

PREPARATION AND CHARACTERIZATION OF ZNO THIN FILMS BY PLD AND HIPIMS

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ZnO thin films were deposited on Si (100) and SiO₂ substrates using two different techniques: high-power impulse magnetron sputtering (HiPIMS) and pulsed laser deposition (PLD). The structure and morphological characteristics of the obtained thin films were compared, along with the optical characteristics. The specific advantages and disadvantages of each deposition technique are presented.

Keywords: pulsed laser deposition, high-power impulse magnetron sputtering, ZnO, thin films, XRD.

1. Introduction

Modern condensed matter physics increasingly deals with the synthesis, analysis and applications of complex materials produced in the form of thin films. Research on the processing of materials has shown that physical and chemical properties of thin films are more different from the bulk material. The parameters linked directly with the growth process of the thin film are: the nature and energy of incoming particles and surface nature, the absorbed particles energy on the substrate (substrate temperature), physical and chemical interactions between atoms and substrate/coating. These parameters are highly dependent on the synthesis method and they have a decisive role on the morphology and texture of the thin film.

ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group, n-type, with a band gap of ~ 3.37 eV at 300 K [1] due to the large difference between the mass of the zinc atom and the oxygen atom. The range of applications for this material is extremely broad from gas sensors, cantilevers,

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solar cells to common applications such as field effect transistors or LCDs (liquid crystal displays) [2-5].

ZnO thin films are typically deposited using techniques such as thermal evaporation [6], metal organic chemical vapour deposition [7], sol-gel [8], molecular beam epitaxy (MBE) [9] and PLD [10].

High quality ZnO films required for device manufacturing are typically deposited using PLD, but in the present work we've managed to obtain similar ZnO thin films using high-power impulse magnetron sputtering. The PLD and the HiPIMS setup were custom build in order to better suit our needs. The innovative feature of the HiPIMS setup consists in controlling the deposition process by managing the sputtered material losses. This is possible by exploiting one of the main advantages of the HiPIMS process, namely the high degree of ionization of the sputtered material obtained in the discharge. Despite neutral atoms, the ions of the sputtered material can be controlled by electric and/or magnetic fields. Additionally to the magnetic confinement inherent to the magnetron cathode, a secondary magnetic field is applied. Thus, due to the successful combination of the pulsed power supply with the additional magnetic confinement, the sputtered material losses at the walls are considerably reduced.

2. Experimental method and results

For the PLD experiment we have used a UV KrF* ($\lambda = 248$ nm, τ_{FWHM} aprox. 25 ns) excimer laser source, operated at 3.1 J/cm^2 incident fluence value, target diameter 1". Before each deposition event, the vacuum chamber was evacuated down to a residual pressure lower than 10^{-4} Pa. The chamber walls were also heated up to 70°C for 15 minutes in order to facilitate the desorption of water vapors and other possible contaminants. The ZnO target was made of 99.9% pure commercial ZnO raw powder. After pressed at 20 MPa into pellets they were sintered in air at 1100°C for 8 h. The precleaning treatments were addressed both to target and substrates. The substrates were cleaned in acetone, alcohol and deionized water in an ultrasonic bath for 15 minutes each. The target surface was cleaned by applying 3000 laser pulses. A shutter was interposed between the target and substrate during the cleaning process. For avoiding the drilling effect and uniform surface usage, the target was submitted to a rotational movement at a frequency of 2 Hz. The distance between the target and the substrate was fixed at 50 mm and at an angle of 45° . The films were grown by applying 15,000 and 25,000 subsequent laser pulses on the undoped ZnO target. The depositions were performed in a uniform dynamic oxygen flow of 10 and 20 Pa monitored by an MKS 50 controller. The substrates were deposited at RT and at 500°C . The used substrates were SiO_2 and Si (100).

For the HiPIMS setup, we have used a circular magnetron, target diameter 2", magnetic field induction at the target surface of 1000 Gauss, a high voltage pulse generator for HiPIMS technology, power density: $0.5\text{--}10\text{ kW cm}^{-2}$, adjustable pulse duration 2- 50 μs , adjustable pulse period between 0.2 and 6 ms, with a response time of less than 500 nanoseconds. The depositions were performed in a uniform dynamic flow of 2 Pa monitored by an MKS 50 controller. There were two gases used, Ar and O₂ at different ratios 1:1 and 4:1. The pulse duration was set to 5 μs , at different frequencies (0.6, 0.75, 1.2 and 1.5 kHz). The average power was set to 50 and 100 W, the deposition time was one hour and the substrates were heated up to 500°C and placed at a distance at 50 mm from the target [11-12]. The external magnetic fields, created by the exterior coils were set to the following values: $B_j=300\text{ Gauss}$ and $B_s=100\text{ Gauss}$ (Fig. 1).

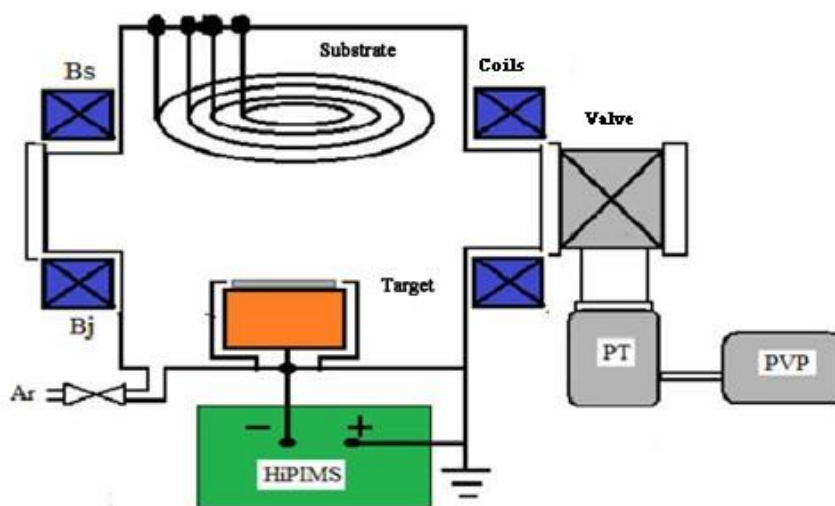


Fig. 1 Block diagram for the HiPIMS setup

In table 1 and 2 we have summarized the deposition conditions for the PLD and HiPIMS experiments.

Table 1

Deposition conditions for the PLD experiment

Name	Temp.(°C)	O ₂ pressure [Pa]	Number of pulses
ZnO1P	500	10	25000
ZnO2P	rt	10	25000
ZnO3P	rt	20	25000
ZnO4P	500	20	25000
ZnO5P	rt	10	15000
ZnO6P	500	10	15000
ZnO7P	500	20	15000
ZnO8P	rt	20	15000

Table 2

Deposition conditions for the HiPIMS experiment

Name	Ar/O ₂	Frequency [kHz]	Average power [W]
ZnO1H	4/1	0.75	50
ZnO2H	4/1	1.5	100
ZnO3H	1/1	0.6	50
ZnO4H	1/1	1.2	100

According to the diffraction patterns from Fig. 2 the ZnO thin films obtained by PLD have a preferential growth direction in the (002) direction and for the HiPIMS thin films we have two preferential growth directions, namely (100) and (101) (Fig. 3). In both cases the films are polycrystalline, even those obtain at room temperature. The XRD analysis reveal a high (002) textured structure for the PLD films and the diffraction line for the 34,4° confirms the stoichiometry and the crystallinity of the nanostructures. The grain sizes are between 15 and 80 nm.

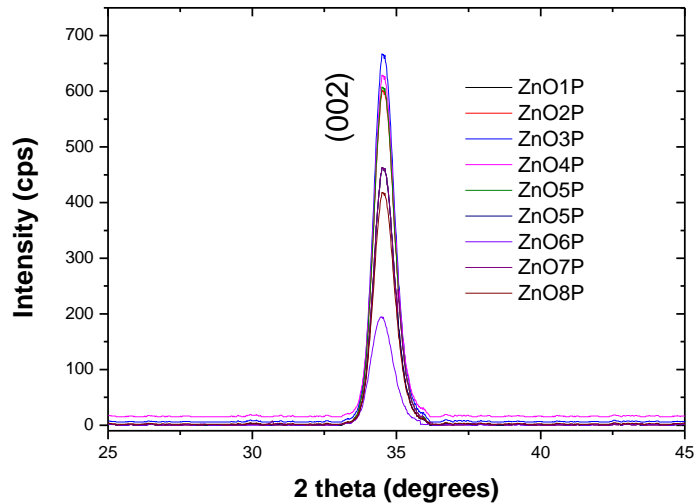


Fig. 2. XRD diffraction pattern for PLD films

The lines attributed to the reflection planes (100), (002) and (101), respectively, 31,7°, 34,4° and 36,2° shows that lowering the average power we will have an attenuation on the (100) and (101) reflection planes especially.

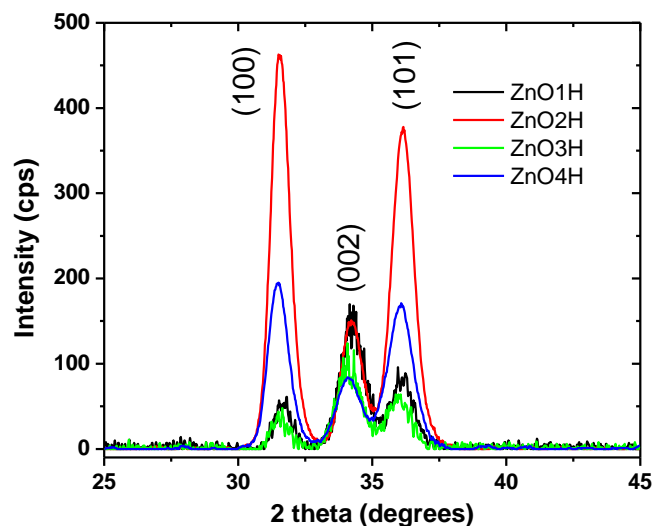


Fig. 3. XRD diffraction pattern for HiPIMS films

The XRD analysis was done with a Shimadzu D6000 system and for the SEM analysis we have used FEI Inspect S. For the ZnO4P and ZnO1P films we have obtained a relatively smooth surface, uniform and with a low density of drops. ZnO8P has craters and droplets, ZnO2 and ZnO7 have a granular morphology and films ZnO3P, ZnO5P and ZnO6P are revealing a particular morphology. The surface has a repetitive structure of segments, similar with ZnO nanowires (Fig. 4). The ZnO1H film is similar with ZnO4P, both having smooth and uniform surfaces. ZnO2H has a scales type structure and ZnO3H and ZnO4H are revealing a rough surface, mainly due to Ar/O₂ flow ratio and we can easily see exploded target parts deposited on the substrate (Fig. 5).

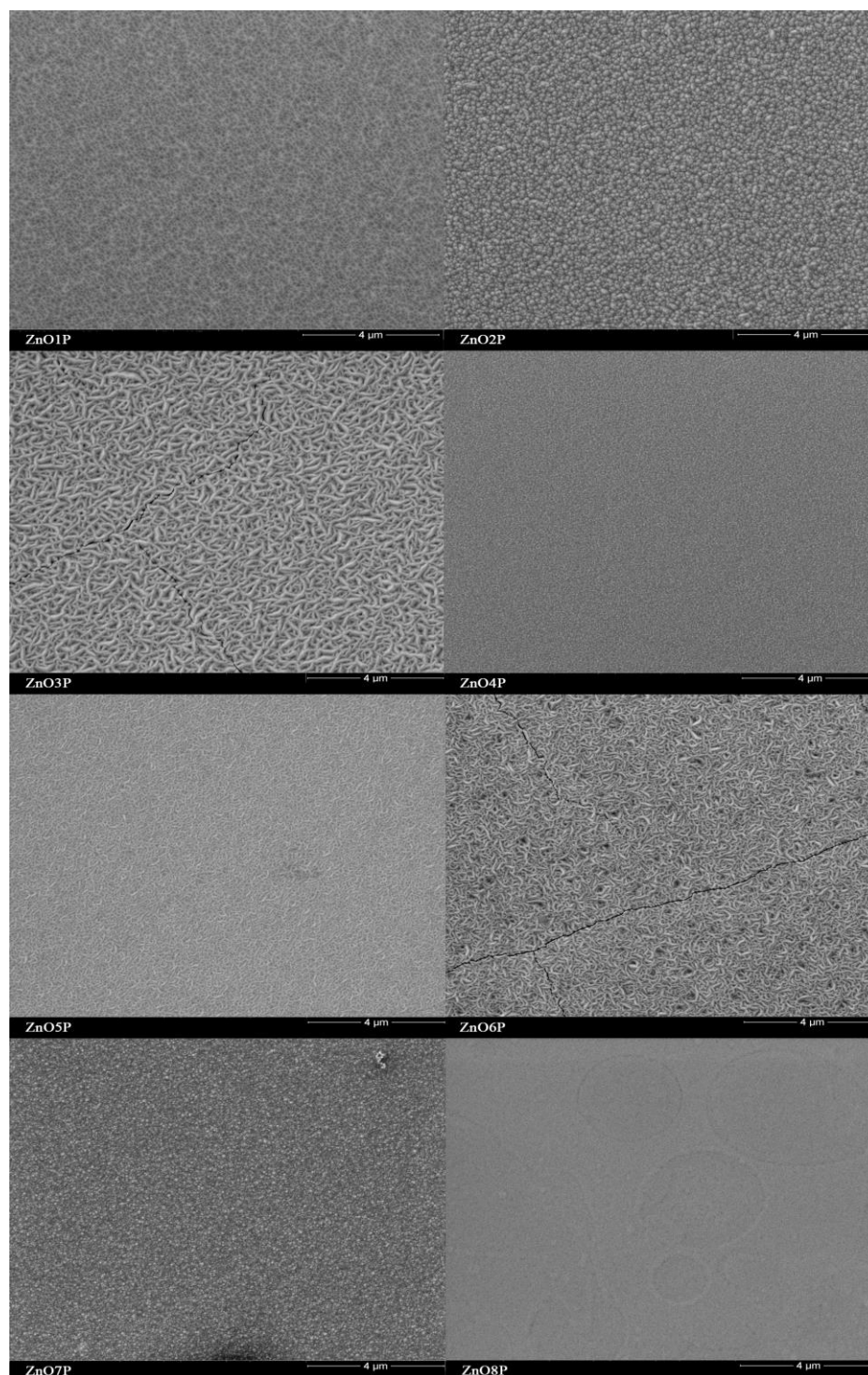


Fig. 4. SEM images for the PLD films

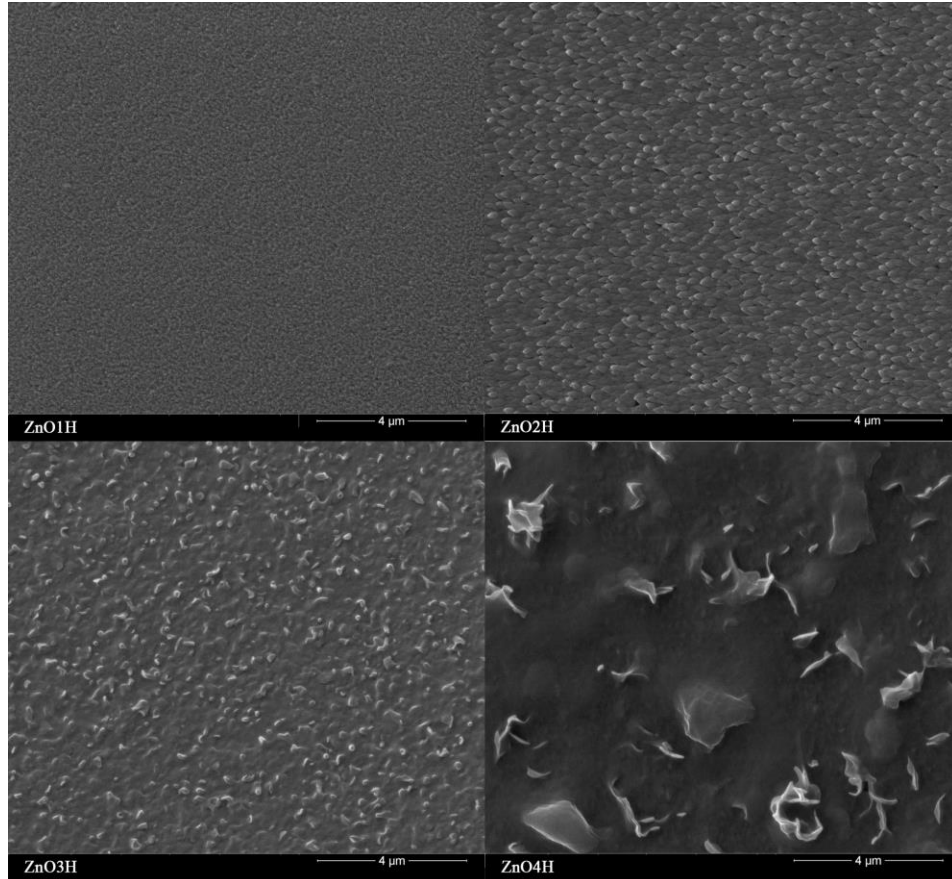


Fig. 5. SEM images for the HiPIMS films

The optical properties were investigated with an Evolution 300 UV-Vis spectrophotometer equipped with a holographical diffraction grating with 1200 lines/mm. Most of the PLD films show a good transmittance, reaching even 90% in the visible and NIR region and sharp absorption edge at about 380 nm, indicating high crystal and optical quality. The exceptions are films ZnO1P and ZnO3P and one of the main reasons is that due to the high number of applied laser pulsed the films are quite thick. Films ZnO2P and ZnO4P were deposited using the same amount of laser pulses, but due to the O₂ pressure and substrate temperature their transmittance is much higher (Fig. 6).

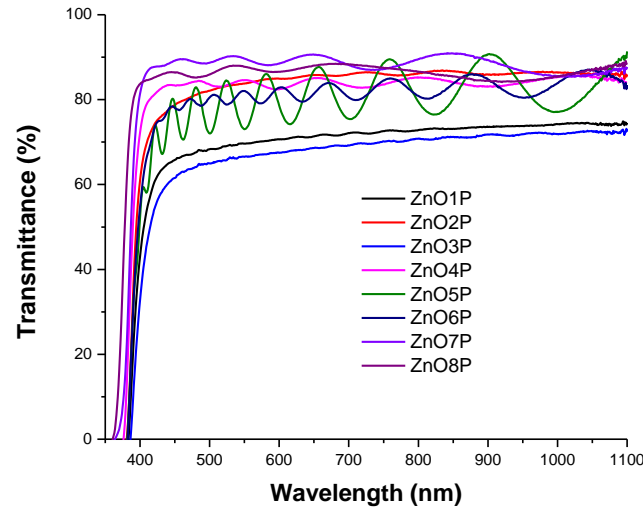


Fig. 6. Transmittance spectra of ZnO films grown by PLD

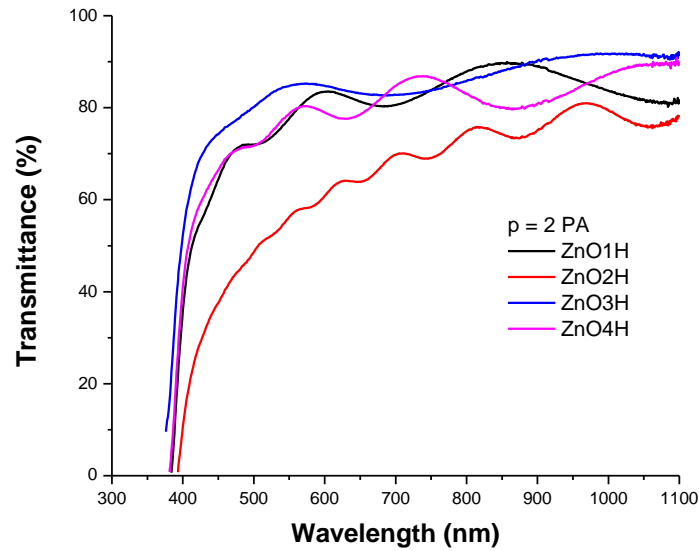


Fig. 7. Transmittance spectra of ZnO films grown by HiPIMS

The HiPIMS films are showing a good transmittance, but still quite different for the PLD films. For ZnO3H we see a transmittance spectrum is shifted to higher wavelengths (Fig. 7).

3. Conclusions

The XRD patterns of ZnO films grown by PLD shows no other peaks except (002). The ZnO films are strongly c-axis oriented and the increasing of

substrate temperature is in favor to the diffusion of atoms absorbed on the substrate. This also accelerates the migration of atoms to a favorable energy positions, inducing a strong crystallinity and c-axis orientation. The situation is different for the ZnO films grown by HiPIMS, but nevertheless the results are more than comparable.

The SEM images shows that in both cases we have high quality films, that are compact and in some cases a granular, polycrystalline morphology which is in good agreement with the XRD analysis.

The optical absorption at absorption edge corresponds to the transition from valence band to the conduction band, while the absorption in the visible region relates to some local energy levels caused by intrinsic defects. A higher transmittance in visible spectra reveals that the film has less defects and better crystallinity. This is one of the main reasons why PLD films are of better quality in terms of transmittance than HiPIMS films. These results are in good agreement with the XRD analysis.

REFERENCES

- [1]. *Satishchandra B. Ogale*, Thin Films and Heterostructures for Oxide Electronics, Springer, 2005, pp. 303.
- [2]. *O. Lupan, S. Shishiyanu, V. Ursaki, H. Khallaf, L. Chow, T. Shishiyanu, V. Sontea, E. Monaico, S. Railean*, Synthesis of nanostructured Al-doped zinc oxide films on Si for solar cells applications Solar Energy Materials & Solar Cells 93 (2009) 1417–1422
- [3]. *L. Oleg, L. Chow, S. Shishiyanu, M. Eduard, T. Shishiyanu, V. Sontea, B. Roldan Cuenya, A. Naitabdi, S. Park, A. Schulte*, Nanostructured zinc oxide films synthesized by successive chemical solution deposition for gas sensor applications, Materials Research Bulletin 44(1):63-69 · January 2009
- [4]. *Zhong Lin Wang*, Zinc oxide nanostructures: growth, properties and applications, J. Phys.: Condens. Matter 16 (2004) R829–R858.
- [5]. *Byeong-Yun Oh, Min-Chang Jeong, Tae-Hyoung Moon, Woong Lee, Jae-Min Myoung, Jeoung-Yeon Hwang, Dae-Shik Seo*, Transparent conductive Al-doped ZnO films for liquid crystal displays, J. Appl. Phys. 99, 124505 (2006).
- [6]. *Kumar, MS; Chhikara, D; Srivatsa, KMK*, Structure-controlled growth of ZnO nanonails by thermal evaporation technique, CRYSTAL RESEARCH AND TECHNOLOGY, 09/2011, Volume 46, Issue 9.
- [7]. *Y. Liu, C. R. Gorla, S. Liang, N. Emanetoglu, Y. Lu, H. Shen, M. Wraback*, Ultraviolet detectors based on epitaxial ZnO films grown by MOCVD, Journal of Electronic Materials, January 2000, Volume 29, Issue 1, pp 69-74.
- [8]. *Ivanova, T; Harizanova, A; Koutzarova, T; Vertruyen, B*, Study of ZnO sol–gel films: Effect of annealing, Materials Letters, 2010, Volume 64, Issue 10.
- [9]. *F. Vigue, P. Vennegues, S. Vezian, M. Laugt, J.-P. Faurie*, Defect characterization in ZnO layers grown by plasma-enhanced molecular-beam epitaxy on (0001) sapphire substrates, Appl. Phys. Lett. 79, 194 (2001).
- [10]. *V. Craciun, C. Martin, G. Socol, D. Tanner, H. C. Swart, N. Becherescu, D. Craciun*, Optical properties of amorphous indium zinc oxide thin films synthesized by pulsed laser deposition, Applied Surface Science 306:52-55 · July 2014.

- [11]. *V. Tiron, I-L. Velicu, F. Ghiorghiu and G. Popa*, „The effect of the additional magnetic field and gas pressure on the sheath region of a high power impulse magnetron sputtering discharge”, *Romanian Reports in Physics*, 67 (2015) 1004-1017.
- [12]. *Jouan, PY; Le Brizoual, L; Ganciu, M; Cardinaud, C; Tricot, S; Djouadi, MA* HiPIMS Ion Energy Distribution Measurements in Reactive Mode *IEEE TRANSACTIONS ON PLASMA SCIENCE*, 11/2010, Volume 38, Issue 11