Pulsed methods of thin film coatings deposition

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Abstract. The most known methods of pulsed thin film deposition such as magnetron sputtering HiPIMS, pulsed laser deposition PLD, vacuum arc pulsed deposition, high-intensity pulsed ion beams deposition HIPIB, as well, were described and analysed. It was shown that the stream of material, generated by means of a pulsed action, impacts to substrate and creates preconditions for nanocrystalline amorphous coating manufacture with superhigh hardness.

Pulsed thin film deposition methods such as magnetron sputtering HiPIMS, pulsed laser deposition PLD, vacuum arc pulsed deposition, high-intensity pulsed ion beams deposition HIPIB, as well, permit to produce, for example, nanocrystalline amorphous coatings with superhigh hardness. One of the urgent task in the field of strengthening carbon coatings today is to obtain DLC coatings with the structure of tetrahedral amorphous carbon ta-C, containing a significant proportion of \(sp^3\) bonds and having high hardness values from 60 to 80 GPa. According to many specialists [1], pulse methods are the most promising for obtaining such coatings, allowing to ensure minimum internal stresses in ta-C coatings, as well as to optimize the technological modes to increase the coating deposition rate.

The advantage of pulsed methods as compared to continuous devices is the possibility to obtain a plasma of higher density and higher energy of the flux of deposited particles. In addition, the pulsed mode of operation allows to minimize the heat load on the processed product.

Methods of pulse coating deposition in vacuum are considered and analyzed in [2] (figure 1): HiPIMS (High power impulse magnetron sputtering) [3], PLD (Pulse laser deposition) [4], VAPD (Vacuum arc pulse deposition) [5] and HIPIB (High-intensity pulsed ion beams) [6].

High power impulse magnetron sputtering HiPIMS is characterized by a specific power at the cathode of 1 - 3 kV/cm\(^2\), which is 100 times higher than in conventional magnetron sputtering. As a result of a short pulse of high voltage (1 - 10 kV) on the target, a plasma with high density and high degree of ionization of the deposited material is formed. The power is transmitted in short pulses of 60 μs duration with a frequency of 0.1 - 4 kHz and a small fill factor equal to 1%, which avoids overheating of the target. The ion current density can reach \(3 \times 10^4\) A/m\(^2\), and the film deposition rate is 0.5 nm/s.

The main advantages of the HiPIMS method are high coating density and hardness, low roughness and complete absence of droplets in the coating. Method HiPIMS is a universal method which combines advantages of arc evaporation and classical magnetron sputtering - possibility to form highly concentrated ion-plasma flows without any microdroplets.

The PLD laser ablation method of thin film deposition in a vacuum has the following modes: pressure in a vacuum chamber \(10^{-5}\) Pa, laser beam energy density 2 - 3 J/cm\(^2\), pulse frequency 30 Hz, pulse duration 25 ns, particle energy resulting from ablation 10 eV, the thickness of deposited film in
one pulse 0.022 nm/imp. At a higher laser beam energy density of 10 J/cm² the thickness of the deposited film in one pulse can reach 0.112 nm/imp. At a pulse frequency of 30 Hz the film deposition rate is 0.66 nm/s and 3.36 nm/s, respectively.

High power impulse magnetron sputtering HiPIMS: 1 - target, 2 - gas discharge, 3 - working gas, 4 - heating stage, 5 - substrate, 6 - power supply, 7 - magnetic system, 8 - water cooling.

Pulsed laser deposition (laser ablation) PLD: 1 - laser, 2 - Kerr cell, 3 - polaroid, 4 - focusing lens, 5 - target, 6 - vacuum window, 7 - flux of deposited material, 8 - substrate, 9 - vacuum chamber, 10 - heated stage.

Vacuum arc pulse deposition VAPD method: 1 - anode, 2 - cathode, 3 - cathode spot, 4 - flux of deposited material, 5 - heated stage, 6 - substrate, 7 - ignition electrode, 8 - pulse power supply (PPS), 9 - insulator, 10 - water cooling.

High-intensity pulsed ion beams HIPIB: 1 - pulsed ion source, 2, 3 - ion-optical accelerating system, 4 - high-intensity ion beam, 5 - target, 6 - ablative plasma flow of deposited material, 7 - substrate, 8 - vacuum chamber, 9 - heated stage.

**Figure 1.** Methods of pulse coating deposition in vacuum.

The vacuum arc pulse deposition VAPD method, compared to other methods, has a significant advantage in coating deposition rate due to the significantly higher plasma density. However, this method has its limitations related to the presence of macro-droplets in the cathode erosion products, which deteriorates the quality of the coating surface. Vacuum electric arc is a low-voltage discharge between a cold cathode and anode, burning in the eroding cathode vapor with formation of cathode spots [3]. The processes associated with the erosion of the cathode material are explosive in nature. The coating has an amorphous-crystalline structure with an average grain size of 5 nm.

Method of high-intensity pulse ion deposition HIPIB [2] is implemented in the TEMP-4M apparatus, its basic parameters are: accelerating voltage 250 - 300 kV, accelerating pulse duration 150 ns, ion current density on a target 50 - 250 A/cm², pulse frequency 5 - 10 pulses/min. The plasma flux formed as a result of ablation of the near-surface layer of the target propagates at a speed of $10^3 - 10^5$
m/s in the direction normal to the target surface. The density of particles in plasma flux can reach $10^{19}$ cm$^{-3}$, and their energy is 0.2 - 2 eV.

The main advantages of the HIPIB thin film deposition method are: high deposition rate, coating stoichiometry corresponds to the stoichiometry of the target material including multicomponent materials, no high substrate heating temperature (573 - 723 K), high coating purity and homogeneity.

To obtain thin-film coatings with a given structure, for example, with the structure of tetrahedral amorphous carbon ta-C, it is necessary to learn how to model the modes of thin-film formation. For this purpose, methods based on pairwise interaction models [7], molecular dynamics with different interatomic interaction potentials: Brenner potentials [8], Tersoff [9,10], environment dependent interaction potential (EDIP) [11], potential based on density functional theory (DFT) [12], Gaussian approximation potential (GAP) [13] are used.

The methods based on modeling the process of particle motion in solids use paired collision models or models of classical dynamics (molecular dynamics method). In the first case, only atoms bombarding the surface of a solid and moving in it, as well as primary and secondary knocked out atoms are considered. The choice of the free path for such model atoms is made by the Monte Carlo method and is based on the given properties of the solid [14]. The problem with this approach is the accounting of changes in the chemical bonding of carbon atoms.

This problem is solved by molecular dynamics simulation, where the displacements of both the deposited atoms and the atoms of the solid are tracked. The large computational cost of this problem imposes certain restrictions related to the number of atoms considered, the number of which is usually $10^3 - 10^4$. However, given the particularity of growth of this type of film, where there is no surface diffusion phenomenon, we can limit the model crystal to a small size (about $10\times10\times30$ atoms). Periodic boundary conditions are often used to simulate a bulk crystal and to reduce the influence of boundaries.

Due to their unique characteristics, such as high hardness, low friction coefficient, chemical inertness and biocompatibility, tetragonal amorphous carbon (ta-C) films find their application in various fields of science and technology, from mechanical engineering to biomedical technologies. The choice of a method of film deposition and optimization of technological process parameters require not only a qualitative understanding of the physics of film formation, but also a quantitative assessment of the structural characteristics of ta-C films.

These films contain three carbon phases formed by $sp$, $sp^2$ and $sp^3$ bonds. Increasing the concentration of $sp^3$ bonds in the film increases its hardness and thermal conductivity, and brings its characteristics closer to the properties of diamond. Thus, the goal of modeling is to predict the distribution of $sp^3$ bond concentration in the formed film. The objectives of this work are: 1) definition of a physical model describing the formation of ta-C films; 2) analysis of existing methods for modeling the deposition process of ta-C films; 3) selection of a modeling method for further studies.

The proposed model of subplantation [7] describes the $sp^3$ phase formation as a result of local density increase when high-energy (1 - 1000 eV) atoms of the deposited substance penetrate into the near-surface layers of the growing film. This approach reduces the problem to the analysis of particle motion in a solid and modeling of the process of chemical bond change. Molecular dynamic simulation of the effect of the angle of incidence of the carbon atom accelerated to an energy of 70 eV on the structure and properties of the DLC film is presented in figure 2 and table 1.

The results of studying the structure properties and growth evolution of DLC films as a function of incident ion energy using the molecular dynamics method using the interatomic interaction potential (EDIP) are presented in table 2 (4000 atomic collisions were simulated in which the transition from $sp^2$ to $sp^3$ phase took place).

For a long time, there was a discussion about the choice of the most suitable interatomic interaction potential for modeling the formation of diamond-like films. The method based on the density functional theory (DFT) [12] was considered to be more accurate, but because of extremely high computational costs (it was possible to simulate only for 250-300 atoms) it did not allow full-fledged simulation. There were used "classical" interatomic potentials of Brenner, Tersoff, EDIP, which did
not give sufficient correspondence with experimental data. The best result was achieved using the Gaussian approximation potential (GAP) obtained with machine learning algorithms. Training was performed on data obtained from simulations using a method based on density functional theory (DFT) [13]. This approach combines relatively low computational cost and high agreement of simulation results with experiment.

**Figure 2.** Structure of the DLC film when it is formed by accelerated ions at the angle $\alpha$.

**Table 1.** Effect of the angle of incidence of the accelerated carbon ion on the structure of DLC films.

| Angle of incidence of $\alpha$ ions, deg. | 0  | 15 | 30  | 45  | 60  |
|-----------------------------------------|----|----|-----|-----|-----|
| Transition region depth, nm             | 0.5| 0.3| 0.3 | 0.5 | 0.4 |
| Stable area thickness, nm               | 2  | 1.8| 1.5 | 1.0 | 1.5 |
| Surface layer thickness, nm             | 0.7| 1.0| 0.9 | 1.2 | 0.6 |

**Table 2.** Number of new $sp^3$ bonds as a function of energy of added carbon atoms

| Energy, eV | 1.0 | 3.0 | 40 | 70 | 100 |
|------------|-----|-----|----|----|-----|
| Number of added atoms | 400 | 400 | 400 | 400 | 400 |
| Number of $sp^3$ links | 100 | 300 | 400 | 220 | 380 |

For further studies, it is assumed to use the molecular dynamics method as the most fully describing the processes occurring during the growth of ta-C films and predicting the main characteristics of the film.

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