*Raport stiintific privind implementarea proiectului in perioada ianuarie – decembrie 2015* Programul: **IDEI** 

Tipul proiectului: Proiecte de cercetare exploratorie

Cod proiect: PCE\_PNII-ID-PCE-2011-3-0522

# *Titlul proiectului:* Giga and tera-watt laser interaction with carbon, tungsten and beryllium films »

# Director de poriect: Dr. Cristian P. LUNGU, INFLPR, Magurele

Obiectiv (5.1): Interactia filmelor compozite ternare (Be-C-W) cu plasma produsa in aer de laserul de mare putere (TEWALAS)

Activitati:

(5.1.1): Caracterizarea depunerilor de Be-C-W inainte de expunerea la fasciculul laser utilizand metodele: AFM, SEM, XPS, XRD, Raman, TDS.

(5.1.2): Caracterizarea depunerilor de Be-C-W dupa expunerea la fasciculul laser utilizand metodele: AFM, SEM, XPS, XRD, Raman, TDS.

(5.1.3): Denumire Activitate: Pregatire prezentari la Conferinte Internationale

(5.1.4): Pregatirea si transmiterea unei lucrari la reviste de specialitate ISI

Obiectiv (6.1): Interactia filmelor compozite ternare (Be-C-W) cu plasma produsa in deuteriu de laserul de mare putere (TEWALAS)

Activitate 6.1.1: Caracterizarea depunerilor de Be-C-W inainte de expunerea la fasciculul laser utilizand metodele: AFM, SEM, XPS, XRD, Raman, TDS

# Rezumat in limba romana

In perioada ianuarie-decembrie 2015, au fost abordate si indeplinite activitatile prevazute in cadrul obiectivului 5.1 respectiv depunerea de filme compozite Be-C-W in configuratie stationara, analiza acestora, pregatirea si publicarea unuor lucrari stiintifice cu cotatie ISI (trei lucrari fata de una singura prevazuta in planul de lucru si trei prezentari la conferinte international, dintre care o lucrare invitata, fata de 2 prezentari prevazute initial). Au fost abordate si indeplinite o parte din activitatile prevazute de obiectivul 6.1 prin decalarea acestora din anul 2016 in anul 2015, conform sumei suplimentare primite in cadrul programului.

Au fost publicate 3 lucrari in reviste cotate ISI si au fost prezentate 3 comunicari la conferinte internationale

# Publicatii in reviste

1. M. Lungu, I. Tiseanu, C. Dobrea, C. Porosnicu, I. Jepu, Preparation and analysis of functional fusion technology related materials, Rom. J. of Phys, 60, (2015), 560-572

2. A. Marcu, F. Stokker, R.R. Zamani, C.P. Lungu, Glancing angle deposition in a pulsed laser ablation/vapor–liquid–solid grow system, *Applied Surface Science*, *327 (2015)*, *262-267* 

3. Marcu, L. Avotina, C. Porosnicu, A. Marin, C.E.A. Grigorescu, D. Ursescu, M. Lungu, N. Demitri, C.P. Lungu, Spatially resolved nanostructural transformation in graphite under femtosecond laser irradiation, *Applied Surface Science*, *355*, (2015, 477-483)

# Prezentari la Conferinte Internationale

1. C. P. Lungu, Ternary composite films interactions with high power laser beam / invited lecture, 15th International Balkan Workshop on Applied Physics and Materials Science/ 2-4 July, Constanta, Romania

2. C. P. Lungu, C. M. Ticos, C. Porosnicu, I. Jepu, M. Lungu, P. Dinca, O. Pompilian, B. Butoi, D. Ursescu, R. Banici, G. Cojocaru, R. Ungureanu, C. Luculescu, A. Marcu, A. Marin, P. Osiceanu, I. Feraru, C. Grigorescu, Plasma plume analysis and the effect of terawatt laser system irradiation on C, W layers/ poster, cc, July 26-31, 2015, Iasi, Romania

3. A.Marcu, M.Lungu, C.Porosnicu, L.Avotina, D.Ursescu, C.A.Grigorescu, C.P. Lungu, A.Marin, G.Kizane and S.Antohe, Laser Irradiation of Materials for Fusion Devices/oral, LAMP 2015, Fukuoka, Japan, March 26-29, 2015

4. C. Porosnicu, I. Jepu, C. Lungu, M. Lungu, P. Dinca, O. Pompilian, I. Tiseanu, Laser Induced Tribological modifications of Composite Layers Obtained by TVA, 15th International Balkan Workshop on Applied Physics and Materials Science, Romania, Constanta, 2-4 iulie 2015, oral presentation

# Detailed report on the implementation of the project during January-December 2015.

#### 1. Introduction

The production of mixed films that simulate re-deposition of materials that may occur in fusion reactors as JET and ITER is of high interest in our days. Production of mixed layers with mechanical and especially tribological characteristics is of great importance for industry. Low Temperature Plasma Physics laboratory produces currently tungsten and beryllium coatings on the first wall tiles used at the JET reactor in Culham, UK. The coating of these materials are few micrometer in thickness and are prepared using the thermionic vacuum arc (TVA) technology. During fusion operation of the ITER reactor mixed films containing Be, C and W layers will be formed due to erosion and redeposition processes that will ocurr during the operation, as it happened in JET. It is a great importance to study these mixed materials in a wide range of relative concentrations from the fuel retention point of view as well as their mechanical properties. We developed a method to simulate either uniform mixed layers formation or a wide range of consentrations that are characterised by X-ray micro-beam fluorescence (µXRF) from the point of view of concentration and using SEM, AFM, XRD, XPS, Raman and RBS methods. Their morphological and structural changes were studied before and after interaction using indirect iradiation produced by plasma ignited by TEWALAS laser in air. The reason the HHF test was performed is that mixed redeposited layers that will form during fuison device operation will be subject to plasma particles that will not be properly confined by the magnetic field and also be suject to plasma disrubtions (ELMs) that induce to these a large amount of energy (kJ) in a short period of time (ns). This was simulated using a laser pulse that had comparable time of operation and local energy.

#### 2. Deposition concept of mixed Be-C-W layers

Using thermionic vacuum arc method mixed films containing Be-C-W were produced using three independent evaporators. Two deposition campaigns were conducted with rotated (as produced for studies related with the **Objective 5.1**) and fixed geometry (as produced for studies related with the **Objective 6.1**). Glass and silicon rectangular substrates of 11 mm x 11 mm were settled on a 320 mm diameter stainless steel probe holder. The distance between the anodes and the sample holder was 210 mm, while the distance between the centers of the probes was kept constant at 19 mm (*Fig. 1*).



Figure 1. dimension specification of probe spatial distribution on sample holder

# 2.1 Samples distribution on the deposition holder

The position of the investigated samples for rotated geometry are marked with blue background; whereas the fixed centre in this case is marked with red background (Table 1). The projections points of the anodes position for the W, Be and C elements are marked with grey background. All indexed samples were subject to micro-XRF measurements. The detection of low-Z elements such as Be or C on a Si substrate is especially difficult because of the presence of much stronger W fluorescence signals at 8.39, 9.67 keV that creates an Raman scattered background signal.

			Be											
						7.3	8.3							
					6.4	7.4	8.4	9.4						
				5.5	6.5			9.5	10.5					
			4.6	5.6					10.6	11.6				
		3.7	4.7	5.7	6.7					11.7	12.7			
	2.8	3.8	4.8			7.8	8.8				12.8	13.8		
	2.9	3.9						9.9	10.9			13.9	14.9	
W	2.10	3.10								11.10	12.10		14.10	С
	2.11	3.11	4.11	5.11	6.11	7.11	8.11	9.11	10.11	11.11	12.11	13.11	14.11	
		3.12	4.12	5.12	6.12	7.12	8.12	9.12	10.12	11.12	12.12	13.12		

Table1. Distribution and marks of the samples on the deposition holder

# 3. Characterizations of the prepared samples

### 3.1 µ-XRF characterization method

The investigation method named micro X-ray fluorescence ( $\mu$ -XRF) technique is a low energy based method (17.5 KeV) using an X-ray excitation source with molybdenum target. The X-ray excitation source with molybdenum target also combines into its experimental setup a specific polycapillary X-ray optics (*Fig. 2*) which determines a focal spot on sample surface in tens of microns range. Applying voltage of 45kV and a current of 700  $\mu$ A as primary working parameters, single point per sample investigation was carried out with at a fixed integration time of 40 sec for fixed geometry samples (total number of 62) respectively 240 seconds integration time for the 5 samples deposited in rotated geometry.



Fig.2 Experimental µ-XRF setup

In order to provide a quantitative result, several calibrated samples were investigates in same conditions and with the same working source parameters. Measured calibration samples for W in the interval 10 - 400 nm on Si allowed the conversion between integrated peak area (*Fig.3*) and layer thickness. These samples were deposited with the TVA method and calibrated using a method based on quartz crystal microbalance technique (QCM).



Fig.3 Tipical analized spectrum with evidenced  $W L\alpha$ ,  $L\beta$  peak of interest

The resulted calibration curve for W could be fitted using a linear fit such as a fit equation

The conversion from layer thickness (nm) to surface atomic concentration (at/cm2) was based on the formula:

$$T(cm) \cdot \rho \left(\frac{g}{cm^3}\right) \cdot \frac{N_A\left(\frac{at}{mol}\right)}{M\left(\frac{g}{mol}\right)} = A_c\left(\frac{at}{cm^2}\right)$$

whereas  $N_A$ =Avogadro number (6.022\*10<sup>23</sup>), *P* material density, T the thickness (cm), M the molar mass of element;

Element	W
Molar mass (g/mol)	183.85
Density (g/cm3)	19.3

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Measurements results for rotated geometry TVA deposited Be-C-W samples in thickness (nm) and two dimensional concentrations of atoms in the film (atoms/cm<sup>2</sup>) (Fig. 4 a,b).

![](_page_6_Figure_0.jpeg)

![](_page_6_Figure_1.jpeg)

Fig.4 a W thickness (nm) variations dependent on the position of the sample related to the fixed center holder

Fig.4 b W atomic concentration (atoms/cm<sup>2</sup>) variations dependent on the position of the sample related to the fixed center holder

![](_page_6_Figure_4.jpeg)

Fig. 5a W spatial deposition expressed in thickness (nm) on Be-C-W samples deposited with TVA method (fixed geometry)

![](_page_7_Figure_0.jpeg)

Fig.5b W spatial deposition expressed in atomic concentration (atoms/cm<sup>2</sup>) on Be-C-W samples deposited with TVA method (fixed geometry)

![](_page_7_Figure_2.jpeg)

Fig.5c W spatial deposition expressed in atomic concentration (atoms/cm2) on Be-C-W samples deposited with TVA method (fixed geometry)

Measurements results for fixed geometry TVA deposited Be-C-W samples in two dimensional concentrations of atoms in the film (atoms/cm<sup>2</sup>) (Fig. 6 a, b, c, d) dependent on the Be, C, W anode projections on the sample holder marked with dots in different color in *Fig.5c*.

![](_page_8_Figure_0.jpeg)

Fig.6.a W at/cm2 in the Be-C W layers between W to Be anode projections (black dots)

![](_page_8_Figure_2.jpeg)

Fig.6.c W at/cm2 in the Be-C W layers between middle distance of W-Be to C anode projections (grey dots)

![](_page_8_Figure_4.jpeg)

Fig.6.b W at/cm2 in the Be-C W layers between W to C anode projections (green dots)

![](_page_8_Figure_6.jpeg)

Fig.6.d W at/cm2 in the Be-C W layers between Be to C anode projections (red dots)

#### 3.2 Rutherford backscattering spectrometry measurements.

Rutherford backscattering spectrometry(RBS) measurements were performed on the Be-C-W layers deposited on silicon substrates with TVA method. For this purpose the 3MV Tandem Accelerator facility available at IFIN-HH was used.

RBS measurements are very useful for providing reliable quantitative information regarding the sample composition and the elements depth profile.

The samples were mounted on a 3-axes goniometer with an accuracy of  $0.01^{\circ}$ . Slits were employed to limit the fascicle divergence to a minimum. The Silicon solid state detector with an energy resolution of 20 kev for He particles was positioned at an angle  $\theta$ =165° in respect with the ion beam. The samples were tilted at an angle of 7° in respect with the beam. A broad beam with dimensions

around 0.5 mm<sup>2</sup> was focused on the samples and monoenergetic He ions with an energy of 3 Mev were used to bombard the sample in order to determine the elemental area density and impurity distribution. The final acumulated charge was  $10\mu$ C. This energy was chosen to be below the threshold of <sup>13</sup>Be composed nuclei formation. These instable isotope decays into more stable <sup>12</sup>Be with the release of a neutron which can activate the materials inside the reaction chamber. It is important to specify that for these measurements no standard or withness sample calibration was needed except the energy calibration. The different atomic species, areal density, elemental deth profile and the layer's thickness were obtained by fitting the simulated spectrum on the experimental one. This was done by using specialized RBS spectrum simulation program SIMRA developed by Matej Mayer.

![](_page_9_Figure_1.jpeg)

Figure 7a Simulated RBS spectra ploted on Be-C-W experimental spectra.

Due to fact that the samples were deposited on silicon substrates the RBS signal for silicon is superimposed on the Beryllium signal and also on the carbon and oxygen signals (fig 7 a). This overlapping doesn't allow a correct simulation and approximation of the concentration for Oxygen, Carbon and Beryllium . In the case of tungsten this method has a very good sensitivity and the simulated spectra fits on the experimental spectra with good precision. The tungsten areal density derived from simulations of the RBS spectrum were listed for all samples in the below table.

Sample index	W: 1E15 Atoms/cm <sup>2</sup>
2_8	471
3_7	489
4_6	415.82
5_5	457.3
6_4	514.95
7_3	322.8
8_3	360.875

8_8	483.8
9_4	374.4
10_5	366.1
11_6	347.6
12_7	301.22
13_8	261.05
14_9	208.6

The position of the RBS investigated sample was in the outer layers of the holder from the W anode projection on the holder to the C anode. In order to observe a tendency for tungsten areal density the above results were plotted as function of sample position between the tungsten-beryllium and beryllium –carbon anode projection (Fig. 7c, 7d).

![](_page_10_Figure_2.jpeg)

Fig.7.b W at/cm2 in the Be-C-W layers between W to Be anode projections

![](_page_10_Figure_4.jpeg)

Fig.7.c W at/cm2 in the Be-C-W layers between Be to C anode projections

Between the W anode projection and Be anode projection (Fig. 7.c)the areal density value has some fluctuation with its peak value for sample 6\_4 but the main tendency is to decrease. In the case of

Be to C anode projection the tungsten quantity shows a obvious decrease (Fig. 7.d) starting from the sample positioned near the Be anode to the lowest value near the C anode. Also a comparison between RBS and  $\mu$ -XRF results was made (Fig .7.e). The values obtained with  $\mu$ -XRF method are in good accordance with the RBS results.

![](_page_11_Figure_1.jpeg)

Fig.7.e Comparison between RBS and µ-XRF results (atoms/cm2)

#### 4. Be-C-W films irradiation and characterizations

Be-C-W (3:2:1) amorphous films were irradiated with three laser wavelengths of 300, 550 and 1350 nm having a comparable energy and respectively power density. Ablated volume and preferential ablation of lighter elements seemed independent of the photon's energy, but rather on their number. Carbon and Be clustering and crystal formation into the amorphous coating were more effective with more energetic photons. Graphite structures were recorded for fluencies below the ablation threshold. For longer laser wavelengths, carbon atoms tend to organize in ring structures and fullerene formation was also recorded around the ablation zones. Be crystals formed in the ablation zone vicinity tend to be stretched toward the film surface and toward the ablation center suggesting more defects into the formed structures for these zones.

Exact atomic ratios of the tested Be-C-W films were 50%; 33% and 17% for Be, C and W, respectively. Film thickness was about 100 nm.

Coating irradiation was performed with a Continuum FX-1 Sunlite Nd:YAG tunable laser, having the pulse length 7 ns and using the burst mode. It was used a  $17.7\pm1.7$  mJ energy/pulse for three different wavelengths 300, 550 and 1350 nm, representing ultraviolet, visible and infrared radiation, respectively. A generic experimental scheme of the experimental system is presented in Fig. 8.

![](_page_12_Figure_0.jpeg)

Fig. 8. Experimental system

One pulse ablated area can roughly be approximated as circular with energy distribution over the irradiated zone described by a Gaussian function in the form of:

$$f(x) = \frac{E_n}{\sigma_x \sqrt{2\pi}} e^{\frac{(x-\mu_x)^2}{2\sigma_x^2}}$$
(1)

where:  $E_n$  is the spot energy,  $\mu_x$  and  $\sigma_x$  are spot center position and respectively dispersion on the axis (approximated with pulse width/6).

Morphology investigation were made by a Scanning Electron Microscopy (SEM) using a 'FEI– INSPECT S' microscope. Raman spectra were recorded using Jasco Raman spectrometer with 532 nm Nd:YAG laser, 633 nm HeNe and 785 nm diode laser. In our experiment, Raman laser parameters for mapping were,  $\lambda$ = 532 nm, exposure time: 30s, accumulations: 3, objective: 20x, resolution: 10 cm<sup>-1</sup> and laser power 3mW.

In a hexagonal graphite single crystal structure correspond to the  $D_{6h}^{4}$  (=P6<sub>3</sub>/mmc) space group. The Raman active mode in graphite (G-peak) at 1581 cm<sup>-1</sup> has  $E_{2g}$  symmetry. In the highly oriented graphite, nanocrystalline graphite and glassy carbon the G-peak does not disperse, (does not change the position with excitation wavelength). With increase of disorder the dispersion of G-peak increases, the position of G-peak increases as excitation energy increases. Dispersion of Raman modes is characteristic for the disorder related (D-peak) in polycrystalline graphite as well. Similar as for the G-peak, position of D-peak increases as increases excitation energy. For excitation energy 1.5 eV the position of D-peak is closing to 1300 cm<sup>-1</sup>, while for excitation energy around 3 eV D-peak position reaches 1380 cm<sup>-1</sup>. For characterization of various carbon materials (disordered graphite, diamond-like carbon materials) another feature from Raman spectra is widely used – the intensity ratio between D- and G-peak (I<sub>D</sub>/I<sub>G</sub>). Tuinstra and Koenig noted that I<sub>D</sub>/I<sub>G</sub> varies inversely with graphite crystallite size L<sub>a</sub>. As well as an increase of I<sub>D</sub>/I<sub>G</sub> correspond to increasing disorder of graphite. In case if L<sub>a</sub> is below 2 nm, the Tuinstra and Koenig relation is not valid and L<sub>a</sub> is proportional to square root of I<sub>D</sub>/I<sub>G</sub>.

For the metals, the surface plasmons limit the penetration of light and therefore the Raman signal usually is extremely weak. However, beryllium with a hexagonal close packed structure is an exception. The hexagonal close packed (hcp) structure allows one Raman-active phonon mode in single crystal 463 cm<sup>1</sup>. The only Raman active mode of the space group of Be lattice  $D_{6h}^4$  is  $E_{2g}$ . In polycrystalline beryllium the signals are observed at 455 cm<sup>-1</sup> (514 nm) and 457 cm<sup>-1</sup> (488 nm).

Raman spectra were measured using three different wavelengths – 532, 633 and 785 nm. From Beer-Lambert law with increasing wavelength it also increases the penetration depth. For carbon the penetration depth of 532 nm is around 50 nm and for 633 nm -  $\sim$ 70 nm. Respectively with 633 and 785 nm laser additional information about deeper layers of the BeCW coating can be obtained. However, in Raman spectra measured with 532 and 633 nm beryllium signal is quite intensive and narrow, in Raman spectra measured with 785 nm the signal/noise ratio being too low to distinguish a beryllium signal.

**FT-IR spectroscopy** measurements were performed with a Perkin Elmer Spotlight 400 FT-IR apparatus. The measurements were made in reflection mode with accumulations: 20, aperture 10, objective: 20x, resolution:  $2 \text{ cm}^{-1}$  and recorded spectra between 450 and 1500 cm<sup>-1</sup>.

**X-ray Photoelectron Spectroscopy (XPS)** - analysis was used to determine the chemical states of the elements present on the surface and, after quantitative analysis, to find out the element and the chemical state relative concentrations, as well. After scanning survey XPS spectra, the high resolution photoelectron spectra of the most prominent XPS transitions (C1s, O1s, Be1s and W4f) were recorded.

It is appropriate to note here that all the calculations were performed assuming that the samples were homogeneous within the XPS detected volume (<10nm). We have to emphasize that the errors in our quantitative analysis (relative concentrations) were estimated in the range of  $\pm$  10 %, while the accuracy for Binding Energies (BEs) assignments was  $\pm$  0.2 eV.

![](_page_13_Figure_4.jpeg)

Fig. 9 Be1s and W4f XPS depth profile spectra.

XPS method was used to establish the chemical states of the elements present on the surface and subsurface region and after quantitative analysis to find the element and chemical state relative concentrations. Fig. 9 shows the high resolution depth profile spectra of Be1s and W4f from a Be-C-W mixed film prepared by TVA method. The metallic feature among oxides of beryllium can be detected).

The W4f core level spectra display also the metallic contribution. A broadening of W4f photoelectron peak is primarily due to a mixture of different tungsten chemical species.

**X-ray diffraction (XRD)** analysis The structural and compositional properties of the samples were investigated by regular and Grazing Incidence X-Ray diffraction (XRD). The measurements have been performed at room temperature with a Bruker type (AD 8 ADVANCED) diffractometer using Cu(K<sub> $\alpha$ </sub>) radiation ( $\lambda_{K\alpha} = 0.154$  nm).

The XRD spectra rewealed the crystalline structure of the film in the zones with high W content

![](_page_14_Figure_2.jpeg)

Fig. 10 XRD typical spectrum

Among the metallic crystalline structure of W, was observed an intermettalic phase of BeW, as shown in Fig.10.

#### 5. Results

During laser irradiation in the central part of the ablated areas, the coating is partially or completely removed and silicon substrate is uncovered and even damaged. Electron microscopy images of the irradiated surfaces are presented in the Fig. 11. As could be seen in the inset presenting the center of the ablation zones, after irradiation with 300 nm, in the central part the coating is removed and the substrate and the damaged Si surface is rather rough. For the 550 nm pulse, the central part of irradiated spot is also affected, but, as can be seen in inset of the Fig.11, the surface is more smooth than for 300 nm pulse, while the spot size is larger. After 1350 nm irradiation seems to be less increased in comparison with 300 and 550 nm zones. The surface modification seems to be less intense than for visible and UV pulses. Unlike for the other two wavelengths, some structures seems to be present in central part of irradiated spot, as can be seen in inset of 1350 nm irradiated spot area. Further from the central part and exfoliation of Be-C-W coating from Si, where the substrate was less affected by the laser pulse, a change in the coating color is visible around all spots, but without significant changes in the morphology, suggesting the presence of structural modification for these zones.

![](_page_15_Figure_0.jpeg)

#### Fig. 11. SEM images of irradiated spot areas 300, 550 and 1350 nm

The elemental composition in the irradiated areas were analyzed by energy dispersion X-ray spectroscopy (EDX) and comparative results for the three film constituents over the three spots are presented in Fig. 12.

![](_page_15_Figure_3.jpeg)

Fig. 12 EDX analysis of element distribution on the ablation spots for: a) beryllium, b) carbon, c) Be, C and W variation over the 300 nm irradiation spot and d) element distribution on the ablation spots for tungsten

As visible in Fig. 12a in the central part of irradiated areas the amount of beryllium is decreased. The EDX results confirm the SEM results regarding dependence of the size of the ablated areas on the

laser wavelength. The strongly affected area is having a smaller diameter for the shorter irradiation wavelengths. As can be seen in Fig.12a, for 300 nm spot close to edge of ablated area and around it, appear some sharp changes in the recorded amount of beryllium. For longer wavelengths, respectively for 1350 nm pulse spot, the change in Be amount is less sharp than for 300 and 550 nm spots.

Carbon ablation after irradiation with 3 different wavelengths is inhomogeneous. In all three cases amount of carbon is decreasing towards central part of irradiated area. However, in all cases a slight increase on edges of the ablated area and few peaks in the central zones are visible (Fig. 12b). The agglomeration effect in the central part and on the edges of the central part seems to be more intense for 300 nm pulse spot than for other wavelengths. However, for the 1350 nm spot, the amount of carbon even increases somewhere in the middle of the irradiated spot, supporting a diffusion or redeposition process.

It should be further emphasized that carbon distribution is in most of the zones, comparable but less uniform with the beryllium distribution. While comparing the Be and C distribution for the 300 nm irradiated zone (Fig.12c) the peaks are mostly fluctuating together. However, the carbon increase near the ablation zone edges and two more individual peaks marked on the image do not have a correspondent in the Be peaks. In one case it even corresponds to a decrease of the Be. Thus, we can not talk about a 'preferential' ablation of the carbon in some zones but rather about a carbon cluster formation through re-deposition or diffusion processes, that takes place in these zones. The presence of such clustering in the presence of high temperature generated by the photonic interaction suggest possible formation of C and Be structures in these zones.

In contrast to Be and C behavior, relative amount of tungsten in the central part of ablated areas is higher than in non-ablated parts (Fig.10d). Since the W concentration is about 1/6 in the initial coating, the increased amount of tungsten in the central parts of the irradiated spots shows preferential ablation of beryllium and carbon in comparison with tungsten, while the slight decrease in amount of tungsten in some points of the central parts of the spot are correlated with the inhomogeneous distribution of carbon in those zones.

By using both SEM and EDX results and approximating the energy distribution on a beam diagonal we were estimating the ablation threshold for the three laser wavelengths. In the case of the SEM images we mediated the diameter of the ablation on the spot diagonal on several direction, while from the EDX data were measured the distances between the sharp edges of the C and Be spatial variations. The obtained results are presented in Fig 13, together with an averaged curve for all obtained results.

If we roughly estimate the number of atoms in film and divide the number of photons per number of atoms in the film volume, we obtain the dependence of the ablation threshold (in this case for a complete 100 nm film removal) on the incident number of photons per atom presented in the inset of the Fig. 11.

![](_page_17_Figure_0.jpeg)

Fig.13. Ablation threshold (for a 100 nm film removal) dependence on the laser wavelength, estimated from SEM and EDX results. Inset: threshold number of photons/atoms as a function of laser wavelength.

As could be seen, the efficiency of the photons is quazi-linearly decreasing with the photon energy for the given film thickness of about 100 nm. However, since the material is extracted from a smaller area for shorter beam wavelength we could conclude that overall, the more energetic photons are depositing more energy out of the beam into the substrate. Thus, it should be natural to expect more structural modifications for shorter radiation wavelengths induced the injected energy.

Spot trace of the 300 nm beam, was investigated by Raman spectroscopy using a 532 nm Raman laser wavelength on a 2D matrix points presented in Fig.14a. Thus, Raman measurements were performed with a 40  $\mu$ m step, covering an area of 640x440  $\mu$ m. A highlighted area in optical microscope image corresponds to the uncovered Si substrate. From each Raman spectrum the intensity of Be peak of a E<sub>2g</sub> mode was obtained and the be peak intensity values were plotted accordingly to the previously settled matrix in Fig.5b. We noticed, that the Be peak intensity variation shows significant similarities with the optical image. Peak intensity decreases towards the central part of ablated area. However, some signs of Be presence can be seen in zones, where substrate is highly modified (ablated), as well. That shows some Be migration or re-deposition processes in the areas with a higher surface roughness.

![](_page_18_Figure_0.jpeg)

Fig. 14. a) Optical image of 300 nm irradiated spot area with a matrix for Raman mapping, b) Be peak intensity from Raman spectra

While examining the Be peak position in Raman spectra, we noticed that Raman shift of Be peak decreases towards the center of irradiated spot. A Be peak Raman shift map is represented in Fig. 15a. Around the ablated zone, Be peak Raman shift value is as low as 441 cm<sup>-1</sup>. With increasing the distance from ablated are Be peak value increases up to 447-449 cm<sup>-1</sup>.

![](_page_18_Figure_3.jpeg)

Fig.15. Be peak position in Raman spectra a) around edges of ablated spot, b) from the edge of ablated area

Raman measurements with a step of 100  $\mu$ m were further extended from the ablated zone edge. In order to obtain in depth information of Be structure, two different Raman laser wavelengths were used – 532 and 633. The obtained results are represented in Fig.6b. It can be seen that on the edge of ablated area Be peak Raman value is lower than at larger distances from the ablated zone. We emphasize a tendency of more decreased Be peak value with a shorter Raman laser wavelength. That shows a higher influence of the irradiation on the superficial layers. Nevertheless, a slight trend in decreasing of Be peak position with the decrease of irradiation laser wavelength is visible in inset of Fig.15b. This shows that shorter irradiation wavelength produces more distorted Be crystals. One possibility would be a higher transferred energy to the non-ablated material generating more diffused material (e.g. carbon) or Be bonds (e.g. BeO, since the irradiation was performed in air)

In the Raman spectra mapping, carbon related peaks were observed as well. Around 1500 cm<sup>-1</sup> was observed a peak, assigned as graphite G-peak, present in graphitic and disordered carbon materials. G-peak arises in the same mode as in Be structure,  $E_{2g}$  mode vibrations. The size of the graphite crystallites is estimated to about 1.6 nm (+/- 0.4 nm) with no particular trend variation. (However we should mention that the due to the noise spectra, reasonable estimation could be made only for deeper layers by using the 785 nm Raman laser wavelength.) The variation of full width in half maximum (FWHM<sub>G</sub>) of this peak is shown in Fig.16a. G-peak is hardly visible in the central part of irradiated spot in spite of the carbon presence shown in the EDX measurement. This suggest that in the central area, agglomerated carbon is hardly forming crystals. Towards the edges of the ablated zone, a decrease in FWHM<sub>G</sub> occurs. At larger distances from the edge of ablated area was investigated with different Raman laser wavelengths as well.

![](_page_19_Figure_2.jpeg)

Fig.16. Full width in half maximum of G-peak a) around edges of ablated spot, b) from the edge of ablated area

As seen in the image 16b) there is decreasing trend toward the ablation zone only for the 300 nm spot and only on the surface. All other curves present no clear trend in spatial variation of the FWHM of the G-peak. However, closer to the surface (analyzing with 532 nm), G-peak is very broad (Fig.16b) comparing with deeper layers. Such information was obtained by infrared, 785 nm Raman laser. Thus, it seems that the carbon tend to form graphite structures in the vicinity of the ablation zone, but, on the surface they tend to have defects. Somehow, more energetic photons manage to prevent that even on the surface but only in the ablated zone close vicinity.

FT-IR investigations were made in order to analyze the chemical composition of the irradiated surfaces. Main FT-IR results are represented in Fig.17.

![](_page_20_Figure_0.jpeg)

Fig.15. SEM images of 300, 550 and 1350 nm irradiated areas with points where specific structure's spectra were observed

A broad peak 900-1000 cm<sup>-1</sup> correspond to C=C sp<sup>2</sup> deformation vibrations (Fig.17) and they are tend to be present for 550 nm irradiation wavelengths from the edge of the ablation zone, while for the 1350 nm only further from the central zone. Peaks at 810, 850 and 900 cm<sup>-1</sup> show to presence of SiC and they tend to be present in all the spectra. They suggest a reaction between the carbon and the substrate. Signals in range 1000-1200 cm<sup>-1</sup> approve the presence of BeO in the ablation zone periphery. As also seen in the Fig.17, by FT-IR mapping, fullerene C<sub>60</sub> peaks were observed in the vicinity of the 550 nm irradiated area and at bigger distances for 1350 nm irradiation area, while for the 300 nm there were only some possible signals from the Raman investigations. It should be mentioned that the small Raman peak could also be attributed to this structure since a peak ~1450cm<sup>-1</sup> could correspond to a shifted fullerene C<sub>60</sub> peak. Thus, for this laser irradiation wavelength, the presence of the fullerene is also very probably among the other formed structures. Actually by FT-IR mapping for the 1430 cm<sup>-1</sup>, (that corresponds to C-C stretch in ring) the data presented in Fig. 18 were obtained. Thus, after laser irradiation, carbon atoms tend to organize in ring like structures, leading to graphitization but also possible formation of spherical structures as fullerene-like particles.

![](_page_21_Figure_0.jpeg)

Fig.18. 1428 cm<sup>-1</sup> peak reflection mapping for 300 nm laser wavelength trace on the Be-C-W film

# 6. Conclusions

While irradiating beryllium-carbon-tungsten coatings with different wavelengths, the ablation efficiency depends on number of photons rather than their energy, and higher energetic photons will mainly deposit more energy into the coating enhancing structural modification as observed for 300 nm beam in comparison with the 1350 nm one. In the mixture of beryllium-carbon and tungsten a preferential ablation of beryllium in comparison to other elements takes place. The less affected element by laser irradiation is tungsten.

In the ablation zone vicinity, irradiated below the ablation threshold, through the injected energy and carbon diffusion, Be and C structures are formed. After laser irradiation, carbon atoms tend to organize in ring structures, but fullerene structures are mostly present for the more energetic photons of 300 nm. Present in the ablation zone periphery for all irradiation wavelengths are graphite (distorted) structures. In general, all the structures are more distorted closer to the surface than in depth. Be forms metallic structure and BeO could be seen in the ablation zone periphery but also for more energetic photons of 300 nm.

#### 7. DISEMINATION

The activities provided in the frame of the project were successfully accomplished. The scientific results were disseminated by presentations (invited lecture, oral, poster) in international conferences, workshops and pub; ications in ISI ranked journals as mentioned below:

Article titleJournalAuthors namesISI impact	1 1 /	5			
	Article title	Journal	Authors names	ISI	impact

			factor
Preparation and analysis of	Rom. J. of Phys,	M. Lungu, I. Tiseanu,C.	0.924
functional fusion technology	60, (2015), 560-	Dobrea, C. Porosnicu, I.	
related materials	572	Jepu,	
Glancing angle deposition in a	Applied Surface	A. Marcu, F. Stokker, R.R.	2.771
pulsed laser ablation/vapor-	Science, 327	Zamani, C.P. Lungu	
liquid-solid grow system	(2015), 262-267		
Spatially resolved nanostructural	Applied Surface	A. Marcu, L. Avotina, C.	2.771
transformation in graphite under	Science, 355,	Porosnicu, A. Marin,	
femtosecond laser irradiation	(2015, 477-483	C.E.A. Grigorescu, D.	
		Ursescu, M. Lungu, N.	
		Demitri, C.P. Lungu	

Presentation title	Conference	Authors names
Ternary composite films	15th International Balkan	C. P. Lungu
interactions with high	Workshop on Applied	
power laser beam / invited	Physics and Materials	
lecture	Science/ 2-4 July,	
	Constanta, Romania	
Laser Induced	15th International Balkan	C. Porosnicu, I. Jepu, C. Lungu, M.
Tribological modifications	Workshop on Applied	Lungu, P. Dinca, O. Pompilian, I.
of Composite Layers	Physics and Materials	Tiseanu
Obtained by TVA,	Science, Romania,	
	Constanta, 2-4 iulie 2015	
Plasma plume analysis and	32nd ICPIG, July 26-31,	C. P. Lungu, C. M. Ticos, C. Porosnicu,
the effect of terawatt laser	2015, Iasi, Romania	I. Jepu, M. Lungu, P. Dinca, O.
system irradiation on C, W		Pompilian, B. Butoi, D. Ursescu, R.
layers/ poster		Banici, G. Cojocaru, R. Ungureanu, C.
		Luculescu, A. Marcu, A. Marin, P.
		Osiceanu, I. Feraru, C. Grigorescu
Laser Irradiation of	LAMP 2015, Fukuoka,	A.Marcu, M.Lungu, C.Porosnicu,
Materials for Fusion	Japan, March 26-29,	L.Avotina, D.Ursescu,
Devices/oral	2015	C.A.Grigorescu, C.P. Lungu, A.Marin,
		G.Kizane and S.Antohe