Frictional Characteristics of Nano-Scale Mesoporous SiO$_2$ Thin Film Formed by Sol–Gel and Self-Assembly Method

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The pores on the surface function as an outlet for wear particles and enhance the storage of lubricants, which improves lubrication effectiveness. Mesoporous SiO$_2$ thin films were formed by the sol–gel and self-assembly methods to have a porous structure. One of the important issues in the manufacturing of the films involves the control of the porous structure to ensure proper mechanical properties. Mesoporous materials were manufactured with two surfactants, Pluronid Polyol (F127) and Cetyltrimethylammonium Bromide (CTABr). The pores were then exposed on the surface by chemical mechanical polishing (CMP) and plasma-etching. Ball-on-disk tests with mesoporous SiO$_2$ thin films on glass specimens were conducted. The results show that the friction coefficient and wear volume of a specimen with F127, which has a 8 nm pore size, are far lower than those of CTABr, which has a 3 nm pore size at both the dry condition and at boundary lubricated condition. This proves a significant dependency of friction and wear on pore size of mesoporous SiO$_2$ thin films.

Keywords: Mesoporous SiO$_2$ Thin Film, Sol–Gel, Self-Assembly Method, Friction, Wear.

1. INTRODUCTION

Thin films with mesoporous structure can be used to improve surface interactions, including reducing friction. They can be stored with lubricating materials, such as oil or carbon. Films can be formed easily by the sol–gel method.\(^1\) In particular, uniform films can be formed at low temperature.\(^4\) The process used to form the porous film is the liquid crystal templating mechanism.\(^5,6\) One of the important issues for forming the films is the control of the porous structure to ensure the proper mechanical properties. In this study, mesoporous materials are formed with two surfactants of F127 and CTABr. After treatment with CMP\(^7\) and plasma etching,\(^8\) the films are evaluated with a ball-on-disk type friction and wear tester.\(^9\)–13

2. EXPERIMENTAL DETAILS

Films with nanoporous structure on glass are made of SiO$_2$ with a surfactant of CTABr and F127 as a pore generator using the sol–gel method, a process which was described in detail in Refs.\(^1, 3, 14–16\). The synthesis condition is as follows.

TEOS (Tetraethylorthosilicate, 98%) is mixed with ethanol and hydrochloric acid, and then mixed one is hydrated using reflux method. Then refluxed one is cooled to a room temperature quickly, and a surfactant is added and is melted completely. After then, spin coating is performed on a glass plate. Coating speed is 1,700–2,000 rpm and coating is performed for 1 min. Then, spin coated plate is aged for 24 hours at 40 °C and the surfactant is burned out from heat treatment for 2 hours at 450 °C.

Depending on the surfactant used, the films have different pore sizes. Figure 1 shows the result of X-ray diffraction analysis (XRD). In the case of F127, the position of the peak was lower than that of CTABr. Therefore, the pores from F127 were larger than the pores with CTABr. Figure 2 shows Transmission Electron Microscope (TEM) images of the porous films. F127 produced uniform pores of 8 nm, which was analyzed by XRD data and TEM images. In the case of CTABr, the pore size was 3 nm.
The film thicknesses were 200 nm with F127 and 900 nm with CTABr, which were measured by Scanning Electron Microscope (SEM), as shown in Figure 3.

CMP and plasma etching was performed on the films to expose the pores. Experimental condition of CMP is that pressure is 4 psi, spindle velocity is 50 rpm, plate velocity is 50 rpm, operation time is 30 sec, and slurry flow is 0.14 lpm.

Plasma etching is performed by plasma enhanced chemical vapor deposition (PECVD). Plasma power is 100 W, pressure is 25 mTorr, and each flow rate of CF4 and H2 is 20 sccm. The temperature of substrate is 300 K and etching time is 120 sec.

The ball-on-disk type friction tests were performed as shown in Figure 4. Commercial bearing ball with a diameter of 10 mm was used as the upper specimen, which was fixed to the load cell to measure the friction forces. Normal load of 2.6 N was applied. The ball was made of AISI 52100 steel with a hardness of 62 HRC, and the surface roughness was 0.02 μm in Ra. The mesoporous SiO2 thin films on glass are fixed as a lower specimen, and were rotated at a sliding speed of 15 rpm (11.78 mm/s). The wear track had a diameter of 30 mm.

3. RESULTS AND DISCUSSION

After forming porous films, surface roughness was measured with Atomic Force Microscope (AFM). The roughness of the film using CTABr was 2.9 nm, and for F127 it was 1.9 nm. Figures 5 and 6 show AFM images of the CTABr and F127 specimens. The plasma etching process did not change the surface roughness of either specimen. However, the CMP process made the surfaces smoother than before.

Figure 7 shows the coefficients of friction of porous films on glass using CTABr and F127 surfactants. Friction coefficients of the films with F127 were higher than those with CTABr. These two films represented much lower friction values than the glass without films. Thus, the porous films played a role in reducing friction.

To control the pores, the etching was performed on the porous films. The etching process was performed for 120 s by PECVD. The film thicknesses before etching were 230 nm with F127, and 900 nm with CTABr. After the etching process, the film thicknesses were 200 nm with F127 and 860 nm with CTABr. The surface roughness was not changed by the etching process. Figure 8 shows the changes in friction coefficients. Friction coefficients of the etched films were similar to those of films without the...
The porous films were treated by CMP to remove rough asperities, thereby making the surface smoother. The roughness of film using CTABr was 0.44 nm, and for F127 it was 0.86 nm. The coefficients of friction are shown in Figure 9. The porous film with large pores shows lower values of friction than the film with small pores. F127 produced pores of 8 nm, and the pore size of CTABr was 3 nm. As increasing the cycles of sliding, the films were damaged and broken with high values of friction. To prolong the cycles for low friction, the strength of the films should be increased.

In order to investigate the wear resistance of the films, a surface profile meter with a mechanical stylus (Tencor Alpha-Step 500) was used to scan the wear track. Figure 10 shows the wear amounts of the films after 200 sliding cycles. The wear volume of the film with F127 was less than the film with CTABr. As shown in Figure 9, the porous film with F127 exhibited lower values of friction than the film with CTABr. The low value of friction was related to low values of wear volume.

To investigate lubricating characteristics, sliding tests were performed with mineral oil, especially under the
boundary lubrication. Figure 11 shows the changes in friction coefficients of two sliding surfaces lubricated with mineral oils. The film with F127 showed lower friction than the film with CTABr. Porous film with large pores was relatively effective in retaining the lubricant on the surface.

**Fig. 8.** Friction coefficients of porous films with F127 and CTABr after etching process.

**Fig. 9.** Friction coefficients of porous films after CMP.

**Fig. 10.** Wear volume of mesoporous films after test.

**Fig. 11.** Friction coefficients of porous films after CMP process under the boundary lubrication using mineral oils: (a) CTABr, and (b) F127.

**4. CONCLUSIONS**

Friction coefficients of mesoporous SiO$_2$ thin films were evaluated using a ball-on-flat tester. The pores were exposed on the surface by CMP or plasma-etching after forming the porous films. The results show considerable dependency of friction and wear on the pore size of mesoporous SiO$_2$ thin films. The pore size of the film by F127 is larger than that by CTABr. The friction coefficient decreased with increasing pore size. The CMP process was very useful in exposing the pores on the surface. However, the etching process was not effective in decreasing the friction coefficient. For CMP process, the films were damaged and broken as increasing cycles of sliding. Therefore the strength of the film should be improved.

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**References and Notes**

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