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Fine Pattern Fabrication by the Molded Mask Method (Nanoimprint Lithography) in the 1970s

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Nanoimprint lithography has recently been attracting the attention of many researchers in the field of nanofabrication technology. Although the study of nanoimprint lithography was initiated by Chou *et al.* around 1995, a fine-pattern fabrication technology, whose concept is similar to nanoimprint lithography, had been proposed and studied at NTT Laboratories in Japan as early as in the 1970s. The technology was based on the combination of the molding of plastic film on a substrate and dry etching of the molded film and substrate surface. It is considered that most of the basic concepts in current nanoimprint lithography were included in this early study. Some demonstration experiments using diffraction gratings, microsized test patterns, LSI patterns and microlenses were carried out to verify the feasibility of the technology at that time. The key point of the technology to fabricate fine patterns accurately was the fluidity of the plastic film. It was called the "Molded Mask Method" and this paper introduces the study on the molded mask method of those days.

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1. Introduction

With the advance of integrated electronic components, a variety of fine-pattern fabrication technologies such as photolithography, extreme ultraviolet (EUV), X-ray and electron beam lithographies have made considerable progress in the last few decades.[1,2] Nanoimprint lithography was proposed by Professor Chou *et al.* in the 1990s as a new nanofabrication technology,[3,4] which has recently been attracting so many researchers worldwide. However, a technology that is similar to nanoimprint lithography was invented and studied at NTT Laboratories in Japan as early as in the 1970s. The technology, which was called the "Molded Mask Method" at that time, is introduced in this paper.

In the 1970s, there had been growing interest in the study of fine-pattern replication technology to realize highly integrated components such as LSI. Although photolithography had predominated the pattern replication technology, it was considered difficult to fabricate submicron patterns by photolithography because of the diffraction limit of light focusing.[1,2,5] Therefore, new exposure technologies using shorter wavelength light such as EUV and X-ray had been proposed and studied.[6,7] In this environment, we conceived that very fine structures may be replicated by making use of molding technology, similarly to the preparation of specimens for electron microscope observation, which brought the idea of the molded mask method.

The concept and demonstration experiments of the method are shown hereinafter.[8–14] In this paper, redrawn copies of original figures and photographs are used to describe the study as it was carried out thirty years ago.

2. Concept of the Molded Mask Method

Figure 1 shows the concept of the molded mask method.[8–10] Other technologies such as photolithography are based on exposure technology in which a two-dimensional pattern is printed on resisit film through a photomask;[1,2,5] however, this new method is based on molding technology, in which the three-dimensional shape of a mold is directly imprinted on the plastic film coated on a substrate. Even patterns as small as 10 nm were expected to be fabricated using the technology, considering the resolution of replica technique in specimen preparation for electron microscopy.[9,15] The molded mask method consists of the following processes.

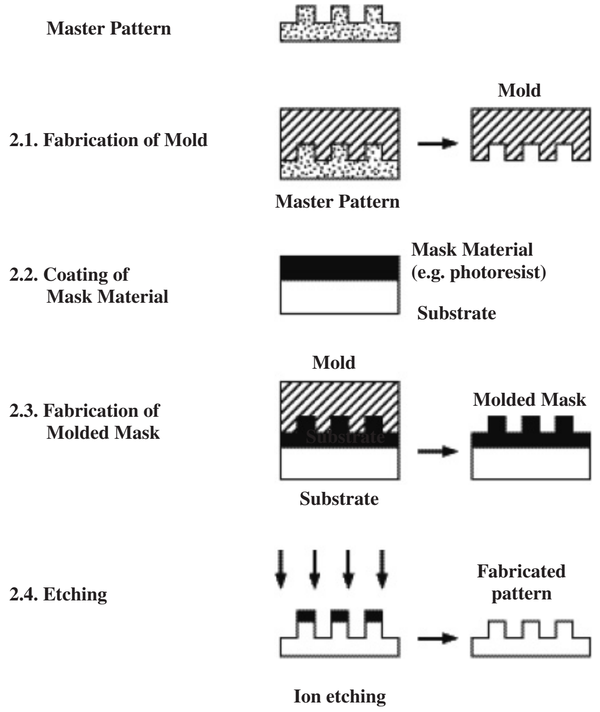

Fig. 1. Concept of the molded mask method, reported in 1976.[8]

2.1 Fabrication of the mold

A plastic resin mold is fabricated from a master pattern. In this process, liquid plastic resin is poured on the master pattern prepared in advance, which results in a mold where the surface concavity and convexity are reversed. The master pattern was, for example, the microstructure created by electron beam writing or focused ion beam machining. A silicone resin [poly(dimethylsiloxane), PDMS] was used as a material for the mold in many cases, because the PDMS has excellent mold releasability.[9,10] Some other plastics such as polypropylene, acetylcellulose, epoxy resin, and polyester resin were also tried as materials for the mold.[9,14] The pattern obtained on the resin in this process is used as the mold in the following process (see §2.2).

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The quality of a mold is very important in the molded mask method. The shape of the final replicated pattern, obtained after the pattern molding on a thin film (§2.3) and etching process (§2.4), strongly depends on the shape and property of the mold.

This process of mold fabrication may be carried out over multiple generations, from an original master pattern to the first replicated mold, from the first replicated mold to the second replicated mold and so on. Thus, a number of molds can be prepared, which enables low-cost nanofabrication as a whole. Good mold releasability is also needed to use one master pattern or one mold repeatedly.

2.2 Coating of the mask material

A mask material is coated on the substrate, from which a thin film is then produced that represents the fine structure to be fabricated. For example, a photoresist was used as the mask material and a Si wafer or quartz glass was used as the substrate. In some cases, PDMS and epoxy resin were also used as the mask material.[9,14)] It is preferable that the mask material film is sufficiently fluid so as to be molded correctly in the next process.

2.3 Fabrication of the molded mask

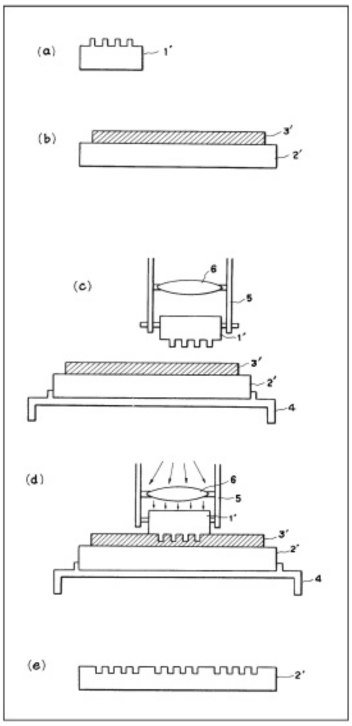
The mold is pressed onto the mask material film on a substrate. After the mask material is hardened, the mold is removed. A molded mask is formed on the substrate. The molded film is called the "molded mask" because it functions as the mask for etching in the subsequent process. Depending on the type of material, room-temperature curing, heat treatment or UV exposure is used to harden and solidify the mask material.[9,11,12)] It is important to make the concave part of the molded pattern (so-called residual layer) as thin as possible[9,10)] (see §2.4).

A step-and-repeat method in this process of molding and hardening of mask material film was also proposed for the case of UV exposure.[12)] As illustrated in Fig. 2, the processes of (c) alignment of the substrate with the mold and (d) UV exposure to harden the mask material film pressed by the mold are repeated in the step-and-repeat manner. Multiple sets of patterns are obtained as shown in (e).

2.4 Etching

Etching is carried out by dry etching technologies such as plasma etching and ion etching.[8–10)] The molded mask is etched at first and the concave part (the residual layer) is etched out, which is followed by the etching of the substrate exposed on the surface. Finally, the remaining molded mask is removed and the intended pattern is obtained on the substrate surface. If the residual layer is sufficiently thin, the shape of the replicated pattern on the substrate becomes closer to that of the molded mask in general. It is also possible, in principle, to fabricate the pattern on the substrate deeper than that of the molded mask, by controlling the conditions of the initial molded mask's etching and the subsequent substrate material's etching.[10)]

These processes seem very similar to those of nanoimprint lithography.



1': Mold
2': Substrate
3': Mask material film
(e.g., photoresist)
4: Movable stage
5: Cylindrical holder
6: Condenser lenr

Fig. 2. Step-and-repeat method in molding and UV exposure in molded mask fabrication process, described in the patent filed in 1975.[12)] The processes of (c) alignment of the substrate with the mold and (d) UV exposure to harden the mask material film pressed by the mold are repeated in the step-and-repeat manner. Multiple sets of patterns are obtained on the substrate after the etching process, as shown in (e).

Thus, the idea of the molded mask method is based on the combination of the molding of three-dimensional fine structure in a plastic thin film and the dry etching of the molded plastic thin film (the molded mask) to engrave the replicated structure into a substrate. Dry etching technologies such as plasma etching, ion etching and reactive ion etching, which began to be developed in the 1970s,[16)] had played an important role in the molded mask method because they enabled the directional and selective etching of the molded mask and substrate to obtain a high-quality fine structure on the substrate surface.

3. Demonstration Experiments

Some demonstration experiments were carried out in the 1970s to verify the feasibility of the molded mask method.

3.1 Fabrication of diffraction grating

At first, the replication of planar reflective diffraction gratings was attempted as an example of fine pattern fabrication using the molded mask method.[8–10)] A diffraction grating of 300 lines/mm (pitch: 3.3 µm) was typically employed as a master pattern in this experiment.

3.1.1 Fabrication of mold

The mold was prepared by pouring a liquid PDMS resin onto the master pattern, solidifying the resin by room temperature curing or heat treatment, and demolding it from the master pattern. Such usage of PDMS is considered to be similar to a process of microcontact printing in the current soft lithography.[17)] Figure 3 shows the typical structure of the mold. Deterioration in the shape of the molded grating was not observed in optical microscope observation and it was

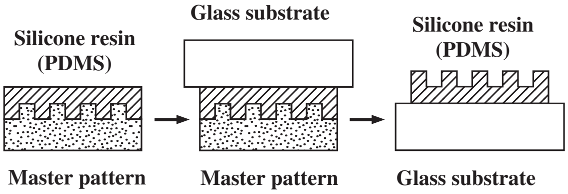


Fig. 3. Preparation of PDMS resin mold.[14] It corresponds to the process of 2.1. Fabrication of Mold in Fig. 1.

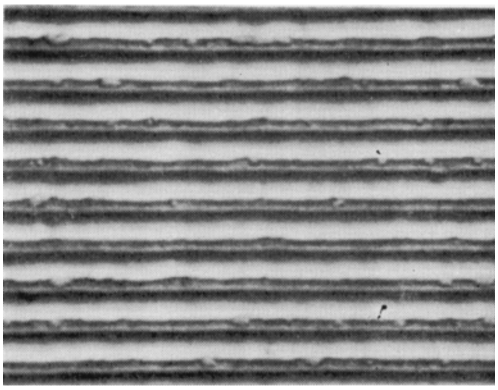


Fig. 4. Example of diffraction grating replicated on Si wafer (pitch: 3.3 µm), reported in 1976.[8]

considered that the grating pattern replication was correctly made on the PDMS resin mold.

3.1.2 Coating of mask material

Si wafer was used as a substrate and a negative-type photoresist was spinner-coated on the substrate as a mask material.

3.1.3 Molded mask fabrication

The photoresist film was pressed using the PDMS resin mold with the grating pattern, and polymerized and hardened by UV exposure using a high-pressure mercury lamp. Then, the PDMS resin mold was removed and the molded mask made of the photoresist film was formed on the substrate.

3.1.4 Etching

Plasma etching or ion etching was used in this experiment. The concave part of the molded mask (the residual layer) was etched out at first and then the Si wafer substrate appearing on the surface was etched. As a result, the diffraction grating pattern was formed on the surface of the Si wafer.

As an example, the 3.3 µm pitch grating pattern finally obtained on Si wafer by this method is shown in Fig. 4. It was demonstrated in this experiment that fine patterns can be fabricated with good accuracy by the molded mask method. The replication of the diffraction grating with 3,600 lines/mm (pitch: 0.28 µm) was also tried at that time and it was observed that the grating pattern was transferred on the mask material film.[9]

3.2 Fabrication of microsized test pattern

Following the success in the replication of the diffraction grating, the fabrication of microsized test patterns was studied to examine the features of the molded mask method.[8–10] The microsized test patterns were composed of the line-and-space of various sizes from 1 to 20 µm width.

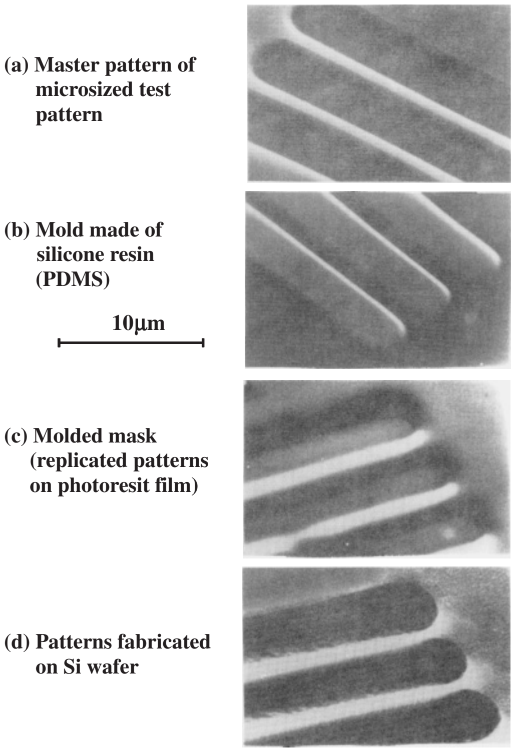


Fig. 5. Microsized test patterns fabricated by molded mask method, reported in 1977.[9]

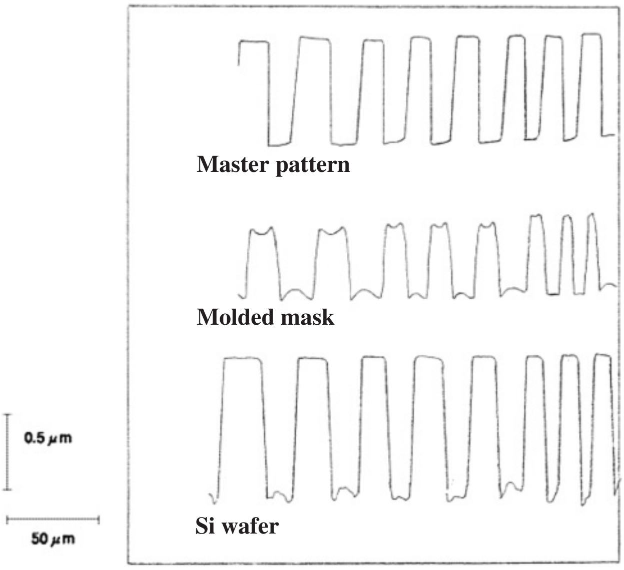
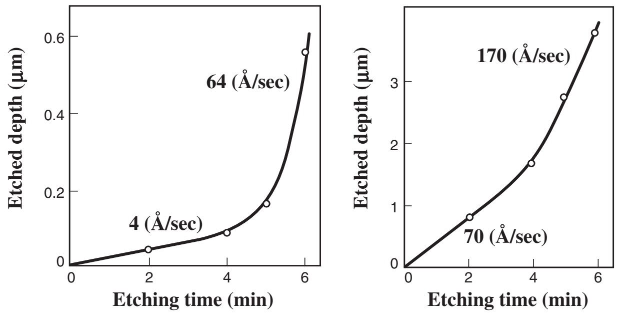


Fig. 6. Surface profiles of master pattern, molded mask, and Si wafer, reported in 1977.[9]

Figure 5 shows the photographs of patterns obtained in the experiment.[9,14] These are (a) original master pattern, (b) mold made of PDMS resin, (c) molded mask made of photoresist, and (d) pattern obtained on Si wafer after etching process. Figure 6 shows surface profiles of the patterns for each of the master pattern, molded mask and Si wafer.[9,14] It is noted that the depth of the patterns formed on Si wafer became larger than that of the original master pattern, that is, the aspect ratio of patterns can become higher by the molded mask method. It is because the etching rate for Si wafer is



Plasma etching of photoresist

Plasma etching of Si wafer

Fig. 7. Etching rate for molded mask (photoresist) and substrate (Si wafer).[14)]

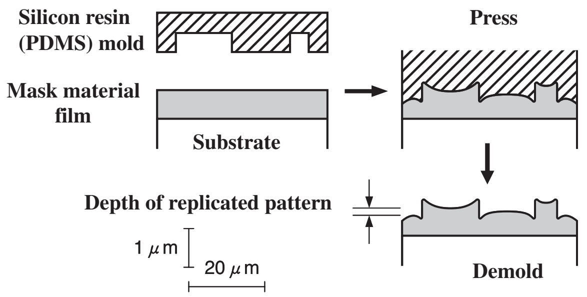


Fig. 8. Schematic of distortion of pattern shape in the molded mask fabrication process.[14)]

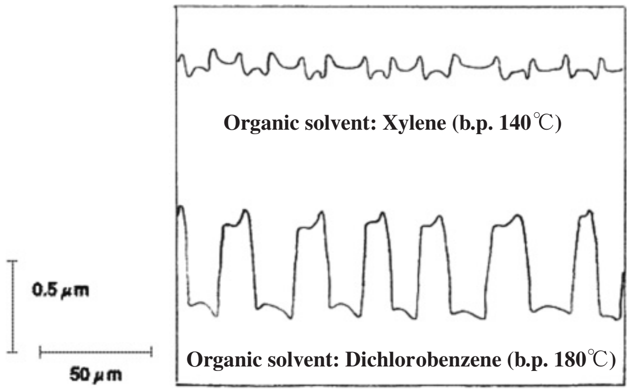


Fig. 9. Surface profile of patterns replicated on mask material film (molded mask), reported in 1977.[9)]

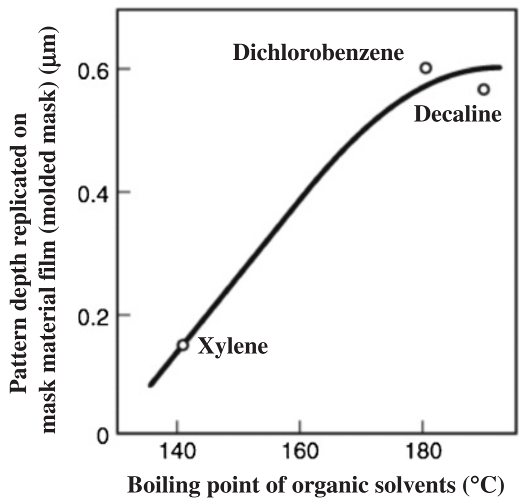


Fig. 10. Depth of pattern replicated on mask material film (molded mask) versus boiling point of organic solvent of photoresist, reported in 1977.[9)]

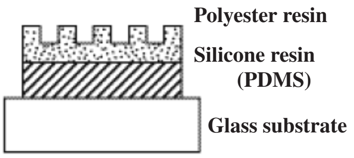


Fig. 11. Schematic of the mold with polyester resin on the surface supported by PDMS resin.[14)]

larger than that for photoresist, as seen in Fig. 7 showing the etched depth versus etching time.[14)] The etching gas, $CF_4 + O_2$, which etches Si swiftly, was used in this experiment.

The surface profile of the patterns in Fig. 6 also indicates an important point of nanoimprint lithography. Regarding the shape of the pattern in the molded mask, the center of the concave part (the residual layer) tends to rise and the center of the convex part tends to indent, particularly in wide patterns. We speculated on the cause of this pattern distortion as illustrated in Fig. 8. When the mask material film is pressed by the mold, it has to flow along the shape of the mold and move to the concave part of the mold, to make the molding accurate.[9,10)] However, if the mask material is not sufficiently fluid but too viscous, it cannot flow and move to the concave part. In such a case, because the PDMS resin mold is a soft material, it tends to be deformed as shown in Fig. 8. Therefore, the pattern distortion occurs in the molded mask fabrication process.

To avoid such pattern distortion, we decreased the viscosity of the mask material using an organic solvent with a high boiling point.[9,10)] It was considered that photoresist with less volatile solvent would remain fluid even when coated in the form of thin film and pressed by the mold. Figure 9 shows a result of the experiment. The shape of the molded pattern was much improved with the use of dichlorobenzene with the boiling point of 180 °C, as compared with xylene with the boiling point of 140 °C. Figure 10 also shows the improvement in the depth of the molded pattern versus the boiling point of organic solvents.[9)]

Furthermore, we hardened the surface of the mold to avoid the pattern distortion. Figure 11 shows the mold, with hard and stiff polyester resin on the surface, supported by soft and flexible PDMS.[14)] The flexible PDMS was considered still useful to make a uniform pressing over the whole substrate with warpage and undulation,[9,10)] while the surface of the mold needed to be covered by a hard and stiff material like polyester resin to make the molding accurate without pattern deformation.

PDMS was also used as a mask material in some experiments to improve the molding accuracy, because the liquid PDMS is sufficiently fluid to be molded when coated in the form of thin film on a substrate. Figure 12 shows the surface profile of patterns obtained from the combination of hard polyester resin as a mold and fluid PDMS film as a mask material, in comparison with the combination of soft PDMS resin as a mold and photoresist film as a mask material.[14)] These surface profiles were measured for the finally transferred patterns on Si wafer surface after the

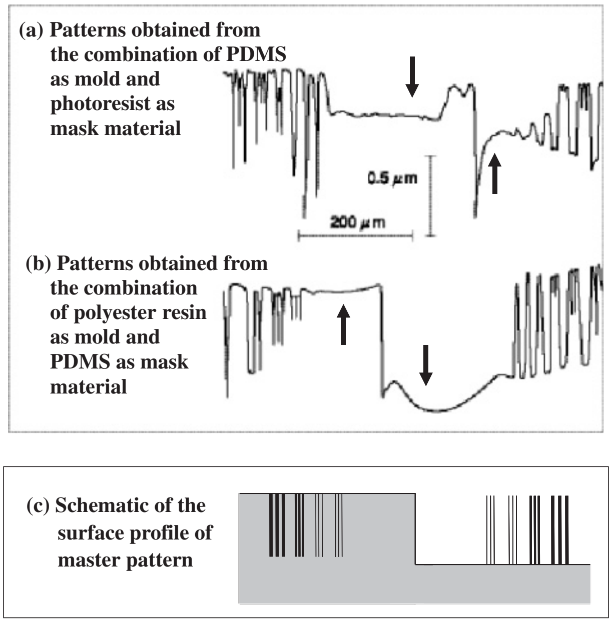


Fig. 12. Surface profile of pattern replicated on Si wafer substrate obtained from (a) the combination of soft PDMS resin as a mold and photoresist film as a mask material and (b) the combination of hard polyester resin as a mold and fluid PDMS film as a mask material.[14] The wide patterns indicated by arrows are distorted in (a), but the distortion is much reduced in (b). Schematic of the surface profile for an original master of microsized test pattern is shown in (c) for reference.

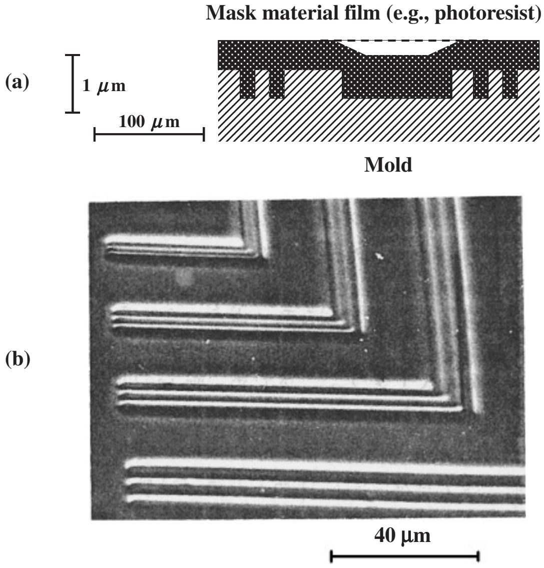


Fig. 13. Molded mask fabrication by the alternative approach in which the mask material is coated on the surface of the mold, reported in 1977.[9] (a) Concept of the alternative approach: mask material (photoresist) coated on a mold fills in the concave part of the patterns, while the surface of the mask material film tends to be flattened due to surface tension. (b) An example of the molded mask fabricated by this alternative method.

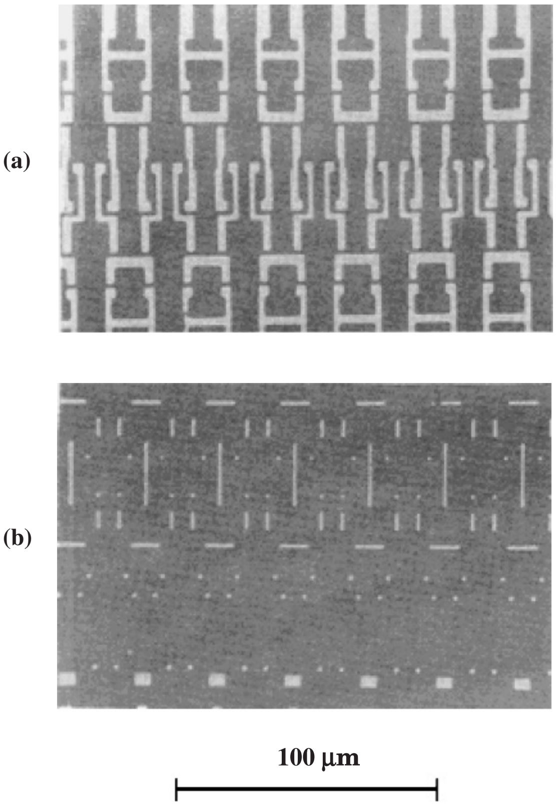


Fig. 14. LSI patterns fabricated on Cr-coated glass, reported in 1977.[10]

etching process, because the molded mask made of the PDMS resin film was too soft to be measured by a stylus-type surface roughness meter. The pattern distortion in wide patterns indicated by arrows in Fig. 12 became very small for the combination of the hard polyester resin as a mold and the fluid PDMS film as a mask material.

An alternative approach in which the mask material is coated on the surface of the mold, rather than on the surface of the substrate, was considered and tried as shown in Fig. 13.[9,10] It was considered that in this coating method, the mask material flows on the surface of the mold with fine pattern and fills in the concave part without trapping air at the bottom of the pattern, while the surface of the mask material film tends to be flattened owing to surface tension. The substrate is then attached to the flattened surface of the mask material film. The mold is removed from the mask material film after the film is hardened, and the molded mask is obtained on the substrate. The pressing force needed for molding and the pattern distortion in the molded mask fabrication process were expected to be much reduced in this alternative method.

Thus, the pattern distortion that occurred in the molded mask fabrication was considerably improved in this study. However, as a general nature of this process, the volume of the mask material to be moved is larger in wide patterns than in narrow patterns;[9] thus, the optimum conditions for mask material coating and molded mask fabrication processes may differ depending on the pattern size to be replicated.

3.3 Fabrication of LSI photomask pattern

The 1970s were really the days when LSI fabrication technologies had been rapidly advancing.[1,2] We also tried to apply the molded mask method to the fabrication of a photomask that was used in LSI fabrication.[10,14] The master pattern was prepared by electron beam writing in advance and the plasma etching or ion etching was employed in the etching process. Figure 14 shows the LSI patterns finally replicated on Cr-coated glass substrate for the photomask.

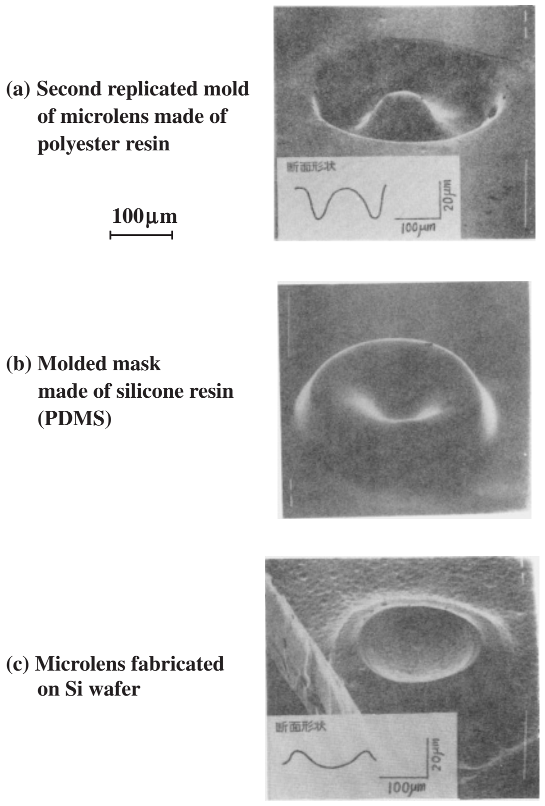


Fig. 15. Replication of microlens by the molded mask method.[14] (a) Second replicated mold made of polyester resin. (b) Molded mask made of PDMS resin. (c) Microlens pattern finally obtained on Si wafer surface.

The thickness of the Cr was approximately 100 nm. As seen in Fig. 14(b), $2 \times 2\,\mu\text{m}^2$ square windows, which are important in LSI pattern, were obtained, and thus, the applicability of the method to LSI fabrication was demonstrated.

3.4 Fabrication of microlens

We also carried out an experiment on the replication of three-dimensional shape such as microlens pattern.[14] The master pattern was prepared by focused ion beam machining of chalcogenide glass in advance. Figure 15 shows the result of the experiment: (a) the second replicated mold made of polyester resin, (b) the molded mask made of PDMS, and (c) the lens pattern finally obtained on Si wafer after etching. As seen in Figs. 15(b) and 15(c), the shape of curved surface changed in the etching process and the curvature radius of the lens obtained on Si wafer became larger than that of the molded mask. This was because the etching of the molded mask was made by isotropic plasma etching in this experiment and the etching condition was not optimized at that time. It was considered that if an anisotropic and directional ion etching was used and the condition was optimized, the curvature of the lens would be improved.

3.5 Prototyping of pressing machine

In the study of the 1970s, even the pressing machine for the molded mask fabrication process was designed and prototyped, in order to make the molding mechanical and quantitative.[12,14] Figure 16 shows a schematic of the machine, in which a mold is set at the upper part and a mask-material-coated substrate is set at the lower part. The substrate is aligned and contacted with the mold using X-, Y- and Z-axes fine manipulators. The semispherical movable stage, on which the substrate is placed, is used to make a uniform contact of the substrate with the mold. Then the substrate is pressed up against the mold by a piston with high-pressure gas. The gas pressure was changed from 0.5 to $5\,\text{kg/cm}^2$ at that time. It was mainly used to study the relation between the pressing force and the pattern-transferred area on the substrate. This machine was operated with optical microscope observation, and also with UV exposure equipment when the photoresist was used as a mask material.

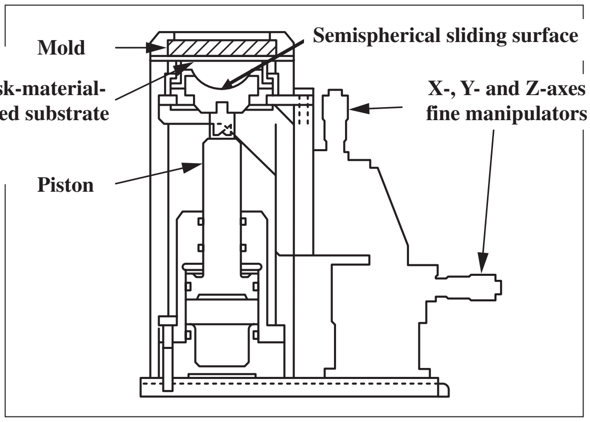


Fig. 16. Schematic of the pressing machine for molded mask fabrication process.[14]

4. Features of Molded Mask Method (Nanoimprint Lithography)

As suggested by the demonstration experiments, the molded mask method, the same as nanoimprint lithography, has some strong and weak points as a novel nanofabrication technology. It is fitted for replicating periodic fine patterns over a substrate surface, but may not be fitted for replicating various sized patterns at one time. A drop-on-demand dispensing method in mask material coating on a substrate can be a possible solution to this problem.[18] It provides a more inexpensive nanofabrication technology than other advanced technologies such as liquid immersion lithography with an excimer laser and EUV lithography.[19] On the other hand, it seems disadvantageous when the defect density should be very small.

Therefore, the most promising application at present is considered to be, for example, the patterned media for high-density magnetic storage.[20,21] The applications to the fabrication of optical components, biochip, LSI memory,[22] and optical discs with very fine grooves, seem also interesting. A so-called 2P process in the optical disc fabrication, in which fine grooves and pits are molded onto photopolymer,[23] seems similar to the molded mask fabrication process using photoresist as a mask material in this early study.

5. Summary

To summarize the study carried out in the 1970s, the invented molded mask method is considered to be almost the same as nanoimprint lithography, in principle. Demonstra-

Fig. 17. (Color online) Samples fabricated by molded mask method in the 1970s. From left to right: master pattern, mold, molded mask, and pattern fabricated on Si wafer substrate. Top: microsized test pattern. Bottom: diffraction grating.

tion experiments using diffraction gratings, microsized test patterns, LSI patterns and microlenses were carried out. Key points of the technology to make an accurate molding were the fluidity of the mask material on a substrate and the stiffness and flexibility of the mold. The pressing machine for the molded mask fabrication process was also prototyped to make the molding mechanical and quantitative.

Figure 17 shows the photograph of actual samples fabricated by the molded mask method thirty years ago. These samples were prepared for a public opening day of laboratories in the 1970s. They are considered to have a historical value in the new technology development.

Current nanoimprint lithography initiated by Professor Chou has enabled considerable progress in practical technology through the efforts of many researchers worldwide.[3,4,18–28] It is sincerely expected that the technology and experience of the molded mask method will be merged into the flow of research and development of the current nanoimprint lithography, and will enable further progress in additional practical development.

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