

Large Variations of the Raman Signal in the Spectra of Twisted Bilayer Graphene on a BN Substrate

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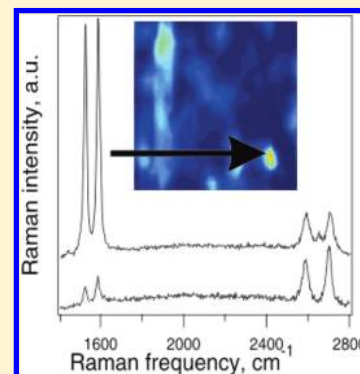
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ABSTRACT: We report an unusual enhancement of the Raman signal of the G mode in a twisted graphene bilayer (2-LG) on a hexagonal single-crystalline boron nitride substrate. We used an isotopically engineered 2-LG, where the top layer was composed of ^{13}C atoms and the bottom layer of ^{12}C atoms. Consequently, it was possible by Raman spectroscopy to distinguish between the enhancement coming from the top and bottom layers. The enhancement of the G mode was, however, found to be similar for the top and bottom layers, and this enhancement effect was observed only at certain locations on the substrate. The experiment with two different laser excitation energies showed that the location of the enhanced spots is dependent on the laser excitation energy. Therefore our results suggest that the enhancement comes from new states in the electronic structure, which are a consequence of a local specific rotation of the grains in graphene layers.



SECTION: Nanoparticles and Nanostructures

Raman spectroscopy has been shown to be a convenient tool for characterizing graphene. It can distinguish between single-layer (1-LG), bilayer (2-LG), and multilayer graphene,¹ and it is also highly sensitive to the doping^{2,3} and stress applied to these materials.⁴ The main features observed in the Raman spectra of graphene are the G mode and the G' mode. In some graphene samples, the D line is also found, indicating the presence of defects or the breakdown of the local graphene symmetry.⁵

The chemical vapor deposition (CVD) process allows the preparation of large and uniform 1-LG flakes.^{6,7} These flakes can be transferred to different substrates^{6,7} including other graphene layers.⁸ 2-LG is an important material suggested for applications in electronic devices. A 2-LG can be prepared by exfoliation from graphite.⁹ This procedure produces AB-stacked graphene. However, the production of double layers is random and the flakes are small. Another approach is to use Ni as a catalyst in the CVD process.¹⁰ The CVD growth process can make large areas of graphene, but again the formation of the 2-LG stacking arrangement is random.¹⁰ Recently, it was suggested to use 1-LG and perform two transfer steps for the preparation of 2-LG.⁸ The 1-LG can be produced almost as a pure monolayer using a Cu catalyst since such a growth process is supposed to be self-limiting.⁶ The subsequent transfer of two 1-LG sheets on top of each other can, in principle, be used for the production of large and uniform 2-LG sheets.⁸ The latter

procedure also allows one to combine ^{12}C and ^{13}C graphene layers, which facilitates the study of the interaction of graphene with a substrate or the charge distribution between the two graphene layers in 2-LG using Raman spectroscopy.⁸

It has been reported previously that graphene can be responsible for the enhancement of the Raman spectra of molecules in proximity to graphene.¹¹ This phenomena is known as graphene-induced enhancement of Raman spectra (GERS).¹¹ Recently, an unusual enhancement of the graphene G mode in 2-LG was reported, but the mechanism of such an enhancement was not understood.⁸ Also it was not clear in that work whether the effect is general or localized at specific areas and whether a specific interaction with the substrate or with local charges in the substrate might play any role. Most of the studies of graphene up to now have been performed on a substrate that is typically SiO_2/Si . This substrate strongly affects the properties of graphene.^{12,13} The typical signature of the substrate interaction is a decreased mobility of the graphene contacting the substrate or localized doping. Recently, a new substrate, namely, hexagonal single-crystalline boron nitride (BN), has been suggested as a noninteracting and more passive substrate for graphene.¹⁴ Indeed the measurements of graphene

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on BN provided superior results regarding carrier mobility compared to graphene on other substrates.¹⁴ The measurements of graphene on a BN substrate are preferable to that on a free-standing graphene due to the large stress in the free-standing graphene.

In the present paper we examine the enhancement of the G mode in the Raman spectra of the two layers of graphene in 2-LG. In order to determine the interaction of graphene with the substrate and to distinguish the top from the bottom graphene layer in 2-LG, we used isotopically engineered 2-LG, where one layer was composed of the natural isotope C (mostly of ¹²C atoms) and the second layer was labeled by the ¹³C isotope. The role of the substrate was determined from the comparison of the effects of the SiO₂ and BN substrates on the Raman spectra of 2-LG. In addition, Raman maps of 2-LG on a BN substrate were measured in order to identify specific spots showing unusually strong enhancement of the G mode intensity.

For our study we used isotopically engineered 2-LG, which we deposited on a Si/SiO₂ substrate (later on we refer to this substrate as SiO₂ since only SiO₂ is in contact with graphene), which was already covered with flakes of hexagonal single crystalline BN. Graphene samples were synthesized using the CVD method as reported previously.⁶ In brief, a Cu (as received) foil was heated to 1000 °C and annealed for 20 min under flowing H₂ gas (50 sccm). Then the film was exposed to H₂ (50 sccm) and CH₄ (1 sccm) for 20 min, and finally the substrate was cooled under flowing H₂ and CH₄ gas. The pressure in the reaction chamber was kept at 1.3 Torr. For the preparation of ¹³C graphene, ¹³CH₄ was used as a feedstock (¹³C content 99%, Aldrich). The as-grown graphene on Cu was covered by polymethylmethacrylate (PMMA).⁷ In the next step, the Cu was etched, and the PMMA film was transferred to a SiO₂/Si substrate with predeposited BN flakes. Finally, the PMMA residual was removed by heating at 500 °C in a flow of hydrogen (250 sccm) and argon (150 sccm). In order to obtain 2-LG, the second layer was transferred onto 1-LG using the same procedure for the second time, thus obtaining two layers with no interlayer stacking order. The BN flakes on a SiO₂ substrate can be easily identified by optical microscopy, and therefore it is possible to select the areas of 2-LG on BN or on SiO₂ substrates for the following measurements. The Raman spectra were excited by a Nd:YAG or Kr+ laser (Coherent). The spectrometer resolution was about 5 cm⁻¹. The spectrometer was interfaced to a microscope (Carl-Zeiss, objective 100X). The size of the laser spot was about 0.5 μm.

Figure 1 shows the Raman spectra of 2-LG on a SiO₂ substrate (top trace) and on a BN (bottom trace) flake. The 2-LG sample is composed of a ¹²C graphene (bottom layer) and ¹³C graphene (top layer) sheet. Note that the ¹²C sample is expected to contain the natural isotopic abundance, that is, 1.07% of ¹³C, and the ¹³C 1-LG sample has 99% content of ¹³C graphene (taken from the declared precursor's purity). The frequency shift of the Raman bands in the ¹³C-enriched material compared to ¹²C graphene originates from the increased mass of the ¹³C isotope, which is given by eq 1:

$$(\omega_0 - \omega)/\omega_0 = 1 - [(12 + c_0)/(12 + c)]^{1/2} \quad (1)$$

where ω_0 is the frequency of a particular Raman mode in the ¹²C sample, $c = 0.99$ is the concentration of ¹³C in the enriched sample, and $c_0 = 0.0107$ is the natural abundance of ¹³C.

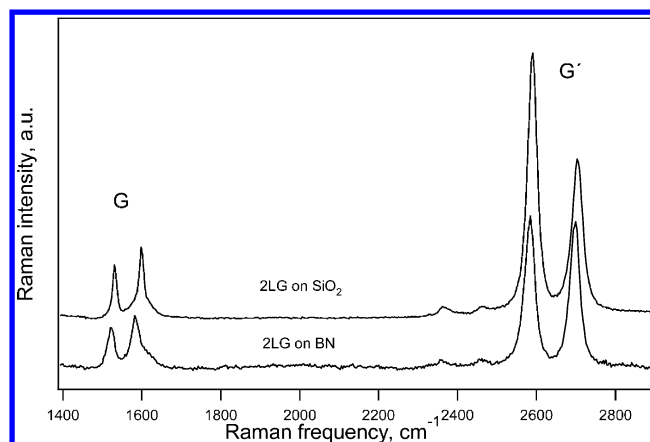


Figure 1. Raman spectra of the ¹³C/¹²C 2-LG on SiO₂ (top trace) and BN (bottom trace) substrates. The spectra are excited using 2.33 eV laser excitation energy.

The spectra of 2-LG on BN and SiO₂ substrates are obviously different, which reflects the specific interactions of 2-LG with these two substrates (Figure 1). The most significant difference between the Raman spectrum of 2-LG on BN and SiO₂ can be seen in the case of the G' mode. The intensity of the G' mode is about the same for both the bottom and top layer in the case of the BN substrate. On the other hand, the G' mode intensity of the ¹²C top layer is significantly smaller compared to the G' mode intensity of the ¹³C bottom layer, for the SiO₂ substrate. The interaction between the BN substrate and graphene is considered to be negligible at least in comparison to that for SiO₂.¹⁴ On the other hand, SiO₂ is known to dope graphene samples.¹³ In general, the doping of graphene leads to a decrease of the intensity of the G' mode.³ The intensity of the G' mode decreases both for positive and negative potentials during doping of the graphene sheet. It can therefore be suggested that the Raman spectra of the bottom layer of 2-LG on a SiO₂ substrate are affected by local charges in the SiO₂. The higher intensity of the G' mode of the top graphene layer, on the other hand, suggests that the local charges in the SiO₂ do not propagate through the bottom layer to affect the top graphene layer. Local charges are not expected in the BN substrate, and therefore the G' mode Raman intensity should be the same for the top and bottom layer, which is consistent with our experimental observation in Figure 1. A slight difference between the intensity of the G' mode between the top and bottom layer of 2-LG on a BN substrate can be rationalized by the interaction of the top layer with absorbed atmospheric gases.¹⁵ Nevertheless, the latter effect is obviously negligible as compared to the effect of the SiO₂ substrate.

The doping of graphene from the SiO₂ substrate should also be reflected in the change of the frequency of the G mode.^{2,3} Indeed, the frequency of the bottom layer is significantly upshifted (to about 1600 cm⁻¹) with respect to the frequency of the G mode of the bottom layer (1580 cm⁻¹) of 2-LG graphene on the BN substrate.

Figure 2 shows the Raman spectra of 2-LG at two different locations on a BN flake. While the Raman spectrum on one spot exhibits a "normal" intensity for the G mode (similar to Figure 1), in the case of the spectra at a second location, there is a strong enhancement of the G mode signal. A similar enhancement was also observed for the SiO₂ previously.⁸ In the present work, the integrated area of the G modes is 4 times

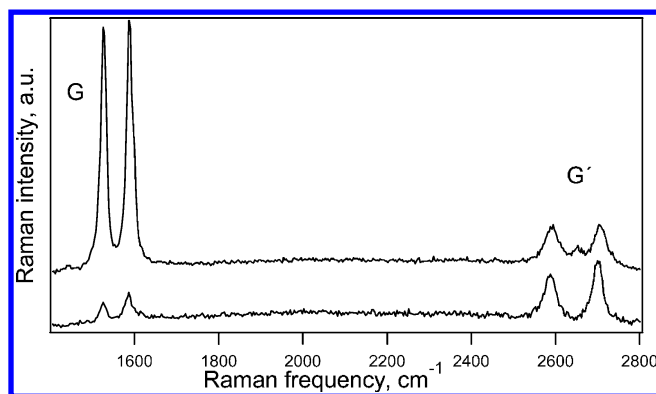


Figure 2. Raman spectra of the $^{13}\text{C}/^{12}\text{C}$ 2-LG on BN substrates at a location with a “normal” G mode signal (bottom trace) and at another location with an enhanced G mode signal (top trace). The spectra are excited using 2.33 eV laser excitation energy.

higher than the integrated area of the G' modes. The isotopic engineering allows us to distinguish between the top and bottom layers of 2-LG. Hence it can be clearly seen that the enhancement is observed for both layers, and, in addition, the enhancement is similar for both layers. It is important that the enhancement can be seen on different substrates and even on BN flakes. Therefore, the enhancement should be attributed to the intrinsic properties of 2-LG and not to extrinsic effects.

Obviously, the enhancement of the Raman spectra is specific for a special location of the measured Raman spot. In order to further analyze the enhancement effect, we measured a Raman map of 2-LG on the BN substrate. It was found that the intensity of the G' mode is only very weakly dependent on the Raman spot. Therefore, the G' mode intensity was used to normalize the intensity of the G mode. Figure 3 shows a Raman map of 2-LG on a BN flake. The color code corresponds to the $A_{\text{BT}}^{\text{G}}/A_{\text{BT}}^{\text{G'}}$ ratio, where A_{BT}^{G} is the integrated area of the G mode for the top plus the bottom layer, and $A_{\text{BT}}^{\text{G'}}$ is the integrated area of the G' mode for the top plus the bottom layer.

It can be clearly seen that the $A_{\text{BT}}^{\text{G}}/A_{\text{BT}}^{\text{G'}}$ ratio varies with the location of the Raman spot. There are only a few regions with a very high $A_{\text{BT}}^{\text{G}}/A_{\text{BT}}^{\text{G'}}$ ratio (up to 6–8). The size of these “hot” spots is about $1\text{--}2\ \mu\text{m}^2$. The focused laser spot size is about $0.5\text{--}1\ \mu\text{m}^2$, and the spectra were measured every $0.5\ \mu\text{m}$. Consequently, the area with maximum enhancement can actually be smaller than $1\ \mu\text{m}^2$. Then there is a large area where the enhancement is moderate, with the $A_{\text{BT}}^{\text{G}}/A_{\text{BT}}^{\text{G'}}$ ratio between 1 and 2, and finally there are spots with a “normal” intensity for the G mode (Figure 1). However, the regions where the intensity enhancement of the G mode is moderate are relatively extended, and in fact they cover about 2/3 of the

analyzed area of the BN flake. Hence, the area without any enhancement of the G mode comprises about 1/3 of the total area of the BN flake. Consequently, we believe that the observation of such large areas with an enhanced signal means that the enhancement is not caused by a surface enhanced Raman scattering (SERS) active particle or local defect (such as wrinkles or local variations). By contrast, the G-band enhancement effect must span over several micrometers square, and its intensity is gradually varied.

Figure 3B shows the Raman map of the same area as shown on Figure 3A, but in this case the spectra were excited by 1.91 eV laser excitation energy. Obviously, the locations of the spots where the G mode is enhanced do not correspond to the location of the spots where the enhancement was observed using 2.33 eV laser excitation energy. This is true both for the “hot” spots with very strong enhancement as well as for the larger number of locations with moderate enhancement. In other words, the enhancement is sensitive to location on the sample and also to the laser excitation energy used.

One can therefore suggest that the change in the absolute intensity of the Raman spectra may be attributed to an interference effect.¹⁶ However, the interference effect is dependent on the SiO_2 thickness, which is almost constant. Also an interference effect¹⁷ would cause the enhancement of all Raman modes, while our experiments show only the enhancement of the G mode. It was shown recently that the Raman signal of molecules attached to graphene can be strongly enhanced due to the chemical mechanism of an effect called GERS.^{18,19} The distance between the two graphene layers is assumed to be about 0.335 nm, which is small enough to observe the enhancement effect. Consequently, the top layer would cause an enhancement of the bottom layer, and the bottom layer would cause an enhancement of the top layer, which would lead to the simultaneous enhancement of the Raman spectra of both layers. Also the specific enhancement of the G mode may be understood because the strength of the GERS effect, similarly to the strength of the SERS effect, is different for different Raman modes. Nevertheless, the enhancement of the Raman spectra of the G mode should not be dependent on the spot location. Furthermore, a similar effect would be also expected for exfoliated AB-stacked 2-LG, but no such effect was observed in that case. Finally, the location where the GERS is observed should not be dependent on the laser excitation energy.

Since the present G band enhancement effect is sensitive to the location on the sample and is not observed in AB-stacked graphene, the anomalous enhancement of the G mode is attributed to a specific orientation of the top and bottom layers with respect to each other. The CVD graphene contains grains that are generally randomly oriented with respect to each other.

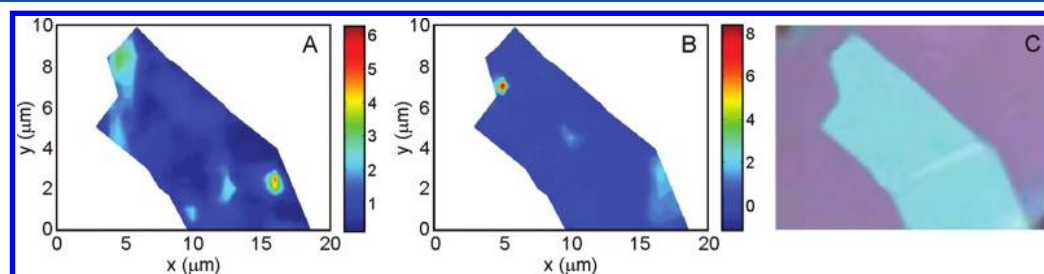


Figure 3. The $A_{\text{BT}}^{\text{G}}/A_{\text{BT}}^{\text{G'}}$ ratio (color code) dependence on the location of the laser probe on the sample. The spectra are excited by 2.33 eV (A) and 1.91 eV (B) laser excitation energy. (C) Optical image of the BN flake on a SiO_2/Si substrate, which corresponds to the Raman maps.

Combining two CVD graphene layers into one 2-LG may result in many different relative orientations between the two graphene layers, which may lead to specific interactions at a given location. It was shown recently that graphene layers that are slightly rotated with respect to each other (up to 10°) may exhibit singularities in their electronic structure with an enhancement in their joint density of states.²⁰ This enhanced density of electronic states can be responsible for a stronger Raman resonance and consequently lead to an increased G mode intensity. Since the position of the singularities would vary with angle of rotation, different laser excitation energies would lead to the appearance of the enhancement at different locations. This is in agreement with our experimental observation.

In conclusion, we studied the Raman spectra of isotopically engineered 2-LG samples on BN single crystal flakes. The 2-LG was prepared by a subsequent deposition of one layer of ^{12}C graphene and one layer of ^{13}C graphene. We observed an unusual enhancement of the Raman signal of the G mode, which was a function of the Raman spot location and the laser excitation energy. The origin of the enhancement effect can be understood and is attributed to a specific rotation angle between grains in the principal crystallographic axes of the top and bottom layers of the two layer graphene sample, resulting in the formation of van Hove singularities in the band structure of twisted 2-LG, which are resonant only for certain laser excitation energies.

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Notes

The authors declare no competing financial interest.

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