

# MECHANICAL PROPERTIES OF SILICON CARBIDE FILMS PREPARED BY RF MAGNETRON SPUTTERING USING TARGETS WITH DIFFERENT CARBON CONTENTS

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## INTRODUCTION

Silicon carbide is an attractive thermally and chemically stable material. Its mechanical properties, such as low friction coefficient and high hardness, make it promising for use as a wear resistance coating for different types of steel. Among the many methods of growing silicon carbide films on steel substrates, radio-frequency (rf) magnetron sputtering, which permits low-temperature film deposition, is most effective because high-temperature film deposition causes damage to the substrate. However, there is very little information on silicon carbide films deposited by rf magnetron sputtering [1]. We do not know of any studies in which the hardness, internal stress, friction coefficient, and other mechanical characteristics of silicon carbide films, all of which are important factors when such films are used for surface protection, were examined. If a target containing a volatile element, that is, carbon, oxygen or nitrogen, is used for sputtering, a film without this volatile component is generally produced. Therefore, in sputtering with a compound target containing a volatile element, volatile component gases contained in the target are often added to the gas for reactive sputtering [2-5]. The silicon carbide film composition improved when acetylene or methane was added to argon gas. However, it is difficult to determine the optimum partial pressure of such a gas mixture for obtaining films with excellent mechanical properties. Four silicon carbide mixture targets (mixture targets) with carbon contents of 50 mol%, 55 mol%, 60 mol% and 67 mol% were used to evaluate the characteristics of sputtered silicon carbide films as functions of the carbon content of the target. Furthermore, the stoichiometric SiC target (compound target) was

also used to enable comparison with the characteristics of films sputtered with mixture targets.

## EXPERIMENT

### Sputter deposition

Figure 1 shows a schematic view of the rf magnetron sputtering apparatus used in this work. Four mixture targets with carbon contents of 50 mol%, 55 mol%, 60 mol% and 67 mol% and the compound target, with diameters of 50 mm and thicknesses of 5 mm were used. Three types of substrate were used: borosilicate glass plates of 26×36 mm<sup>2</sup> and 1.2 mm thickness for monitoring film thickness; stainless-steel plates (SUS304) of 10×26 mm<sup>2</sup> and 70 μm thickness for internal stress measurements; and SUS304 of 26×36 mm<sup>2</sup> and 1.4 mm thickness for all other measurements. The substrate was cleaned in a supersonic bath of acetone for 15 min and then

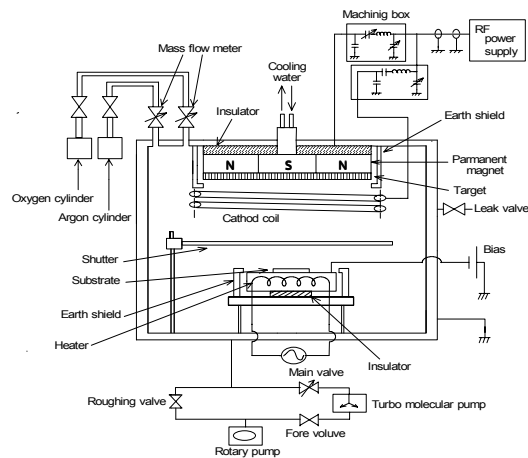


Figure 1: Schematic view of RF magnetron sputtering apparatus.

TABLE 1. Sputtering and sputter etching conditions.

	rf power (W)	rf power density (W/cm <sup>2</sup> )	Working pressure (Pa)	Argon gas flow rate (sccm)	dc bias (kV)
Sputtering	150	7.7	8×10 <sup>-2</sup>	10	0
Sputter etching	30	1.54	1×10 <sup>-1</sup>	30	1

TABLE 2. Hardness and chemical composition (mol. %) of pin (SUJ2) and substrate (SUS304)

	Fe	C	Cr	Ni	Mn	Si	DH (GPa)
SUS304	72.92	0.08	18.0	8.2	0.8	—	3.7
SUJ2	97.25	0.95	1.6	—	—	0.20	5.5

placed on a substrate holder. The sputtering apparatus was first evacuated to  $5 \times 10^{-4}$  Pa with a turbomolecular pump to reduce the influence of residual gases, and then the working gas (99.99% pure argon) was introduced into the chamber through an electrically controlled mass flow controller. After the pressure was stabilized at  $4 \times 10^{-1}$  Pa, the substrate and target were cleaned by sputter etching for 10 min. The film deposition was carried out under the conditions shown in Table 1. In all cases, the pressure of the gas during film deposition was  $8 \times 10^{-2}$  Pa.

#### Hardness test

Film hardness was measured with a nanoindentation tester (Shimadzu, DUH-201) using a Berkovich indenter at room temperature. A load of 30 mN was employed with a dwell time of 15 s. To obtain reasonably good accuracy, ten impressions were made on each specimen and their values were averaged.

#### X-ray diffraction test

The crystallographic structure of the films was examined by X-ray diffraction (XRD) analysis using a Shimadzu XRD-7000 goniometer with a constant incidence angle of  $1^\circ$  using  $\text{CuK}\alpha$  radiation. The excitation voltage and current were 40 kV and 30 mA, respectively.

#### Electron probe microanalysis

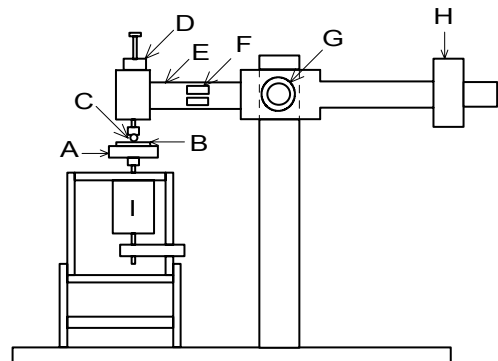
An electron probe microanalyzer (EPMA) was used to analyze the composition ratio of Si and C, the Ar content in the films and the composition in the wear region. The measurements were performed under the following conditions: an accelerating voltage of 10 kV, a sample current of 100 nA and a beam diameter of  $1 \mu\text{m}$ .

#### Atomic force microscopy

Atomic force microscopy (AFM) was also performed to observe the surface topography of the films prepared. The tip used in the AFM was a rectangular microcantilever, with a radius of  $20 \mu\text{m}$ , made of  $\text{Si}_3\text{N}_4$ . The images were obtained in the constant-force mode at a tip load of 40-50 nN.

#### Friction and wear test

The friction and wear test apparatus is of the pin-on-disk type, as shown in Fig. 2. The pin (SUJ2, diameter=2 mm) was pressed onto the rotating table at a normal load. A new pin was used for each test and it was cleaned in a supersonic bath of acetone for 15 min before each run. Friction force was measured by strain gauges located on both sides of the plate spring. Sliding velocity was maintained constant by adjusting the rotation speed of the pulse motor and the radius of the wear track. Experimental



A: Rotation table B: Sample C: Pin D: Normal load  
E: Plate spring F: Strain gauge G: Bearing H: Weight balance  
I: Pulse motor

Figure 2: Schematic view of pin-on-disk wear apparatus.

conditions throughout the test were a load of 0.4 N, a sliding velocity of 4 mm/s, and dry friction in open air. The hardnesses and chemical compositions of the pin and the substrate (SUS) are shown in Table 2.

## EXPERIMENTAL RESULTS AND DISCUSSION

### Film hardness

Hardness is one of the importance factors governing wear resistance, as reported by Rabinowicz et al. [6], who showed that the inverse of abrasive wear resistance is proportional to hardness. A hardness test, therefore, was carried out to evaluate the hardness of SiC films sputtered using mixture targets and the compound target. Figure 3 shows the results. The hardness of films sputtered with the mixture targets increases with increasing carbon content of the target. On the other hand, the hardness of film sputtered with the compound target was comparable to that of the film sputtered using the target with a carbon content of 60 mol%.

The most influential factors affecting film hardness are the crystal structure,[7] composition,[8-9] and particle size.[10] Therefore, these factors were measured in this study by XRD analysis, AFM and EPMA. First, XRD was used to determine whether the film was crystalline or amorphous. It was found that the crystal structure of the sputter-deposited films was amorphous with all targets investigated. This suggests that the crystal structure does not affect film hardness in this study. The film composition was further examined by EPMA. The silicon and carbon contents in sputter-deposited SiC films using the mixture target and the compound target are shown in Fig. 4. The carbon content in the film increases with increasing carbon content of the target, whereas the silicon content in the film decreases. These EPMA results indicate that a film sputtered using a mixture target with a carbon content of 60 mol%

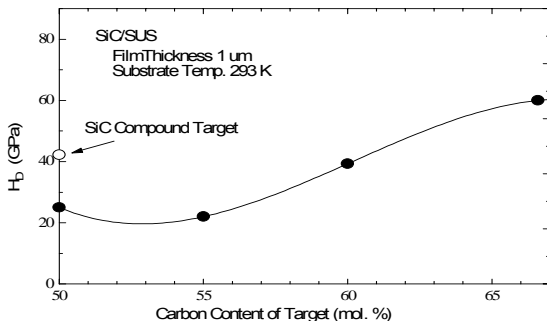


Figure 3: Film hardness with a load of 30mN as a function of carbon content of mixture target (●) and SiC compound target (○).

has the optimum stoichiometry. On the other hand, the film hardness increases to a maximum value at the carbon content of 67 mol%; this indicates a good correlation with the carbon content in the films. Therefore, the film composition might be one of the factors affecting film hardness. To verify the influence of particle size, the surface shape of the films was observed by AFM. Figure 5 shows

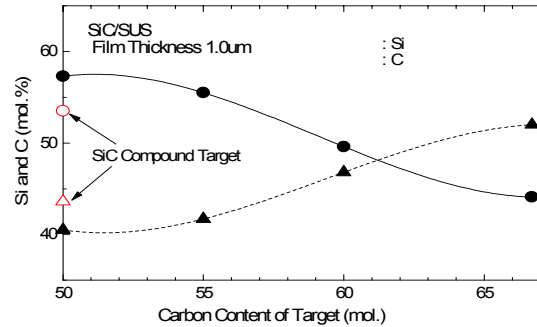


Figure 4: Silicon and carbon contents in sputter-deposited SiC films as a function of carbon content of mixture target (●: Si ▲: C) and compound SiC compound target (○: Si △: C).

### SiC/Si

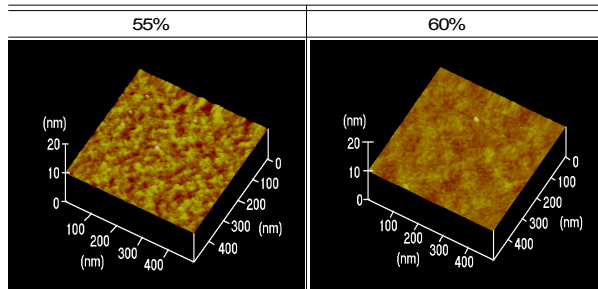


Figure 5: Atomic force microscopy image of SiC films sputter-deposited using targets with carbon contents of 55 mol% and 60 mol%.

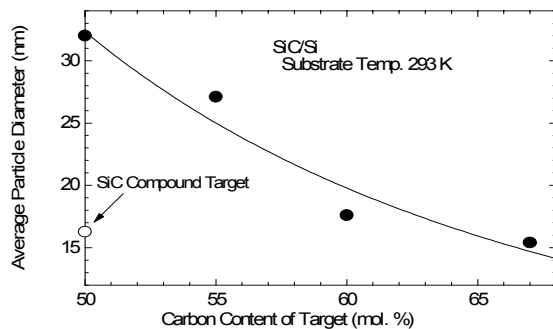


Figure 6: Number of particles per unit area in atomic force microscopy image as a function of carbon content of mixture target (●) and SiC compound target (○).

the AFM images of SiC films sputtered using the mixture targets with carbon contents of 55 mol% and 60 mol%. As can be seen, the surface of the former tends to have a more acicular structure and that of the latter has structures that are more spherical in shape. Figure 6 shows the relationship between the carbon content of the mixture target and the diameter of the surface structures obtained from AFM images. It was found that the average particle diameter decreases with increasing carbon content of the mixture target. This correlates well with the film hardness. On the basis of these results, the film composition and particle size might be the factors affecting the film hardness.

It is thought that the film sputtered by adjusting composition ratio of a mixture target offers stoichiometric compound and desired properties to compound target and indicates the possibility of great development industrially.

#### Friction coefficient and wear resistance

Figure 7 shows the friction and wear test results for the SUS304 substrate and SiC films sputter-deposited using the mixture targets and the compound target. It can be seen that the friction coefficients of the SiC films sputter-deposited using the mixture targets with carbon contents of 60 mol% and 67 mol% and using the compound target are small after 3000 or more wear test cycles. In particular, the films sputter-deposited using the mixture target with a carbon content of 67 mol% shows a steady low friction coefficient of 0.2 after 10000 wear test cycles. According to these results, the carbon content of the target might be expected to affect mechanical properties such as the hardness, the friction coefficient and the wear resistance of the film.

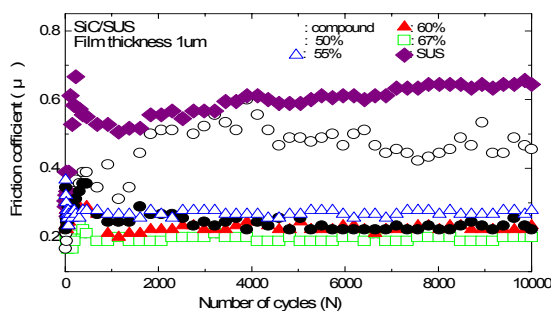


Figure 7: Change in friction coefficient with number of cycles for SUS substrate and SiC films sputtered using mixture targets with different carbon contents and using compound target

#### **CONCLUSION**

The mechanical properties of SiC films deposited by rf magnetron sputtering using mixture targets with different carbon contents and using the compound target were studied. The following results were obtained.

1. Film hardness increases with increasing carbon content of the mixture target.
2. The crystal structure of the films is amorphous at all the carbon contents investigated.
3. The carbon content increases with increasing carbon content of the mixture target, whereas the silicon content of the films decreases.
4. The average particle diameter of the film decreases with increasing carbon content of the mixture target.
5. The friction coefficient of the films decreases from 0.5 in the case of using a mixture target with a carbon content of 50 mol% to 0.2 in the case of using a mixture target with a carbon content of 67 mol%.

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