

Effect of chlorine doping on tribological properties of amorphous carbon films deposited by plasma-based ion implantation and deposition

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ABSTRACT

Many efforts to improve the tribological properties of amorphous carbon films have been reported. We used chlorine doping to reduce the friction coefficient of amorphous carbon films under non-lubricated conditions. This forms chlorine compounds, such as chlorinated tribofilm, at the sliding interface between films and counter parts. A friction test indicated a lower friction coefficient and lower attackability for chlorine-containing amorphous carbon films compared with hydrogenated amorphous carbon films. Time-of-flight secondary-ion mass spectroscopy (TOF-SIMS) confirmed the existence of chlorine-bonded ions along the wear track of chlorine-containing amorphous carbon films suggesting that chlorinated compounds improve the friction properties of these films.

1. Introduction

In recent years, the use of hydrogenated amorphous carbon films has attracted attention as a surface improvement technology. These films exhibit excellent friction properties such as high mechanical hardness, high wear resistance, and low friction [1–4]. These carbon films have an amorphous structure that is generally composed of sp^2 - and sp^3 - hybridized orbitals of carbon and hydrogen. Thus, these carbon films take on a complicated bonding state in spite of their simple elemental composition and have attracted interest from within academia and industry because of their extraordinary structure. Amorphous carbon films are expected to be useful in various industrial applications, including machine tools, steel molds, and sliding parts, and their fields of application are expanding [5–7]. On the other hand, new methods for improving the frictional properties of amorphous carbon films have been demanded in recent years. Many efforts to improve the frictional properties of amorphous carbon films, for example, doping with different elements, have been reported [8–10].

In this regard, a variety of methods for doping amorphous carbon films with different elements, such as Si, F, and metal atoms, are known. These efforts have led to the discovery of ways to improve the properties of the film, for example enhancing the thermal stability and adhesion, and lowering the surface energy, internal stress, and the friction. Researchers have reported a study in which they used Si- and F-doping of amorphous carbon films. These reports suggest that Si-

containing amorphous carbon films induce the reduction of the friction coefficient depending on the relative humidity, and that these mechanisms are caused by forming hydrated silica at the sliding interface [11,12]. Other workers investigated the effect of using Si as a dopant on the thermal stability of amorphous carbon films [13]. The effect of F-containing dopants on the surface energy of amorphous carbon films was attributed to the reduction of the size of the polar part contributing to the surface energy, owing to a decrease in the amount of sp^2 - hybridization and the number of dangling bonds [14]. The ability of surface fluorination to reduce the friction and micro-wear of amorphous carbon films has been demonstrated [15]. Metal doping of amorphous carbon films has been accomplished with various materials such as those containing Ti, Cr, Mo, and W [16–20]. The structure of metal-doped amorphous carbon films can be considered to contain metals in the form of small nanocrystallites of pure metal or metal carbide. The advantage of incorporating metals into amorphous carbon films is well known to reduce internal stress and enhance adhesion. Moreover, metal-doped amorphous carbon films are able to activate tribochemical reactions against oil additives. As described above, the use of different elements as dopants has the potential to improve the properties of amorphous carbon films.

For several decades, a chlorine additive has been used to reduce the friction coefficient between cutting tools and materials in machining work, thereby making it possible to improve the cutting performance. Chlorine additives are known to contribute to forming chlorine

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compounds, such as chlorinated tribofilm, at the sliding interface between the film and counter parts [21–23]. This film plays an important role to reduce the friction coefficient between sliding interfaces. In this study, we focused on the use of chlorine doping for the improvement of the tribological properties of amorphous carbon films under non-lubricated conditions. Our work aimed to research about the effect of chlorine on tribological phenomena of amorphous carbon films. Chlorine-containing amorphous carbon films were deposited by using a plasma-based ion implantation and deposition (PBII & D) method using a gas mixture containing toluene ($C_6H_5CH_3$) and tetrachloroethylene (C_2Cl_4). Several analyses using micro-laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), and time-of-flight secondary-ion mass spectroscopy (TOF-SIMS) were employed to investigate the structure and friction mechanism of chlorine-containing amorphous carbon films. This paper presents the results of the analytical and tribological studies we carried out on chlorine-containing amorphous carbon films.

2. Experimental setup

2.1. Deposition of the amorphous carbon films

The hydrogenated amorphous carbon films and chlorine-containing amorphous carbon films used in this study were deposited on an aluminum alloy (ISO- $AlMg1SiCu$) via the PBII & D system (PBII-R1000/ KURITA seisakusho Co Ltd.). The disk diameter was 28 mm. Before amorphous carbon was deposited, the substrate surface was cleaned by Ar bombardment to remove contaminants and activate the surface. Fig. 1 shows a schematic diagram of the PBII & D system. The PBII & D method, which uses high voltage to implant ions into a three-dimensional substrate, relies on the substrate itself playing the role of an RF antenna. The RF pulse generates the initial plasma around the substrate, and the negative-pulsed voltage induces ion implantation [24,25]. It is well known that amorphous carbon films possess various structures depending on the precursor gases that are employed to deposit the films [26]. Vaporized toluene ($C_6H_5CH_3$) and tetrachloroethylene (C_2Cl_4) are typically applied to deposit these films. Table 1 lists the deposition parameters reported in this article. Hydrogenated amorphous carbon films were deposited using vaporized $C_6H_5CH_3$ gas for 120 min under vacuum. In the case of chlorine-containing amorphous carbon films, the hydrogenated amorphous carbon films were deposited using vaporized $C_6H_5CH_3$ gas in the first step of 60 min duration. Subsequently, the chlorine-containing amorphous carbon

films were deposited on the upper surface of the hydrogenated amorphous carbon films using a gas mixture consisting of toluene and tetrachloroethylene ($C_6H_5CH_3 + C_2Cl_4$) as the second step of 60 min duration. The deposition carried out in the first step is an effort to prevent corrosion between the chlorine-containing amorphous carbon films and the aluminum substrate. And before the deposition of amorphous carbon films, Si interlayer was deposited using hexamethyldisiloxane (HMDS) in 60 min duration.

It is well known that the structure of amorphous carbon films varies depending on the deposition parameters [27,28]. In this study, several kinds of chlorine-containing amorphous carbon films were prepared by controlling the deposition parameters to enable us to examine the effect of chlorine content on the tribological properties. The structural and tribological properties of the hydrogenated and chlorine-containing amorphous carbon films were compared.

2.2. Structural analysis of each of the amorphous carbon films

After deposition, a structural analysis of both the hydrogenated and chlorine-containing amorphous carbon films was performed using Raman spectroscopy and XPS. These two techniques are popularly used for probing the structure of amorphous carbon films [29–31]. The internal structure of the films was analyzed by Raman spectroscopy, and the existence of chlorine inside the film was investigated by XPS. Raman spectroscopy was performed using a Raman spectrometer (In Via Reflex/ RENISHAW Co Ltd.) equipped with a YAG laser with a wavelength of 532 nm. The laser power was 0.25 mW, the spot size was 5.0 μm , and the spectra were recorded in the range of 800–2000 cm^{-1} . XPS analysis was accomplished using an XPS apparatus (QUANTERA/ ULVAC-PHI Co Ltd.), and measurements were performed after pre-sputtering. The $sp^3/(sp^3 + sp^2)$ bonding ratio of carbon was investigated using XPS analysis by adopting the method described in Riedo's report [32]. The $sp^3/(sp^3 + sp^2)$ of all sample reported in this article were calculated using same methods as shown above. It enabled us to accomplish relative comparison of each films structure.

A nano-indentation hardness tester (TI-950/HYSITRON Co Ltd.) was employed to compare the hardness of the hydrogenated amorphous carbon films with that of the chlorine-containing amorphous carbon films. In nano-indentation hardness test, applied load was increased stepwise and measurement was finished when the indentation depth reached to 100 nm.

2.3. Friction test

The friction and wear properties of both the hydrogenated and chlorine-containing amorphous carbon films were investigated by using a reciprocating type ball-on-disk tester (Tribometer/CSM Co Ltd.). An aluminum alloy (ISO- $AlMg1SiCu$) ball, 6 mm in diameter, was used as the ball specimen. The applied load, sliding speed, sliding distance, and total number of sliding cycles were 5 N, 20 mm/s, 10 mm, 4000 cycles, respectively. The friction test was performed under non-lubricated conditions.

2.4. Surface analysis of amorphous carbon films after friction test

After the friction test, we employed an optical microscope to observe the surface condition of each amorphous carbon film. The wear volume of films was measured using a confocal laser-scanning microscope (OLS-4000/ OLYMPUS Co Ltd.). Surface analysis was accomplished using a TOF-SIMS apparatus (TRIFT/ ULVAC-PHI Co Ltd.) to investigate the existence of chlorine compounds along the wear track of chlorine-containing amorphous carbon films.

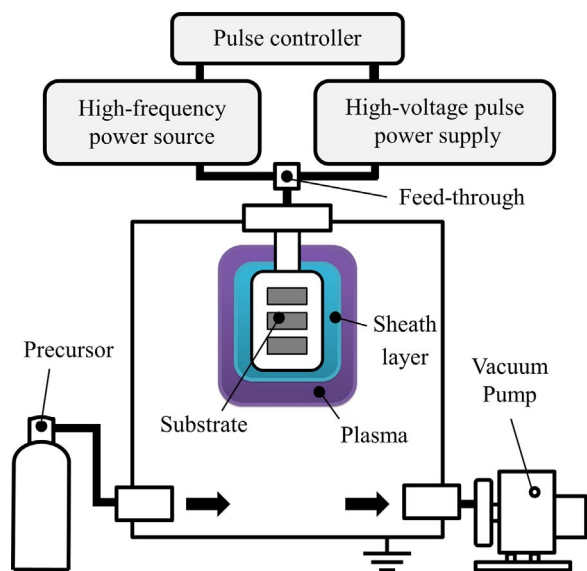


Fig. 1. Schematic diagram of PBII & D system.

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