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Nanostructured Silicon Carbide Molds for Glass Press Molding

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Abstract—**This paper reports the first result of press molding of Pyrex glass using a silicon carbide (SiC) mold with nanopatterns. First, the nanopatterns were formed on a silicon substrate by electron beam lithography and fast atom beam (FAB) etching. To transfer these patterns to SiC, SiC was deposited on the patterned silicon substrate, and the SiC surface was polished to mirror finish. Subsequently, a SiC ceramic plate was bonded to the polished SiC surface using sputter deposited nickel as an interlayer. Finally, the silicon substrate was etched to release the SiC mold. Using the fabricated SiC molds without an anti-sticking layer, we succeeded in press-molding Pyrex glass (Corning 7740) at 800 °C. In this process, we found surface roughening problem, which occurs in SiC atmospheric vapor deposition on FAB-etched areas. This is due to damage in silicon by FAB, and enhanced under the existence of surface natural oxide.**

Index Terms— **Silicon carbide, Press molding, Glass, APCVD**

I. INTRODUCTION

Glass has excellent chemical, mechanical and optical characteristics. From these properties, micro/nanofabricated glass parts are useful for high-end or advanced applications. For low-end or economical applications, plastic microoptics mass-produced by injection molding or press molding are used. To expand the future application of micro/nanofabricated glass parts, glass press molding technology for their mass-production is expected.

Because glass press molding is preformed at high temperature (600–1400 °C), the molds must be made of heat resistive materials such as cemented carbide, glassy carbon and silicon carbide (SiC), which remain chemically and mechanically stable at such a high temperature. However, it is difficult to fabricate micro/nanopatterns directly on such materials. To the contrary, silicon is easy to fabricate by well-established semiconductor micromachining technology, although it is not suitable for glass press molds due to its chemical instability and creep above 500 °C.

Thus, we have developed a novel SiC lost molding process to transfer micropatterns on silicon to SiC by SiC chemical vapor deposition (CVD) and SiC-SiC bonding. This process enjoys both matured silicon micro/nanomachining technology and superior SiC properties. In the previous study [1], we fabricated microstructured molds by anisotropic wet-etching of silicon, and demonstrated the press molding of Pyrex glass at 820 °C. This study expands the glass press molding technology to nanometric regions.

II. PROCESS

Figure 1 illustrates the experimental process. In the process, there are two pattern transfer steps. Original nanopatterns are formed on a silicon substrate by electron beam lithography and fast atom beam (FAB) etching. The silicon substrate with the nanopatterns is referred as silicon mold. The first transfer step occurs from the silicon mold to a SiC mold. SiC is deposited on

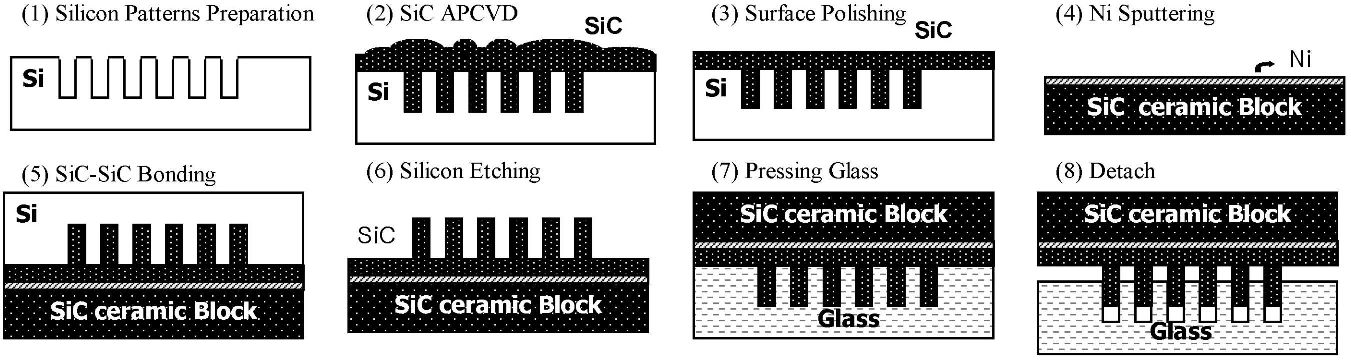
(1) Silicon Patterns Preparation
(2) SiC APCVD
(3) Surface Polishing
(4) Ni Sputtering
(5) SiC-SiC Bonding
(6) Silicon Etching
(7) Pressing Glass
(8) Detach

Fig. 1 Experimental process of a SiC mold and glass press molding using the SiC mold.

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the silicon mold by atmospheric pressure chemical vapor deposition (APCVD) technique (2), and then the surface is polished to mirror finish (3). A mirror-finished SiC ceramic block with a Ni film is prepared (4), and bonded to the CVD SiC (5). By etching away the silicon substrate, the SiC mold is obtained (6).

The second transfer step is from the SiC mold to glass, that is, glass press molding (7). The SiC mold and a glass substrate are set in a vacuum hot press machine with special sample stages. After the samples are heated to a process temperature, the press force is applied to the sample stages using a feed-back-controlled oil cylinder. After demolding, the samples are cooled down to room temperature.

III. EXPERIMENTAL

A. *Fabrication of Silicon Mold*

Lines with widths from 900 nm to 300 nm and square dots with widths from 900 nm to 250 nm were fabricated on a silicon substrate. First, positive electron beam resist was spin-deposited on the silicon substrate with a thickness of 350 nm, and the patterns were drawn using an electron beam lithography system. Using the patterned resist as a mask, the silicon substrate was etched to 300 nm depth by FAB. Figure 2 shows the fabricated pattern on the silicon mold, which has a trench width of 300 nm and a pitch of 900 nm.

The fabricated silicon mold was cleaned to remove surface natural oxide using hydrofluoric acid. This process is important to keep the etched surface of the silicon mold. The surface of the silicon mold etched by FAB is damaged due to the bombardment of atoms accelerated at 3 kV. This damaged surface can be attacked by hydrogen at high temperature during 1100 °C preheating step in SiC APCVD. We found that the silicon surface was more easily attacked by hydrogen, if surface natural oxide remained.

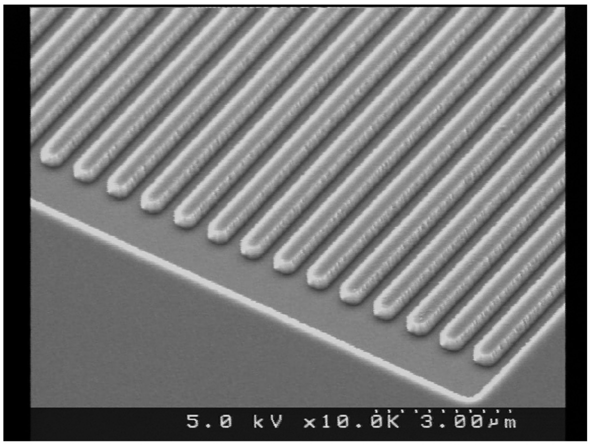
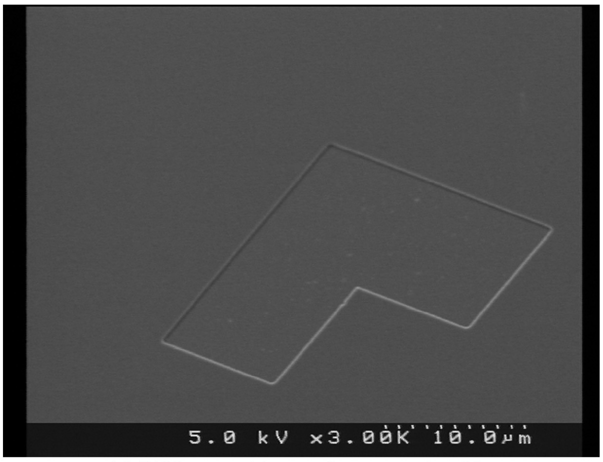


Fig. 2. Trench patterns on the silicon mold with 300 nm width and 600nm interval.

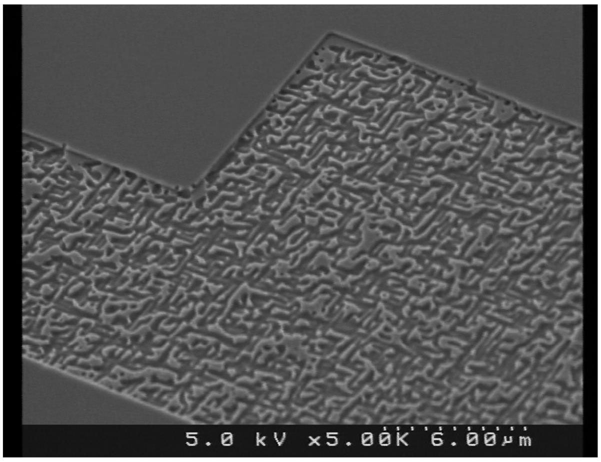
Figure 3 confirms the effect of surface natural oxide. A sample etched by FAB was prepared, and a half of the sample was dipped in hydrofluoric acid to remove surface natural oxide. The sample was heated in a SiC APCVD furnace at 1100 °C for 30 min by flowing 3 l/min hydrogen. Figure 3 (a) shows the area where surface natural oxide was removed, while (b) shows the area which was not etched by hydrofluoric acid. Although some pits are found in the former area, the surface is kept almost as it was etched by FAB. In the latter area, however, the surface etched by FAB considerably roughened.

It was reported that silicon etching is promoted by the following chemical reactions to produce volatile SiO_2 under the existence of SiO_2 [2]:

$$Si\text{-}H + SiO_2 \rightarrow Si^* + H_2O(g)$$
$$Si^* + SiO_2 \rightarrow SiO_2(g)$$
$$Si + H_2O(g) \rightarrow SiO_2 + H_2$$



(a) Without etching surface natural oxide.



(b) With etching surface natural oxide.

Fig. 3. Comparison of silicon surface with and without etching surface natural oxide after heating at 1100 °C with hydrogen flowing.

This can explain the result shown in Fig. 3. In the previous study [1], we fabricated silicon molds by alkaline wet etching or reactive ion etching. In addition, patterns on the silicon molds had sizes of 10 μm to several hundreds μm, which were much larger than those in this study. Thus, this problem did not emerge.

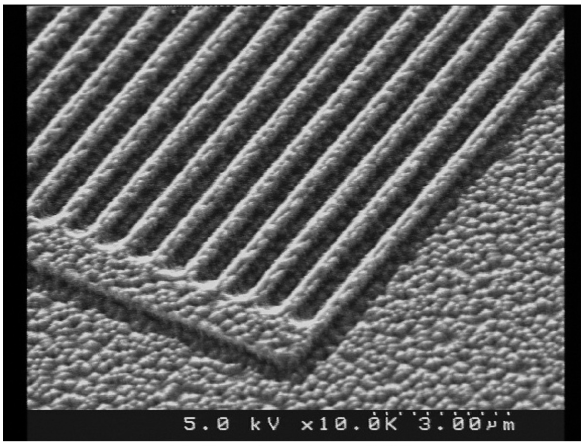
B. Fabrication of SiC Mold

On the silicon mold after the removal of surface natural oxide, 8–10 μm thick SiC film was deposited by APCVD. The APCVD was performed at 1100 °C using tetramethylsilane ($Si(CH_3)_4$) and hydrogen as a source and carrier gas, respectively. After that, the surface of the APCVD SiC film was mechanically polished using 0.25 μm diamond slurry until mirror finish. A 5 mm thick SiC ceramic block was prepared for supporting the APCVD SiC film, and 0.3 μm thick nickel bonding interlayer was sputter-deposited on it. The CVD SiC film and the SiC ceramic block were bonded in vacuum at 900 °C for 2 hours with a pressure of 1 MPa. The fabrication process of the SiC mold was completed by dissolving the silicon mold using the mixture of hydrofluoric acid and nitric acid.

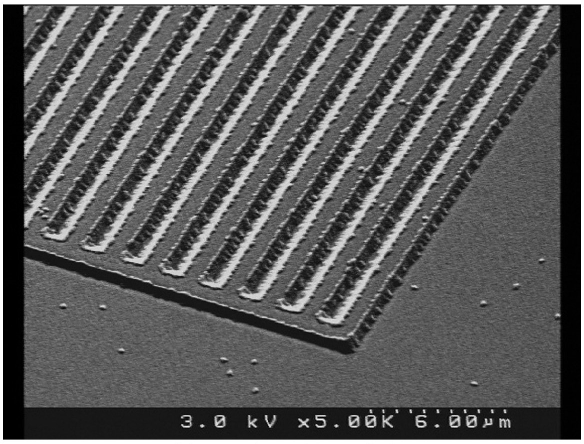
In this process, the conditions of SiC APCVD must be tuned. Figure 4 compares SiC mold fabricated on different SiC APCVD conditions. For Fig. 4 (a), SiC was slowly deposited by flowing 0.5 sccm source gas and 4 l/min carrier gas. As a result, the grains of SiC grew large, and the surface became rough. For Fig. 4 (b), SiC was faster deposited by flowing 2.5 sccm source gas and 2 l/min carrier gas. As a result, a smoother surface was obtained. However, the silicon mold shown in Fig. 4 (b) is still unsatisfactory. The edges of the patterns are rough, and there are some small protrusions. It was reported that grains were more easily grow at pattern edges [3], but the reason of this edge roughening must be investigated in the future.

C. Glass Press Molding

In the previous study [1], the SiC molds were coated with 1

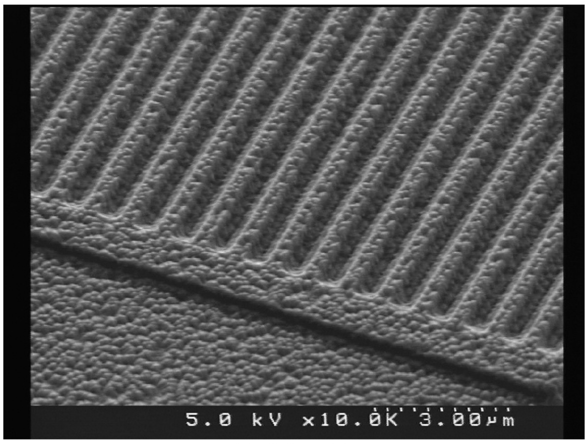


(a) Slow deposition of SiC.

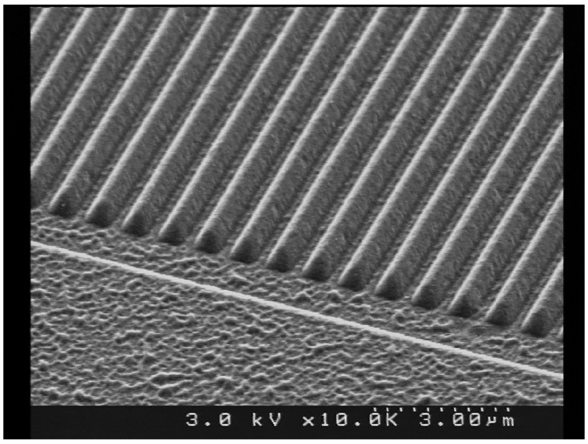


(b) Fast deposition of SiC.

Fig. 4. Comparison of the SiC mold surfaces fabricated by slow and fast SiC deposition.

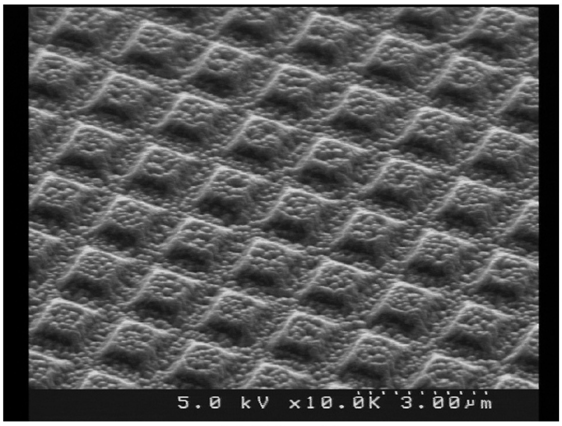


(a) SiC mold.

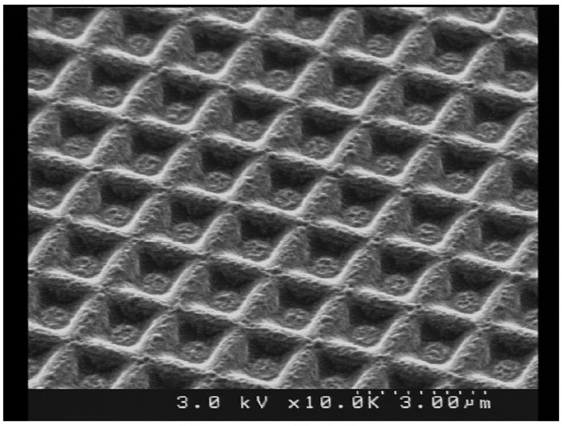


(b) Press-molded glass.

Fig. 5. Result of the press molding of Pyrex glass using the SiC mold with 300 nm wide protruding lines.



(a) SiC mold.



(b) Press-molded glass.

Fig. 6. Result of the press molding of Pyrex glass using the SiC mold with 900 nm wide squares.

µm thick diamond-like carbon as an anti-sticking layer. However, such an anti-sticking layer fills or changes nanopatterns, and glass press molding was performed without an anti-sticking layer in this study. The tested glass is Pyrex glass (Corning 7740). A glass sample was heated at 800 °C in vacuum, and pressed at 1 MPa for 40 s. Subsequently, the sample was cooled down to 560 °C, which is around the transition point, and the second press was done at 0.5 MPa for 40 s. After demolding, the sample was cooled down to room temperature.

Figure 5 and figure 6 show the SiC mold and corresponding press-molded patterns on the glass. The patterns on the SiC mold including roughness were well transferred to the glass. After the molding, no obvious damage and contamination was observed on the SiC mold.

IV. CONCLUSION

Hundreds of nanometers wide patterns were fabricated on a silicon substrate by electron beam lithography and fast atom beam (FAB) etching, and then transferred to silicon carbide (SiC) by atmospheric vapor deposition (APCVD), SiC-SiC bonding and silicon etching to make SiC molds. In this process, the following two things must be taken care.

The first one is the roughening of the surface etched by FAB during preheating step in SiC APCVD. The surface etched by FAB is damaged by the bombardment of accelerated atoms, and easily subjected to hydrogen attack at high temperature. This effect is enhanced under the existence of surface natural oxide, and thus the removal of surface natural oxide before APCVD must be done carefully.

The second one is SiC grain growth in APCVD. To obtain smooth surfaces, excess SiC grain growth on a silicon surface must be avoided. It was found that SiC grains grew more easily at the pattern edges. It is necessary to tune the condition of SiC APCVD. In this study, we could not obtain a perfect SiC mold, but demonstrated the possibility of nano press molding of Pyrex glass using the fabricated SiC mold.

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