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Effects of substrate bias voltage and target sputtering power on the structural and tribological properties of carbon nitride coatings

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HIGHLIGHTS

- Various CN_x coatings are produced using a unique hybrid coating process.
- Structural and tribological properties of CN_x coatings are investigated.
- The lowest friction coefficient of 0.12 is achieved at −800 V 100 W.
- Friction is controlled by the directly sliding between coating and steel pin.
- Friction reduction is due to decrease of sp^3 carbon bonding in the coating.

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ABSTRACT

Effects of substrate bias voltage and target sputtering power on the structural and tribological properties of carbon nitride (CN_x) coatings are investigated. CN_x coatings are fabricated by a hybrid coating process with the combination of radio frequency plasma enhanced chemical vapor deposition (RF PECVD) and DC magnetron sputtering at various substrate bias voltage and target sputtering power in the order of −400 V 200 W, −400 V 100 W, −800 V 200 W, and −800 V 100 W. The deposition rate, N/C atomic ratio, and hardness of CN_x coatings as well as friction coefficient of CN_x coating sliding against AISI 52100 pin in N_2 gas stream decrease, while the residual stress of CN_x coatings increases with the increase of substrate bias voltage and the decrease of target sputtering power. The highest hardness measured under single stiffness mode of 15.0 GPa and lowest residual stress of 3.7 GPa of CN_x coatings are obtained at −400 V 200 W, whereas the lowest friction coefficient of 0.12 of CN_x coatings is achieved at −800 V 100 W. Raman and XPS analysis suggest that sp^3 carbon bonding decreases and sp^2 carbon bonding increases with the variations in substrate bias voltage and target sputtering power. Optical images and Raman characterization of worn surfaces confirm that the friction behavior of CN_x coatings is controlled by the directly sliding between CN_x coating and steel pin. Therefore, the reduction of friction coefficient is attributed to the decrease of sp^3 carbon bonding in the CN_x coating. It is concluded that substrate bias voltage and target sputtering power are effective parameters for tailoring the structural and tribological properties of CN_x coatings.

1. Introduction

Excellent performances of carbon nitride (CN_x) coatings, such as low friction and high wear resistance make them good candidates for the demanding mechanical systems [1,2]. Particularly, CN_x coatings produced by the ion beam assisted deposition (IBAD)

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technique can give super-low frictions ($\mu < 0.01$) in N_2 gas environment [3–6]. According to previous research, the structural and tribological properties of CN_x coatings are strongly related to the coating deposition methods [3,4,7–10]. However, the key deposition parameter in controlling the tribological behavior as well as structural behavior of CN_x coatings is still not clearly identified. To obtain a clear relationship among deposition parameter, tribological behavior, and structural behavior of CN_x coatings, a unique hybrid coating process [11–14], combining radio frequency plasma enhanced chemical vapor deposition (RF PECVD) and DC magnetron sputtering and possessing the advantage of separately adjusting the various deposition parameters (e.g. pressure, source gases, RF power, substrate bias voltage, target materials, and DC sputtering power) have been applied for the development of high performance CN_x coatings in our recent work [15]. It has been clarified that the structural properties (i.e. deposition rate, residual stress, and hardness) of hybrid CN_x coatings are greatly affected by the N_2/Ar flow ratio in the coating process. However, the friction behavior of hybrid CN_x coatings in N_2 gas stream shows less dependency on the N_2/Ar flow ratio. The friction coefficients of hybrid CN_x coatings sliding against AISI 52100 pins in N_2 gas stream are in the ranges of 0.33–0.42, at least 10 times higher than those observed in IBAD CN_x coatings. Low friction coefficient of hybrid CN_x coatings is not achieved, although the atomic composition of the hybrid CN_x coating (81.4% C, 10.8% N, and 7.8% O) is similar to that of the IBAD CN_x coating (81.8% C, 11.2% N, and 7.0% O). Therefore, it is argued that the bonding structure other than the composition of CN_x coating is paramount important for achieving low frictions of CN_x coatings in N_2 gas environment [15].

The structural properties of CN_x coatings can be tailored by the nitrogen ion energy in the plasma during the coating deposition process [16–19]. It has been revealed that both N/C atomic ratio and sp^3/sp^2 carbon ratio of IBAD CN_x coatings decrease with increasing bombarding energy of nitrogen ions from 300 eV to 1000 eV [19]. On the other hand, the nitrogen ion energy in the hybrid coating process could be well controlled by adjusting the substrate bias voltage and target sputtering power. Therefore, in this study, effects of substrate bias voltage and target sputtering power on the structural and tribological properties of hybrid CN_x coatings are investigated, with the objective to get lower friction coefficient of the hybrid CN_x coatings and further clarify the friction mechanisms of hybrid CN_x coatings from the viewpoint of bonding structure as well.

2. Experimental

2.1. Coating deposition

CN_x coatings (400 nm thick) were grown on Si (100) substrates using a hybrid coating process with the combination of RF PECVD and DC magnetron co-sputtering of a graphite target [11–15]. A high purity graphite target (>99.99%) with dimensions of $\varphi 76.2 \times 5$ mm was mounted on the water cooled cathode at a distance of 100 mm from the substrate. A stainless steel shutter was placed between the target and substrate. The base pressure of depositing chamber was pumped down to 4.0×10^{-4} Pa by utilizing a turbomolecular pumping system. First of all, the silicon substrates were etched by argon plasma for 10 min to remove contamination. Thereafter, the shutter was closed and argon plasma was generated on the surface of the graphite target by applying 200 W d.c. power to pre-sputter the target and stabilize the sputtering condition at the surface. The shutter was then opened and CN_x coatings were deposited onto the silicon substrates at a pressure of 1.3 Pa. A mixture of nitrogen and argon gas with N_2/Ar flow ratio of 0.1 was applied as source gas. The detailed deposition conditions are listed in Table 1.

To get higher nitrogen ion energy during the coating deposition process as much as possible, four combinations of substrate bias voltage and target sputtering power in the order of −400 V 200 W, −400 V 100 W, −800 V 200 W, and −800 V 100 W, were employed. The substrate bias voltage increased from −400 V to −800 V, whereas the target sputtering power decreased from 200 W to 100 W. In the hybrid coating process, −800 V was the maximum value of substrate bias voltage, beyond which the re-sputtering rate of the coating by nitrogen and argon ions was larger than the deposition rate of coating, and thus the coating cannot be prepared on the substrate. 200 W was the maximum value of sputtering power, beyond which a strong reaction between nitrogen gas and carbon atom occurred, the reaction product then covered the surface of graphite target and prohibited the deposition process (so-called target poison).

2.2. Coating characterization

A surface profiler (Alpha-Step 500 KLA-Tencor Ltd., USA) was employed for thickness and residual stress measurement. The deposition rate was calculated from the thickness of coating, which was determined from a step between the CN_x coating and silicon substrate generated by a shadow mask. Another purpose to use the surface profiler is to calculate the residual stress of the coating. The residual stress was calculated from the Stoney equation after the measurement of the curvature of CN_x coated substrate [15,20].

Hardness of CN_x coatings was evaluated under both single stiffness mode and continuous stiffness mode for confirmation of the results. In case of the single stiffness mode, the hardness of CN_x coatings was characterized on a Nano Indentation tester (ENT-2100, Elionix Inc., Japan) using a Berkovich diamond tip with a load of 0.4 mN. The depth of indentation was below 10% of the coating thickness in order to exclude the influence of substrate. In case of the continuous stiffness mode, the hardness of CN_x coatings was determined on a Nano Indenter (Nano Indenter XP, MTS Systems Corporation, USA) using a Berkovich diamond tip with a load of 50 mN. Before and after each experimental series, the tip shape calibration procedure was repeated by indenting a standard fused silica specimen to monitor the possible wear of tip shape. In both conditions, the measurement was conducted ten times on each sample to ensure data accuracy.

Chemical composition and bonding structures of CN_x coatings were characterized by an X-ray photoelectron spectroscope (XPS, PHI1600, Physical Electronics Inc., USA) operating with a monochromated Mg Kα irradiation. The structure of carbon bonds of CN_x coatings was analyzed by a Raman spectroscope (NRS-5100, JASCO Corporation, Japan) operating with a 532 nm green laser as the excitation source. The fitting of XPS and Raman spectra were both conducted in Origin 8.0 software (OriginLab Corporation, USA).

Tribological properties of CN_x coatings were measured by using a pin-on-plate reciprocating tribometer. CN_x coated Si substrates (10×20 mm) were driven to run against AISI 52100 balls ($\phi = 6$ mm) with a normal load of 1 N, a sliding speed of 3 mm s^{-1}, a

Table 1
Deposition conditions of CN_x coatings.

Deposition parameters	Value
Operation pressure (Pa)	1.3
N_2 gas flow rate (ccm)	1.0
Ar gas flow rate (ccm)	10.0
Substrate bias voltage (V)	−400, −800
Target sputtering power (W)	100, 200