

Research of Anti-reflective and Protective Symmetrical DLC Films Deposited by Pulsed Laser

Shuyun Wang^{*}, Xu Liu, Weibing Bai

Wuhan Mechanical Technology College, Wuhan Hu Bei, 430075, China

paper1511@sina.com

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Abstract. Femtosecond pulsed laser(800nm, 120fs, 1000Hz) was used. And methods of element doping, abaxially rolling and moving were applied. Problems of conflict between transmission and inner-stress, and large area asymmetric of diamond like carbon (DLC) films deposited by pulsed laser were overcome. Hydrogen-free DLC film was deposited on silicon substrates. The transmission at 3-5 μ m of the silicon sample coated by DLC film on one side was larger than 68%. The nano-hardness was up to 40-50GPa. Asymmetry of DLC film in size of ϕ 125mm was smaller than 2%. Furthermore there was no nicks on the film after rubbed 105 times by 9.8N rubber.

Introduction

Silicon and germanium are the main optical materials at 3-5 μ m or 8-12 μ m^[1,2]. But the transmission, hardness and stability of these materials are not high enough, and they are easy to be nicked and mildewed. As DLC films have many merits similar to diamond, such as high hardness, anti-reflective at wide spectrum and high stability. One effective approach is to plate common infrared anti-reflective film on the inside surface and plate DLC films on the outside surface. This method will not only improve the infrared transmission, but also advance performances such as mechanical and chemical stability.

Chemical vapor deposition(CVD) has developed as a ripe method to deposit DLC films. But it need high temperature and the film contain hydrogen. The performances such as hardness, thermal and chemical stability are not excellent enough. As one new technic, pulsed laser deposition(PLD) can deposit hydrogen-free DLC films under room temperature with high speed^[3,4]. Even so, there are still some problems in PLD method. DLC films with high sp^3 bonds content show high transmission but at the same time their inner-stress are also high. Furthermore, the plasma sputtered by laser is similar to taper, it's difficult to deposit uniform film on large area.

In our research, femtosecond pulsed laser was used to deposit DLC films. Through a great lot of experiments, we validated the impact rules of DLC films by laser parameters, such as laser intensity^[5-7]. Through means of element doping, abaxially rolling and moving, we deposited excellent DLC films on silicon substrates and resolved the problems of DLC films by PLD.

The effect of element doping to DLC film

To reduce the inner-stress of DLC film, researchers tried to mix some elements to DLC film, such as Si, Ti, W, B, P^[8-10]. Many elements have big extinctive coefficient, if doped into DLC film, the transmission of DLC film will be reduced. Compared to other elements, Si has some merits. Si fits well with silicon substrate and impossibly to form π bonds which indwell in sp^2 . It's helpful to increase sp^3 bonds content to dope Si into DLC films whose sp^3 bonds content are not too high. And this will also improve the transmission. Besides, as the energy of Si-C bond (3.21eV) is smaller than that of C-C bond (3.70eV), aberrance of C bonds can be slacked which will make the inner-stress decline greatly.

Only few people have studied doped silicon DLC film. Earliest overseas report about doped silicon DLC film was in 1998^[9], and while domestic until recent years^[10]. Anyway, the actions of doping silicon have been found. It's useful to decrease inner-stress and improve adhesion.

Experiments research

Experiment equipment

Ti:Sapphire femtosecond laser(800nm , 120fs , 1000Hz) was used. The vacuum limit of deposition chamber is 6×10^{-5} Pa. The schematic deposition system is shown in figure 1. Laser beam is focused onto graphite target by a 50cm focal length lens with an incidence angle of 55° . The 99.999%-purity graphite target and the n-type single crystal silicon(100) substrates are placed parallel into the chamber. And their distance can be changed from 40mm and 80mm. Both the target and substrate holders can rotate round their main axis during the irradiation to make the films uniform. Furthermore, the substrate holder can move up and down. Ambient atmosphere channels and ion sputtering devices are equipped to the chamber. The graphite was ultrasonically cleaned in distilled water and alcohol for 5 minutes respectively. The silicon slices were firstly dipped in 5% HF for 10 minutes, then cleaned in alcohol with ultrasonic wave for 5 minutes. Both graphite and substrates should be put into the chamber immediately after drying. To improve the adhesion of film we use Ar^+ plasma to sputter sample surface for 10 minutes before deposition.

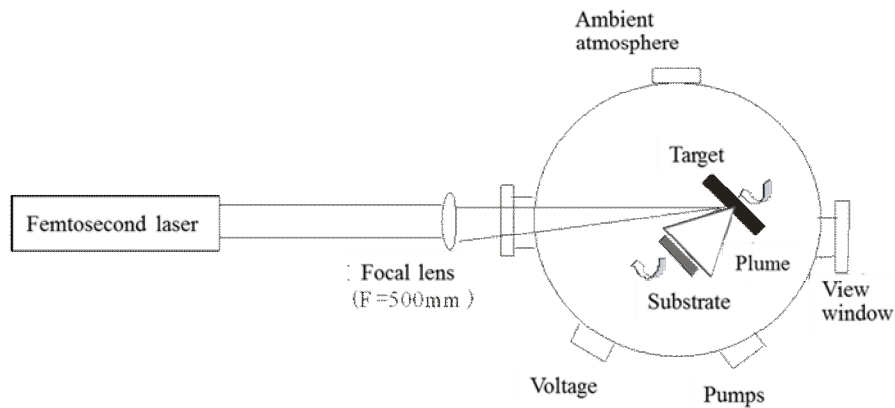


Fig.1 Schematic PLD system

Experiment process and results

In our experiments, we firstly deposited DLC films in vacuum and to find best distance between target and substrate. Under single pulse energy of $1.1\text{mJ}(8.7 \times 10^{13}\text{W}/\text{cm}^2)$, we deposited films on silicon substrates at 4cm and 5cm distance for 4min respectively. Through these experiments, we found the transmission at 5cm was better than 4cm^[5].

Deposit Si doped DLC films

We stuck Si slice onto graphite target surface to dope Si to the film, as shown in figure 2. When target holder rotated, laser ablated graphite and Si by turns and deposited Si doped DLC film. Through changing the width of silicon slice, DLC films with different Si quantity doped can be deposited.

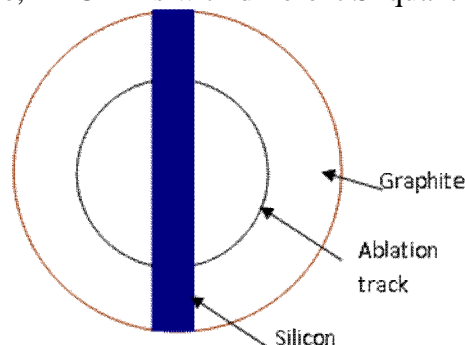


Fig. 2 Laser ablation track while doping Si to DLC film

We deposited films with different Si quantity doped. Si quantity doped in sample SiI、SiJ、SiK was 4%、7%、11% respectively. We tested performances of these samples and discovered that all transmissions of these three samples were higher than those pure DLC films. Furthermore, the quantity of Si doped was not the higher, the better. The transmission of sample SiJ was highest. Transmission peak at 3~5 μm reached 68.2%. Ellipsometer was applied to test the optical characteristics of the films. Refraction index of film doped silicon was lower than that of non-doped. This also explained the reason of transmission improved after doped silicon. To sample SiJ, the refractive index of DLC film was 2.17. The academic transmission simulated by film design software was 68.7%. The actual transmission 68.2% was only smaller 0.5% than 68.7%, as shown in figure 3. Furthermore, we plated common 3~5 μm anti-reflection film on other side of sample SiJ. The transmission peak at 3~5 μm was 93% and average $\geq 91.7\%$. Nano Indenter was used to test film nano-hardness and the hardness up to 40-50GPa. Furthermore, after rubbed by 9.8N rubber for 10^5 times, there was no nicks on the film. This proved that the adhesion performance of DLC film could meet the demand of common optical application.

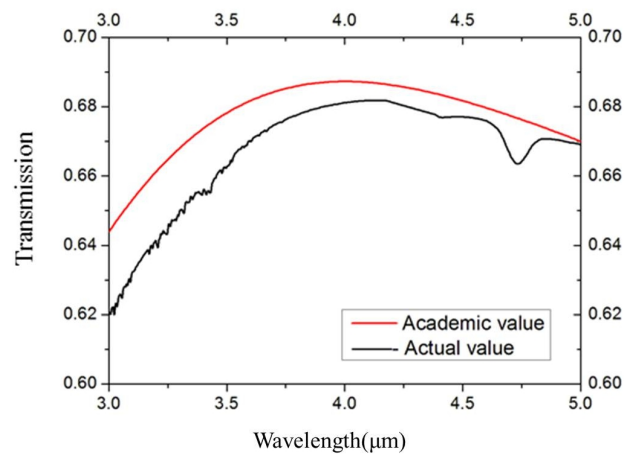


Fig. 3 Academic and actual transmission compare of Si doped DLC film

Symmetrical DLC film on large area

The shape of plasma generated in PLD was similar to taper. The distribution of kinetic energy and numbers of particles was very asymmetric, so the performances and thickness of films deposited by PLD was also asymmetric. The thickness of film by PLD was usually thick on center and thin on edge. This restrict the application of PLD. We adopted abaxially rolling and moving method to improve uniformity. As shown in figure 4, the initial center of substrate was apart from the center of plasma, and the substrate holder moved along its radial direction with variational velocity. The substrate holder moved quickly when it moved close to the center of plasma. When the substrate holder moved far from the center of plasma, it moved slowly. Furthermore, the substrate rotated round its own axis. Through this method, the film thickness on the center would not be too thick, and the film thickness on the edge would not be too thin. Symmetrical DLC film on large area would be deposited by optimizing the distance between substrate, the range of substrate holder moved, time of substrate holder stopped at different position. In our experiments, we found that the optimal conditions were as follows: the initial distance between substrate center and plasma center was 22mm, the substrate holder moved under velocity from 0.5mm/s to 2mm/s. The biggest distance between substrate center and plasma center was 75mm, and the substrate holder stayed 4s at this position, then the substrate holder moved to its initial position under velocity from 0.5mm/s to 2mm/s. After this process repeated for many times, symmetrical DLC film on $\phi 125\text{mm}$ silicon substrate was deposited. The film thickness was tested by ellipsometer, and the film thickness changed between 404.9nm and 412.9nm, average thickness was 407.8nm. The thickness asymmetry of film was smaller than 2%, and the transmission of different position all larger than 68%.

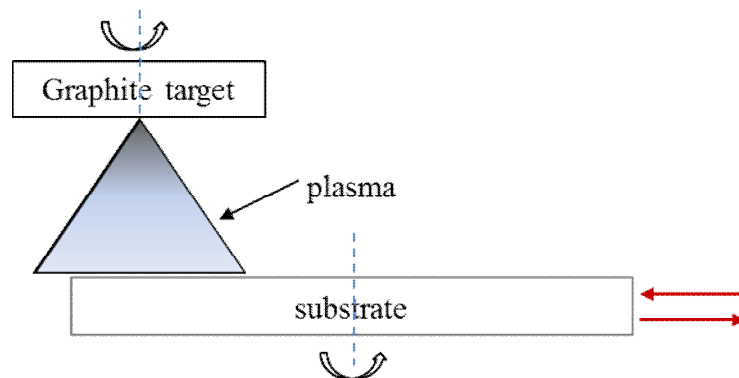


Fig. 4 Abaxially rolling and moving method

Conclusions

New technic of femtosecond pulsed laser deposition was used to prepare DLC films. Method of doping Si element was used to improve the performances of DLC film. Experiments proved that doping suitable Si element was useful to improve the integrated performances of DLC film, including transmission, inner-stress and adhesion. The transmission at 3-5 μ m of the silicon sample coated by DLC film on one side was larger than 68%. The nano-hardness was up to 40-50GPa. Through method of abaxially rolling and moving, symmetrical DLC film on large area was gained. Asymmetry of DLC film in size of ϕ 125mm was smaller than 2%.

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