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Friction properties of surface-modified polished chemical-vapor-deposited diamond films under boundary lubrication with water and poly-alpha olefin

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ABSTRACT

To reduce the friction coefficient of chemical-vapor-deposited diamond films, the films were surface modified by fluorination, oxidation, or nitrogen ion implantation. Surface modification of diamond surface structures (especially of the N^+-implanted diamond film) was confirmed by Raman spectroscopy. Fluorinated diamond film demonstrated the lowest surface free energy, whereas the nanoindentation hardness and nanowear resistance were lowest in the N^+-implanted diamond film. Boundary lubrication properties were evaluated by an oscillating friction test. The friction coefficient and surface damage of the oxidized and N^+-implanted diamond films (with high surface free energies) were effectively reduced by boundary lubrication. Fluorinated and untreated diamond films exhibited low-friction and little damage under dry and boundary lubrication.

1. Introduction

The performance of advanced mechanics equipment is gradually degraded by wear and friction. Surface modification seems to effectively improve these tribological properties [1–10]. In these modifications, the usual self-sacrificial solid lubricant is replaced with a wear-resistant lubricating material. Hard, low-friction materials such as diamond and diamond-like carbon (DLC) are recognized for their low-friction and wear. The concepts of tribological surface material design have been discussed, and a feasible surface material composition that ensures zero microtribological wear has been suggested [10].

The tribological properties of diamond, the hardest natural material, have been extensively investigated. Bowden showed that natural diamond has excellent tribological properties, such as low-friction and high wear-resistance [1]. Many researchers have demonstrated the wear resistance and low-friction of CVD diamond films [2–8]. Reducing the friction coefficient of diamond and DLC films by fluorination and ion implantation has also been trialed. Fluorinated diamond films [9] and fluorinated amorphous-carbon films [10] have been fabricated and evaluated. Fluorination was found to improve the tribological properties of carbon films.

On the other hand, boundary lubrication is important in many mechanical systems, such as automobiles, manufacturing machines, magnetic disk systems, and medical and biotechnology equipment [8,11,12]. In practical applications, boundary lubrication is more important than fluid lubrication, because it amplifies the drive torque. However, after long-term sliding, the surface deteriorates due to chemical conversion by the wear debris.

In our previous studies, we confirmed the microtribologically low-friction and wear resistance of diamond films [4]. On the other hand, the friction coefficient of polished diamond films is high under vacuum conditions, but can be lowered by N^+-implantation [13]. However, the amorphous layer formed by N^+-implantation increases the nanowear of polished CVD diamond films [14].

Because the performance of mechanical parts depends largely on the boundary lubrication properties, these properties have been well-clarified in diamond films. Miyake studied the low-friction properties of diamond films under dry and water boundary lubrication conditions [15]. The friction coefficient of polished diamond film with a diamond tip is extremely low ($\mu = 0.01$) [9], by virtue of the reduced contact area and low shearing strength of water absorbed on diamond surfaces. The diamond tip protects the opposite silicon surface from damage, regardless of water boundary lubrication. To clarify why the diamond tip ensures damage-free sliding, Miyake and Kinjyo conducted a stress analysis using the boundary element method [16]. They confirmed

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that the diamond tip exerts low shearing stress on the sliding silicon surface.

The boundary lubrication properties of various films have also been evaluated. For instance, to maximize the fuel efficiency of automobile engines, Kano et al. investigated whether coating DLC films on the shim of a follower series could reduce the friction in engine oil. Hydrogen-containing DLC films have poor boundary lubrication properties, resulting in higher friction than that of polished diamond films PAO and GMO lubrication. This is because of the lower affinity between the hydrogen-containing DLC film and the lubricant [17]. Although the coating the shims with hydrogen-containing DLC films has a minimal effect, the friction was effectively reduced in hydrogen-free DLC films, which similar to that of diamond films. Hydrogen-free DLC films have superior lubrication properties and have been used in the shims of automobile engines [18]. Although friction can be significantly reduced by applying lubricants such as poly(alpha-olefin) (PAO) mixed with glycerol mono-oleate (GMO), the boundary lubrication properties should be improved in the presence of hydrogen-free DLC films [19]. The boundary lubrication properties of DLC films should be further improved by incorporating metals into them. The effect of adding metals to hydrogen-free DLC films was investigated by Okamoto et al. [20] and Miyake et al. [21]. Hydrogen-free DLC films have been impregnated with cobalt (Co), cerium (Ce), magnesium (Mg), nickel (Ni), and Ti, which are expected to react with PAO and GMO additives. The friction coefficient of a Co-containing hydrogen-free DLC film is extremely low ($\mu = 0.02$) [22]. (DLC/Au) and (TiC/DLC) multilayer films composed of hydrogen-free DLC and gold or TiC layers exhibit superior boundary lubrication properties in water and PAO (with and without GMO) [23,24].

In this study, we hypothesize that the friction coefficients of surface-modified diamond films are lower than those of conventional boundary lubricants, since diamond film increases the hardness and Young's modulus, while the surface modification decreases the shear resistance. Surface modification can achieve a multitude of surface structures and compositions, enabling compatibility with a variety of lubricants. Polished CVD diamond films were surface-modified by fluorination, oxidation, or N^+-implantation, and their boundary lubrication properties were tested in different lubricants (water and PAO). The effects of surface modification on the structure, surface free energy, and nanometer scale-mechanical and boundary lubrication properties of the diamond films were also evaluated.

2. Experimental methods

2.1. Deposition and surface modification of diamond films

Diamond films were deposited on a rectangular silicon nitride (Si_3N_4) substrate surface by thermal filament CVD in an atmosphere of 99% hydrogen and 1% methane at 900 °C. The diamond surface was then polished to a surface roughness of less than 5 nm Sy (measured by atomic force microscopy (AFM)). The structure and surface energy of the polished diamond surface were then altered by modifying the surface with CF_4 and O_2 plasmas in an RF plasma apparatus with power 50 W. Nitrogen ions (N^+) were implanted into the diamond films under an accelerating voltage of 120 keV. The dose was 5×10^{16} ions/cm^2, as shown in Table 1. The thickness of these diamond films was around 27 μm. The adhesion strengths of the polished diamond films on the silicon nitride substrate were in excess of 500 mN, as evaluated by oscillating scratch tests, much higher than those of the DLC films deposited by an ion-enhanced method [25].

Table 1
Deposition condition of diamond.

Film name	Processing condition
Untreated diamond film	Filament CVD Substrate: silicon nitride (Si_3N_4) Atmosphere: hydrogen 99%, Methane 1% Temperature:900 °C
Fluorinated diamond film	RF plasma treatment Flow:5 CCM, RF:50 W Processing time:60 min
N^+-implanted diamond film	Ion implantation Acceleration energy:120 keV, Dose:5×10^{16} ions/cm^2 Processing time:60 min
O_2 plasma treated diamond film	RF plasma treatment Flow:5 CCM, RF:50 W, Bias: −100 V Processing time:60 min

2.2. Evaluation

2.2.1. Surface structure, composition and surface free energy

The structures of the surface-modified diamond films were evaluated by Raman spectroscopy (JASCO NRS-1000 DT, Raman spectrophotometer, 532 nm). The composition of the surface-modified diamond films were evaluated by X-ray Photoelectron Spectroscopy (XPS). The nitrogen depth profile of the N^+-implanted diamond film was evaluated by secondary ion mass spectrometry (SIMS).

The surface free energy of the diamond films was determined by the liquid drop method using a contact angle gauge (Kyowa kaimen kagaku, CA-V) and three liquids (water, methylene iodide, and *n*-hexadecane). First, the contact angle of each liquid on the surface-modified diamond films was measured. Based on these measurements, the surface free energy was evaluated using the extended Folks method [26].

2.2.2. Nanoindentation and nanowear tests

The nanoindentation properties of the surface-modified diamond films were investigated by an AFM (Digital Instruments Nanoscope III) with a nanoindentation measurement system (Hysitron Inc.) [27]. The hardness was derived from the load indentation depth curves. The loading time was 20 s and the load was 500 μN. Here, the hardness was evaluated from the plastic deformation depth.

The nanometer-scale wear resistance was evaluated in a nanowear test conducted under AFM [6,14,27]. The surface profile and nanowear profiles were observed using a sharp diamond tip (approximate radius = 0.1 μm). The diamond tip was slid against the specimen surface by a piezoelectric ceramic material (lead zirconate titanate; PZT) scanner, forming square wear marks. One scan consisted of 100 repeated slidings with a span of 1 μm. The test conditions were: applied load = 50 μN; scan area = (1×1) μm^2; friction speed = 4.0 μm/s. Using the AFM, the nanowear was measured from the change in surface profile under a load of less than 1 μN after the nanowear test. To maintain a consistent tip profile, the surface profiles were evaluated on a standard specimen before and after the nanowear test. On the other hand, the oxidized diamond film was as coarse as 120 nm Sy, precluding a nanoscale mechanical evaluation.

2.2.3. Evaluation of boundary lubrication properties

The effects of surface modification on the boundary lubrication properties of diamond films were evaluated for various lubricants. The boundary lubrication properties were investigated by an oscillating friction tester (Optimol Instruments SRV4). During the