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Structure and microtribological behavior of Teflon and Teflon/Si_3N_4 micro-assembling film

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Abstract

Micro-assembling Teflon/Si_3N_4 multilayer film was developed by ion beam alternating sputtering Teflon and Si_3N_4 ceramic targets. The structural, mechanical and microtribological properties were studied by PHI-5300, FTIR, XRD and atomic force and friction force microscope (AFM/FFM). The results show that the multilayer consists of Si_3N_4 component and crystalline Teflon. The hardness of the multilayer is less than that of Si_3N_4; but the toughness of Teflon/Si_3N_4 is greatly improved. The friction coefficient of Teflon/Si_3N_4 multilayer is lower than that of Si_3N_4 film, and the wear resistance of Teflon/Si_3N_4 multilayer is much greater than that of Teflon film. The friction force of Teflon/Si_3N_4 film is linear with the load in nanoscale. The worn track will be formed in Teflon and Teflon/Si_3N_4 film when the load is greater than 70 nN. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Multilayer polymer; Atomic force and friction force microscope

1. Introduction

It is well known that there are two kinds of materials to reduce friction and wear in tribology, one is the soft materials such as gold, silver, MoS_2, graphite and Teflon, etc. These materials have low shear strength and low wear resistance, and are often referred to as solid lubricants. The other is the hard materials which have high wear resistance such as TiN, BN, Al_2O_3, Si_3N_4, DLC, etc. But there are a few materials which have low friction coefficient and high wear resistance.

Teflon possess the combination of chemical inertness, low friction coefficient, electrical insulation, and biological compatibility. It has been widely used as corrosion resistant, biomedical and biological material, but its strength and wear resistance are very low. Silicon nitride can be used as a protective coating of functional devices because of its high strength and wear resistance, but the low toughness limits its applications in industry.

Natural biomimetic materials have superior comprehensive properties because of their special structure such as particulate, fiber, whisker or laminate reinforced characteristics [1–3], for example, the pearl layer of sea shell has high fracture toughness because the pearl layer is composed of alternatively organic matrix and aragonite layers [4]. So it was recognized that the composite can be designed by the combination of soft and hard phases, such as SiC_p/Al, Al_2O_3/C, etc. As for the matrix multilayer, the emphasis was focused on the study of metal/metal layers, and there have been a few investigations on the organic or ceramic matrix multilayers. With the development of material science and information technology, the organic matrix multilayers with special function such as optical, electrical and mechanical requirement have a wider and wider application [5,6].

In this paper, according to the characteristics of Teflon and Si_3N_4, the idea of laminate structure was chosen to design a multilayer with relative low friction coefficient and high wear resistance. The micro-assembling Teflon/Si_3N_4 multilayer was prepared by ion beam alternatively sputtering Teflon and Si_3N_4 target, and then the structural, mechanical and microtribological properties were investigated.

2. Experimental procedures

2.1. Sample preparation

The sample preparation process was carried out by ion beam assisted deposition system. The micro-assembling Teflon/Si_3N_4 multilayer was prepared by Ar^+ ion beam

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Table 1
Parameters of ion beam enhanced deposition

Samples	Base pressure (Pa)	Sputtering energy (KeV)	Sputtering current (mA)	Pressure of argon (Pa)	Pressure for deposition (Pa)	Temperature (°C)
Teflon	1.3×10^{-3}	1.5	30–40	5.3×10^{-3}	$1.3–1.7 \times 10^{-3}$	25
Si_3N_4	1.3×10^{-3}	3.0	100	5.3×10^{-3}	$1.3–1.7 \times 10^{-3}$	25

alternatively sputtering pure Teflon and Si_3N_4 ceramic target. Si(100) wafer was used as the substrate. The multilayer is designed to 11 layers with alternatively Teflon and Si_3N_4 layer, the inner and outer layers are Si_3N_4 films. The deposition rate of Teflon and Si_3N_4 layer is separately 15 nm/min and 7.5 nm/min. So the sputtering time is chosen 5 min for each Teflon layer, and 10 min for each Si_3N_4 layer. The thickness of each Teflon layer is almost the same as that of Si_3N_4 layer (about 80 nm). Detail parameters of the sputtering process are shown in Table 1.

In order to compare the Teflon/Si_3N_4 multilayer, pure Teflon and pure Si_3N_4 films were also prepared using the same sputtering parameters as shown in Table 1. The sputtering time is 1 h for pure Teflon film, and 2 h for Si_3N_4 film. The film thickness of pure Teflon or pure Si_3N_4 films is almost equal to that of whole Teflon/Si_3N_4 multilayer.

2.2. Test procedures

2.2.1. Structure analysis

The chemical bonding, structure and phase composition were determined by PHI-5300 X-ray photoelectron spectrum, FTIR2000 infrared absorption spectrum and X-rays diffraction patterns.

2.2.2. Mechanical properties

The micro-hardness of multilayer was measured by Knoop indenter, the measuring load is 25 g. As for the toughness, Liu [7] evaluated the relative toughness of multilayer film by examining the micro-indentation with a Vickers indenter at different loads, and the critical load F_c to a fracture indentation is taken as the relative toughness of the films on the silicon substrates. The higher the critical load F_c, the higher the relative toughness is. So in this paper the relative toughness of multilayer was carried out through the indentation method by a Vickers indenter, and then determined by the critical load F_c under which the indentation mark started to crack.

2.2.3. Micro friction and micro wear

The microtribological behavior was carried in a CSPM-930a atomic force and friction force microscope (AFM/FFM), the normal spring constant of Si_3N_4 cantilever (scanning tip) is 0.38 N/m. During the micro friction test, the tip scanned back and forth on the sample surface in the y direction at a given load (normal force). The normal force and friction signals were, respectively, recorded by upper and lower halves, left and right halves of the quadrant photo diode. The friction force signal value is half of the difference between the average $+y$ (scanning in positive y direction) and $-y$ (scanning in negative y direction) friction signals. For wear, the cantilever scanned for 50 times in the area 1×1 μm along the x direction at a given load, and then

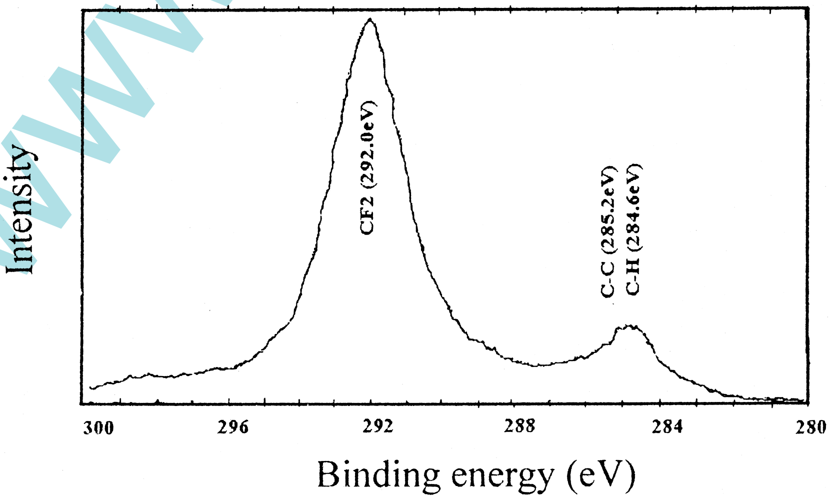

Fig. 1. C1s spectrum of the as-deposited Teflon film.

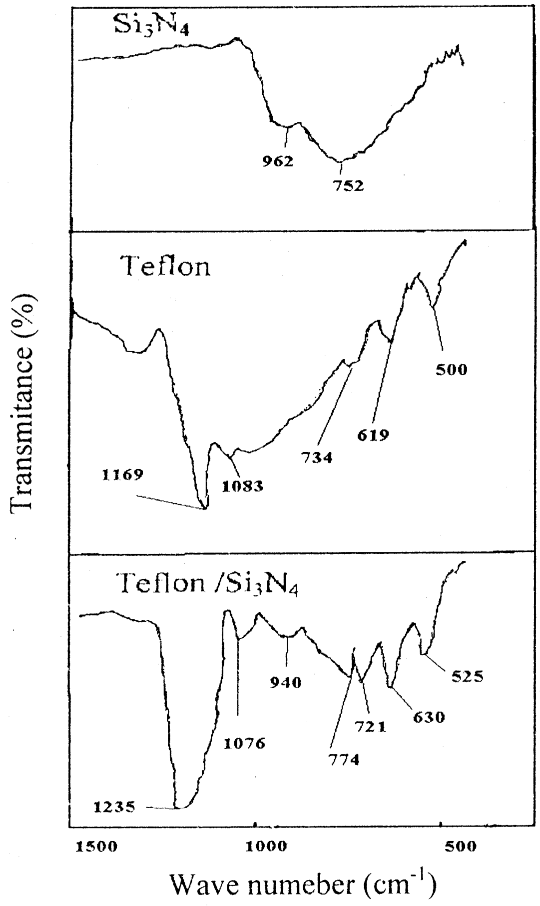

Fig. 2. FTIR spectrum of Si_3N_4, Teflon and Teflon/Si_3N_4 film.

measured the worn surface morphology in the area 2×2 μm. The worn depth can be calculated through measuring the difference between the worn area and initial area which was not worn.

3. Results

3.1. Structure

The C1s spectrum of the thin Teflon film is shown in Fig. 1. It can be observed that the thin film is mainly composed of CF2 (292.0 ± 0.1 eV) bond. Meanwhile there is a small amount of C—C (285.2 ± 0.20 eV) and C—H (284.6 ± 0.20 eV) bonds. These results show that the chemical bond state of the deposited film coincides with the bulk Teflon.

Fig. 2 is the infrared absorption spectrum of the pure Teflon, pure Si_3N_4 and Teflon/Si_3N_4 multilayer. It can be seen that: (1) In the absorption spectrum of Teflon/Si_3N_4 multilayer, there are not only strongest C—F absorption peaks near 1169 and 1083 cm^{-1} but also characteristic peaks near 734, 619 and 521 cm^{-1} which are the strongest and characteristic absorption peaks of pure Teflon film. (2) Coinciding with the absorption peaks of pure Si_3N_4 film, the absorption peaks at 940 cm^{-1} and 774 cm^{-1} also appear in the absorption spectrum of Teflon/Si_3N_4 multilayer. All these show that Teflon/Si_3N_4 multilayer consists of Si_3N_4 and Teflon.

The X-ray diffraction pattern of the pure Teflon, pure Si_3N_4 and Teflon/Si_3N_4 multilayer is shown in Fig. 3. In the X-ray diffraction pattern of Teflon/Si_3N_4 multilayer, there are not only pure Teflon's diffraction peak at $2\theta \approx 25°$ but also pure silicon nitride's peak at $2\theta \approx 35°$. Apart from these two peaks, there are no another peaks in the multilayer. Teflon component in pure Teflon film and Teflon/Si_3N_4 multilayer is in the crystalline state, but Si_3N_4 component in pure Si_3N_4 film and Teflon/Si_3N_4 multilayer appears to be in the diffused scattering pattern. This proved that the multilayer consists of Si_3N_4 component and crystalline Teflon.

3.2. Mechanical properties

Table 2 shows the film thickness, microhardness and critical load *Fc* of pure Teflon, pure Si_3N_4 and Teflon/Si_3N_4 multilayer. The thickness of Teflon/Si_3N_4 multilayer is almost the same as that of pure Teflon and pure Si_3N_4 film. The hardness of the Teflon film is very low, but its critical load is very high. The mechanical properties of Si_3N_4 film which has high hardness and low critical load (toughness) are different from Teflon film. Through micro-

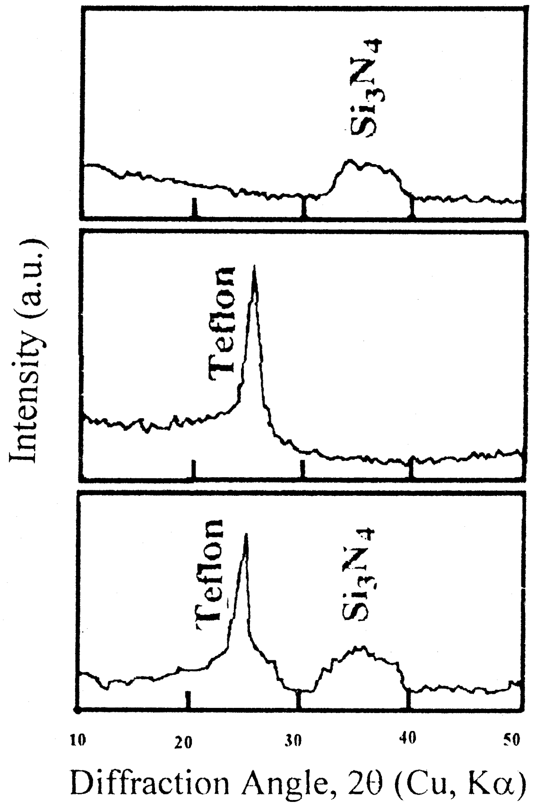

Fig. 3. X-ray diffraction pattern of Si_3N_4, Teflon and Teflon/Si_3N_4 film.

Table 2
Film thickness and mechanical properties of deposited film

Samples	Film thickness (nm)	Microhardness (HK)	Critical load F_c (g)
Teflon	820	60	> 100
Si_3N_4	920	2016	7
Teflon/Si_3N_4	870	1578	30

assembling of Teflon and Si_3N_4 film, the Teflon/Si_3N_4 multilayer not only has high hardness but also has relatively high critical load (toughness), i.e. the comprehensive properties of multilayer are superior to pure Teflon and pure Si_3N_4 film. We found through a series of experiments that the strength and critical load (toughness) of the Teflon/Si_3N_4 multilayer can be varied with the thickness and numbers of Teflon and Si_3N_4 layers.

3.3. Characteristics of micro friction

Fig. 4 shows the dependence of micro friction force signal of pure Teflon, Si_3N_4 and Teflon/Si_3N_4 multilayer on load. It can be observed that the micro friction force signal of Si_3N_4 film and Teflon/Si_3N_4 multilayer is almost linear with load. Through the linear regression, the following formula can be obtained:

$$f = 0.170p + 9.97\ (Si_3N_4)$$

$$f = 0.115p + 1.68\ (Teflon/Si_3N_4)$$

As for pure Teflon film, when the load is less than 70 nN, the micro friction force signal increases linearly with the load:

$$f = 0.057p + 2.78\ (Teflon)$$

But when the load is greater than 70 nN, the micro friction force signal does not increase with the load, the friction force stays about constant. Through the observation of the surface morphology after micro friction process when the load is above 70 nN, it is found that the surface of the pure Teflon film and Teflon/Si_3N_4 multilayer is scratched, but for pure Si_3N_4 film, there is no observed worn mark under the maximum load in the micro friction test (Fig. 5).

According to the principle of FFM, the friction force can be calculated by multiplying the torsion stiffness of the cantilever by the distance that the cantilever is turned around in the friction test along y or $-y$ directions, i.e. the friction force signal. The torsion stiffness is related to the geometry of the cantilever and the mechanical properties of the made material Si_3N_4, and can be calculated by finite element method [8]. Because the size of cantilever is so small that we can not measure it precisely, and there is a slight difference between different cantilevers, the precise value of the friction force is very difficult to calibrate. So if only the difference of friction behavior between different samples is required to be found, the friction force signal can be used as the representative of the real friction force to be compared. On the other hand, according to friction theory, the friction force can be expressed as following [9]:

$$f = \mu\left(L_{\text{applied}} + F_{\text{adhesion}}\right)$$

Here μ is the friction coefficient, L_{applied} is the applied force, F_{adhesion} is the adhesion force. Corresponding to the relationship between the friction force and friction force signal, the slope of friction force signal vs. load is referred as the friction coefficient factor (equivalent of friction coefficient) under the micro friction test [10].

From the above formula, it is shown that the friction coefficient factor of pure Teflon film (0.057) is very small, the friction coefficient factor of Teflon/Si_3N_4 multilayer (0.115) is located between the pure Teflon and Si_3N_4 film (0.171), and is about two thirds of Si_3N_4 film's friction coefficient factor.

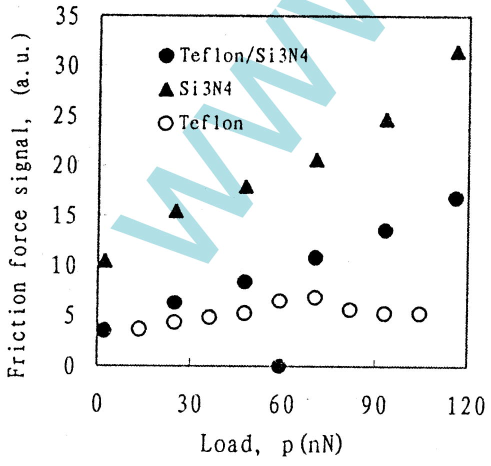

Fig. 4. Dependence of friction force of Teflon, Si_3N_4 and Teflon/Si_3N_4 film on load.

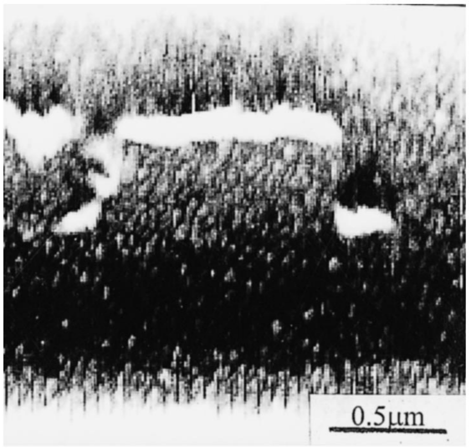

Fig. 5. Morphology of Teflon/Si_3N_4 film after 116 nN load and 10 cycles' friction (2 × 2 μm).

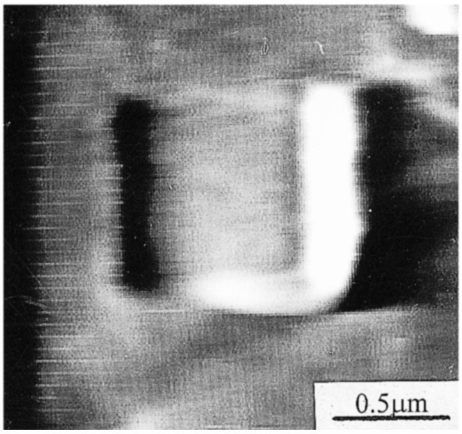

Fig. 6. Worn morphology of Teflon under 110 nN load and 50 cycles (2 × 2 μm).

3.4. Micro wear

Through the friction and wear tests, it is seen that when the load is greater than 70 nN, the worn mark is started to form in the pure Teflon and Teflon/Si_3N_4 film, but there is no obvious worn mark in pure Si_3N_4 film under the load range 10–40 nN. Fig. 6 shows the worn morphology of Teflon film under 110 nN load and 50 scanning times.

After the micro wear tests, the dependence of worn depth of Teflon and Teflon/Si_3N_4 film on load is shown in Fig. 7. It can be seen from Fig. 7 that the worn depth of Teflon and Teflon/Si_3N_4 film is also in nanoscale, and the worn depth increases linearly with load. The worn depth of Teflon/Si_3N_4 multilayer is about one tenth of Teflon film at the same load. Although the wear resistance of multilayer is less than that of Si_3N_4, the wear resistance of Teflon/Si_3N_4 multilayer is much greater than that of Teflon film.

4. Discussion

From the above experimental results, it can be seen that the deposited Teflon component of pure Teflon film and Teflon/Si_3N_4 multilayer is in the crystalline state, and its structure is the same as that of bulk Teflon. The molecular structure of Teflon is the zigzag backbone or rod-like of —CF_2—CF_2— groups. The Teflon molecule exhibits extremely high cohesion, but the intermolecular strength is not high because there is van der Waals force between molecules, so the Teflon with rod-like molecule has very easy slip under the shear stress. In the friction and wear process, Teflon has high lubricity, low friction coefficient and low wear resistance [11].

During the friction and wear tests, two periods can be distinguished according to the load. One is the load below 70 nN, the friction force which created in friction and wear tests is so small that it does not make the Teflon film shear. So in this period the friction force increases linearly with the load, and there are no transfer of atoms and no worn marks. The second period is the load above 70 nN, the friction force created in the friction and wear tests would make the Teflon molecular atom to slip. So there would be obvious worn mark and projection in the film, and the friction force would not increase with the load.

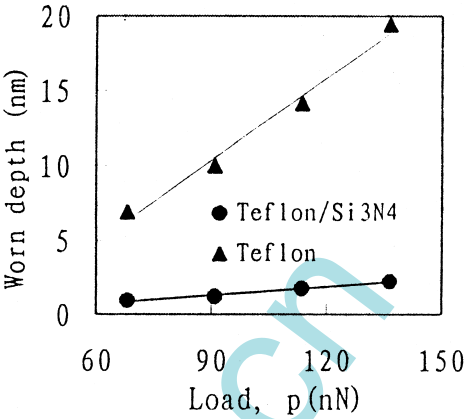

Fig. 7. Dependence of worn depth of Teflon and Teflon/Si_3N_4 film on load.

Through micro-assembling of Teflon and Si_3N_4 layers, the Teflon layer in Teflon/Si_3N_4 multilayer is located between two Si_3N_4 layers. Because of the interaction between Teflon and Si_3N_4 layer, the multilayer combines the superior characteristics of Teflon and Si_3N_4 film, so the multilayer has high comprehensive properties, i.e. the combination of high hardness, high toughness, low friction coefficient and high wear resistance.

5. Conclusions

1. The Teflon/Si_3N_4 multilayer was developed, and the multilayer consists of Si_3N_4 component and crystalline Teflon.
2. Through micro-assembling of Teflon and Si_3N_4 film, the Teflon/Si_3N_4 multilayer not only has the characteristics of Teflon's relatively low friction coefficient and high toughness but also has characteristics of silicon nitride's high hardness and wear resistance. The comprehensive properties of Teflon/Si_3N_4 multilayer are greatly improved.
3. The micro friction force of Si_3N_4 film and Teflon/Si_3N_4 multilayer increases linearly with load, the worn tracks will be formed in the Teflon/Si_3N_4 multilayer surface when the load is greater than 70 nN. But for pure Teflon film, there are two regions in the friction and wear tests. When the load is less than 70 nN, the micro friction force is linear with the load. When the load is greater than 70 nN, the friction force of Teflon film will stay about constant, and worn marks will be created in the friction and wear process.

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