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Raman probing of hydrogen-intercalated graphene on Si-face 4H-SiC

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Abstract

We report the results of in-depth Raman study of quasi-free-standing monolayer graphene on the (0001) Si- face of 4H-SiC, which contains $\sim 0.1\text{-}2 \cdot 10^{11} \text{ cm}^{-2} sp^3$ defects that have been introduced by hydrogen intercalation. The nature of the intercalation-induced defects is elucidated and ascribed to the formation of the C-H bonds. At the higher intercalation temperature in the formed monolayer graphene the defect-related Raman scattering displays a great enhancement and new spectral features attributed to D' and $D+D'$ modes appear. Comprehensive statistical analysis of the Raman data enabled us to estimate the homogeneity of the Raman scattering processes and to separate strain and doping effects. Analysis of the compressive strain and carrier density maps revealed that the intercalation temperature of 900°C and intercalation time of 1h are more favorable conditions for conversion of the buffer layer to uniformly relaxed and p -doped monolayer graphene in comparison to annealing at 1100°C for 30 min.

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Keywords: Raman spectroscopy, graphene, SiC, hydrogen intercalation, strain, doping

1. Introduction

During the last decade, epitaxial graphene (EG) on SiC has attracted much attention due to its fascinating physical properties, which are, in most cases, similar or even superior to those of free-standing graphene [1-3]. The well-revealed advantages of the EG over other graphene-family materials, namely, high quality and uniformity, large area, transfer-free processing, technology scale-up, chemical stability, high adhesion strength to SiC substrate, ability to be used as a template for growth of wide class of two-dimensional materials, are excellent prerequisites for utilization of EG as an active element in electronic devices [4-6], sensors [7-9] and quantum metrology [10, 11]. Since 2009, significant progress in scaling-up

graphene (towards graphene on 8-inch diameter SiC wafers) has been made, thereby enabling the realization of the quantum Hall effect chip with hundreds of Hall bars, miniaturized field-effect transistor (FET) and sensor arrays. At the same time, it is important to note that the huge promise of EG to be used in realistic practical applications has been overshadowed by the presence of the buffer layer (carbon-rich interfacial layer, which is referred to $6\sqrt{3}\times 6\sqrt{3}$ R30° SiC surface reconstruction during the incongruent SiC evaporation at temperatures $> 1400^\circ\text{C}$) [12]. Even though formation of the buffer layer favors some unusual properties of EG [13], this layer is partly covalently bonded to the topmost SiC layer and, as a result, plays a negative role in electron transport through graphene, introducing additional carrier scattering mechanisms that limit carrier mobility. More specifically, the buffer layer with sp^3 -type Si-C bonding causes the appearance of the out-of-plane acoustic phonon modes contributing to surface phonon scattering [14] and induces additional electron scattering related to considerable doping variations [15]. By performing Hall measurements, Lin *et al.* [16] established that the carrier scattering by the SiC substrate is a dominant scattering mechanism in EG on SiC. The reduced electrical performance of EG can also be attributed to the residual strain, which permanently occurs in the as-grown samples because of difference in thermal expansion coefficients of graphene and SiC. Abovementioned limiting factors can be combined and regarded as one complex problem, which needs to be addressed in order to uncover the full potential of EG, especially for electronic applications. The most challenging way to tackle this drawback is to separate the buffer from the substrate via intercalation by appropriate species [17-19]. Such approach implies that intercalants could penetrate beneath the buffer layer, destroy the Si-C covalent bonds and passivate the remaining Si dangling bonds on the surface. Whenever this happens, the buffer layer immediately detaches from the SiC surface and transforms into a first graphene layer. In this regard, hydrogen intercalation is believed to be the most effective way to provide the decoupling of the buffer layer, since the formation of Si-H bonds is more energetically favorable than that of Si-C bonds even at moderate temperatures [20]. The mechanisms of the hydrogen-intercalated epitaxial graphene on SiC has been extensively investigated in numerous works by *ab initio* methods and comprehensive experimental characterization [21-29]. In particular, strain relaxation in EG after H intercalation [27], carrier density reduction [28] as well as reversal of the carrier type upon hydrogen intercalation from *n*-type to *p*-type [29] have been observed. The most important attributes indicating successful hydrogen intercalation process can be identified through monitoring Raman scattering in epitaxial graphene. Indeed, disappearing the spectral features within the frequency range from 1355 to 1600 cm^{-1} [30], which are related to the buffer layer, as well as an appearance of the

phonon peak at 2131 cm^{-1} ascribed to Si-H vibrations [31] are reliable indicators of a complete buffer layer detachment. In this regard, Raman spectroscopy is a powerful tool for probing structural changes in epitaxial graphene upon hydrogen intercalation [32]. Furthermore, micro-Raman mapping followed by statistical analysis has been shown to be an effective way to determine quality characteristics such as the intercalation uniformity [33] and thickness homogeneity [34]. This method has been used to assess both spatial distribution of hydrogen intercalants forming chemical bonds and distribution of stacked layers of graphene. It is also known that intrinsic Raman modes (namely G and $2D$) of graphene are very sensitive to strain and doping effects [35, 36]. Any changes in the position of these Raman modes after conversion of the buffer layer into graphene will correlate with strain/doping changes. Therefore, the statistical analysis of the Raman data would also allow to estimate the degree of spatial fluctuations of the strain and carrier concentration in the intercalated graphene samples. Reaching a control of these parameters is an imperative requirement for many electronic applications. Lee *et al.* [37] proposed the graphical method to extract strain and carrier density magnitudes by using mutual dependence of the $2D$ peak position on G peak position. However, strain and doping mapping have been surprisingly little used to collect the critical information about structural evolution upon hydrogen intercalation of EG on Si-face 4H-SiC.

In the present paper, we apply the optical separation approach to distinguish between two mechanisms. A deep understanding of the strain evolution and carrier density modulation during intercalation process is of special interest because it provides critical knowledge towards optimization of the graphene growth conditions. Our data confirm that a careful temperature and time control during the intercalation procedure is required to provide strain relaxation and reduction of the defect density in epitaxial graphene.

2. Experimental method

The intercalation process was investigated via monitoring structural conversion of the buffer layer (BL) to quasi-freestanding monolayer graphene. For this task, we synthesized BL samples ($15\times 15\text{ mm}^2$) by high-temperature thermal decomposition of the Si-face 4H-SiC bulk substrate (nominally on-axis) in argon atmosphere [38]. To achieve full coverage of the SiC surface with the targeted $(6\sqrt{3}\times 6\sqrt{3})R30^\circ$ reconstruction the growth process was carried out in an inductively heated reactor under highly controlled conditions. We note that the formation of BL in our experiment occurred at lower temperatures than upper temperature limit required for self-assembling of monolayer graphene through the silicon carbide decomposition (sublimation) approach. The presence of the BL was confirmed by the observation of the characteristic Raman features within the frequency range of 1355 to 1600 cm^{-1} (see Figure S1,

Supplementary Information). The BL-covered SiC wafer was cut into two similar samples (with area of about $7 \times 7 \text{ mm}^2$). Both samples were subjected to hydrogen intercalation by means of high-temperature annealing in a gas-flow of H_2 at a pressure of 200 mbar in a hot-wall MOCVD reactor [39]. The first sample was annealed at 1100°C for 30 min, while the second one was annealed at 900°C for 60 min (hereafter we call these samples SL2920 and SL2921, respectively). These conditions followed pre-selection test runs.

Firstly, the morphology of the samples subjected to different intercalation processes was evaluated by tapping mode atomic force microscopy (AFM) using Si probes and a DI3100 equipment with a Nanoscope V controller. To evaluate the uniformity of the hydrogen intercalation, the defectivity, strain and doping of graphene intercalated under the two conditions, as-intercalated samples were further characterized by micro-Raman spectroscopy, including mapping analysis and statistical analysis. The Raman spectra were registered by using micro-Raman setup based on a monochromator (Jobin-Yvon, model HR460) equipped with a CCD (couple-charged device) camera. The objective lens has a magnification of $100\times$ and numerical aperture $\text{NA} = 0.95$ resulting in a $\sim 0.85 \text{ }\mu\text{m}$ diameter of the laser spot focused on the sample surface. A 532 nm diode-pumped solid-state laser with 17 mW power was used as an excitation source. We notice that laser power of the order of few tens of milliwatts, which is destructive for many other materials when focused through a microscope, seems to be well below the damage threshold for graphene on SiC (including H-intercalated samples), probably because of the excellent thermal conductivity of the substrate. The spectral resolution of the system is $\sim 5.5 \text{ cm}^{-1}$. The statistical analysis applied to processing Raman spectral data has been performed for two representative samples.

3. Results and discussion

Two typical AFM morphologies of the samples SL2920 (intercalated with H_2 at 1100°C for 30 min) and SL2921 (intercalated with H_2 at 900°C for 60 min) are reported in Fig.1(a) and (c), respectively. In both cases, the usual stepped morphology of the SiC substrate underlying graphene can be observed. For the sample subjected to the higher intercalation temperature, some additional peculiar features are superimposed to the substrate morphology and are responsible for the increased root mean square roughness ($\text{RMS}=0.66 \text{ nm}$) with respect to the sample SL2921 ($\text{RMS}=0.42 \text{ nm}$). Fig.1(b) and (d) show two representative height profiles, extracted along the dashed lines in Fig.1(a) and (c), respectively. From Fig.1(b), it is evident how these features correspond to nanometric corrugations and cracks of the quasi-free-standing-graphene membrane and cracks of the graphene membrane.

Figure 1. AFM images and representative line scans of the SL2920 ((a), (b)), and SL2921 ((c), (d)) samples

In order to get a full picture of optical phonon response of hydrogen-intercalated graphene and to ascertain the uniformity of the Raman scattering process, micro-Raman spectroscopy measurements were performed to obtain Raman maps containing 324 Raman spectra from different regions within the sample (scanning area: $5.1 \mu\text{m} \times 5.1 \mu\text{m}$; $0.3 \mu\text{m}$ pitch). Contour plots of Raman data (see Figure 2) indicate that the intensity over 324 spectra is quite uniform, implying that the complete homogeneous hydrogen intercalation is reached for both considered cases. This is evidenced by the full absence of the structured band related to BL (Raman spectra of BL are not shown here) and observation of the two main intensive peaks of monolayer graphene (so-called *G* and *2D* modes). What is most strikingly revealed for the present light scattering geometry is the presence of the defect-related *D* peak, which is originating from in-plane “breathing” vibrational mode with A_{1g} symmetry at the Brillouin zone. In addition, due to the difference in intercalation conditions the structural changes from sample to sample are illustrated by the changes in the intensity of the Raman signal in the spectral regions of interest. A straightforward interpretation of the Raman data is that higher intercalation temperature (sample SL2920) caused the generation of larger number of defects

and formation of the graphene sheet with higher degree of mosaicity, whereas lower intercalation temperature (sample SL2921) favored the formation of the less-defective monolayer graphene with larger size of domains. Furthermore, a close look at contour plots (shown in Figure 2) allows to conclude about more complicated nature of Raman scattering in sample SL2920. More specifically, it is manifested by the appearance of the additional Raman peaks corresponding to D' and $D+D'$ vibrational modes, which are seen due to the defect-induced relaxation of the selection rules. Another important aspect is that the larger intercalation time applied to sample SL2921 can be also a reason of observation of D peak quenching, pointing to either self-healing of defects in graphene or less probability of defects' formation. The first factor implies a complete reconstruction of vacancy defects or breaking the sp^3 covalent bonds between host carbon atoms and external adsorbates (if we would assume that carbon vacancies or sp^3 defects, i.e. C-H bonds, are dominant defects in graphene). Indeed, by performing *ab initio* molecular dynamics simulations, Özçelik *et al.* [40] predicted a perfect self-healing of Stone-Wales type defects even at 300 K. The second factor means that the intercalation conditions in the case of sample SL2921 do not favor the formation of vacancy-type or sp^3 defects. To understand the type of preferential defects generated during intercalation processes, more evidences including careful statistical analysis are needed (see discussion below).

Figure 2. Two-dimensional contour plots of the unnormalized (raw) Raman data, showing the intensity of the Raman signal as a function of coordinate and Raman shift. The top panel and bottom panels represent the uniformity of Raman scattering processes in samples SL2920 and SL2921, respectively. The whole Raman fingerprints of the hydrogen-intercalated

freestanding graphene samples and the regions zooming near the G and $2D$ peaks are illustrated from left to right, respectively.

To better visualize the difference between considered hydrogen-intercalated samples, we also demonstrate the average normalized Raman spectra (Fig. 3a). It is clearly seen that all Raman peaks for sample SL2921 (namely G , D , $2D$, G' , $2D'$ modes) show a redshift and become narrower in comparison to those for sample SL2920. $2D$ peaks for both intercalated samples are symmetric and can be well fitted by single Lorentzian. In this regard, the shape of the $2D$ bands is most informative parameter to distinguish between single layer and few-layer graphene [40]. We estimated I_{2D}/I_G amplitude and area ratios. It was found that I_{2D}/I_G amplitude ratio for both samples is higher than 1 (1.02 and 1.25 for SL2920 and SL2921 samples, respectively), suggesting the formation of graphene. Furthermore, mean FWHM value of $2D$ band of SL2921 (lower intercalation temperature) is only 28.05 cm^{-1} , which is a main indicator of the formation of the single layer graphene [41]. The area ratio was estimated to be 2.33 and 3.96 for SL2920 and SL2921 samples, respectively. This reveals a higher structural quality of the SL2921 sample compared to the SL2920 sample. Indeed, in their earlier work Zhen Hua Ni *et al.* [42] showed that the $2D/G$ intensity ratio is very sensitive to charged impurity concentrations in single layer graphene. In particular, the higher the I_{2D}/I_G ratio points into the smaller impurity density in graphene. The results are summarized in Figure S2 (Supplementary Information).

As was mentioned before, in addition to the strong defect-related D peak, the sample SL2920 somewhat surprisingly reveals several relatively sharp peaks which are absent in the sample SL2921. Furthermore, when we have plotted the zoomed region between 1850 and 2350 cm^{-1} after normalizing both spectra we notice the presence of weak Raman band at 2132 cm^{-1} corresponding to the Si-H stretch mode (Figure 3b). Conventionally, this Raman process is very faint, and the plasmonic metal nanoparticles should be used to produce SERS enhancement of the intensity for this stretching mode. In our case, this band is distinguishable for both samples even without the SERS effect, indicating the formation of new Si-H chemical bonds instead of the host covalent bonding between carbon atoms of the buffer layer and Si atoms belonging to the topmost layers of the SiC. In the following analysis, we will use the D/G intensity ratio to estimate the degree of structural perfection of the hydrogen-intercalated graphene and to extract the crystallite size (average distance between two neighboring disruptions in the graphene). Corresponding histograms (including the mean value, μ , and relative standard deviation, σ) for both samples are presented in Fig. 3c. It is obvious that the higher intercalation temperature causes larger value of D/G amplitude ratio (0.625 vs. 0.046) and, as a result, smaller value of

the crystallite size (13 vs. 49 nm). In a recent work [43], it was shown that there is a direct correlation between crystallite size and defect density. Our estimations showed that the defect density in sample SL2920 is about $1.91 \cdot 10^{11} \pm 2.6 \cdot 10^{10} \text{ cm}^{-2}$, which is about an order of magnitude larger than $1.31 \cdot 10^{10} \pm 1.9 \cdot 10^9 \text{ cm}^{-2}$ for sample SL2921. In addition, the D/G intensity ratio enables to determine roughly the type of possible defects, which potentially could activate D Raman process. In other words, using this ratio it is possible to distinguish between sp^3 defects and vacancy-type defects. If this ratio is less than 1, then sp^3 defects are dominant [44]. While the $D/G > 1$ points to the dominant role of vacancies as symmetry-breaking defects allowing the disorder-induced Raman scattering. In our study, for both samples, D/G ratio is less than 1, which is indicative of sp^3 defect generation upon hydrogen intercalation process. This, and the fact that the D peak was absent on the Raman spectra of the as-grown BL, led to the conclusion that the high-temperature annealing under hydrogen is related to the generation of the sp^3 defects. While suggestive, this finding itself does not fully clarify the nature of defects in the hydrogen-intercalated sample. To get deeper insights into the origin of the defect-related Raman processes in graphene, we considered also the relationship between D and D' peak intensities. As was reported in an earlier work [45], this ratio can be used rather than the D/G ratio to identify the nature of defects in graphene. The estimated mean value of this ratio is about 12 for sample SL2920, which can be definitively ascribed to on-site defects related to sp^3 hybridization. We have been unable to determine the D/D' ratio for sample SL2921 due to the absence of D' peak, but we suppose that for this sample very small fraction of on-site sp^3 defects is also available. It is important to note that a careful inspection of the spectral region associated with $D+D'$ Raman process ($2850\text{-}3100 \text{ cm}^{-1}$) revealed the presence of a wide Raman band composed of several overlapping components. As far as we know from literature data, the Raman features in the frequency range from 2857 and 2915 cm^{-1} may be originating from the symmetric and asymmetric C–H stretching vibrational modes [33]. Therefore, the most likely explanation of activation of the forbidden D breathing mode and combined $D+D'$ mode is the formation of C-H bonds in nominally defect-less sample during hydrogen intercalation.

Figure 3. (a) Average normalized Raman spectra (after background subtraction) for samples SL2920 and SL2921. (b) Zoomed spectral region of the average Raman spectrum, which corresponds to frequency position of Si-H stretching mode observed in both samples. (c) Histograms of the D/G amplitude ratio distribution fitted with a Gaussian function for samples SL2920 and SL2921.

Figs. 4(a) and (b) report two maps showing the spatial distribution of the D peak intensity (integrated area under the D peak) for the SL2920 and SL2921 samples. These maps are clearly related to the spatial uniformity of defectivity for the two H₂ intercalation conditions. For the lower temperature intercalated sample (Fig. 4(b)), a low and uniform defects density on all the investigated area is observed. On the contrary, for the higher intercalation temperature, an inhomogeneous distribution of defects can be observed (Fig. 4(a)). According to the morphological AFM studies, SL2920 sample demonstrates the presence of the corrugations/cracks of the graphene membrane, which can explain the high D -peaks intensity regions.

Figure 4. Maps of the *D* peak intensity (integrated area) distribution the samples SL2920 (a) and SL2921 (b).

Statistical analysis of the Raman data (*G* and *2D* peak positions) for hydrogen-intercalated graphene makes it possible to evaluate the uniformity of the corresponding first-order and second-order Raman scattering processes as well as to separate the strain and doping effects on these processes. The results of such analysis are presented in Fig. 5 depicting Raman maps and histograms of *G* and *2D* peaks position distribution (Fig. 5b-g). The quasi-freestanding graphene processed at the higher intercalation temperature (sample SL2920) shows a broad distribution around 1603.75 ± 10 (2718.86 ± 20) cm^{-1} for *G* (*2D*) peak in comparison to the theoretical value for freestanding graphene of 1582 (2670) cm^{-1} suggesting strong compressive strain ($\sim 0.45\%$). After longer annealing at lower intercalation temperature (900°C), *G* (*2D*) peak position distribution becomes very narrow with mean value of 1595.21 ± 3 (2686.04 ± 6) cm^{-1} , which points to a decrease in compressive strain. We believe that the quasi-freestanding graphene at such intercalation conditions appears to be relaxed due to the low probability of the formation of the out-of-plane bonding with host carbon atoms and subsequent reduction of the lattice distortion.

Figure 5. (a) Mutual dependence of 2D peak position and G peak position for quasi-freestanding graphene obtained from two-dimensional Raman mapping: sample SL2920 (empty blue circles) and sample SL2921 (magenta asterisks). The light red point (with coordinates of $G_{\text{pos}}=1582 \text{ cm}^{-1}$ and $2D_{\text{pos}}=2670 \text{ cm}^{-1}$) corresponds to the case when the graphene is subjected to neither strain nor doping effect. Blue and red lines represent the theoretical pure strain and pure hole doping dependences of the 2D and G peak positions (also called strain and doping lines). Raman maps of free-standing graphene samples, (b) 2D peak position map for sample SL2920, (c) G peak position map for sample SL2920, (d) 2D peak position map for sample SL2921, (e) G peak position map for sample SL2921. Histograms of the (f) 2D and (g) G peak positions fitted with a Gaussian function for samples SL2920 and SL2921.

It is instructive to compare the statistical data describing the mutual dependence of 2D peak position and G peak position to theoretically calculated strain and doping lines (Figure 5a). For the higher intercalation temperature, we can see the data points are evenly distributed along the strain line with a slope of 2.3, suggesting the presence of the biaxial compressive strain in the hydrogen-intercalated sample SL2920. On the other hand, judging from the scatter plot for the sample SL2921 one would say that the data points are concentrated in very narrow region and this group of points is parallel to the similar one for sample SL2920. This can be explained by a decrease in the degree of local strain fluctuations in graphene and by more uniform and stronger doping. By projecting the experimental points to theoretical strain and hole doping lines and using corresponding vector decomposition analysis, it is possible to ascribe the carrier concentration and strain values to each of the data points. This allowed to construct the strain

distribution and carrier (hole) concentration maps (shown on Fig. 6). The obtained maps are clearly consistent with our abovementioned suggestions; the decrease in intercalation temperature followed by longer annealing results in a decrease in spatial fluctuations of compressive strain. Less well understood is the increase in the carrier concentration, which is observed for sample SL2921. One possible explanation for this phenomenon may be related to the fact that there is a fundamental relationship between carrier concentration and strain. Indeed, Schmidt *et al.* [46] proposed a phenomenological model, which gives a clear understanding of the strain-doping correlation. More specifically, an increase in the compressive strain will cause the decrease in C-C bond lengths (within hexagonal rings) and, as a result, the increase in Fermi velocity. Whenever this happens, carrier concentration becomes smaller. Bearing this in mind, it is reasonable to assume that the strain relaxation in graphene can be reached by enlargement of the local electron concentration. This is the main reason why we observe simultaneously a reduction of compressive strain and increase in carrier concentration for quasi-freestanding graphene grown at the lower intercalation temperature. On the other hand, *p*-type doping observation is typical for hydrogen-intercalated graphene samples, originating from spontaneous polarization of the substrate [47]. Any changes in the hole density from sample-to-sample correlate with the efficiency of the hydrogen intercalation. Indeed, less-efficient hydrogen intercalation implies incomplete hydrogen passivation of the donor-like states associated with the buffer layer and its interface to SiC, thereby causing smaller values of hole doping.

Figure 6. Spatial compressive strain (a and b) and carrier density (c, d) fluctuations showing the effect of intercalation conditions on intrinsic properties of the samples SL2920 and SL2921, respectively.

4. Conclusions

In conclusion, we have studied the structural conversion of the buffer layer to quasi-free-standing monolayer graphene upon temperature- and time-controlled hydrogen intercalation process by using Raman mapping and subsequent in-depth statistical analysis. A successful intercalation was confirmed by the vanishing of the buffer layer related structured band and observation of the faint, but distinguishable Si-H stretch vibrational mode. We observed upward frequency shifts of characteristic Raman modes with increasing the intercalation temperature, followed by the Raman peaks' broadening due to high degree of spatial fluctuations of strain and carrier density. It was revealed that the higher intercalation temperature has led to formation of more defective monolayer graphene (with defect density of $\sim 1.9 \cdot 10^{11} \text{ cm}^{-2}$) subjected to compressive strain of 0.4%. This is evidenced by the appearance of the intense defect-induced Raman peaks corresponding to nominally forbidden D , D' and $D+D'$ vibrational modes. The magnitudes of the D/G and D/D' ratios as well as the appearance of the broad band possibly related to C-H stretching mode allowed us to assume that the on-site sp^3 hybridization defects are dominant defects in quasi-freestanding monolayer graphene. By applying the so-called optical separation approach, we distinguished between strain and doping effects and constructed the corresponding maps. It was found that the reduction of the intercalation temperature from 1100°C to 900 °C caused the reduction of the degree of the strain fluctuations and overall reduction of the compressive strain. We ascribe such phenomenon to an effective strain relaxation through a local enhancement of the carrier density. Our results give deep insights into the nature of the physical processes underlying the structural changes of the buffer layer upon hydrogen intercalation.

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Supplementary Information for paper

Raman probing of hydrogen-intercalated graphene on Si-face 4H-SiC

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Figure S1. Raman data for buffer layer (BL) on Si-face 4H-SiC bulk substrate

Figure S2. Statistics of 2D/G ratio and FWHM of G and 2D peaks for the intercalated samples.