Pulsed laser deposition of high-quality diamond-like carbon films under an inhomogeneous magnetic field

Guojun Huang1,a, Yimin Lu1,b, Sai Wang1,c, Fangzheng Ding1,d, Shangfang Wei1,e, Chaowei Mi1,f, Fangtao Tian1,g, Hua Chu1,h, Yong Cheng1,i,

1Ordance NCO Academy, Army Engineering University of PLA, Wuhan, 430075, China

Corresponding author’s e-mail: gdyjs@263.net

Abstract. High-quality diamond-like carbon film was deposited on silicon substrate by magnetic field-enhanced pulsed laser deposition. The motion tracks of carbon ions in the inhomogeneous magnetic field were simulated. The thickness and surface morphology of carbon film were characterized by surface profilometer and atomic force microscopy, respectively. Mechanical property was evaluated by an indenter. The results showed that the deposition rate of the carbon film prepared under the magnetic field increased 1.7 times than that of the carbon film without magnetic field. The surface of the carbon films constructed of columnar particle arrays with the size ranging from 20 nm to 30 nm was improved and the roughness was decreased from 3.22 nm to 0.93 nm. The nano-hardness of the carbon film was 53.4 GPa, which increased by 18.1% than that of carbon film deposited without magnetic field. The experiment and simulation on the magnetic field-enhanced pulsed laser deposition proved that the new method of film preparation by magnetic filtration laser plasma deposition is feasibility.

Keywords. pulsed laser deposition, external magnetic field, filtered plasma, carbon film, nano-hardness

1. Introduction

Pulsed laser deposition (PLD) is one of the advance technologies for growing nano-films. The plasma with high temperature and high pressure is generated by the laser beam with high fluence from the target, and is cooled on the substrate, forming the film. PLD process has the advantages of high ionization, high ion kinetic energy, and deposition at low temperature. However, with the high inner stress, the drops and clusters are present in the coating grown by PLD to reduce the performance seriously. Meanwhile, it’s difficult to prepare uniform film on large-area substrate. These disadvantages have obstructed the development and commercialization of PLD technology[1-2]. Therefore, many methods like gradient structure, doping and annealing are used to reduce these bad effects. And more importantly, the plasma generated by laser with high fluence includes a lot of clusters and drops to increase the optical absorption and stress concentration, leading to several problems such as the reduction of the optical property and the exfoliation of broken film.

Magnetic field is used to guide the ions and reduce the drops or clusters. An initial study is carried out in our research. In the synthetize of the materials, the magnetic field as a non-contact driving force can increase the active effect of the ions, and induce the arrange changes among the atoms, molecules and ions, influencing seriously the structure and properties of the materials[3-4]. Magnetic field-assisted technology has been applied in the laser process fields such as laser repair, laser cladding welding and so forth. Wang Xiaoming employed revolved magnetic field-assisted laser cladding to prepare the five-metal cladding layer with the Al-Ni-Y-Co-La elements. The stir effect of magnetic field increased the amorphous phase content from 10.2% to 30.7% in the cladding layer, and restrained the growth of the crystalline grain in the refused zone during the multi-channel lap and multi-layer accumulation, improving the residual stress, micro-hardness and toughness[5]. Magnetic field-assisted laser cladding
was used to generate the Fe60 composite coating and made the crystalline grains refined, increasing the micro-hardness and anti-wear property[6]. The stir effect of the magnetic field during laser repair reduced the viscous powder and accordingly smoothed the surface of the titanium alloy, increasing the micro-hardness[7]. The rotated magnetic field-assisted pulsed laser deposition was used to prepare the Fe106 and nickel-packaged tungsten carbide composite coating, and strengthened the thin crystalline grains, improving the wear resistant[8]. It’s indicated that the magnetic field is useful to reduce the disadvantage of the PLD process.

This research shows that magnetic field has the good assisted effect on the laser plasma in growth of the functional films, influencing the deposition rate and thickness distribution of the DLC film. And more importantly, it can improve the structural and mechanical properties of the DLC film such as micro-surface, nano-hardness and so on.

2. Experimental

2.1. Film deposition

The substrate is polished crystal silicon with the size of Φ25 mm × 4 mm, and a permanent magnet is fixed closely on the substrate. Magnetic field between substrate and target is shown in figure 1, and the substrate-to-target distance is 100 mm. figure 1(a) shows the distribution of the magnetic field lines between substrate and target. figure 1(b) shows the distribution of magnetic field intensity on the plane with different distances below the magnet.

![Magnetic distribution of permanent magnet between substrate and target.](image)

The nano-second KrF laser with the emitting wavelength and pulse energy of 248 nm and 400 mJ was used. The pure graphite target (99.99%) was ablated by the focused laser with the fluence of about 7.2 J/cm². 40000 shots were used, and the DLC film sample A was prepared in the free space while the DLC film sample B was prepared under magnetic field.

2.2. Film characterization

Film thicknesses of the DLC films were measured by probe profilometer of Bruke Dektak XT. Surface of the DLC film at different positions were measured by AFM (atomic force microscope) of VEECO Multimode 8. Nano-hardnesses of the films were measured by MTS Nano Indenter XP with the B-R92 Berkovich.

3. 3 Result and discussion

3.1. Deposition rate of the DLC films

Film thicknesses of the samples A and B are shown in figure 2.

As seen in figure 2, the film thickness of the sample A prepared in the free space is 217.0 nm, and the film thickness of the sample B prepared under magnetic field is 364.7 nm. In the experiment, both of them were deposited by 40000 shots. Therefore, the deposition rates of the samples A and B are 5.42 nm and 9.12 nm per thousand pulses, respectively. It’s indicated that the deposition rate under magnetic field is increased to 1.7 times against that in the free space.
Figure 2. Profile graphs of the carbon films.

The Lorentz force, magnetization and magnetic moment of magnetic field against the ions will affect the growth of the film materials, improving their electrical, magnetic, thermic and mechanical properties obviously\(^9\)\(^{10}\). The laser-induced plasma includes the C\(^+\), C\(^{2+}\) ions, C, C\(_2\) atoms, carbon clusters and other particles. Firstly, the flying path of the carbon ions will be affected by the magnetic field, as shown in figure 3.

Figure 3. The trajectory of carbon ions in the magnetic field.

As seen in figure 3, the carbon atoms or clusters are not affected by the magnetic field, and keep their lineal flying paths. On the other hand, the flying paths of the C\(^+\) and C\(^{2+}\) ions change to be helix shape due to the Lorentz force under the magnetic field. And some ions those fly away from the substrate by lineal path in the free space can fly onto the substrate because of helix-shaped flying path. Therefore, the deposition rate is increased.

3.2. Micro-surface imaging of the film samples

Figure 4 and figure 5 show the AFM surface morphology of DLC films prepared in the free space and under magnetic field. The view fields are 500 nm × 500 nm.

Figure 4. Surface morphology of carbon film without magnetic field.
According to figure 4, the surface of the DLC film sample A prepared in the free space is smooth and compact, and its RMS roughness is about 3.22 nm in the view field of 500 nm × 500 nm. On the other hand, there is no grain or cluster on the surface of the DLC film sample B prepared under magnetic field as seen from figure 5. The sample B has smoother surface, and its RMS roughness is just 0.93 nm, which is 72% lower than that of the sample A.

And more importantly, the column-shaped crystal structure is present in the DLC film prepared under magnetic field. The crystal structure shows the uniform pyramid-like shape, and its grain size is about 20 ~ 30 nm. It’s possible that the ions were drove by the Lorentz force under magnetic field, flying onto substrate by the same or similar deposition angles. Therefore, the crystal growth mode was generated, and showed the order micro-structure in the carbon film.

3.3. Nano-hardness of the samples
The diamond tip is indented into DLC films under the increasing load. The max indentation load was 4 mN, and the load rate is 8 mN/min, and 10% film thickness was estimated the average nano-hardness of the DLC film samples. The functions between load and depth are recorded, as shown in figure 6.

![Figure 6. Nano-indentation curves of carbon films.](image)

When the load increases to its maximum, the lower indentation into surface (depth) means to the higher film hardness. As seen in figure 6, the indentations of the samples A and B are 110.2 nm and 89.3 nm, respectively. It is indicated DLC film prepared under magnetic field has higher nano-hardness, compared with DLC film deposited in the free space. The indentation curve with the depth can be calculated by the Oliver-Pharr method, and the average nano-hardnesses of the various DLC film prepared in the free space and under magnetic field are estimated as 45.2 GPa and 53.4 GPa, respectively. Therefore, the magnetic field increased the nano-hardness of DLC film sample by 18.1%.

It is assumed that the concentration of the carbon ions onto the substrate, which is due to the Lorentz force, increases local stress of the surface, promoting the transformation of sp² bonds to sp³ bonds[11]. Then, the optical absorption and mechanical hardness will be reduced and increased, respectively.

4. Design of magnetic field-filtered laser-induced plasma and its simulation
Laser-induced plasma filtered by magnetic field is designed to grow the film. The elbow magnetic field, as shown in figure 7, is used to generate the Lorentz force just to the ions, drives them flying as the curved path that is similar to the elbow. Therefore, the ions can fly out the elbow and onto the substrate. On the other hand, the atoms, molecules and clusters fly as straight line since they are not affected by the magnetic field, and they will be obstructed by the elbow wall. In a word, the laser-induced plasma is
purred. After flying out the elbow, the ions will be controlled by the negative voltage in deposition chamber. And the uniform film can be prepared by scan of the negative voltage.

![Figure 7. Schematic diagram of the magnetic filtration laser plasma deposition system.](image)

The corresponding simulation is shown in figure 8. With the circle current is adjusted to gain the max magnetic field intensity of 0.2 T, the caliber and curvature radius of the elbow are optimized to be 0.3 m and 0.8 m, respectively.

![Figure 8. Simulated distribution of the magnetic field.](image)

Under the optimized condition, most of the carbon ions (C⁺, C²⁺) can fly out the elbow by their curved paths, as seen in figure 9(a). The angles marked in this figure are the initial emitting angles of the ions generated by laser. Positions of the emergent ions in exit plane of the elbow (XOZ plane) are shown in figure 9(b). The red broken ring is denoted as the elbow exit.

![Figure 9. Simulation of the carbon ions under magnetic field.](image)

According to figure 9, some ions cannot fly out from the elbow exit, and the rate is about 37.3%. It is assumed that the rate could be reduced if the condition is optimized further.

5. Conclusions
A novel PLD method of laser-induced plasma filtered by magnetic field was designed to grow the film, and an elbow-shaped magnetic field was simulated to filter the atoms and clusters. As an important example, the flying paths of the carbon ions drove by Lorentz force were simulated.

DLC film was deposited under magnetic field, and measurements showed that its deposition rate and nano-hardness were increased by 68.3% and 18.1%, respectively, compared with the DLC film prepared in the free space. In addition, the RMS roughness of the DLC film deposited under magnetic field is
improved to 0.93 nm from 3.22 nm. It is indicated that the sp³ bond content was increased because of the increasing local stress in the DLC film. And more importantly, the magnetic field facilitated the column-shaped crystal structure with grain size of about 20–30 nm in DLC film, since the Lorentz force drove the ions to fly onto substrate by the similar deposition angles.

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