure S9. (A) Calculated GEF plots of 13 different tBLGs with RAC using anti-Stokes scattering. (B) Calculated GEF patterns at 2.33 eV using anti-Stokes shift.



Figure S10. R_{net} spectra of tBLGs without RAC. The spectra were offset upward by 0.05 for visual clarity.



Figure S11. R_{net} spectra of tBLG before and after 350°C annealing under air.



Figure S12. Reflection and Raman of additional tFLGs without RAC, showing intensified vHs peak. (A)
False-color composite reflection image of tFLGs adjacent with tBLG. Yellow-dotted box indicates twisted graphene regions. (B) Reflection spectra with tFLGs with increasing layer number. (C) The corresponding widefield G-band image. (D) G-band spectra from respective regions. Inset: plot of GEF *vs.* background-subtracted *R*_{net} at 2.33 eV.



Figure S13. Reflection and Raman of additional tFLGs without RAC, showing double vHs peaks. (A) False-color composite reflection image of tFLGs adjacent with tBLG. Yellow-dotted box indicates twisted graphene regions. (B) Reflection spectra with tFLGs with increasing layer number.

Refl	ection					
$E_{ m vHs}$	θ , based on	Enhancen	nent factor [†]	$\omega_{ m R}$	θ based on	$\Delta heta$ [°]
[eV]	$E_{\rm vHs}$ [°]	G-band	R-band	$[cm^{-1}]$	ω _R [°]	
2.21	11.5	35.8±2.1	0.37±0.10	1501.5±1.4	11.8	0.3
2.23	11.6	34.7±1.1	0.45 ± 0.05	1499.9±2.4	11.9	0.3
2.37	12.5	32.7±3.2	0.62	1490.5	12.9	0.4
2.43	12.8	23.4±1.3	0.18	1490.8	12.9	0.1
2.45	13.0	17.6±1.1	0.27 ± 0.03	1481.0±1.9	13.9	0.9
Average	12.28				12.68	

Table S1. R band properties of several tBLGs and calculated θ based on ω_R .

[†]Enhancement factor = $I_{G \text{ or } R, tBLG}/I_{G, SLG}$

Table S2. vHs peak properties of adjacent tFLG regions without RAC from Samples 1 and 2.

Sample	Layer No.	$E_{\rm vHs}$ [eV]	FWHM [eV]	Area	Backgrou	CEE	
No.					$R_{\rm net}$ at $E_{\rm vHs}$	$R_{\rm net}$ at 2.33 eV	GEF
Sample 1	tBLG	2.65	0.25	0.012	0.032	0.004	4.0
	tTLG	2.67	0.34	0.015	0.028	0.006	5.2
	t4LG	2.53	0.46	0.019	0.027	0.015	15.4
Sample 2	tBLG	2.13	0.25	0.015	0.038	0.011	5.2
	tTLG	2.11	0.26	0.023	0.056	0.015	15.0
	t4LG	2.09	0.27	0.035	0.081	0.020	11.8