DEVELOPMENT OF PLASMA AND ION BEAM TECHNOLOGY FOR MATERIAL ENGINEERING AT NCBJ

K. Nowakowska-Langier

Plasma/Ion Beam Technology Division (FM2), Material Physics Department (DFM), National Centre for Nuclear Research (NCBJ), Otwock-Świerk, Poland

E-mail: k.nowakowska-langier@ncbj.gov.pl

The Plasma/Ion Beam Technology Division is one of several laboratories forming the Material Physics Department at the NCBJ in Świerk, Poland. Scientific activity of the Division concerns different aspects of research related to material engineering, surface engineering, functional properties characterization, as well as synthesis and modification of different materials.Plasma surface engineering methods like cathodic arc UHV deposition and pulsed magnetron sputtering methods as well as ion beam implantation methods are intensively exploited and developed in our laboratory.

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INTRODUCTION

The main tools used by our research groups in The Plasma/Ion Beam Technology Division are plasma and plasma-related techniques. The plasma surface engineering, as an important scientific field investigated at the laboratory, allows improve, modify and develop modern and unique methods of the material synthesis. The investigations include also research on plasma diagnostics, which is important and indispensable part of studies performed by our teams. Basic features of plasma-surface interactions, as well as the characteristics of the plasma generation in various experimental and technological facilities, are studied extensively [e.g. 1-6]. Other very important tools used in our research are ion- and electron-beams produced by various implantation devices. These corpuscular beams are considered as a promising technique for modifications of a material structure, and synthesis of non-equilibrium structures [e.g. 7-11].

Innovative work is being carried out related to the development of surface engineering, including the synthesis of layers of different materials e.g. metallic, oxide and nitride layers, multi-component and composite layers [12-14]. Plasma surface engineering methods are used like cathodic arc UHV deposition and pulsed magnetron sputtering methods as well as ion/electron implantation methods. In case of our methods we still need some improvements and changes or adaptations which are carried out simultaneously with conducted study. Synthesis processes of the materials in case of our research, means the synthesis from the moment when plasma is generated; and from the process of nucleation itself, through transport, growth of layers, structure and properties of the obtained final structure of materials, at the end. It is very important to try to get to know the behavior of the environment, that exists in the conditions that we can create therefore. It worth to notice that plasma diagnostics techniques are very helpful in our development. Everything is very important when it comes to the development of this scientific domain that is plasma and ion beam technology for material engineering.

1. PLASMA TECHNOLOGY

1.1. PLASMA IN PULSE PROCESS

The studies implemented in the area of plasma technology are focused on the synthesis of non-equilibrium structures in chosen materials and determination of their influence on the material properties, as well as on the synthesis of completely new materials. Studies perform by this groups are also focused on the development of plasma surface engineering techniques.

The main potential is no-equilibrium plasma and the use of pulsed plasma glow discharge in a magnetron system (pulsed glow discharge assisted by magnetic field) [e.g. 4, 5, 13, 14, 19, 21]. Magnetron sputtering is well known and the most commonly used method for synthesis of material in the form of layer [e.g. 15-17]. In our studies we focus on the use of conditions that increase the degree of thermodynamic non-equilibrium of plasma and at the same time can exploit of other forms of energy in the synthetic process, by use of pulsed changeable condition of generation [18-21].

The one of example is the PMS process (pulse magnetron sputtering) [e.g. 19, 21]. This technique provides the ability to initiate a discharge in a pulsed manner by the task of electric impulses of medium order of 100 kHz; using a voltage exceeding the voltage corresponding to the characteristics of glow discharge (Paschen curve [22]), thus providing a non-equilibrium conditions during the synthesis of the material. A second variant provides for the use of a new method of plasma generation causing the intensification of this nonequilibrity (that provides PMS), by using pulsed changeable concentration of working gas particles (pulsed gas injection). It is a solution that has been recently introduced to the knowledge, is involve the use of a pulsed changeable concentration of the working gas particles during the synthesis process. In standard operating conditions during the process, plasma working gas is delivered continuously and its pressure is of the order of $10^0…10^1$ Pa. The continuous way of the gas supply (constant concentration of gas particles during the synthesis process) was replaced by the pulsed gas injection that works as a gate for the electric circuit. Pulsed changeable concentration of gas during the synthesis process, allows to work in conditions of reduced gas pressure (~10^{-4} Pa) which changes the intensity of the elementary phenomena characteristic for synthesis. Therefore recently proposed, in the case of magnetron sputtering method, the glow discharge by the pulsed gas injection, resulted in a new type of pulsed process GIMS ("Gas Injection Magnetron Sputtering") [23-25]. This method from the point of application are characterized by big improvements of adhesion of the layers, obtained on a cold, not heated substrate. In our laboratory we use two kinds of magnetron sputtering technique that are characterized by above mentioned pulse process. It is pulsed magnetron sputtering (PMS) and gas injection magnetron sputtering method (GIMS). Examples of some conducted research in the domain of the synthesis and characterization of various layers deposited upon chosen materials will be discussed below.

1.2. IMPACT OF PULSE PLASMA ON MORPHOLOGY AND PHASE COMPOSITION

It is known that typical structure obtained by magnetron sputtering method is characterised by columnar structure [26]. The morphology of structure depends on temperature of the substrate material, pressure and energy. Therefore, it can be modified As reported by the results of our previous research, we are able to succeed in eliminating the columnar structure of layers of various materials. Example are shown in Fig. 1 and Fig. 2. Figures show a cross section views of aluminium nitride and copper nitride layers obtained during different magnetron sputtering synthesis processes. As one can see we can synthetize structure without columns by using a different frequency of modulation (PMS) as well as in case of pulse gas injection (GIMS) [14].

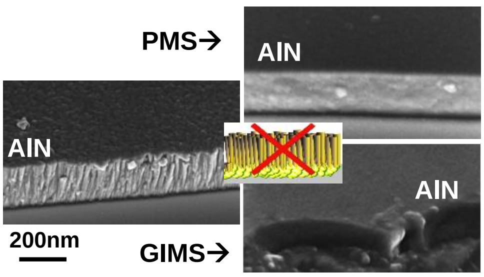

Fig. 1. Cross section view of different structure of the AlN layers obtained by magnetron sputtering technique

In case of the structure of copper nitride layers in most of cases the structures are columnar one. But some process parameters are favourable to finer columnar structure, and also structure without columns. Finally, the received finer structure of the Cu-N layers improved the nanohardness properties [27].

The GIMS synthesis allows the ability to control the phase composition in a final structure of layers. For example, in titanium oxide layers, depending on the pulsed process parameters we can obtain anatase or/and rutile structure [25, 27]. Therefore, taking into account the properties of these two phases and possibility of technology we can control the nanohardness properties of the layers [25]. We can also control the decoration effects [25, 28] as is shown on Fig. 3.

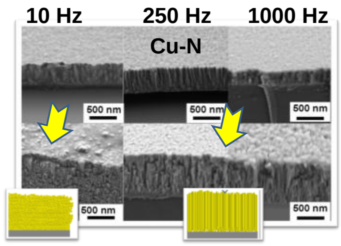

Fig. 2. Cross section view of different morphology of the Cu-N layers obtained by magnetron sputtering with different frequency of modulation

Fig. 3. Photography of coloured Ti/Ti-O layers deposited on polymer substrates by used a PMS and GIMS method

In case of PMS synthesis influence of different frequency modulation on phase compositions of copper nitride layers were observed. Cu_3N is a metastable phase, very difficult to synthesis because of the low temperature decomposition. there is very difficult to obtain a one phase structure of layers. The using a various frequency modulation with combination of other process parameters, allowed us for the control of phase composition. But in this case of investigation plasma diagnostics, optical emission spectroscopy, was very helpful [14]. These studies allowed to propose dependence between the process parameters and phase structure. They allowed the estimation of the range of process parameters favouring the synthesis of single-phase copper nitride, and two-phase material with additions of pure copper [14].

1.3. OPTIMIZATION OF CATHODIC ARC DEPOSITION FOR GROWING SMOOTH SUPERCONDUCTING PB PHOTOEMISSIVE LAYERS

The cathodic arc deposition is a well-known method. It is one of the first method of plasma technology used in our institute. The method has been developed and improved for years. Currently, the main goal of research conducted with the use of this method are investigation concerning optimization of synthesis process for growing smooth superconducting photoemissive layers. As one know the technological problem in the arc method is the production of microdroplets and their gathering on the surface of the layers. That phenomenon prevents achieving a flat, low roughness surface. There are two generic approaches to microdroplet elimination: removal from the plasma flux on its way from the cathode to the substrate with various filtering methods, or by using a postdeposition processes leading to the droplets melting, dissolution and surface flattening. To achieve a sufficiently low roughness, several methods based on these approaches have been tested.

Over the years we've used different configuration of various cathodic arc filtering systems for elimination of micro-droplets [29, 30]. Finally, we are able to obtain a good smooth lead layers. The first experiments included the micro-droplets removal from a lead plasma stream was attempted by separating the cathode and substrate with a plane slit or a chicane [31, 32]. Both filters blocked the plasma streams straight towards the substrate and enabled a sharply bent path through apertures. Unfortunately, the deposition rate was to low [32] and a long deposition time caused a large amount of Pb to stick to the filters and to the arc chamber wall. Additionally, the use of such a system excluded application of constant voltage bias between the arc chamber and the substrate. This resulted in a very low energy of ions, and finally leads to insufficient film adhesion. The next approach was based on magnetic filtering. That method had been previously used successfully for arc deposition of niobium layers on to copper walls of accelerating cavities [23, 24, 33, 34]. For Pb/Nb layers, a bent knee-like magnetic filter has been developed and inserted between the arc cathode and a substrate.The target was biased relative to the grounded wall to accelerate ions to improve the adhesion. It was concluded from the experiments with mechanical and magnetic filters that tight filtering is required to eliminate droplets during the deposition. On the other hand, the film clean lines requires a high deposition rate, which in turn demands loosening of the filtering and in evitable entails micro-droplet deposition and unacceptable surface roughness. This contradiction excluded the use of a filtering-based approach to smooth surface preparation and pointed to using a simple planar UHV arc geometry without any flux damping, but supplemented by a postdeposition treatment. The applicability of two approaches was compared in terms of the achieved surface flatness: filtered arc deposition and direct arc deposition followed by a surface treatment [35]. Currently our investigations resulted in an optimal, repeatable procedure for Pb/Nb film photocathode preparation that consists of direct cathodic arc deposition of layers, followed by the pulsed plasma melting [35]. The sample surface roughness reached in this way is 1μm in amplitude. The recent achievements and progress in smoothness of the Pb coatings were realize with a new setup. The position of the substrate montage was changed. Now the substrate is mounted perpendicular to the axis of arc. Obtained results show a considerable improvement of the roughness and significant reduction of micro-droplets (Fig. 4). We obtained a very smooth layers with the roughness of about 10 nm. The obtained results is a great success of our laboratory. The properties of the layers are currently being studied.

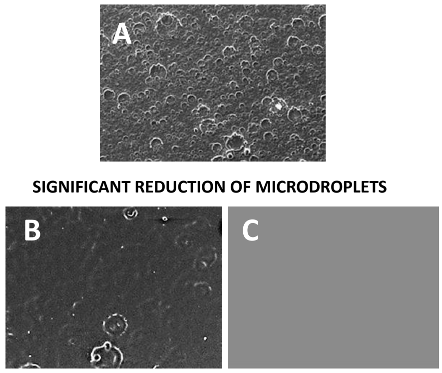

Fig. 4. Topography of Pb layers obtained by cathodic arc deposition. (A) directly after deposition process with using a simple planar UHV arc geometry, (B) direct arc deposition followed by a surface treatment post-process, (C) directly after deposition process with different configuration of substrate montage

2. ION BEAM TECHNOLOGY

Ion implantation is a low-temperature process by which ions of one element are accelerated into a solid target, thereby changing the physical, chemical, or electrical properties of the implanted material. This technology is considered as promising modification method of different materials especially in case of semiconductor materials and is studied by many research groups.

In our laboratory runs research on material modifications, which covers issues related with the modification of different material surfaces by means of ion beams [7-9].

The most interesting investigations concerning the ion beam technology include the study of the ion implantation doping of semiconducting the zirconium oxide layers. ZnO is probably the most extensively studied semiconductor over the last decade. Primarily, due to the fact that it is a promising material for optoelectronic and microelectronic applications [36]. With this respect ZnO is expected to be a cheaper replacement for GaN. The depth distribution of dopant and their concentration is precisely controlled in ion implantation technique, but the ballistic nature of this process produces lattice damage**.**

Moreover, in the as-implanted stage most of dopants are optically inactive. Therefore, annealing leading to the lattice recovery and optical activation of dopants is necessary.

The ZnO layers are implanted by rare Earth elements and this modification finally causes a very good optical properties of the material. Currently, very promising research in this field is carried out concerning optimization of technology, optimization of heating post-processes and investigation of influences of implantation on the structure [7-9].

The other example can be study concerning to the ion irradiation as an interesting method of modification of elastomers [11]. In this case we use a gaseous ion implantation for Improvement of functional properties. Fig. 5 shows a cross section view of morphology before and after irritation. As results a 4 – 6 folds reduction of friction forces and 9-folds improvements of nanohardness of elastomers were obtained. Finally, the improves of the functional properties of the material were achieve.

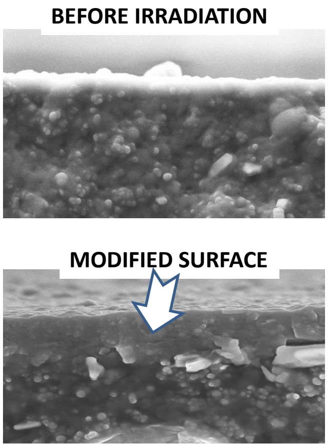

Fig. 5. A cross section view of morphology of elastomer before and after irritation process. Irradiated 160 keV HE^{+}, $3E16C^{2}$

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REFERENCES

1. K. Nowakowska-Langiera, R. Chodun, K. Zdunek, S. Okrasa, R. Kwiatkowski, K. Malinowski, E. Skladnik-Sadowska, M.J. Sadowski. OES studies of plasmoids distribution during the coating deposition with the use of the Impulse Plasma Deposition method controlled by the gas injection // *Vacuum*. 2016, v. 128, p. 259-264.

2. K. Nowakowska-Langier, K. Zdunek, R. Chodun, S. Okrasa, R. Kwiatkowski, K. Malinowski, E. Składnik-Sadowska, M.J. Sadowski, et al. On coatings adhesion during the Impulse Plasma Deposition // *Phys. Scr*. 2014, № 25, v. T161, p. 014063.

3. K. Nowakowska-Langier, L. Jakubowski, E.O. Baronova, K. Czaus, M. Rabiński, M.J. Jakubowski. Observations of extreme ultraviolet emission from plasma produced by capillary discharges // *Eur. Phys. J. D*. 2009, № 54, p. 377-382.

4. B. Wicher, R. Chodun, K. Nowakowska-Langier, S. Okrasa, M. Trzciński. Relation between modulation frequency of electric power oscillation during pulse magnetron sputtering deposition of MoNx thin films // *Applied Surface Science*. 2018, № 456, p. 789-796.

5. K. Zdunek, R. Chodun, B. Wicher, K. Nowakowska-Langier, S. Okrasa. Characterization of sp [3] bond content of carbon films deposited by high power gas injection magnetron sputtering method by UV and VIS Raman spectroscopy // S*pectrochim Acta.* 2018, v. 194, p. 136-140.

6. R. Chodun, K. Nowakowska-Langier, K. Zdunek, P. Konarski, S. Okrasa. Characteristic STATE of substrate and coatings interface formed by Impulse Plasma Deposition method // *Thin Solid Films*. 2018, № 663, p. 25-30.

7. R. Ratajczak, E. Guziewicz, S. Prucnal, G. Łuka, R. Böttger, R. Heller, C. Mieszczyński, W. Wozniak, A. Turos. Luminescence in the visible region from annealed thin ALD-ZnO films implanted with different Rare Earth ions // *Phys. Status Solidi A.* 2018, p. 1700889.

8. R. Ratajczak, S. Prucnal, E. Guziewicz, C. Mieszczyński, D. Snigurenko, M. Stachowicz, W. Skorupa, A. Turos. The photoluminescence response to structural changes of Yb implanted ZnO crystals subjected to non-equilibrium processing // *J. Appl. Phys.* 2017, v. 121, p. 075101.

9. R. Ratajczak, C. Mieszczyński, S. Prucnal, E. Guziewicz, M. Stachowicz, D. Snigurenko, J. Gaca, M. Wójcik, R. Böttger, R. Heller, W. Skorupa, J.V. Borany, A. Turos. Structural and optical studies of Pr implanted ZnO films subjected to a long-time or ultra-fast thermal annealing // *Thin Solid Films.* 2017, v. 643, p. 24-30.

10. J. Jagielski, L. Thomé, A. Chartier, O. Dorosh, C. Mieszczyński, I. Jozwik. Damage accumulation studies in ion-irradiated oxides: Current status and new perspectives // *Nucl. Instr. and Meth. B.* 2018, v. 435, p. 2-7.

11. J. Jagielski, A. Kosińska, U. Ostaszewska, M. Romaniec, Ł. Kurpaska, I. Jóźwik. Ion-irradiated butadiene acrylonitrile rubber reinforced with graphene filler // *Nucl. Instr. and Meth. B.* 2018, v. 3, p. 26.

12. K. Nowakowska-Langier, K. Zdunek. Nanostructured alloy layers with magnetic properties obtained by the impulse plasma deposition // *Plasma Proc. Polymers*. 2009, v. 6, № S1, p. 826.

13. K. Nowakowska-Langier, R. Chodun, R. Minikayev, S. Okrasa, G. Strzelecki, B. Wicher, K. Zdunek. Phase composition of copper nitride coatings examined by the use of X-ray diffraction and Raman spectroscopy // *J. Mol. Struct*. 2018, v. 1165, p. 79-83.

14. K. Nowakowska-Langier, R. Chodun, S. Okrasa, G. Strzelecki, K. Zdunek, R. Minikayev. Copper nitride layers synthesized by pulsed magnetron sputtering // *Thin Solid Films*. 2018, v. 645, p. 32-37.

15. R. Cremer, M. Witthaut, D. Neuschutz, C. Trappe, M. Laurenzis, O. Winkler, H. Kurz // *Mikro. Acta A*. 2000, v. 133, p. 299.

16. K.J. Kim, J.H. Kim, J.H. Kang // *J. Crystal Growth*. 2001, v. 222, p. 767.

17. X. Li, Q. Bai, J. Yang, Y. Li, L. Wang, H. Wang, S. Ren, S. Liu, W. Huang // *Vacuum.* 2013, v. 89, p. 78-81 (in Russian).

18. K. Zdunek, K. Nowakowska-Langier, et al. Properties of tin coatings deposited by the modified ipd method // *Vacuum*. 2010, v. 85, p. 514(in Russian).

19. K. Nowakowska-Langier, R. Chodun, R. Nietubyć, R. Minikayev, K. Zdunek. Dependence of the specific features of two PAPVD method: Impulse Plasma Deposition (IPD) and Pulsed Magnetron Sputtering

(PMS) on the structure of Fe-Cu alloy layers // *Appl. Surf. Sci*. 2013, № 30, v. 275, p. 14-18.
20. K. Nowakowska-Langier, R. Chodun, K. Zdunek. Synthesis of multicomponent metallic layers during impulse plasma deposition // *Materials Science-Poland*. 2015, № 15, v. 33(3), p. 841-846.
21. K. Zdunek, K. Nowakowska-Langier, R. Chodun, S. Okrasa, M. Rabiński, J. Dora, P. Domanowski, J. Halarowicz. Impulse Plasma in Surface Engineering - a review // *J. Phys. Conf.* 2014, v. 564, p. 012007.
22. F. Paschen // *Annalen der Phys. und Chemie*. 1889, № 273, p. 69.
23. K. Zdunek, K. Nowakowska-Langier, J. Dora, R. Chodun. Gas injection as a tool for controling plasma process during coating deposition // *Surf. Coat. Technol*. 2013, № 35, v. 228, p. S367- S373.
24. K. Zdunek, R. Chodun, L. Skowronski, K. Nowakowska-Langier, S. Okrasa, et al. Novel GIMS technique for deposition of coloured Ti/TiO_2 coatings in industrial scale // *Materials Science-Poland*. 2015, v. 15.
25. L. Skowronski, R. Chodun, K. Nowakowska-Langier, K. Zdunek, Ł. Kurpaska, et al. Characterisation of microstructural, mechanical and optical properties of TiO_2 layers deposited by GIMS and PMS methods // *Surf. Coat. Technol.* 2015, № 35, v. 282, p. 16-23.
26. J. Thornton // *J. Vac. Sci. Technol.* 1974, v. 11, p. 666.
27. K. Nowakowska-Langier, R. Chodun, R. Minikayev, L. Kurpaska, L. Skowronski, G. Strzelecki, S. Okrasa, K. Zdunek. Structure of Cu–N layers synthesized by pulsed magnetron sputtering with variable frequency of plasma generation // *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*. 2017, v. 409, p. 167-170.
28. R. Choduna, L. Skowronskib, S. Okrasaa, B. Wichera, K. Nowakowska-Langierc, K. Zduneka. Optical TiO_2 layers deposited on polymer substrates by the Gas Injection Magnetron Sputtering technique // *Applied Surface Science*. 2019, v. 466, p. 12-18.
29. R. Nietubyć, J. Lorkiewicz, A. Kosińska, M. Barlak, Ja. Sekutowicz, D. Kostin, R. Barday, R. Xiang, R. Mirowski, J. Witkowski, W. Grabowski. Coating and processing of thin lead layers on niobium for photocathodes in superconducting RF electron injectors // *Phys. Scr.* 2015, v. 25.
30. R. Nietubyć, J. Lorkiewicz, J. Sekutowicz, J. Smedley, A. Kosińska. Optimization of cathodic arc deposition and pulsed plasma melting techniques for growing smooth superconducting Pb photoemissive films for SRF injectors // *Nucl. Instr. Meth. A.* 2018, v. A 891, p. 78-86.
31. R. Nietubyć, J. Lorkiewicz, R. Mirowski, M. Barlak, J. Witkowski, J. Sekutowicz. Recent development in optimization of superconducting thin film lead photocathodes at NCBJ in Świerk // *Proc. SPIE*. 2013, v. 8903, p. 89032B.
32. J. Lorkiewicz, R. Nietubyć, M. Barlak, R. Mirowski, A. Bartnik, J. Kostecki, J. Sekutowicz, A. Malinowska, P. Kneisel, J. Witkowski. Deposition and optimization of thin lead layers for superconducting accelerator photocathodes // *Phys. Scr.* 2014, v. T161, p. 014071.
33. R. Russo, L. Catani, A. Cianchi, D. DiGiovenale, J. Lorkiewicz, S. Tazzari, C. Granata, P. Ventrello, G. Lamura, A. Andreone. Nb coating of cavities using cathodic arc, IEEE // *Trans. Appl. Supercond.* 2009, v. 19(3), p. 1394-1398.
34. R. Russo, A. Cianchi, Y. Akhmadeev, L. Catani, J. Langner, J. Lorkiewicz, R. Pollini, B. Ruggiero, M.J. Sadowski, S. Tazzari, N.N. Koval. UHV arc for high quality film deposition // *Surf. Coat. Technol*. 2006, v. 201(7), p. 3987-3992.
35. A. Kosińska, M. Barlak, D. Derewnicka-Krawczynska, J. Lorkiewicz, J. Sekutowicz, R. Nietubyć. Investigation of the intermediate layers located between niobium substrate and lead films destined for superconducting photocathodes // *Surf. Coat. Technol.* 2018, v. 352, p. 501-507.
36. C. Jagadish, S.J. Pearton. *Zinc Oxide Bulk, Thin Films, and Nanostructures*. New York: “Elsevier”, 2006.

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РАЗВИТИЕ ПЛАЗМЕННЫХ И ИОННО-ПУЧКОВЫХ ТЕХНОЛОГИЙ ДЛЯ МАТЕРИАЛОВЕДЕНИЯ В НЦЯИ

K. Nowakowska-Langier

Отделение плазменных и ионно-пучковых технологий – одна из лабораторий отдела физики материалов НЦЯИ в Сверке, Польша. Научная деятельность отделения связана с различными аспектами исследований в области материаловедения, технологии поверхности, определения характеристик функциональных свойств, а также синтеза и модификации различных материалов. В лаборатории активно используются и разрабатываются методы плазменной обработки поверхности, такие как электронно-дуговое осаждение при сверхвысоком вакууме (UHV deposition), методы импульсного магнетронного распыления, а также методы ионной имплантации.

РОЗВИТОК ПЛАЗМОВИХ ТА ІОННО-ПУЧКОВИХ ТЕХНОЛОГІЙ ДЛЯ МАТЕРІАЛОЗНАВСТВА У НЦЯД

K. Nowakowska-Langier

Відділення плазмових та іонно-пучкових технологій – одна з лабораторій відділу фізики матеріалів НЦЯД у Свєрці, Польща. Наукова діяльність відділення пов’язана з різними аспектами досліджень у галузі матеріалознавства, технології поверхні, визначення характеристик функціональних властивостей, а також синтезу й модифікації різних матеріалів. У лабораторії активно використовуються та розробляються методи плазмової обробки поверхні, такі як катодно-дугове осадження за надвисокого вакууму (UHV deposition), та методи імпульсного магнетронного розпилення, а також методи іонної імплантації.