Applicability of Atmospheric Pressure Plasma Jet (APPJ) Discharge for the Reduction in Graphene Oxide Films and Synthesis of Carbon Nanomaterials

Sri Hari Bharath Vinoth Kumar 1,2, Josefia Ibaceta-Jaña 1, Natalia Maticiuc 2,*, Krystian Kowiorski 3, Matthias Zelt 2, Ulrich Gernert 4, Ludwika Lipińska 3,*, Bernd Szyszka 1, Rutger Schlatmann 2, Uwe Hartmann 5 and Ruslan Muydinov 1,2,*

1 Institute for High-Frequency and Semiconductor-System Technologies, Technische Universität Berlin, Einsteinufer 25, 10587 Berlin, Germany; s.vinothkumar@tu-berlin.de (S.H.B.V.K.); josefa.ibaceta@gmail.com (J.I.-J.); bernd.szyaska@tu-berlin.de (B.S.)
2 Pvcmb, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Schwarzschildstraße 3, 12489 Berlin, Germany; natalia.maticiuc@helmholtz-berlin.de (N.M.); matthias.zelt@helmholtz-berlin.de (M.Z.); rutger.schlatmann@helmholtz-berlin.de (R.S.)
3 Graphene and Composites Research Group, Łukasiewicz Research Network—Institute of Microelectronics and Photonics, Aleja Lotników 32/46, 02-668 Warsaw, Poland; krystian.kowiorski@itme.edu.pl (K.K.); ludwika.lipinska@itme.edu.pl (L.L.)
4 Zentraleinrichtung Elektronenmikroskopie (ZELMI), Straße des 17. Juni 135, 10623 Berlin, Germany; ulrich.gernert@tu-berlin.de
5 Impellis GmbH & Co., KG, Am Försterberg 12, 32805 Horn-Bad Meinberg, Germany; u.hartmann@impellis.de
* Correspondence: ruslan.muydinov@helmholtz-berlin.de

Abstract: Atmospheric pressure plasma jets (APPJ) are widely used in industry for surface cleaning and chemical modification. In the recent past, they have gained more scientific attention especially in the processing of carbon nanomaterials. In this work, a novel power generation technique was applied to realize the stable discharge in N2 (10 vol.% H2) forming gas in ambient conditions. This APPJ was used to reduce solution-processed graphene oxide (GO) thin films and the result was compared with an established and optimized reduction process in a low-pressure capacitively coupled (CCP) radiofrequency (RF) hydrogen (H2) plasma. The reduced GO (rGO) films were investigated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Effective deoxygenation at longer exposure times was found to proceed with the expense of GO–structure integrity. By adding acetylene gas into the same APPJ, carbon nanomaterials on various substrates were synthesized. The carbon materials were characterized by Raman spectroscopy, scanning electron microscopy (SEM), and energy-dispersive X-ray (EDX) analyses. Fullerene-like particles and graphitic carbon with short carbon nanotubes were detected on Si and Ag surfaces, respectively. We demonstrate that the APPJ tool has obvious potential for the versatile processing of carbon nanomaterials.

Keywords: atmospheric plasma; carbon nanomaterials; graphene oxide; plasma treatment

1. Introduction

Plasma techniques have been part of the material science and technology domain for the past several decades [1]. They are well integrated with today’s research and industries in diverse applications due to high versatility, flexibility, and scalability. Recently, there has been a growing interest in the use of atmospheric plasma systems, and the APPJ systems, in particular [2–5]. The fundamentals of this technology have been reviewed in the literature [6–14]. APPJ can generate a high flux of various metastable but chemically very active species. Its use in ambient conditions allows setting up smaller, modular, and low-cost plasma sources for surface treatment. Since APPJs work with a gas flow, the
ignition of plasma is spatially separated from the treatment surface [15]. This attribute has the following advantages: (i) the surface to be treated is safe from damage caused by arcs or discharge currents; and (ii) surfaces of objects with various shapes, geometries, and sizes can be treated. A limitation of the APPJs is the small area of a treatment restricted to a few millimeters. This limitation can be successfully overcome by scanning [16], using robotic arms [17], or an array of APPJs [18,19].

The applications of APPJs are numerous and can be broadly summarized into (i) surface modification; (ii) deposition of coatings, and (iii) biomedical applications [2,3,5]. This article relates to the former two themes. The crossover of the APPJ applications with the synthesis and processing of carbon nanomaterials is particularly interesting [20–23].

In the last four decades, the field of carbon materials has been extended with fullerenes, carbon dots, nanodiamonds, nanofibers, nanotubes, and graphene [24]. From these carbon-allotropic forms, the growth and prospects of graphene have been compelling [25]. In our previous work, we highlighted the importance and scope of atmospheric plasma such as APPJ in the reduction in GO, which is one of the strategies to produce graphene films [26].

There is also an emerging interest in the production of free-standing graphene (gas-phase synthesized graphene, GSG) at atmospheric pressure. The GSG is formed in the afterglow region of plasma discharge where nucleation and growth take place [27,28]. Microwave (MW)-induced plasma is predominantly utilized for such synthesis [29–31]. Jašek et al. [31] deposited GSG layers from ethanol vapors in argon in this way. Such plasma heated the Si/SiO$_2$ substrate to ~650–1150 °C, depending on plasma conditions. The results are commendable, but the approach needs further development to operate at lower temperatures suited for sensitive (e.g., flexible) substrates. Researchers have also synthesized GSG using high-power APPJ (30–40 kW power, 300–400 A) fixed and enclosed in a reactor with graphitic walls [24,32–34]. The reactor was further enclosed in a vacuum chamber with helium or argon feed-through. As a graphene forming admixture, propane/butane or methane, or acetylene were used. A drastic cooling of the discharge flow resulted in the formation of a solid form of carbon. Crumbled graphene sheets of various sizes (up to a few hundred nanometers) with the number of layers in the range of 1–10 have been obtained. Although this technique is attractive, some of the downsides are [32–34]: (i) a very high power consumption; (ii) the necessity of special auxiliary systems including a vacuum chamber with cooling; and (iii) the crumbled nature of graphene, and the need for a post-synthesis solution process to realize particular applications such as transparent conductive layers, sensors, and other functional coatings.

Motivated by the need for an atmospheric plasma system to be able to deposit graphene films in ambient conditions, we developed a low-power APPJ system. Although the glowing gas jet is named “Plasma” in the literature, it is not strictly correct in our case since most gas species are not ionized but excited. Our free jet system provides a lower temperature of neutrals as compared to the known APPJs. Due to the discontinuity of power coupling, not all the flowing gas is electrically affected. The potential applications of this system are demonstrated for: (i) reduction in GO films and (ii) deposition of carbon nanomaterials on various substrates (described in Sections 3.1 and 3.2, respectively).

2. Materials and Methods

As substrates, an Eagle XG® (Corning Inc., Corning, NY, USA) glass of 1.1 mm thickness and p-type (100)–oriented Si (Microchemicals GmbH, Ulm, Germany) were used. Before deposition, the substrates were sonicated at 50 °C in organic solvents (acetone, isopropanol) and washed in a glass-washer using a universal detergent (Hellmanex®) and deionized water.

All GO samples were prepared only on Si substrates. The aqueous dispersion of GO was prepared with flakes obtained from graphite by a modified Hummers method. Further experimental details are described in the literature [35–37]. The 2 mg/mL GO dispersion in deionized water (DI) (flake size 1–100 µm) was spin-coated at 2000 rpm for 30 s on a 1.5 × 1.5 cm$^2$ substrates. The films were dried at room temperature (RT) overnight in a N$_2$–filled
glovebox. As found by SEM and confirmed by ellipsometry these films had a thickness of ~20 nm and a multilayered porous microstructure.

The commercial PlasmaJet® (Raantec GmbH & Co., KG, Borgholzhausen, Germany) system was specially redesigned for our purposes. Since molecular H\textsubscript{2} inhibits plasma generation, the electronic components of the power generator have been modified. Power generation was also optimized for the gas mixtures used and thus operated at an MF-induced (31.8 kHz) direct current (DC) power (480 W). The free jet nozzle was constructed to provide a vortex-like flow of gas. The nozzle head design details are available in the patent DE 195 32 412 C 2. The internal glowing chamber was equipped with a ring-electrode, which also worked as an outcoupling window. Another electrode was placed in the middle of the chamber on the back side. Fine-tuning of the power generation provided the following gas excitation conditions:

- high enough excitation degree;
- gas leaving the nozzle electrically unchanged;
- gas species remaining excited outside the nozzle;
- the relaxation of excited species producing energy in the infrared (IR) range.

So far, no detailed optical emission spectroscopy (OES) analysis of our free jets has been performed, however, it is planned for future work. The GO–reduction treatment was performed in a flow (30 L/h) of forming gas (10 vol.% H\textsubscript{2} in N\textsubscript{2}). The substrate to nozzle distance was 8 mm, and the plasma irradiation time was varied at 2 s, 5 s, and 10 s. To avoid rGO reoxidation in air, the freshly treated surfaces were exposed to the same flow for 20 s after the plasma power supply was turned off. For all treatments/deposition with the APPJ, no external sample heating was used. The GO reduced with APPJ in ambient conditions was compared to rGO reduced in a H\textsubscript{2}-plasma environment. For this, an RF-plasma treatment was carried out in the AKT 1600 system (Applied Materials, Santa Clara, CA, USA) described elsewhere [38]. After comprehensive optimization where RF-power, temperature, and treatment time were varied, the conditions chosen were: 100 W RF power, 30 s treatment, and 200 °C substrate temperature. The heating was performed in hydrogen for 10 min and the cooling in the load lock chamber for 5 min under vacuum. A pure H\textsubscript{2} (99.9999%) environment at a process pressure of 133.3 Pa was used during the treatment.

The in-house prepared RF-sputtered Corning®-glass/~20 nm i-ZnO/~20 nm Ag film stack (referred to as ZnO/Ag from here onwards) and Si were used as substrates for carbon APPJ deposition. A Corning®-glass of size 2.5 × 2.5 cm\textsuperscript{2} was used for the sputtering of ZnO/Ag. The sputtering process for i-ZnO was described in previous work [39]. Silver films were deposited in the DC magnetron sputtering system A600V7 (Leybold Optics Dresden GmbH, Dresden, Germany) at a 75-mm target–to–substrate distance. The base pressure was 5.37 × 10\textsuperscript{−4} Pa, the process was performed in Ar (99.9999%) at a pressure of 5.16 × 10\textsuperscript{−1} Pa. The power density was 1.33 W/cm\textsuperscript{2}, no intentional heating of a substrate was used. The substrate holder oscillated with a 4.8 m/min speed. No special pretreatment such as etching of SiO\textsubscript{x} from silicon wafer was applied before carbon depositions. The metallic silver film grew (111)-textured on (0002)-ZnO seed layer (Figure S1a), which was in good agreement with the literature [40]. Herewith, the Ag-film was not textured in-plane (Figure S1). For carbon synthesis, the APPJ discharge contained a mixture of C\textsubscript{2}H\textsubscript{2} (feedstock gas, 0.5 L/h flow) and forming gas (10 vol.% H\textsubscript{2} in N\textsubscript{2}, 30 L/h flow). The substrate to nozzle distance varied between 3 and 6 mm. The 1 × 1 cm\textsuperscript{2} cut ZnO/Ag films, optimized based on resistance measurements in Van der Pauw geometry (Rsh ≈ 10 Ω), were chosen for the carbon depositions. The photographs of the APPJ working with two considered gas mixtures are shown in Figure S2. All freshly treated or deposited samples were immediately packed into vacuum-sealed plastic bags for transport or storage until the next processing step or analysis.

Scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDX) were performed on a Hitachi SU8030 SEM (Tokyo, Japan) with a CFEG (cold field emitter gun) and EDX analyzer EDAX TEAM system with a 30 mm\textsuperscript{2} Octane SDD (silicon drift detector). XRD measurements were completed on the Bruker Discovery D8 (Karlsruhe, Germany).
system using Cu K$_\alpha$ radiation and the high-resolution mode of the 1D-LYNXEYE XE-T detector. For the acquisition of the pole figure, Polycap optics were installed.

XPS measurements were carried out using nonmonochromatic Mg K$_\alpha$ radiation (1254 eV) [41]. The raw XPS spectra of the various GO were fit using the XPSPEAK 4.1 software by non-linear least-squares fittings with a Gaussian/Lorentzian ratio of 80:20 [42]. Micro-Raman spectroscopy was performed in a high-resolution Horiba Jobin Yvon LabRAM HR800 (Bensheim, Germany) spectrometer. Samples deposited with the C$_2$H$_2$ plasma on Si and ZnO/Ag substrates were measured with an excitation source of 633 nm and a power of 2.49 mW. The GO and rGO (reduced with APPJ) on Si were measured with an excitation wavelength of 532 nm with a power of 5 mW. Different Raman excitation wavelengths used during the investigation were solely due to lab availability. The acquisition parameters were grating of 600 lines per millimeter, an aperture of 400 µm, and an objective of 100 ×. The Raman spectra were fit using Fityk software (version 1.3.1).

3. Results and Discussion

3.1. Reduction in GO

The fitted Raman spectra for the GO and various rGO are presented in Figure 1 where a combination of three pseudo-Voigt and two Gaussian functions were used [43]. The fit data such as peak centers, intensity, and full width at half maximum (FWHM) have been summarized in the supplementary information, Table S1. In pure graphite, the peak at ~1580 cm$^{-1}$ corresponded to the G-band arising from the E$_{2g}$-symmetry of the carbon lattice [44]. In the case of GO/rGO, this peak either blueshifted or redshifted based on the excitation laser frequency. The spectra also exhibited peaks at ~1350 cm$^{-1}$ (D–band) and ~1620 cm$^{-1}$ (D$'$–band) corresponding to the disorder-induced phonon mode due to the finite size of crystals and defects [45]. The D$'$–band has also been attributed to vacancy defects in pentagonal and octagonal rings in the literature [46]. The shoulder at ~1200 cm$^{-1}$ was the D*–band also arising from disordered graphitic lattice provided by the sp$^2$–sp$^3$ bonds at the edges of the network [44]. The attribution of the D$''$–band at ~1480 cm$^{-1}$ was ambiguous [43] as it has been assigned to (i) phonon density of states in finite-sized crystals [47], (ii) amorphous lattices, since the intensity of the D$''$ band was found to decrease with an increase in crystallinity [48], (iii) amorphous sp$^2$–bonded forms, including functionalized small molecules [44,49], and (iv) a double resonance process with the iTO phonon branch [50].

In the literature, the peak at ~1447 cm$^{-1}$ has been attributed to either the scissoring mode of –CH$_2$ [51–53] or the C=C ring stretching in thiophene (containing nitrogen) [54,55]. Moreover, a peak ~1450 cm$^{-1}$ in nanocrystalline diamond is said to arise from the sum modes of sp$^2$ C=C and C–H vibrations of trans-polyacetylene type segments at grain boundaries [42,56]. In the case of the rGO samples here, this peak is likely to be from the mode of –CH$_2$ as it was confirmed with XPS analysis that foreign atoms were not incorporated into the rGO. Therefore, the emergence of these peaks indicated that the sample structure deviated from the typical GO structure [57]. With a 10 s APPJ-reduction, the structure of rGO seemed to further deviate from the 5 s APPJ-reduced sample (see supplementary information, Figure S3). The overtone bands (2D or G', D + G, and 2G [58,59]) were found in the region 2500–3300 cm$^{-1}$ for the GO and they decreased in intensity with increasing free-jet exposure time (supplementary information, Figure S3). This can be attributed to the formation of defects and diminishing sp$^2$–C domains [59–61].
Figure 1. Fitted Raman spectra of GO (a), 2 s APPJ reduced GO (b), 5 s APPJ reduced GO (c), and 30 s RF plasma reduced GO (d) on Si substrates.

The XPS survey of the various GO is shown in the supplementary information, Figure S4. As expected, peaks arising from carbon (~284 eV) and oxygen (~531 eV) were observed along with silicon (99–169 eV) from the substrate. Interestingly, nitrogen signals were not found in the APPJ–processed GO samples, which were exposed to plasma containing nitrogen species. This suggested that nitrogen doping did not occur for the rGO. For samples treated with APPJ for 5 and 10 s, traces of iron (Fe) were found originating from the sample holder (supplementary information, Figure S4). Figure 2 presents the XPS core levels of the GO and various rGO. The chemical components identified from the spectra were sp²–hybridized carbon (sp²–C), sp³–hybridized carbon (sp³–C, C–C/C–H), hydroxyl–(C–OH), epoxide–(C–O–C), carbonyl–(C=O), and carboxyl–(CO(OH)) groups, respectively [60,62–67]. For the sample rGO–APPJ–5s, a feature at binding energy >290 eV was distinctively observed. In the literature, this has been assigned to energy losses due to π–π* excitations, which is typical for carbonaceous systems with delocalized π–electrons [68], as well as to carbon atoms bonded to metals [69].

The increasing trend of the I_D/ (I_G + I_D′) ratio from Raman spectroscopy was an indicator of deoxygenation in GO (Table 1). The increasing ratio arose from the increasing quantity of disorder, which in turn was associated with the appearance of new sp²–C domains with the loss of carbon–oxygen bonds [70]. The loss of oxygen bonds was also verified from the XPS quantification of the components’ fit for the C1s spectra. The crystallite size was calculated from the areas of the D band and G band in Raman spectra using the Tuinstra and Koenig relation [71–73]. The calculated average crystallite size (La) for GO was 10.8 nm when the Raman signals were measured with a 532-nm laser. It reduced to 9.6 nm and 8.4 nm when the GO was reduced with APPJ plasma for 2 and 5 s, respectively. In the case of RF plasma treatment, the crystallite was reduced to 9.2 nm from 10.2 nm (Raman signals recorded with 633 nm laser). The average distance between the defects reduced to 7.9 nm and 7.4 nm from 8.4 nm for an APPJ treatment time of 2 and 5 s,
respectively. With the 30 s RF plasma treatment, the distance between defects reduced to 7.9 nm from 8.2 nm. This suggests that with plasma irradiation defects were created in the rGO which is already well established in the literature. The 30 s RF plasma irradiation produced similar defects as the 2 s APPJ exposure, indicating that the APPJ had higher energetic plasma species than the RF-plasma used.

The hydrogen RF plasma typically constitutes free electrons, neutrals (molecular H\(_2\), atomic H), and charged ions (H\(^-\), H\(^+\), H\(_2^+\), and H\(_3^+\)) \[74\]. The plasma composition is relatively stable and homogeneous stipulating nearly equilibrium conditions for chemical interactions. At the same time, the electrodeless RF-coupling powers the high temperature of neutrals. Hydrogen-containing APPJ reveals mostly nitrogen second positive system bands and NH \[75\]; typical species from N\(_2\) discharge are N, NO\(\cdot\), OH\(\cdot\), N\(_2\), N\(_2^+\), and CN.
bands and NH [75]; typical species from N₂ discharge are N, NO•, OH•, N₂, N₂⁺, and CN [76]. As pointed above, the gas in our free jet was expected to be negligibly ionized, especially at the distance of the surface reaction event. In GO, the carbon bonded to oxygen accounted for nearly 79% of the total carbon bonds. In the case of carbon-to-carbon bonds (Table 1), the fraction of sp³-hybridized content (12.9%) was found to be higher than sp²-hybridized bonds (8.2%). Even with a short 2 s APPJ-treatment, the oxygen-containing group loss was observed, and the amount of sp²-carbon content (~21%) increased relative to sp³-carbon (~16%). With a 5 s APPJ-treatment, the net oxygen-containing group fraction reduced to ~23%, and the restoration of sp²-C increased to 52%. To compare, the optimized hydrogen RF-plasma reduced net oxygen-content in the GO film down to ~24%, while the sp²-C content increased to ~61%. Compared to the 5 s APPJ-treatment, the RF plasma treatment yielded a lower content of C-OH and O=C-OH groups, whereas the APPJ-treatment yielded a lower content of C-O-C and C=O groups.

3.2. Synthesis of Carbon Nanomaterials

3.2.1. Deposition on ZnO/Ag Substrates

It is known, that the (111)-facet of fcc-metals such as Cu and Ni serve as a template for the honeycomb carbon network [77,78]. The lattice mismatch with graphene in these cases exceeds −10%. According to our estimation, the 111-Ag lattice would have less than +2% mismatch at normal conditions. That is why we have chosen it as a substrate, which is a standard for low-emissivity coating technology. Figure 3 presents the Raman spectra of carbon deposited on ZnO/Ag substrates, and they were fitted with a combination of Lorentzian and Gaussian (only for D3 band) functions [44]. The parameters extracted from the fitted peak are summarized in the supplementary information, Table S2 and the broad Raman spectrum is presented in the supplementary information, Figure S5. In the 250–750 cm⁻¹ region (Figure S5), several peaks and bands were strongly observed for samples deposited at a distance of 3 mm for 1 s (and weakly when deposited at a distance of 6 mm from the substrate). These features are attributed to the underlying glass substrate [79], ZnO [80], and Ag–O [81]. Except for the sample deposited at 3 mm and 1 s, the samples portrayed well-separated D and G bands suggesting relatively low amorphous content or high crystalline (graphitic) content [82].

The G band split into G⁻ band and G⁺ band (Figure 3), which is usually observed in carbon nanotubes (CNT) as a result of curvature [83]. This splitting has also been observed when graphene sheets are strained [84], wrinkled [85], or folded and scrolled [86].

A weak 2D band (~2700 cm⁻¹) was detected in all the samples (supplementary information, Figure S5). The 2D band is a well-known characteristic feature of all the sp²-C based materials [87–89]. The films deposited for 2 s revealed relatively prominent 2D peaks, as well as the G + D band (~2900 cm⁻¹) (supplementary information, Figure S5). The existence of these features is assessed as a lower disorder in the films [60]. The D3 band (~1500 cm⁻¹) is assigned to the presence of amorphous carbon [44,90]. The D4 band (~1200 cm⁻¹) is assigned to the aliphatic compounds grafted on the disordered carbon network [90,91] or defective graphite [90,92]. In some samples (Figure 3b,c), a weaker D′′ band (1076–1095 cm⁻¹) is also additionally observed originating from defects [90,92,93].

The estimated crystallite size (Lₐ) from Raman spectroscopy were 8.7 nm, 10.2 nm, 10 nm, and 11.6 nm for the samples Ag–C–D3–1S, Ag–C–D3–2S, Ag–C–D6–1S, and Ag–C–D6–2S, respectively [71–73]. Similarly, these samples had an estimated defect between the point defects (L_D) as 7.5 nm, 8.2 nm, 8 nm, and 8.7 nm, in the same order. The SEM images (supplementary information, Figures S6 and S7) evidenced several microstructural changes as compared to the initial silver surface (Figure S7a,b). Silver recrystallized and probably shrank, which led to a formation of pores (dark regions ranged in size from a few 10s of nm to ~100 nm). Point EDX analysis of the largest dark areas revealed greater Zn and lesser Ag-content as compared to the flat particle-free areas. These relatively homogeneous areas were notably smoother in treated samples than the surface of the initial silver film. One can also distinguish in a few places an increase in the size of Ag grains, but the surface
appears to be coated with carbon. Nano needle-like structures (or short nanotubes) were also observed, whose diameter was ~50 nm, and length was in the range of 100s of nm. Similar to the pores, the number of short nanotubes also decreased at a higher nozzle distance and longer deposition time. Bright dots observed in the SEM images with higher magnification represent silver particles according to EDX.

3.2.2. Deposition on Si Substrates

It is known that native Si-wafers are oxidized from the surface. This oxide is very smooth and dense but not crystalline. We took this substrate for the next experiments to discard the template impact of a substrate. The dynamic linearly oscillating deposition was undertaken at the nozzle-to-substrate distance of 6 mm to avoid overheating the substrate. The Raman spectra of the carbon deposited on Si substrates are shown in Figure 4 and the peak assignments are summarized in Table 2. The carbon deposited for 2–20 s displayed a similar spectral feature, and their interpretation was not straightforward. Some prominently observed features in the spectra were the bands in the range 1050–1100 cm\(^{-1}\) coinciding with C–C stretching observed in hydrocarbon chains [94,95] and several peaks up to 1450 cm\(^{-1}\) which are observed in C60/C70-fullerene materials (see Table 2) [96,97].

It should be also noted that the region 1100–1150 cm\(^{-1}\) and 1430–1470 cm\(^{-1}\) were related to the trans-polyacetylene segments at the grain boundaries [98]. The peaks ~1060 cm\(^{-1}\) and ~1180 cm\(^{-1}\) also have been reported for the nanocrystalline phase of carbon [99]. The sp\(^2\)–C phase or the G band (1560 cm\(^{-1}\)) from the in-plane stretching mode of carbon is observed only when the deposition time is high at 30 s [100,101]. The carbon with the broad G and D bands indicates the existence of an amorphous structure [82]. However, features of the fullerene-like structure were also superimposed into the dominant broad G and D bands. This suggests a possible composite structure of fullerene-like matter and amorphous films. The SEM images of the carbon samples are presented in the supplementary information, Figure S8. For up to a deposition time of 20 s, the surface
coverage was nonuniform and low with clusters of spherical particles. In the sample deposited for 30 s, spherical particles of various sizes (several 10s of nm) were observed with some in aggregated form. These aggregates (supplementary information, Figure S5d) were comparable to onion-like fullerene/nanocarbon (fullerenoid) structures reported in the literature [20,102–105].

The idea of using acetylene to synthesize or to deposit the sp²-carbon network was based on the corresponding catalytic synthesis of benzene. This can proceed for instance via adsorption on Pd-surface [106], or be promoted by transition metals, which are known to catalyze the so-called [2 + 2 + 2]-polymerization [107]. Silicon atoms may also form intermediates driving the polymerization process [108]. In combination with admixtures increasing the Lewis acid character of the promoter (e.g., Si⁺⁴), the reaction in question can proceed at much lower temperatures than the established 500–600 °C [109]. The entire mechanism of polymerization in plasma from a single carbon atom to fullerenes was proposed and described in detail elsewhere [110]. In the case of a plasma torch process at atmospheric pressure, the formation of a similar carbon-onion-like structure passes through dissociation, nucleation, and agglomeration events in the carbon feedstock gas [102]. The spherical agglomerates form owing to defects in fullerene molecules, which fulfill the role of reactive centers [111]. Further investigation of our free jet must provide the information on existing reactive species and give an idea of polymerization mechanism.

**Table 2.** Features observed in the Raman spectra of Carbon deposited on Si substrates.

| Peak (cm⁻¹) | Vibrational Assignment | Reference |
|------------|------------------------|-----------|
| 1080       | C–H bend + C–C stretch | [112,113] |
| 1175       | C–H bend or E1'' (C70) or H₃(5) (C60) | [98,113,114] |
| 1232       | A₁' (C70)              | [96]      |
| 1320       | G₅(5) (C60) or E₁' (C70) or the D-band | [82,97] |
| 1350       | T₂g(4) (C60) or E₂' (C70) | [97]      |

**Figure 4.** Raman spectra of the carbon deposited on Si substrates for various time and nozzle distances.

![Raman_spectra](Figure_4 популярный заголовок по английски)
Table 2. Cont.

| Peak       | Vibrational Assignment | Reference |
|------------|------------------------|-----------|
| 1360 cm$^{-1}$ | D band related sp$^2$-C | [114] |
| 1370 cm$^{-1}$ | H$_2g$(C60) or E$_2'$ (C70) | [97] |
| 1414 cm$^{-1}$ | H$_u$(6) (C60) or E$_1'$ (C70) | [97] |
| 1439 cm$^{-1}$ | T$_{1u}$(4) (C60) or E$_1'$ (C70) | [96,97] |
| 1449 cm$^{-1}$ | H$_u$(7) (C60) or E$_1''$ (C70) | [97] |
| 1560 cm$^{-1}$ | H$_u$(7) (C60) or the G band | [115,116] |

4. Conclusions

In this work, a novel free jet system was evaluated in ambient conditions. The optimized MF-power generation could produce excited species in hydrogen-containing gas mixtures making them chemically active. Using 10% vol. H$_2$/N$_2$ forming gas, ~20 nm GO-films were successfully reduced within a processing time of 2 s according to XPS and Raman analyses. The rGO films thus obtained were comparable in quality with the rGO films reduced in RF hydrogen plasma under optimized and established conditions. A longer free jet treatment resulted in further deoxygenation with the appearance of a strong Raman peak at 1447 cm$^{-1}$, which was attributed to trans-polyacetylene (–CH$_2$) chains. The appearance of such chains reflects the breaking of the honeycomb carbon network in GO. A closer analytical look into the free-jet constituents and their energies is planned to control and improve the process, e.g., to not damage the GO surface at longer treatment.

By introducing the acetylene admixture into the forming gas, we realized the deposition of carbon films by our free jet system. Multiple activations of the depositing surface via dynamic oscillating treatment resulted according to Raman spectroscopy analysis in a formation of the fullerene C70-like matter. SEM revealed the presence of aggregated spherical nanoparticles from a few-10s to over a few-100s of nm. These particles resembled the onion-like nanostructure, which contains fullerene-like particles, as reported in the literature. The carbon films deposited on (111)-textured Ag surface had nano needle-like structures (a few 10s nm in diameter and a few 100s nm long). Raman spectroscopy also revealed the presence of graphitic carbon (estimated crystallite size, $L_a \approx 9$–12 nm). The number of nanocrystalline carbon needles reduced with increasing deposition time and nozzle-to-substrate distance.

The preliminary results based on our free jet system demonstrated unique simplicity in the synthesis of various carbon nanostructures at atmospheric pressure. The presented method opens an inexpensive, scalable, and entirely vacuum-free way to produce rGO coatings. The low gas temperature of the jet enables using any sensitive substrates including flexible ones. Furthermore, we believe that a much faster (seconds vs. tens of minutes) and vacuum-free reduction process has more potential to be realized on an industrial scale, e.g., in reel-to-reel production concepts. A deep scientific understanding of the excitation processes occurring in gases coupled electrically in this way is of imperative importance.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/c7040071/s1: Figure S1: XRD pattern and pole-figure of the ZnO/Ag substrate, Figure S2: Photographs of the APPJ used in this work, Figure S3: Raman spectra of GO and rGO prepared with APPJ, Figure S4: XPS survey spectra for Si, GO, and various rGO, Figure S5: Wide Raman spectra of carbon deposited on ZnO/Ag substrates. Figures S6 and S7: SEM images of carbon deposited on ZnO/Ag substrates, Figure S8: SEM images of carbon deposited on Si substrates, Table S1: Parameters from Raman spectroscopy of GO and various rGO, Table S2: Parameters from Raman spectroscopy of various carbon deposited on ZnO/Ag substrates.

Author Contributions: The conceptualization, organization, supervision, XRD measurements, review, and editing of the draft, R.M.; development of the special APPJ system, U.H.; experimental realization, analyses of data, and writing of the original draft, S.H.B.V.K.; Raman measurements and support with data analyses, J.I.-J.; XPS measurements and support with data analyses, N.M.; synthesis of GO and rGO powders and preparation of their stable suspensions, K.K., RF-plasma
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