Raman spectra of misoriented bilayer graphene

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We compare the main feature of the measured Raman scattering spectra from single layer graphene with a bilayer in which the two layers are arbitrarily misoriented. The profiles of the 2D bands are very similar having only one component, contrary to the four found for commensurate Bernal bilayers. These results agree with recent theoretical calculations and point to the similarity of the electronic structures of single layer graphene and misoriented bilayer graphene. Another new aspect is that the dependance of the 2D frequency on the laser excitation energy is different in these two latter systems.

Single-layer graphene (called graphene in the following), defined as a two-dimensional honeycomb lattice of carbon atoms, has rencently attracted major attention from the physics research community [1, 2]. Part of the interest lies in the nature of the electronic band structure which permits carriers to behave as massless Dirac fermions with a vanishing density of states at the Fermi level [3]. These properties are destroyed as soon as two graphene layers are staked in Bernal AB configuration (referred in the following as Bernal bilayer) as the electronic dispersion curve is no longer linear [4, 5]. The two main processes that are mostly used for the production of graphene are mechanical exfoliation [6] and expitaxial growth on SiC [7]. Epitaxial growth is well adapted to scaling-up and electronic integration, but is controversial because until now several graphene layers are produced, although on rotational disordered configuration (no Bernal AB stacking). Mechanical exfoliation is a convenient and inexpensive way to produce graphene but has the main drawback of producing huge amounts of multilayer graphitic pieces. The biggest issue for SiC epitaxial growth concerns its ability to preserve the linear electronic structure of graphene despite the presence of several misoriented layers. According to Hass *et al.* [8], the interesting electronic transport properties are preserved. Recent calculations by Latil *et al.* [9] seems to comfort these results. The first step in understanding this important system consists in studying two misoriented graphene sheets and comparing them to graphene.

The main difficulty in this experiment consists in making sure that the observed system is indeed what we seek: i.e. a superposition of two graphene layers which are arbitrarily misoriented one with the respect to the other (a rotational stacking fault). The work of Ferrari *et al.* [10] has pointed out the importance of Raman spectroscopy in order to identify unambiguously single layer graphene from Bernal multilayers graphene. However, if the calculation by Latil *et al.* [9] turns out to be correct, graphene and misoriented bilayer graphene will exhibits identical Raman signature. We need to use an other independant technique to characterize our system.

In this paper, we focus mainly on the study of misoriented bilayer graphene although an example of a graphene misoriented on top of a Bernal bilayer will be shown. We took advantage of overlapping samples to probe graphene and misoriented bilayer graphene. These systems are characterized with Atomic Force Microscopy [13] and probed using Raman spectroscopy. We will show that the Raman spectrum of a misoriented bilayer graphene exhibits a single Raman peak, its position depending on the excitation energy. We will state that the use of Raman spectroscopy to identify unambiguously the nature of multilayer graphene is not as simple as previously thought.

Graphene layers were prepared by using mechanical exfoliation of graphite [6] and deposited on Si/SiO_2 substrate with 290-295 nm thermally grown oxide (commercially available from IBS [11]). This oxide thickness allows rapid localization of interesting pieces with an optical microscope. After selecting the most promising pieces, we perform AFM measurements(tapping mode, 300 kHz cantilever with 40 N/m spring constant).

Raman spectra were recorded using two spectrometers. For 488 and 514.5 nm excitation wavelenghts, we use a Jobin-Yvon T64000 spectrometer operating in triple configuration (1800 gr/mm grating mode) coupled with a liquid nitrogen cooled CCD camera. For 633 nm excitation wavelenght, we use a Jobin-Yvon Aramis spectrometer, (1800 gr/mm grating configuration), with a Pelletier cooled CCD camera. Excitation laser light was focussed on the substrate using a confocal microscope with a 1 μm typical spot size. The 633 nm laser spot on sample was smaller than at 514.5 nm and 488 nm, due to the different experimental setup. The laser beam power was set to 3.5 mW on sample for all studied wavelengths. We also measured Raman spectra between 2 and 6 mW and observed no adverse heating effects.

Our principal sample consists in two overlapping graphene which were rotationally disordered. The AFM image of the two graphene (α' and α") and their overlap (α'+α") is shown in figure 1. We checked it was indeed two overlapping graphene as follows: the thickness of each layer relative to the substrate was measured to be 0.7±0.1 nm. The edge of the overlapping graphene (α") on top of the underlying graphene (α') was found to be 0.4±0.1 nm. Finally, the total thickness (α'+α") on top of the SiO_2 was measured at 1.0±0.1 nm. The color, observed through optical microscope, also confirms the thickness of the sheets. Concerning their stacking configuration, we do not know, a priori, if the overlapped layers will be Bernal or misoriented (rotationally disordered). However, it is clear that random overlapping pieces of graphene will not, with a high probability, be stacked following a Bernal configuration with the lower layer. Anyway, as the AB-bilayer Raman fingerprint is well known [10, 12], a straightforward comparison will show if the stacking is or is not Bernal like.

Figure 2 shows the Raman spectra for 633 nm excitation wavelength recorded on the two graphene and compared to the overlap area. We can immediately see that the spectrum of overlapping layers strongly differs from a reference Bernal bilayer Raman spectrum. The unique 2D peak compares well to graphene signature although its energy dependance is different. These two observations suggest that the overlapping is indeed a misoriented bilayer graphene.

Interestingly, the width (FWHM) of the 2D band of the misoriented bilayer graphene is smaller (19 cm^{-1}) than for graphene (26 cm^{-1}). This result should be compared with turbostratic graphite which also exhibits a single 2D peak, but with a width of about 40 cm^{-1} [14].

Figure 2 also compares the G and D bands in graphene and misoriented bilayer graphene. For the graphene, the G peak has been measured at 1585.6 cm^{-1} while it is at 1583 cm^{-1} for the overlapping area (2.6 cm^{-1} shift). The small shift in G peak as a function of the number of layers has already been mentioned in the literature [15]. Note as well that despite the rotational disorder, the D band is identical on graphene alone and on the overlapping area.

In the following, we focus on the excitation dependence of the position of the 2D peak in graphene and misoriented bilayer graphene. When the laser wavelength is reduced to 514.5 nm, the difference between the positions of the two peaks reduces (figure 3, bottom). The small asymmetry in the 514.5 nm spectrum can be explained rather simply by a small contribution of the single graphene sheet; the laser spot been slightly larger on the T64000 spectrometer than on the Aramis spectrometer, thus a part of the beam probes the monolayer near by. The up shift is still measurable. When a laser excitation wavelength of 488 nm is used, the difference between the positions of the two peaks vanishes (Figure 3, top). For 514.5 nm and 488 nm wavelengths, the graphene signal contribution does not allow accurate determination of the width of the misoriented graphene bilayer 2D peak. As the overlapping signal plus a graphene contribution gives a narrower peak than graphene alone, it is clear that the peak width reduction is still present.

Table I summarize the results for two misoriented graphene sheets for the three wavelengths used.

The first conclusion to draw from these measurements is that the interaction between the misoriented graphene layers is weak as it does not split the electronic dispersion curve because only one component is observed contrary to the case of a Bernal bilayer (four components). This observation is in agreement with theoretical calculation [9] as well as transport measurement carried out on rotationnally disordered graphene multilayer grown on SiC [8]. However, the different energy dependence of the 2D band shows that the two systems are not completely equivalent. As the 2D band Raman shift involves both the electronic band structure and the phonon dispersion curve [17], change in either (or both) distribution could induce a shift. In the framework of an intervalley double-resonance process (DR), the incident photon selects the k vector of the resonant electronic state (E_{elec}(k)) in the vicinity of the K point. The enegy loss $E2_D$ depends on the iTO phonon with wavevector q=2k involved in the DR process as $E2_D(q) = 2E_{iTO}(q)$ [19].

In order to explain the misoriented bilayer graphene 2D peak shift compared to graphene, a first hypothesis could be that the interaction opens a gap in the electronic band structure. In this case, we expect the electronic band structure of the misoriented bilayer graphene, for a given k, to be above the graphene band structure. Indeed, for an identical excitation energy, the selected k vector should be smaller due to the gap opening. Thus we expect a down shift of the 2D band (q been smaller as q = 2k) contrary to what is observed. Another argument against this first hypothesis is that we expect a broadening of the 2D band if the electronic band structure is disturbed (e.g. like for the Bernal-Bilayer case). In our case, the width of the 2D band does not increase in the misoriented bilayer compared to graphene. The unique narrow 2D peak and the shift toward high wave number compared to graphene leads us to propose a second hypothesis: for a misoriented bilayer, the weak interaction modifies the phonon dispersion curve while leaving the electronic band structure typically unaffected.

Within this proposition, and from our experimental data, we can extract linear fits for the dispersion of the phonon mode. These coefficients are reported in table II.

It was shown that two misoriented graphene layers exhibit, like a single layer, a single peak around 2700 cm^{-1}. Is it still possible then to discriminate a graphene from misoriented bilayer graphene using only Raman spectrometry? The peak frequency shift is clearly of little use if the excitation wavelength is at 514.5 nm or 488 nm. We suggest that the G to 2D intensity ratio can be used. It is known that, for the first layers, the G peak intensity increases very fast with the number of layers [20]. For the overlapping configuration studied above, at 633 nm excitation wavelength, we found a ratio of 0.46 for the overlap. Measurements over five different graphene sheets (including the two that partially overlap) yield a ratio between 0.8 and 1.5. Note however, that the ratio G/2D is wavelength [10] and gate dependent [18]. Despite these constraints, measuring the G/2D ratio in addition to the unique 2D peak may be the only technical means to recognize graphene from misoriented bilayer graphene using only Raman spectroscopy.

The difficulty in identifying graphene by using only Raman spectra is also illustrated in the following example: among our samples, we have a graphene partially covered by a torn thicker layer (figure 4). We recorded a Raman spectrum (633 nm) on spot (1) and confirmed it was graphene (single 2D peak with G/2D ratio 0.82). On spot (2), where the thick layer is isolated, we identify unambiguously it as a Bernal bilayer from the specific features of its 2D band. The color, which depends on the number of layer, whatever their stacking is, also confirms these conclusions. The overlapping part (spot 3) could then be either a Bernal trilayers (ABA) or a Bernal bilayer plus a misoriented graphene (ABA').

Figure 4 also displays the experimental 2D Raman spectra from spot 3 compared with a known Bernal trilayer recorded at 633 nm. As the signature is clearly different, we propose it is a graphene misoriented on top of a Bernal bilayer (ABA'). According to the calculation of Latil *et al.* [9], a Bernal bilayer plus a rotationally disordered graphene (ABA') should simply exhibit the sum of the spectra from a bilayer (i.e. a broad band with 4 components) plus the unique peak of graphene. The experimental fingerprint indeed shows several contributions, a broad base that is compatible with a Bernal bilayer contribution and a single peak which could correspond to shifted graphene peak. However, their relative intensity is not what is expected for a simple addition of Bernal bilayer and graphene signal. Note that on a noisy background this 2D band could be mistaken for a graphene. The color observed on optical microscope will however rule out this type of error.

Finally one can ask if we were able to measure deviation in inter-plane spacing between A-B and non A-B staking. Unfortunately, even with a higher quality substrate, Atomic Force Microscopy is not accurate enough to measure such deviation, STM analysis will be required.

In conclusion the principal point we have shown is that two misoriented graphene layers still exhibit a single Raman 2D peak contrarily to a Bernal bilayer. This confirms the weak interaction between misoriented layers and brings arguments in favor of the conservation of the linear dispersion of electronic band in multilayer rotationally disoriented graphene on SiC. The different dependence in laser excitation energy of the 2D position does however show that the phonon dispersion curve is modified. Another important information is that the unicity of a Raman 2D spectra is not enough to unambiguously identify graphene, the G over 2D ratio should also be measured.

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TABLE I: Dependence on excitation wavelength (nm) of the 2D frequency (cm^{-1}) for graphene and misoriented graphene bilayer.

Laser excitation wavelength (nm)	488	514.5	633
Graphene (cm^{-1})	2701	2688	2641
Misoriented bilayer graphene (cm^{-1})	2703	2694	2650

TABLE II: Dispersion relation for iTO phonons fitted from experimental Raman shift, for excitation between 633 nm and 488 nm, within the hypothesis of identical electronic band structure for graphene and misoriented bilayer graphene (using linear electronic dispersion with $v_F = 10^6$ m.s^{-1}).

iTO phonon energy (eV) = a.q+b	Graphene	Misoriented bilayer graphene
a (eV.Å)	0.0415	0.0372
b (eV)	0.1514	0.1532

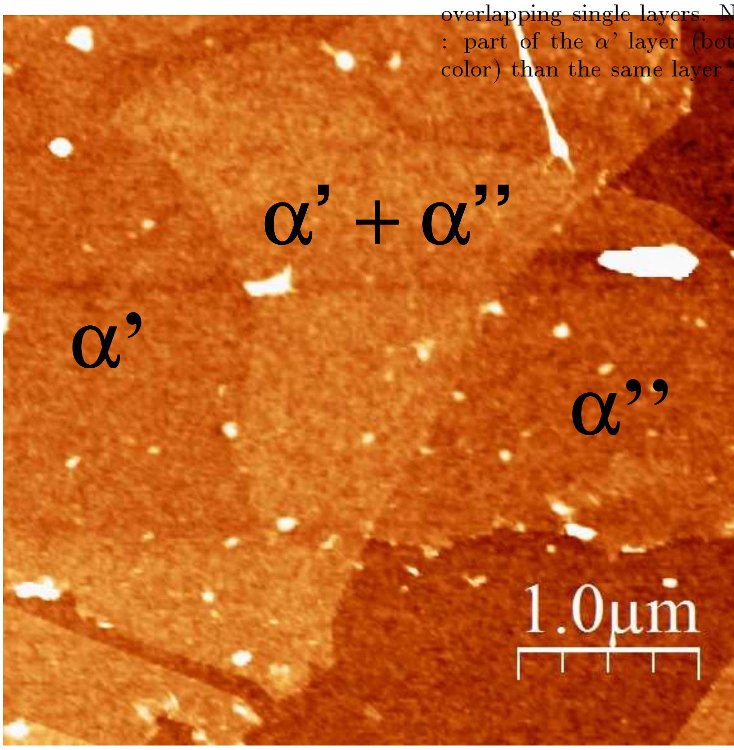

FIG. 1: (color online) AFM image of two graphene layers (α' and α") and their overlap (α'+ α"). All measurements (thickness of α" on top of α' and thickness of each layers on top of SiO_2) are consistent with the hypothesis of two overlapping single layers. Note an image "flattening artifact" : part of the α' layer (bottom left) appears higher (lighter color) than the same layer just above.

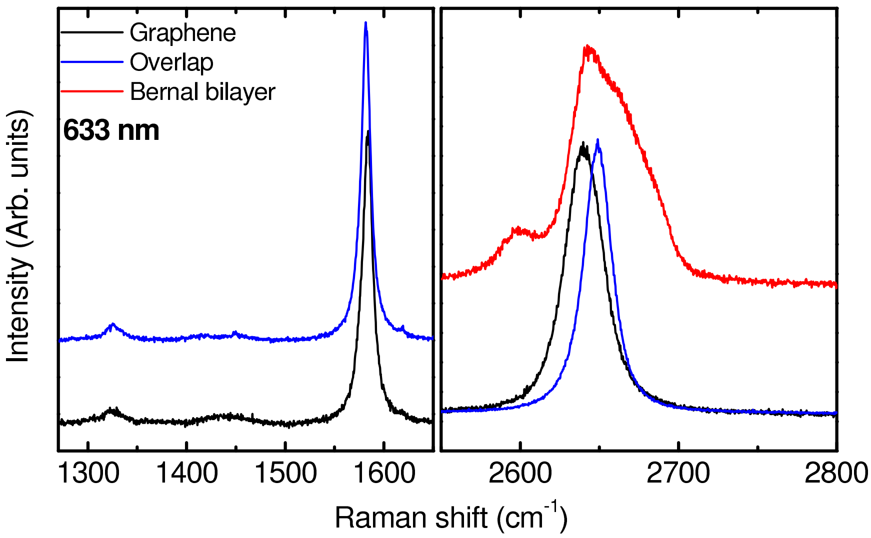

FIG. 2: (color online) Raman spectra of a single graphene sheet (α', black lines), Bernal bilayer (red line) and two overlapping misoriented graphene sheets (α' + α", blue lines) at 633 nm. Left : G and D band range of the graphene and overlapping configuration. Curves have been vertically offset for clarity and normalized on the G peak. The frequency shift is about 2.6 cm^{-1} and comparable to what is reported in the literature. Right : 2D band region for single graphene sheet (α') and overlap (α' + α") compared to Bernal bilayer. The spectrum of α" is almost identical to α' and will hardly been seen if plotted on the same figure. The overlapping graphene spectrum consists in a single peak clearly shifted compared to single graphene. It strongly differs form Bernal stacked bilayer (above curve). Its width (19 cm^{-1}) is smaller than the single graphene peak (26 cm^{-1}).

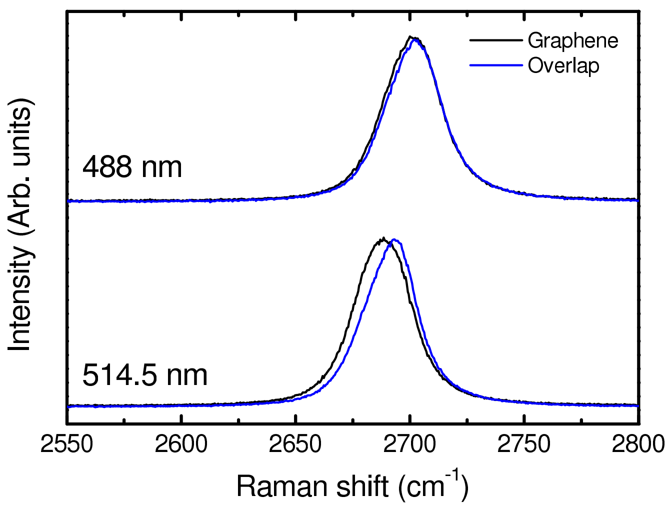

FIG. 3: (color online) Raman spectrum of graphene (black lines) and misoriented bilayer graphene (blue lines) at 488 nm (top) and 514.5 nm (bottom). The difference in Raman shift is reduced compared to 633 nm. The slight asymmetry is due to a contribution of the individual graphene sheet (see text).

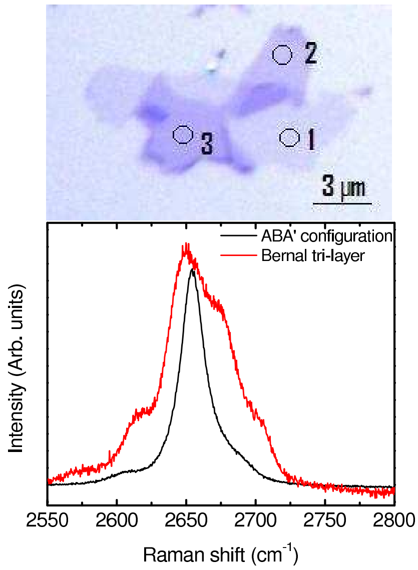

FIG. 4: (color online) Top : Optical microscope image of a thin layer (1) covered by a torn thicker layer (2). Both layers have been independantly probed, (1) has been found to be graphene and (2) identified as a Bernal bilayer. The color also confirms these conclusions. The overlapping area (3) could be ABA (Bernal trilayer) or ABA' (Bernal bilayer plus a rotationally disordered graphene). Bottom : measured Raman signal on (3) (black line) compared to a reference Bernal trilayer (red line) at 633 nm. The clear difference make us state that (3) is a graphene misoriented on top of a Bernal bilayer.