A new method to fabricate micro-structured products by using a PMMA mold made by X-ray lithography

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Abstract

A new method is proposed to fabricate micro-structured products, in which a PMMA mold prepared by X-ray lithography is combined with silicone replication. Line/space structure and column structure have been constructed to demonstrate the feasibility of the method. The durability of PMMA as a mold and the smallest structure feasible were also examined. This method is much simpler and easier than the conventional LIGA process and has several potential applications in the field of optics, chemistry and biology.

Introduction

Today the mass production technology is most important in order to reduce the price of products. The mold method has been adopted widely in the mass production processes in industry. Usually metal molds are used for the injection molding and the printing. To obtain plastic products, they are heated above the melting temperature and plastic material is injected into the metal mold, or they are heated to the softening temperature of the plastic material and it is pressed against the mold. In these processes the accuracy in the mold structure is very important because the accuracy of the products depends on that of the mold.

In the LIGA process [1-6] using X-ray lithography, a PMMA master is formed by the X-ray lithographic technique, and Ni plating is performed on the PMMA master. The mold is finally obtained by cutting the Ni plating and integrating it into the mold. A lot of plastic products are made by using the Ni metal molds.

The previous paper [7] reported the fabrication of micro lens arrays. In the process, the PMMA master made by the X-ray lithography was used as the mold, and the products were made of silicone. Many other products by using this method could be made, of course. The combination of the PMMA/silicone is possible because PMMA and silicone do not bind each other. The advantage of this method is that the Ni plating process is omissible. This method, however, must be used by paying attention on the reliability of PMMA as the mold and the accuracy of the structure of the products.

Thinking of the application of this method, the character of silicone must be considered. From its visible light transparency, it could be used as optical components [7]. Since it is non-conductive, the chip for high-speed capillary electrophoresis could be produced [8-10]. The silicone casting application is increasing now, e.g., micro printing [11] and micro-molding in capillaries [12]. In this paper, the silicone casting method using X-ray lithography will be described.

Experiments and Results

For the comparison purpose, the LIGA process is schematically drawn in Fig.1a. Next the new method is given in Fig.1b. This new method is simpler, easier and of lower cost because it needs no Ni plating process. This method will be called “PMMA mold method”.

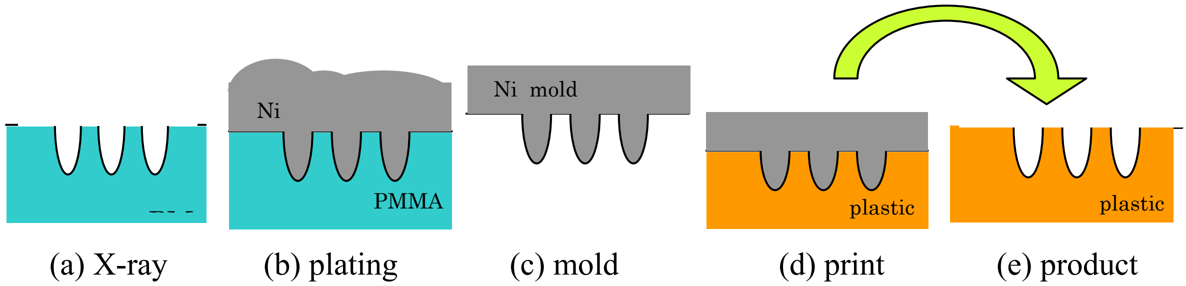


Fig.1a. The LIGA process.

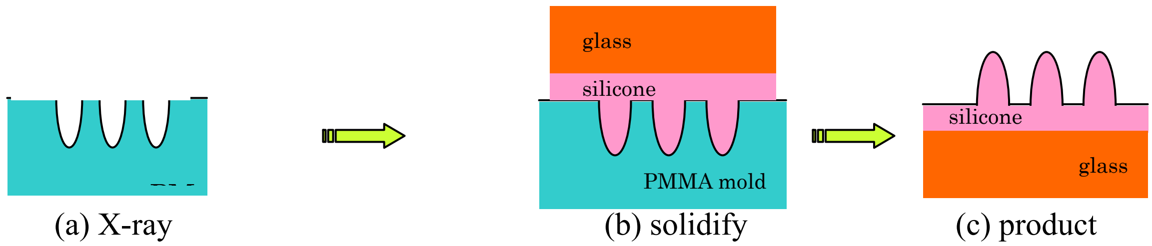


Fig.1b. The PMMA mold method.

In order to apply this new method to many fields, the following points must be studied.

1. Durability of the PMMA mold.
2. Limitation in size and structure of the product made of silicone.
3. Waiting time for silicone to solidify.

A. *Durability of the PMMA mold*

Silicone oil mixed with the curing agent was put on the PMMA mold. They were placed on a hot plate heated at 90℃ for about 30 min to solidify the silicone. Next the silicone was separated from the PMMA mold and thus the copy was produced. The separation process was very easy because it is soft and can be bent. One of the risks this method might have is the damage of the PMMA mold during the separation process. The number of copying process attainable is limited by the PMMA damage received during the whole process. The damage can be introduced at X-ray exposure, heating, and separation. In this respect, the advantage of using silicone is its very softness which leads no damage to the PMMA mold. After twenty replicas were produced using the same PMMA mold, no problem was found expect for generating the rubbish of silicone. On a 300μm thick PMMA sheet the mold for a 40μmϕ lens array was formed (over the area of 100mm^2). This is shown in Fig.2.

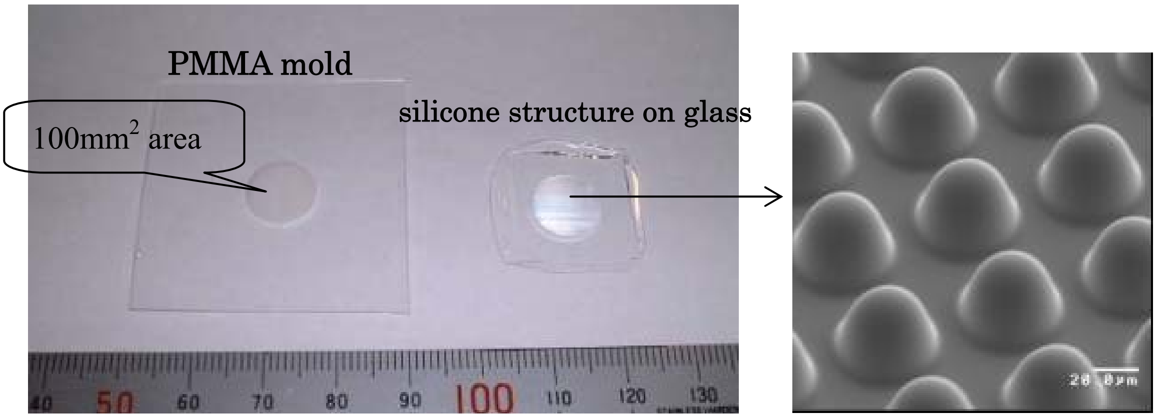


Fig.2 The PMMA mold and the silicone product.

micro lens array

B. *About the product*

The silicone is so soft that the silicone thin film can not keep its shape by itself. The adequate solution might be holding the silicone film on a hard support. In this case the sticking strength is a very important factor from the point of view of reliability. Generally the silicone is stable and not adhesive. Therefore, the sticking strength on Si substrate was checked by changing several curing conditions, for instance, temperature, time and others. Eventually, it was found that the silicone's curing agent worked as glue to the Si substrate. It was confirmed that the sticking strength was high when large amount of the curing agent was used. The silicone replica samples were fabricated on glass, Si and PET substrates. All of them were firmly held on the substrates and the silicone did not come off easily. They are shown in Fig.3. In this process, it is important to remove air in the silicone oil. Of course, when it is thick, the removal of the air is unnecessary. Because of it was keep by itself.

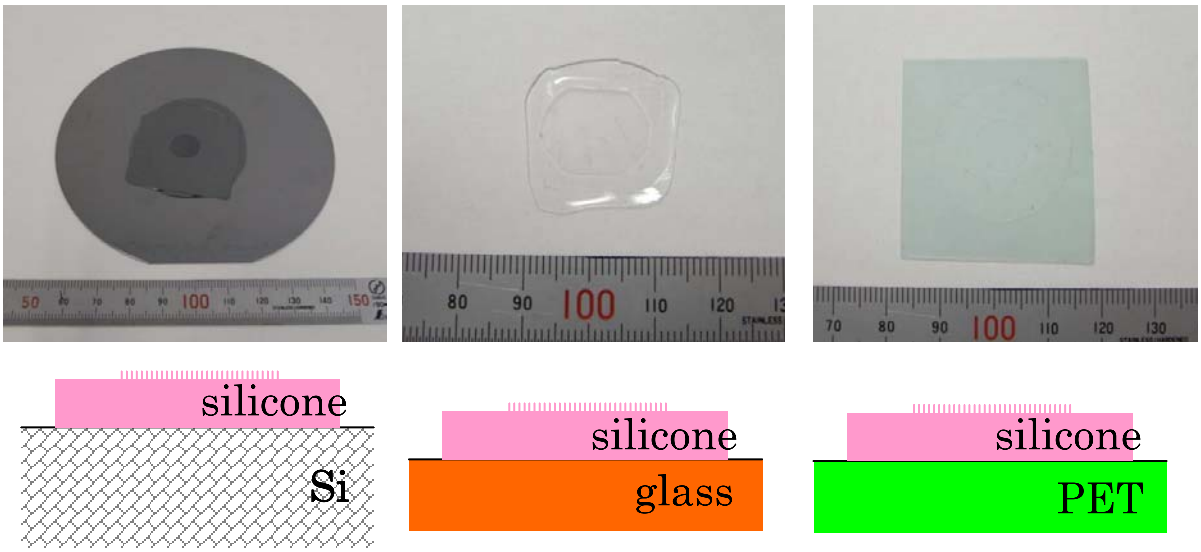


Fig.3 The silicone product on each material

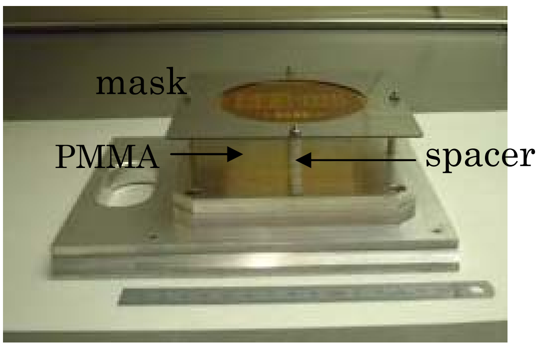
C. *Silicone as a replica material*

In the present PMMA mold method silicone oil was used as the replica material. The silicone has several advantages: ①high optical transparency, ②good chemical resistance, and ③high temperature resistance. It is considered that the silicone is able to be used as the component material in the field of optics, and chemical and biological equipments.

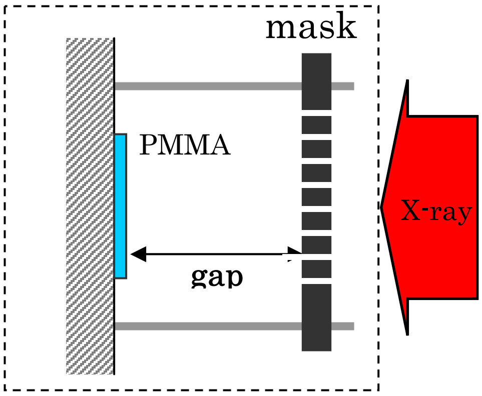
In the present study, the silicone oil was solidified by adding curing agent. When considered this method as a means of mass-production, the slow solidifying process of about 30min might become a problem. In that case, the solidifying time can be shortened by curing at higher temperature or the solidification can be performed by light.

D. *Apparatus to form tapered shape on the PMMA mold*

The silicone replica must be pulled out from the mold without causing any damage on the mold, therefore, the technology to form a tapered shape in the mold is very important, since the taper will reduce the damage of both the mold and the replica. There are some methods to make the taper by the X-ray lithography. In this study was used a method in which the X-ray mask and the PMMA resist were placed at a distance between them. The picture of the apparatus and its schematic diagram are given in Fig.4. The apparatus is simple and can be constructed easily, but the taper formed becomes “S” shaped.



the apparatus



exposure condition

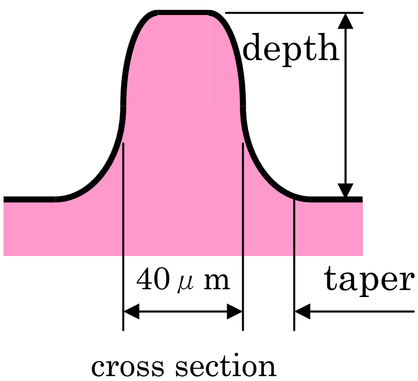
Fig.4 Apparatus and the diagram for exposure

E. *The shape of the taper and aspect ratio*

The combination of PMMA mold/silicone replica is possible because of no strong bonding formation between them. However, if the mold has a complex structure, the separation process is not easy. It is rare but sometimes the replica sticks to the mold and the replica structure breaks at the separation process. For the successful separation two factors are important, i.e. the aspect ratio (width/depth) and the taper structure. The deeper the depth and the finer the structure, the separation becomes more difficult. For such difficult structure, tapered structure makes the separation process easier. Therefore it is important to know how much aspect ratio can be attained and what kind of taper shape is necessary.

F. *X-ray mask with 40μmϕ holes*

By using an X-ray mask with 40μmϕ holes, a micro lens array can be made. The exposed area is about 1 mm^2. The replica formed on a glass support is shown in Fig.2. As mentioned above, the separation is harder with the deeper structure on the PMMA mold and with the smaller angle of the taper structure. If hard replica/mold bonding was formed on the glass substrate (the cover glass for microscope), the glass could be broken at the separation process. The separation tests were repeated with the samples having different etching depth and taper value. The results are given in Fig.5. The tests were repeated several times for each taper and etching depth values. The mark "○" means all of them are successfully separated, the "×" mark for no success, and "△" for occasional success. The etching depth was controlled by changing the X-ray exposure time and the taper width by the gap between the mask and PMMA. If the taper width was zero, the separation was difficult for the 60μm depth sample. If given the 10μm taper width, the separation was easily for the same depth sample. This examination suggested that two is the aspect ratio (taper/depth) limit attainable.

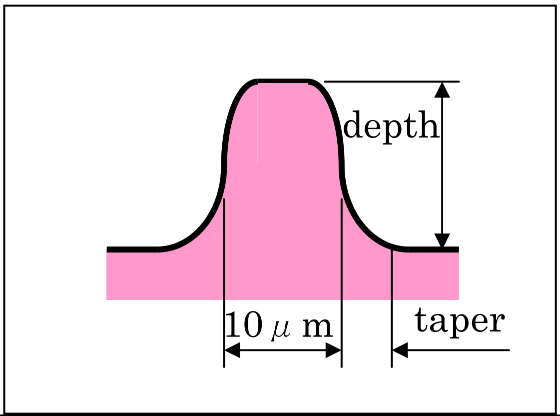


	depth			
taper	42μm	60μm	66μm	80μm
0μm	○	△		
5μm	○	○		×
10μm	○	○	○	
20μm	○	○		
30μm	○			

Fig.5 The cross section of the structure and the separation conditions

G. *X-ray mask with 10μmϕ holes*

By using an X-ray mask with 10μmϕ holes in row, the structure of rows of micro columns can be made. The variation of etching depth and taper width for 10μmϕ column sample did not necessary affect the obtained replica structure in a similar way to that for the 40μmϕ lens array but the silicone columns were broken under harsh conditions. The microscope photographs are given in Fig.6. This relates very much with the very soft character of silicone. Without tapered structure, the two rows of silicone columns were successfully formed for the 14μm depth sample, but they bended when the depth was 33μm. However, by applying the taper to the 33μm depth sample good results could be obtained. From this examination, it is suggested that 2～5 is the aspect ratio (taper/depth) limit.



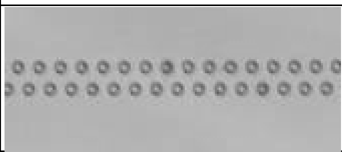
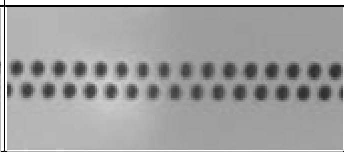
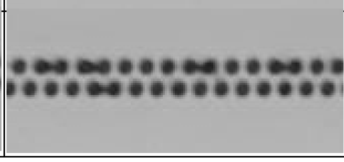
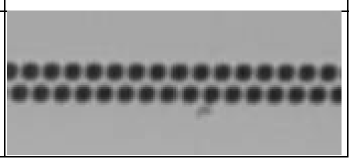
depth	taper: 0(μ m)	taper: 5(μ m)	taper: 10(μ m)
6(μ m)			
14(μ m)			100 μ m
39(μ m)			

Fig.6　The cross section of structure and the photograph

H. *X-ray mask of the line and space structure*

If compared with the mold with holes, that with line structure is easy to handle. The test sample had a structure of 100μm lines and spaces with 500μm depth and the result was quite satisfactory. The more complex structures have been tried. Such examples are shown in Fig.7. They may be used as liquid paths.

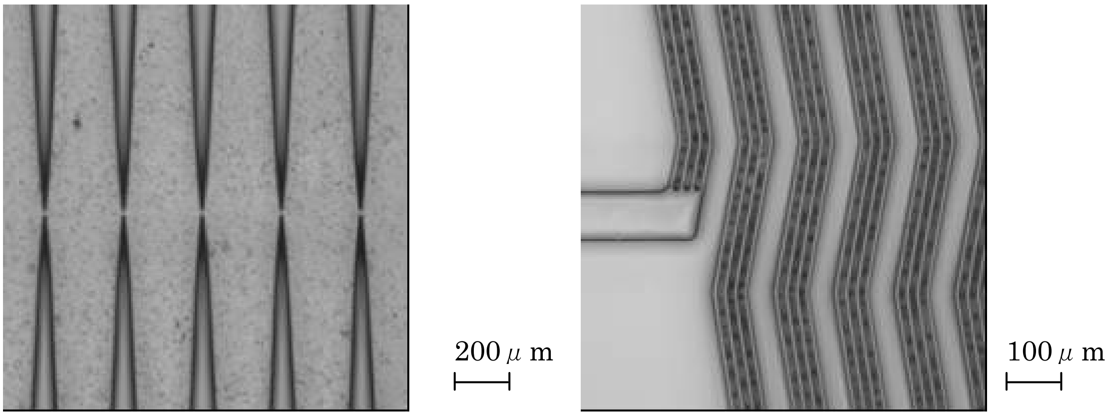


fig.7 The complex line and space structure photograph

Summary

A new method to produce many replicas was proposed. It is not the method called “LIGA”, but here it is named “PMMA mold method”. This method uses PMMA mold made by X-ray lithography and silicone as the replica material. This paper reports ① the reliability of PMMA as the mold material and ② the structural limit of the silicone replica products for the automatic mass production.

No damage was found on the PMMA mold by the microscope observation after continuous production of 20 replicas. This must be due to the very soft character of silicone and also to the bendable character of PMMA. The bendable character of PMMA makes the separation process easy. This is important for an industrial practicality.

The silicone thin film is too soft to be self-supporting. Then it needs a substrate for instance glass etc. But this may not be so serious problem in some cases, e.g. for the application to the LED lamp in which the silicone thin film can be directly bonded on the LED lamp. There may be a peel-off problem between the silicone and the support after the use for a long time.

Thinking of the applicable field, the character of silicone is very promising. On the contrary this silicone stability might limit the development of “PMMA mold method”.

Compared to the column structure, producing replicas of a line and space structure is easier by using the PMMA mold method. Even a structure with several hundred μm depth can be easily fabricated with no defects. In case of the column structure, it is considered that the aspect ratio limit is about 2. When a 10μm taper is integrated to the mold structure, the value increases to 5. The effect of the taper structure was confirmed for the column structure as small as a 5μmϕ.

This new method can be used in the field of the optics, and chemical and biological equipment.

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