Modification of thin carbon films by UV_C light

T Milenov^1,5, I Avramova^2, A Dikovska^1, G Avdeev^3, J Mladenoff^1, S Kolev^1 and E Valcheva^4

^1 Acad. E. Djakov Institute of Electronics, Bulgarian Academy of Sciences, 72 Tzarigradsko Chaussee, 1784 Sofia, Bulgaria
^2 Institute of General and Inorganic Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria
^3 R. Kaishev Institute of Physical Chemistry, Bulgarian Academy of Sciences, Acad. G. Bonchev Str., Bl. 11, 1113 Sofia, Bulgaria
^4 Faculty of Physics, St. Kliment Ohridski University of Sofia, 5 James Bourchier Blvd. 1164 Sofia, Bulgaria

E-mail: tmilenov@ie.bas.bg

Abstract. We modified by UV_C light single to few-layered nano-sized graphene films deposited by pulsed laser deposition (PLD) on ~300-nm SiO_2/Si substrates. The samples were irradiated by UV_C lamps (wavelength of 254 nm) for 15, 30, 60 and 90 minutes in air. The influence of the modification was evaluated by following the changes in the X-ray photoelectron and Raman spectra of the samples after UV_C irradiation.

1. Introduction
Graphene is a two-dimensional (2D) material consisting of a single layer of sp^2 hybridized carbon atoms and has attracted interest for application in many areas – microelectronics, energy storage, composite materials, medicine etc. [1]. However, researchers found that the high-quality graphene does not possess a forbidden gap and is thus useless in field-effect transistors. Additionally, due to its hydrophobicity it cannot be used in composite materials based on aqueous solutions. Overcoming these problems necessitates that the material be modified. Zhang et al. [2] established by molecular dynamic calculations that oxygen functionalization may tailor the thermal transport properties of high-quality graphene. According to ab initio simulations, it was concluded that the presence of a graphene buffer layer at the SiC/graphene interface opens an energy gap that can be modulated by changing the height of corrugation of the graphene buffer layer [3]. Using UV irradiation conducted in ozone atmosphere as a very simple and reproducible method for introducing defects (mainly by changing the carbon hybridization from sp^2 to sp^3) was studied theoretically [4] and experimentally [5]. Later on, two mechanisms were discussed of graphene oxidation by UVc treatment (254-nm Hg lamp irradiation source) in oxygen and hydrogen atmosphere [6]. Mulyana et al. [7] reported on reversible oxidation of graphene by UV irradiation, while Gao et al. [8, 9] showed that extreme UV (13.5-nm wavelength) could induce defects in single-, bi- and in few-layered graphene. We present here results on modifying nano-sized graphene by irradiation with 254-nm UVc light.

---

5 To whom any correspondence should be addressed.
2. Experimental

Nano-sized single to bi-layered graphene was deposited by pulsed layer deposition (PLD) on 300-nm SiO₂/Si substrates [10] and used in the experiments. The thickness of the specimens was determined by ellipsometry measurements.

The modification was performed by 254-nm Hg lamps (2.7 W radiation power) in a 200×200×200 nm³ stainless-steel box and air atmosphere for 15, 30, 60 and 90 minutes. The specimens were characterized by X-ray photoelectron spectroscopy and Raman spectroscopy, as the former method is usually the first choice whenever surface analysis of the top few nanometers and the sp²/sp³ hybridized carbon fractions are to be determined quantitatively [11,12]. On the other hand, the number of graphene layers and the defects existing in graphene films can be distinguished by the latter method [13, 14]. It has also been established that the phase composition of mixed carbon films could be determined by Raman spectroscopy [15]. In the study reported here, the characterization measurements were carried out before irradiation and immediately after it. We denoted by C2, C4, C6 and C8 the specimens C1, C3, C5 and C7 after irradiation of 15, 30, 60 and 90 min, respectively.

We performed the XPS measurements on a Kratos AXIS Supra spectrometer with a monochromatic Al X-ray source under vacuum better than 10⁻⁶ Pa at a 90-degree take-off angle. We recorded the C1s, O1s, N1s and Si2p lines for each specimen; the C1s lines were then subjected to an additional fitting procedure with the XPSPEAK4.1 software. The Raman measurements were performed using a HORIBA Jobin Yvon Labram HR 800 micro-Raman spectrometer with a He-Ne (633 nm) laser. The laser beam (0.5-mW power) was focused on a spot of about 2 μm in diameter on the surfaces studied. The spectral resolution was 1 cm⁻¹ or better.

3. Results and discussion

The phase analysis performed by XPS showed the presence of carbon, oxygen and silicon (table 1). The sp²/sp³ hybridized carbon fractions and the existing C-O, C=O etc. bonds were determined by deconvoluting the C1s line of the X-ray photoelectron spectrum – figures 1 a and b, 2 a and b, 3 a and b and 4 a and b for C 1-8 specimens, respectively. The different time of irradiation initiated diverse changes in the surface chemical bonds in comparison with the bonds initially existing on the graphene film surfaces. We distinguished the four components of the C1s spectrum corresponding to sp² bonds in graphitic-like carbon (284.3 eV), sp³ hybridization (285.2 eV), hydroxyl (C-OH) and (C-O-C) groups (286.5 – 287.0 eV), and carboxyl (C=O) groups (288 – 288.5 eV) (figures 1-4). The sp³ to sp² hybridized carbon ratio varied between 0.23 and 0.28 in the non-irradiated samples (C1, C3, C5 and C7) and between 0.17 and 0.26 in most of the UVc-light-treated samples (C4, C6 and C8), while it was 0.44 in the sample C2 irradiated for a short time.

![Figure 1](Image)

**Figure 1.** Deconvoluted XPS C1s lines obtained from C1 (a) and C2 (b) specimens.

![Figure 2](Image)

**Figure 2.** Deconvoluted C1s XPS lines obtained from C3 (a) and C4 (b) specimens.
The Raman spectra of all specimens are typical for sp²-carbon-based materials and have two high-intensity features – D and G bands, as well as several weakly pronounced overtones and combination bands: 2D and (D+D’) (figure 5 a). Additionally, the Raman spectra of specimens C 1, 3, 5 and 7 are very similar to those of the single to bilayer nano-sized graphene, as it was reported by Milenov et al. [10] (figure 5 a).

We present the summarized results from all measured Raman spectra in Table 2, which provides a clearer interpretation of the irradiation effect on the samples. In addition, we show the results of deconvoluting the spectrum of C 8 specimen only, since the intensities and positions of this Raman spectrum features are typical for all specimens (figure 5 b and Table 2). All defect-related bands (D, D’ and D”) [16,17] are distinguishable in all specimens, which can be related to the large number of defects (mainly flake boundaries) in our samples. The D and G bands are clearly but not completely separated, which indicates a low amorphous content. The D and G bands positions are close to their typical values for graphene and nano-crystalline graphite [13-17]. The related intensity of the 2D to G bands varies (I_{2D}/I_G) between 17 – 30 % in the C1 – C8 specimens. It is worth noting that the intensities of the Raman features of the specimens irradiated for a long time (C 6 and C 8) varies

Table 1. Summarized XPS results for the samples’ surface composition before and after irradiation by UVc light.

| Experiment | C at.% | O at.% | Si at.% | N at % | O/C | sp³/sp² | C-O | C=O |
|------------|--------|--------|---------|-------|-----|---------|-----|-----|
| C 1        | 39.90  | 40.74  | 18.91   | 0.45  | 1.02| 0.28    | 6.5 | 7.1 |
| C 2        | 47.35  | 31.33  | 21.32   | -     | 0.66| 0.44    | 10.2| -   |
| C 3        | 44.97  | 37.03  | 17.63   | 0.38  | 0.82| 0.28    | -   | 3.1 |
| C 4        | 39.24  | 35.28  | 25.48   | -     | 0.89| 0.26    | 6.4 | -   |
| C 5        | 43.22  | 38.96  | 17.82   | -     | 0.90| 0.24    | 4.2 | 4.6 |
| C 6        | 39.17  | 41.41  | 18.72   | 0.70  | 1.05| 0.23    | -   | 12.9|
| C 7        | 45.25  | 36.57  | 17.56   | 0.61  | 0.80| 0.19    | -   | 9.0 |
| C 8        | 17.26  | 13.83  | 68.91   | -     | 0.80| 0.17    | -   | 3.0 |
significantly at different points of the surface, which indicates a significant worsening of the layer’s quality and a probable violation of its continuity. The values presented in Table 2 for the Raman features for C6 and C8 are typical for these specimens.

**Table 2.** Results from Raman spectra deconvolution: position of the D, G, D’ and 2D bands, intensity ratios of G and D bands \(I_D/I_G\) and of 2D and G bands \(I_{2D}/I_G\) of C1 – C8 specimens.

| Experiment | D, cm\(^{-1}\) | G, cm\(^{-1}\) | \(I_D/I_G\), % | D’, cm\(^{-1}\) | 2D, cm\(^{-1}\) | \(I_{2D}/I_G\), % |
|------------|----------------|----------------|----------------|----------------|----------------|----------------|
| C 1        | 1330           | 1586           | 121            | 1613           | 2658           | 19             |
| C 2 (15 min UVc) | 1332          | 1588           | 145            | 1610           | 2652           | 15             |
| C 3        | 1328           | 1581           | 140            | 1609           | 2663           | 27             |
| C 4 (30 min UVc) | 1326          | 1584           | 162            | 1608           | 2636           | 24             |
| C 5        | 1330           | 1586           | 134            | 1610           | 2641           | 20             |
| C 6 (60 min UVc) | 1330          | 1584           | 167            | 1609           | 2649           | 21             |
| C 7        | 1330           | 1584           | 142            | 1611           | 2651           | 28             |
| C 8 (90 min UVc) | 1328          | 1585           | 128            | 1615           | 2644           | 30             |

The short UVc irradiation (15 min) increases the amount of sp\(^3\) hybridized carbon most probably due to dangling of sp\(^2\) and formation of sp\(^3\) bonds (Table 2) and preserves the carbon amount of the film, as expected according to Gao et al. [8, 9]. Further treatment by UVc significantly decreases the total carbon content (twice in C 6 and about threefold in C 8), which explains the different Raman spectra measured at different points on the surface. Surprisingly, while the sp\(^3\) to sp\(^2\) hybridized carbon ratio for 15-min irradiation increases, we observe an insignificant predomination of the sp\(^2\) fraction after 30-, 60- and 90-min UVc light treatment (Table 1). This result points to an enhanced evaporation of the sp\(^3\)-hybridized carbon as part of the oxygen-containing radicals after an extended UVc-light treatment. A longer irradiation causes formation of C=O and C=O bonds due to oxidation in general as the irradiation process takes place in air. Additionally, the 30-min irradiation leads to a full transformation of C=O bonds to C=O bonds. After a 60-min irradiation, the C-O bonds are damaged and C=O type bonds appear as an alternative. The Raman spectroscopy results confirm the above conclusions: the 2D band intensity in C 6 and C8 specimens increases after UVc irradiation in the area where the nano-sized graphene film remains continuous. The increased sp\(^3\) fraction (specimen C 2) results in a significant drop (about 25 %) of the relative intensity \(I_{2D}/I_G\) (Table 2).
4. Conclusions

The short-time modification (irradiation of up to 15 min) of nano-sized defected predominantly single layered graphene by 254-nm UVc light causes an increase in the carbon sp³ fraction in the film. Further irradiation for 60 and 90 minutes eliminates much of the carbon phases (the amount of carbon-containing phases decreases about two- and threefold, respectively), which can be related to oxidation of graphene flakes, dangling of C-C bonds and evaporation of oxygen containing species. It seems also that this process affects predominantly the sp³-hybridized carbon fraction, as the sp³ fraction decreases by 1 – 2 % after irradiation.

Acknowledgements

The work was supported in part by the Bulgarian National Science Fund under grant DN18/9-11.12.2017. The work of J. M. was partially supported by the Bulgarian Ministry of Education and Science under the National Research Program “Young scientists and postdoctoral students” approved by DCM # 577 / 17.08.2018.

References

[1] Ferrari A et al Nanoscale 2015 7 4598
[2] Zhang H, Fonseca and A Cho K 2014 J. Phys. Chem. C 118 1436
[3] Kolev S, Atanasov V, Aleksandrov H and Milenov T 2018 Eur. Phys. J. B 91 272
[4] Lecente N, Moser J, Ordejon P, Tao H, Lherbier A, Bachtold A, Alsina F, Sotomayor Torres C, Charlier C and Roche S 2010 ACS Nano 4 4033
[5] Moser J, Tao H, Roche S, Alzina F, Sotomayor Torres C and Bachtold A 2010 Phys. Rev. B 81 205445
[6] Günes F et al 2011 J. NANO: Brief Reports and Reviews 6 409
[7] Mulyana Y, Uenuma M, Ishikawa Y and Uraoka Y 2014 J. Phys. Chem. C 118 27372
[8] Gao A, Rizo P, Zoethout E, Scaccabarozzi L, Lee C, Banine V and Bijkerk F 2013 J. Appl. Phys. 114 044313
[9] Gao A, Lee C and Bijkerk F 2014 J. Appl. Phys. 116 054312
[10] Milenov T, Dikovska A, Avdeev A, Avramova I, Kirilov K, Karashanova D, Terziyska P, Georgieva B, Arnaudov B, Kolev S and Valcheva E 2019 Appl. Surf. Sci. 480 323
[11] Gorham J et al 2016 Carbon 96 1208
[12] Lascovich J, Giorgi R and Scaglione S 1991 Appl. Surf. Sci. 47 17
[13] Ferrari A et al 2006 Phys. Rev. Lett. 97 1
[14] Gupta A, Chen G, Joshi P, Tadigadapa S and Eklund P 2006 Nano Lett. 6 2667
[15] Ferrari A and Robertson J 2004 Philos Trans. R. Soc. A 362 2477
[16] Ferrari A and Basko D 2013 Nat. Nanotechnol. 8 235
[17] Herziger F, Tyborski C, Ochenedowski O, Schleberger M and Maultzsch 2014 J. Phys. Rev. B 90 245431