Corrosion resistance of optical diamond-like carbon film

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Abstract: KrF laser and Ti:Sapphire femto-second laser were used to deposit diamond-like carbon (DLC) films on silicon substrates which were double polished. Optical transmittance and corrosion resistance of these samples were compared. The transmittance of DLC film sample which was deposited by Ti:Sapphire laser in oxygen atmosphere was higher than the sample which was deposited by KrF laser in vacuum. Both samples could pass the salt solubility test and salt fog test. But when dipped in NaOH liquor, the result showed that surface of the sample deposited by Ti:Sapphire laser in oxygen atmosphere appeared corrosive spots first. Reasons were analyzed according to corrosive mechanism.

1. Introduction
Silicon and germanium are used as optical windows commonly. But these materials have some shortcomings, such as the transmission and hardness are not high enough, easy to be nicked and corroded. As DLC films have many merits similar to diamond, such as high hardness, anti-reflection at wide spectrum and high stability. DLC films can be used as anti-reflective and protective materials for optical windows [1-3]. One effective approach is to plate common infrared anti-reflection film on the inner surface and plate DLC films on the outer surface. DLC films deposited by chemical vapor deposition (CVD) were mature, the transmission was high enough. But as the DLC films deposited by CVD method contain hydrogen element, their chemical stability are not excellent enough [4]. They can be corroded easily and can’t protect the optical windows perfectly in the marine, acidic and alkaline environment [5]. The transmission of optical windows will be affected once they were corroded. So it’s very important to study the corrosion resistance ability of DLC films.

Some researchers [6,7] studied the corrosion resistance ability of DLC film deposited on alloy substrate, they found that the corrosion resistance ability of these substrates improved evidently after coated by DLC films. The research about corrosion resistance ability of DLC film in optical application was rare. Some researchers [8] deposited DLC film on germanium window by radio frequency plasma CVD (RF-CVD). They compared the corrosion resistance ability of this window to another germanium window which was uncoated by DLC film. The test was carried out in marine environment. They found corrosion resistance ability of the window coated by DLC film was much better. For all that, some points of the DLC film still fell off after 3 months, and the substrate was corroded at the position where the film fell off.

Pulsed laser deposition (PLD) is a new method to deposit DLC film. High power laser is used to bombard graphite target to produce plasma which will grow DLC film on substrates. DLC films deposited by PLD contain no hydrogen element and no telescopic vibration at 3.4μm owing to C-H bond. Furthermore, PLD method has other merits such as room temperature, high speed and fastness[9-11]. It was used more and more popular. In this article, two kinds of laser were used to deposit DLC films on silicon substrates. The transmission of these samples could meet the demand. Factors
which influenced the corrosion resistance ability were analyzed. Corrosion resistance effect of two different craft was compared qualitatively.

2. Experiments

The sketch map of deposition system is shown in figure 1. KrF excimer laser (248nm, 20ns, 50Hz) and Ti:Sapphire femto-second laser(800nm, 120fs, 1000Hz) were used to deposit DLC film. Laser beam was 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) substrates were placed parallel into the chamber. Both the target and substrate holders could rotate round their main axis during the irradiation to make the films uniform. Ambient atmosphere channels and ion sputtering devices were equipped to the chamber. Before put into the chamber, the substrates were scrubbed by diamond power suspension to generate microdefects. Then they were ultrasonic cleaned in alcohol for 10 minutes and washed by distilled water. After blowed dry by nitrogen, the substrates were put onto the holder and sputtered by 400eV Ar⁺ for 10 minutes.

Figure 1. The scheme of pulsed lasers deposition system

After many experiments, the deposition parameters were optimized. We found that the peak transmission at 3~5μm of silicon sample coated by DLC film on single side deposited by KrF laser was bigger than 65%. The experimental parameters were energy 500mJ and frequency 30Hz of KrF laser in vacuum. Under the condition of energy 1.7mJ, frequency 1000Hz and vacuum, the peak transmission at 3~5μm of silicon sample coated by DLC film on single side deposited by Ti:Sapphire laser was smaller than 60%. If deposited in oxygen ambient, the peak transmission could reach to 68%[12,13]. Transmission curves were shown in figure 2. After coated by common optical anti-reflective film on other sides, all the transmission of these samples reached bigger than 90% and could meet the demand of optical windows.

Figure 2. Transmittance of different samples
Sample A: DLC film deposited by KrF laser; Sample B: DLC film deposited by Ti:Sapphire laser
3. Corrosion resistance test and analysis of the film

There are many methods to assess the corrosion resistance of DLC films. As corrosion resistant film for metal materials, it was usually assessed by electrochemistry method[6,7]. In this article, according to universal standard of optical films, salt solubility test and salt fog test were used to assess the corrosion resistance of DLC films.

In salt solubility tests, the samples were dipped in 4.5% NaCl solution for 24h under temperature between 16°C and 32°C.

For salt fog tests, the samples were sprayed by NaCl solution for 24h. The concentration of the solution was between 4.9% and 5.1%, pH value was between 6.5 and 7.2, and the temperature was between 33°C and 37°C.

After these two tests, all the films of the samples were intact. There was no peeling, abscission or crackle on the sample surfaces. The transmission had no change almost. These results showed that DLC films deposited by pulsed lasers could meet the common corrosion resistant demand.

To compare further performances of these samples, more strict tests were carried out. The samples were dipped in 10% NaOH solution. Corroded spots appeared on sample B first as shown in figure 3.

![Figure 3. Sample B after dipped in NaOH solution](image)

Corrosion mechanism for DLC films deposited by different parameters were various, common mechanism was pitting and uniform corrosion [4]. Dense structure could prevent ion seeped into the film, corrosion would only occur on the surface. Even the films were dipped in corrosive solution, the corrosive velocity would be very low and this kind of corrosion was due to uniform corrosion.

In the deposition progress, sputtering of Ar⁺ and defects of substrates would both cause defects in DLC films, such as pinhole and weak combination. The corrosion resistance of those defective positions would decline, corrosive solution could reach to the substrates and pitting formed.

Sample B was deposited in oxygen ambient, so there were C-O bonds in the film. The bond energy of C-O was smaller than that of C-C, so the density was lower and ions could easily penetrate into the film. Furthermore, oxygen element might be residual in the film. These substances were unstable and easy to react with corrosive solution. This would make the corrosion resistance of the film inferior.

4. Conclusions

In this article, two kinds of lasers were used to prepare DLC film on silicon substrate. All the transmissions could meet the demand, and transmission of DLC film deposited by Ti:Sapphire laser in oxygen ambient was larger than that by KrF laser in vacuum. According to universal optical standard, corrosion resistance was compared qualitatively, all the samples passed the salt solubility test and salt fog test, and could meet the demand for general conditions. Through dipping the samples into NaOH solution, corrosion resistance of sample A was better than sample B. The reasons might be density reduced and oxygen residual. In actual applications, we should balance the demand of transmission and corrosion resistance, and choose the deposition parameters synthetically.

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