UNIVERSITY POLITEHNICA OF BUCHAREST

Doctoral School of Applied Chemistry and Materials Science

SUMMARY OF DOCTORAL THESIS

Single layer graphene from synthesis to integration in medical applications

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ABSTRACT

The doctoral thesis addresses a novel topic and has as main objective the integration of single layer graphene in medical applications. In order to achieve this objective, we have fallowing main activities i) synthesis of single layer graphene by the chemical vapor deposition (CVD) method, ii) transfer of single layer graphene from the catalyst substrate to different types of substrates depending on the application concerned, iii) functionalization of single layer graphene and control of the remarkable properties of this material and iv) integration of single layer graphene in different applications: membranes, microfluidic platforms and electrochemical sensors. This thesis is the foundations for the further development of theranosctics medical devices: diagnosis and therapy.

This doctoral thesis is structured in 2 parts: in part I present the Critical Stage of Literature Data. This part comprises 2 chapters: Chapter 1: Current state of research on single layer graphene and Chapter 2: Use of graphene in applications.

Part 2 presents the Original Contributions structured as follows: Chapter 3: presentation of characterization methods, Chapter 4: Experimental data: obtaining single layer graphene on target substrate: synthesis, transfer and characterization methods, Chapter 5: Properties of graphene obtained and their modification for use in applications, Chapter 6: Integration of single layer graphene in applications - Manufacture of graphene-based membranes, Chapter 7: Integration of single layer graphene in microfluidics and Chapter 8: Graphene - use as electrode material for electrochemical sensors.

Prior to the 2 parts I presented: List of figures, List of tables, List of abbreviations, Acknowledgments and Summary.

The thesis ends with a chapter of general conclusions, the dissemination of the results presented in the doctoral thesis, and the references consulted.

Keywords: Single Layer Graphene, Chemical Vapour Deposition, Graphene- based membrane, microfluidics, electrochemical sensors

ORIGINAL CONTRIBUTIONS

Chapter 4. Experimental data: single layer graphene synthesis on target substrate: synthesis, transfer and characterization

Cu foil with a thickness of 35 μm and a purity of 99.95% (Graphene Platform Corporation, Japan: Cooper Foil Special for CVD Single Layer Grapehene) was used as the catalyst for the experiments of growing single layer graphene at high temperature (1080˚C). Precursor gases, specially attached to Nanofab equipment, used in the process of obtaining graphene: CH_4: 99.9%, H_2: 99.9%. Acetic acid, isopropyl alcohol, Polymethylmethacrylate (PMMA), useful substances for the processes targeted in single layer graphene transfer experiments were purchased from Sigma Aldrich [134-136].

For the single layer graphene synthesis, the PlasmaPro100 equipment was used, Nanofab 1000 model (Oxford Instruments, UK) dedicated to the growth processes of carbonic materials, which can operate in both thermal (CVD) and plasma assisted (PECVD) procedures.

The standard production process has 5 steps: 1) vacuum - at a base pressure of 6 mTorr and a target temperature of 650˚C, 2) heating: the sample is subjected to heating, up to 1080˚C, in an atmosphere of Ar and H_2, 3) heat treatment: for the formation of binding sites, 4) growth: the surface migration of the precursors to the nucleation centers, surface reactions, increase of the atomic layer, 5) cooling: the system is cooled to 200˚C temperature, then the sample is removed in Load-Lock [134-137].

From an optical point of view, the difference in the surface morphology of the catalyst metal is visible, before and after the CVD process. After the process of growing single layer graphene, the Cu surface has a degree of coverage of about 99%.

Improving the CVD process for single layer graphene synthesis

The wrinkles specific to the catalyst substrate are also identified by SEM in figure 4.8. Single layer graphene is transparent, but due to the overlapping areas of the graphene domains, the presence of wide domains on the Cu surface can be distinguished. Graphene domains are in the hundreds of microns.

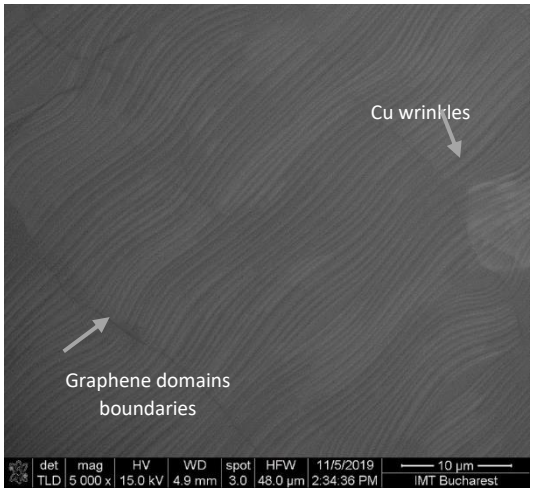

Figure 4.8 *SEM Micrograph – single layer graphene on Cu substrate*

In the Raman spectrum from Figure 4.9, acquired on CVD graphene, the existence of G and 2D bands corresponding to monoatomic graphene is observed. The qualitative indicator I_{2D}/I_G = 3.72 indicates the increase of the qualitative single layer graphene domains. The half-widths for

the G and 2D bands take values close to the equilibrium values (FWHM (G) - 14.85 cm^{-1}, FWHM (2D) - 20.75 cm^{-1}). The Raman spectrum of the CVD graphene was acquired with λexcit = 633 nm in the range 1000 – 3500 cm^{-1}.

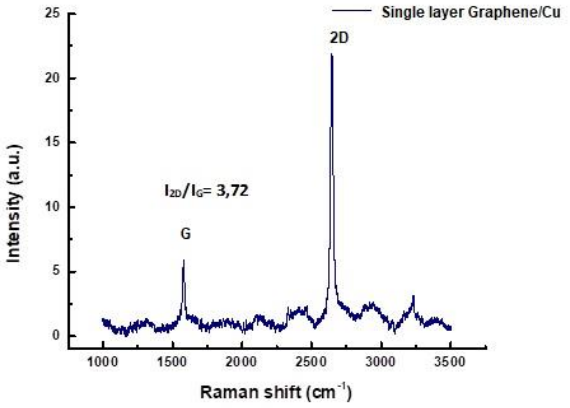

Figure 4.9 *Raman spectrum- single layer graphene on Cu substrate*

The implementation of the single layer graphene growth process at high temperatures was successful obtained, and has large areas of single layer graphene with a coverage of about 90% of the copper substrate.

Improved single layer graphene transfer processes on substrates of interest

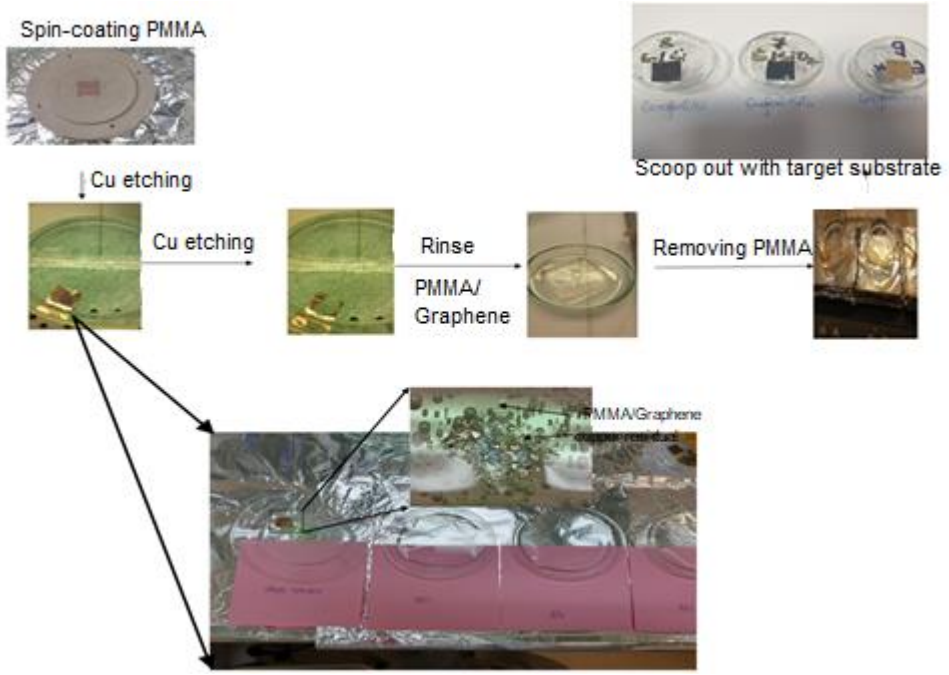

Figure 4.20 *Optimized transfer process: Cu etching (during the process the formation of air bubbles is observed, the presence of traces of uncorroded Cu and PMMA)*

The morphological and structural characterization of the sample was obtained by scanning electron microscopy - SEM (FEI Nova NanoSEM 630 Scanning Electron Microscope) and Raman spectroscopy (LabRAM HR 800 (Horiba Jobin Yvon, Japonia).

4.5.1 Single layer graphene on Si substrate

To obtain the single layer graphene on Si substrate, used a Si <100> wafer, from it we cut pieces with an area of 1cm x 1cm and then we chemically cleaned them with Piranha. Following the standard transfer process, samples are obtained and characterized to identify the control and quality of graphene.

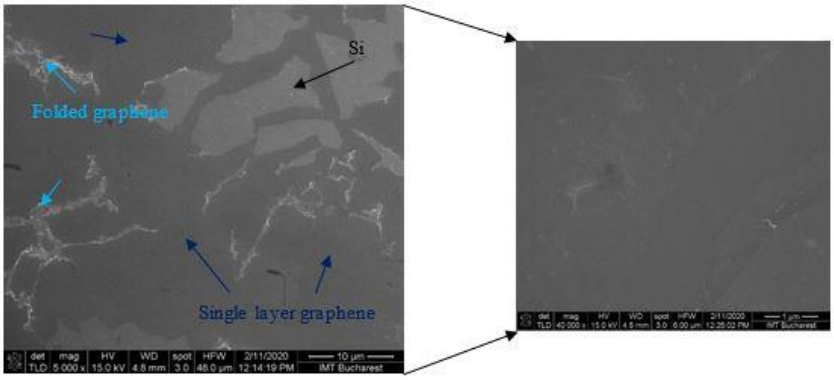

Figure 4.21 *Scanning electron microscopy of single layer graphene on Si substrate*

The SEM image (Figure 4.21) shows the morphology of single layer graphene, with continuous graphene domains, with occasional small islands of folded graphene. Following the transfer on Si, areas with holes are observed, where Si is marked.

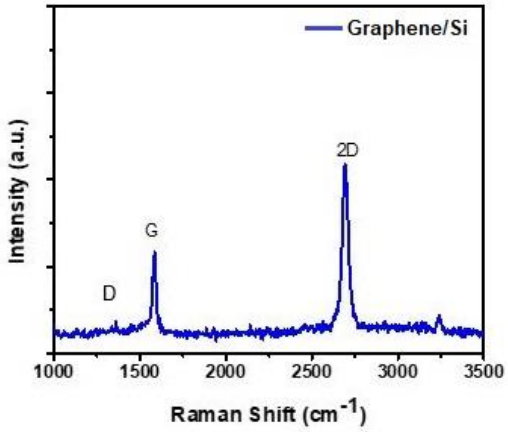

Figure 4.22 *Raman spectrum- single layer graphene on Si substrate*

The Raman spectrum shown in Figure 4.22 confirms the presence of single layer graphene on the Si substrate. The Raman spectrum of graphene/Si contains the 2 unique signatures of graphene: the G band appears at 1582.5 cm^{-1} and the 2D band at about 2693.6 cm^{-1}.

4.5.2 Single layer graphene on SiO_2 substrate

To obtain single layer graphene on a SiO_2 substrate, a Si <100> wafer, thermally oxidized at 1100 ° C, was used. From the wafer we cut pieces with an area of 1cm x 1cm and then we chemically cleaned them with Piranha.

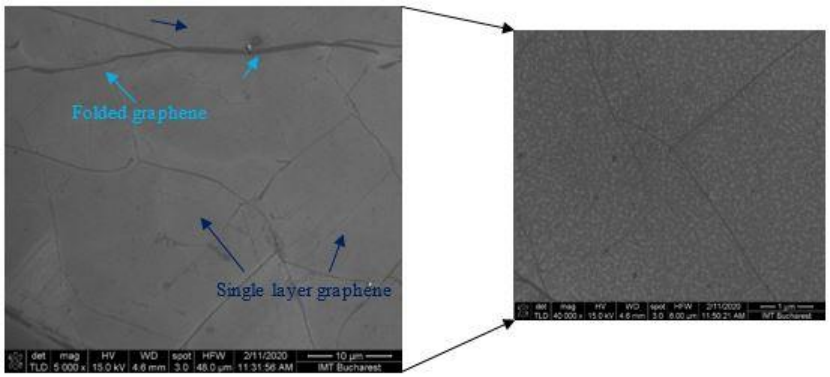

Figure 4.26 *Scanning electron microscopy of single layer graphene on SiO_2 substrate*

Figure 4.26 shows the controlled transfer with continuous single layer graphene domains. Folded graphene areas are identified at the intersection of the domains.

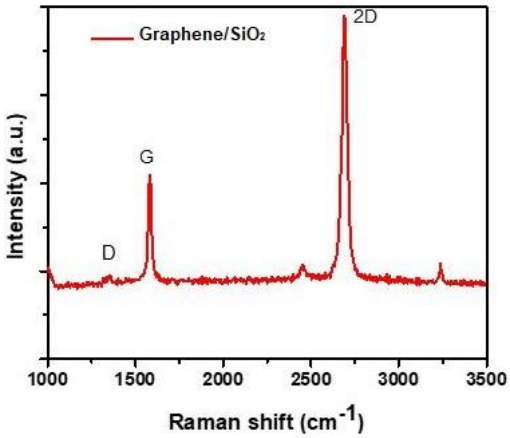

Figure 4. *Raman spectrum- single layer graphene on SiO_2 substrate*

The Raman spectrum of single layer graphene on SiO_2 substrate, shown in Figure 4.27, contains the bands characteristic of single layer graphene: the G band appears at 1581.4 cm^{-1} and the 2D band at approximately 2691.4 cm^{-1}.

4.5.3 Single layer graphene on Au substrate

To obtain the single layer graphene on Au substrate, a Si <100> wafer is used, on which Cr-Au (20/200 nm) is deposited, 1cm / 1cm, from the plate we cut pieces with an area of 1cmx1cm and then we chemically cleaned them with Piranha.

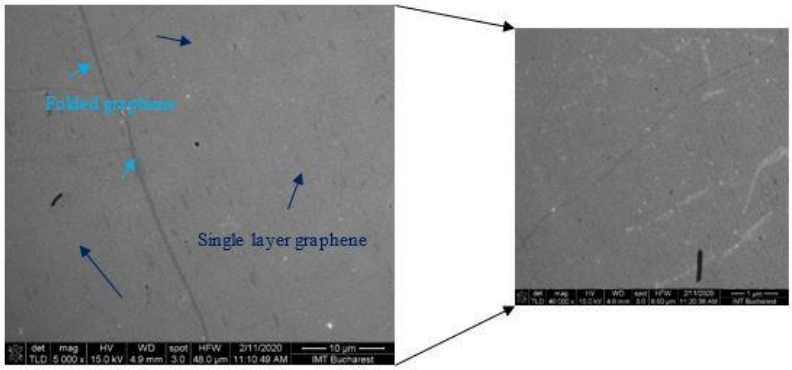

Figure 4.30 *Scanning electron microscopy of single layer graphene on Au substrate*

Figure 4.30 shows the controlled transfer of the single layer graphene on the Au substrate. Graphene domains are predominantly single-layer (> 90%) with occasional small multilayer islands (approximately 10%).

Table 4.1. Quality parameters of single layer graphene, related to the previous Raman spectra

Sample	G		2D		I_{2D}/I_G	I_D/I_G
	Raman spectrum (cm^{-1})	FWHM (cm^{-1})	Raman spectrum (cm^{-1})	FWHM (cm^{-1})		
Graphene/Si	1582.5	25.38	2693.6	45.83	2.18	0.2
Graphene/SiO_2	1581.4	0.85	2691.4	40.47	1.86	0.46
Graphene/Au	1579.2	29.32	2678.4	54.64	1.56	0.42

Figure 4.31 shows the Raman spectrum acquired on the graphene sample transferred to the Au substrate. The Raman lines characteristic of monoatomic graphene D (1337.9 cm^{-1}), G (1579.2 cm^{-1}) and 2D (2678.4 cm^{-1}) are observed. The intensity of the D-band in relation to the intensity of the G-band suggests a low density of defects, which is also indicated by the I_D / I_G defect ratio> 0.42.

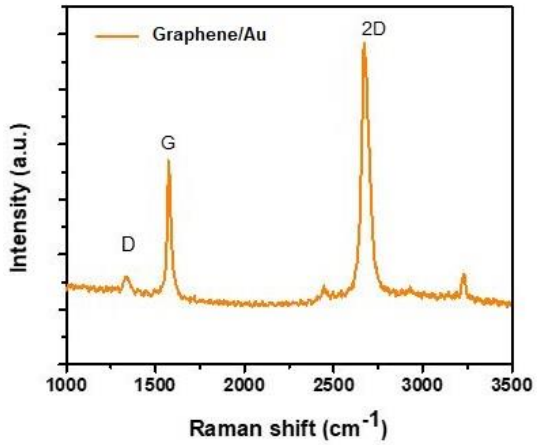

Figure 4.31 *Raman spectrum- single layer graphene on Au substrate*

4.6. Conclusions

The single layer graphene was successfully obtained on a Cu substrate, by the chemical vapor deposition method and was transferred to the Si, SiO_2 and Au substrate by a wet chemical process.

SEM micrographs have shown successful transfer, but the process must be optimized to control graphene folding and domain overlap. This folding of graphene does not induce changes in the Raman spectrum, so although in SEM the folding of graphene is observed, in Raman this folding does not initiate the presence of multilayer graphene.

Raman spectra confirm the growth of the single layer graphene on the defect-free catalyst substrate and the successful transfer to the target substrate, in order to select the ideal substrate for the theranostics platform.

Graphene on the Au substrate induces an increase in Raman intensity due to the surface plasmons of the metal nanostructures. Graphene domains are predominantly single-layer (> 90%) with occasional small multilayer islands (approximately 10%).

Graphene is the basic material targeted for these theranostics platforms, demonstrating from the experimental analysis outstanding results and successful control of diagnostic functions by integration into electrochemical sensors.

Chapter 5. Properties of graphene obtained and their modification for use in applications

5.1 Introduction

This chapter highlights the properties of single layer graphene theoretically identified in Chapter I and the possibility of modifying and improving some properties through a conversion of pure graphene into oxidized graphene, through the plasma treatment of O_2.

5.2 Single layer graphene properties

5.2.1 Optical properties

Figure 5.3 shows the optical transmittance from 250 nm to 800 nm for a single layer of graphene on a quartz substrate. The transmittance for 0.34 nm related to the graphene layer shows a transmission of at least 90%. The optical absorption measured on the graphene film on the quartz substrate has a maximum absorbance at 260 nm. The transmittance of the graphene layer transferred to the quartz substrate is over 97.4%.

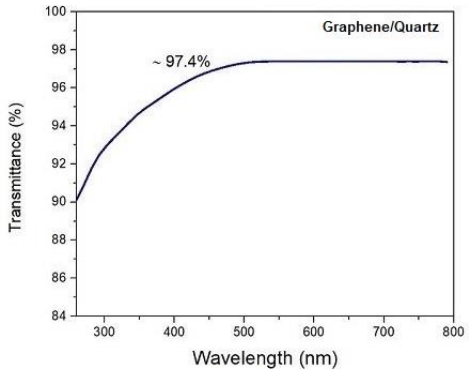

Figure 5.3 *Transmittance of single layer graphene on quartz substrate*

5.2.2 Electrical properties

The electrical characterization was performed in a controlled atmosphere, using the characterization system for 4200S/C/Keithley semiconductors (IMT Bucharest). When the contacts are on graphene, we can observe we have ohmic characteristics and on Au we have a very good stability. When the contacts are on the graphene-free Au structures, the recorded response was only that of background noise. The calculated resistance at the surface of the Au electrodes, after the graphene transfer was 950 Ω, this being higher in the areas where the graphene is suspended, measuring values of approximately 12 kΩ.

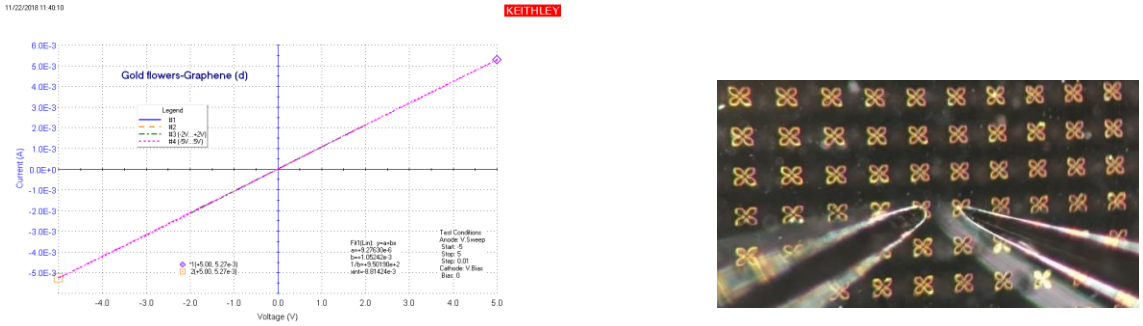

Figure 5.4 *I-V characteristic of graphene transferred to Au structures*

I-V characteristic of graphene between 2 gold flowers, located at a distance of 150 μm, indicates a constant, linear electrical resistance of approximately 950 Ω. In Figure 5.4, the current characteristics of graphene for different voltage ranges are reported. The stability of the I-V curve is due to the Au electrodes which play a role of support layer for graphene.

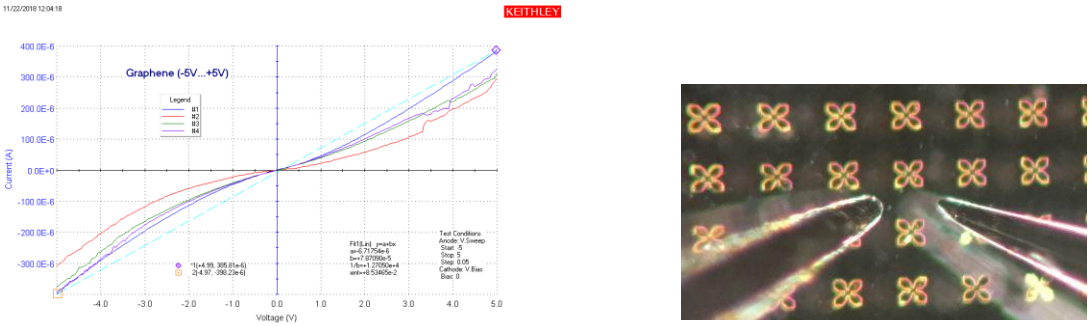

Figure 5.5 *I-V characteristic os suspended graphene*

The area between the suspended points on the graphene indicates a damaging character with instabilities of the material, at the same point, the same current. Compared to the electrical resistance measured on graphene, between 2 gold flowers, we determine the stability of the graphene transferred to Au. The electrical resistance of the suspended graphene was 12 kΩ. Following each measurement we made a change in contact, practically trying to break through the graphene, this was not achieved, due to the strength of this material.

5.2.3 Electrochemical properties

Electrochemical measurements were performed in the presence of a 0.1 M KCl redox solution containing 5.0 mM $K_3[Fe(CN)_6]$ and 55.0 mM $K_4[Fe(CN)_6]$. Cyclic voltammetry is the most adaptable electroanalytical technique for the study of electroactive species.

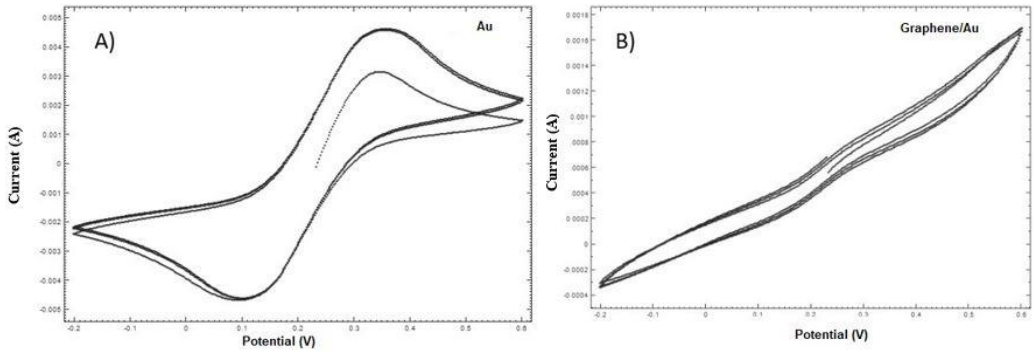

Figure 5.6 *Cyclic voltamograms recorded for the characterization of Au electrodes A) without graphene and B) with graphene in 0.5 M KCl*

Figure 5.6 shows 3 consecutive scans of the applied potential between -0.2V and + 0.6V, a field in which the tested structures are electroactive. In the presence of $Fe(CN)_6$ ions, the appearance of anodic peaks and cathodic peaks around 0.12V and 0.33V, respectively, is observed. The shape of the voltamograms did not change during the sweep of the potential, confirming a good stability.

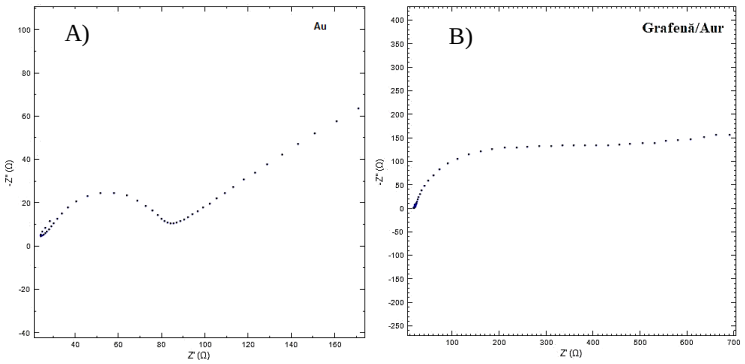

Figure 5.7 *Nyquist diagram for the electrode of A) Au, B) Graphene/Au*

We observe the linear variation of the imaginary impedance as a function of the real impedance, due to the diffusion process and this variation is called Warburg impedance. In the presence of graphene, a decrease in impedance is observed and the diffusion process is much more active.

5.2.5 Biocompatibility evaluation

The MTS kit was used to investigate cell viability. The tests were performed in the Laboratory for the Evaluation of the biocompatibility of medical materials and devices (BIOEVAL), within the National Research-Development Institute for Physics and Nuclear Engineering "Horia Hulubei" (IFIN-HH). No differences in cell proliferation / viability were identified.

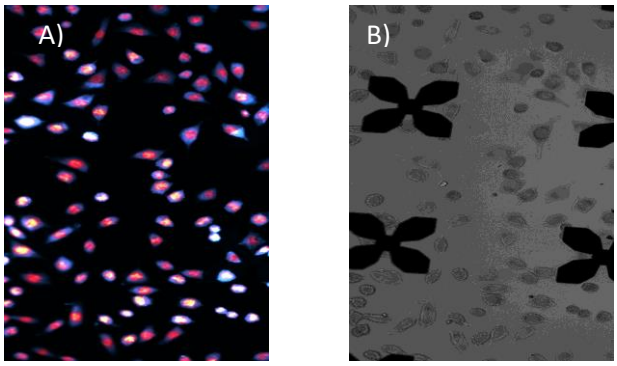

Figure 5.12 *Cell morphology by A) fluorescent microscopy and B) by transmission microscopy on the glass substrate structured with Au electrodes control*

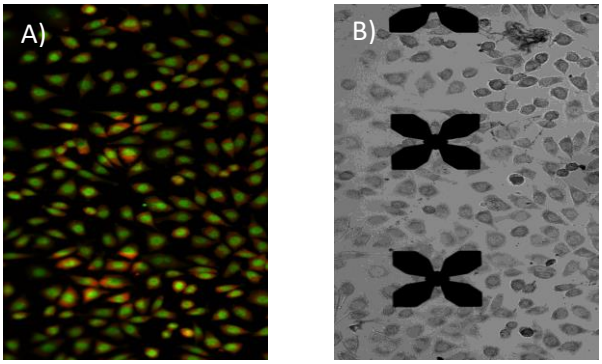

Figure 5.13 *Cell morphology by A) fluorescent microscopy and B) by transmission microscopy on the glass substrate structured with Au- graphene electrodes*

Graphene monolayer is not toxic to L929 fibroblast cells (mouse fibroblasts) and has no induced effects on their morphology and proliferation within 24 hours of culture.

5.3 Modification of single layer graphene properties by conversion to oxidized graphene

Oxidized graphene is a type of chemically activated graphene with hydroxyl and epoxy groups. O_2 plasma treatment has proven to be an effective method of introducing defects and active bonds into the structure of single layer graphene.

The Raman spectrum of the pure or inert graphene (grown by CVD method) shows the presence of the G and 2D bands that can be attributed to the theoretical structure of pure graphene. Band D requires a defect for its activation. Band D requires a defect for its activation.

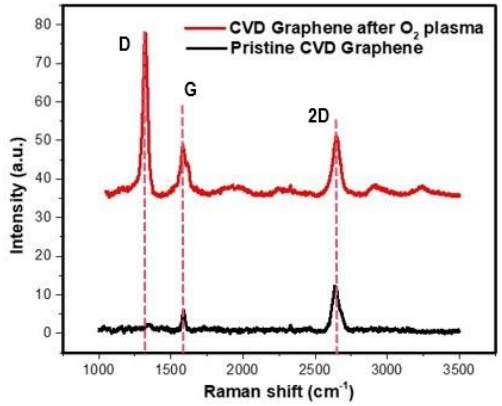

Figure 5.15 *Raman spectra of graphene samples before and after plasma treatment of O_2*

After plasma exposure of O_2 at 50 W RF for 1 min, substantial variations in graphene-specific Raman spectra were detected. In the spectrum of graphene CVD after plasma treatment of O_2 there is also a displacement of the bands G (1583 cm^{-1}) and 2D (2648 cm^{-1}) and a lower intensity compared to band D, due to the increase in the number of defects by activation of atoms. These bands confirm the change in graphene structure resulting from O_2 plasma exposure.

5.3.5 Structural characterization of CVD graphene and oxidized CVD graphene in O2 plasma by FT-IR spectroscopy

Fourier transform IR spectroscopy can be exploited to detect chemical structures in graphene samples before and after the plasma process. The FT-IR spectra of pure CVD graphene and CVD graphene after O_2 plasma exposure were shown in Figure 5.16. There are no functional bonds present on the spectrum of pure CVD graphene.

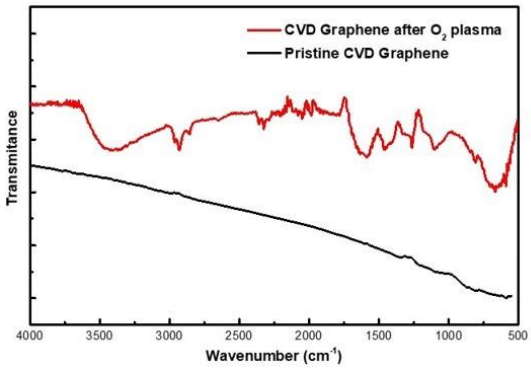

Figure 5.16 *FT-IR spectra of graphene samples- before and after plasma treatment of O_2*

From a structural point of view, FTIR spectroscopy exposed the modification of graphene by introduction the O_2 atoms and the possibility of converting inert graphene into oxidized graphene.

5.3.6 SEM and EDX analysis after process in plasma O_2

The morphological characterization of graphene was performed using a secondary electron detector (SE (UL)) of the electron scanning microscope. The SE (UL) detector has rich topographical information, high resolution and good voltage contrast.

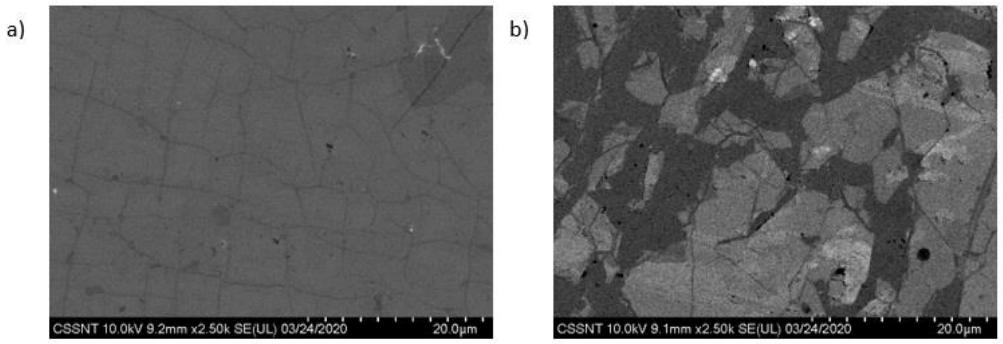

Figure 5.21 *SEM images for a) CD graphene before plasma treatment and b) after O2 plasma treatment*

The obtained images are presented in Figure 5.21 Figure (a) shows the CVD graphene transferred on the Au substrate: it can be noticed that the single layer transferred on the surface of the target substrate is uniform. After plasma O_2 treatment (Figure 5.21 (b)), the graphene surface has irregularities, with different contrast zones, therefore confirming the changes in plasma treatment.

5.4 Conclusions

The study and control of graphene properties are of a great interest for integration into medical devices. The manufacture of graphene-based devices can be achieved by controlling the stability of graphene in terms of quality and properties. In this chapter we analyzed the control of the influence of O_2 plasma in the functionalization of the surface of single layer graphene, a chemically inert material.

The manufacture of graphene-based devices can be achieved by controlling the stability of graphene, very well identified on areas where there is perfect adhesion of graphene on Au electrodes. Au electrodes have a well-established structure, identified by the images taken after modeling the device, but also by the linearity of the I-V characteristics. Following the electrical and electrochemical characterizations, we noticed an improvement of the performances, the presence of graphene and its large surface being useful characteristics in different applications, especially in the manufacture of detection biosensors.

The surface changes, highlighted from a morphological point of view, by SEM micrographs, show irregularities, with different contrast areas, thus confirming the changes in plasma treatment. Raman spectra confirm the qualitative transfer of monolayer graphene. During exposure to O_2 plasma we obtain a good control of the oxidation degree of graphene. This study shows promising results that can be further used to improve the functionalization of graphene and the attachment of biomolecules for biomedical applications.

Chapter 6. Integration of single layer graphene in applications - Manufacture of graphene-based membranes

In this chapter we followed the integration of single layer graphene on holes configured in SiO_2. The single layer graphene will performance as a membrane. Previous research reports experiments to obtain graphene-based membranes, the main key factors being the transfer process, the choice of specific substrate and the influence of the substrate on the adhesion and properties of graphene.

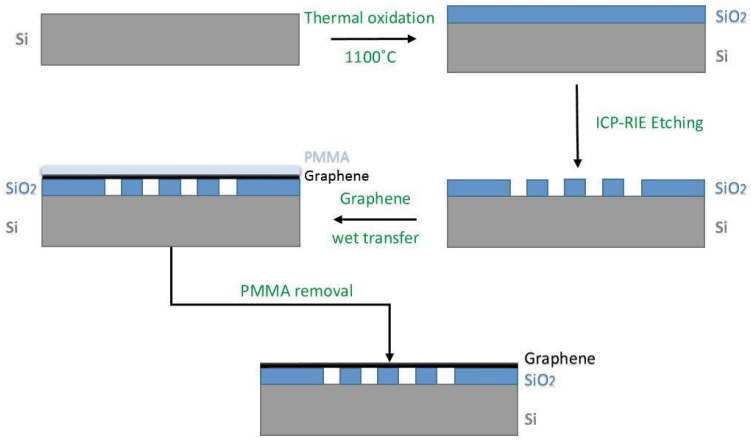

Figure 6.1 *Schematic of the manufacturing process of single layer graphene-based membranes [134]*

For the microfabrication of graphene-based membranes, we transferred the single layer graphene onto an oxidized silicon wafer, in which the holes with a diameter of 7 μm were etched. The process flow used to manufacture the membranes is briefly described in Figure 6.1. Initially, the Si wafer is cleaned in a Piranha solution (H_2SO_4: H_2O_2, 10: 1 ratio) at 120 ° C for 30 minutes, followed by a thermal increase of the 300 nm layer of SiO_2.

For graphene transferred to Si / SiO_2 holes we used three different methods of wet chemical transfer, highlighted in Table 6.1.

Table 6.1 *Sample definition: Sample 1: transfer method by wet-standard etching, Sample 2: transfer method by wet etching assisted by 1 vacuum step; Sample 3: Wet etching method with 2 vacuum steps.*

Sample 1	1. PMMA spin-coating	**Sample 2**	1. PMMA spin-coating	**Sample 3**	1. PMMA spin-coating
	2. Copper etching		2. Copper etching		2. Copper etching
	3. DI water rinsing		3. DI water rinsing		3. DI water rinsing
	4. Graphene “fishing”		4. Graphene “fishing”		4. Graphene “fishing”
	5. 120˚C, 2 h		5. 120˚C, 2 h		5.***Stored in vacuum, 1 h***
	6. PMMA removal		6. PMMA removal		6. 120˚C, 2 h
	7. 170˚C, 2 h		7. ***Stored in vacuum, 1h***		7. PMMA removal
			8. 170˚C, 2 h		8. ***Stored in vacuum, 1 h***
					9. *8. 170˚C, 2 h*

6.1.1 Sample 1

For sample 1, prepared by a standard process, the holes array coated with single layer graphene is shown in figure 6.2. Raman spectroscopy, shown in Figure 6.3, confirms the presence of graphene on holes and surrounding areas.

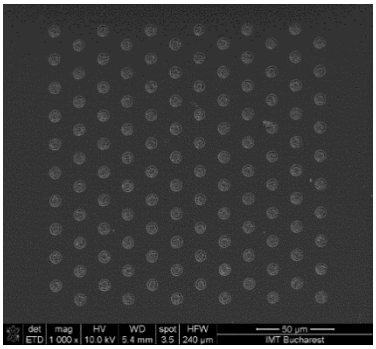

Figure 6.2 *SEM morphology for Sample 1: wet-standard transfer method*

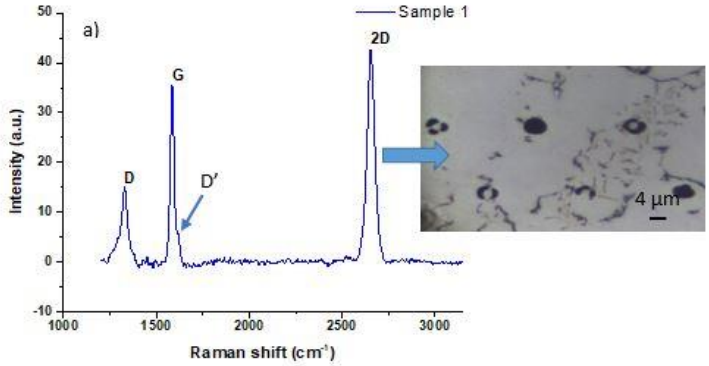

Figure 6.3 *Raman spectrum for Sample 1: wet-standard transfer method and specific optical microscopy*

Figure 6.3 shows the Raman spectrum acquired on sample 1 in the area of the holes and the image associated with the surface from where the spectra were taken. It is observed that the size of the holes is smaller in the case of this sample.

Table 6.1 shows parameters extracted from Raman spectra confirming the presence of graphene on sample 1. The half-width of the G-band is typical of folded graphene. The I_{2D} / I_G quality indicator confirms the presence of at least 2 layers of graphene. The defect density varies to high values as indicated by the I_D / I_G value. From the investigations we can conclude that the graphene membrane is not a continuous and uniform layer, the presence of cracks and domains without graphene can be highlighted.

6.1.2 Sample 2

Figure 6.4 shows an image of the configured area with holes coated with a single layer of graphene for sample 2, while figure 6.5 shows Raman spectroscopy.

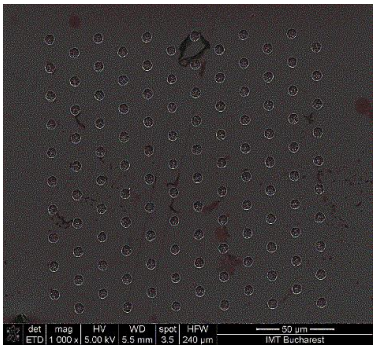

Figure 6.4 *SEM morphology for Sample 2: wet transfer method with 1 vacuum assisted step*

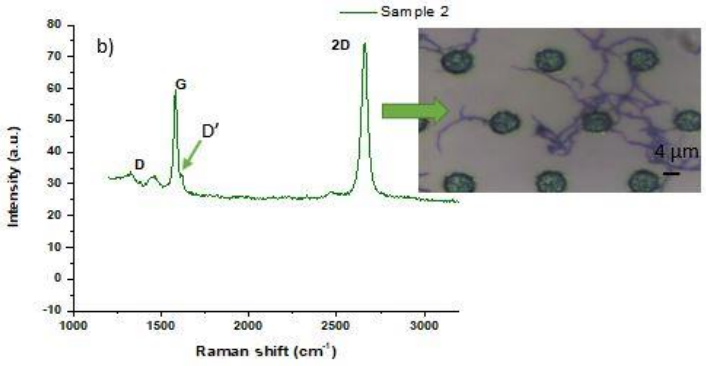

Figura 6.5 *Raman spectrum for Sample 2: 1-step vacuum assisted wet transfer method and specific optical microscopy*

Figure 6.5 shows the Raman spectrum acquired on sample 2 in the area of oxide-corroded holes. Raman bands characteristic of graphene are observed. The optical image indicates the area of Raman spectra and it is clear the presence of graphene, both in the area of the holes, indicating their coverage and on their edges, by optical contrast. The Raman spectra obtained from sample 2 showed representative characteristics of the monolayer graphene: the G band at 1583 cm^{-1} and the 2D band at 2658 cm^{-1} appeared with precision.

6.1.3 Sample 3

For sample 3, the morphological investigations, presented in figure 6.6, and the Raman spectroscopy, presented in figure 6.7, indicate a qualitative transfer process, compared to the two previous methods. Wrinkles, cracks or areas without graphene are significantly reduced for this sample compared to the previous two.

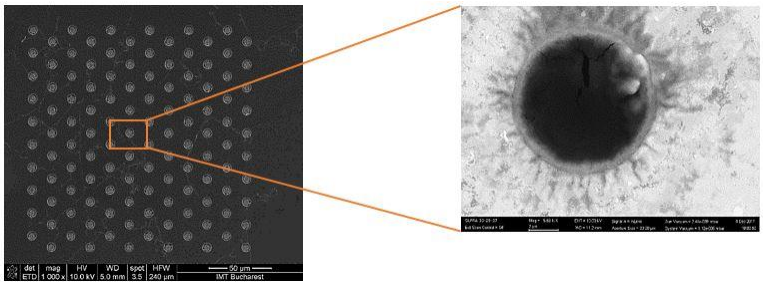

Figure 6.6 *SEM morphology for Sample 3: wet transfer method with 2 vacuum assisted steps*

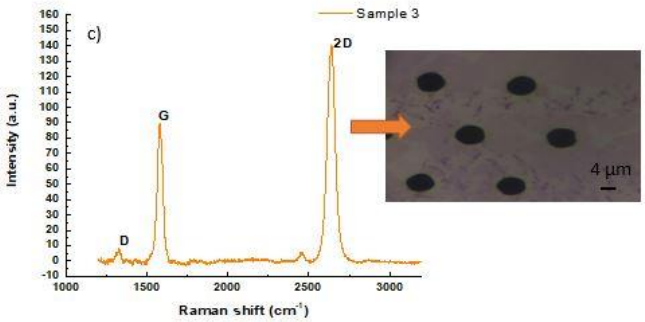

Figure 6.7 *Raman spectrum for Sample 3: 2-step vacuum assisted wet transfer method and specific optical microscopy*

Figure 6.7 shows the Raman spectrum purchased on sample 3 which confirms the presence of monoatomic graphene. Raman D, G, 2D bands characteristic of graphene are observed.

Tabel 6.2 *Raman features of samples*

Sample	D band	G band		D` band	2D band		I_D/I_G	I_{2D}/I_G
	ω (cm^{-1})	ω (cm^{-1})	FWHM (cm^{-1})	ω (cm^{-1})	ω (cm^{-1})	FWHM (cm^{-1})		
Sample 1	1330	1589.0	17,61	1610	2646.0	37,45	0,42	1,25
Sample 2	1351	1583.0	22,06	1613	2658.4	38,22	0,15	1,34
Sample 3	1350	1582.1	39,96	-	2640.5	52,63	0,15	1,57

6.2 Conclusions

A technological method for the manufacture of graphene membrane on SiO_2 holes has been successfully manufactured and implemented. The key factor in this proposed method is the vacuum step introduced into the transfer process which results in a single layer suspended graphene membrane.

Based on the characterization results, the single layer graphene obtained by CVD was transferred to Si / SiO_2 holes without significant defects. SEM images show the morphology of the single layer graphene after transfer and coating of holes. Raman spectra confirmed the control of quality single layer graphene transfer on 7 µm holes.

The new vacuum-assisted step technique reported in this chapter opens up new possibilities for the manufacture of graphene devices with different configurations and improved performance. The vacuum stages led to a uniform membrane, with fewer wrinkles and defects.

Chapter 7. Integration of single layer graphene in microfluidics

For the integration of monolayer graphene in microfluidics, this chapter presents an optimized method of channel transfer and microfabrication, processes that lead to increasing the potential use of graphene in microfluidics and the development of a wide range of graphene-based medical devices. Optical microscopy detail images (Figure 7.3) after microchannel etching are presented on each specific area of the microchannel.

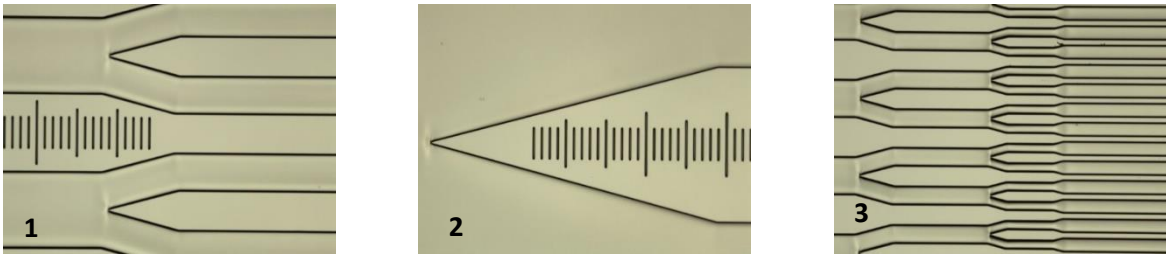

Figure 7.3 *Optical microscopy images after microchannel etching in Si.*

The integration of the single layer graphene in the microfluidic channel was done by the method of transferring the graphene monolayer from the Cu catalyst substrate on Si microchannel.

7.2.2 Single layer graphene integration in microchannel

Single layer graphene (SLG) was synthesized on the catalyst by the CVD method in a mixture of CH_4 and H_2 at 1080˚C. Figure 7.4 shows the scheme of the proposed transfer method for SLG integration in the microfluidic channel.

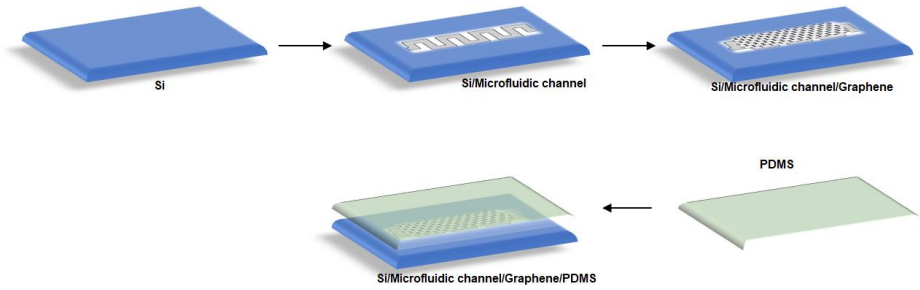

Figure 7.4 *Schematic of the integration process of single layer graphene in microfluidic platforms*

RIE etching was a 2 min process with a low O_2 concentration: 50 sccm. Removal of the photoresist used in M2 (AZ 4562) was performed by immersion in 2 steps in heated acetone, followed by immersion in Piranha solution at 40˚C.

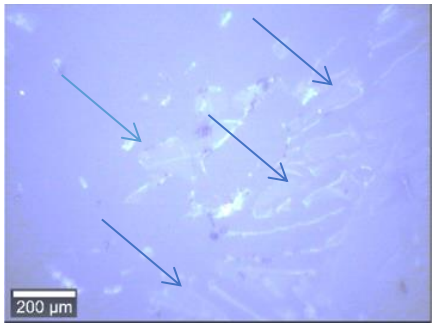

Figure 7.5 *Optical microscopy image with graphene integrated in the microchannel*

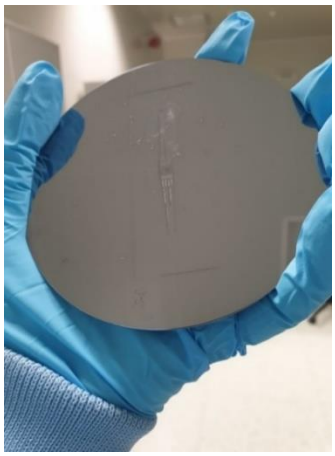

Figure 7.6 *SLG integrated in the microchannel corroded on the Si plate*

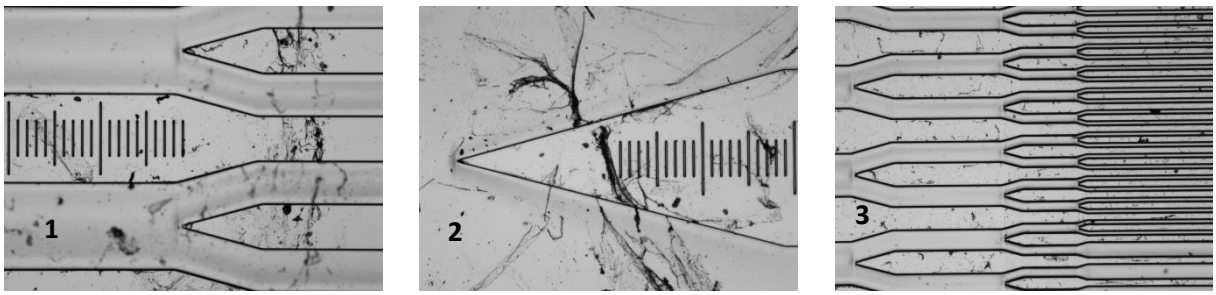

Figure 7.7 *Optical images after SLG transfer on the Si microchannel*

7.3 Results and discussions

Following the characterization of optical microscopy on the entire surface of the microchannel, the presence of areas isolated with SLG is observed, and it is not found on the entire surface of the microchannel. In the channel, both before and after the etching of the single layer graphene, areas are identified in which the SLG is transferred to the microchannel, detected with the Raman Spectroscopy.

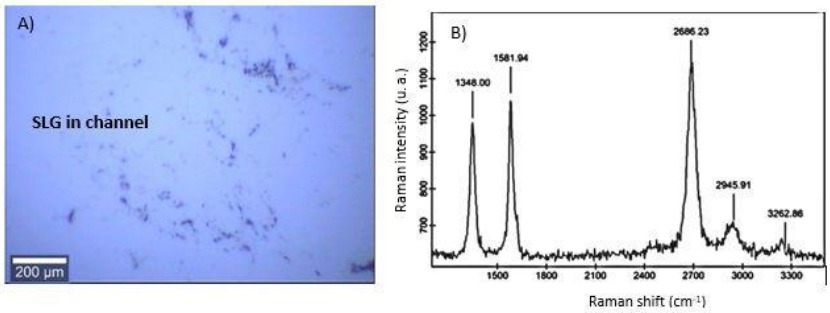

Figure 7.9 *SLG optical microscopy image, after etching, isolated in the microchannel made of Si (A) and the Raman Spectrum of SLG after RIE etching, in the background, in the microchannel (B)*

The vibrational modes of graphene by the presence of graphene-specific G (1581.9 cm^{-1}) and 2D (2686.2 cm^{-1}) bands are present in the spectrum from the microchannel, on the inferior plane. The I_{2D} / I_G ratio~ 1.38 indicates the folding of graphene in the microchannel due to the graphene domains falling into the microchannel, without control over the overlapping process. The I_D/I_G ratio~0.88 indicates an increase in the degree of defects following the etching process.

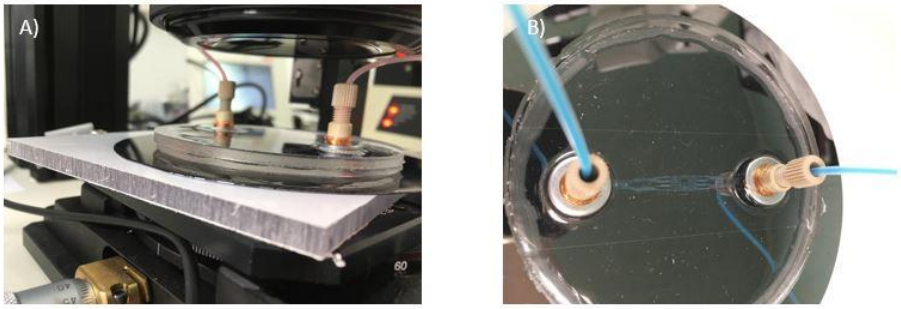

Figure 7.10 *Side view - SLG microfluidic device (A) and Top view - SLG microfluidic device (B)*

7.4 Conclusions

In this chapter we presented the single layer graphene integrated in microfluidic devices manufactured of Si. Graphene integration before and after graphene etching was verified by Raman spectroscopy. After integrating the graphene into the Si microchannels, it was encapsulated with a layer of PDMS and sealed with another layer of PDMS, containing microfluidic ports.

In conclusion, this chapter aimed to successfully improve the processes of integration of monolayer graphene in microfluidic channels.

Raman spectroscopy provides information about the presence of a single layer of graphene in the microchannel, which allows the transfer and successful integration of graphene with large and good quality domains.

Preliminary results are the basis for controlling the integration of monolayer graphene in the microfluidic channel. The approaches presented establish a great potential for the use of graphene in the manufacture of transparent and flexible devices with a high level of complexity.

Chapter 8. Graphene- use as electrode material for electrochemical sensors

In this chapter are presented the single graphene as an electrode material. Raman spectroscopy is used to analyze the characteristics of graphene, such as: the number of graphene layers, the presence of defects, the effects of deformation, the interaction between graphene and the support layer. When graphene is transferred to a substrate, the interaction of the interface can introduce changes in the structure of the material. The morphological characterization of graphene on gold substrate is investigated by SEM. The first characterization to certify the synthesis of the material is Raman spectroscopy. Raman spectra were obtained with a red laser: 633 nm.

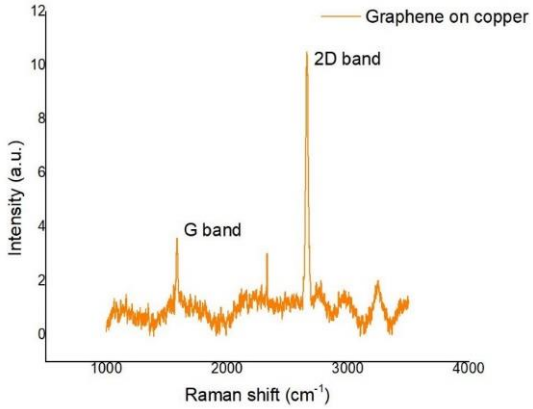

Figure 8.1 *Raman spectra graphene on Cu*

In figure 8.1 is presented the specific Raman spectra of single layer graphene on Cu foil after CVD process. Is observed presence of the G and 2D bands representative to graphene. The number of graphene layers is established by the intensity ratio of feature bands: G and 2D. Defects band is not present, representing an increase with a low density of defects in the graphene lattice.

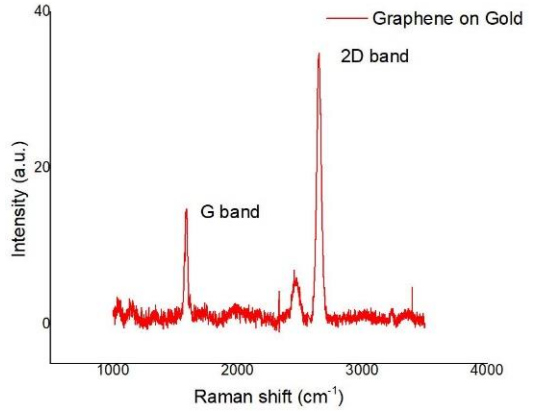

Figure 8.2 *Raman spectra of graphene on Au*

Raman spectra of CVD graphene on Au substrate show a good transfer of single layer graphene free defects. It is observed an increase in intensity with approximately three times. Figure 8.2 shows the Raman spectra in the 2450 cm^{-1} due to a double resonant Raman scattering explaining by interface between the gold substrate and the graphene layer.

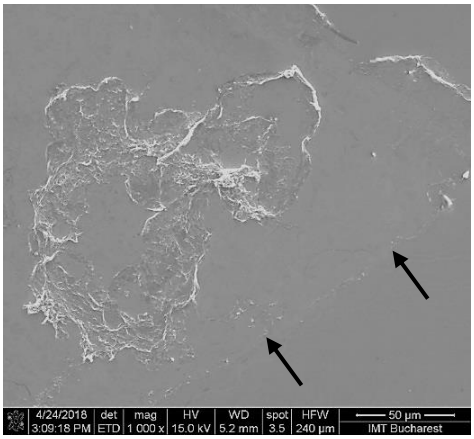

Figure 8.3 *SEM Micrograph of single layer graphene on Au substrate*

Figure 8.3 shows the transfer of graphene on the Au substrate. The arrows indicate the boundary between the graphene layer and the Au substrate. In the SEM micrograph on the Au substrate appear a zone with graphene overlaid due to sample folding tendency. Due to its properties, graphene has an affinity for the dielectric substrate and adheres excellently to Au, but in the air it has a very high tendency to folding.

8.1 Electrochemical measurements

Figure 8.5 shows the CV specific curves of the Au and Graphene / Au electrode recorded in the electrolyte solution containing redox mediator, which is sensitive to the groups present on the surface of the electrodes. Compared to the voltamogram recorded for the control, a reversible redox process characteristic of graphene on Au is observed, displaced from that of the control, the Au electrode, with a ΔEp = 109 mV.

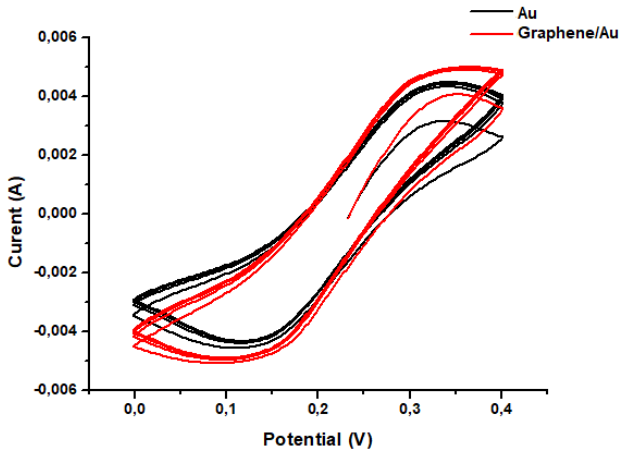

Figure 8.5 *CV curves of gold working electrode and gold working electrode with graphene in 0.1 M KCl mixed with 5.0 mM $K_3[Fe(CN)_6]$ and 5.0 mM $K_4[Fe(CN)_6]$*

Nyquist plots show the imaginary impedance (Z″) versus the real impedance (Z′). From the semicircular curve corresponding to the high frequencies, we can determine the charge transfer resistance (Rct). Rct (960 Ω) for Au working electrode is much larger than that of Au working electrode with graphene layer (Rct= 13.6 Ω), exhibited better charge transfer performance when

graphene is used and had excellent conductivity. The Randles circuit involves: a solution resistance (Rs), a double layer capacitance (Cdl) and Rct. These parameters are presented in Table 8.1.

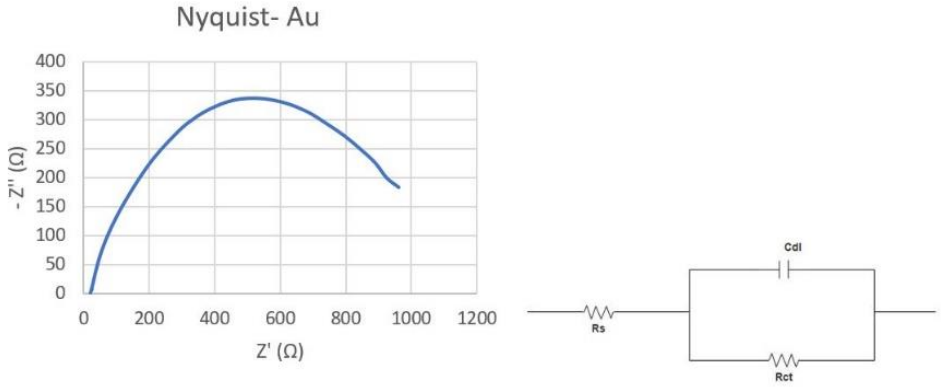

Figure 8.6 *Nyquist plot of Au working electrode and circuit characteristic in 0.1 M KCl mixed with 5.0 mM $K_3[Fe(CN)_6]$ and 5.0 mM $K_4[Fe(CN)_6]$*

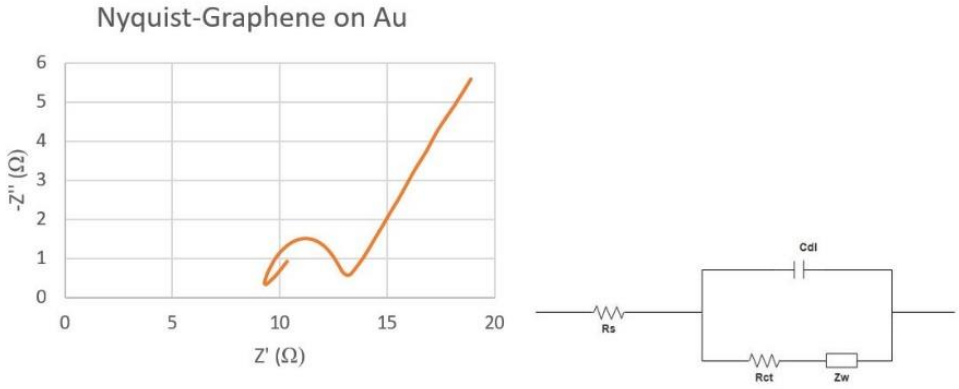

Figure 8.7 *Nyquist plot of Au working electrode with graphene and Randles circuit 0.1 M KCl mixed with 5.0 mM $K_3[Fe(CN)_6]$ and 5.0 mM $K_4[Fe(CN)_6]$*

Table 8.1 *Electrochemical characteristics*

Working electrode	**Cdl**	**Rs**	**Rct**
Au	0.5 mF	25.7 Ω	960 Ω
Graphene on Au	0.13 mF	10.35 Ω	13.07 Ω

The diffusion phenomenon occurs due to the presence of the graphene layer and generates a Warburg impedance. Electrochemical characterization is a versatile method for the quantitative biomolecules' detection. The electrochemical activity of the graphene coating the Au electrode is more stable than that of the graphene-free Au electrode. The low electrochemical activity of graphene implies a positive effect on the study of cellular activity, increases biocompatibility and wettability.

Figure 8.8 shows the Bode diagram of the frequency impedance and phase angle versus frequency modules for the working electrode in Au (Figure 8.8 a)) and for the working electrode-Au modified with graphene (Figure 8.8 b)).

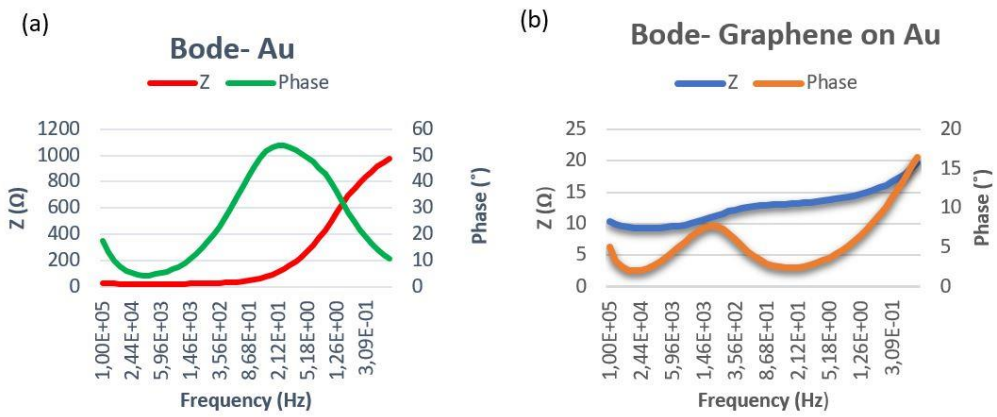

Figure 8.8 *Bode plot of a) Au working electrode and b) Au working electrode with graphene in 5,0 mM $K_3[Fe(CN)_6]$ și 5,0 mM $K_4[Fe(CN)_6]$*

Applying the results obtained from the Nyquist and Bode diagrams, we calculated Cdl. Cdl for Au was 0.5 mF, and for Graphene / Au, the calculated Cdl was 0.13 mF, data indicating an improvement in working electrode performance and excellent graphene conductivity. The resistance is high for the working electrode in Au due to the substrate.

8.2 Conclusions

Graphene on the Au working electrode, with high quality and SERS effect, is an ideal candidate for medical imaging and biosensors as applications.

The surface / volume ratio specific to graphene and the possibility of numerical control of graphene layers are important advantages in functionalization and integration in applications, particularly in the field of biosensors. Au substrate improves the properties of graphene.

Based on the electrochemical experimental results, the performances of a single layer of graphene obtained by CVD on Cu catalyst and transferred to the working electrode from Au were highlighted. Raman confirmed control of the transfer of a single layer of graphene.

SEM highlighted the morphology of the single layer of graphene on Au electrodes. The Graphene / Au interface plays an important role in the properties of graphene by the interfacial coupling of single layer graphene and gold electrodes due to the attractive synergy between the π orbitals of the graphene structure and the d orbitals of the gold atoms. Higher values of the double layer capacity were obtained on Au working electrodes. Graphene on the working electrode shows electrocatalytic activity, stability and strong transfer control.

General Conclusions and Original Contributions

General conclusions

The doctoral thesis entitled "Single layer graphene from synthesis to integration in medical applications" is the result of research in projects in the Laboratory of Micro and Nanotechnology - National Research and Development Institute for Microtechnology, IMT Bucharest and the University Politehnica of Bucharest, Faculty of Applied Chemistry and Materials Science, Department of General Chemistry and led to the following general conclusions:

- ✓ Single layer graphene was successfully obtained on Cu catalyst substrate, by the chemical vapor deposition method, with large domains and a superior quality, demonstrated by morpho-structural characterizations: SEM and Raman.
- ✓ Graphene was successfully transferred to different substrates: glass, quartz, Si, SiO_2 and Au by the wet chemical etching method of the Cu catalyst substrate, optimized and controlled by the quality of the obtained single layer graphene.
- ✓ The study and control of the properties of graphene-based materials are a great interest for integration in medical devices, so the control of the influence of O_2 plasma in the functionalization of the single layer graphene surface was analyzed.
- ✓ The structural changes of pure CVD graphene were confirmed, by the treatment with O_2 plasma, as a results of O_2 bonds introduced at the edge of the graphene domains, as an alternative of surface activation. This study shows promising results that can be further used to improve the functionalization of graphene and the attachment of biomolecules for biomedical applications.
- ✓ Implementation of a technological method for the development of single layer graphene-based membrane on SiO_2 holes.
- ✓ The proposed method of manufacturing the membrane eliminates most of the water residues under the graphene membrane. Based on the characterization results, the single layer graphene obtained by CVD was transferred to Si/SiO_2 holes without significant defects.
- ✓ The new vacuum assisted step transfer method reported in this thesis opens new possibilities for the manufacture of graphene devices with different configurations and improved performance. The vacuum stages conducted to a uniform membrane, with fewer wrinkles and defects.
- ✓ The electrical and electrochemical study of single layer graphene is of great interest for medical biosensors. When graphene is transferred to Au, improved the performance of the working electrode and an excellent conductivity of graphene is observed.
- ✓ Graphene on the Au substrate is an ideal candidate for medical imaging and biosensors, as applications. Raman spectra confirmed control of the transfer of the single layer graphene. SEM highlighted the morphology of the single layer graphene on Au electrodes.
- ✓ The Au / graphene interface has an important role in the properties of graphene through the interfacial coupling of single layer graphene and gold electrodes due to the attractive synergy between the π orbitals of the graphene structure and the d orbitals of the gold atoms.
- ✓ Graphene on the working electrode shows electrocatalytic activity, stability and strong transfer control.

- ✓ The results and conclusions of this thesis represent a stable and promising basis for the development of medical devices for detection and treatment.

Original contributions

The originality elements and the contributions of this thesis are identified in the second part of the doctoral thesis, as follows:

- Selection of the material type, from the class of carbon materials with unique properties, namely single layer graphene.
- The CVD synthesis method of single layer graphene, a method rarely used at national level. Optimization of the method and morpho-structural characterization of the material obtained successfully.
- Optimized transfer method by wet chemical etching of the Cu catalyst substrate and control of the single layer graphene on different substrates and configurations. Characterization and comparative analysis of graphene on different substrates in order to choose the ideal substrate for applications.
- Single layer graphene functionalization by using oxygen plasma and highlighting the oxidation process of the active edges of graphene.
- Integration of single layer graphene in applications: material synthesis, preparation and obtaining of the configured substrate, control of the transfer of the graphene layer over holes. Observations and discussions on the optimal vacuum steps, necessary to obtain membranes based on single layer graphene.
- Integration of single layer graphene in microfluidics: material synthesis, preparation and microfabrication of microfluidic channel, control of single layer graphene transfer in microfluidic channel.
- Integration of single layer graphene in electrochemical sensors: material synthesis, and preparation of working electrodes. Electrochemical characterization and single layer graphene evaluation as electrode material for electrochemical sensors.

Through this doctoral thesis the author contributes with important novelty elements at national level, and the affiliation to the IMT Bucharest and implicitly the possibility to work within the Research Center for Nanotechnologies Dedicated to Integrated Systems and Advanced Nanomaterials based of Carbon- CENASIC, directed to the optimization of the single layer graphene synthesis process with large domains and the possibility of integration in applications including different nanostructured surfaces, important aspects and interest for the Romanian scientific field, with a strong applicative character.

Last but not least, the novelty character is also presented by the author's contribution to the upgrading of the specialized literature in the field of single layer graphene.

Future research directions

- Electrochemical sensors development for tumor cell detection: single layer graphene will be used as electrode material for the working electrode of an electrochemical sensor. The single layer graphene will be functionalized in the first step by O_2 plasma, for the activation of the edges, followed by the functionalization with Gold nanoparticles. Next is the attachment of antibodies specific to the cell lines to be tested. Cell detection will be performed by the electrochemical impedance spectroscopy method.
- Development of the single layer graphene field effect transistor (GFET) for electrical detection of SARS CoV-2.

Dissemination of results

I. ARTICLES PUBLISHED IN ISI JOURNALS

1. 1. **B. Tincu**, I. Demetrescu, A. Avram, V. Tucureanu, A. Matei, O. Tutunaru, T. Burinaru, F. Comanescu, C. Voitincu, M. Avram, „Performance of single layer graphene obtain by chemical vapor deposition on gold electrodes", Diamond & Related Materials 98 (2019) 107510, ISSN 0925-9635, WOS:000488305000028, **IF: 3,31**;
2. **B. Tincu**, M. Avram, A. Avram, O. Tutunaru, V. Tucureanu, A. Matei, T. Burinaru, F. Comanescu, I. Demetrescu, „Progress and control in development of single layer graphene membranes", Vacuum 175 (2020) 109269, **IF: 3,62**;
3. Tiberiu A. Burinaru, Marioara Avram, Andrei Avram, Cătălin Mărculescu, **Bianca Țîncu**, Vasilica Țucureanu, Alina Matei, Manuella Militaru „Detection of circulating tumor cells using microfluidics", ACS Combinatorial Science (2018), **IF: 3,78**;
4. **Bianca Țîncu**, Andrei Avram, Vasilica Țucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, Florin Comănescu, Raluca Gavrila, Marioara Avram, „Study of the CVD graphene transferred from copper to gold substrate", UPB Scientific Bulletin, 2019, Series B: Chemistry and Materials Science 81(3):29-38.
5. **B. Tincu**, M. Avram, V. Tucureanu, C. Mihailescu, O. Tutunaru, A. Avram, E. Anghel, "Single Layer Graphene and Vertical Graphene as a Promising Candidate for Electrochemical Biosensors", Rev. Chim., 71 (5), 2020, 24-29, (trimisă în 2019: IF: 1.75).

FI cumulat: 3,31+ 3,62 + 3.78= 10,71

II. BOOK CHAPTER

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III. PATENTS

1. CBI Nr. A/00486/18.07.2017 - „Procedeu chimic de transfer a grafenei de pe un substrat pe altul", autori: Țucureanu Vasilica, Matei Alina, **Țîncu Bianca Cătălina**, Avram Marius Andrei, Mărculescu Cătălin Valentin, Burinaru Tiberiu Alecu, Avram Marioara, publicata in Buletinul Oficial de Proprietate Intelectuala, sectiunea Brevete de Inventie, RO-BOPI 1/ian.2019, pag. 21, 133042 A2 (51) C01B 32/182(2017.01); B05D 5/12

2. CBI Nr. A/100494/iun.2018: Avram Marius Andrei, Avram Marioara, **Țîncu Bianca Cătălina**, Voițincu Corneliu, Țucureanu Vasilica, Matei Alina, Burinaru Tiberiu Alecu, Mărculescu Cătălin Valentin, „Procedeu de realizare a senzorului de presiune bazat pe emisie în câmp".

IV. PAPERS PUBLISHED IN SPECIALTY VOLUMES OR PROCEEDINGS CONFERENCES INDEXED IN INTERNATIONAL DATABASES

1. **B. Tincu**, M. Avram, C. Pachiu, E. Chiriac, C. Voitincu, A.C. Costache, Maria-Roxana Marinescu, "Microfluidic device based on graphene", CAS 2020 PROCEEDINGS, ISBN: 978-1-7281-1072-1.

2. **Bianca Ţîncu**, Andrei Avram, Marioara Avram, Vasilica Țucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Alecu Burinaru, Florin Comănescu, Iuliana Mihalache, Marian Cătălin Popescu, and Ioana Demetrescu "Spectroscopic investigation of CVD graphene", Proc. SPIE 10977, Advanced Topics in Optoelectronics, Microelectronics, and Nanotechnologies IX, 109770C (2018), doi: 10.1117/12.2324261, WOS: 000452925200006.
3. **Bianca Țîncu**, Andrei Avram, Marioara Avram, Vasilica Țucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, "Graphene post-processing", acceptata pentru publicare, IOP Conference Series: Materials Science and Engineering (MSE) (2018), IOP Conf. Ser.: Mater. Sci. Eng. 485 012027, doi: 10.1088/1757-899X/485/1/012027.
4. **Bianca Țîncu**, Andrei Avram, Marioara Avram, Vasilica Țucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, Florin Comănescu, Iuliana Mihalache, Marian Cătălin Popescu, and Ioana Demetrescu, „Investigation of graphene on quartz substrate", AIP Conference Proceedings 2071, 040007 (2019), doi: 10.1063/1.5090074, WOS: 000452925200006;
5. Tiberiu Alecu Burinaru, Marioara Avram, Andrei Avram, Cătălin Mărculescu, **Bianca Țîncu**, Vasilica Țucureanu, Alina Matei, Roxana Marinescu, „Microfluidic device for circulating tumor cell quantification and capture", AIP Conference Proceedings 2071, 040006 (2019); https://doi.org/10.1063/1.5090073 (2018).
6. Burinaru Tiberiu Alecu, Avram Marioara, Țucureanu Vasilica, Avram Andrei, **Țîncu Bianca**, Mărculescu Cătălin, Matei Alina, Marinescu Roxana, Volmer Marius, „Antibody functionalized magnetic nanoparticles for circulating tumor cells detection and capture using magnetophoresis", IOP Conf. Ser.: Mater. Sci. Eng. 485 012005 (2018).
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V. PARTICIPATION IN NATIONAL AND INTERNATIONAL TECHNICAL-SCIENTIFIC EVENTS

National conferrences

1. **B. Tincu**, M. Avram, V. Tucureanu, C. Pachiu, O. Tutunaru, E. Chiriac, I. Demetrescu, "Noi investigații ale grafenei monostrat: sinteză, funcționalizare și integrare în platforme microfluidice", Aplicații Ale Chimiei În Nanostiinte Si Ingineria Biomaterialelor", Conferinta Stiintifica- AOSR- 17 Iulie 2020.
2. **Cătălina Bianca Țîncu**, Ioana Demetrescu, Mariana Prodana, Andrei Marius Avram, "Grafena Single Layer- CVD", Sesiunea de Comunicări Ştiinţifice Studenţeşti 2017, SECŢIUNEA 14-01, Inginerie Medicală, BIOMATERIALE ȘI DISPOZITIVEMEDICALE, Premiul 2.
3. Andrei Avram, **Bianca Țîncu**, Florin Comănescu, Vasilica Țucureanu, Adrian Dinescu, "Monostraturi de grafenă crescute prin metoda CVD", INCD pentru Microtehnologie – IMT Bucuresti, A 16-a editie a SEMINARULUI NATIONAL DE NANOSTIINTA SI NANOTEHNOLOGIE 6 iunie 2017, Amfiteatrul "I.H. Radulescu", BibliotecaAcademieiRomane;

International conferrences

1. **B. Tincu**, M. Avram, C. Pachiu, E. Chiriac, C. Voitincu, A.C. Costache, Maria-RoxanaMarinescu, "Microfluidic device based on graphene", 43rd International Semiconductor ConferenceCAS 2020- Poster.

2. **Bianca Ţîncu**, Andrei Avram, Marioara Avram, Vasilica Ţucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, Florin Comănescu, Oana Tutunaru, Ioana Demetrescu, THE STRUCTURAL MODIFICATION OF SINGLE LAYER GRAPHENEBY OXYGEN PLASMA TREATMENT, 2nd InternationalConference on Emerging Technologiesin Materials Engineering EmergeMAT, 6-8 November 2019, **Premiul 1**.
3. **B. Tincu**, M. Avram, A. Avram, V. Tucureanu, A. Matei, T. Burinaru, O. Tutunaru, I. Demetrescu, "Influence of polymethyl-methacrylate in graphene functionalization" 21st Romanian International Conference on Chemistry and Chemical Engineering (RICCCE21), S6(New Materials andNanomaterials) – P089, [2019]
4. **B. Ţîncu**, A. Avram, V. Ţucureanu1, A. Matei, C. Mărculescu, T. Burinaru, F. Comanescu, M. Avram, „GRAPHENE BASED ON SEPARATION MEMBRANE", BRAMAT 2019, 11TH INTERNATIONAL CONFERENCE ON MATERIALS SCIENCE & ENGINEERING Transilvania University of Brasov – Romania.
5**. Bianca Tincu**, Andrei Avram, Marioara Avram, Vasilica Tucureanu, Alina Matei, Catalin Marculescu, Tiberiu Burinaru, "Spectroscopic investigation of CVD graphene", ATOM-N 2018, Session Biomedical optoelectronics, Poster PS2-22, OMN100-52, [2018]- **Excellent PaperAward**.
6. **Bianca Ţîncu**, Andrei Avram, Marioara Avram, Vasilica Ţucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, "Graphene post-processing", 8th Conference on Material Science & Engineering (UgalMat 2018), Book of Abstract, p. 66, Section I: AdvancedMaterialsAnd Technologies (TMA2018) Poster Session P55 [12 oct 2018].
7. **Bianca Ţîncu**, Andrei Avram, Marioara Avram, Vasilica Ţucureanu, Alina Matei, Cătălin Mărculescu, Tiberiu Burinaru, Florin Comănescu, Marian Popescu, Ioana Demetrescu, „Investigation of graphene on gold flowers", 1st International Conference on Emerging Technologies în Materials Engineering EmergeMAT and 4th International Workshop on Materials under Extreme Conditions SUPERMAT, Additive manufacturing of metallic and composite materials, Book of Abstracts, No1/2018, p. 72 [nov.2018].
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9. **B. Ţîncu**, A. Avram, V. Ţucureanu, A. Matei, C. Mărculescu, T. Burinaru, B. Bitza, M. Avram, „Importance of post-processing for CVD graphene" BRAMAT 2017, Surface Engineering, Book of Abstracts, IV.PO.12, p.173, Brasov, Romania [2017];
10. **Bianca Ţîncu**, Andrei Avram, Tiberiu Burinaru, Vasilica Ţucureanu, Marioara Avram, Cătălin Mărculescu, Iuliana Gâjâilă, Gabriel Gâjâilă, „CVD Graphene Growth For Antibacterial Study", The 16th International Symposium Prospects For The 3rd MillenniumAgriculture, Section 7: Biotechnologies, Cluj-Napoca, Romania,28-30 septembrie 2017 — Prezentare Orală;

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