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# FRICTIONAL BEHAVIOR OF NANO-UNDULATED SURFACE OF DIAMOND-LIKE CARBON FILMS

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## ABSTRACT

Frictional behavior of nano-undulated diamond-like carbon (DLC) films deposited by plasma assisted chemical vapor deposition (PACVD) process was investigated. In order to prepare the nano-undulated DLC film, a Si wafer with nano-sized Ni dots was prepared by rapid thermal annealing of Ni thin films. Since the structure of DLC film deposited by PACVD was independent of the substrate materials and that the size of Ni nano dots could be controlled in a systematic way by changing the thickness of the Ni film, we could investigated the effect of nano-scale surface roughness on the tribological behavior of DLC films. The friction coefficient between steel ball and undulated DLC films of the roughness varying from 0.6 to 13.7 nm was measured by using a ball-on-disk type wear rig in ambient environment. The friction coefficients were in the range from 0.15 to 0.2, independent of the surface roughness. Wear of the steel ball was much enhanced with higher content of Fe in the debris as the roughness increased. However, the size of the debris decreased with increasing roughness. Raman spectrum analysis revealed that the chemical bond structure of the debris is significantly dependent on the surface roughness. The friction behavior was discussed in terms of the chemical compositions and the agglomeration behavior of debris.

**Keywords**: Nano-undulated surface, Friction behavior, Diamond-like carbon film
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## INTRODUCTION

Surface roughness of materials has been considered to affect significantly on their tribological behaviors (ref. 1). In macro-scale tribology, it was reported that the surface roughness could reduce the friction coefficient by suppressing the wear particle generation, removing the wear particle from sliding interface or/and preventing the wear particle agglomeration (refs. 2 and 3). This artificial rough surface has the potential for artificial joint because of the low friction coefficient and the suppression of the wear particle generation (refs. 4 and 5). However, systematic investigation on the dependence of the tribological behaviors on the surface roughness in nano-scale was yet to be reported.

Recently, we suggested a method to manipulate the microstructure of tetrahedral amorphous carbon (ta-C) films deposited by filtered vacuum arc process (ref. 6). By incorporating the nano-sized Ni dots on the substrate surface, we could obtain nano-sized graphitic phases grown from the Ni dots to the surface. In addition to the possibility of nano-scale manipulation of the ta-C films, this method can also be used to control the surface roughness in nano-scale by adjusting the size of Ni dots. In contrast to the filtered vacuum arc process, PACVD deposition resulted in the homogeneous microstructures of carbon regardless of the substrate materials. By employing PACVD method for carbon deposition, nano-scale undulated surface of the DLC film could be obtained. In the present work, the DLC film of nano-scale undulated surface was used to investigate the tribological behaviors for various values of surface roughness. In the present range of the surface roughness (from 0.5 to 14 nm), the tribological behavior was independent of the roughness presumably due to the smaller size of debris and suppressed tribo-chemical reactions in rough surface.

## EXPRIMENTAL PROCEDURE

Nano-sized Ni dots on Si substrate were prepared by annealing Ni thin films of thickness ranging from 3 to 14 nm. The Ni thin film was deposited on the 600-μm-thick Si (100) wafers by DC magnetron sputtering method. In order to change the deposited Ni film to nano dots, the specimen was annealed in a rapid thermal process (RTP) at 800°C for 15 min in hydrogen environment. Hydrogen pressure during the annealing was kept at 1 Torr by adjusting the flow rate of hydrogen. Ni dots of diameter ranging from 15 to 90 nm were uniformly distributed on the substrate. The average size of nano Ni dots monotonically increased with the thickness of the Ni film.

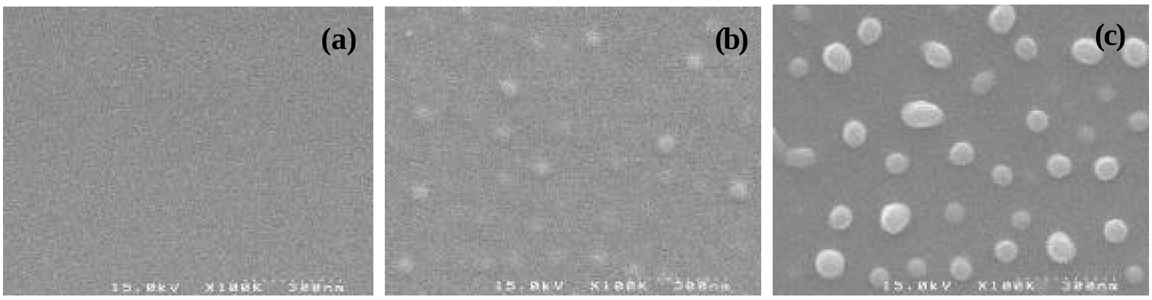


Figure 1. SEM microstructure of DLC films surface. (a) rms=0.6nm (b) rms = 5.1 nm (c) 13.7 nm

DLC film was deposited by radio frequency plasma assisted chemical vapor deposition (r.f.-PACVD) using methane as precursor gas. The film was deposited at the negative bias voltage –150V and deposition pressure 1.33 Pa. Thickness of the film was fixed at 100 nm in all samples. Roughness of the film measured by an atomic force microscope ranged from 0.6 to 13.7 nm depending on the thickness of the Ni films. SEM microstructure of the surface was shown in Fig. 1. Tribological properties were characterized by using ball-on-disk type wear rig using steel ball (AISI 52100) of diameter of 6 mm as the counter face materials. Normal load was fixed at 4 N (0.53GPa) and the sliding speed 17.3 cm/s. The test environment was in ambient air at room temperature. After the tribological characterization, SEM, Auger electron spectroscopy and Raman spectroscopy were employed to analyze the morphologies and chemical bond structure of the debris and the wear track.

## RESULTS AND DISCUSSION

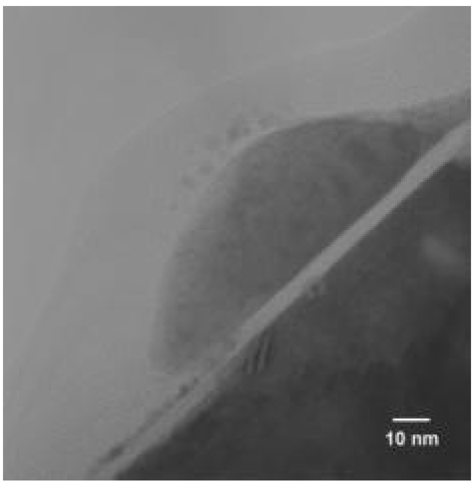


Figure 2. TEM cross-sectional microstructure of the specimen of Fig. 1 (c).

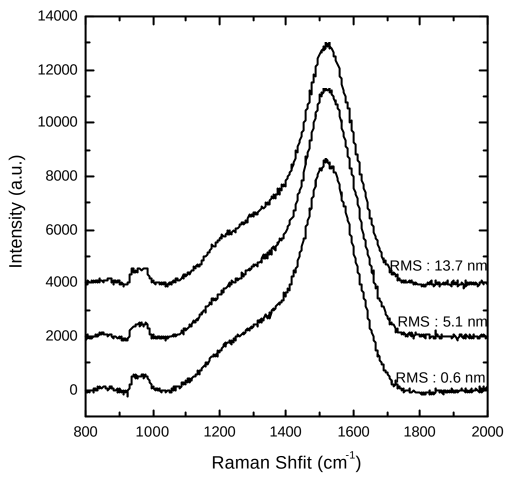


Figure 3. Raman spectra of DLC films for various surface roughness.

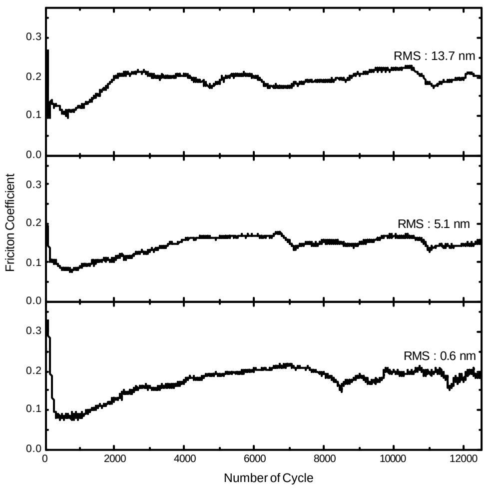


Figure 4. Evolution of friction coefficient for various values of surface roughness.

Microstructure of the DLC films and the interface was investigated by cross sectional TEM microscope. Figure 2 shows the TEM microstructure of the sample of Fig. 1 (c). In contrast to the case of ta-C films, growth of second phase on Ni catalyst could not be observed in the present work. Instead, amorphous layer was uniformly covered both Si substrate surface and Ni nano dots. EDS analysis showed that the composition of the deposited film was pure carbon. Homogenous single phase of carbon film deposition could also be confirmed by Raman spectroscopy. Figure 3 shows the Raman spectra of the films. All the spectra were essentially same regardless of the thickness of Ni film, i.e. the size of Ni dots. No significant change in wetting angle of pure water, electrical resistivity and residual compressive stress could be observed. These results thus showed that the homogeneous DLC films of different surface roughness could be prepared by the present method.

Figure 4 is the evolution of friction coefficient with increasing the number of contact cycle. After the initial transient period, steady state of the friction occurs after 2,000 cycles. Even if the increase in the friction coefficient to the steady state coefficient occurred earlier in the roughest film, the steady state friction coefficients were independent of the surface roughness. However, the roughness of the surface significantly enhanced the wear of the steel ball. The wear rate of the ball increased from $3.8\times 10^{-10}$ to $1.8\times 10^{-9}$ $mm^3$/cycle as the roughness increased from 0.6 to 13.7 nm. Composition analysis by Auger electron spectroscopy also showed that the amount of Fe in the debris increased with the surface roughness.

SEM microstructures of the debris near wear track were shown in Fig. 5. The SEM microstructure showed that the debris agglomeration was suppressed with the surface roughness. Raman spectra of the debris shown in Fig. 6 revealed a significant difference in the chemical bond structures of the debris. Raman peak near 700 $cm^{-1}$ is the characteristic line of Fe oxide. D and G peak, centered at 1300 and 1550 $cm^{-1}$ respectively, composed the carbon Raman peak. As the roughness increased, intensity of Fe oxide peak decreased. This result implies that the tribo-chemical reaction to oxidize Fe originated from the wear of steel ball was considerably suppressed in rough surface. Another significant observation in Raman spectra would be the changes in carbon Raman peak. The shape of carbon peak changed from that of typical DLC films to graphitic one with decreasing the surface roughness. This observation also confirmed that the tribo-chemical reaction was suppressed in the case of rough surface.

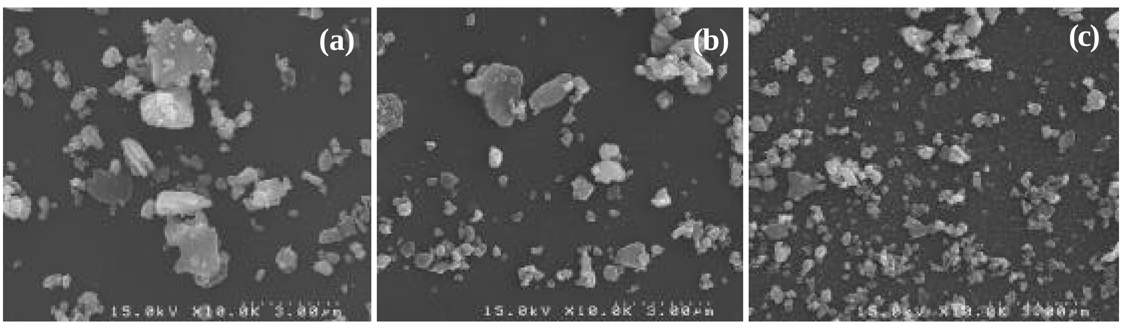


Figure 5. SEM microstructures of the debris near the wear track. (a) rms=0.6nm (b) rms = 5.1 nm (c) 13.7 nm

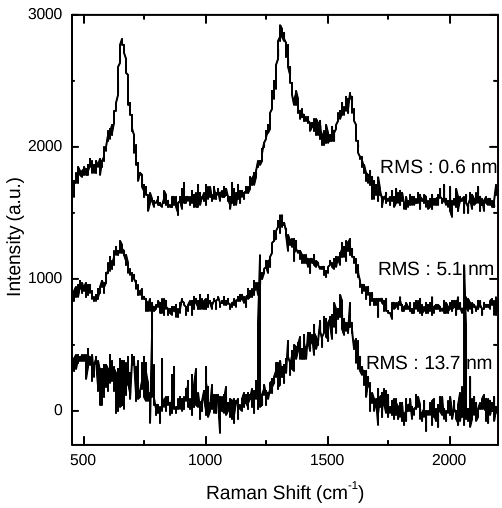


Figure 6. Raman spectra of the worn scar debris on the steel balls

It was reported by the present authors that the debris composition and their agglomeration during sliding play an important role to determine their tribological behaviors (ref. 7). The humidity dependence of the friction between DLC film and steel ball was shown to be due to the Fe oxide debris and their agglomeration. In high humid environment, Fe oxide debris dominates in the sliding environment, resulting in higher friction coefficient. The present observation can be understood based on the same conjectures. Increasing surface roughness can resist the sliding as can be deduced from the increased wear of the ball. However, smaller debris of DLC structure might have an opposite effect on the friction coefficient. Furthermore, reducing amount of Fe oxide with increased surface roughness could decrease the friction coefficient. These two opposite effects seem to result in the friction behavior independent of the surface roughness.

## CONCLUSIONS

Nano-scale undulated DLC films prepared by PACVD using Ni nano dots on the Si substrate made it possible to investigate the friction behavior of DLC films for various surface roughness in nano-scale. Although the friction coefficient appeared independent of the surface roughness, the tribo-chemical reactions such as debris shape, composition and chemical bond were intimately related with the surface roughness. Surface roughness enhanced the wear of counter face materials, which might increase the friction coefficient. However, oxidation of Fe and graphitization of the debris were suppressed by the surface roughness, which would suppress the agglomeration of the debris. These changes in the case of rough surface might reduce the friction coefficient. These two opposite effects seem to be balanced in the present experimental condition resulting in the friction behavior independent of the surface roughness. More elaborate experimental work is in progress to separate the opposite effects.

## ACKNOWLEDGEMENTS

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