# 論文 / 著書情報
# Article / Book Information

| | |
|---|---|
| Title | Surface modification of silicon carbide films by silicon elimination process |
| Authors | Shoutarou Andou, Tatsuya Nishio, Yuko Aono, ATSUSHI HIRATA |
| Citation | Proceedings of 5th BIT-TIT Workshop on Mechanical Engineering, , , pp. 215-220 |
| Pub. date | 2014, 8 |

# Surface Modification of Silicon Carbide Films by Silicon Elimination Process

Shotaro ANDO Tatsuya NISHIO Yuko AONO Atsushi HIRATA
(Dept. Mechanical Sciences and Engineering, Tokyo Institute of Technology, Ookayama 2-12-1, Meguro-ku, Tokyo 152-8550, Japan)

**Abstract:** This study demonstrated the surface modification of SiC coating in which their lubrication property has been improved with retaining their high hardness. Amorphous SiC films were deposited by RF sputtering. To break Si-C bonds and eliminate silicon atoms, heat-treatment was conducted with a heater or a laser beam to the films. After the treatment, elementary analysis, friction test, and hardness measurement were carried out for modified layers. As the result of Auger electron spectroscopy, the outermost surface of the film was found to be covered with oxide film, and the content of silicon and oxygen decreased while carbon relatively increased underneath this oxide film. According to the boll-on-disk friction test, the friction coefficients of as-deposited and heat-treated SiC films were 0.7 and 0.2, respectively. On the other hand, the results of the friction test at ultralow load less than 10 μN using a scanning probe microscope showed that the friction coefficient of heat-treated films was not lower than that of as-deposited SiC film. Nanoindentation hardness measurements indicated that the hardness of heat-treated SiC film was about 1.5 times as high as that of as-deposited SiC film.

**Key words:** silicon carbide; film; carbide-derived carbon; friction; laser irradiation; sputtering

## 1. Introduction

Silicon carbide (SiC) coating is a promising material to improve surface properties of various machine parts because of its high hardness and thermal stability. When thin film coatings are practically applied to slide members, additional properties, for example, wear resistance and low friction coefficient are required. While wear resistance of SiC is relatively strong due to its hardness, friction coefficient of SiC is generally too high in atmosphere without lubricant. Therefore the ways for decreasing the friction coefficient of SiC have been studied and, for example, the addition of solid lubricant or metal atoms [1, 2] were proposed. However, because these ways have to be processed at the same time of depositing, they cannot be applied to SiC films that have been already deposited.

This study proposed a new surface modification process of SiC coating in which its lubrication

**Biography** Shotaro Ando, graduate student, andou.s.ab@m.titech.ac.jp
Tatsuya Nishio, garaduate
Yuko Aono, assistant professor, Dr.Eng., yaono@ctrl.titech.ac.jp
Atsushi Hirata, associate professor, Dr.Eng., ahirata@ctrl.titech.ac.jp

property is improved with retaining its hardness of as-deposited thin films. The new process is based on several studies regarding carbon layers produced on bulk SiC surface by eliminating silicon from SiC, which revealed high lubricity of this carbide-derived carbon layer [3-5]. Etching in the presence of halogen gas have been applied to provide the energy required for breaking Si-C bond and to eliminate silicon from SiC [6-8], whereas the current study selected heating process in reduced pressure considering safety and hazard prevention for experimental environment.

## 2. Deposition and surface modification of SiC films

SiC thin films were deposited on silicon or sapphire substrates by RF sputtering under the conditions listed in Table 1. A graphite disk on which silicon chips were placed was used as a composite target. The analysis of chemical composition of the as-deposited films by Auger electron spectroscopy (AES) resulted in the surface oxide covering the film and the inside consisting of 32.4 % carbon, 30.0 % silicon and 37.6 % oxygen in atomic ratio. The crystalline structure of the film was analyzed by X-ray diffraction method and identified to be amorphous. The thickness of the film was about 1.1 μm.

**Table 6 Deposition conditions**

| | | |
|---|---|---|
| RF power | [W] | 150 |
| Process gas | | Argon |
| Gas flow rate | [sccm] | 30 |
| Pressure | [Pa] | 8.0 |
| Deposition temperature | | Ambient temperature |
| Deposition time | [hour] | 3 |

To break Si-C bond and eliminate Si atoms from SiC film surface, heat-treatment was conducted with a heater or a laser beam to the films. Induction heating was used to anneal the whole surface of the film. The film for annealing was deposited on a sapphire substrate because melting point of silicon is too low for heating over 1400°C. The SiC film was put inside a carbon case because sapphire substrate was an insulator. The carbon case was placed in the induction heater. Then inside of the heater was evacuated to 5.0 Pa with a rotary pump. After that, the substrate was heated up to 1400°C for 30 minutes. The temperature at the surface of SiC film was monitored with a radiation thermometer.

Argon ion laser was used for the purpose of heating film locally. SiC film deposited on a silicon substrate was placed in a chamber inside of which was evacuated to $4.0\times10^2$ Pa. Then an argon ion laser beam, which was scanned at 1 mm/s, was irradiated onto the film surface under the conditions listed in Table 2.

**Table 7 Laser scanning conditions**

| | | |
|---|---|---|
| Wavelength | [μm] | 514.5, 488.0, etc. |
| Spot diameter | [μm] | 28 |
| Power | [W] | 4.0 |
| Scan speed | [mm/s] | 1 |

## 3. Properties of modified SiC films

### 3.1. Elementary analysis of the films

Figure 1 shows the result of depth analysis of AES for (a) annealed film and (b) irradiated film. It is clearly found that both films are covered with oxide film. The ratio of carbon increases and that of silicon decreases underneath the outermost oxide surface compared with as-deposited film consisting of 32.4 % carbon, 30.0 % silicon and 37.6 % oxygen.

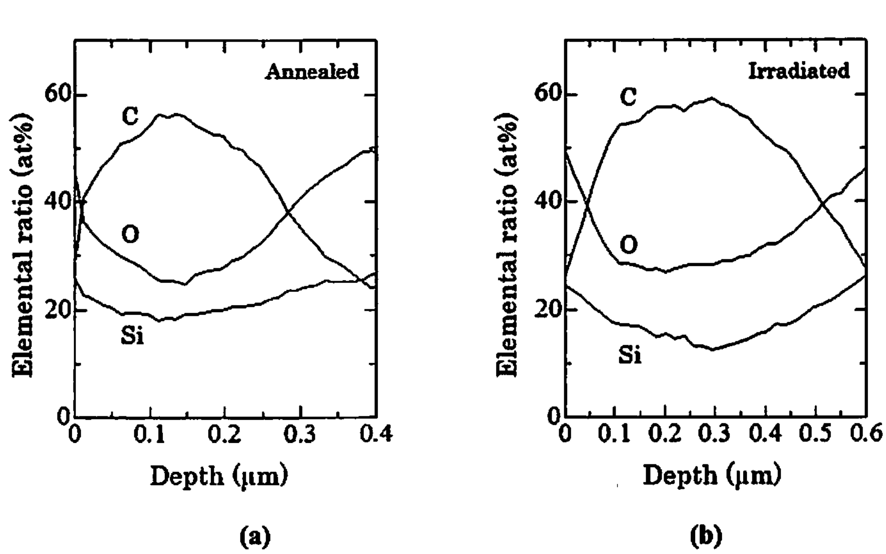



**Fig. 1 Depth profiles of elemental ratio on (a) annealed and (b) irradiated film**

### 3.2. Chemical bonding structure of the films

The chemical bonding structure of the films was analyzed by Raman spectroscopy. Figure 2 shows the Raman spectra having two broad peaks around 1350 $cm^{-1}$ (D band) and 1550 $cm^{-1}$ (G band) for both modified films. The appearance of the spectra is similar to the spectrum of micro-crystalline graphite containing minute $sp^2$ bonding sites of carbon atoms [9]. Full widths at half maximum of D and G bands of laser-irradiated film are smaller than those of annealed film. The carbon layer with higher crystallinity could be produced by laser irradiation process.

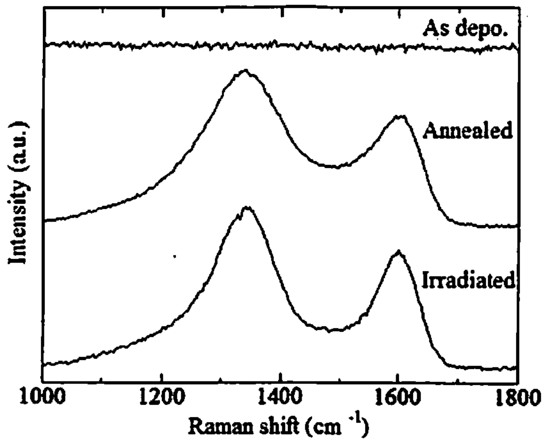



**Fig. 2 Raman spectra of as-deposited, annealed and laser-irradiated film**

3.3. Friction coefficient of the films

The friction coefficients were measured by ball-on-disk friction test. The test was carried out with a normal load of 0.1 N under standard temperature and pressure. The variations of friction coefficient for as-deposited and annealed films are shown in Fig. 3. The friction coefficient of as-deposited film is 0.7-0.8, on the other hand the friction coefficient of annealed film is apparently reduced to about 0.2. The carbon layer formed through heating process is believed to contribute to lower friction.

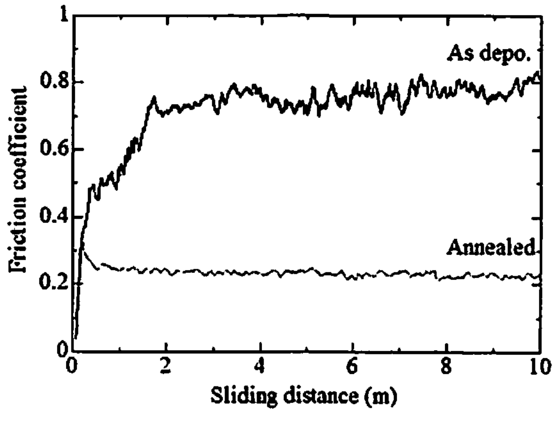



**Fig. 3 Friction coefficients of as-deposited and annealed film**

When the modified film is used for MEMS, the lubrication behavior of the film in micro-scale should be known. The result of friction test in micro-scale using a scanning probe microscope (SPM) is shown in Fig. 4. The test was carried out with the loads under less than 10 μN. In this test, the reduction of friction by heating process is not observed. Considering these results, carbon layer would behave as a solid lubricant when the outermost oxide film is rubbed off at higher load.

Because the outer most oxide films of each SiC films would be responsible for the lubrication dominantly under ultralow load, the friction coefficients are almost the same.

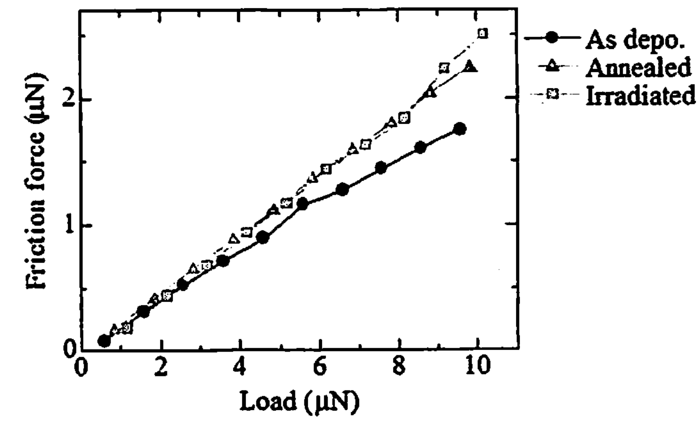
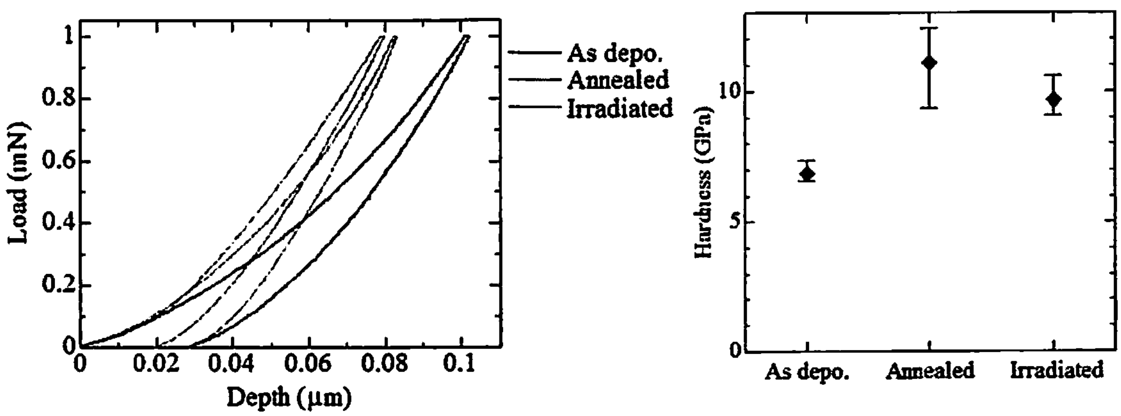



**Fig. 4 Friction coefficients of as-deposited, annealed and irradiated film measured with SPM**

3.4. Hardness of the films

Nanoindentation test was carried out to measure the hardness of modified films. Figure 5 (a) shows load-depth curves. The maximum load is 1.0 mN. The thickness of the film was 1.1 μm and the maximum indentation depth is 70-110 nm. Each calculated hardness of the films is shown in Fig. 5 (b). While the hardness of as-deposited film is 6.9 GPa, the hardness of annealed film and irradiated film are 11.0 and 9.7 GPa, respectively. Through heating process, the hardness of film is improved by 40-60 %.




(a) (b)

**Fig. 5 Nanoindentation (a) load-depth curves and (b) hardness of as-deposited, annealed and irradiated films**

## Conclusion

Improvement of tribological properties of SiC films has been attempted by silicon elimination process through heating of the film surface. Following results are obtained in this study; (1) By heating SiC film, carbon ratio increased and silicon and oxygen ratio decreased in the film; (2) Raman spectrum of modified film was similar to that of micro-crystalline graphite; (3) Friction coefficient of modified film was about 0.2, which was approximately 25 % of that of as-deposited SiC film; (4) Decrease of friction coefficient was not observed in friction test in micro-scale; (5) Hardness of modified films is 40-60 % higher than that of as-deposited film.

## References


[1] Michita HOKAO, Hiroshi SASAKI, Seiichiro HIRONAKA; Friction and Wear Properties of Carbon/Silicon Carbide Composites, Journal of the Ceramic Society of Japan, 108, 1254, 2000: 191-195.

[2] Masahiko KATO, Keijiro NAKASA, Jinhua ZHENG, Satoshi HIROTA; Friction and Wear Properties of SiC-Ti and SiC-Al Films Deposited by Simultaneous RF Magnetron Sputtering ,The Japan Society of Mechanical Enginners, 71, 702, 2005: 359-366.

[3] Kazuhisa MIYOSHI, Donald H. BUCKLEY; XPS, AES, and friction studies of single-crystal silicon carbide, Application of Surface Science, 10, 3, 1982: 357-376.

[4] A.Erdemir, A.Kovalchenko, C.White, R.Zhu, A.Lee, M.J.McNallan, B.Carroll, Y.Gogotsi; Systhesis and tribology of Carbide-Derived Carbon Films, International Journal of Applied Ceramic Technology, 3, 3, 2006: 236-244.

[5] Michael McNallan, Daniel Ersoy, Ranyi Zhu, Allen Lee, Christopher White, Sascha Weltz, Yury Gogotsi, Ali Erdemir, Andriy Kovalchenko; Nano-Structured Carbide-Derived Carbon Films and Their Tribology, Tsinghua Science & Technology, 10, 6, 2005: 699-703.

[6] Sascha Welz, Michael J. Mcnallan, Yury Gogotsi; Carbon structures in silicon carbide derived carbon, Journal of Materials Processing Technology, 179, 1-3, 2006: 11-22.

[7] A.V. Zinovev, J.W. Elam, J.F. Moore, J.N. Hryn, O. Auciello, J.A. Carlisle, M.J. Pellin; Coating of SiC surface by thin carbon films using the carbide-derived carbon process, Thin Solid Films, 469-470, 2004: 135-141.

[8] Tatiana Gorelik, Sabine Urban, Fritz Falk, Ute Kaiser, and Uwe Glatzel; Carbon onions produced by laser irradiation of amorphous silicon carbide, Chemical Physics Letters, 373, 5-6, 2003: 642-645.

[9] J.Robertson; Diamond-like amorphous carbon, Materials Science and Engineering, 37, 4-6, 2002: 129-281.