

Article

Evolution of Nanocrystalline Graphite's Physical Properties during Film Formation

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Abstract: Nanocrystalline graphite (NCG) layers represent a good alternative to graphene for the development of various applications, using large area, complementary metal-oxide semiconductor (CMOS) compatible technologies. A comprehensive analysis of the physical properties of NCG layers—grown for different time periods via plasma-enhanced chemical vapour deposition (PECVD)—was conducted. The correlation between measured properties (thickness, optical constants, Raman response, electrical performance, and surface morphology) and growth time was established to further develop various functional structures. All thin films show an increased grain size and improved crystalline structure, with better electrical properties, as the plasma growth time is increased. Moreover, the spectroscopic ellipsometry investigations of their thickness and optical constants, together with the surface roughness extracted from the atomic force microscopy examinations and the electrical properties resulting from Hall measurements, point out the transition from nucleation to three-dimensional growth in the PECVD process around the five-minute mark.

Keywords: nanocrystalline graphite film; PECVD; ellipsometry; Raman; AFM; hall effect; Romania sensor applications



Citation: Gartner, M.; Anastasescu, M.; Stroescu, H.; Calderon-Moreno, J.M.; Preda, S.; Simionescu, O.-G.; Avram, A.; Buiu, O. Evolution of Nanocrystalline Graphite's Physical Properties during Film Formation. *Coatings* **2022**, *12*, 1274. <https://doi.org/10.3390/coatings12091274>

Academic Editor: Marco Laurenti

Received: 8 June 2022

Accepted: 25 August 2022

Published: 1 September 2022

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1. Introduction

Graphene has generated—since its discovery [1]—an enormous interest; initially limited to theoretical studies, the topic quickly transitioned to a more application-orientated field of focus after its empirical finding by Novoselov et al. A broad spectrum of applications was unveiled [2,3] since but, device integration with current production techniques and equipment was shown to be inefficient compared to other state-of-the-art materials. Therefore, manufacturing and integration constraints are the main drivers in identifying other carbon-related materials, which could be compatible with complementary metal-oxide semiconductor (CMOS) technologies, thus enabling more accessible and faster integration into different applications. Nanocrystalline graphite (NCG), which can be described as a collection of sp^2 hybridised carbon nanodomains delimited by amorphous carbon and various other defects, can represent a feasible alternative [4,5]. NCG thin films have already shown immense versatility, bringing tremendous contributions to various applications: from FETs and sensors to protective coatings and supercapacitors [4].

Its “less ordered” nature allows NCG thin films to be synthesised through a large variety of techniques and retain the critical properties of graphene [4], thus providing them with a significant advantage in research and development and large-scale production. From the broad assortment of deposition techniques, plasma-based methods see the most frequent use, as they provide additional energy in the form of ion bombardment and allow for lower substrate temperatures during growth. Plasma-enhanced chemical vapor

deposition (PECVD) is one of the most used plasma-based methods to grow NCG thin films due to its great capability of fine-tuning the film's properties through the multitude of available parameters [4–6]. Parameters such as discharge power, pressure, gas ratio, and substrate temperature can provide a high degree of control over the thin films' crystallinity, electrical conductivity, and even the type of growth (i.e., planar or vertical) [4,6–10]. Another notable process parameter that may not seem highly impactful at first is the plasma growth time, with which the film thickness can be controlled. Although film thickness is the direct consequence of varying the exposure time to the plasma phase, other intrinsic properties also suffer significant changes (e.g., electrical conductivity [6,11]).

The simple variation of the growth time can impart significant modifications to several physical properties. Thus, it can be a valuable parameter for adjusting the film's properties for specific applications. Moreover, it is arguably the easiest one to modify and is readily available to do so on any deposition system. Although studies that include time-dependent deposition properties have been presented in the past, they usually focus more deeply on other process parameters, and the scope of said papers is not solely aimed at the investigation of growth time dependence [6,7,11]. For example, Schmidt et al. [7] presented a comprehensive study of NCG thin films' properties with respect to several growth parameters, including deposition time, but the paper concentrates on a larger array of parameters and analyses a growth period of only 15 min. We believe it is important to investigate the films' properties over a larger growth period to better observe how the thin films' properties evolve with further three-dimensional growth. Therefore, in this paper, we aim to provide a systematic study of NCG's properties strictly with respect to the deposition time for growth periods of up to 60 min. Several NCG thin films were grown by capacitively coupled radio frequency (RF) PECVD for different periods of time, and properties such as crystallinity, surface morphology and topography, and several electrical properties were investigated through X-ray diffraction (XRD), spectroscopic ellipsometry (SE), scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectroscopy, and Hall measurements.

2. Experimental

2.1. Samples Preparation

Prior to the NCG deposition, the 4" Si wafers were coated with a low-temperature oxide (LTO) by PECVD with the LPX-CVD equipment (SPTS, Newport, UK). The deposition occurred at a substrate temperature of 300 °C, using SiH₄ and N₂O as precursors. The NCG growth was accomplished using the PECVD NANOFAB 1000 (Oxford Instruments, Abingdon, UK) equipment. First, the wafers were loaded from a load-lock chamber into the PECVD reactor at 200 °C, and the substrate temperature was gradually raised (15 °C·min^{−1}) to 900 °C in an Ar/H₂ (5%) atmosphere. The wafers were kept in these conditions for 10 min, thus completing the post-deposition densification of the LTO layer. Next, the hydrogenation of the surface is carried out for 5 min in an Ar/H₂ (10%) atmosphere.

The growth of the NCG thin films was completed in a CH₄:H₂ plasma, at the same substrate temperature of 900 °C, for various growth intervals between 1 and 60 min. After the plasma was switched off, the wafers were cooled down to 200 °C in Ar atmosphere at a rate of 9 °C·min^{−1}. They were then transferred back into the load-lock chamber (5×10^{-2} Torr) and cooled down to room temperature (RT). The process used to obtain the thin films described here is commonly used for synthesising the bulk-NCG subclass, as designated in Ref. [4]. For better readability, the samples are herein referred to as NCG_x, where *x* represents the plasma growth time (in minutes) to each sample subjected to (i.e., NCG1, NCG2, NCG5, NCG15, NCG30, and NCG60).

2.2. Sample Characterization

The obtained samples were characterized from structural, optical, morphological, vibrational (modes of molecules), and electrical points of view.

Structural characterization was performed by XRD. The measurements were carried out using the Rigaku Ultima IV equipment (RIGAKU, Tokyo, Japan), with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) and a fixed power source (40 kV and 30 mA). The diffractometer was used in the grazing incident X-ray diffraction (GIXRD) mode, with an incidence angle of $\alpha = 0.5^\circ$.

Optical characterizations of the samples were performed by SE with a J. A. Woollam VASE[®] ellipsometer (J. A. Woollam Inc., Lincoln, NB, USA). The measurements were executed in the 280–1700 nm spectral range at three incident angles (65° , 70° , and 75°) and with a 10 nm wavelength step. Data acquisition and analysis were realised using the WVASE[®] software package (version 3.92, J. A. Woollam Inc., Lincoln, NB, USA).

The surface morphology of the samples was analysed by SEM in FEG Quanta 3D (Thermo Fisher Scientific, Waltham, MA, USA) operating at 15 kV. The average grain size was determined by the linear intercept method using ten random straight lines through the SEM micrographs and dividing the number of grain boundaries intersecting each line by the actual line length.

The morphological features of the samples were analysed by AFM with the XE-100 microscope (Park Systems, Suwon, Korea) in true non-contact mode, using flexure-guided, cross-talk eliminated scanners. All AFM measurements were performed with NCHR sharp tips (NanosensorsTM, Neuchatel, Switzerland), with less than 8 nm tip radius, $\sim 125 \text{ }\mu\text{m}$ length, $\sim 30 \text{ }\mu\text{m}$ width, spring constant of $\sim 42 \text{ N}\cdot\text{m}^{-1}$, and $\sim 330 \text{ kHz}$ resonance frequency. The topographical 2D AFM images were acquired over $8 \times 8 \text{ }\mu\text{m}^2$ and $1 \times 1 \text{ }\mu\text{m}^2$ areas. The XEI Image Processing Program (v.1.8.0, Park Systems, Suwon, Korea) was used to display the results and for subsequent statistical data analysis, including calculating the root mean square (RMS) roughness.

The Raman spectra were recorded with a Horiba Jobin Yvon LabRam HR spectrometer (Horiba Jovin Yvon, Paris, France) using a 325 nm He-Cd laser, with a spot size of around 1–2 μm , as a light source. The measurements were carried out under a microscope objective of $40\times$ magnification, and a Raman Shift range between 1000 and 3500 cm^{-1} was covered. The positions (w_G and w_D) and maximum intensities (I_G and I_D) of the G and D Raman bands were determined by fitting the raw spectra with Lorentzian peaks.

Electrical characterization was accomplished by Hall measurements based on the Van der Paw effect with the HMS-5000 equipment from Ecopia (Anyang, Korea). The measurements were conducted in direct mode at RT.

3. Results and Discussions

3.1. X-ray Diffraction

The structural variation of the NCG thin films with respect to various growth times, investigated by GIXRD, is presented in Figure 1. The LTO-coated Si wafer was also analyzed, and its diffraction pattern is shown alongside the NCGs' as a reference. The XRD spectra serve only for a qualitative evaluation of the NCG films due to the overlapping of the broad line of the amorphous SiO_x (LTO) and that of the C (002) crystal plane of graphene. The intensity and width of diffraction lines are related to the number of layers and the variations in the interlayer distance [12]. In addition to the diffraction line around 26° , corresponding to the C (002) crystal plane, two broad and diffuse diffraction lines can be observed at around 43° . The latter two are attributed to contributions of the C (100) and C (101) planes, which are often denoted as the C (10) single reflection. The intensity of the NCG diffraction lines increases as the plasma growth time is extended from 1 to 60 min, which corresponds to a restacking/overlapping of the graphitic domains. The structural parameters, L_a and L_c , representing carbon crystallites' stacking weight and lateral crystallite size, cannot be calculated from the recorded XRD data due to the above-mentioned overlapping around 26° , the low intensity, and the signal-to-noise ratio. Therefore, L_a was calculated solely from the intensities ratios of the Raman G and D bands, and the results are presented in Section 3.5.

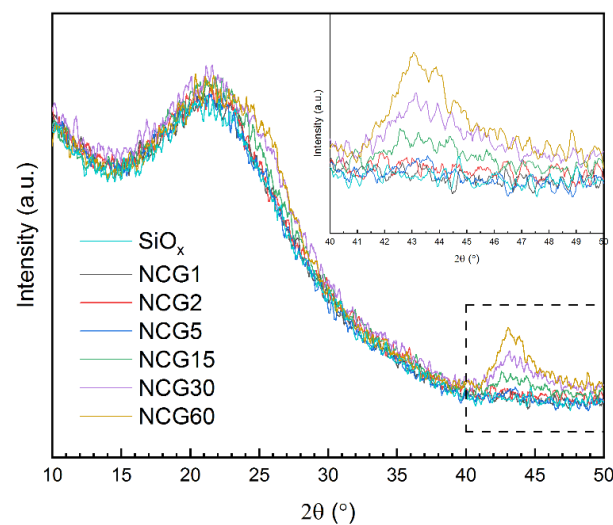


Figure 1. X-ray diffractograms of the low-temperature oxide (LTO) reference wafer and the nanocrystalline graphite (NCG) samples grown at different time periods. (Inset: enhancement of the dotted square, evidencing the C(10) peak at $2\theta = 43^\circ$). The spectra are smoothed with the Savitzky-Golay method over an 11-point window, with a second-order polynomial, for better differentiation of the lines.

3.2. Spectroscopic Ellipsometry

To determine the films' thickness and their optical constants, the ellipsometric measurements were analysed using a four-layers model (i.e., roughness/NCG/SiO_x/Si). A Cauchy equation was initially used for the approximation of the NCG layer's thickness, while the roughness was modelled with the Effective Medium Approximation (EMA). In the next step, the thickness fit parameter was maintained fixed, and a General Oscillator layer was used to describe the optical behaviour of the NCG layers. In this approach, the best fit was obtained using a few Tauc–Lorentz oscillators. To illustrate the efficiency of our chosen model, both the raw experimental data and the calculated data for the amplitude ratio (Ψ) and phase difference (Δ) at an incidence angle of 70° are presented in Figure 2. As observed from the overlapping of the presented spectra, a very good agreement was reached between the modelled and experimental data. Furthermore, the lowest value of the Mean Square Error (MSE) obtained by the Levenberg–Marquardt regression algorithm (~ 6 for the thickest sample) further supports that the model used for fitting was correct. Finally, the thickness and the optical constants of each sample were extracted from the best fit of the SE measurements and are showcased in Figures 3 and 4, respectively.

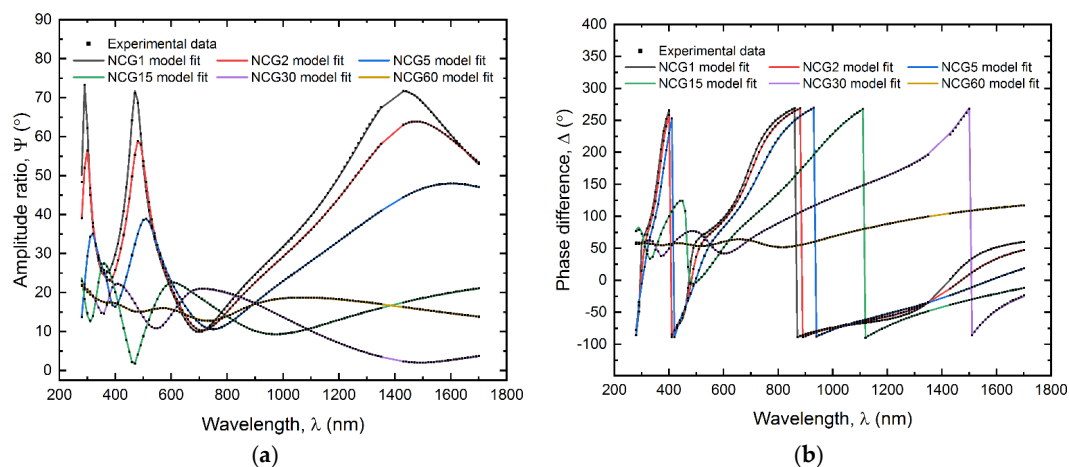


Figure 2. Comparison of the measured and calculated (a) amplitude ratio and (b) phase difference spectra, at a 70° angle of incidence, of the thin NCG films grown at different time periods.

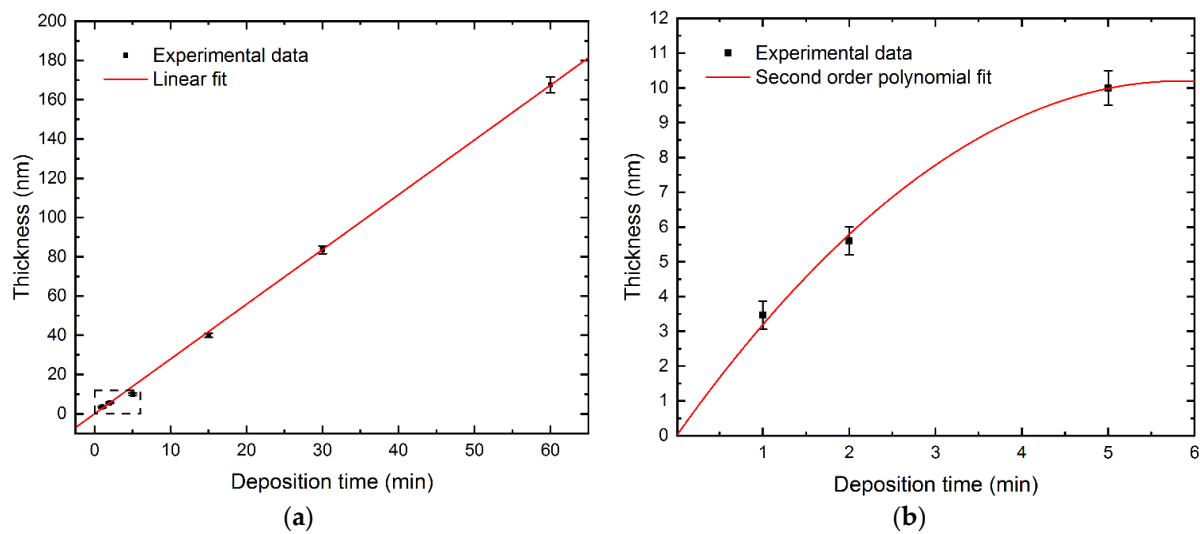


Figure 3. (a) Thickness evolution, with a linear fit, of the NCG films over the full range deposition time. (b) Enhancement of the dotted squared area in (a), representing the thickness evolution over the first 5 min of growth, with a second order polynomial fit.

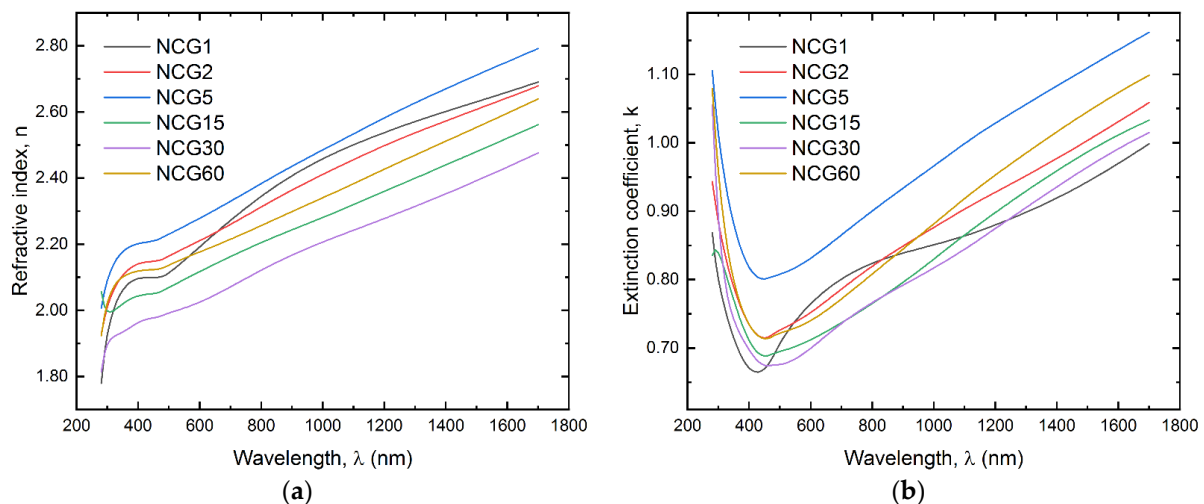


Figure 4. The (a) refractive index and (b) extinction coefficient of the NCG samples.

We noticed that, while the film thickness varies relatively linearly with respect to deposition time for large growth periods (Figure 3a), for the first three samples (NCG1, NCG2, and NCG5), the film thickness varies based on a second-order polynomial function (Figure 3b). This change in variation reveals the transition from the nucleation stage in the NCG's development to the actual growth and lateral expansion of the layers [5,6].

The results of the optical constants of the investigated NCG films (Figure 4) demonstrate that NCG5 exhibits the highest refractive index. This possibly indicates that the homogeneity of the graphitic thin film is attained at a deposition time of around 5 min. Further increasing the plasma exposure time leads to a higher thickness of the deposited NCG layer and, consequently, slightly lower values of the refractive index. This observation is supported by the fact that the growth rate appears to stabilise after 5 min of growth, as evidenced in the already presented thickness evaluation and other studies [6]. As graphene and graphene-derived materials can be obtained through several methods and in various nanostructures, their optical properties vary accordingly. To better showcase the variance of graphene-based materials' optical constants, we extracted some of the optical constants presented in a few recent literature studies regarding graphene's optical constants obtained

by SE measurements. The constants mentioned above, together with those from our present work, are displayed in Table 1 for a direct comparison. From the multitude of articles published on this topic, the ones that describe synthesis by the CVD method and measurements performed on SiO₂/Si substrates were mainly chosen.

Table 1. Recent studies of graphene and graphene-derived materials' optical constants, refractive index (n) and extinction coefficient (k), obtained by spectroscopic ellipsometry analysis.

Synthesis Method	Substrate	Number of Graphene Layers or Film Thickness	Measurement Wavelength Range	Optical Constants ($\lambda = 630$ nm)	Ref.
CVD *	SiO ₂ /Si	Bilayer	218–1200 nm	n = 2.95 k = 1.78	[13]
CVD *	Si PET	Monolayer Bilayer Trilayer	0.38–6.2 eV 0.38–5.2 eV 4.00–5.2 eV	n = 1.36 k = 0.06	[14]
CVD *	Glass Quartz SiO ₂ /Si	Monolayer	240–1000 nm	n = 2.7 k = 1.48	[15]
CVD *	SiO ₂ /Si	0.334 nm	250–1100 nm	n = 2.16 k = 1.06	[16]
Drop casting	SiO ₂ /Si	r-GO film 1500–2500 nm	193–1690 nm	n = 1.86 k = 0.83	[17]
CVD *	Fused silica	0.335 nm	0.7–9.0 eV	n = 2.91 k = 1.51	[18]
Exfoliation	SiO ₂ /Si	0.34 nm	210–1000 nm	n = 2.73 k = 1.26	[19]
Exfoliation	SiO ₂ /Si Amorphous quartz	0.335 nm	240–750 nm	n = 2.8 k = 1.45	[20]
PECVD	SiO ₂ /Si	bulk-NCG thin films 3.4–167 nm	280–1700 nm	NCG5: n = 2.29, k = 0.84 NCG15: n = 2.13, k = 0.71 NCG30: n = 2.03, k = 0.71	This work

* The graphene samples prepared by CVD were initially grown on Copper foils and transferred onto the respective substrate.

For a better depiction, the refractive index of NCG5, NCG15, and NCG30 is graphically represented in Figure 5 alongside some of the results [13,16,17] listed in Table 1, over the full investigated wavelength range. The additional experimental data sets were extracted from the literature using the WebPlotDigitizer software (Version 4.5) [21]. As can be observed from Figure 5, even the optical constants' behaviour of graphene is slightly different in the published literature. This occurs due to some independent factors, such as the preparation method, the use of other substrates for the graphene deposition, and the number of graphene layers, or could even be linked to the investigation methods.

3.3. Scanning Electron Microscopy

The granular morphology of the NCG films is more visible from the SEM micrographs of the NCG15, NCG30, and NCG60 films (Figure 6) than those of the thinner samples. This is because the average grain size slightly increases with the deposition time, ranging from ~19 nm for NCG15 to ~21 nm for NCG60. As the grain size shows an increasing trend with deposition time and due to the low RMS roughness of the samples, the grains for the thinner films are harder to distinguish by top-view SEM micrographs. Hence, all samples' topography was further evaluated by AFM.

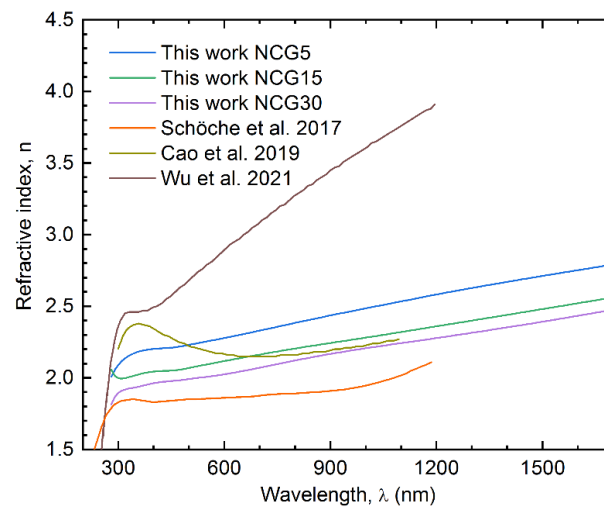


Figure 5. Comparison of the refractive index of graphene obtained from Refs. [13,16,17] with this work.

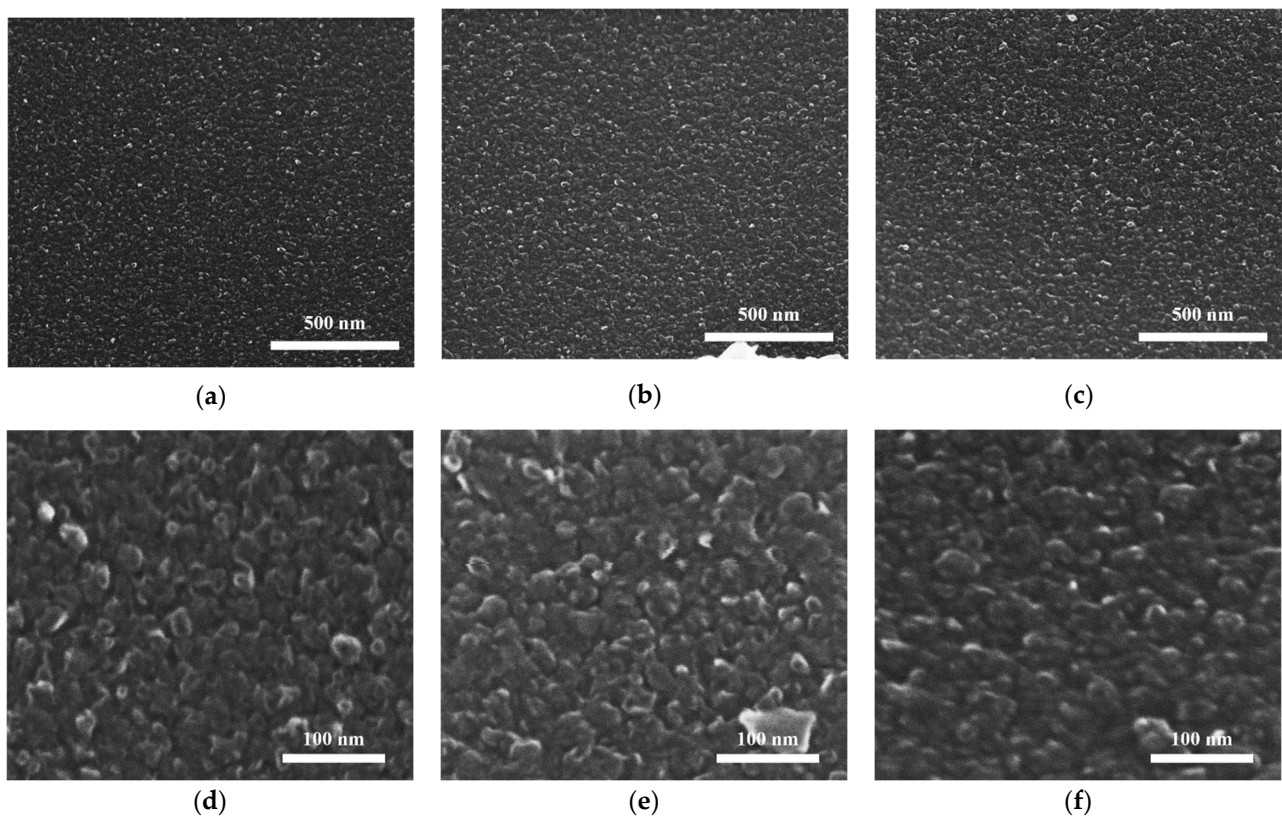


Figure 6. Top-view SEM micrographs at (a–c) 150 k $\times$ and (d–f) 600 k $\times$ magnification of the NCG films grown for (a,d) 15, (b,e) 30, and (c,f) 60 min.

3.4. Atomic Force Microscopy

The AFM images of the NCG samples and the substrate used for deposition (SiO_2/Si) are displayed in Figure 7, together with their respective height histograms. The AFM topography was recorded at an $8 \times 8 \mu\text{m}^2$ and an $1 \times 1 \mu\text{m}^2$ scale. The images recorded at $8 \times 8 \mu\text{m}^2$ were registered to check the uniformity of the NCG deposition or the existence of defects induced during NCG layer formation. After 1 min of plasma growth, a few droplets of deposited material appear on the sample's surface, visible as rounded white spots in Figure 7a (middle). These droplets, marked by yellow arrows in Figure 7b (left), become more visible after 5 min of NCG deposition as new carbonic layers nucleate and

expand laterally on the already formed NCG layers. Otherwise, no other defects, such as cracks or exfoliations, are visible in the recorded AFM images. The lower $1 \times 1 \mu\text{m}^2$ scale (Figure 7c,d) offers a better view of the NCG samples' morphology. The granular morphology of NCG1 is not much different as an aspect from the SiO_2 substrate, most probably indicating the formation of just the first NCG nucleation sites. After 2 min of deposition, the sample's morphology is less uniform, revealing the appearance of parcels with small particles and few material deposits. After 5 min of deposition, the film's surface is still covered only with small particles, with a few large deposits of material visible on both NCG5 and NCG15 (marked by blue arrows in Figure 7d—left and middle). When extending the deposition time to 15 and 30 min, these small particles start to nucleate themselves, and the diameter of the surface particles increases. Some double-sized (or larger) surface particles (marked by green arrows in Figure 7d—right) can be observed on the surface of the thicker samples. The current AFM observations are consistent with the previously presented top-view SEM micrographs, suggesting that larger grains are formed as the films grow thicker. This complies with the PECVD synthesis of NCG films, as the upper layers nucleate and grow on an already partially sp^2 bonded carbon film and are further away from the SiO_2 substrate, which should allow for a better lateral expansion of the nucleation sites [6].

The RMS roughness histogram (Figure 8a) pointed out a slight increase in roughness values for the NCG films after 1 or 2 min of deposition, probably related to the formation of the nucleation sites. As pointed out before, after 5 min, the film is formed and continuous, and the appearance of some droplets of material (see Figure 7b—left) leads to an abrupt increase in roughness. Further on, the thickness of the NCG films increases and the films become more uniform, stabilising the RMS roughness around 4 nm after 60 min of deposition (Figure 8b).

3.5. Raman Spectroscopy

In order to check the crystallisation of our samples and determine if the trend of crystallite size matches the predictions from the SEM and AFM results of the PECVD process's evolution, Raman spectroscopy was conducted. Raman analysis of sp^2 bonded carbon nanostructures, such as ours, is typically conducted in the visible spectral range. Nevertheless, we thought it would be interesting to analyse the Raman response of our samples with a 325 nm He-Cd laser, as numerous investigations in the visible spectral range of this type of carbonic film have already been published [4–6,22]. Although the UV excitation causes dispersion of the D band and may suppress its intensity [23–26], the acquired spectra can still be utilised as a qualitative comparison of each sample's crystallinity relative to each other. The extracted Raman parameters are listed in Table 2. The spectra show the typical features of disordered graphitic carbon at $\sim 1430 \text{ cm}^{-1}$ (D mode) and $\sim 1600 \text{ cm}^{-1}$ (G mode)—see Ref. [24] and references therein. The position of the D and G bands, ω_D and ω_G , shifts to lower values as the deposition time increases and the I_D/I_G ratio decreases from 0.59 for NCG2 to 0.36 for NCG60 (Table 2). This indicates the growth of the typical width, L_a , of the nanographite domains along the hexagonal plane. The lateral crystallite size values L_a were calculated according to Ref. [27], and they show steady growth with respect to the deposition time (from 4.5 nm for NCG2 to 7.4 nm for NCG60—see Table 2). The proportionality of this relation implies a higher crystalline order of the nanographite domains as the films are grown for a larger period of time and further reinforces the implications inferred from the SEM and AFM results.

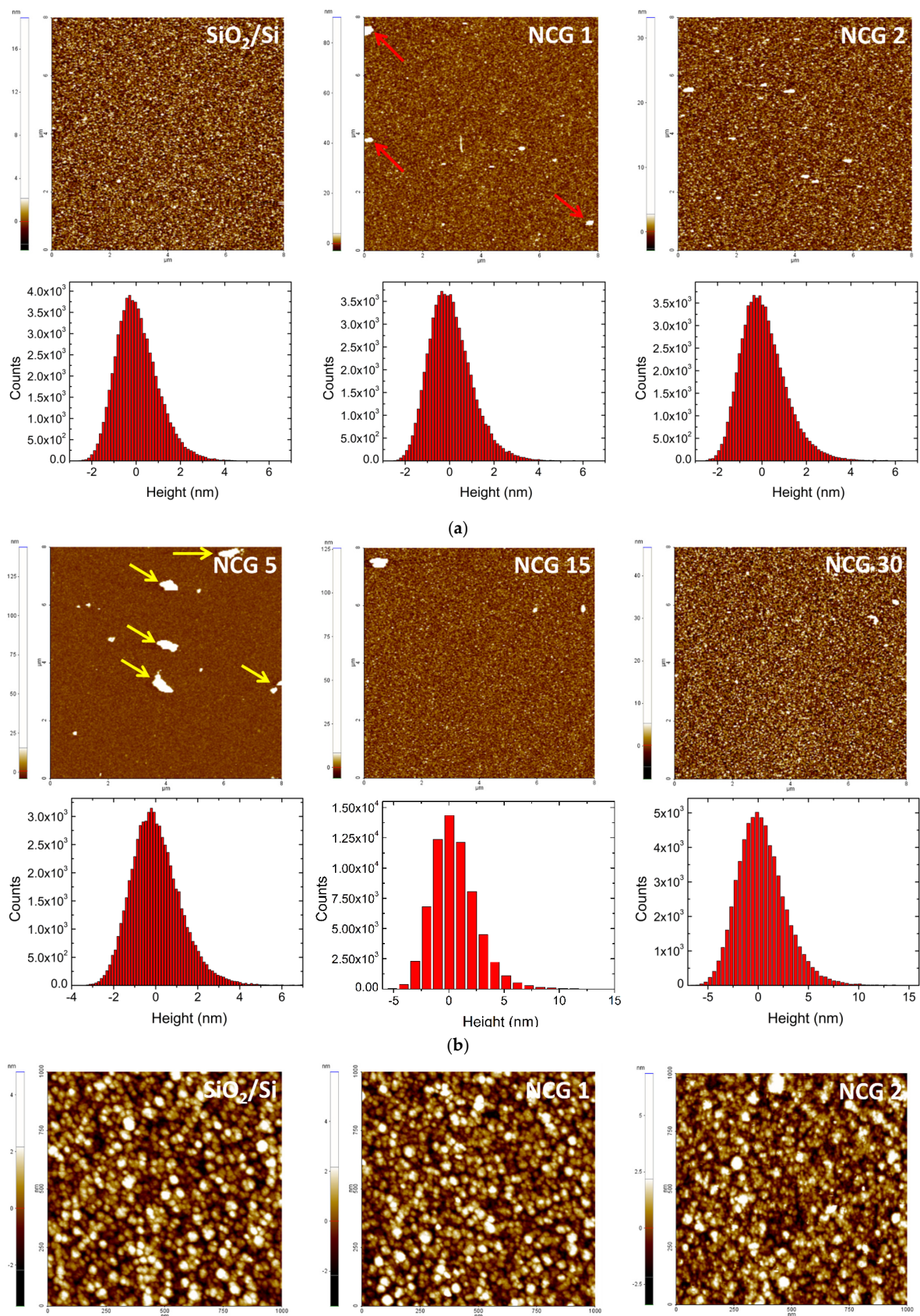


Figure 7. Cont.

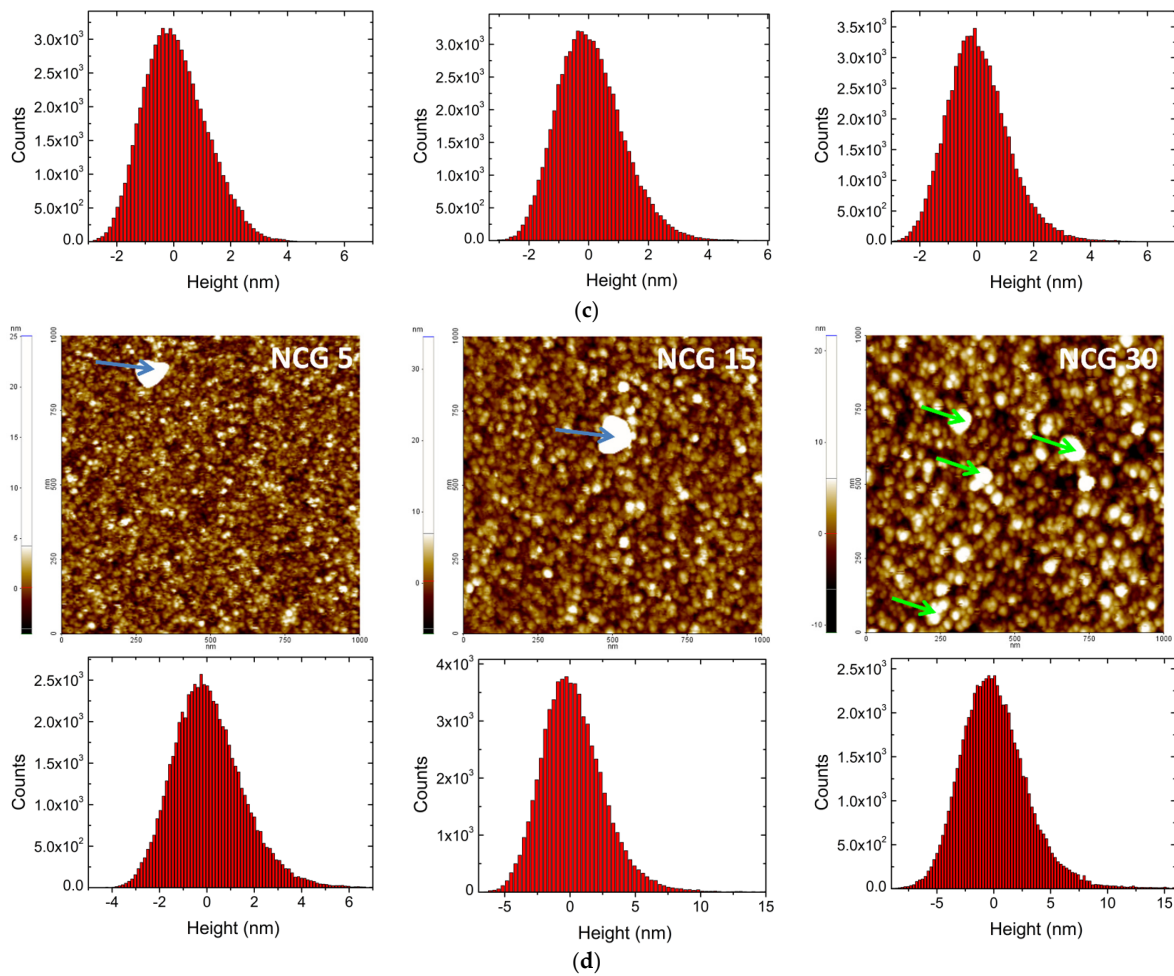


Figure 7. Two-dimensional AFM images of the LTO reference substrate and the NCG samples (top row of each subfigure), with the respective height histograms below each image, taken at an (a,b) $8 \times 8 \mu\text{m}^2$ and (c,d) $1 \times 1 \mu\text{m}^2$ scale.

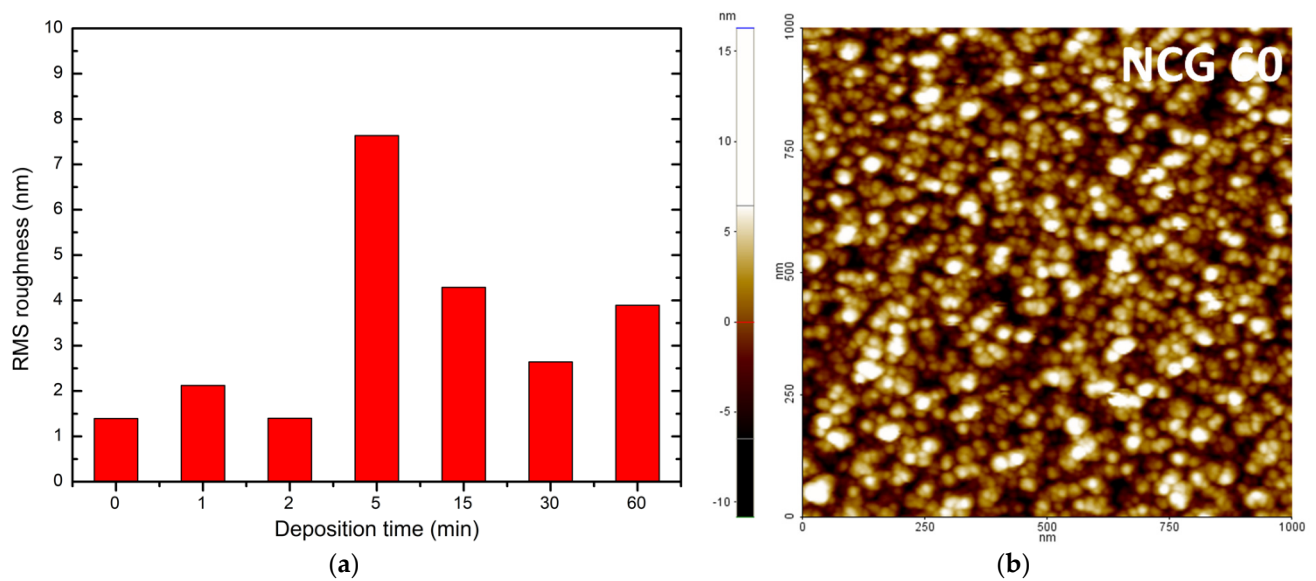


Figure 8. (a) The root mean square (RMS) roughness histogram of the NCG samples versus deposition time (evaluated from the corresponding AFM images recorded at a $8 \times 8 \mu\text{m}^2$ scale). (b) AFM image of NCG60 at a $1 \times 1 \mu\text{m}^2$ scale.

Table 2. Raman spectra parameters: ω_D , ω_G , I_D/I_G , I_{2D}/I_G and the calculated basal plane domain size.

Sample	ω_D (cm ⁻¹)	ω_G (cm ⁻¹)	I_D/I_G	L_a (nm)	I_{2D}/I_G
NCG2	1441.7	1598.9	0.59	4.5	0.1041
NCG5	1437.4	1594.6	0.51	5.2	0.1020
NCG15	1431.4	1593.0	0.45	6.0	0.0869
NCG30	1430.0	1592.9	0.37	7.2	0.0729
NCG60	1429.2	1592.8	0.36	7.4	0.0581

The 2D band is present at ~ 2860 cm⁻¹, and the I_{2D}/I_G ratio decreases with deposition time from ~ 0.104 for NCG2 to ~ 0.058 for NCG60 (Table 2). The relative decrease in the 2D band's intensity is in agreement with the enhancement of crystalline order and indicates the formation of layered nanographitic domains due to the superposition of single-layer domains. Typical Raman spectra of the thinnest and thickest samples, together with the Raman spectrum of commercial single-layer graphene, are presented in Figure 9 for a better visual depiction of the NCG films' transformation.

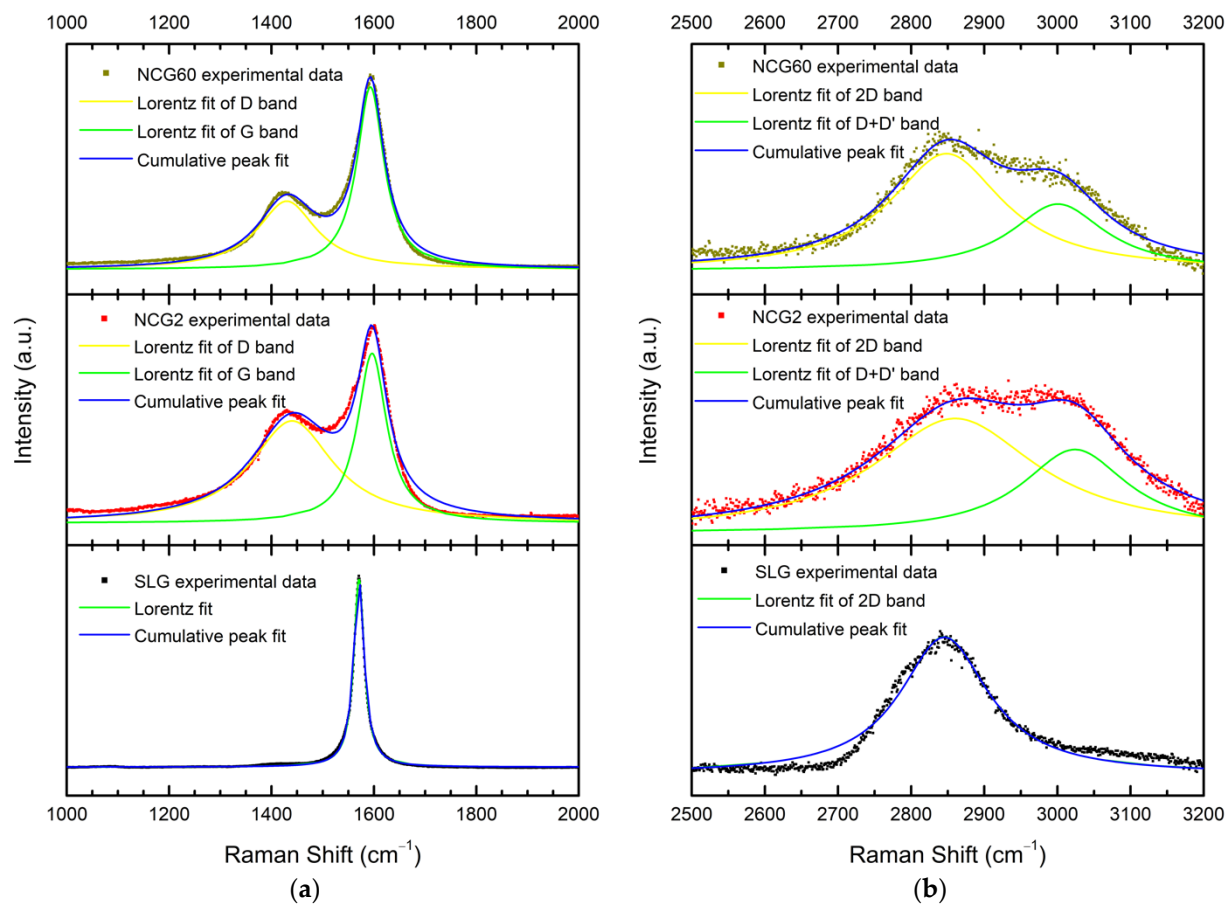


Figure 9. Raman spectra of commercial single-layer graphene (SLG), NCG2, and NCG60 acquired with a 325 nm He-Cd laser, showcasing the (a) D and G, and (b) 2D and D + D' Raman bands fitted with Lorentzian peaks.

3.6. Hall Measurements

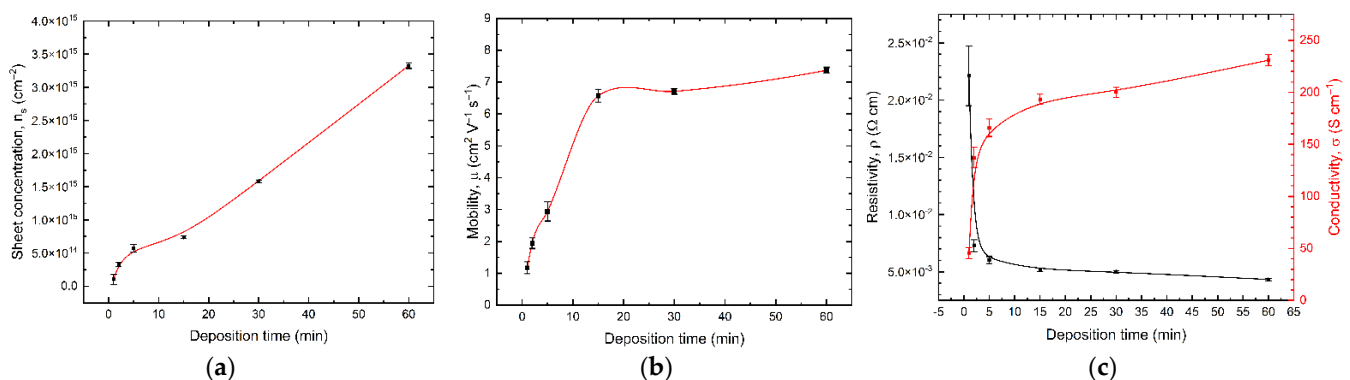
The increasing degree of crystallinity of the presented samples should also involve an increase in electrical conductivity. Therefore, to evaluate the electrical properties of our samples and establish a relative dependence/trend with their growth time, Hall measurements were performed. The obtained results for bulk and sheet concentrations, resistivity, conductivity, and mobility are presented in Table 3.

Table 3. The electrical properties of the NCG thin films resulted from Hall measurement.

Sample	Current (mA)	Bulk Conc. n_c (cm ⁻³)	Sheet Conc. n_s (cm ⁻²)	Resistivity ρ ($\Omega \cdot \text{cm}$)	Conductivity σ (S·cm ⁻¹)	Mobility μ (cm ² ·V ⁻¹ ·s ⁻¹)
NCG 1	0.05	1.67×10^{20}	1.25×10^{14}	2.21×10^{-2}	4.52×10^1	1.69
NCG 2	0.1	4.27×10^{20}	2.99×10^{14}	7.28×10^{-3}	1.37×10^2	2.01
NCG 5	0.5	2.47×10^{20}	3.70×10^{14}	6.02×10^{-3}	1.66×10^2	4.20
NCG 15	1	1.88×10^{20}	7.52×10^{14}	5.17×10^{-3}	1.93×10^2	6.42
NCG 30	3	1.84×10^{20}	1.57×10^{15}	4.99×10^{-3}	2.00×10^2	6.78
NCG 60	5	1.97×10^{20}	3.36×10^{15}	4.33×10^{-3}	2.31×10^2	7.30
-	-	-	↑	↓	↑	↑

All investigated samples possess a “p-type” conductivity, and their electrical properties show improvement for higher deposition times. The carrier concentration (n_s), electrical conductivity (σ), and mobility (μ) increase from NCG1 to NCG60, while the resistivity (ρ) decreases, from $2.2 \times 10^{-2} \Omega \cdot \text{cm}$ (NCG1) to $4.3 \times 10^{-3} \Omega \cdot \text{cm}$ (NCG60), showing better conduction due to the improved crystallinity. The high values of the bulk concentration (10^{20} cm^{-3}) and transmittance make them suitable as transparent conducting materials for solar cell applications.

For a better depiction of the electrical properties’ trend, the sheet concentration, mobility, resistivity, and conductivity are plotted with respect to deposition time, and the respective graphical representations are showcased in Figure 10. All electrical measurements exhibit a trend consistent with the prior investigations presented in this work, indicating a superior crystallisation for the samples grown for a larger period of time.

**Figure 10.** (a) Sheet concentration, (b) mobility, (c) resistivity, and conductivity of the NCG thin films as a function of deposition time.

4. Conclusions

A comprehensive study of the physical properties of PECVD NCG was conducted, including establishing the spectral dispersion of the complex dielectric function and the Raman response as a function of the incident wavelength. Firstly, a change in growth rate after 5 min of plasma growth is found from the evaluation of film thickness by SE, suggesting the transition from nucleation to film growth. This is further confirmed by analysing the optical constants of the NCG films. SEM and AFM investigations show an increase in grain size as the deposition time increases. Furthermore, the RMS surface roughness investigations show a maximum value at a deposition time of 5 min, again touching on the transition in growth at around the 5 min mark. The Raman analysis of our samples reveals a layered structure of nanographitic domains with an improved crystallinity for higher deposition times. The enhancement of crystallinity is also reflected in the electrical properties of the NCG films, which become more conductive as the deposition time is increased. Moreover, the process evolution before and after the 5 min mark is further reflected in the films’ electrical properties, as can be seen in the respective graphical

representations. All investigations of the presented samples show an increase in crystallinity and improvement of electrical properties with higher deposition times. Additionally, we conclude that the transition between the nucleation of the first few NCG layers and the three-dimensional growth of the bulk-NCG film takes place around the 5 min mark in the PECVD process under these specific parameters. As was shown in this study, the physical properties of NCG thin films can vary considerably by only modifying their growth time and so, the evolution of the NCG layer's properties as a function of deposition time is highly relevant from the perspective of application development (e.g., field emission, electrochemical sensing, photodetectors, etc.).

Author Contributions: Formal analysis, M.A., H.S., J.M.C.-M. and S.P.; Sample preparation, A.A. and O.-G.S.; Investigation, O.-G.S., A.A., O.B.; Writing—original draft preparation, M.G., O.B. and A.A.; Writing—review and editing, O.-G.S., O.B., H.S. and M.A.; Project management, O.B. All authors have read and agreed to the published version of the manuscript.

Funding: The authors from ICF Bucharest would like to acknowledge the financial support of the project PN-III-P2-2.1-PED-2019-2073 (UEFISCDI) and of the Romanian Government that allowed for the acquisition of the research infrastructure under POS-CCE O 2.2.1 project INFRANANOCHEM—No. 19/01.03.2009. The authors from IMT—Bucharest would like to acknowledge the funding support offered by project MICRO-NANO-SIS PLUS, 2019-2022, Cod: 1916—Romanian Ministry for Digitization, Innovation, and Research; and the PN-III-P1-1.2-PCCDI-2017-0619 project (UEFISCDI) “Nanostructured carbonic materials for advanced industrial applications” (NANOCARBON+).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available in this paper; To access specific experimental data, please contact the corresponding author.

Acknowledgments: Gabriel Crăciun's (IMT Bucharest) support for acquiring SEM images is greatly acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

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