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Structure analysis of topmost layer of CN_x after repeated sliding using scanning transmission electron microscopy electron energy-loss spectroscopy

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ABSTRACT

Carbon nitride (CN_x) coating has been found to exhibit an ultra-low friction coefficient (less than 0.01) when sliding against a silicon nitride (Si_3N_4) ball in a dry nitrogen gas (N_2) atmosphere; however, no direct surface analysis of the topmost layer of the ultra-low friction coating has been conducted. In the present study, we examine the wear tracks formed on a CN_x coating after a sliding test in both dry N_2 and air atmospheres, using scanning transmission electron microscopy combined with electron energy-loss spectroscopy, to elucidate the structure of the surface transition layer quantitatively on the nanometer scale. After the sliding test in dry N_2, a measurement taken from the surface towards the material bulk indicates that the plasmon peak has shifted. We discuss the plasmon peak shift in terms of the density and chemical bonding nature, as a measure of the microscopic structural change.

1. Introduction

In recent years, hard carbon films have attracted considerable attention as promising coating materials that exhibit low friction and high wear resistance [1–5]. Thus, their applications as sliding parts in machinery, particularly in the precision machinery industry, have been studied extensively [3]. In the field of magnetic storage, carbon nitride (CN_x) coatings have been used as protective coatings on hard disks and recorder heads, with the aim of reducing the friction property [2]. The present authors' research group has focused on CN_x coating [4,5] with 20-GPa of a nanoindentation hardness in sliding tests, in which the CN_x slides against a silicon nitride (Si_3N_4) ball in a dry nitrogen gas (N_2) atmosphere. In a previous study, it was reported that the initial friction coefficient μ for this sliding scenario was as high as approximately 0.16; however, this value decreased with increasing sliding distance, finally reaching 0.007 [4].

In order to elucidate the microscopic mechanism behind the appearance of this ultra-low friction in response to repeated sliding tests in dry N_2, the effect of local structural changes in the CN_x coating and the thickness of the transfer layer onto the Si_3N_4 ball have been investigated. Raman and X-ray photoelectron spectroscopy analyses [4,5] have confirmed that CN_x coating samples exhibit a relative increase in the fraction of sp^2 carbon as well as structural changes in the surface when ultra-low friction in dry N_2 is generated. Further, Auger electron spectroscopy analysis has indicated a relative decrease in the N content after a sliding test, compared to the initial state [5]. Thus, it is expected that a structurally modified thin layer is generated on the surface of the ultra-low-friction CN_x coating, and that this structurally modified layer acts as a low-shear-strength layer with a graphite-like structure [5]. However, it is known that graphite does not exhibit low friction in vacuum, whereas the present CN_x coating has low friction even under vacuum conditions [4]. Thus, it is believed that the structure of the modified layer formed by the friction differs from that of ordinary graphite, but this hypothesis must be clarified from a microscopic perspective. With regard to whether or not the structure contains a large sp^2 fraction, information on the coating space structure and the structural changes has not yet been obtained.

Analysis of the plasmon peak in the coating can be used to examine the structures of the coating and the surface transition layer, as the plasmon peak corresponds to the density (ρ) of the solid, which is related to the space structure. Plasmon peaks are produced by plasma oscillations that originate from collective excitations of valence electrons. Two types of plasmon peaks are observed in C-based materials (such as graphite, amorphous carbon (a-C), and diamond-like carbon), namely, the σ-plasmon (23–28 eV) originating from the sp^2-σ and sp^3-σ bonding states, and the π-plasmon (5–8 eV) characteristic of the sp^2-π bonding states in graphite and a-C [6–9]. In the free electron-gas model, the

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plasmon energy E_p is proportional to the square root of the valence-electron density and, if unaccompanied by major changes in composition or the chemical bonding state, is an approximate reflection of the ρ of the material [8]. Furthermore, the σ-plasmon or ρ of C-based amorphous films is known to be closely linked to the sp^2/sp^3 ratio [10].

This paper presents evidence regarding the nature of the CN_x coating structure and the surface transition layer following sliding testing in both dry N_2 and air atmospheres, at nanometer resolution and based on the plasmon peak in the coating. In order to obtain further details of the microscopic structural information on the disk-side wear tracks, scanning transmission electron microscopy (STEM) and electron energy-loss spectroscopy (EELS) are employed for depth-dependent analysis at nanometer resolution. The depth dependence of the plasmon peak positions is investigated for the wear-track cross sections of the CN_x coating on the disk-side, which are generated during sliding tests performed in a dry N_2 atmosphere and in open air. Information on the structural changes near the wear-track surface is then obtained by comparing the results with those for non-contact areas of the coating. Hence, we investigate the coating density, sp^3 fraction, and the hexagonal structure connected with the sp^2 fraction in the wear tracks, and reveal the unique characteristics of the structurally modified layer located within the wear tracks, which exhibits ultra-low friction.

2. Experimental details

2.1. CN_x coating deposition

The CN_x coating was deposited on a 2-in. diameter Si(100) wafer using ion-beam-assisted deposition [4–5], as follows. First, a vacuum chamber was evacuated to 1.0×10^{-4} Pa using a cryogenic vacuum pump. The Si substrate was then sputter-cleaned for 5 min using N^+ ions at a current density of 100 μA/cm^2, in order to remove any contaminants from the surface. The deposition was then performed using a C target (purity: 99.999%) sputtered with Ar^+ ions having an energy of 1.0 keV at a current of 100-mA, while the Si substrate was simultaneously irradiated by N^+ ions at a current density of 30 μA/cm^2; thus, a mixture of C^+ and N^+ ions was deposited on the Si substrate. The accelerating voltage was 1 kV. The deposition yielded a disk with a CN_x layer thickness of ca. 165 nm. Table 1 shows the chemical composition ratio, indentation hardness, Young's modulus, and surface roughness of the CN_x coating. The chemical composition ratio was measured by the EELS analysis (a JEOL, JEM-2100 TEM operated at 200 kV and a Gatan ENFINA 1000 spectrometer). The surface roughness was measured by an atomic force microscope (Seico Instruments Inc., SPA400). The indentation hardness and the Young's modulus were measured by a nanoindentation hardness tester (Elionix Co. Ltd, ENT110a).

2.2. Sliding test

The μ values for the CN_x coated surface sliding against the Si_3N_4 ball were measured with a customized pin-on-disk friction tester, using the method reported previously [5]. The load is applied by moving a pin (in this case, a Si_3N_4 ball) that is installed in the chamber up and down, so that the pin is pressed onto the disk. The load and friction force are measured by strain-gauge-type load cells affixed to linear leaf springs.

The sliding test conditions were as follows: Temperature: 23 °C; load: 0.1 N; sliding speed: 0.13 m/s. A maximum Hertzian contact pressure of 314 MPa under the normal contact load of 0.1 N was employed. A Si_3N_4 ball with 8-mm diameter was used as a pin specimen, having 15-GPa hardness according to micro-Vickers hardness measurements. The CN_x-coated Si wafer, which had nanoindentation hardness of 20 GPa, was used as a disk specimen. Si_3N_4 ball have been widely used in industrial applications as ball bearings. For one of the future applications of CN_x coatings, our research group previously selected the sliding pair of CN_x coatings and Si_3N_4 balls to examine the friction property [4]. The specific sliding property of the CN_x coatings against the Si_3N_4 balls in dry N_2 atmosphere was investigated [4,5]. Note that the Si_3N_4 ball was cleaned prior to the sliding test via a 15-min ultrasonic cleaning treatment with acetone and then dried. The sliding tests were performed in a dry N_2 atmosphere and in open air, so as to investigate the effect of the gas atmosphere on the structural changes. For the sliding tests in the dry N_2 atmosphere, the chamber was evacuated to 270 Pa by a rotary pump, before the N_2 was supplied. The sliding tests were repeated for a number of sliding cycles N of up to 8300.

Table 1
Properties of CN_x coating.

N/C ratio	Hardness H GPa	Young's modulus E GPa	Roughness Ra nm
0.12	20	200	0.72

2.3. EELS analysis of wear tracks and non-contact areas

After performing the sliding tests in both the dry N_2 atmosphere and in open air, the wear tracks in the disk-side CN_x coatings were observed via scanning electron microscopy.

For transmission electron microscopy (TEM) analysis in the depth direction of the specimens, cross-sectional samples at the wear-tracks were obtained using a focused ion beam (Hitachi, FB-2100; accelerating voltage: 40 kV). Hence, TEM samples of 40-nm thickness from the surface towards the bulk of the material (Si substrate) were obtained, as shown in Fig. 1. This sample thickness corresponds to one fifth of the inelastic scattering mean free path, which allows nonlinear superposition of the EELS spectral intensities due to the effects of multiple scattering to be avoided. For comparison, a TEM sample was also produced in a similar manner from the framed area (II) of Fig. 2(a). This specimen was obtained from a region that was slightly removed from the wear track of the CN_x coating, after sliding testing in dry N_2.

STEM-EELS measurements were performed on the selected samples in the depth direction from the surface, as indicated by the dotted lines in Fig. 1, using a JEOL JEM-2100 STEM operated at 200 kV and a Gatan ENFINA 1000 spectrometer. Fig. 3 is a schematic of the experimental set-up used for these measurements. Each sample was scanned with an electron probe of 2 nm in diameter in the Y direction with a 3-nm step width, and the EEL spectra were recorded. This process was repeated four times, with the scanning positions being varied in the X direction

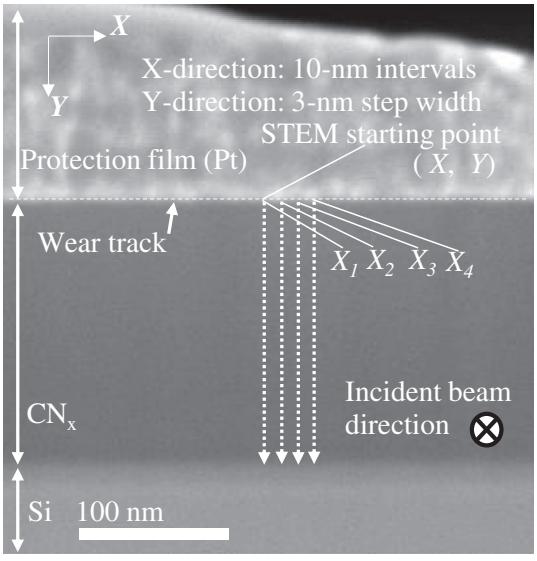

Fig. 1. Measurement area of cross-sectional TEM sample. (X, Y) indicates the measurement starting point. The Y axis is in the depth direction. EELS spectra were measured from the surface of the wear track to the Si substrate along the dotted lines shown in the figure and at 3-nm intervals, using STEM EELS. The same measurement was repeated four times along the dotted lines, which have 10-nm separation.