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Hybrid Laser Technology for Composite Coating and Medical Applications

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Abstract: *Nano-composite layers were synthesised by pulsed laser deposition (PLD) combined with magnetron sputtering, ion gun modification and RF discharges, and by dual pulsed laser ablation using simultaneously two KrF excimer lasers and two targets. Diamond-like carbon (DLC), Cr-containing diamond-like carbon (Cr-DLC), silver-doped hydroxyapatite (Ag-HA) and silver doped 316L steel and Ti6Al4V were prepared by hybrid laser technologies for potential coating of medical implants. Growing DLC films were modified during the laser deposition (10 J cm*$^{-2}$*) by ion bombardment. Energy of argon ions was in the range between 50 eV and 210 eV. Content of sp*^{2} *"graphitic" and sp*^{3} *"diamond" bonds, doping, structure, mechanical and biocompatible properties were tested. Deposition arrangements and experiences are presented.*

Keywords: Hybrid technology, pulsed laser deposition, biocompatible composites, doped coating, composite coating

1. INTRODUCTION

Laser is a unique device which can be used for fabrication of thin films of multicomponent materials, thin nanocomposite films, nanocrystalline, amorphous, polycrystalline or monocrystaline films, and multilayers and superlattices. Hybrid laser based systems were historically used for deposition of special types of layers and multilayers. Usually, combinations of pulsed laser deposition (PLD) with magnetron or PLD with discharges were used.[1–7] In our work, we present a wide range of laser based hybrid systems for creating novel and special types of biocompatible materials. Over the last years it has become apparent that a very few materials implanted in the body are truly biocompatible.[8] Therefore, there is a goal to develop novel types of biocompatible layers to cover implant materials and hence improve biocompatible and mechanical properties. The main focus is on the diamond like carbon (DLC) layers, hydroxyapatite (HA) layers, TiO_2 layers, and on the doped modifications of DLC, HA and TiO_2 materials.

DLC is a metastable form of amorphous carbon containing bonded carbon atoms in sp^1, sp^2 and sp^3 hybridised orbitals. Properties of DLC layers are impressed with sp^3/sp^2 bond ratio and concentration of hydrogen or other elements in layers. DLC layers exhibit extreme mechanical hardness, good biocompatibility, high chemical inertness, nano-smooth surfaces and a low coefficient of friction (lowest among solids).[9] DLC layers have potential applications in cardiovascular areas for coating and improving hemocompatibility of prosthetic valves, stents, artificial heart and heart-lung machines; orthopedic areas for coating of hip and knee implants; ophthalmic areas for improving lenses; and for conformal coating of medical and surgical instruments. Content of sp^3 bonds can be modified using ions bombardment.

The problem with DLC layers is their poor adhesion to biomedical alloys such as steel, titanium and cobalt alloys. This problem can be overcome using interlayers and doped DLC layers.[10] Some of the interlayers which can be used are carbides, nitrides, metal layers and the gradient layers. Dopants in DLC layers change the hardness, coefficient of friction, surface roughness, adhesion and biocompatibility, etc. For example, the hemocompatibility of implants can be improved by doping the DLC with phosphorus,[10] fluorine,[11,12] nitrogen,[13,14] silicon[15,16] and silver.[17] Their biocompatibility was found to be better than that of low-temperature isotropic carbon (LTIC).[10,14,17]

Silver-doped DLC has an excellent antibacterial effect.[17,18] Also, phosphorus-doped DLC upholds growth of cortical neurons.[19] This property has been used for generation of neuronal networks. Silicon-doped DLC has a better adhesion[15] and the layers are more hydrophilous.[20] Silver, argon, nitrogen and fluorine-doped DLC layers shows a decrease in the sp^3-hybridised C bondings,[18,21,22] while silicon doped shows an increase.[16] The surface roughness of the fluorine and silicon-doped DLC layers is very low.[22,23] Chromium[24,25] and titanium[26,27,28] doping DLC layers exhibit better adhesion to the substrate than without the doping. Chromium and titanium reduce internal stress and lower the risk of cracking and peeling layers from the substrate.[24–28]

Metallic silver and silver compounds such as HA silver composites are widely used in medical devices and healthcare products.[29] Besides the mechanical properties, the antibacterial properties and cytotoxicity are important for medical applications. Bacterial infections are usually caused by the adherence and colonisation of bacteria on coated implants.[2,30] Silver and silver ions have long been known to have strong inhibitory and bactericidal effects as well as a broad spectrum of anti-microbial activities.[30] Various opinions concerning silver biocompatibility have been presented in the literature.[31] The conclusions published in the mentioned studies are somewhat different and making a comparison is a challenge. This is because the properties of doped materials depend on the dopand concentration, shape of material (bulk, thin layer, nanoparticles) and on the methods and parameters used to introduce silver into the material.

In this hybrid laser research, we concentrated on development and construction of new technological systems, and on the study of DLC, doped (nanocomposite) DLC, doped HA and doped metallic layers for medical applications.

2. EXPERIMENTAL

Our PLD system consists of excimer laser and deposition chamber (Figure 1). Laser beam is focused on a target, placed in a vacuum chamber. Chamber input window is large in diameter to be able to scan laser beam over the target and to ensure the same conditions for material evaporation. Laser beam evaporate (ablate) target material is in a form of plasma plume.

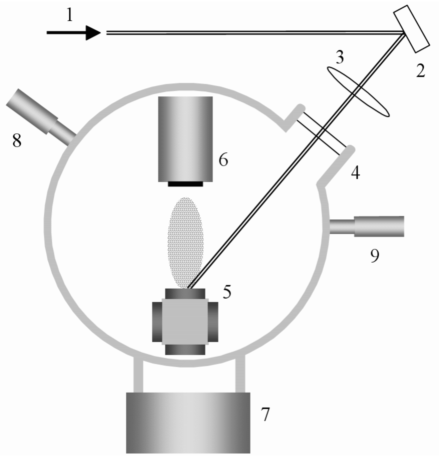

Figure 1: Scheme of PLD deposition chamber. 1: laser beam, 2: reflecting mirror, 3: focusing lens, 4: carousel with four targets, 6: rating table with substrate, 7: vacuum system, 8 and 9: vacuum gauge.

Material condensates on a substrate are placed on a heating element. The stream of material from a target (plasma plume) is very directional and is perpendicular to the target. Simple deposition of multilayers is one of the advantages of PLD. In this case, several different targets are placed in a deposition carousel. The substrate is usually heated during the deposition process. For majority of materials, the substrate temperature is not higher than about 800°C. Another PLD advantage is in its stoichiometric deposition and relatively simple and economical pumping system (10^{-3} Pa). The spectrum of materials created using PLD is very wide. With PLD, the majority of inorganic materials and composites can be created.

2.1 Hybrid PLD

In some cases, it is better to use combination of PLD with some other deposition techniques or discharges. Here, we are referring to hybrid PLD. For example, when we tried to synthesise the beta phase of C_3N_4, we were not able to reach PLD due to high content of nitrogen in the created layers. Using combination of PLD and discharges (13.56 MHz) we managed to reach PLD because additional RF source for higher excitation of nitrogen was used.[1–3] Hybrid PLD can be used for creating nanocrystalline diamond embedded in carbon matrix to produce crystalline BN or TiO_2 layers at lower substrate temperatures, etc.

Another example of hybrid PLD is a combination of PLD and Magnetron Sputtering (PLDMS) deposition (see scheme in Figure 2). We see that streams of materials from PLD target and from MS target intersect on the substrate. The combination of high energetic material flow from PLD and low energetic from MS makes it possible to synthesise materials of new properties at technologically reasonable conditions. By changing the laser repetition rate and magnetron power, it is possible to modify flows of materials on the target and to create gradient layers or layers with a special material distribution along a thickness profile. Using this method we synthesised TiC, TiCNx and SiC films.[4–7]

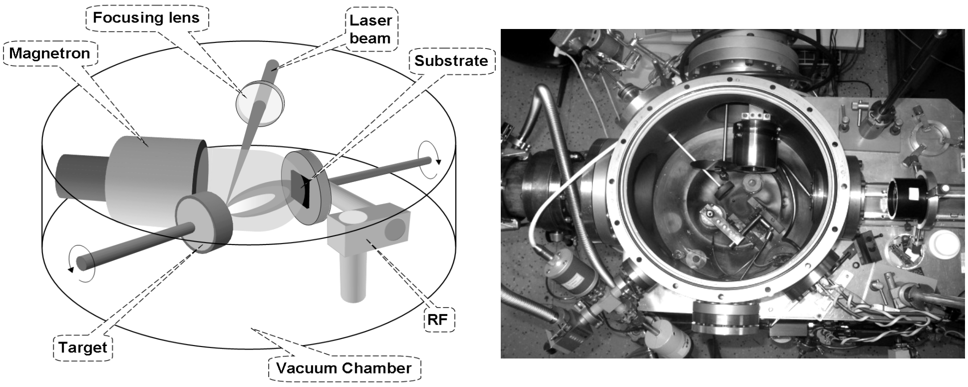

Figure 2: Scheme of hybrid PLD with magnetron deposition system (left) and photo of real chamber (right).

Another type of hybrid system is based on a combination of two lasers, depositing material from two targets (Figure 3). By changing the repetition rate of lasers, the multilayer systems, and doped and graded layers can be easily fabricated. We tested such system for deposition of DLC doped with Cr. The Cr content changed from 2.2 to 17.9 at%. The contact angle of Cr-DLC films (90°) was higher than DLC film (70°) and surface free energy of Cr-DLC films (43 mN m^{-1}) was lower than DLC film (33 mN m^{-1}). Their biological properties were also studied.[32]

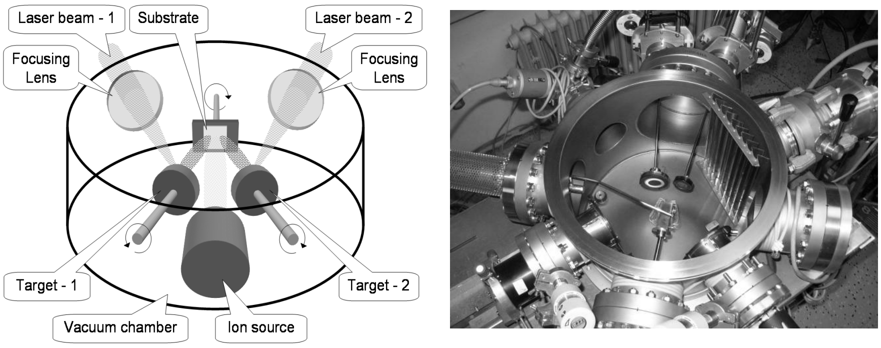

Figure 3: Hybrid PLD system, combining two laser beams with ion beam gun.

All hybrid systems can be combined with ion beam gun. The ion gun can be used to modify growing film, e.g., to increase film density, crystallinity and to improve morphology, etc. (see Figure 3). The ion gun has been successfully tested in fabrication of DLC films. The ion energies up to 210 eV for cathode currents of 0.15 A and 0.5 A were adjusted. We found the influence of ions energy and cathode current on the development of sp^3 bond. The maximum of sp^3 bond (81%) was measured for layer bombarded with argon ions of energy of 40 eV and cathode current of 0.15 A. Compared to non-bombarded DLC layers the increase in sp^3 bonds was from 68% to 81%.[33]

Using segmented target (HA covered with a plate of silver), the hydroxyapatite layers with silver dopation from 0.06 at% to 14 at% were prepared by laser deposition. Films were amorphous or polycrystalline in dependence on deposition temperature (from RT to 600°C). The antibacterial efficacy changed with silver dopation from 70% to 99.9%. Cytotoxicity was studied by a direct contact test. Depending on dopation and crystallinity, the films could be non-toxic or mildly toxic.[31]

Nanocomposite silver doped titanium alloy (Ti6Al4V) and 316L steel can be a suitable antibacterial material to reduce the possibility of infection or severity of infection complications in patients after the surgical treatment of fractures. Silver doped layers of titanium alloy and steel were prepared by dual laser ablation using a KrF excimer laser and target composed from metal and silver segments. Concentration of silver in metal was up to 13 at% (depending on deposition conditions). The adhesion of coating to metallic prostheses was outstanding. The prepared layer exhibits good antibacterial properties for gram negative and gram positive bacteria.[34]

3. CONCLUSION

Laser based hybrid systems for depositing new composite biomaterials have been described. The arrangements of combination of PLD with RF discharges, magnetron sputtering, ion gun and dual laser ablation were applied to create nanocomposite biomaterials. Schemes and photos of real systems were presented. Thin films of DLC, DLC doped with chromium, hydroxyapatite, hydroxyapatite doped with silver, and chromium doped titanium alloy and steel were fabricated and characterised. Materials of new properties can be synthesised. Finally, the results were explained.

4. ACKNOWLEDGEMENT

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