Fabrication of micro segment structured DLC film

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Abstract

DLC films have many excellent properties, such as high wear resistance and a low friction coefficient, and are used in an increasing range of application fields. However, their low transmission of visible light prevents DLC films from being used for transparent materials. Nano-segment structured DLC (S-DLC) film with a segmented pitch equal to or less than the wavelength of visible light is supposed to not only solve this problem but also improve its mechanical properties. In this study as preliminary stage of nano S-DLC film, we fabricated DLC films consisting of 1-µm-size segments which have not only high wear resistance but also unique optical characteristics. This structure on DLC film was fabricated by electron beam lithography followed by liftoff method, which is suitable for nanoscale micromachining. The micro segment structured DLC films with groove width of 1 µm and pitch of 20 µm had rounded edges because the resist mask acted as an electrode. Micro S-DLC film exhibited structural colors because of the reflection-type diffraction grating and its transmittance was lower than that of continuous DLC films. From ball on disk test, it was found that the wear resistance of the micro S-DLC film with a groove of 1 µm was superior to that of a normal continuous DLC film and the small edge curvature could improve wear resistance furthermore.

Key words : DLC film, Segment structure, Electron beam lithography, Micro, Texture, Optical properties, Mechanical properties

1. Introduction

Diamond-like carbon (DLC) film which consists of \(sp^2\) and \(sp^3\) bonding carbon and hydrogen have many excellent properties such as high wear resistance, low friction coefficient, and high hardness. Therefore, the demand for DLC film is expanding (Grill, 1997); for instance, this is applied to frictional parts of automotive parts and cutting tools. The application of DLC films to glass and plastic materials has recently been increasing because of their function as high corrosion and wear resistance. However, DLC films have low transparency and black color; the thicker the DLC films are, the blacker it appears. This prevents DLC films from being used as transparent materials from the view points of design and the visibility of the content inside. Although, increasing the hydrogen content of DLC films improves their transmission, the hardness decreases and wear resistance is worsened. Therefore, it is difficult to apply high hydrogen content DLC films as a hard coating.

We supposed that this problem can be solved by applying “nano-segment structure” to DLC film. Segment structure DLC film is a film consisting of divided discontinuous latticed pattern. This discontinuous structure improves flexibility against the deformation of the substrate and prolongs the lifetime of films because of suppressing abrasive wear during friction. DLC films having the discontinuous structure are called “Segment-structured DLC (S-DLC) film.” On the other hand, by forming cyclical conical asperities on the substrate, whose cycle is approximately equal to or less than the wavelength of visible light, the refraction index gradually changes towards the inside of the substrate. Almost all the light doesn’t reflect, then transmittance is improved and we can see opposite side mediated glass clearly (Clapham and Hutley, 1973). From the above, nano S-DLC film is supposed to improve both transmittance and
mechanical properties as compared with conventional continuous DLC film.

Texturing procedure used to apply cyclical irregularities to DLC film are divided into two methods. One is a texturing of a substrate and deposition of DLC film. The other is a mask process. The former method includes photolithography (Petterson and Jacobson, 2004) (Zhao, et al., 2013) and laser beam methods (Ding, et al., 2011), whereas the latter process includes a photolithography (Chouquet et al., 2010), a nanoimprinting, a mesh masking (Aoki and Ohtake 2004) and an inkjet method (Takashima, et al., 2011). With the exception of mesh masking, these methods are usually used for micromachining of electronic devices. S-DLC film is generally fabricated by mesh masking method. DLC film is deposited on a metal mesh covered substrate and the mesh is removed after deposition. However, the diameter of the metal mesh can’t be minimized less than several µm. Therefore this method can’t be applied to micro/nano S-DLC films with a sub-micrometer groove size.

The final goal of this study is to fabricate a nano S-DLC film with higher mechanical properties and unique optical characteristics. In this paper, we developed a new masking method utilizing an electron beam (EB) lithography, which enabled fabrication of a stable submicron-order pattern. Micro S-DLC film with groove width of 1 µm and pitch of 20 µm was attempted as a preliminary stage of nano S-DLC film in this paper. Furthermore, optical properties and tribological properties of micro S-DLC films were evaluated.

2. Fabrication process of micro/nano segment structured DLC film

In this study, electron beam (EB) lithography followed by liftoff method was proposed to fabricate micro/nano segment structured DLC films. The process to apply segment structure to DLC films is described in Fig. 1. First, a resist is coated uniformly on a substrate by spin-coating (Fig. 1(1)). Before coating the resist, the substrate was pretreated with HMDS (hexamethyldisilazane) to promote adhesion between the resist and the substrate by eliminating –OH groups existing the substrate surface. Then a lattice pattern is formed by EB lithography to leave the resist after development where the grooves will be finally formed in the S-DLC film (Fig. 1(2)). EB lithography can fabricate fine patterns by using an electron beam to damage a surface, enabling finer lines to be drawn than can be drawn by other drawing technologies. After developing the resist, DLC film is deposited on the substrate by a plasma CVD method (Fig. 1(3)). Finally, the resist mask is lifted off by soaking and ultrasonic cleaning with acetone (Fig. 1(4)).

![Fabrication process of micro/nano S-DLC film used EB lithography followed by liftoff process.](image)

Micro S-DLC film was fabricated by the proposed process. A lattice resist pattern with a line width of 1 µm and a line pitch of 20 µm was formed on a Si substrate by EB lithography. The resist was OEBR-CAP 112PM (Tokyo Ohka Kogyo Co., Ltd.) which is made of propylene glycol monomethyl ether acetate. It is a positive-type resist with high chemical stability and line width controllability. The developer of the resist was NMD-3 (Tokyo Ohka Kogyo Co., Ltd), which is made of tetramethylammonium hydroxide. The conditions of the forming resist mask process are shown in Table 1. The conditions of DLC film deposition by pulse plasma CVD are shown in Table 2. The thickness of the DLC film was measured by a stylus-type surface profile measuring instrument. Before DLC film deposition, the surface of the substrate was sputter-cleaned in Ar plasma for 30 min to remove the contaminated layer on the substrate surface. The sputtering process also led to increase substrate temperature up to approximately 100°C. After DLC film deposition, the substrate was soaked for 30 min in acetone and cleaned by ultrasonic cleaning in acetone for 30 min.

After fabricating micro S-DLC film, the surface profiles were evaluated by a scanning electron microscope (SEM) and an atomic force microscope (AFM). Cross-sectional images were taken by AFM and a laser micro scope. Structure of the film was evaluated by Raman spectroscopy. Optical properties of the film were discussed by observing its appearance and UV-VIS, and tribological properties are checked by a ball-on-disk (BoD) test.
Table 1  Conditions of patterning resist mask by EB lithography

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<table>
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<tr>
<td>Thickness of resist [µm]</td>
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<tr>
<td>EB lithography dose [µC/cm²]</td>
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</tr>
<tr>
<td>Electron accel voltage [kV]</td>
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Table 2  Conditions of Ar sputter cleaning and DLC film deposition by pulse plasma CVD method

(a) Ar sputter cleaning          (b) DLC film deposition

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<tr>
<td>Gas</td>
<td>Ar</td>
<td>Source gas</td>
<td>C\textsubscript{3}H\textsubscript{2}</td>
</tr>
<tr>
<td>Flow rate [cm\textsuperscript{3}/min]</td>
<td>20</td>
<td>Flow rate [cm\textsuperscript{3}/min]</td>
<td>20</td>
</tr>
<tr>
<td>Pressure [Pa]</td>
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<td>Pressure [Pa]</td>
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</tr>
<tr>
<td>Bias voltage [kV]</td>
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<td>Bias voltage [kV]</td>
<td>-4.5</td>
</tr>
<tr>
<td>Pulse frequency [kHz]</td>
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<td>Pulse frequency [kHz]</td>
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</tr>
<tr>
<td>Sputtering time [min]</td>
<td>30</td>
<td>Film thickness [nm]</td>
<td>300</td>
</tr>
</tbody>
</table>

3. Results and discussions

3.1 Fabrication of micro segment structured DLC film

A cross-sectional SEM image of the resist after patterning and development is shown in Fig. 2(a). The bottom width of the resist is less than the top width (reverse tapered shape). SEM images of the micro S-DLC film after liftoff are shown in Fig. 2(b). The image suggests that the proposed process can be used to fabricate segment structures in a DLC film. However, some residues were observed at the edge of the grooves as shown in Fig. 2(c). These residues are considered to be remaining resists.

![SEM images](image)

The cause of the rounded edge formation is attributed to the resist mask that plays a role of an electrode. The carbon ions were affected by the electric potential of the substrate as well as the resist as an electrode. A part of the carbon and hydrogen ions were prevented from reaching the substrate by the mask. The fluxes of ions that can reach a given point on the surface of the substrate depend on two-dimensional view angle formed by the point and the top of masks. The nearer the point comes to the mask electrode, the smaller two-dimensional view angle \( \alpha \) becomes smaller and also the DLC film becomes thinner. In the case of the C-DLC film, two-dimensional view angle is \( \alpha = 2\pi \) because there are no masking walls and nothing blocks the ions to reach the substrate.

Two types of S-DLC films with groove width of 1 µm and pitch of 20 µm were fabricated to confirm the effect of two-dimensional view angle to the curvature at the edge of S-DLC films; the thicknesses of the resist mask were respectively 1.3 µm and 2.0 µm. The thicknesses were controlled by changing rotation speed of spin coater while resists were coated on the substrate. The results of the cross sectional observations by laser microscope are shown in Fig. 4. The edges of S-DLC film which the thickness of resist mask was 2.0 µm had smaller curvatures than those which the thickness of resist was 1.3 µm. The relations between the thickness of the resist mask and the edge of the...
DLC film were summarized in Table 3. By assuming a segment and the cross sections of the segment A-A', we can derive the two-dimensional view angle along x-axis. The view angles at the center and the edge of the segment (a) are 157.4 degree and 84.29 degree, respectively. Therefore, $\alpha_2/\alpha_1 = 0.536$. In contrast, $\beta_2/\beta_1 = 0.522$ for the segment (b), the ratio is smaller than $\alpha_2/\alpha_1$. The deposition rate of DLC film is considered to be decreased with the view angle.

The deposition rates at the vicinity of the edge of films (a) and (b) are smaller than that in the middle. The difference in the deposition rate between the middle and the edge in film (b) is larger than that of (a), because $\beta_2/\beta_1$ is smaller than $\alpha_2/\alpha_1$. Therefore, the curvature at the edge of the S-DLC film is large in film (b) which is deposited with a low-height resist mask.

![AFM image of micro S-DLC film](image1)

Fig. 3 AFM image of micro S-DLC film with groove width of 1 µm and pitch of 20 µm.

![Raman spectra](image2)

Fig. 4 The cross-sectional images of the edge of two type micro S-DLC films. “$t_R$” at the legend means the thickness of the resist.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>The summary of the relation between two-dimensional view angle and curvature at the edge of S-DLC film.</th>
</tr>
</thead>
<tbody>
<tr>
<td>The thickness of resist mask</td>
<td>(a) $t_R = 2.0 \mu m$ (Large)</td>
</tr>
<tr>
<td>Schematic images of cross-section A-A’</td>
<td><img src="image3" alt="Schematic image" /></td>
</tr>
<tr>
<td>$\alpha_2/\alpha_1$, $\beta_2/\beta_1$</td>
<td>0.536</td>
</tr>
<tr>
<td>Radius of curvature at the edge of S-DLC film</td>
<td>0.837-1.911 µm Av. 1.149 µm</td>
</tr>
<tr>
<td>Curvature at the edge of S-DLC film</td>
<td>Small</td>
</tr>
</tbody>
</table>

Figure 5 shows the Raman spectra of the C-DLC film and micro S-DLC film. Raman spectroscopy was used to analyze the structure of these films. A Nd:YVO4 pump laser with a wavelength of 532 nm was used. The spectra of both the C-DLC film and the micro S-DLC film at the center of film had two broad bands centered at approximately 1360 cm$^{-1}$ (D-band) and 1580 cm$^{-1}$ (G-band), indicating that these films were similar and of similar quality. However, the spectrum obtained between the grooves was typical of that for Si, with peaks at 520 and 950 cm$^{-1}$, indicating that the Si substrate is exposed at the grooves.

In hardness measurement by nano indentation test showed that the hardness of the C-DLC film and micro S-DLC film were 18.2 GPa and 18.4 GPa respectively. Ra’s measured by AFM were 2.04 nm and 3.02 nm respectively. These measurement results indicate that these films were similar quality and there were few influences by resist mask during Ar sputtering and DLC film deposition.
3.2 Optical properties of micro segment structured DLC film

The appearance of the S-DLC film and C-DLC film were observed from two directions (5 and 45 degrees from the above of the films). S-DLC films with groove width of 30 µm and pitch of 250 µm were fabricated by the proposed process and compared with C-DLC film. The 250 µm pitch film is the same size as S-DLC film generally fabricated by metal mesh method. The observation results are shown in Fig. 6. The images labeled (a), (b) and (c) show S-DLC film with a groove size of 1 µm and a pitch of 20 µm, S-DLC film with groove size of 30 µm and pitch of 250 µm, and C-DLC film, respectively. C-DLC film and S-DLC film with groove width of 30 µm appeared black from all angles. In contrast, micro S-DLC film with groove width 1 µm appeared black and blurred when viewed from above, it exhibited the structural color when viewed from some angles which mean that it exhibit white and the colors of the rainbow due to angle of the observed direction. This phenomenon will be attributed to the reflection-type diffraction grating (Kinoshita, 2010).

![Raman spectra of C-DLC film and micro S-DLC film. S-DLC film was measured two points at the center point of film and the groove.](image)

![Fig. 5 Raman spectra of C-DLC film and micro S-DLC film. S-DLC film was measured two points at the center point of film and the groove.](image)

![Fig. 6 Appearances of S-DLC films and C-DLC film from two directions. (a) S-DLC film groove width (w) of 1 µm and pitch of 20µm. (b) S-DLC film with groove width of 30 µm and pitch of 250µm. (c) Continuous (C-DLC) film](image)
To evaluate quantitatively, reflectance of DLC films coated on the Si substrate was measured by UV-VIS. Incident angle was 5 degree. Reflectance of DLC films were waved depending on the wavelength because of thin film interference as shown in Fig. 7(a). Furthermore, reflectance of micro S-DLC film is smaller than that of C-DLC film at all wavelengths, so the S-DLC film with groove width of 1 µm appeared blurred.

The micro S-DLC film was fabricated on a 7059 optical glass substrate and its reflectance and transmittance were measured next. In the case of fabricating S-DLC films on glass substrate, an Au thin film of 10 nm thickness was sputtered before resist coating because the glass is an insulator and was charged up due to EB drawing. The appearance of DLC films was shown in Fig. 7(b). The black of the S-DLC on glass substrate looked lighter than that on the Si substrate because the effect of the reflection at the surface of the substrate was smaller. Therefore the difference of reflectance between C-DLC films and S-DLC films on glass substrate became larger as shown in Fig. 7(c). It is clear from Fig. 7 (d) that the transmittance of the micro S-DLC film is approximately 2 % larger than that of the continuous film at wavelength $\lambda = 550$ nm and approximately 10 % larger at $\lambda =1100$ nm. The increase in transmittance should be attributed to not only the transmission at the grooves but also micro segment structure, because the change in transmittance increases with wavelength. These results of quantitative measurement were seemed appropriate because the opposite side of the substrate can be seen clearly. Therefore, if the groove width and pitch were minimized, the transmittance will increase more in the visible light range.

### 3.3 Tribological properties of micro segment structured DLC film

The tribological properties of the DLC films were evaluated by BoD test under the condition shown in Table 4. The friction coefficient was calculated from the normal load, and the frictional force was measured using a load cell. The relative wear rate was determined by measuring the cross-sectional area of the wear track using a laser microscope after BoD test. The specific wear rate ($W_p$ [mm$^3$/mN]) was determined using the formula below, where $V$, $F$ and $l$ are...
relative wear rate \( [\text{mm}^3] \), normal load \([\text{N}]\) and total rotating distance \([\text{m}]\), respectively. When the specific wear rates of S-DLC films were calculated, the volume of the grooves was excluded.

\[
W_p = \frac{V}{Fl}
\]

The results of the BoD test under the condition of Table 4(i) are shown in Fig. 8(1). The friction coefficients of both of the S-DLC films which had different sized groove width were around 0.25-0.4 and stable, but higher than that of the C-DLC film. The S-DLC film with groove width of 30 \( \mu \text{m} \) showed strong fluctuations in the friction coefficient after 90000 revolutions. As shown in the laser microscope images in Fig. 9(b), the S-DLC film with groove width of 30 \( \mu \text{m} \) was worn out; therefore friction coefficient was changed drastically. This result is totally different from previous results that S-DLC films have excellent tribological properties (Aoki and Ohtake 2004). Including the other films, the wear tracks of the two S-DLC films were wider than that of the C-DLC film as shown in Fig. 9. The specific wear rates of C-DLC film and micro S-DLC film with groove width of 1 \( \mu \text{m} \) were 2.36×10^{-8} \( \text{mm}^3/\text{Nm} \) and 1.33×10^{-8} \( \text{mm}^3/\text{Nm} \), respectively i.e., the specific wear rate of the micro S-DLC film with groove width of 1 \( \mu \text{m} \) decreased by about 44% compared with that of the C-DLC film as shown in Fig. 8(2). The remaining resist at the edge of the grooves formed a protuberance as shown in Fig. 2(c) and Fig. 3. It appears that this remaining resist was shaved off by contact with the touching sliding ball in the BoD test, resulting in adhesive wear. Thus, the shearing force generated during the adherence of the resists resulting in the higher friction coefficient of the S-DLC films. However, the specific wear rate was hardly affected by the resist and decreased over time because wear debris and adhesive resist soon became trapped in the grooves.

Finally, the influences of the curvature at the edge of S-DLC film on the tribological properties were evaluated with BoD test under the condition of Table 4(ii). Two types of micro S-DLC films were used; the resist thicknesses were respectively 1.3 and 2.0 \( \mu \text{m} \). These cross sectional profiles at the edge of the micro S-DLC film were shown in Fig. 4. Before the BoD test, ST-120 (Tokyo Ohka Kogyo Co., Ltd) which had stronger removal effect was used in the resist liftoff process to minimize the bad influences by the remaining resist. The result of BoD test was shown in Fig. 10 (1). The friction coefficients of the two micro S-DLC films were around 0.25-0.3 and almost the same as that of the C-DLC film because there was few remaining resists. These results coincide with the previous results on the tribological properties of S-DLC films (Aoki and Ohtake 2004). The friction coefficient of the C-DLC film was around 0.2-0.5 between 0 and 20000 revolutions before friction coefficients were stable around 0.25, but the these trends couldn’t be seen in the case of S-DLC films. The initial increasing of friction coefficient was caused by the surface roughness. The specific wear rate of the C-DLC film, micro S-DLC film with a resist thickness of 1.3 \( \mu \text{m} \) and micro S-DLC film with a resist thickness of 2.0 \( \mu \text{m} \) were respectively 9.96, 8.23 and 6.43 × 10^{-7} \( \text{mm}^3/\text{Nm} \) as shown in Fig. 10(2). Specific wear rates measured under the condition of Table 4 (ii) increased ten times more than those measured under the condition of Table 4(i), because of difference of the substrates. Specific wear rate of micro S-DLC film with a resist thickness of 1.3 \( \mu \text{m} \) decreased as well under the condition of Table 4(ii). As for comparison between the two micro S-DLC films with different resist thicknesses, specific wear rate of the micro S-DLC film with a resist thickness of 2.0 \( \mu \text{m} \) was lower than that with a resist thickness of 1.3 \( \mu \text{m} \). Namely, it was suggested that the smaller the curvature at the edge of S-DLC film, the less wear resistance became. The ball sliding on the film was touched many times at the edge of S-DLC film. At this time, a part of the edge of DLC film was considered to be scratched by the ball and wear debris. Therefore, the edge was easier to wear than that with the small curvature, so wear debris are more likely to be generated and cause abrasive wear when S-DLC film which has the large curvature at the edge is tested with BoD test. Considering the high wearing of S-DLC film with the groove width of 30 \( \mu \text{m} \), the pitch of resist mask was wider than that of the micro

<table>
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<th>Table 4</th>
<th>Conditions of BoD test.</th>
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<td>Ball material</td>
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<td>Diameter of ball [mm]</td>
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<tr>
<td>Load [N]</td>
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<td>Temperature [°C]</td>
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<td>Humidity [%]</td>
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S-DLC film with the groove width of 1 µm. The wider the pitch of resist mask is, the larger the curvature at the edge of S-DLC film becomes. In the case of the S-DLC film fabricated by mask mesh method (Aoki and Ohtake 2004), DLC film was deposited between a metal mesh and a substrate, so the edges which have sufficiently small curvature for sliding test are formed. It is necessary to consider the resist thickness to form sufficiently small curvature at the edge when S-DLC film is fabricated by liftoff process.

Fig. 8  Friction coefficients and specific wear rates measured by BoD test compared between different groove widths of S-DLC films.

Fig. 9  Laser microscopic images of wear tracks after BoD test which the result of friction coefficient was Fig. 8 (1).

Fig. 10 Friction coefficients and specific wear rates measured by BoD test compared between different resist thicknesses (curvature at the edge of S-DLC film). “t_R” means thickness of resist.
4. Conclusions

Micro segment structured DLC films with groove width of 1 µm and pitch of 20 µm was fabricated by electron beam lithography followed by the liftoff process. A patterned resist was used as a mask to form a groove area before DLC film deposition. The resist was patterned by EB lithography. The cross-sectional image showed that the edge of the DLC film was rounded by the resist mask, which acted as an electrode and the curvature depended on the height of the resist.

Fabricated micro segment structured DLC film was found to have unique optical properties, which exhibited structural colors when observed at certain angles because of the effect of the reflection-type diffraction grating. The transmittance of micro segment structured DLC film was lower than that of continuous DLC film. Although some resist remaining at the edge of the micro segment structured DLC film after liftoff poorly affected its friction coefficient, the debris-trapping effect of the grooves lead to decrease the specific wear rate in the case of segment structured DLC film with groove width of 1 µm. Finally, the effect of the curvature at the groove edge to the tribological properties was evaluated. Smaller curvature at the groove improved wear resistance.

References