Structural analysis of polycrystalline graphene systems by Raman spectroscopy

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ABSTRACT

A theoretical model supported by experimental results explains the dependence of the Raman scattering signal on the evolution of structural parameters along the amorphization trajectory of polycrystalline graphene systems. Four parameters rule the scattering efficiencies, two structural and two related to the scattering dynamics. With the crystallite sizes previously defined from X-ray diffraction and microscopy experiments, the three other parameters (the average grain boundaries width, the phonon coherence length, and the electron coherence length) are extracted from the Raman data with the geometrical model proposed here. The broadly used intensity ratio between the C—C stretching (G band) and the defect-induced (D band) modes should be used to measure samples with crystallite sizes larger than the phonon coherence length, which is found equal to 32 nm. The Raman linewidth of the G band is more appropriate to characterize the crystallite sizes below the phonon coherence length, down to the average grain boundaries width, which is found to be 2.8 nm. "Ready-to-use" equations to determine the crystallite dimensions based on the Raman spectroscopy data are given.

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1. Introduction

Most of the potential applications of graphene as a two-dimensional system are dependent on large area sample production, which can be achieved by the deposition of chemical vapor [1,2] or exfoliated graphite [3,4]. In both cases, polycrystalline samples are usually obtained, and the key aspects defining the material properties are the atomically-organized crystallite size and the grain boundaries structure [5–9]. Although the use of Raman spectroscopy as a quick technique to measure the crystallite size (L_a) of nanostructured graphitic samples is a procedure that was introduced 45 years ago [10], the protocols developed up to date are still empirical and dominated by large uncertainties. However, the basis for developing an unified and accurate model for the Raman-based procedure for addressing these key structural aspects are now in place, mostly due to recent work performed on graphene [11–16].

In 2010, Raman scattering from defects in graphene was used to define the coherence length (ℓ_A) of electrons/holes excited in the visible range [11,12]. The results were found in the range of $\ell_A = 2$–4 nm, roughly independent on the excitation laser energy [17], consistent with theoretical expectations [13]. In 2014, near-field Raman scattering in graphene was used to confirm $\ell_A \approx 4$ nm [18], and to define the coherence length for optical phonons (ℓ_C), with an observed value of $\ell_C \approx 30$ nm [14,15]. Finally, atomically resolved scanning tunneling microscopy (STM) imaging of grain boundaries elucidated the structural aspects on the merging between two misoriented graphene planes [16]. This merge region of lateral extension ℓ_B is a periodic perturbation on

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the C—C bonding along the boundary axis, necessary to accommodate the connection between two neighboring hexagonal lattices which are not in the same crystallographic orientation [16]. This perturbation is characterized by the presence of localized electronic states near the grain boundary, and recent scanning tunneling spectroscopy (STS) measurements showed that the height of these localized states decay exponentially from the grain boundary with a half-decay length of ≈ 1.6 nm, which defines $\ell_B \approx 3.2$ nm [16].

With this information in hand, it is now possible to show how the carbon—carbon stretching (G band at 1584 cm^{-1}) and the disorder induced (D band near 1350 cm^{-1}) spectral features can be used to describe the average size L_a of crystallites and the average width of the grain boundaries ℓ_B in graphene systems. The experimental results and the model are presented in Sections 2 and 3. In Section 4 we elaborate on the novelties of this model as compared to previous research on this topic, demonstrating why the field matured enough to reach an unified model that accounts for crystallites with L_a ranging from a few nanometers up to infinity. Besides the model, this development makes it possible to build "ready-to-use" formulae for accurate determination of crystallite sizes in polycrystalline graphene systems, which are given in Section 5.

2. Experimental results

2.1. Sample preparation and structural characterization

The samples were produced by the well-established heat treatment of diamond-like amorphous carbon (DLC) [19], which is known to produce graphite nanocrystallites with lateral dimension (L_a) defined by the heat treatment temperature (HTT) [20]. A representative structural image is presented in Fig. 1(a), which shows an STM image of a sample with HTT = 2200° C (see the Supplemental Material for experimental details). This image clearly shows that the sample is polycrystalline. Consecutive zooms at the border between two neighboring crystallites are shown in Fig. 1(b) and (c). From the image in Fig. 1(c), the disordered border of thickness $\ell_B \approx 3$ nm is clearly seen, with two well-organized hexagonal lattices at each side, corresponding to the atomic structure of two neighboring crystallites. This atomically-resolved image shows that the neighboring crystallites have different lattice orientations. Fig. 1(d,e) show a scanning transmission electron microscopy-bright field image (STEM-BF), and a transmission electron microscopy-dark field image (TEM-DF), respectively, of the sample with HTT = 2300° C. In panel 1(d), the STEM-BF image reveals the presence of Moiré patterns generated by rotation between the hexagonal lattices of adjacent layers. The TEM-DF image [panel 1(e)] clearly shows well-defined crystallites, and similar images were used to extract the average L_a values of selected samples (see details in the Supplemental Material available).

The model used to describe the Raman spectral response from the nanocrystallites is illustrated in Fig. 1(f), and it will be discussed in Section 3. For this development, twelve different HTTs were used to produce polycrystalline graphenes with twelve different L_a values, which were characterized using X-ray diffraction, transmission electron microscopy (TEM), and STM (see the Supplemental Material for experimental details). These three different techniques were used to accurately measure the mean values of L_a, and the results are plotted in Fig. 1(g) as a function of the HTT. Most important, the results from the surface technique (STM) are consistent with the results from X-ray and TEM, which probe the volume. This result, together with the fact that the Raman features that will be analyzed here do not change significantly with the number of layers,[1] indicates that our results apply to single and N-layers graphene systems.

2.2. Raman spectroscopy measurements and analysis

Fig. 2 shows representative first-order Raman spectra of heat-treated polycrystalline graphene samples with different HTTs values and correspondingly different crystallite sizes L_a. The values of HTT and L_a (obtained by X-ray diffraction) are indicated in the plot, at the left and right sides of each spectrum, respectively. For samples with HTT = 2200° C and upwards (the five top spectra in Fig. 2), the Raman spectra are fitted using Lorentzians (green lines). Two main peaks are related to the D and G bands (named here D^A and G^A), plus a weak disorder-induced D' feature at ~1610 cm^{-1} for the lower HTT values; for these HTT values the D' feature is well defined and can be clearly distinguished from the G peak. At HTT = 2800° C, the disorder-induced D and D' bands are no longer observed. The mechanisms giving rise to the G, D, and D' peaks have been vastly discussed in the literature, and the details can be reviewed in Refs. [22—27].

For samples with HTT ≤ 2000° C (five bottom spectra in Fig. 2), the spectra are fit using four peaks (or five if the D' band is still noticed as a shoulder in the right side of the G band, e. g. samples with HTT = 1800 and 1600° C). Of the four peaks, two are lined in green (Lorentzians), related to the D^A and G^A peaks, which are also observed for HTT = 2200° C and upwards. The other two peaks, lined in red (Gaussians), are new and are here designated as D^S and G^S peaks. A more detailed description about the protocol to fit the Raman spectra is provided in the Supplemental Information.

3. Theoretical model

A single crystallite is idealized as illustrated in Fig. 1(f): a square-shaped graphene of side L_a, formed by a perfect graphene lattice ($\mathbb{A}$ domain) surrounded by the structurally-disordered area (red) of thickness ℓ_S ($\mathbb{S}$ domain). Since two neighboring crystallites share one border of thickness ℓ_B, $\ell_S = \ell_B/2$. L_a and ℓ_S are the two relevant structural parameters on polycrystalline graphene. There are also two other relevant parameters related to the scattering dynamics, which are represented by the electron and phonon coherence lengths. These dynamic parameters have already been measured using Raman spectroscopy in graphene: $\ell_A \approx 3$ nm for electrons [11,12], and $\ell_C \approx 30$ nm for phonons [15]. These definitions are summarized in Table 1.

The importance of ℓ_A is that this dynamics parameter defines how far from the edge the defect-induced scattering can occur. Therefore, ℓ_A defines the thickness of the D band scattering within the $\mathbb{A}$ domain, which is the green area in Fig. 1(f). The reason why these areas are considered here in two of the faces is due to the D band dependence on the laser polarization. The D band scattering is maximum if the polarization of the exciting field is parallel to the edge, and minimum (null for perfect edges) if the exciting field is polarized along the direction perpendicular to the edge [28,29]. Considering the excitation field as parallel to a pair of opposite edges in the squared crystallite, the D band scattering originates

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[1] The stacking properties of the samples used in this work have been previously investigated by X-ray diffraction and Raman spectroscopy, and the results are reported in Ref. [21]. It has been shown that for HTTs below 2300° C ($L_a < 140$ nm), the samples do not present any detectable stacking order (turbostratic structure). For HTTs = 2300° C and upwards ($L_a \geq 140$ nm) the crystallite size along the c axis (L_c) increases with HTT. Although the shape of the D band can be slightly influenced by stacking, its relatively low intensity (compared to the G band intensity) obtained for samples with $L_a \geq 140$ nm ensure that the analysis presented here is not significantly affected by the occurrence of stacking order in those particular samples.