Thin film coatings material particles creation by pulsed methods in vacuum

Y V Panfilov, L L Kolesnik and A V Gurov
Bauman Moscow State Technical University, 105005 Moscow, Russia
E-mail: panfilov@bmstu.ru

Abstract. Thin film materials particles creation pulsed methods such as magnetron sputtering HiPIMS, pulsed laser deposition PLD, vacuum arc pulsed discharge, high-intensity pulsed ion beam impact HIPIB, as well, were described. It was shown that the stream of material, created by means of an explosion action such as ablation, avalanche paired impacts and microsecond electrical disruption as well creates preconditions for nanocrystalline thin film coating manufacture.

One of the most actual tasks in the field of thin film deposition with unique characteristics is a pulsed methods development and practice. By means of pulsed methods it is possible to deposit, for example, strengthening carbon coatings with ta-C structure and 60 – 80 GPa hardness as well [1]. The advantages of pulsed methods in comparison with classical methods of thin film deposition are an opportunity to obtain more power and concentrated stream of deposited particle.

Most known methods of pulsed impact of high energetic particles to target of deposit material surface were described and analysis at this article. The next thin film deposition methods such as high power impulse magnetron sputtering (HiPIMS) [2], pulse laser deposition (PLD) [3], vacuum arc pulse deposition (VAPD) [4] and high-intensity pulsed ion beams (HIPIB) [5] are realized by beams of pulsed methods. HiPIMS method is characterized of specific power on cathode in approximately 100 times more in comparison with traditional magnetron sputtering. High density plasma is formed as a result of short pulse impact on target and ion bombardment of surface with high specific power takes place (figure 1). The power is transmitted in short pulses that permits to avoid of target overheat. In this case we can suppose that the physical effect of ions to target impact is an excitation of double encounter avalanche and pulsed flow of atoms and ions is generated.

HiPIMS method incorporates advantages of two methods – arc evaporation and classical magnetron sputtering so pulsed high density ion-plasma flows without micro-drops are generated.

PLD method has manyfold fields of application due to simplicity of realization and availability of industrial equipment. Laser ablation is physical effect of laser beam with high density power impact to target (figure 2). Pulsed laser beam with high density power has explosion nature of impact to target material. As a result of this impact, crater with molten borderline layer on crater walls is formed and target material particles are injected with high speed.

VARD method is characterized of like explosion erosion of target (figure 3). Pulsed electric arc is low voltage discharge between cold cathode and anode which burn at vapor of cathode erosion material as a cathode spot. The large part of cathode material takes away in ablation regime at pulsed arc charge. High energy concentration and like explosion electronic emission leads to like explosion
erosion of target in the result of this a number of cathode spots are generated on cathode surface microdefects.

**Figure 1.** Scheme of pulse magnetron discharge impact to a target surface: 1 – pulsed ions flow from magnetron discharge, 2 – atoms and ions of target material, 3 – target, 4 – zone of ion impulse impact with explosion effect of double encounter.

**Figure 2.** Scheme of pulse laser beam impact to a target surface (a) and laser ablation effect (b): 1 – target, 2 – target material explosion, 3 – works of explosion, 4 – pulse laser beam, 5 – injected particles of target material, 6 – crater, 7 – molten borderline layer, 8 – zone of pulsed laser beam impact.

**Figure 3.** Scheme of pulsed arc discharge impact to a target surface: 1 – target-cathode, 2 – like explosion emission center, 3 – electron emission, 4 – pulsed flow of ions and electrons and neutral atoms, molecules and target material drops, 5 – plasma pressure, 6 – plasma cathode spot, 7 – pulsed arc discharge, 8 – anode.
The temperature of cathode spot can reach 15 000 K and plasma pressure has magnitude of 20 GPa so pulsed arc discharge forms craters on cathode surforcer. The craters have diameters of $1 - 10$ microns and one- or multicharged ions and neutral atoms and molecules take away by plasma high pressure action. Time of cathode spot existence is equal approximately $10^7$ seconds. Cathode materials atoms number and mass take away of cathode surface for singular impulse are equal, approximately, $10^{18}$ - $10^{16}$ atoms and $10^8$ kg respectively [4].

Thin film coatings with ultra high hardness can be deposited at ablation regime by means of high-intensity pulsed ion beams impact to a target surface [5]. Physical effects such as ablation plasma of target material emission and ions penetration into target with surface layer modification and crystal lattice of target material compress as well start up in the result of high-intensity pulsed ion beams impact to a target surface (figure 4).

Figure 4. Scheme of high-intensity pulsed ion beams impact to a target surface: 1 – ion beam HIPIB, 2 – ablation plasma, 3 – ion path and target surface modification area, 4 – stress waves, 5 – target.

Plasma stream formed in the result of surface layer ablation adiabatically spread with speed of $10^3 - 10^5$ m/sec to a target surface normal direction, likewise laser ablation but with higher energy and from bigger area and with more intensity of particles formation. Thin film deposition high rate and the same stoichiometry of coating and target material including multicomponent coatings and coatings high purity and homogeneity as well are the most advantage of this method.

In the dependence of ion beam power density on a target surface the next fields of HIPIB method applying take place [5]: ion implantation and annealing by $10^6 - 10^7$ W/sm$^2$, surface strengthening and modification by $10^7 - 10^8$ W/sm$^2$, thin film deposition from ablation plasma with energy density more than $3$ J/sm$^2$ by $10^8 - 5.10^9$ W/sm$^2$.

The comparison of described pulse methods of thin film deposition (table 1) indicates that the next certain logic takes place: thin film deposition rate minimum (0.02 nm/impulse) corresponds of deposited particles energy maximum (10 – 50 eV) and thin film deposition rate maximum (40 nm/impulse) corresponds of deposited particles energy minimum (0.2 – 2.0 eV) on the contrary. Pressure from 1 to $10^5$ Pa and substrate heating temperature of 723 K are the standard processing regimes.

Thin film formation essence by impulse deposition is differ than known essence of thin film growth: island, two-dimensional and combined growth, when adatom is diffusing on substrate surface as long as his temperature become equal a substrate temperature. The essence of thin film formation by impulse method corresponds in interfusion of deposited atoms because of free surface lack for atoms moving. In the result deposited atoms come to thermodynamics equilibrium by means of energy dispersion on surrounding atoms. So, presupposition of nanocrystalline and radiographical amorphous
thin film forming are established. Then more atoms were deposited to surface unite per one impulse but smaller grains were formed with more probability and consequently such parameter of thin film coating as hardness, for example, became more higher [1].

Table 1. Comparison of characteristics of thin film deposition pulse methods.

| Method                              | HIPIBS                  | PLD                   | VAPD                  | HIPB                  |
|-------------------------------------|-------------------------|-----------------------|-----------------------|-----------------------|
| Physical effect of impact to target | Stream of ions          | Laser beam            | Vacuum electric arc   | Ion bombardment       |
|                                     | with high power density | with high energy density | with like explosion cathode erosion | with high ion energy |
| Impulse frequency, Hz              | 100 – 4000              | 30                    | 3 – 1000              | 0,08 – 0,18           |
| Impulse lasting, microsecond       | 60                      | 2,5 10^2             | 250 – 1200            | 1,5 10^1             |
| Ion current density, A/m^2         | 3 10^4                  | 100                   | 40 – 250              | 400                   |
| Energy density, J/sm^2 or power density, W/sm^2 | 10^3 – 3 10^3         | 2 – 10 J/sm^2         | 10^8 W/sm^2           | 10^6 – 10^9 W/sm^2    |
| ion energy of target bombardment, keV | 0,9 – 1,0              |                       |                       | 573 – 723             |
| Substrate heating temperature, K   | 293 – 473               | 293 – 423             | 293 – 343             |                       |
| Vacuum chamber pressure, Pa        | 1,0                     | 10^5                  | 8 10^-3              | 10^2                  |
| Particle energy, eV                | 10 – 50                 | 0,1 – 10              | 10 – 12               | 0,2 – 2,0             |
| Film deposition rate, nm/impulse   | 0,02                    | 0,04 – 0,1            | 1,8                   | 40                    |

One of the further research tasks are modeling of thin film deposition regimes with predetermined structure, let us say, tetrahedral amorphous carbon – ta-C. At the present time application program packages are existed for modeling of thin film deposited by means of standard PVD and CVD methods. This packages are based on models of interatomic potential interaction, Gaussian approximation potential (GAP), density functional theory (DFT) [6, 7], and so on. Plurality of the packages require very large calculation power because the modeling can be carried out for small number of atoms (250 – 300) only. Furthermore, an examples of computer modeling of thin film coatings by impulse regimes did not find yet. So, further research will be carried out by combination of modeling with relatively small calculation expenses and results of experimental investigations.

References
[1] Panfilov Y V 2021 Strengthening technology and coatings 2 93–6
[2] Capek J, Hala M, Zabeida O, Klemberg-Sapieha J E and Martinu L 2013 J. Phys. D: Appl. Phys. 46 205205 doi: 10.1088/0022-3727/46/20/205205
[3] Devitsky O V, Nikulin D A and Sysoev I A 2020 Science and technical digest of informational technology, mechanics and optics 20 2 doi: 10/175862226-1494-2020-2-177-184
[4] Brown I and Oks E 1999 NATO science series II. Mathematics, Physics and Chemistry 88 1–14
[5] Remnev G E at al. 1999 Surface and Coatings Technology 114 206–12
[6] Caro M A, Zoubkoff R, Lopez-Acevedo O and Laurila T 2014 Carbon 77 1168
[7] Caro M A, Deringer V L, Koskinen J, Laurila T and Csánya G 2018 Phys. Rev. Lett. 120 166101