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To cite this article: Thonimar V Alencar et al 2018 J. Phys.: Condens. Matter 30 175302

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Twisted bilayer graphene photoluminescence emission peaks at van Hove singularities

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Received 30 December 2017, revised 2 March 2018
Accepted for publication 13 March 2018
Published 3 April 2018

Abstract
We report on photoluminescence emission imaging by femtosecond laser excitation on twisted bilayer graphene samples. The emission images are obtained by tuning the excitation laser energies in the near infrared region. We demonstrate an increase of the photoluminescence emission at excitation energies that depends on the bilayer twist angle. The results show a peak for the light emission when the excitation is in resonance with transitions at the van Hove singularities in the electronic density of states. We measured the photoluminescence excitation peak position and width for samples with various twist angles showing resonances in the energy range of 1.2 to 1.7 eV.

Keywords: graphene, twisted bilayer, luminescence, femtosecond excitation

(Some figures may appear in colour only in the online journal)

1. Introduction

The optical properties of twisted bilayer graphene (tBLG) samples show interesting dependence on the rotation angle between the two graphene layers, the twist angle. The understanding of these properties are important both from the fundamental point of view and for device applications. For the tBLG, the van Hove singularities (vHs) in the electronic density of states (DOS) appear at lower energies than in single layer graphene (SLG) due to the coupling between the layers, represented by two Dirac cones separated by a wavevector depending on the twist angle [1–5]. Recent results showed the application of a tBLG as a photodetector with selectively enhanced photocurrent generation due to strong light-matter interaction at the vHs [6]. Also fast dynamics of the photoexcited electrons in bilayer graphene has been observed using transient-absorption microscopy [7, 8] and time- and angle-resolved photoemission spectroscopy [9–11].

In contrast to graphene, that shows a broad and almost flat optical absorption in the visible and near-infrared spectral region [12], tBLG presents peaks in the optical absorption that depends on the twist angle due to the presence of the lower energy vHs [13–15]. The theoretical and experimental studies until 2016 are discussed in the review by Rozhkov and co-workers [1] and the references therein. For a very small twist angle, 1.2°, a peak was observed in the terahertz frequency range [13]. Wang et al [14] presented results for the optical conductivity in the visible range, 505 nm (2.46 eV) to 705 nm (1.76 eV), and they observed peaks for samples with twist angles of 7.5° and 13.7°. Havener et al [15] presented a more comprehensive study and showed peaks at the absorption spectra for samples with angles ranging from about

\textsuperscript{4}The authors contributed equally to this work.
8°–25°. For twist angles smaller than about 12° the observed vHs energy transitions show a linear behaviour with the twist angle. However, to date, the reported results are mainly on light absorption measurements. Here we present studies that show photoluminescence (PL) emission from tBLG samples after femtosecond laser excitation showing a broad wavelength light emission. As in SLG the emission due to direct electron–hole recombination is not detectable [16–23] and the observed emission presents the black body thermal like behaviour. We show PL excitation (PLE) measurements by confocal scanning optical microscopy imaging to map the thermal emission intensity in the single layer and the bilayer regions in the samples. We observe an increase of the PLE intensity at excitation energies that depends on the bilayer twist angle due to resonances with the vHs. Also the laser excitation in the near infrared region, 1.2–1.7 eV covers transitions in resonance with vHs for twist angles in the range 5.5° to 7.5°, that is an angle range not yet studied in the literature. Some of our preliminary PLE results were presented at the Lasers and Electro-Optics Europe & European Quantum Electronics Conference 2017 and is published in the extended abstract [24]. The application of graphene as light emitting devices has been recently demonstrated [23, 25]. This observation of PL emission from tBLG showing a twist angle dependence may lead to the use of tBLG for tunable light emitting devices.

2. Experimental

The tBLG single crystals were prepared by ambient pressure chemical vapor deposition synthesis on polycrystalline Cu foils. The nucleation conditions on Cu foils are controlled to allow both constituent layers to form as hexagonal single crystals, and each tBLG grain has a specific twist angle. The samples were transferred to a transparent amorphous quartz substrate for the optical images and spectroscopy measurements. The transfer was made using a polycarbonate film that was then removed using chloroform. More details about the sample preparation are presented in the [26].

To select the samples for the PLE studies we first measured the sample twist angle by an analysis of the flake shapes on optical microscopy images. The optical images were obtained using a Olympus microscope (DP72) in reflection mode with a 100× objective lens. To obtain the twist angle we drew a hexagon for each layer and measured the angle between the edges of the two hexagons [27], as can be seen on the left hand side sample in figure 2(a). We also characterized the sample twist angle by Raman spectroscopy using an alpha300R WITec confocal Raman spectrometer with an excitation laser at 633 nm. The Raman spectra were measured in backscattering geometry on a triple monochromator spectrometer equipped with a liquid-N$_2$ CCD. All measurements were performed at room temperature.

To obtain samples with vHs in the wavelength range of the Ti:sapphire laser we estimated the twist angle from the optical images and from the Raman spectra analysis. Figure 1 shows the normalized Raman spectra for the samples studied, A$_1$–A$_2$. The Raman modes G, L and 2D can be observed for all the samples. The L peak observed in the Raman spectra of tBLG samples comes from phonons within the interior of the Brillouin zone (BZ) of graphene that are folded to the centre of the reduced Moiré pattern BZ. The wavevector of these phonons corresponds to the wavevector of the Moiré pattern, therefore their frequencies depend on the twisting angle $\theta$. The L label is related to a folding from the LO branch [28]. Thus, the angle can be obtained from the position, width and intensity of the Raman peaks as described in [28–35]. The calculated twist angles are in the range of 5.8° to 7.6°. Nonetheless due to the low dispersion of the LO branch for angles lower than 10° the error on the obtained angle value is large. Thus, these values were used only for selecting the samples for the PLE measurements and not for a precise angle measurement.

The PL imaging was performed using a modified confocal microscope (Olympus FV300) with infrared 140 fs laser pulse excitation from a Ti:sapphire laser (Chameleon from Coherent Inc). The excitation laser wavelength is tuned from 800 nm to 1000 nm (i.e. from 1.24 eV to 1.55 eV) for the PLE measurements. After the scanning mirrors the laser is focused on the flakes at normal incidence using a 60× objective lens. The images are obtained with the scanning rate of 2.71 s/scan for a 512 x 512 pixel scan area (pixel size of 0.092 μm) and an average intensity of 1 mW (fluences on the range of 25.1 to 39.3 J m$^{-2}$). The emission signal is measured on back scattering, it is separated from the laser by a dichroic mirror (Semrock FF665-Di02) and detected by a time-correlation single-photon counting PMT (Becker–Hickl). A band-width filter (75 nm centred at 610 nm) is used in front of the detector to further block any scattered laser light (Chroma 610/75M). For some samples (A4 and A6 in figure 3) the measurements were performed using a picosecond laser (APE PicoEmerald) with 6ps pulse width and 76 MHz repetition rate. However, it should be noted that as the intensities are presented normalized by the single layer graphene under the same excitation conditions, the PLE measurements show the same
behaviour. The average intensity at each sample region (tBLG and SLG) in the PL images were measured using the ImageJ software [36]. For the PL spectra measurements the emission signal was directed to a spectrometer (Andor, Shamrock 303 with a CCD DU401A).

3. Results and discussion

Figure 2(a) shows an optical image for three tBLG samples where it is possible to observe the optical contrast between the bilayer (central hexagon) and the single layer (outer hexagon) regions on the substrate. It is well-known that each irregular hexagon preferably has the edge in the zigzag direction of the graphene honeycomb lattice [26]. Then, the optical image can be used to estimate the stacking angle between the layers. The twist angle is measured between the edges of the two hexagons [27]. The PL images for the same tBLG samples are shown in figure 2(b). The images are intensity maps where high intensities are in brighter colours and low intensities in black. Note that the sample with twist angle of 6.4° shows more intense emission at the bilayer region than the other flakes in the image. As it is going to be shown along the paper this brighter emission occurs only for samples with the twist angle such that the excitation energy is in resonance with the vHs transition, sketch in figure 2(c). The PL spectra show a broad wavelength light emission, figure 2(d). After excitation by a pulsed laser, the photoexcited electrons and holes thermalize through carrier–carrier scattering on a time scale of tens of femtoseconds and a quasi-equilibrium distribution of hot-electrons is formed with an effective temperature higher than the lattice temperature and these hot electrons can emit light as a thermal black body like radiation, with a broad range of energies well above of the excitation energy [16–23]. The enhanced absorption for transitions in resonance with the vHs at the tBLG leads to higher electron temperature ($T_e = 2900$ K) at the tBLG and hence higher emission intensity than the SLG ($T_e = 2500$ K). The radiation emission efficiency considering the Stefan–Boltzmann law is on the order of $10^{-6}$, see [25].

The enhanced thermal emission for the excitation in resonance with the vHs would allow to map the singularities. Thus to study this intensity dependence we perform imaging measurements varying the laser excitation wavelength in steps of 10 nm. The excitation dependence were obtained measuring an PL emission image for each laser excitation wavelength, the PLE. The PLE spectra have the same thermal like shape for all the excitation wavelengths, only the overall intensity changes. From each image we analyse the PL intensity at
As the PLE peak is due to an increase of the absorption at the vHs transitions as for these samples the vHs is not in this wavelength range. The observed intensity for the normalized peaks, between 2 and 3 times that of single layer graphene, are comparable with theoretical calculations of the optical absorption enhancement at vHs transitions [4].

The samples A5 and A6 show no emission enhancement at the vicinity of the overlap of the two Dirac cones where the DOS acting graphene [29]. The transition energy between the conduction and the valence vHs, $E_{vHs}$, scales with the twist angle, $\theta$, and it can be written as [2]:

$$E_{vHs} = \frac{(8\pi h v_F/3a)}{\sin(\theta/2)},$$

where $h$ is the reduced Planck’s constant, $v_F = 1 \times 10^6$ m s$^{-1}$ is the Fermi velocity of graphene and $a = 0.247$ nm is the graphene lattice parameter. The PLE measurements show that the enhancement of the absorption at the $E_{vHs}$ transitions leads also to an emission enhancement. Thus the peaks in figure 3 appear when the excitation energy matches the vHs energy transition for each sample. Considering the energy obtained from the fitted peak and the equation (1) we calculate the twist angles, the values are shown in table 1. In the work by Havener et al [15] they considered the excitonic effects and proposed an empirical function for their angle measurements in the range 8° to 30°. If we use their expression we would obtain angles that are about 0.2° lower than the ones in table 1.

From the PLE measurements we obtain also values for the vHs resonance width, table 1. The values are close to the ones obtained by Havener et al [15], that are around 0.25 eV, for samples with slightly larger angles, 8°–10°. As the PLE peak is due to an increase of the absorption at the vHs, the peak widths are expected to be similar. Also, values around 0.25 eV were obtained by resonance Raman measurements [37] and values around 0.23 eV by reflection measurements [35].

<table>
<thead>
<tr>
<th>PLE peak (eV)</th>
<th>angle (°)</th>
<th>FWHM (eV)</th>
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<tbody>
<tr>
<td>1.27</td>
<td>6.5</td>
<td>0.22 ± 0.03</td>
</tr>
<tr>
<td>1.32</td>
<td>6.8</td>
<td>0.26 ± 0.01</td>
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<tr>
<td>1.38</td>
<td>7.1</td>
<td>0.23 ± 0.01</td>
</tr>
<tr>
<td>1.40</td>
<td>7.2</td>
<td>0.27 ± 0.03</td>
</tr>
</tbody>
</table>

4. Conclusions

In conclusion we have observed thermal like emission from tBLG samples. The PLE results show that the PL emission presents a wavelength dependence with peaks for the excitation in resonance with the vHs. The enhancement of the emission is due to the increase of the optical absorption at the singularities. The observed PLE resonance peak energies and widths are in good agreement with optical absorption measurements in the literature. Moreover the results expand the range of twist angles studied with optical spectroscopy. The understanding of these features are important for possible applications in tunable optoelectronic devices.

Acknowledgments

We acknowledge financial support from the Brazilian funding agencies: Fapemig, CNPq, Capes and INCT Carbon Nanomaterials.

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References