Research of high-performance DLC Film on Si Substrate by Pulsed Laser Deposition

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Abstract. Femtosecond pulsed laser was used to deposit DLC films. Through methods of oxygen ambient and mixing silicon, no-hydrogen DLC films were deposited with more excellent transmission, hardness, adhesion and stability than those by chemical vapor deposition or traditional pulsed laser deposition (PLD). The transmission of 3~5μm band was larger than or equal to 91.7%, and the hardness up to 40~50GPa. All the films passed the tests of high temperature, low temperature, salt-fog and heavy-friction tests. The performances of the samples satisfied optical engineering need.

1. Introduction
Optical systems are playing a more and more important role in the modern military weapons and equipment. It demands optical windows with more excellent physical and chemical performances. Silicon as optical sensor in 3-5μm wave band is a great military need. But if silicon windows are used on equipment directly, as the transmission and hardness are not high enough, it is easy to be nicked and mildewed. One effective approach is to plate DLC films on silicon sensors.

Chemical vapor deposition has developed as a ripe method to deposit DLC films. But it needs high temperature and the film contains hydrogen. The performances such as hardness, heat and chemical stability are not excellent enough. As one new engineering technique, pulsed laser deposition can deposit no-hydrogen DLC films under room temperature with high speed, and is easy to mixing other substance and ambient gas [1-3]. Even so, there are still some incapable solved problems in traditional PLD method. Factors of low transmission, large stress and difficulty to deposit big uniform film restrict the engineering applications. DLC films for 3~5μm deposited on silicon or germanium in air and hydrogen have been reported, but the anti-reflection effect was not ideal. Besides, the hardness of these films was not strong enough and stability was inferior.

In our research, femtosecond pulsed laser was used to deposit DLC films. Through a great lot of experiments, we discovered the impact rules of DLC films by technical parameters, such as laser intensity. In addition, through means of oxygen ambient and mixing silicon, the performances of DLC film were improved. The average transmission of 3~5μm waveband was larger than 91.7% and hardness up to 40~50GPa. The Si windows deposited DLC films passed the tests of high temperature, low temperature, salt-fog and heavy-friction. They satisfied the needs of optical engineering application.

2. Theory research
Through our early experiments [4-6], we found that the transmission of DLC films deposited in vacuum were not high enough, only higher than or equal to 55% which was the transmission of Si substrate
itself. And the adhesion was very bad, many DLC films couldn’t be deposited on Si samples firmly. The films fell off easily. It is hopeful to improve the transmission, hardness and adhesion through oxygen ambient and silicon mixing which may change the sp³-band content of DLC film.

2.1 Theory of oxygen etching effect to DLC film
The particles which sputtered from the graphite target can collide with oxygen molecules and produce oxygen ions. The etching effect of oxygen ions with sp³ bond is very small while with non-sp³ bond very strong. Thus oxygen ions can decrease the content of sp² bond and increase content of sp³ bond. The sketch map is showed as figure 1. But if the oxygen pressure is too high, only few carbon particles can fly to the substrate. The oxygen etching rate will exceed deposition rate, which leads to no film deposited.

![Figure 1. Etching effect of oxygen to DLC film](image)

2.2 The effect of mixing silicon to DLC film
To reduce the inner-stress of DLC film, researchers [7-9] tried to mixing some elements to DLC film, such as Si, Ti, W, Cu, Ag, Cr and N Compared to other elements, Si has some merits. Silicon fits well with Si substrate and impossibly to form π bonds which indwell in sp². Besides, as the energy of Si-C bond 3.21eV is smaller than that of C-C bond 3.70eV, aberrance of C element bonds can be slacked which will make the stress decline greatly.

Research of mixing silicon DLC film still at germination stage, only few people [7-9] have studied it. Earliest overseas report about mixing silicon DLC film was 1998 while domestic until 2005. Anyway, the actions of mixing silicon have been found. It’s useful to decrease inner-stress and improve adhesion or sp³ bond content.

3. Experiments research

3.1 Experiment equipment
Ti:Sapphire femtosecond laser (800nm, 120fs, 1000Hz, 3.3W) was used. The vacuum limit of
deposition chamber is 6×10^{-5} Pa. The sketch deposition system is shown in figure 2. 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 Si (100) substrate are placed paralleled 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 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 Si slices were firstly dipped in 5% HF for 10 minutes and then ultrasonically cleaned in acetone for 5 minutes. Both graphite and Si should be put into the chamber immediately after drying. To improve the adhesion of film we use Ar⁺ plasma to sputter sample surface for 10min before deposition.

![Fetosecond laser Focal len F 500mm](image)

Figure 2. Schematic PLD system of DLC film

3.2 Experiment process and results

In our experiments, we firstly deposited DLC films in vacuum and found the best distance between target and substrate. Through these experiments, two problems were discovered. One, the transmission was very low. The other one, the films were easy to shed. Thus we must look after else methods to improve the performances of DLC film. We mainly studied the influence of oxygen ambient and mixing silicon to DLC film.

3.2.1 Deposit DLC film in vacuum

In vacuum and under single pulse energy of 1.1mJ (9.6×10¹³W/cm²), we deposited films to find best distance between target and substrate, concrete technical parameters are shown in table 1.

| Sample | Energy(mJ) | Distance(cm) | Time(min) |
|--------|------------|--------------|-----------|
| SiA    | 1.1        | 4            | 4         |
| SiB    | 1.1        | 5            | 4         |

Infrared transmissions of sample Si(uncoated), SiA and SiB were measured and shown in figure 3. From figure 2, we can see that transmission at 4−5μm (2000−2500cm⁻¹) of sample SiB is slightly higher than uncoated Si slice (55%). Transmission of SiA is lower than Si. So the experiments indicated that the better distance was 5cm.
3.2.2 Deposit DLC film in oxygen ambient

In vacuum we found best distance between target and substrate was 5cm. According to the equation of gas molecule average free path:

$$\lambda = \frac{kT}{\sqrt{2\pi d^2 p}}$$

where $k=1.38\times10^{-23}$, diameter of oxygen molecule $d=3.6\times10^{-10}$m, room temperature is 298K, $p$ is oxygen pressure, so we can calculate than when $p=0.14$Pa, $\lambda_{oxygen}=5$cm.

We can deem that when oxygen pressure smaller than 0.14Pa, collisions between carbon particles and oxygen molecules will very few and generate few oxygen ions. When the pressure is larger than 0.14Pa, collisions will be strong to generate enough oxygen ions. The etching effect will be evident and make the content of sp³ bonds increase.

Kept the distance 5cm and laser energy 1.1mJ unchanged, we tried to find the best oxygen pressure. Samples were deposited respectively under 0.03Pa, 0.1Pa, 0.5Pa, 2Pa and 5Pa oxygen pressure. To make the anti-reflection wave center all nearly 4μm, the films were deposited different time. They were deposited 8min, 14min, 20min, 60min and 80 min accordingly. The particles sputtered from the graphite target would collide with oxygen molecules violently. It caused that particles reached onto surface of Si decreased heavily. The deposition rate of DLC film would fall down as the oxygen pressure increase. The technical parameters were shown in table 2.

| Sample | Energy (mJ) | Oxygen Pressure (Pa) | Time (min) |
|--------|-------------|----------------------|------------|
| SiB    | 1.1         | 1×10⁻⁴               | 4          |
| SiC    | 1.1         | 0.03                 | 8          |
| SiD    | 1.1         | 0.1                  | 14         |
| SiE    | 1.1         | 0.5                  | 20         |
| SiF    | 1.1         | 2                    | 60         |
| SiG    | 1.1         | 5                    | 80         |

Experiments proved when oxygen pressure was 5Pa, DLC film couldn’t be deposited on sample SiG. It’s because the oxygen pressure was too high and it matched with the theory analysis. The transmission of sample SiC was nearly to SiB as the oxygen etching effect feeble. Both sp³ bond content and transmission of sample SiD, SiE and SiF increased along with oxygen pressure. The sp³ bond content of sample SiF was 63% and transmission at 3~5μm 62%.

Figure 3. Infrared transmission spectrum of SiA and SiB
Under conditions of 2Pa oxygen pressure and 5cm distance, we deposited DLC films at 1.3mJ, 1.6mJ, 2mJ and 3mJ respectively. We found that when pulse energy was 1.6mJ, the transmission was highest (about 64%). These experiments proved that pulse energy was not the higher, the better. There was a highest threshold in pulse energy.

3.2.3 Mixing silicon to DLC film in oxygen ambient
We stuck silicon slice onto graphite target surface to mixing silicon to the film. When target holder rotated, laser ablated graphite and silicon by turns and deposited mixing silicon DLC film. Through changing the width of silicon slice, DLC films with different mixing silicon quantity could be deposited. The sketch map was shown as figure 4.

![Figure 4. Laser ablation track while mixing silicon to DLC film](image)

We deposited films with different mixing silicon quantity. Silicon ration mixed in sample SiI, SiJ and SiK was respectively 4%, 7% and 11%. We tested performances of them and discovered that all transmissions of these three samples were higher than those non-mixed silicon DLC films. Furthermore, the transmission of sample SiJ was highest. Transmission peak at 3~5μm reached 68.7% and hardness up to 40GPa. Infrared spectroscopic ellipsometer was applied to test the optical characteristics (e.g. refraction index and extinction coefficient) of the films. Refraction index of film mixed silicon was lower than non-mixed. Both refraction index and extinction coefficient decreased as mixing silicon quantity increased. This also explained the reason of transmission improved after mixing silicon. All the films passed the tests of high temperature, low temperature, salt-fog and heavy-friction. Furthermore, we plated common 3~5μm anti-reflection film on other side of sample SiJ. The transmission peak at 3~5μm was 93% and average ≥91.7%.

Technical parameters of best samples under different conditions were contrasted in table 3. Make a comprehensive survey of above experiments, we can found that both oxygen ambient and mixing silicon were helpful to improve performances of DLC film by PLD. Parameters of pulse energy, distance, oxygen pressure and mixing silicon quantity all existed optimal numerical value.

| Sample | Distance(cm) | Energy(mJ) | Oxygen Pressure (Pa) | Mixing Silicon | Time (min) | Transmission (3~5μm) |
|--------|--------------|------------|----------------------|----------------|------------|----------------------|
| SiB    | 5            | 1.1        | 1×10^-4             | 0%            | 4          | 56%                  |
| SiF    | 5            | 1.1        | 2                    | 0%            | 60         | 62%                  |
| SiH    | 5            | 1.6        | 2                    | 0%            | 50         | 64%                  |
| SiJ    | 5            | 1.6        | 2                    | 7%            | 50         | 68.7%                |

4. Conclusions
Femtosecond pulsed laser deposition was used to prepare DLC films. And methods of oxygen ambient and mixing silicon were used to improve the performances of DLC film. Our experiments indicated
that both these two methods were helpful to advance transmission, hardness and adhesion of DLC film. Average transmission at 3–5μm of Si substrate deposited with DLC film was larger than 91.7% and hardness was up to 40–50GPa. All the samples passed the tests of high temperature, low temperature, salt-fog and heavy-friction.

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