Interlayer interaction and disorder in Few Layer Graphene powders prepared by fluidized bed chemical vapor deposition

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ABSTRACT

The growth of few layer graphene (FLG) in powder form by CVD is particularly promising for its large scale production and use in composites as well as electrochemical and energy applications. The electronic and mechanical properties of FLG depends critically on the number of layers and the interlayer interaction. We have recently developed a fluidized bed chemical vapor deposition (FBCVD) process to produce FLG. We present structural measurements on FLG flakes with thickness varying from 3-8 nm prepared FBCVD. While transmission electron microscopy shows the formation of few layer graphene, Raman spectra bear the characteristics of single layer graphene with a relative low defect density indicating that the interaction between layers is reduced in FLG powders. Heat treatment at 2800°C is employed to reduce the number of defects and to study the effect to temperature on the stacking order.

Keywords: provide up to five comma separated, keywords for indexing, don't capitalize

1 INTRODUCTION

The future of making use of the unusual properties of few layer garphene depends crytically on scalable sythesis. Fluidized bed chemical vapor (FBCVD) deposition has been succesfuly implemented for the growth at industral scales of multi wall carbon nanotubes (MWCNT) [1]. Recently FBCVD has been employed to grow few layer graphene (FLG) by optimizing th catalyst and process parameters [2]. The grown graphene flakes are agglomerated and are recovered from the reactor in powder form. The properties of FLG depend strongly on the number of layers and on their interaction. The stacking order of the graphene layers is often not well defined due to weak interlayer van der Waals interaction. The stacking order can be as in graphite o simply disordered as in turbostratic graphite. Recent investigations of FLGs have found that the successif graphene sheets can be twisted giving rise to extra Raman bands [3]. We explore here stacking order through structural measurements using transmission electron microscopy (TEM), Raman spectroscopy (RS) and X-ray diffraction (XRD).

2 STRUCTURAL MEASUREMENTS

The powders consisting of loosely agglomerated FLGs has been dispersed on the holy carbon grids. Figure 1 shows a TEM image of a FLG flake as grown by FBCVD. The sheet in figure 1 measures 500 nm across and consists of a few graphene layers. Several buckling or folding lines and bent edges can be seen.
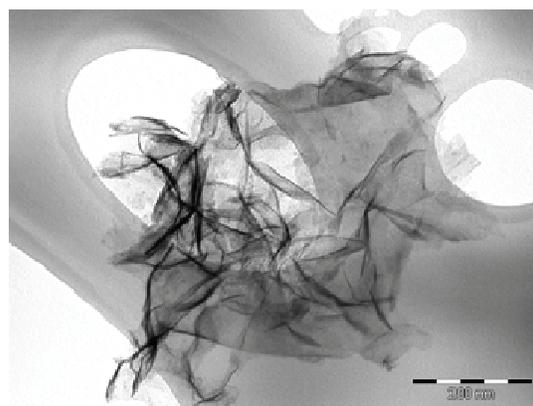

Fig 1. TEM image of FLG flake grwon by FBCVD.

To probe disorder and stacking of the FLG flakes we use micro-Raman spectroscopy (MRS). MRS is one of the most sensitive nondestructive techniques to study disorder in nano-structured carbon through the appearance of diorder induced spectral bands. Disorder breaks the momentum conversation rule and in additon to first order symetry allowed phonons, additional spectral bands are observed. Interestingly the disorder induced bands in the Raman spectrum are enhanced when in resonance with the energy of the incident exciting beam which requires again a form of momentum conservation [4]. Dissorder induced bands are the D band (1350 cm^{-1}), the D' band (1600 cm^{-1}) and the D'' band (1100 cm^{-1}). Two photon scattering can be

observed at higher RS shifts where three bands appear (2D: 2700 cm⁻¹, D+D'': 2450 cm⁻¹, 2D': 3200 cm⁻¹). It is important to remind that the second order spectral lines are not defects induced. However the spectral widths depends on the number of defects as well as on doping (electron-electron scattering). All the D bands mentioned here shift with excitation energy due to the double resonant scattering process and the paticular phonon dipersion in graphene. Important is that intensity of the 2D band is highly sensitive to disorder. Its relative intensity to the G band is taken as a indicator of the presence of defects. Over exposure of graphene results in an decrease of the intensity of 2D band and appearance of a D band due to absorption induced over heating and formation of defects.

We used a Horiba XploRa spectrometer with 532 nm laser excitation and x100 optical objective. Figure 2 shows the 2D band of FBFLGs. The two spectra were recorded from two different locations. The symmetric shape of the 2D has been normally used to indicate the presence of single layer graphene layer [5].
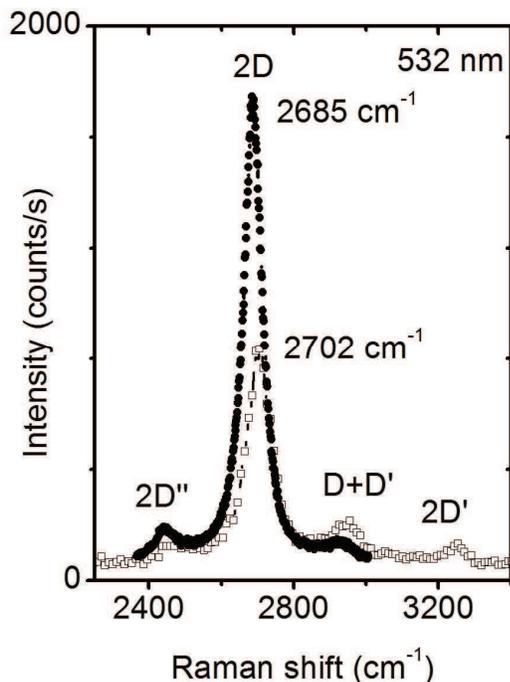

Fig 2. Raman spectra in the spectral range of the two photon 2D band. The band at 2685 cm-1 is three times more intense than the corresponding G band. Its width is 57 cm⁻¹ (FWHM).

However it has been shown that the line shape varies for FLG from highly oriented graphite (HOPG) or grown from SiC [5] which can be attributed to differences in the stacking order of the graphen layers. The intensity with respect to the G band and the spectral position of the 2D

band is a better indicator of the presence of single layer graphene or FLGs. We can see that the two spectra have a different intensity and spectral position. The 2D band at 2685 cm⁻¹ shown in fig. 2 is three times more intense than the G band while the intensity of the D band is 1/3 of the G band (not shown in fig. 2). The band position is compatible with that for graphene. The 2D band at 2702 cm⁻¹ is 1/2 of the G band intensity and the D band is 10% more intense than the G band. The two spectra have similar spectral width (57cm⁻¹) but very different scaled intensities. The upshifted of the 2D band at 2702 cm⁻¹ corresponds to the spectral position of turbostratic graphite [6]. For comparison, the spectral position of the 2D band of highly oriented pyrolytic graphite (HOPG) is at 2721 cm⁻¹ when exited at 532 nm.

We observe that Raman spectra of FBCVD FLG show uniform spectral bands with unifrom band widths but very different spectral intensities. The spectral position of the 2D band indicates falls in range of graphene and turbostratic graphite.

3 STRUCTURAL EVOLUTION WITH HEAT TREATMENT

We studied furthermore the disorder and stacking in FLG by annealing in agon athmosphere up to 2800 C. The structural parameters of the heat-treated FLG were determined by X-ray diffraction and investigated by Raman spectroscopy. The analysis of the XRD profiles of the materials shows that, as the temperature increases from 2200 C to 2800 C, the widths of the (002), (004) and (110) XRD reflections decrease. Additionally, the maximum of the (002) reflection shifts to larger angles in particluar at 2800 C. The reflection peaks get symmetric and increase in intensity with annealing. This means the interlayer distance d_{002} decreases while the crystallites mean size along the c-axis, L_c and the a-axis, L_a increases (Table 1).

d_{002}	L_c	L_a	W_D	W_G	I_D/I_G	$I_{D'}/I_G$
nm	Nm	nm	cm⁻¹	cm⁻¹	%	%
.3400	11.1	20.8	42.7	31.3	73.1	7.8
.3403	13.3	29.9	38.7	23.5	25.0	3.4
.3401	14.0	32.5	39.2	23.1	23.0	3.5
.3401	14.5	31.7	39.0	21.9	19.0	3.0
.3397	15.3	34.7	39.0	21.4	17.8	3.0

Table 1 Crystalline parameters from XRD and Raman parameters of raw and heat-treated FLG. The first line shows the parameters before annealing and the following lines by increasing the temperature from 2200 C to 2800 C in steps of 200 C.

The XRD measurements show that the structural order of the FLG increases with annealing. However, the absence of the (112) reflection in the XRD profiles of the heat-treated FLG even at 2800 C, indicates poor three-dimensional stacking. As the annealing temperature is increased the development of the planar structure is preferred. This is seen by the increase of the crystallite size along the basal plane L_a.
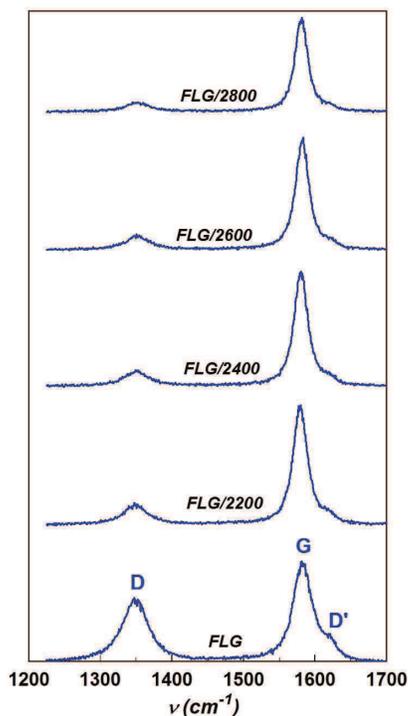

Fig 3. Raman spectra of the D and G band region of FLG and FLG annealed at 2200 - 2800 C.

The extracted Raman parameters are reported in Table 1. The D band gets narrower after heat treatment at 2200 C. The width decreases from ~ 43 cm^{-1} (W_D, FWHM) to ~ 39 cm^{-1} when annealing at 2200 C. Accordingly, L_a values from the XRD measurements increase from ~21 nm and ~30 nm. However, at higher temperature W_D does not decrease further. The width of the D band is associated with the average crystallite size and this shows that the crystallites size does not get larger when increasing the temperature from 2200 to 2800 C. This is consistent with the in-plane L_a value as determined by XRD which increases only by 16% at 2800 C. Simlarly, the width of the G band (W_G) decreases from ~ 31 cm^{-1} to ~ 24 cm^{-1} after annealing reaching a minimum value of ~ 21 cm^{-1} at 2800 C.

The integrated relative intensity of the D band (I_D/I_G) band decreases with higher annealing temperature reflecting improvement of both the degrees of structural order and crystalline orientation of the material. The I_D/I_G

ratio falls from ~73 % in the untreated FLG to ~18 % in FLG annealed at 2800 C. The defect concentration is reduced mainly due to coalescence and growth along the basal plane increasing L_a the lateral dimension of the planes. The D' band has been postulated to be sensitive to the edges [6]. Table I shows the relative itensity of this band ($I_{D'}/I_G$). As expected, the D' band also decreases with annealing consistent with the increase of L_a.

The Raman parameters from the second order spectra are summarized in Table 2. The width of the 2D band (W_{2D}) of FLG decreases significantly after heating a 2200 C. However, this parameter remains nearly constant in the whole annealing range. The number of graphene layers has been reported to strongly affect the shape of the Raman 2D band. Thus, when a single graphene sheet is present, a 2D band composed of a single Lorentzian peak is expected; whereas two or more graphene layers lead to three or four peaks, and finally, as the number of layers in the graphene increases, the 2D band has the shape of graphite, that is, a 2D band consisting of two Lorentzian peaks at around 2687 cm^{-1} and 2727 cm^{-1} [8]. The deconvolution of the Raman 2D band of the FLG and heat-treated FLGs studied here results in three peaks (see Figure 4 in S3); one at the same frequency of the original 2D band at around 2698 cm^{-1} (denoted $2D_{2D}$), 2687 cm^{-1} ($2D_{3DA}$) and 2727 cm^{-1} ($2D_{3DB}$). This suggests that the FLGs are composed of several graphene layers and their structure is a mixture between FLGs and graphite.

W_{2D} cm^{-1}	$I_{2D/3DA}$	$I_{2D/2D}$	$I_{2D/3DB}$
60.4	0.29	0.53	0.18
49.6	0.34	0.53	0.13
50.2	0.36	0.56	0.08
49.0	0.40	0.40	0.20
48.7	0.40	0.48	0.12

Table 2. Raman parameters from the second-order spectra of raw FLG and heat-treated FLG as above between 2200-2800 C.

Table 2 shows the width of the total 2D band and the intensity of the three contributing bands as a function of annealing temperature. The 2D band gets narrower and the contribution of the 2D/3DA band gets more important compared to the other two components. However the evolution is not uniform for the 2D/3DB band which is the least intense band. The evolution of the 2D band is consistent with the trend seen in the XRD measurements; L_c increases when increasing the annealing temperature. In conclusion annealing of FLG improves the graphitic structural ordering increasing L_a as well L_c as observed through XRD and the decrease and narrowing of the Raman

D band. The planar crystalline size increases and the number of defects are reduced.

4 CONCLUSION

FLG grown with FBCVD method show second order Raman bands which are distingtly different to graphite and similar to single layer graphene and turbostratc graphite. XRD and Raman spectroscopy show that annealing of FLG up to 2800 C increases the latreal dimension of the planes and reduces the number of defects and the distance between the layers decreases.

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