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Deposition of carbon nitride films for space application

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Carbon nitride thin films were prepared by electron-beam evaporation assisted with nitrogen ion bombardment and TiN/CN_x composite films were by unbalanced dc magnetron sputtering, respectively. It was found that the sputtered films were better than the evaporated films in hardness and adhesion. The experiments of atomic oxygen action, cold welding, friction and wearing were emphasized, and the results proved that the sputtered TiN/CN_x composite films were suitable for space application.

Keywords: CN_x film, hardness, atomic oxygen, cold welding, friction, wear
PACC: 8115G, 6220M, 6220P, 9490

1. Introduction

Since Liu and Cohen [1] predicted that the hardness of hypothetical β-C_3N_4 is similar to or higher than that of diamond in 1989, many research groups tried to deposit CNx thin film. Various deposition techniques were used: laser ablation,[2] ion-assisted evaporation,[3] ion implantation,[4] reactive sputtering[5−7] and chemical vapour deposition,[8] etc. Although some researchers reported that they had synthesized tiny β-C_3N_4 crystallites, no excellent performance as predicted[1] was achieved.

There are still many groups trying to synthesize the stoichiometric C_3N_4 now, and although some strategies have been summarized for the synthesis of β-C_3N_4[9] many researchers pay more attention to the use of substoichiometric CN_x films and some composite carbon nitrides.[9]

In our laboratory, the deposition of carbon nitride thin films was carried out by electron beam evaporation of high-purity graphite assisted with nitrogen ion bombardment and by unbalanced dc magnetron sputtering graphite in $Ar+N_2$ atmosphere. The TiN/CN_x composite films were sputtered in order to obtain films suitable for space and machine industry application. The experiments of atomic oxygen action, cold welding, friction and wearing were carried out to prove the protection properties of the composite films.

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2. Experimental details

2.1. IBAD technology

To attempt synthesis of high N/C ratio CN_x films, an ion-beam assisted deposition (IBAD) system with an electron gun and ion source were used (see Fig.1). The high current electron beam from the electron gun was used to evaporate the high-purity graphite, at the same time, the assisted nitrogen ion beam from an ion source bombarded on the carbon film (also the substrate), by which the carbon reacted with nitrogen and the carbon nitride films were grown, and some carbon atoms were also sputtered and eroded. The base and operating vacuum were about 10^{-4} and 10^{-2}Pa, respectively.

The purity of the graphite is 99.99%, and the electron beam is of 10 kV. The evaporation rate can be adjusted by changing the working current of the electron gun, the energy of nitrogen ion beam and the $Ar+N_2$ flow rate. The deposition conditions are listed in Table 1.

Table 1. Deposition condition for CN_x films.

electron gun power/W	150–200
ion beam energy/eV	500–1500
operating vacuum pressure/Pa	$2\times10^{-2}-7\times10^{-2}$
N_2 flow/sccm	8–20

Substrates used were Si wafers and high-speed steel. The thickness of CN_x films obtained was about 300–400 nm, and the deposition rate of CN_x films was

about 60 nm/h. It was found that the deposition rate increased with the increase of evaporation rate of graphite.

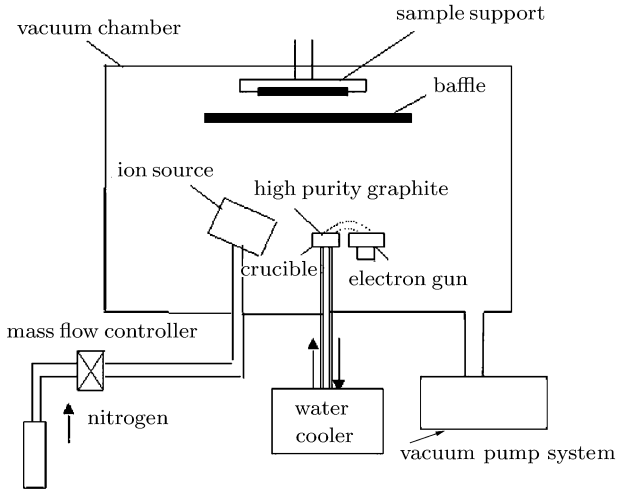


Fig.1. Schematic diagram of the IBAD apparatus.

2.2. Magnetron sputtering technology

For the formation of high-quality CN_x and composite films TiN/CN_x, the unbalanced magnetron field dc sputtering system was also used (see Fig.2).

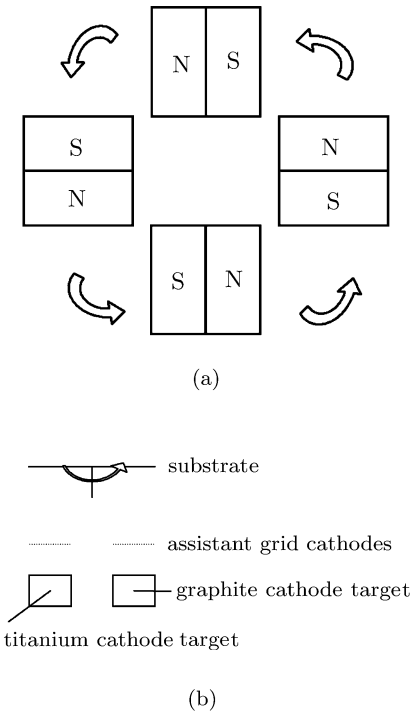


Fig.2. Principle of unbalanced magnetic field dc sputtering. (a) Unbalanced magnetic field; (b) Assistant grid cathodes.

In the system, the assistant magnets were mounted on the places opposite to the cathode targets to form a closed unbalanced magnetic field. Two assistant grid cathodes were placed between the targets and the substrate (see Fig.2(b)). The assistant magnets and cathodes restrained the electron flow and increased the ionization rate.

In the magnetron sputtering system, the titanium and graphite were mounted on the magnetron target, and the substrate were rotated, so that the TiN and CN_x could be deposited on the substrate alternatively. The base vacuum was 10^{-4}Pa and the working vacuum was about 1.0Pa. Deposition conditions are listed in Table 2. TiN/CN_x composite films were sputtered on high-speed steel, carbon fibre reinforced boards and ALY12 plate (hard aluminium alloy). The thickness of TiN/CN_x films was about $1-2$ μm, where the deposition rate of TiN/CN_x films was about 120 nm/min.

Table 2. Deposition condition for TiN/CN_x composite films.

depositing pressure/Pa	0.8–1.0
Ar/N_2/sccm	10–20
substrate rotating speed/(r/min)	5–10
grid bias voltage/V	−400
graphite target sputtering voltage/V	480–550
graphite target sputtering current/A	1–2
titanium target sputtering voltage/V	400–450
titanium target sputtering current/A	1–2

3. Results and discussion

3.1. Film adhesion

It was found that the smoothness and adhesion of CN_x films deposited by IBAD become worse when the evaporation rate of graphite is high. The films with high-energy ion bombardment have better compactness and adhesion. However, the deposition rate of CN_x films decreases with the increase of nitrogen ion bombarding energy because the high-energy ions have a strong sputtering action on the film surface.

The smoothness and adhesion of CN_x films and TiN/CN_x composite films deposited by dc magnetron sputtering are excellent even when the thickness of the films is higher than 1 μm.

3.2. Hardness

The IBAD films are amorphous with tiny crystallites, and the conventional hardness is not suitable for their measurement,[10] a nano-indentation measurement is used. It was found that the elastic modulus of the film was 218 GPa, and the maximum hardness was 23.3 GPa, which was much less than the theoretical result.

The sputtered CN_x and TiN/CN_x composite films were relatively thick, so the conventional hardness measurement was suitable. The hardness of our composite films was measured with a micro indenter MINILOAD-2. The load was 245.2 mN, and the maximum HK hardness was 52.91 GPa, which is less than the hardness of diamond ($\geq$ 70 GPa), but larger than that of c-BN (about 40 GPa). The maximum HK hardness of sputtered CN_x films was 40.2 GPa, which is equivalent to the hardness of c-BN.

The XPS, EDX, XRD measurements were used to test the CN_x films deposited on Si wafers by IBAD so as to explain the poor hardness and adhesion. The XPS measurement showed that more sp^2 hybrids existed in the films than sp^3 hybrids. The EDX measurement showed that the maximum N/C atomic ratio was only 0.43. The XRD showed that no β-C_3N_4 crystal structure existed.

3.3. Atomic oxygen action

Atomic oxygen reactions with spacecraft materials in the low-earth-orbit environment have significant effects on the performance of materials, particularly on those with polymeric base. For example, atomic oxygen has an obvious corrosion to polyimide and carbon fibre configuration. It is essential to make the atomic oxygen protection in the form of films and coatings.[11,12] Carbon fibre board are usually used for structural materials in spacecrafts.[13] The TiN/CN_x composite films are deposited on the carbon fibre board in our laboratory for testing the protection against the atomic oxygen action.

Two carbon fibre boards are selected for the atomic oxygen action tests. One is covered with TiN/CN_x film, the other is bare. The samples are exposed in the atomic oxygen environment for up to 340h and the total flux is 4.3×10^{21} atoms/cm^2. The samples are taken out three times to measure the mass loss during the experiment. The mass loss data and the relative mass loss rate are listed in Table 3.

Table 3. The mass loss rate of samples.

samples(carbon fibre board)	the mass loss per unit area/(g/mm^2)	the relative mass loss rate/%
bare	1.34×10^{-4}	28.2
covered with TiN/CN_x film	2.08×10^{-5}	5.38

After undergoing the atomic oxygen action at the same flux, the mass loss per unit area and the mass loss rate of the two samples are compared. Results show that the TiN/CN_x films can be used for protecting structural materials in spacecrafts from atomic oxygen action.

3.4. Cold welding measurements in ultra-high vacuum environment

The phenomenon of strong adhesion generated between clean metal surfaces in an ultra-high vacuum environment is called cold welding, which may affect the working of the metallic movable equipment in space environment.[14,15] It can be avoided by depositing a protective film on the metal surface. The TiN/CN_x film deposited on ALY12 has been tested by dualization attached in the ultra-high vacuum environment to evaluate its property of cold welding proofing.

The experimental vacuum is $2.6 - 5.9 \times 10^{-8}$Pa and the load is 0.3 N. In room temperature environment, the samples are pulled apart 100 times. The test data obtained are divided into ten groups. The average value per group is listed in Table 4.

Under the same test condition except for the load of 0.5N, the maximum value of the pull-apart force between the bare ALY12 surfaces is 40mN and the adhesion coefficient ranges from 10^{-1} to 10^{-2}. The results show that the TiN/CN_x composite films can be used for cold welding protection in the ultra-high vacuum environment.

Table 4. The data obtained from cold welding test.

group number	pressure/10^{-8}Pa)	I_{adh}/mA	f_{adh}/N	$\alpha/10^{-3}$
1	4.3	8.05	0.000470	1.57
2	5.9	8.04	0.000455	1.52
3	3.9	7.87	0.000188	0.63
4	2.9	8.06	0.000486	1.62
5	3.2	7.68	0.00000	-
6	2.9	7.57	0.00000	-
7	3.2	7.68	0.00000	-
8	3.2	7.07	0.00000	-
9	4.2	7.77	0.000031	0.10
10	2.6	7.82	0.000110	0.37
Average data	3.9	7.90	0.00029	0.97

Note: I_{adh}(mA)—critical current consumed by the lower electric coil to pull the specimen apart; f_{adh}(N)——adhesion force; $\alpha(\times 10^{-3})$—adhesion coefficient.

3.5. Friction and wearing

Thin hard TiN/CN_x composite films are used popularly in many important tribological fields, such as metal cutter, foaming tools, sliding bearing, seals, engine parts and other machine element. The slide wearing properties of bearing is very important for spacecraft on orbit, because it cannot be repaired and lubricated with liquid lubrication.

The tribological properties of composite films are measured in a multi-function vacuum tribology system. The plate diameter is 8mm, the ball material is GCr15, the load is 5N, the touch radius is 12mm, and the rotating speed is 500rpm. The friction experimental results are shown in Table 5.

Table 5. Results of the friction experiment.

No	materials	friction coefficient	wearing time/min	wearing area/mm^2
1	High-speed steel	0.50	47	1.3×10^{-2}
2	TiN/CN_x covered high-speed-steel	0.32	47	9×10^{-3}

It is found that the friction coefficient of coated material decreases about 36%, and the wearing area decreases about 31%.

4. Conclusion

CN_x films and TiN/CN_x composite films have been deposited and their properties measured. The results showed that dc sputtered films are better than the evaporated films, and the sputtered TiN/CN_x composite films are the best. Experiments showed that the sputtered composite TiN/CN_x films are promising materials that can be used for protection of atomic oxygen action, cold welding and wearing in spacecrafts.

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