# Effects of Si incorporation on thermal stability and tribological properties of DLC films

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**Pure and silicon (Si)-incorporated diamond-like carbon (Si-DLC) thin films were deposited onto Si wafers using a reactive sputtering method. By varying the $SiH_4$ flow rate, DLC films of various Si contents were achieved. The effects of Si incorporation on the thermal stability and tribological properties of the DLC films were studied with reference to the modifications to their chemical bonding at elevated temperatures along with their friction mechanisms. Fourier transform infrared spectroscopy (FTIR), optical microscopy, field emission scanning electron microscopy (FESEM) with energy-dispersive X-ray spectroscopy (EDS), and micro-Raman spectroscopy were applied to determine the film's thermal, friction, and wear behaviors. As the Si was incorporated, the Si-O bond intensity increased and the Si-C bond remained within the films, which presumably resulted in the good thermal stability. It was found that the lower friction coefficient of the Si-incorporated films is correlated to the formation of a $SiO_2$ transfer film on the surface of the wear scar.**

**Key words: DLC, Reactive sputtering, Si incorporation, Thermal stability, Friction and wear.**

## Introduction

Silicon (Si)-incorporated diamond-like carbon (Si-DLC) films, owing to their low friction coefficient [1, 2] and high thermal stability [3], among other excellent properties, have been applied to various sliding parts often subjected to localized heating caused by friction in ambient air. It is extremely important, therefore, to investigate these films' thermal stability with respect to structural change and the mechanism of the low friction coefficient at elevated temperatures for a wide range of industrial applications [4]. It is well known that as incorporation of Si forms more sp³-bonded carbon and stabilizes the film structure, this leads to thermal degradation such as graphitization and hydrogen effusion at higher temperatures than is the case with pure DLC films [5, 6]. Such effects of Si incorporation into DLC films are generally attributed to Si-C bond formation [7, 8], as embedded in a carbon matrix. In a previous study, we employed micro-Raman spectroscopy and field emission scanning electron microscopy (FESEM) imaging to clarify the effects of Si incorporation on the structural change of as-deposited and annealed films [9]. However, modification of the chemical bonding configuration of Si-DLC films during the annealing process is required in order to

investigate the resultant improvement of thermal stability.

In the process of wear, DLC films can be subjected to high frictional heat and undergo an in situ bonding-structure change. Generally, the flash temperature exceeds the critical temperature for the sp³-to-sp² phase transition, which is to say that wear-induced graphitization can create a transfer layer on sliding surfaces, leading to a low friction coefficient and the well-known solid lubricant of DLC films [10, 11]. However, under various conditions, the most frequently observed low-friction-coefficient mechanism between Si-DLC films and a steel ball might, alternatively, be due to the formation of a $SiO_2$-layer, possibly arising from friction-produced oxidation [12, 13].

Therefore, in the interests of the reliable long-term thermal stability of Si-DLC films, it would seem prudent to investigate modifications to their chemical bonding configurations at elevated temperatures along with their low-friction mechanism.

In this study, we deposited Si-DLC films of various Si contents by reactive sputtering, and systematically observed, through annealing and wear testing, the effects of Si incorporation on their thermal stability and tribological properties.

## Experimental

Pure DLC and Si-incorporated DLC films were deposited onto Si wafer substrates using a reactive sputtering system composed of the plasma decomposition

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of a CH$_4$ and SiH$_4$ (5% in Ar) gas mixture and RF magnetron sputtering of a graphite target by Ar. The specifications on this reactive sputtering system have been reported elsewhere [14, 15]. The Si incorporation was controlled by varying the SiH$_4$ flow rate from 0 (pure DLC), to 4.49 and to 9.17 sccm, subsequently the Si contents as determined by X-ray photoelectron spectroscopy (XPS, VG Science Escalab 210) were 7 at.% and 15 at.%, respectively. The chemical bonding state within the pure DLC and 7 at.% Si-DLC films before and after annealing treatment was measured by Fourier transform infrared spectroscopy (FTIR, Bruker IFS66v/s & Hyperion 3000) to elucidate the effect of Si incorporation on the films' thermal stability. The thermal annealing was conducted in an open-air tube furnace by heat treating the samples from 200 °C to 700 °C in 100 °C increments. The friction coefficient and wear behavior were evaluated by sliding tests using a ball-on-disk tribometer with a 1.27 cm (1/2 in) AISI 52100 chrome steel ball under a load of 1 N at ambient temperature. The maximum number of contact cycles was 25,000. After the friction and wear tests, the wear track in the films and the wear scar on the balls were examined under optical microscopy, micro-Raman spectroscopy (Horiba Aramis), and field emission scanning electron microscope (FESEM, Hitachi S-4800) with energy dispersive X-ray spectroscopy (EDS, Horiba X-max) to analyze the morphology, microscopic structure, and chemical composition, respectively.

## Results and Discussion

### FTIR analysis

FTIR measurements were performed to reveal the structures of DLC films, thereby yielding a variety of information on the local chemical bonding. Fig. 1 shows the infrared absorption spectra within the 700-4000 cm$^{-1}$ wave-number range for the as-deposited pure DLC and 7 at.% Si-DLC films. It is evident that the spectra of the pure DLC films show the C = C (~ 1700 cm$^{-1}$) and C-H bond-stretching modes (~ 2900 cm$^{-1}$), whereas the 7 at.% Si-DLC films show not only the C = C and C-H peaks but also the Si-O (~ 1040 cm$^{-1}$) and Si-H (~2100 cm$^{-1}$) bond stretching modes [16-18]. The peak at 1700 cm$^{-1}$ due to C = C stretching indicates non-graphite-like C = C bonding; that at 1040 cm$^{-1}$ is attributable to Si-O valence vibration, which confirms the presence of oxygen in the films [3].

Fig. 2 shows the FT-IR spectra of the pure DLC films after annealing at various temperatures. As is apparent that with increasing annealing temperature, the intensity of the C = C bonds increases and that of the C-H bonds decreases. It is well known that increased C = C bond intensity for annealed DLC films is an indication of the relatively higher sp$^2$ contents than in as-deposited films, which is due to the increase of the random network of nanocrystalline graphite with
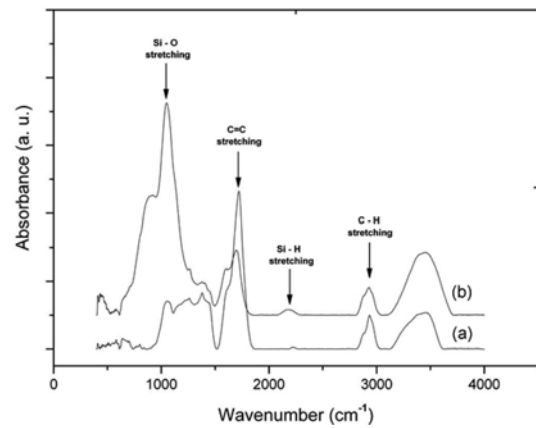


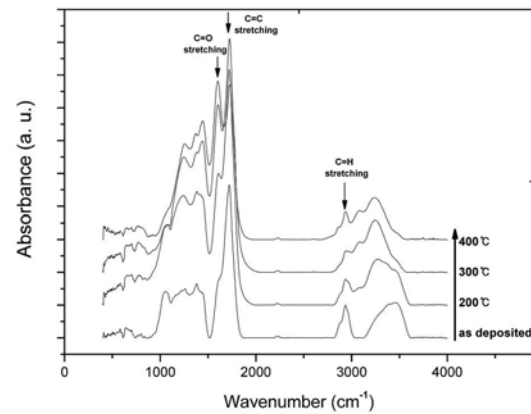**Fig. 1.** FTIR spectra of as-deposited (a) pure DLC and (b) 7 at.% Si-DLC films.



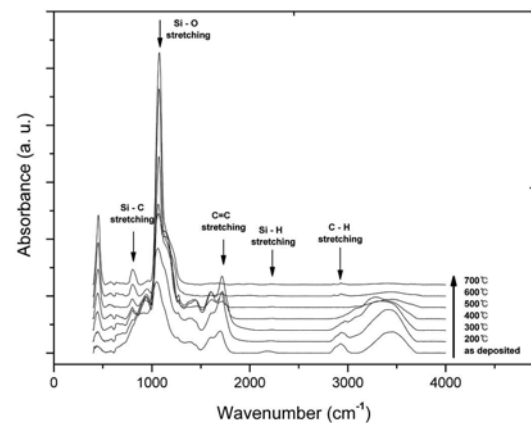**Fig. 2.** FTIR spectra of pure DLC films annealed at various temperatures.



**Fig. 3.** FTIR spectra of 7 at.% Si-DLC films annealed at various temperatures.

increasing annealing temperature [5]. Conversely, decreased C-H bond intensity for annealed films reflects the hydrogen loss attendant on high temperature annealing [19]. From the thermodynamic point-of-view, it is reasonable that the oxygen from air is adsorbed into the DLC film surface during annealing process, forming carbon dioxide [20, 21]. This oxidation reaction is confirmed by the increase in the relative

intensity of the C = O bond stretching modes ($\sim 1600$ cm$^{-1}$) at higher annealing temperatures, which, significantly, is not detected in as-deposited films. It can be assumed, therefore, that with respect to the variation of the intensity of C-H and C = O peaks, hydrogen is removed from films and oxidation is enhanced as annealing temperature increases. Indeed, in our previous study [9], we observed that oxidation resulted in thickness loss and finally disappearance of films annealed at a temperatures higher than 500 $^o$C.

Fig. 3 shows the FT-IR spectra of the 7 at.% Si-DLC films after annealing at various temperatures. It is apparent that the relative intensity of the hydrogen-containing bonds, namely Si-H and C-H, decreases with increasing annealing temperature, and that when annealed over 400 $^o$C, the peaks disappear, which indicates a hydrogen-effusion-effected structural change. The C = O and C = C bond intensity is not significantly changed until annealing at 400 $^o$C, and disappears above 500 $^o$C. By contrast, the intensity of the Si-O bond shows a very appreciable increase as the annealing temperature increases. This high intensity of the Si-O bond indicates the Si-DLC film' considerable oxidation which might remain therein as silicon dioxide (SiO$_2$), where it acts as a barrier to oxygen diffusion. It should be noted that the Si-O bond appears in diamond-like nanocomposite (DLN) films synthesized by addition of the Si-O network for improved thermal stability [22, 23]. It is also found that the intensity of the Si-C bond stretching mode ($\sim 800$ cm$^{-1}$) is significant even after annealing at 700 $^o$C, reflecting the large extent of SiC phase formation in the Si-DLC films. In a previous study, changes to structural and mechanical properties were explained by the existence of SiC phase embedded in an amorphous matrix [24]. Accordingly, in the present FT-IR analysis as a function of annealing temperature, it was determined that the Si-DLC films showed, in comparison with the pure DLC films, good thermal stability, which can be considered to have resulted from the increase of the Si-O bond intensity that prevented oxidation, thereby allowing for the existence of the Si-C bond that formed a stable SiC phase at high annealing temperatures.

**Friction and wear behaviors**

Fig. 4 presents the friction coefficients of the as-deposited pure DLC, 7 at.% Si-DLC and 15 at.% Si-DLC films in ambient air at room temperature. All of the films show nearly constant values of friction coefficient until the final sliding of the ball on their surfaces. The friction coefficient of the pure DLC films is about 0.171, whereas those of the 7 at.% Si-DLC and 15 at.% Si-DLC films are low values, 0.085 and 0.057, respectively, indicating that as the Si content increases, the friction coefficient decreases. This was first shown by Oguri et al. [12], who attributed the lowering of the friction coefficient of Si-DLC films to silica-gel-like
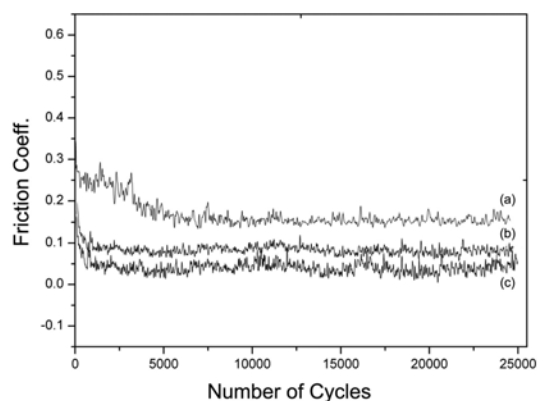


**Fig. 4.** Evolution of friction coefficients of (a) pure DLC, (b) 7 at.% Si-DLC, and (c) 15 at.% Si-DLC films against steel ball in ambient air.
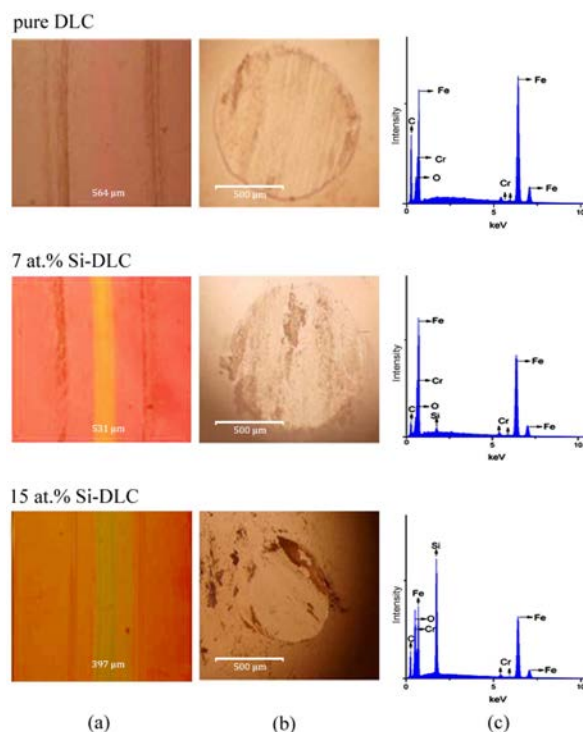


**Fig. 5.** Optical micrographs of wear tracks in films (a), wear scars on mating ball surfaces (b), and EDS spectra of wear scars (c) of pure DLC, 7 at.% Si-DLC, and 15 at.% Si-DLC. Widths of the wear tracks of each film are shown in (a).

sacrificial layers formed during a friction test. To investigate the effects of Si incorporation on the friction and wear mechanisms of DLC films, we carried out the optical microscopy, FESEM with EDS and a Raman analysis of the wear scars of mating steel balls and the wear tracks in the pure DLC and Si-DLC films. Fig. 5 shows optical micrographs of those wear tracks, the wear scars on the mating balls, and the corresponding EDS spectra of the transfer films generated on the ball surfaces. As seen in Figs. 5(a-b), the width of the wear tracks and wear scars decreased with increasing Si content. This trend indicates that in the case of pure DLC films with larger friction
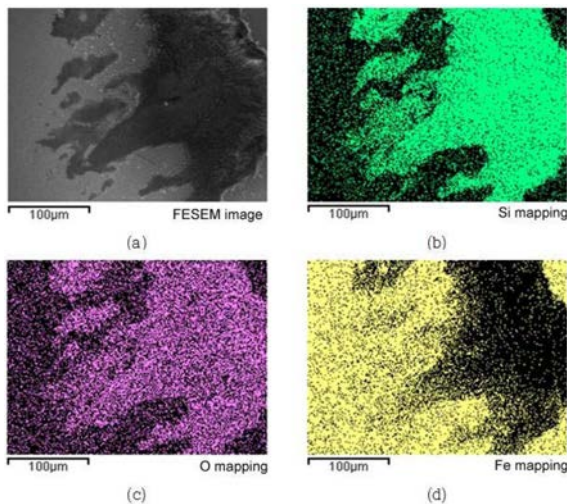
**Fig. 6.** FESEM micrograph of wear scars on mating ball surfaces against 15 at.% Si-DLC films and corresponding elements image maps based on EDS spectra.
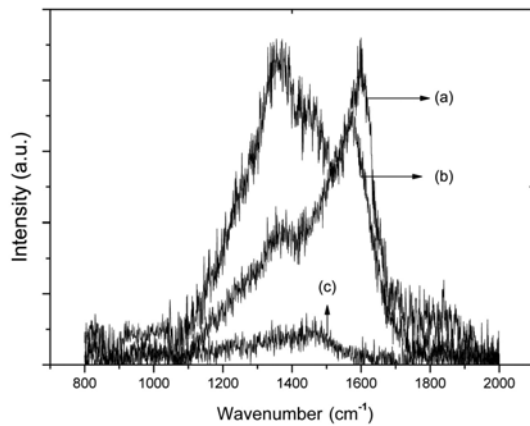


**Fig. 7.** Raman spectra of wear tracks in the films: (a) pure DLC; (b) 7 at.% Si-DLC; (c) 15 at.% Si-DLC.

coefficients, the amount of wear of films and steel balls is relatively large, whereas, with Si-incorporated films with lower friction coefficients, the wear is less extensive [25]. Additionally, the worn surface of the steel balls sliding against the pure DLC films is relatively smooth and becomes rougher as the Si content increases, reflecting the fact that the ball scar is largely covered by the transfer layer [26]. The corresponding EDS ball-scar spectra are shown in Fig. 5(c). The C, O, Fe and Cr elements are detectable in the wear scar generated by the pure DLC films, whereas in the scar effected by the Si-DLC films, the presence of a Si signal is clearly visible. The wear scar of the mating ball moving against the 15 at.% Si-DLC films was analyzed by mapping of the elements on the basis of the EDS spectra, the results of which are plotted in Fig. 6 for the Si, O, and Fe distributions. As noted above, the ball scar corresponding to the 15 at.% Si-DLC films was mainly covered by the transfer layer, which consisted of C, O, Si, Fe and Cr. The localization of Si and O is observable inside of the

transfer film, whereas Fe is located outside. The co-existence of Si and O at the same location within the transfer film indicated that the film was composed mainly of the $SiO_2$ phases, which would be formed by the tribochemical reaction of Si in ambient air and transferred from the films to the mating ball surface [27]. Comparison of this result with the friction behavior plotted Fig. 4 suggests that the lower friction coefficient of Si-incorporated films in ambient air is related to the formation of $SiO_2$-transfer film, acting as a lubricant layer on the top surface [13]. Wear tracks were analyzed also by Raman spectroscopy, as shown in Fig. 7. It can be seen that for the pure DLC films, the D and G peak separation was apparent after the wear test, indicating a pronounced graphitization, resulting in the low friction coefficient. However, the Raman spectra from the Si-incorporated films exhibited no appreciable peak shift; most notably, for the 15 at.% Si-DLC films, the post-wear-test spectra remained unchanged [26]. Resultantly, the friction-induced flash temperature was not sufficiently high to initiate graphitization of the Si-incorporated films, indicating good thermal stability and friction properties.

## Conclusions

We employed annealing process and wear testing to investigate the effects of Si incorporation on the thermal stability and tribological properties of DLC films. From the experimental results, the following conclusions can be drawn.

1. Si-incorporated films show a better thermal stability than the pure DLC films, which fact may be attributed to the increase of Si-O bond intensity, resulting in prevention of oxidation and the existence of the Si-C bond at high annealing temperatures.

2. The lower friction coefficient of Si incorporated films is related to the formation, on the top surface of the wear scar, of $SiO_2$ transfer film formed by the tribochemical reaction of Si in ambient air.

3. Si-incorporated films exhibit no appreciable graphitization of the wear track, indicating good thermal stability and friction properties.

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