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Study of the Initial Stages of Deposition of Graphene-like Films by Sublimation of Amorphous Carbon

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Abstract. The initial stages of deposition of graphene-like thin films have been studied by X-ray photoelectron spectroscopy, scanning electron microscopy, Raman spectroscopy and ellipsometry. The deposition process has been performed by sublimation of amorphous carbon on 330 nm SiO₂/ (001) Si substrates with surface area of 15x 15 mm². The sublimation process was carried out in a quartz tube having an internal diameter of 25 mm at a temperature of 1050°C in which samples were placed in an argon flow of about 1 cm³/s for 3 to 15 minutes. As a source of amorphous carbon, modified carbon blacks SPHERON 5000 were used. We established that an amorphous carbon film with thickness up to 3- 6 nm is always deposited on the SiO₂ after 3- 5 min deposition and the deposition of a few-layered defected graphene as well as nano-sized graphite occurs after 5- 6 min on the surface of substrate. Further on, after 8-10min deposition a non-continuous carbon film is formed and after 12- 13 min the substrate is covered by a smooth and continuous carbon film. The film has extremely low resistivity ($\rho = 2.8 \times 10^{-6} \Omega \cdot m$) and consists of predominantly sp² hybridized carbon with a Raman spectrum similar to those of nano-sized graphene.

1. INTRODUCTION

In simple terms graphene is a sheet of a single layer of carbon atoms, tightly bound in a hexagonal honeycomb lattice. In more complex terms, graphene is an allotrope of carbon in the form of a plane of sp²-bonded atoms with a molecular bond length of 0.142 nm.[1] It is proven that monolayer graphene has unique charge transport properties- its charge carriers move like massless Dirac fermions with mobilities of up to 200000 cm²/Vs.[2,3] The increasing interest in graphene led to the development of a lot of synthesis' methods. The "classical" way is by micromechanical cleavage of a monoatomic layer from graphite single crystal or from highly oriented pyrolytic graphite (usually termed as "exfoliation").[4] An alternative way of synthesis of high-quality graphene is by chemical vapor deposition (CVD) methods on metal foils (Ni, Cu etc.).[5,6] Recently we reported on a possible way for deposition of graphene by sublimation of pyrolytic carbon but the method demands high temperature (over 1150°C) as well as the use of predeposited diamond-like carbon (DLC) film of SiO₂/Si substrate.[7] Here we present

experimental results of deposition of graphene-like films by sublimation at 1060–1080⁰C of chemically and thermally modified carbon black source.

2. EXPERIMENTAL

The deposition processes were carried out in quartz reactor (30 ID) in main gas flow (90- 120 cm³/min) of pure Ar (99.9995 at. %). The chosen source of carbon for sublimation was carbon black as it has a high surface-area-to-volume ratio that is in contact with the environmental gas, in this case Ar. We used Spheron 5000 by Cabot carbon black as it is available as a highly purified carbon product and the chemical processing by HCl additionally removes residual quantities of impurities (see L. Tzonev et al. BPU-10 poster presentation).

The quartz reactor was charged with about 15 x15 mm silicon wafer coated with a layer of SiO₂ (thickness of about 330nm) and behind it the carbon blacks were positioned on a polycrystalline graphite holder. The inert Ar atmosphere in the flow reactor was created for about 15 min at room temperature by Ar gas flow. Then it was shifted in the working space of the furnace which is designed to provide a temperature of about 1080⁰C for carbon black while the temperature of silicon substrate is about 1050- 1060⁰C. The deposition time was varied between 3 and 16 minutes (see Table 1).

The X-ray photoelectron spectroscopy analyses were performed on a Kratos AXIS Supra spectrometer with a unimonochromatic Al X-ray source under the vacuum better than 10⁻⁸ Pa at 90 degree take-off angle. Each analysis started with a survey scan from 0 to 1200 eV, pass energy of 160 eV at steps of 0.5 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV. The C1s photoelectron line at 285 eV was used for calibration of spectra.

We used LYRA TESCAN scanning electron microscope at 10-20 kV accelerating voltage for the SEM studies in both secondary electron image (SEI) and backscattered electron image (BEI) without deposition of any conducting film on the studied specimens. The Raman measurements were carried out using a micro-Raman spectrometer HORIBA JobinYvonLabram HR 800 Visible with a He-Ne (633 nm) laser. The laser beam with 0.5 mW power was focused on a spot of about 1 µm in diameter on the studied surfaces, the spectral resolution being 0.5 cm⁻¹ or better.

To determine the electrical conductivity of the layers four-contact Van der Pauw method as well as two contact schemes have been applied. We used In contacts (~1mm²) situated on the layer surface. All contacts are distanced at about 4-5 mm away from each other. Measurements were done in the dark using HP4140B pA-meter/dc voltage source.

3. RESULTS AND DISCUSSION

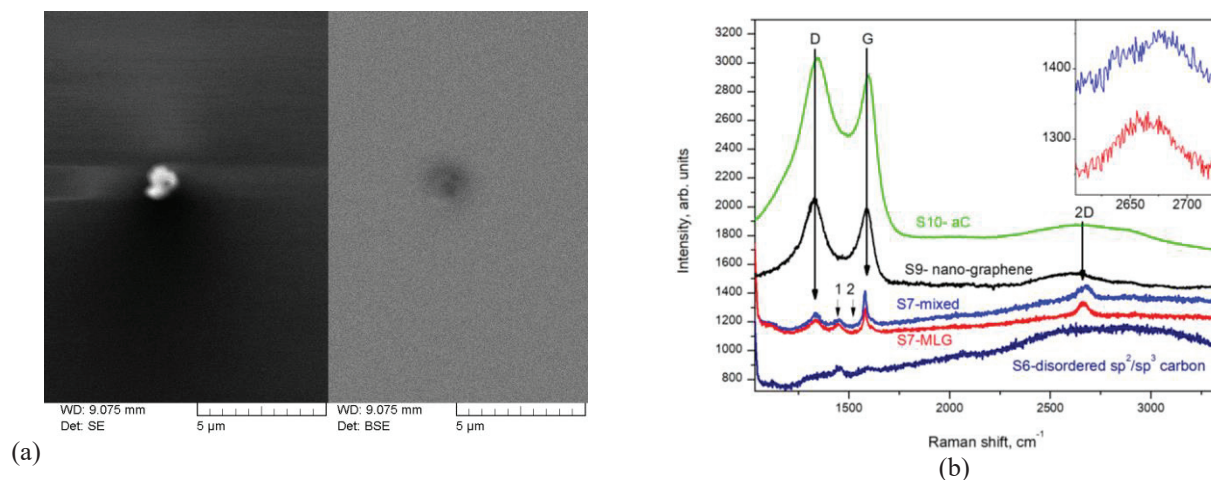


FIGURE 1. a) SEI of a carbon particle on the SiO₂/Si surface of S7 specimen- left panel. SEI of the morphology of the surface of specimen S8- right panel. b) Raman spectra of the specimens S6, S7, S9 and S10. The inset: magnified part of the area of the 2D band of the mixed graphite and multilayered graphene (MLG)- blue trace and MLG (red trace) particles in S7 specimen.

The thickness of the obtained samples was determined by ellipsometry and the results are shown in Table 1.

We did not distinguish by SEM a clear evidence for presence of a deposited carbon film during experiments S1-S6, while some nano-to-micrometer sized flakes were observed in specimen from S7 experiment- see the left panel of Fig. 1a). The corresponding BEI (the right panel of Fig. 1a) shows that the flake has a different composition from the neighboring surface and the energy dispersive X-ray analysis (EDAX) reveals that the flake consists of carbon. The SEI and BEI images of S8 films (the left and the right panels of Fig. 1b, respectively) show that the film is not continuous as it has some roughness (the left panel of Fig. 1b) but it consists from a single phase carbon (the right panel of Fig. 1b). The films deposited by experiment S9 are smooth and continuous.

The Raman spectrum of perfect graphene has several strong bands, namely the G- band (the only first order Raman feature of graphene which appears from E_{2g} phonons at Γ point in the center of the first Brillouin zone) and 2D band (the overtone of the D-band), as well as few combination bands.[8-10] Few additional bands: the D, D' and D'' bands, arise originating from the breathing-like modes of the carbon rings activated by defects via double-resonance Raman process.[8-11] On the other hand the spectrum of mixed sp²/sp³ carbon films has two prominent features: D and G bands which appear at different wavenumbers according to the sp²/sp³ ratio, sample crystallinity etc.[12] It was also established that following the trajectory of graphitization the Raman spectrum of the film transforms from that of perfect graphene, i.e. dominated by the 2D band, to a dominated by D- and G- bands spectrum.[13] Our results show that the films deposited in S1-6 are most probably amorphous- see Fig. 2a. In specimen S7 we established that some of sub-micrometer sized particles have Raman spectrum typical for graphite- the 2D band is centered at 2670-2680 cm⁻¹ as well as it is asymmetrically broaden- see Fig. 2a and the inset of Fig. 2a). Some other particles from S7 possess a Raman spectrum typical for defected graphene as the 2D band is symmetrical and centered at 2660-2665 cm⁻¹ (Fig. 2a and the inset of Fig. 2a). According to the dispersion of the D, G and 2D bands, the Raman spectrum of S9 specimen may be referred as a spectrum of nano-crystalline graphene.[13] The spectrum of S10 specimen (Fig. 2a) is very similar to those of a-C.[12]

The X-ray Photoelectron spectroscopy method was used for controlling the surface bonds that are formed by the sublimation process. The C1s, O1s Si2p as well as N1s and VB photoelectron regions taken from specimens S1,S6, S7, S8 and S9 were characterized. The special attention was paid to C1s photoelectron lines, due to the fact that it can be used for evaluation of sp³ and sp² hybridized carbon. Additionally the C1s photoelectron line gives information for the other bonds as C-O/C-OH or C=O and π - π^* bond.[14] The C1s for all synthesized and examined films are presented on the Fig.2 b. After deconvolution (see the inset of Fig.2b) the sp² and sp³ hybridized components were evaluated and their respective ratio was calculated. The deconvolutions of C1s lines for S1-S8 specimens are not shown here but the summarized data is shown in Table 1. We find out that the distance between the sp² and sp³ is around 0.9 eV, which is in accordance with already reported previously results.[15]

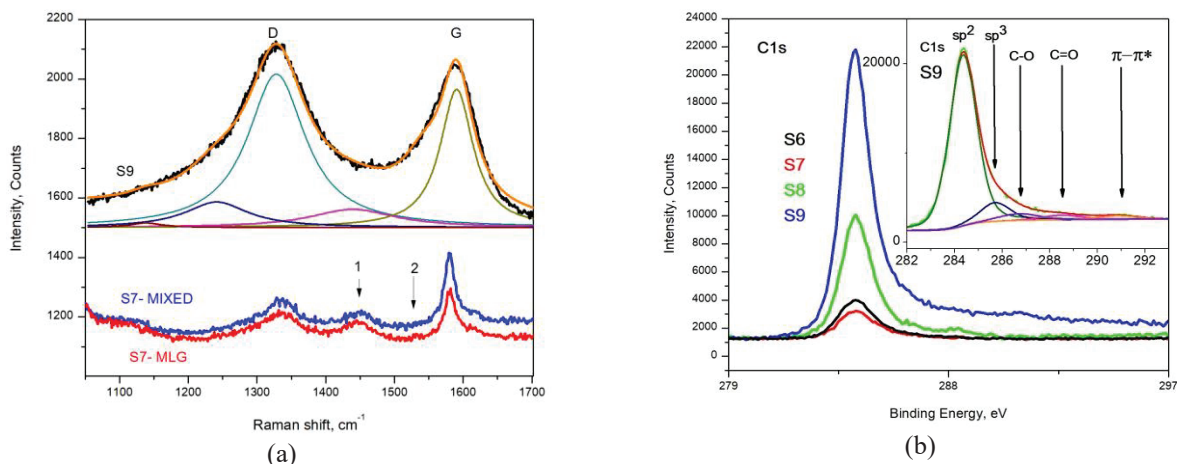


FIGURE 2. a) Deconvoluted Raman spectrum of the specimens S9 (upper traces) as well as magnified parts from the Raman spectra of specimen S7- lower red and blue trace. b) XPS spectra (C1s line) of S6- S9 specimens. The inset: Deconvolution of the C1s line of S9 specimen.

The binding energy which belongs to sp² hybridized carbon for the different studied by us films is shifted to lower binding energy from the 284.4eV, typical for graphite/graphene.[16] The evaluated shift is up to 0.2 eV. The probable reason for that could be the higher density of states at the Fermi level as a result of bond disorder within

the layers. The FWHM of sp² component also narrowed and the FWHM of sp³ hybridized carbon changed due to different amount of SiO₂ that was detected.

TABLE 1. The summarized data of XPS analysis and ellipsometry measurements of S1- S9 specimens.

Sample	Time, min	C, at. %	O, at. %	Si, at. %	N, at. %	sp ³ /sp ²	Thickness, nm
S1	3min	9.28	54.03	36.68	-	0.34	-
S6	6 min	12.87	64.16	22.64	0.33	0.48	4
S7	8 min	9.13	66.90	23.74	0.22	0.19	5
S8	11 min	43.26	41.15	15.32	0.27	0.16	7
S9	16 min	93.24	5.17	1.59	-	0.13	9

The electrical conductivity measurements are carried out at room temperature and the I/V characteristics were plotted- Fig. 3. The determined resistivity at room temperature is $\rho = 2.8 \times 10^{-6} \Omega \cdot \text{m}$ which is extremely low. It is known that such values for resistivity are measured in natural single crystalline graphite, highly oriented pyrolytic graphite (HOPG) and hot-pressed and annealed at $> 2000^\circ\text{C}$ graphite [17,18] and can be expected in high quality graphene[19]. The glassy carbon, the sputtered nano-crystalline carbon as well as the evaporated carbon films possess resistivity in the range 1-3 orders of magnitude higher than those of S9 specimen.[20] Taking into account that the initial 5-6 nm of the carbon film is a predominantly sp³-hybridized (i.e. its resistivity is $> 10^3\text{-}10^4 \Omega \cdot \text{m}$) we can suggest that the top few layers of specimen S9 are most probably a mix of nanosized graphite and graphene.

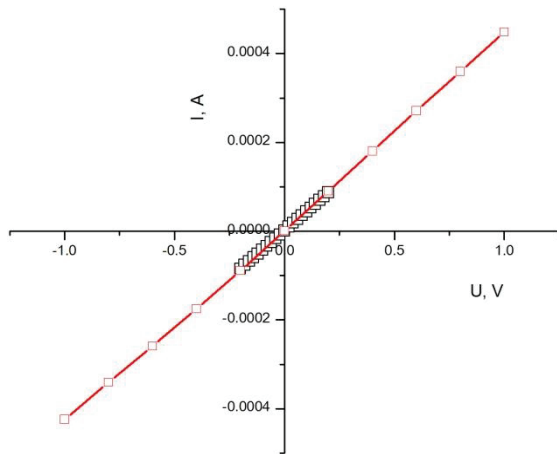


FIGURE 3. I/V characteristics of S 9 specimen measured at room temperature. The measurements in the region from -0.20 to 0.20 V were repeated in a different measurement's run.

It is clear from XPS measurements that the sp³ fraction decreases with the deposition time from about 40 to about 13%. It seems that the film deposited during the initial stages of the process is amorphous and has a sp³-hybridized fraction enriched interface. After the deposition of a sp³ dominated amorphous film (up to 5- 6 nm) the deposition of sp² dominated film occurs and after few (1-2 nm) a mix of nanosized graphite and defected graphene film can be obtained. Similar results were established in cases of deposition of graphene on (001) Si by thermal decomposition of acetone.[21,22] We can relate these results to the origin of the Si-C and Si-O bonds at the interface SiO₂/C: the carbon in Si-C as well as in Si-O bonds should be in sp³ hybridization state. It was established by *ab initio* simulations [23] that such change of hybridization takes place even when few separated Si atoms are situated over a graphene sheet. In this sense we can assume that the formation of a sp³ enriched interface film cannot be avoided completely in cases when carbon films are deposited on Si or SiO₂/Si substrates directly.

4. CONCLUSIONS

We studied the initial stages of deposition of carbon films by sublimation of carbon from modified carbon black source on SiO₂/Si substrate at temperature of about 1050-1060⁰C and established that the initial few nanometers of the deposited film are amorphous and enriched with sp³- hybridized carbon. According to the SEM, XPS and

Raman studies we can assume the next process's consistency: an amorphous carbon film with thickness up to 3- 5 nm is always deposited on the SiO₂ followed-up of precipitation of few-layered defected graphene as well as nano-sized graphite nano-particles on the surface of substrate. Further on, after 8- 10 min a non-continuous carbon film is formed and after 12- 15 min deposition a continuous film of a mix of nanosized graphite and graphene is deposited. The latter has extremely low resistivity ($\rho = 2.8 \times 10^{-6} \Omega \cdot \text{m}$) at room temperature and a completely linear I/V characteristic.

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REFERENCES

1. Jesus de La Fuente, *Www.Graphenea.Com* 1 (2018).
2. K.S. Novoselov, A.K. Geim, S. V. Morozov *et al.* *Science* (80-.). **306**, 666 (2004).
3. J.H. Chen, C. Jang, S. Xiao, M. Ishigami, and M.S. Fuhrer, *Nat. Nanotechnol.* **3**, 206 (2008).
4. H.B. Heersche, P. Jarillo-Herrero, J.B. Oostinga *et al.* *Nature* **446**, 56 (2007).
5. A. Reina, S. Thiele, X. Jia, S. Bhaviripudi, M.S. Dresselhaus *et al.* *Nano Res.* **2**, 509 (2009).
6. X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang *et al.* *Science* **324**, 1312 (2009).
7. T. Milenov and I. Avramova, *Opt. Quantum Electron.* **47**, 851 (2015).
8. Thomsen C, Reich S. *Phys. Rev. Lett.* 2000;85: 5214- 5217
9. A.C. Ferrari and D.M. Basko, *Nat. Nanotechnol.* **8**, 235 (2013).
10. L.M. Malard, M.A. Pimenta, G. Dresselhaus, and M.S. Dresselhaus, *Phys. Rep.* **473**, 51 (2009).
11. Herziger F, Tyborski C, Ochedowski O, Schleberger M, Maultzsch J. *Phys. Rev. B* 2014;90: 245431-1-6
12. A.C. Ferrari and J. Robertson, *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **362**, 2477 (2004).
13. R. Beams, L. G. Cançado, and L. Novotny, *J. Phys. Condens. Matter* **27**, (2015).
14. S. Svensson, B. Eriksson *et al.* *J. Electron Spectros. Relat. Phenomena* **47**, 327 (1988).
15. J. Díaz, G. Paolicelli, S. Ferrer, and F. Comin, *Phys. Rev. B* **54**, 8064 (1996).
16. H.A. Becerril, J. Mao, Z. Liu, R.M. Stoltenber, Z. Bao, and Y. Chen, *ACS Nano* **2**, 463 (2008).
17. C.A. Klein, *J. Appl. Phys.* 1962;33(11):3338-3357.
18. I. Spain, A. Ubbelohde, D. Young *Philos Trans R Soc London Ser A*, *Math Phys Sci.* 1967;262(1128):345-381.
19. I. Vlassiouk, S. Smirnov, I. Ivanov *et al.* *Nanotechnology* **22**, (2011).
20. E. Staryga, G.W. Bąk, K. Fabisiak, K. Paprocki, **35**, 830 (2017).
21. T.I. Milenov, E. Valcheva, and V.N. Popov, *J. Spectrosc.* **2017**, (2017) 3495432/1-8.
22. T.I. Milenov, I. Avramova, E. Valcheva *et al.* *Superlattices Microstruct.* **111**, 45 (2017).
23. T.I. Milenov, Stefan Kolev, Victor Atanasov *et al.* *EPJ(b)* 2018 **submitted**, (2018).