

# THE INFLUENCE OF SILICON ELEMENT-ADDED DLC FILM ON Ti-6Al-4V

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## Abstract

Silicon added diamond-like carbon films fabricated from C<sub>2</sub>H<sub>2</sub>:TMS mixture were used to study the influence of silicon content on the deposition and tribological properties of films prepared on Ti-6Al-4V substrate by using plasma-based ion implantation (PBII). The structure of the film was analyzed by Raman spectroscopy. Hardness and elastic modulus of the film were measured by nano-indentation hardness tester. Tribological properties of the film were performed by using ball-on-disk friction tester. The results indicate that with the increasing silicon content in the pure DLC film, the friction coefficient increases. The hardness and elastic modulus of Si-DLC film can increase to a value of up to 31.1 GPa and 200.1 GPa with a silicon content of 13.1 at.%. This is because the greater C content. The Si-DLC films with Si content of 13.1 at.% (C:Si/1:2) and 14.3 at.% (C:Si/1:6) shows a low friction coefficient of 0.2, which is considerable improvement in the tribological properties. This is due to the high hardness and elastic modulus.

**Keywords:** DLC film; plasma-based ion implantation (PBII); Silicon element; Ti-6Al-4V

## Introduction

DLC films are metastable amorphous films with high hardness, low friction coefficient, good wear resistance, chemical inertness, good biocompatibility, and great corrosion resistance. As a result, these films are extensively used in protective coatings, cutting instruments, biomedical applications, magnetic storage, etc. (Kwak *et al.*, 2005; Cruz *et al.*, 2006; Shirakuna *et al.*, 2006). Moolsradoo and Watanabe (2010) and Yu *et al.* (2005) have published studies demonstrating the improvement of DLC film characteristics by adding elements.

The plasma-based ion implantation (PBII) technique was created to enhance the properties of film coating (Xia *et al.*, 2005). Furthermore, PBII has been demonstrated to be effective for surface modification and the homogeneous fabrication of ions onto three-dimensional substrates with complicated forms. Samples are immersed in plasma and biased to a negative potential in this approach. The exposed surface of the samples is then encased in a plasma sheath, and accelerated ions bombard it. This is a surface modification

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technique that works well (Conrad and Castagna, 1986).

There is currently no report on the PBII method for depositing Silicon enhanced DLC films on Ti-6Al-4V substrates with the goal of comparing mechanical and tribological properties. At three different gaseous flow rate ratios, the PBII process was used to generate pure DLC and silicon added in DLC films in this research. The aim of this study was to study the influence of silicon element on properties of diamond-like carbon film.

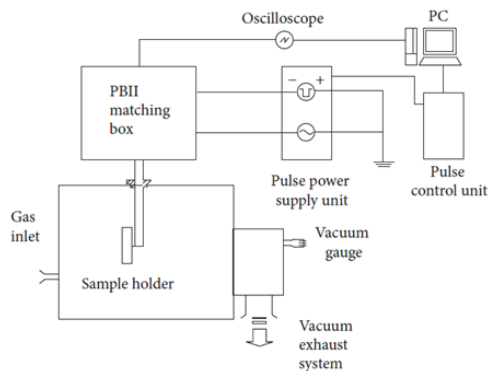


Figure 1. Schematic of the PBII apparatus

## Materials and Methods

Pure DLC and Si-DLC films were fabricated by using the plasma based ion implantation (PBII) technique. A PBII apparatus used in this paper is showed in Figure 1 and early presented by (Moolsradoo and Watanabe, 2010). The dimensions of inner chamber are  $600 \times 630 \times 200 \text{ mm}^3$ . The plasma is generated by RF (13.6 MHz) glow discharge and a high voltage power supply that connected to the samples. Ti-6 Al-4 V alloys were used as substrate material. Prior to the plasma coating, specimens were mirror polished by standard abrasive paper down to 2,000 grit and polished with  $1 \mu\text{m}$  diamond paste, and then cleaned in an ultrasonic cleaning bath. The substrates were cleaned with  $\text{Ar}^+$  sputtering to remove surface contaminants using a negative bias voltage of -10 kV. The inter layer was first deposited with  $\text{CH}_4$  for 60 min by using the bias voltage of -20 kV, to improve adhesion between the film and the substrate. The DLC film was deposited from Acetylene ( $\text{C}_2\text{H}_2$ ) gas. The Si-DLC films were fabricated from  $\text{C}_2\text{H}_2$  and TMS ( $\text{C}_4\text{H}_{12}\text{Si}$ ) mixtures at three different flow rate ratio of 1:2, 1:4 and 1:6. The bias voltage and RF power were set at -5 kV

and 300 W, respectively, and deposition pressure was set at 2 Pa.

The total film thickness was approximately 500 nm, as measured by Stylus Profilometer. The deposition conditions of all films are listed in Table 1. The films structure were analyzed using Raman spectroscopy. The elements composition of films were measured on the top surface using Energy Dispersive X-ray Spectroscopy (EDS). The hardness and elastic modulus of films were determined by a nanoindentation hardness tester using a diamond ball indenter (Berkovich-type) with an indentation load of  $1,000 \mu\text{N}$ . The tribological properties of the films were investigated using a ball-on-disk friction tester under ambient air conditions. For the friction test, ball tester made from AISI 440C with a diameter of 6 mm under a normal applied load of 1 N, a linear speed of 31.4 mm/s, a rotational radius of 4 mm and 3,000 frictional rotations. The friction test was performed at room temperature.

Table 1. G-peak of all films at various flow rate ratios

| Film type | Gaseous mixture              | Gas flow rate ratio | G-peak ( $\text{cm}^{-1}$ ) |
|-----------|------------------------------|---------------------|-----------------------------|
| Pure DLC  | $\text{C}_2\text{H}_2$       | —                   | 1,528                       |
| Si-DLC    | $\text{C}_2\text{H}_2$ : TMS | 1:2                 | 1,462                       |
|           |                              | 1:4                 | 1,460                       |
|           |                              | 1:6                 | 1,451                       |

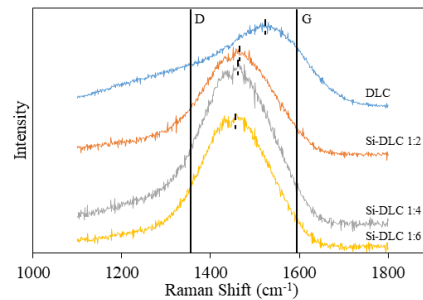


Figure 2. Raman spectra of all films at various flow rate ratios

## Results and Discussion

Figure 2 shows the Raman spectra of the pure DLC and Si-DLC films fabricated at various flow rate ratios, deposited on Ti-6 Al-4 V substrates. DLC films with a broad spectrum composed of a D band ( $1,350 \text{ cm}^{-1}$ ) and G band ( $1,580 \text{ cm}^{-1}$ ) that are similar to the peaks shown in conventional DLC films.

The G-peak of the pure DLC film shifted lower with silicon incorporation.

For the Si-DLC film, the G–peak shifted from  $1,462\text{ cm}^{-1}$  (C:Si/1:2) to  $1,451\text{ cm}^{-1}$  (C:Si/1:6) with silicon incorporation. This could be attributed to a change in microstructure as the formation of more  $\text{sp}^3$  clusters with an increase in the silicon contents (Papakonstantinou *et al.*, 2002).

**Table 2. Relative atomic content of all films at various flow rate ratios**

| Film type | Gas flow rate ratio | Relative atomic content (at.%) |      |     |      |
|-----------|---------------------|--------------------------------|------|-----|------|
|           |                     | C                              | Si   | O   | Ti   |
| Pure DLC  | -                   | 87.8                           | -    | 1.1 | 10.4 |
| Si-DLC    | 1:2                 | 52.6                           | 13.1 | 4.8 | 21.1 |
|           | 1:4                 | 47.9                           | 13.4 | 6.5 | 28.4 |
|           | 1:6                 | 47.1                           | 14.3 | 5.9 | 28.3 |

The relative atomic contents measured on the top surface of the films are shown in Table 2. The carbon (C), silicon (Si), oxygen (O) and titanium (Ti) concentrations were measured using the EDS, and values are always given in units of atomic percent (at.%). Additionally, the hydrogen content is neglected due to the EDS could not be measured.

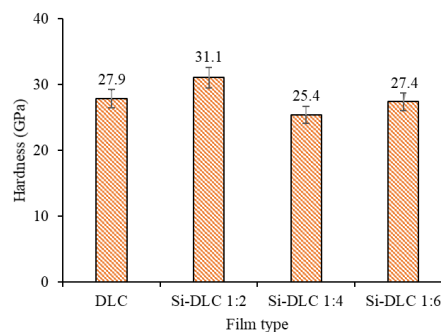
From Table 2, the results show the Ti content appeared in all films. This is due to the very thin film thickness (approximately 500 nm). It is assumed that the penetration depth of electron during test is higher than 500 nm (Moolsradoo and Watanabe, 2017).

From Table 2, the result of Si-DLC film show that the Si content increases from 13.1 at.% to 14.3 at.% when the gas flow rate ratio changed from 1:2 to 1:6.

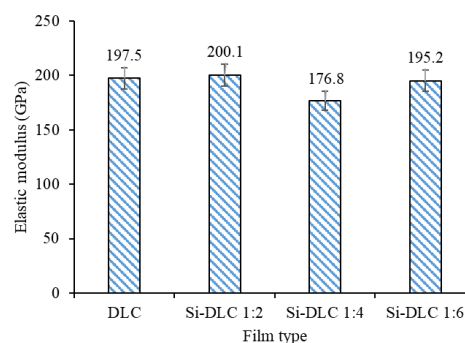
The hardness and elastic modulus values of pure DLC and Si-DLC films are shown in Figures 3-4. The results were calculated from a force curve obtained from the nanoindentation hardness test.

It is clear that the hardness and elastic modulus gradually increased from 25.4 GPa to 27.4 GPa and 176.8 GPa to 195.2 GPa with Si content increased from 13.4 at.% to 14.3 at.%. The increases in the film hardness and elastic modulus are believed to be partly due to the changes in the microstructure, as concluded from the Raman analysis result, that is the formation of more  $\text{sp}^3$  structure with an increase in the silicon contents (Moolsradoo and Watanabe, 2017). Si-DLC film at lowest Si content of 13.1 at.% (C:Si/1:2) shows the highest hardness and elastic modulus, this is because the greater C content. A pure DLC film shows the high hardness and elastic modulus, although the G peak of the pure DLC film was greater than the Si-DLC at silicon content of 13.4 at.% to 14.3 at.%. The high hydrogen content in a pure DLC film prepared from the  $\text{C}_2\text{H}_2$  precursor gas was speculated to have

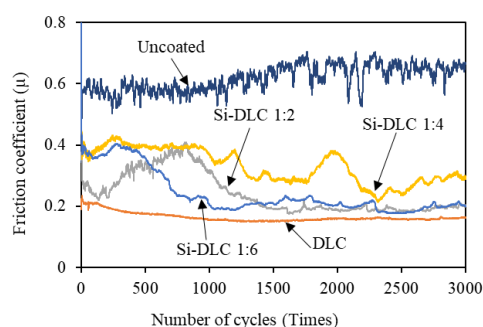
polymer-like chains, resulting to the decreased of film hardness and elastic modulus (Fujimoto *et al.*, 2011), while the greater C content exhibited greater hardness values.



**Figure 3. Hardness of all films at various flow rate ratios**



**Figure 4. Elastic modulus of all films at various flow rate ratios**



**Figure 5. Friction coefficient of all films at various flow rate ratios**

The friction coefficient of pure DLC and Si-DLC films measured under ambient air are shown in Figure 5. The DLC film are stable friction coefficient of 0.18. The Si-DLC films at Si content of 13.4 at.% (C:Si/1:4) had an unstable. It is due to

the lower hardness and elastic modulus, results in difficulty supporting the load, which can increase the contact area at the ball-film interface. Si-DLC films at Si content of 13.1 at.% (C:Si/1:2) and 14.3 at.% (C:Si/1:6), has a low friction coefficient of 0.2. It is due to the high hardness and elastic modulus.

## Conclusions

Silicon added diamond-like carbon films (Si-DLC) were prepared on Ti-6 Al-4 V alloys by using the PBII technique. The films were investigated in term of their structures, mechanical properties, and tribological properties by using Raman spectroscopy, nano-indentation hardness testing, and ball-on-disk friction testing. It was observed that by increasing the silicon content in the pure DLC film, the friction coefficient increased. Moreover, by increasing the silicon content in the Si-DLC film from 13.4 at.% to 14.3 at.%, the hardness and elastic modulus increased. The increases in the film hardness and elastic modulus were due to the increases in  $sp^3$  clusters. The hardness and elastic modulus of Si-DLC film can increase to a value of up to 31.1 GPa and 200.1 GPa with a silicon content of 13.1 at.%. This is because the greater C content. The Si-DLC films with Si content of 13.1 at.% (C:Si/1:2) and 14.3 at.% (C:Si/1:6) shows a low friction coefficient of 0.2, which is considerable improvement in the tribological properties. This is due to the high hardness and elastic modulus.

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