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The Effects of Impurities in Silicon Nitride Substrate on Tribological Behavior between Diamond Film and Silicon Nitride Ball

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Abstract—Diamond films were prepared by a hot filament vapor deposition onto polycrystal silicon nitride substrates. Different kinds of silicon nitride containing CaO and Fe_2O_3 were manufactured to investigate the impurity effect of substrate on the morphology of diamond films and their wear behaviors. Nucleation rates and morphologies of diamond films deposited on various kinds of silicon nitride were compared. The highest nucleation rate was observed in a substrate containing 1% of CaO. Wear tests were performed with a silicon nitride ball on the disk geometry to investigate the tribological behavior of diamond film against silicon nitride. This study demonstrated that different morphologies of diamond film due to substrate impurities produced different wear behavior against silicon nitride.

Key words : Diamond film, Silicon nitride, Impurity, Wear, Friction

1. Introduction

Different experimental synthesis methods for producing diamond films have been reported. [1-3] These diamond films have been considered to use in industrial applications in many fields. The most promising area with diamond films is tribological application since diamond has unique properties such as superhardness, high degree of chemical inertness, and high thermal conductivity [4-5]. Coated tools with diamond films were proved to significantly improve their cutting performance and already introduced in the commercial markets. However, for the success of these applications in the market, the improvement in coating technologies by controlling nucleation and growth rate enhancement and meeting the high degree of adhesion with substrate is needed. During the last decades various new methods have been proposed to enhance growth rate [6-7]. The enhancement of nucleation density is also important since diamond nucleation is sluggish and starts only after a long initial time period. "Scratching" substrate with diamond, SiC, B_4C, or other particles is known to enhance the diamond nucleation [8-10]. However only few reports besides scratching have been published to describe the methods to enhance nucleation density. The nucleation density strongly depend on the balance between the flux of the carbon atoms arriving at the substrate surface and carbon diffusion [11]. The chemical reactions occurring between substrate and reaction gas can be another mechanism for the influence on nucleation [12].

We have recently demonstrated that by adding impurities in the fabrication of silicon nitride such that we could enhance nucleation density [13]. Different microstructure of polycrystalline diamond films is expected to depend on the nucleation density. In this paper we report tribological characteristics of diamond films produced on substrates to understand how these impurities influence microstructures and tribological behaviors of the substrates having different impurities.

2. Experimental Procedures

Three different kinds of silicon nitrides were fabricated to investigate the effect of minor impurities in the substrate on the formation of diamond film and the tribological behavior. The main difference was that silicon nitride B had 1% of CaO and silicon nitride C had 1% of Fe_2O_3, whereas silicon ni-

Table 1. The Composition of Substrates (weight%)

	Substrate A	Substrate B	Substrate C
Si_3N_4	85.5	85.5	85.5
Y_2O_3	13	13	13
Al_2O_3	1.5	1.5	1.5
CaO	-	1	-
Fe_2O_3	-	-	1
Total	100	101	101

tride A had neither CaO nor Fe_2O_3. The phase composition of materials are summarized in Table 1.

The powders were ball-milled for 72 hours by using ethanol, silicon nitride balls, and acetal jar. They were gas-pressure sintered at 1850°C in N_2 gas (300 MPa) for 2 hours after cold isostatic pressing. Silicon nitride specimens were cut to 8 mm×8 mm×1 mm. The specimens were polished up to 6 mm then ultrasonically treated in diamond powder (1 μm) dispersed methanol. The specimens were cleaned in methanol and acetone prior to deposition.

A diamond film was deposited onto silicon nitride substrate by a hot filament chemical vapor deposition apparatus. Fig. 1 is a schematic of the deposition setup.

The diamond films in this study were grown at 110 torr from dilute mixtures of methane in hydrogen. Gas flow rate through reactor and substrate temperature were fixed to 140 cm^3 min^{-1} and 900°C respectively. The concentration of CH_4 was 1 volume %.

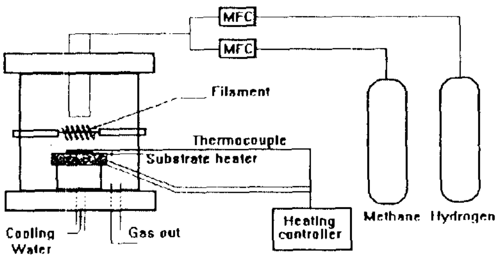


Fig. 1. Schematic diagram of hot filament chemical vapor deposition system.

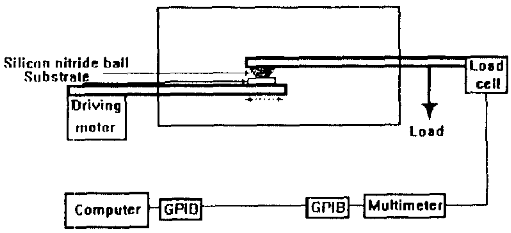


Fig. 2. Schematic diagram of tribo-tester.

The wear tests were performed by pressing 11.7 mm diameter of silicon nitride ball against a reciprocally moving plate as shown in Fig. 2.

Diamond coated substrate was fixed on the moving plate. Wear tests were conducted in air at room temperature without lubricant. Sliding velocity and applied load was maintained at 2.9×10^{-3} m/sec and 10 N, respectively. Diameter of wear scar on silicon nitride ball was measured by optical microscopy. Interruptions after every 20 minutes test was made for periodic measurements of diameter of wear scar.

The coefficient of friction between diamond film and silicon nitride ball was determined by measuring frictional force through the load cell.

Unworn and worn surfaces of diamond films were examined by secondary mode with scanning electron microscopy (SEM).

3. Results and Discussions

Fig. 3 and Fig. 4 show SEM micrographs of diamond deposited on three different kinds of silicon nitride after 2 hours and 20 hours deposition. The density of diamond particle is much higher on the substrate containing CaO in comparison with other silicon nitride substrate as shown in Fig 3. The morphology of the diamond crystals is observed to be different as shown in Fig. 4. High nucleation density observed on substrate B leads to a relatively fine grained film. Ravi et al have shown that as the nucleation density is increased, dendritic growth conditions appear to be operative with long, narrow crystallites growing out from the surface with no specific crystalographically. In this work similar results were observed. Square faces of (100) planes appeared on the films deposited on A and C. Whereas for film deposited on B, triangular faces of (111) planes appeared.

Fig. 5 shows the diameter of wear scar of the silicon nitride ball generated by frictional sliding with uncoated and diamond film coated substrates. Wear scar diameters of silicon nitride were larger with diamond film than with silicon nitride itself. This result can be explained by the greater possibility of abrasive action by diamond film defined direction.

SEM micrographs of wear scar of silicon nitride

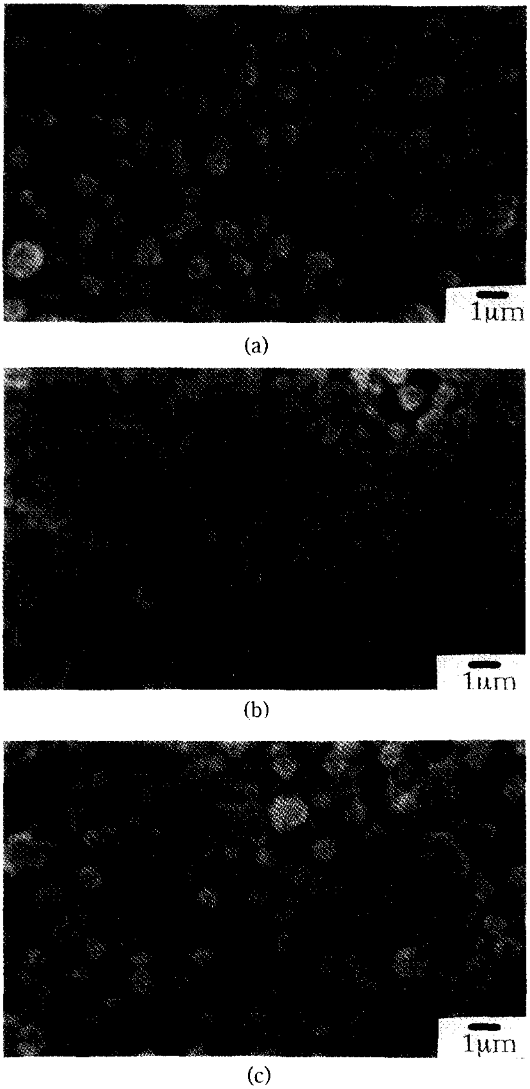


Fig. 3. **Scanning electron micrographs of diamond deposited for 2 hours on; (a) substrate A, (b) substrate B, and (c) substrate C.**

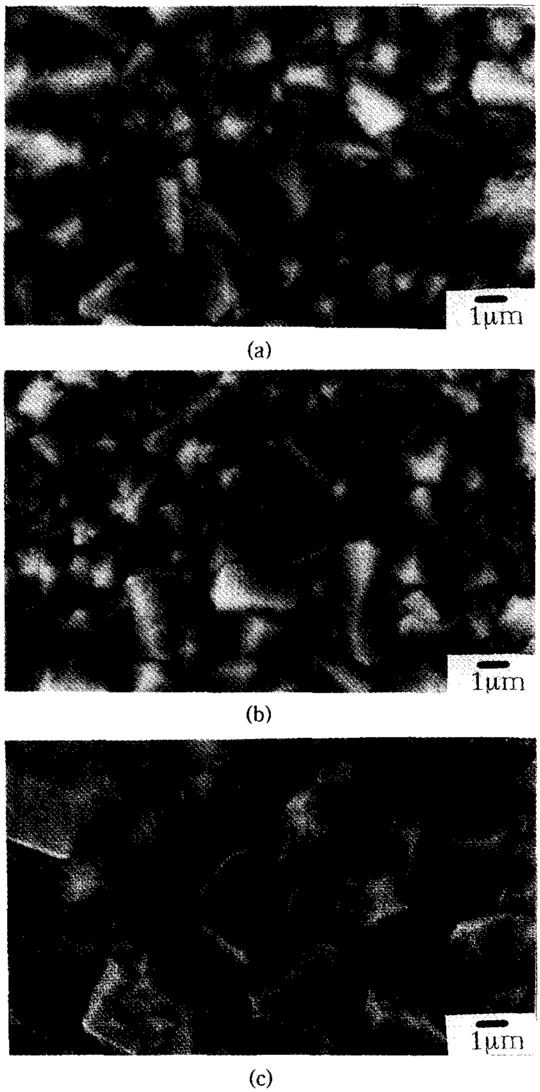


Fig. 4. **Scanning electron micrographs of diamond deposited for 20 hours on; (a) substrate A, (b) substrate B, and (c) substrate C.**

balls were shown in Fig. 6. The size and surface smoothness of wear scar were different depending on the contacting morphology of diamond films.

The wear scar generated by diamond film on B shows a smaller area and smoother damaged surface. The higher magnification of micrograph shows that wear scar was damaged by typical abrasive wear (Fig. 6(c)).

Fig. 7 shows damaged diamond films by frictional sliding of silicon nitride ball. Fig. 7(a) shows that silicon nitride debris and grain pull-out of small crystals have been observed. The sharpness of edge of cube orientations of diamond crystals have been decreased probably due to polishing by frictional sliding. No noticeable change in morphology by diamond film grown on substrate B except silicon nitride debris was observed (Fig. 7(b)). Dramatic change of morphology compared unworn diamond surface was observed in frictionally damaged diamond crystals grown on substrate C. Relatively big octahedron and cube crystals

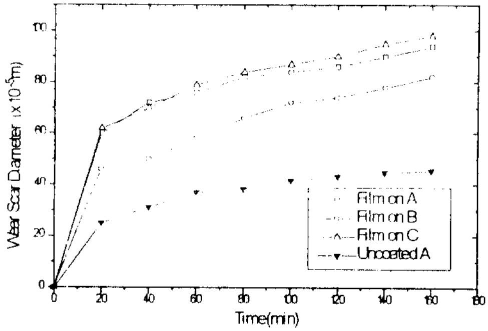
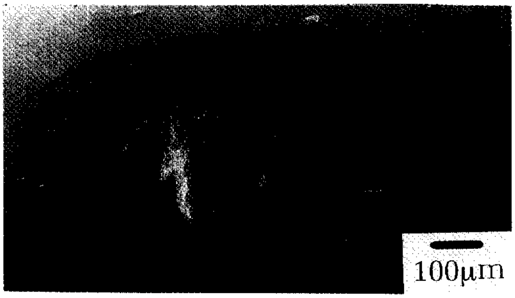


Fig. 5. Wear scar diameter of the silicon nitride ball.

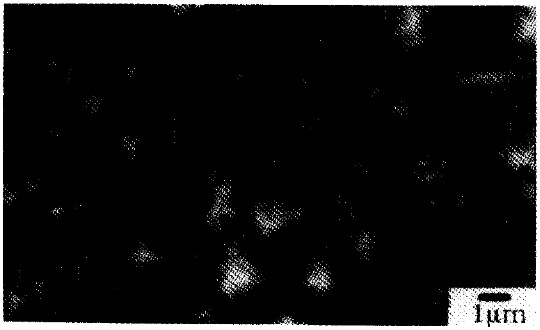


(a)

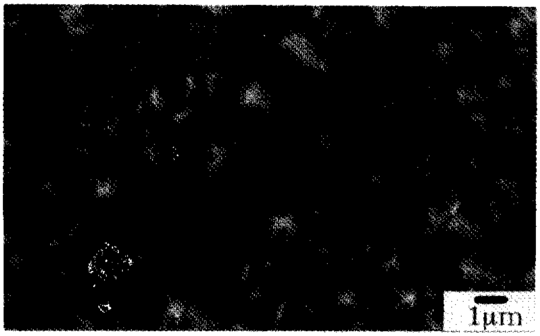
(b)

(c)

Fig. 6. Scanning micrographs of wear scar on silicon nitride ball worn with diamond film on; (a) substrate A , (b) substrate B, and (c) higher magnification of (b) .



(a)



(b)

(c)

Fig. 7. Scanning electron micrographs of diamond films after wear test; (a) film on substrate A, (b) film on substrate B, and (c) film on substrate C.

were worn out by the wear test. The present results indicate that wear of both silicon nitride and diamond film is influenced by morphology of diamond crystals. It is observed that as the crystal size of the diamond decreases, the wear of softer contacting material decreases. It has been reported that specific energy (energy required per unit volume of material removed) required to wear out is a function of grain size of harder material as the grain size decreases, the specific energy increases [14]. So, least wear of both sil-

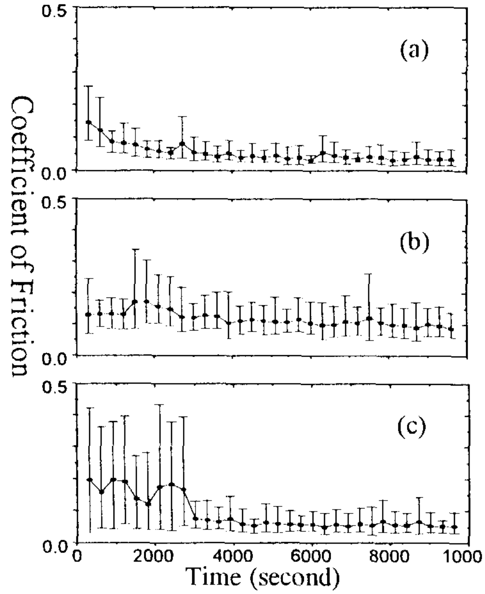


Fig. 8. Coefficient of friction as a function of sliding time; (a) film on substrate A, (b) film on substrate B, and (c) film on substrate C.

icon nitride ball and diamond coated on substrate B when it contacts each other.

Fig. 8. illustrates the behavior of the friction coefficient. The value of the friction coefficient tends to gradually decreased. Depending different friction behavior was observed on the surface morphology of films. The frictional coefficient with diamond on A maintains below 0.1 after 2700 seconds. The variation of the friction coefficient was very smooth. The frictional coefficient with diamond on B reached about 0.1. They display the greatest variability in friction coefficient. The frictional coefficient was about 0.2 during first 2700 seconds, after it decreased to below 0.1. The variation of frictional coefficient was large during initial periods probably due to worn out of diamond crystal. The SEM micrograph of Fig. 7.(c) confirm this explanation. The cube type diamond films deposited on A and C substrate produced the lower frictional coefficients than octahedron type film. Similar results due to cutting and plowing contributions to friction by pyramidal facet was reported by Blau *et al.* [15].

5. Conclusions

The frictional wear behavior of HFCVD diamond films grown on different kinds of silicon nitrides was investigated. It was demonstrated that the nucleation rate and morphology of crystalline were greatly influenced by containing impurities in the substrate. The highest nucleation rate and triangular (111) faces was appeared on a substrate containing 1% of CaO, whereas (100) faces appeared on a substrate containing either Fe_2O_3 or no impurities. The wear rate and friction coefficient were also influenced by the surface morphology and size of crystals. Film with smaller and (111) octahedron shape, which was grown on substrate containing CaO, produced the lowest wear rate of silicon nitride ball and film itself. The cube type diamond films produced a lower friction coefficient except initial period.

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