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Four-fold Raman enhancement of 2D band in twisted bilayer graphene: evidence for a doubly degenerate Dirac band and quantum interference

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Abstract

We report the observation of a strong 2D band Raman in twisted bilayer graphene (tBLG) with large rotation angles under 638 nm and 532 nm visible laser excitations. The 2D band Raman intensity increased four-fold as opposed to the two-fold increase observed in single-layer graphene. The same tBLG samples also exhibited rotation-dependent G-line resonances and folded phonons under 364 nm UV laser excitation. We attribute this 2D band Raman enhancement to the constructive interference between two double-resonance Raman pathways, which were enabled by a nearly degenerate Dirac band in the tBLG Moiré superlattices.

Keywords: twisted bilayer graphene, Raman scattering, quantum interference

1. Introduction

Graphene has been the focus of attention since the first successful fabrication of single-layer film by mechanical exfoliation a decade ago [1]. This excitement stems from the fact that graphene provides, among many other interesting properties, a clean and versatile experimentation platform with which to test various theories. As a result of research over the last decade, the basic properties of single-layer and AB-stacking bilayer graphene have become well understood [2]. Among many graphene characterization techniques, Raman scattering has proven to be a powerful, non-invasive method that can probe graphene band structure and subsequently distinguish single-layer from few-layer graphene [2, 3]. The strong Raman signal is made possible by graphene's unique cone-like band structure and Raman resonance, in which the energy of an excition laser can always match the graphene interband transition [3]. As a two-dimensional, atomically thin film, graphene also provides a new degree of freedom that is not possessed by other nanostructures: relative rotation between the graphene layers [4]. Rotationally twisted bilayer graphene (tBLG) has recently attracted intensive theoretical and experimental investigations [4–23]. As a result, rotation-dependent properties, such as the van Hove singularity [12, 22], G-line resonances [5, 8, 10, 23] and folded phonons, have been revealed [14, 20, 24, 25]. However, unlike AB-

[8] Equal contribution.

stacking graphene, the chemical synthesis of tBLG with a controlled rotation angle has not been reported; many properties, especially those of non-commensurate lattices, are yet to be explored [13, 26–29].

In this letter, we report the observation of a strong 2D band in tBLG with large rotation angles. In contrast to the expected two-fold enhancement, due to the doubling of the sample volume [5], its intensity is about four times as strong as that of monolayer graphene under visible laser excitation. We attribute such enhanced intensity to the constructive Raman interference between the two Raman pathways, enabled by interlayer coupling and the degenerate Dirac band in tBLG. The observation of enhanced 2D Raman, as well as G-line resonances and folded phonons, indicates that twisted bilayer graphene can be effectively described by the Moiré superlattice [7, 14, 20, 21, 25]. A more than two-fold enhancement in the 2D-band intensity in tBLG with large rotation angles can be found from data in previously published papers, but there was no explicit recognition and discussion about this unusual enhancement [5, 8].

2. Raman results

Twisted bilayer graphene was grown on Cu foils by chemical vapor deposition (CVD) at ambient pressure in a quartz tube furnace [15, 25, 30, 31]. The advantage of such CVD graphene bilayers is that they typically contain two single-crystal domains with relative rotation angles that can be determined by their edge misorientations; this property facilitates Raman characterization and interpretation. More descriptions about growth conditions, rotation angle determination and G-line resonances can be found in our previous work [15, 25]. Figure 1 shows scanning electron microscopy (SEM) images of four bilayer graphene samples and their Raman spectra under 638 nm laser excitation. These samples have increasing rotation angles from 9 to 16 degrees, and the expected rotation dependent Raman spectra can be clearly seen [5, 8, 23, 25]. G-line resonances can only be observed in samples with smaller 9° and 11° rotation angles. The folded phonon can also be seen in figure 1(b) near 1500 cm^{-1}. In addition, the 2D intensity has also experienced significant changes; the integrated intensity increases as the rotation angle increases, as summarized in figure 2(a).

These rotation-dependent Raman spectra of the G-line and the 2D band agree with previously reported observations [5, 8, 10, 23, 25]. However, the unusually strong 2D Raman intensity was not discussed there; the 2D intensity becomes more than twice that of the single-layer graphene. This observation regarding our bilayer graphene with a rotation angle larger than 20 degrees is general. Figures 2(b), (c) show typical Raman spectra of two bilayer graphene films with rotation angles of around 25 degrees. As can be seen, while the intensity of the G-line in the tBLG is doubled, the 2D band intensity becomes about four times stronger. As a comparison, for 'decoupled artificial' bilayer graphene made

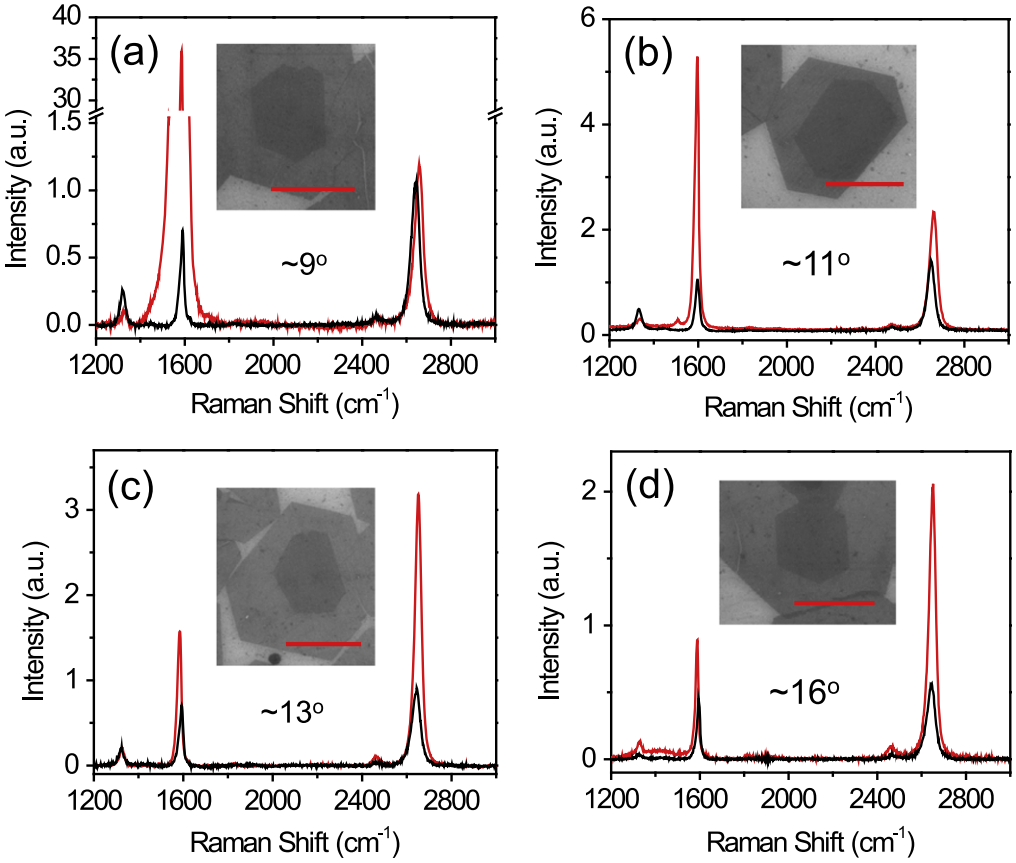

Figure 1. Raman spectra of single-layer graphene (in black) and twisted bilayer graphene (in red) with rotation angles of 9, 11, 13 and 16 degrees. Insets are scanning electron microscopy (SEM) images. The excitation laser wavelength is 638 nm. The scale bar is 5 μm.

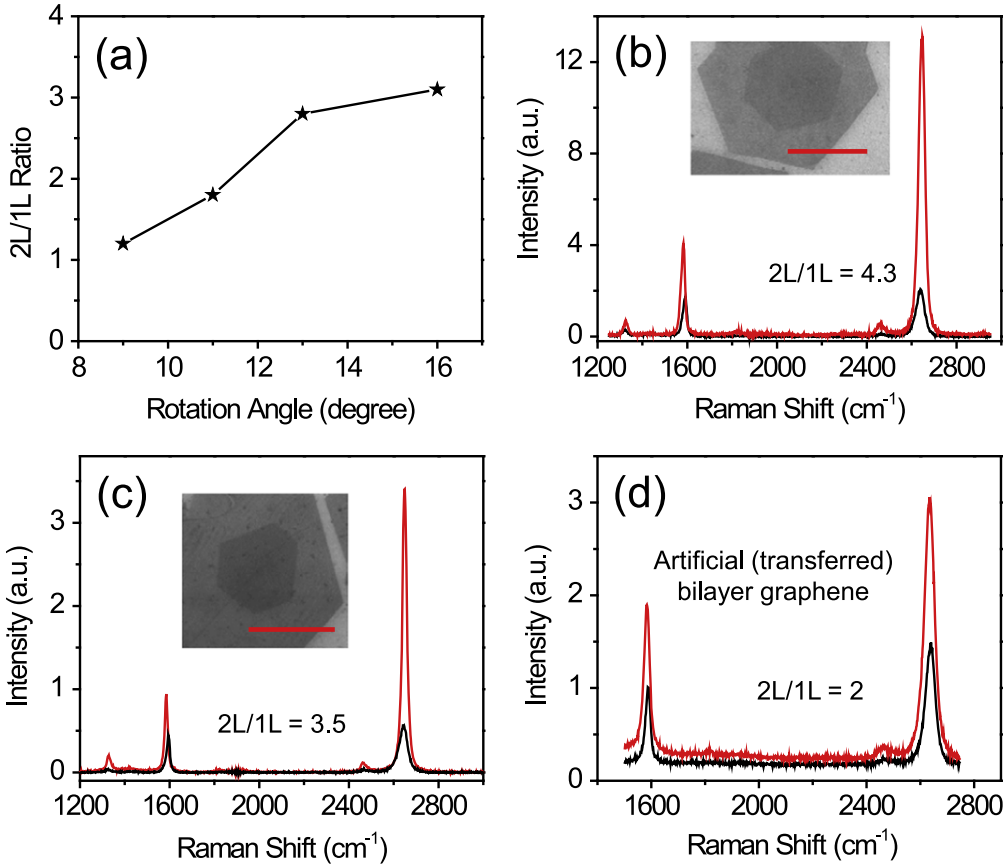

Figure 2. (a) Normalized 2D band intensity of bilayer versus single-layer graphene as a function of the rotation angle. (b), (c) Raman spectra of single-layer (in black) and CVD-grown bilayer (in red) graphene. Insets in (b) and (c) are SEM images of the tBLG with large rotation angles near ∼25°. (d) Raman spectra of single-layer (in black) and uncoupled artificial bilayer (in red) graphene fabricated by transferring one monolayer graphene onto another monolayer graphene. '2L/1L' is the 2D band integrated intensity ratio of the bilayer to the single-layer graphene. The wavelength of the laser is 638 nm. The scale bar is 5 μm.

from simple mechanical stacking by transferring monolayer graphene twice, the 2D band intensity is approximately twice the intensity that was observed in single-layer graphene [8], as shown in figure 2(d). It should be noted that 'coupled artificial' bilayer graphene can be achieved by using a cleaner stacking procedure such as thermal annealing [5, 8], no PMMA [5] or no chemical at all [10, 23].

The observation of a stronger 2D band in twisted bilayer graphene is not limited to 638 nm laser excitation. Figure 3(a) shows Raman spectra under a 532 nm laser from the same sample as in figure 2(c). A strong 2D band is also observed, but when excited by a 364 nm UV laser, a G-line resonance is observed again, and the 2D band becomes weaker and broader, as shown in figure 3(b) [25]. It is important to point out that the peak with a frequency very close to the D-line of single-layer graphene is not the D-line of the bilayer graphene; instead, it is the folded longitudinal optical (LO) phonon of the tBLG superlattice. In addition to a good match between its frequency with the rotation angle [24, 25], the following observation can also rule out the peak as the D band of the bilayer graphene: it is red-shifted but the 2D band shows a blue-shift when compared to the corresponding D and 2D bands of the single-layer graphene. If this peak is the D-line of the tBLG, it is expected to shift in the same direction as the 2D band does. As a matter of fact, both the D and 2D bands in the previous Raman spectra in figures 1 and 2 exhibit the same blue-shifts in the bilayer graphene.

One general observation in the tBLG with large rotation angles is the four-fold enhancement of the 2D band, where the G-line resonances and folded LO phonons were also observed under the 364 nm UV excitation [25]. Because all of the samples with small or the large rotation angles were obtained from the same batch, the Raman measurements were performed under the same conditions, and the only variable among the samples is the rotation angle, the 2D band Raman behavior must be a reflection of the rotation-dependent intrinsic property of the tBLG. Other major factors, such as strain and doping, have been shown to affect graphene Raman spectrum, but they can be ruled out in our case. Recent calculations indicate that twisted bilayer graphene does not show a preferred rotation angle [21]; therefore, the strain is negligible in CVD-grown bilayer graphene. This absence of a strong strain effect is further supported by the Raman spectra of the G-line and the 2D band; both the width and the shape of the G-line remain the same for single-layer and bilayer graphene [32]. The 2D band does not show spectral broadening or red-shift [33, 34]. Raman mappings in figure 4 further show that there is no localized strain in the graphene

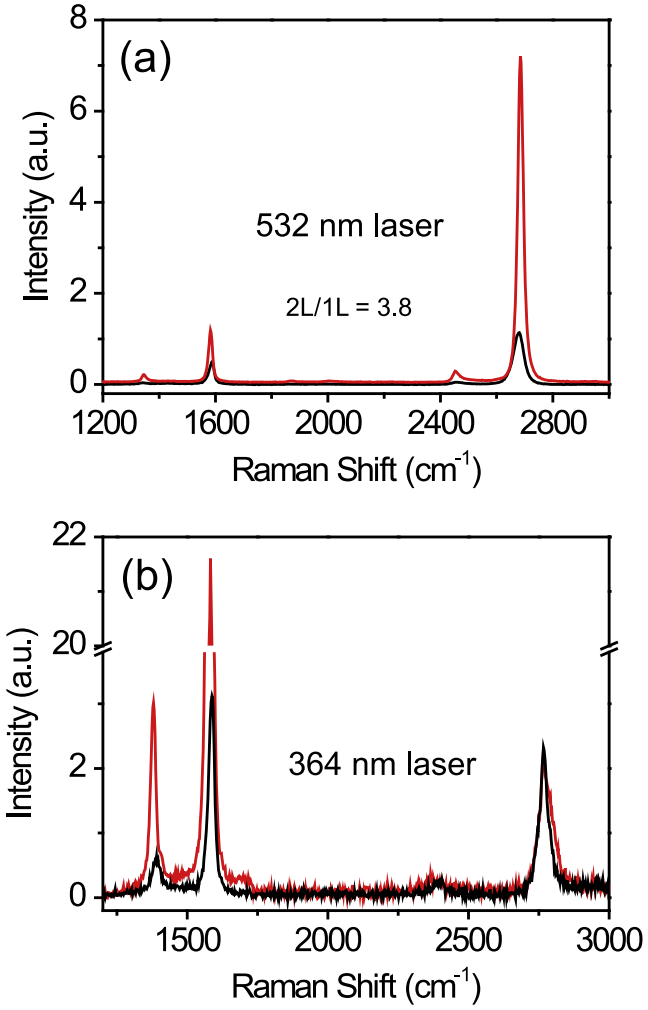

Figure 3. Raman spectra of the sample shown in figure 2(c) under 532 nm (a) and 364 nm (b) laser excitations. Single-layer and bilayer Raman spectra are plotted in black and red, respectively.

bilayer regions, whether they are in AB-stacking graphene or twisted bilayer graphene. An enhanced 2D band was reported in suspended single-layer graphene, and it was attributed to a decreased doping level in the suspended region [35]. This doping effect can be excluded due to the previously-discussed lack of a noticeable change in the G-line width, as well as the blue-shift instead of the red-shift in the 2D band [35].

3. Discussion

The enhanced 2D band intensity in the tBLG is a result of constructive quantum interference between two Raman pathways [36–39]. Figure 5 shows a schematic of the band structures of the tBLG and the representative Raman pathways for the 2D double resonance Raman scatterings [3, 6, 10, 19]. Here, we have assumed that twisted bilayer graphene forms two-dimensional superlattices, defined by the Moiré pattern [7, 13, 14, 20, 40]. For comparison, we only show Raman pathways that involve an interband transition between the two inner Dirac bands: A → B → D and A → C → D, as in AB-stacking bilayer graphene [3].

Let's examine the effect of degenerate pathways on the Raman intensity of the 2D band. First, we note that there are two absorption pathways for an incident photon, either through outer loop interband transition or through inner loop interband transition P_{int}, as shown in figure 5. As a result, the G-line intensity doubles in comparison to the G-line intensity in single-layer graphene. Let's consider the contribution of P_{int} to the 2D band. Because the Raman pathway after A splits into P_{ABD} and P_{ACD}, the total transition amplitude is given by P_{int}* (P_{ABD} + P_{ACD})/sqrt(2), where sqrt(2) is due to the even splitting of the incident amplitude at point A. Assuming P_{ABD} and P_{ACD} have the same amplitude and phase due to a nearly degenerate Dirac band [3, 6, 9, 11, 19, 41], the transition amplitude can be written as P_{int}*P_{ABD}*sqrt(2). Because Raman intensity is the modular square of the transition amplitude, the 2D Raman intensity becomes 2*|P_{int}*P_{ABD}|^2, which is twice the Raman intensity of |P_{int}*P_{ABD}|^2 that is found in single-layer graphene. When the contribution from the outer loop is added, we reach the observed four-fold enhancement of the 2D band in the tBLG.

It should be noted that this Raman quantum interference is enabled by the unique degenerate Dirac band structure of tBLG, which has been calculated for twisted bilayer graphene with a commensurate lattice by many groups [6, 8–11]. In these cases, the degeneracy of the Dirac band is almost guaranteed because bilayer graphene becomes a two-dimensional superlattice with larger unit cells. The band structure of such a superlattice can be constructed by zone folding the monolayer graphene band structure into a reduced Brillouin zone. The band below the M point, or G-line resonance, is a degenerate Dirac band. For twisted bilayer graphene with an incommensurate lattice, there is no simple general theoretical description for the band structure. The observation of rotation-dependent folded phonons, however, indicates that bilayer graphene can be approximated as a Moiré superlattice [7, 13, 14, 20, 23, 40].

It is important to note that there is a finite gap (~20 meV for 13.2 degrees tBLG) between the two Dirac bands [6]. This band splitting is much smaller than ~300 meV in AB-stacking graphene. Besides G-line resonances and folded LO phonons, the low frequency breathing mode of the tBLG is another indication of interlayer coupling [42]. It is the finite interlayer coupling and the finite gap between the Dirac bands that makes it possible to observe such quantum interference between two Raman pathways. For a band splitting of ~20 meV, it is estimated that the Raman peak spacing between the two paths, shown in figure 5, is on the order of 2–5 cm^{-1}, which is much smaller than the measured ~40 cm^{-1} line width of the 2D band [3, 6]. In other words, the two Raman paths are indistinguishable, which is the necessary condition for quantum interference. For a larger gap, as in AB-stacking bilayer graphene, peaks from two Raman pathways can be well resolved, and the pathways become distinguishable, so there is no such quantum interference [3]. When there is no interlayer coupling, as is the case for the decoupled artificial bilayer graphene, the two graphene layers

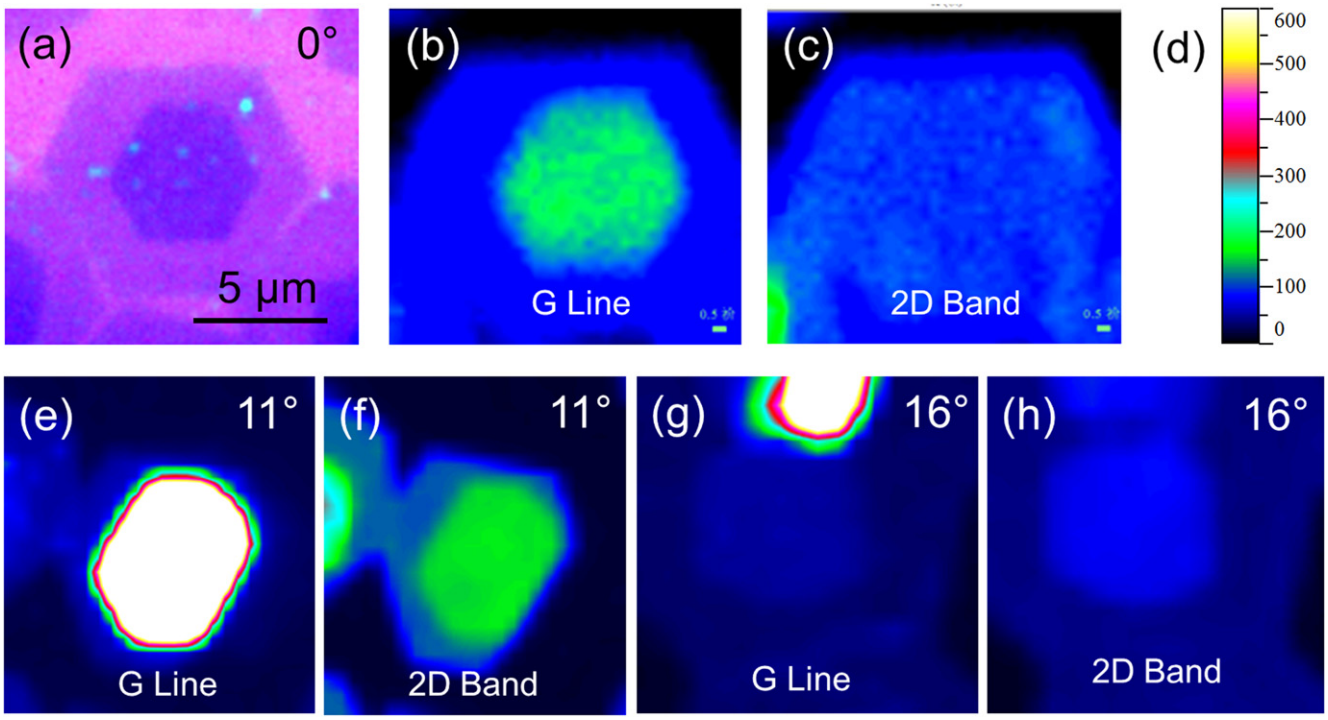

Figure 4. Optical image and Raman mappings of representative bilayer graphene. (a) Optical image, (b) G-line Raman mapping and (c) 2D band Raman mapping of 0 degree (AB-stacking) bilayer graphene. (e) G-line and (f) 2D band Raman mappings of the tBLG with 11 degrees of rotation. (g) G-line and (h) 2D band Raman mappings of the tBLG with 16 degrees of rotation. (d) Color scale.

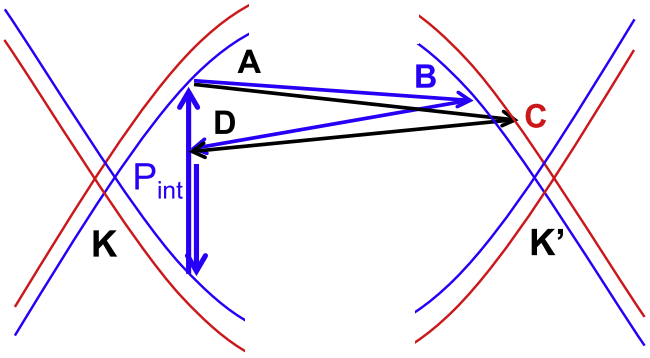

Figure 5. Example of two degenerate 2D Raman pathways involving an interband transition between the inner loops. The excitation laser is tuned below the G resonance of the tBLG.

are then independent from each other, and the total Raman intensity is simply twice that of the single-layer graphene.

Interference phenomena are frequently observed in Raman spectroscopy [36, 37, 41, 43, 44]. The Raman peak can be either enhanced or diminished, depending on the relative contributions from the two Raman paths. The observation of Raman interference typically requires laser excitation energy tuning, such that the incident light is in resonance with two Raman paths simultaneously. The advantage of graphene is that such a resonance condition is naturally satisfied in a wide energy range. As such, twisted bilayer graphene provides us with a unique 2D platform, which we can use to explore distinctive electronic and optical phenomena.

4. Conclusions

To summarize, we have observed four-fold Raman enhancement of the 2D band in tBLG under visible laser excitations, and we have established its correlation with G-line resonances and folded phonons under UV excitation. The enhancement is due to Raman quantum interference, enabled by double resonance and the degenerate Dirac band of the tBLG Moiré superlattice; this cannot be explained using the theory of rotated Dirac bands. We expect that such quantum interference and Raman enhancement can be observed as long as the laser excitation energy is tuned below the G-resonance of the twisted bilayer graphene. The unique property of 2D band Raman allows for the distinction between the twisted bilayer and the other bilayer graphene. The picture of the bilayer Moiré superlattice and its associated band structure will help to reveal more novel properties and applications of twisted bilayer graphene.

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References

[1] Novoselov K S, Geim A K, Morozov S V, Jiang D, Zhang Y, Dubonos S V, Grigorieva I V and Firsov A A 2004 Electric field effect in atomically thin carbon films *Science* **306** 666–9

[2] Castro Neto A H, Guinea F, Peres N M R, Novoselov K S and Geim A K 2009 The electronic properties of graphene *Rev. Mod. Phys.* **81** 109–62

[3] Ferrari A C *et al* 2006 Raman spectrum of graphene and graphene layers *Phys. Rev. Lett.* **97** 187401

[4] dos Santos J, Peres N M R and Castro A H 2007 Graphene bilayer with a twist: electronic structure *Phys. Rev. Lett.* **99** 256802

[5] Kim K, Coh S, Tan L Z, Regan W, Yuk J M, Chatterjee E, Crommie M F, Cohen M L, Louie S G and Zettl A 2012 Raman spectroscopy study of rotated double-layer graphene: misorientation-angle dependence of electronic structure *Phys. Rev. Lett.* **108** 246103

[6] Mele E J 2010 Commensuration and interlayer coherence in twisted bilayer graphene *Phys. Rev.* B **81** 161405

[7] MacDonald A H and Bistritzer R 2011 Materials science: graphene moire mystery solved? *Nature* **474** 453–4

[8] Havener R W, Zhuang H L, Brown L, Hennig R G and Park J 2012 Angle-resolved raman imaging of inter layer rotations and interactions in twisted bilayer graphene *Nano Lett.* **12** 3162–7

[9] Shallcross S, Sharma S, Kandelaki E and Pankratov O A 2010 Electronic structure of turbostratic graphene *Phys. Rev.* B **81** 165105

[10] Ni Z H, Liu L, Wang Y Y, Zheng Z, Li L J, Yu T and Shen Z X 2009 G-band Raman double resonance in twisted bilayer graphene: evidence of band splitting and folding *Phys. Rev.* B **80** 125404

[11] Sato K, Saito R, Cong C X, Yu T and Dresselhaus M S 2012 Zone folding effect in Raman G-band intensity of twisted bilayer graphene *Phys. Rev.* B **86** 125414

[12] Luican A, Li G H, Reina A, Kong J, Nair R R, Novoselov K S, Geim A K and Andrei E Y 2011 Single-layer behavior and its breakdown in twisted graphene layers *Phys. Rev. Lett.* **106** 126802

[13] Bistritzer R and MacDonald A H 2011 Moire bands in twisted double-layer graphene *Proc. Natl. Acad. Sci. USA* **108** 12233–7

[14] Carozo V, Almeida C M, Ferreira E H M, Cancado L G, Achete C A and Jorio A 2011 Raman signature of graphene superlattices *Nano Lett.* **11** 4527–34

[15] Nie S, Wu W, Xing S R, Yu Q K, Bao J M, Pei S S and McCarty K F 2012 Growth from below: bilayer graphene on copper by chemical vapor deposition *New J. Phys.* **14** 093028

[16] Cocemasov A, Nika D and Balandin A 2013 Phonons in twisted bilayer graphene *Phys. Rev.* B **88** 035428

[17] Latil S, Meunier V and Henrard L 2007 Massless fermions in multilayer graphitic systems with misoriented layers: ab initio calculations and experimental fingerprints *Phys. Rev.* B **76** 201402

[18] Hass J, Varchon F, Millan-Otoya J E, Sprinkle M, Sharma N, De Heer W A, Berger C, First P N, Magaud L and Conrad E H 2008 Why multilayer graphene on 4H-SiC(000(1)over-bar) behaves like a single sheet of graphene *Phys. Rev. Lett.* **100** 125504

[19] Hicks J *et al* 2011 Symmetry breaking in commensurate graphene rotational stacking: comparison of theory and experiment *Phys. Rev.* B **83** 205403

[20] Righi A, Costa S D, Chacham H, Fantini C, Venezuela P, Magnuson C, Colombo L, Bacsa W S, Ruoff R S and Pimenta M A 2011 Graphene moire patterns observed by umklapp double-resonance Raman scattering *Phys. Rev.* B **84** 241409

[21] Jiang J W, Wang B S and Rabczuk T 2013 Why twisting angles are diverse in graphene moire patterns? *J. Appl. Phys.* **113** 194304

[22] Yan W, Liu M X, Dou R F, Meng L, Feng L, Chu Z D, Zhang Y F, Liu Z F, Nie J C and He L 2012 Angle-dependent van Hove singularities in a slightly twisted graphene bilayer *Phys. Rev. Lett.* **109** 126801

[23] Carozo V *et al* 2013 Resonance effects on the Raman spectra of graphene superlattices *Phys. Rev.* B **88** 085401

[24] Campos-Delgado J, Cançado L, Achete C, Jorio A and Raskin J 2013 Raman scattering study of the phonon dispersion in twisted bilayer graphene *Nano Research* **6** 269

[25] Wang Y N *et al* 2013 Resonance Raman spectroscopy of G-line and folded phonons in twisted bilayer graphene with large rotation angles *Appl. Phys. Lett.* **103** 123101

[26] Bistritzer R and MacDonald A H 2011 Moire butterflies in twisted bilayer graphene *Phys. Rev.* B **84** 035440

[27] Ponomarenko L A *et al* 2013 Cloning of Dirac fermions in graphene superlattices *Nature* **497** 594–7

[28] Dean C R *et al* 2013 Hofstadter's butterfly and the fractal quantum Hall effect in moire superlattices *Nature* **497** 598–602

[29] Hunt B *et al* 2013 Massive Dirac fermions and Hofstadter butterfly in a van der Waals heterostructure *Science* **340** 1427–30

[30] Yu Q K *et al* 2011 Control and characterization of individual grains and grain boundaries in graphene grown by chemical vapour deposition *Nat. Mater.* **10** 443–9

[31] Wu W, Liu Z H, Jauregui L A, Yu Q K, Pillai R, Cao H L, Bao J M, Chen Y P and Pei S S 2010 Wafer-scale synthesis of graphene by chemical vapor deposition and its application in hydrogen sensing *Sensors Actuators* **150** 296–300

[32] Huang M Y, Yan H G, Chen C Y, Song D H, Heinz T F and Hone J 2009 Phonon softening and crystallographic orientation of strained graphene studied by Raman spectroscopy *Proc. Natl. Acad. Sci. USA* **106** 7304–8

[33] Huang M Y, Yan H G, Heinz T F and Hone J 2010 Probing strain-induced electronic structure change in graphene by Raman spectroscopy *Nano Lett.* **10** 4074–9

[34] Yoon D, Son Y W and Cheong H 2011 Strain-dependent splitting of the double-resonance Raman scattering band in graphene *Phys. Rev. Lett.* **106** 155502

[35] Berciaud S, Ryu S, Brus L E and Heinz T F 2009 Probing the intrinsic properties of exfoliated graphene: Raman spectroscopy of free-standing monolayers *Nano Lett.* **9** 346–52

[36] Duque J G, Telg H, Chen H, Swan A K, Shreve A P, Tu X M, Zheng M and Doorn S K 2012 Quantum interference between the third and fourth exciton states in semiconducting carbon nanotubes using resonance Raman spectroscopy *Phys. Rev. Lett.* **108** 117404

[37] Menendez J and Cardona M 1985 Interference effects: a key to understanding forbidden Raman scattering by LO phonons in GaAs *Phys. Rev.* B **31** 3696–704
[38] Burke B G, Chan J, Williams K A, Wu Z L, Puretzky A A and Geohegan D B 2010 Raman study of Fano interference in p-type doped silicon *J. Raman Spectrosc.* **41** 1759–64
[39] Clark R J H and Dines T J 1981 Interference between a-term and b-term resonance Raman-scattering for totally symmetric modes *Chem. Phys. Lett.* **79** 321–5
[40] de Laissardiere G T, Mayou D and Magaud L 2010 Localization of Dirac electrons in rotated graphene bilayers *Nano Lett.* **10** 804–8
[41] Chen C F *et al* 2011 Controlling inelastic light scattering quantum pathways in graphene *Nature* **471** 617–20
[42] He R, Chung T-F, Delaney C, Keiser C, Jauregui L A, Shand P M, Chancey C C, Wang Y, Bao J and Chen Y P 2013 Observation of low energy Raman modes in twisted bilayer graphene *Nano Lett.* **13** 3594–601
[43] Bussi G, Menendez J, Ren J, Canonico M and Molinari E 2005 Quantum interferences in the Raman cross section for the radial breathing mode in metallic carbon nanotubes *Phys. Rev.* B **71** 041404
[44] Ralston J M, Wadsack R L and Chang R K 1970 Resonant cancelation of Raman scattering from CdS and Si *Phys. Rev. Lett.* **25** 814