Rapid Replication of High Aspect Ratio Molds for UV Embossing

Yehai Yan, Mary Bee-Eng Chan-Park, and Chee Yoon Yue

***Abstract*—This paper describes a promising fabrication technique for rapid replication of high aspect ratio microstructured molds for UV embossing. The process involves casting silicone rubber on a microstructured master, replicating an epoxy mold using the PDMS rubber mold and finally, metallizing the surfaces of the epoxy mold by electroless plating nickel (EN). The preliminary study suggests that this technique is feasible for rapid replication of high aspect ratio molds for UV embossing. Uniform molds can be replicated rapidly through this technique making the process economical and accessible.**

***Index Terms*—rapid replication, high aspect ratio microstructured mold, UV embossing**

I. Introduction

Polymeric micro-electro-mechanical systems (pMEMS) are important as low–cost alternatives to silicon or glass-based MEMS technologies for a range of present and future commercially viable products in the field of life science, [1] micro-optics, [2], [3] display technology [4] and so on. Hence, pMEMS are attracting considerable attention in both the scientific and industrial communities.

The creation of polymeric MEMS typically involves the use of a microstructured mold to replicate polymeric materials with the features in micron scale dimensions. Most present techniques for microstructured moldmaking rely on conventional semiconductor materials such as a silicon wafer and standard microlithographic techniques originally developed for the microelectronics industry. These materials and techniques are relatively expensive and they are not routinely accessible to most scientists and industrialists. Recently, alternative technologies for micropatterning and lithography using polymeric materials have been presented. [5] Soft lithography using Polydimethylsiloxane (PDMS) is receiving much attention as an alternative method of rapid replication. [5]-[8] This polymer is not only a low-cost material but also particularly suitable for use as a mold in replica molding because it can be separated easily from the master without damaging the latter.

Ultraviolet (UV) embossing is a technique for making polymeric MEMS components with high aspect ratio. It offers many advantages such as rapid processing, operation using low pressure and room temperature, outside-the-cleanroom operation, and good dimensional replication. However, the polymeric microstructured molds used in high aspect ratio embossing must have sufficient rigidity to withstand the stresses of demolding. In addition, the surfaces of the mold need to be metallized and coated with anti-stick coating in order to decrease the interaction between the mold and UV embossing resins. To fabricate molds from a rigid microstructured master mold, PDMS mold can be used as a 2nd generation mold and other rigid polymers such as epoxies, polyurethanes, and poly (acrylic acid) can be molded against it [6]. The 3rd generation polymeric mold made of a rigid polymer with relatively higher surface energy can then be metallized so that the metal layer acts as a diffusion barrier between the mold and the photopolymerizable resin. [9]-[11] Electroless nickel plating was explored as the metallizing technique as it does not require sophisticated equipments.

In this paper, a promising replication technique for UV embossing molds is presented. The method allows the rapid replication of fairly rigid metallized polymeric microstructured molds with high aspect ratio for UV embossing. In this technique, no clean room is needed and many inexpensive daughter molds can be made from each expensive master. It is therefore an accessible and economical technique.

II. Experimental

A. Materials

The master employed in this study was prepared by exposing and developing a photoresist coating, specifically SU-8 supplied by MicroChem Corporation (MA, USA), on a silicon wafer through a mask. PDMS used in this work for casting is supplied by Dow Corning Corporation (MI, USA). The epoxy casting resin is Epoxfix Kit supplied by Struers A/S (Denmark) and is a Biphenol A epoxy resin (M_n<700). The viscosity of the epoxy resin at 20°C is 550 mPa.s.

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Pallidum choride ($PdCl_2$) and 1-vinylimidazole were purchased from Aldrich Chemical Company and used as received. A commercial product electroless nickel plating solution 'PEN-99' supplied by Plaschem Specialty Products Pte. Ltd (Singapore) was used.

B. Procedure

Figure 1 illustrates the procedure used in this study for microstructured mold replication. Many aspects of this procedure are not novel; a similar but somewhat less elaborate procedure has been employed previously for the fabrication of stamps and molds for soft lithographic techniques. [5] Prior efforts using similar procedures to create molds using soft lithography have addressed neither the goal of high aspect ratio microstructure nor the goal of mold metallization to promote mold durability and the release of molded structures.

The mechanical and thermal processing conditions which dictate the use of rigid metallic molds in many applications are greatly relaxed in the UV embossing process, which involves low-pressure and room-temperature processing. A new problem, which arises in application of UV embossing to high aspect microstructures, however, is cohesive failure within the embossed structures. This can be addressed through surface pretreatment of the molds to promote release of the embossed structures.

Fabrication of PDMS mold ---- The microstructured silicon wafer was stiffened by attaching it to a glass plate using room-temperature curing epoxy adhesive. The PDMS prepolymer and its curing agent were thoroughly mixed with a 10:1 weight ratio. Before use, the prepolymer mixture was degassed at 30 mtorr for 30 min to remove air bubbles. A cavity was formed around the master with a 2mm thick aluminum spacer; the prepolymer mixture was poured into this cavity. A 1 cm thick PTFE block was carefully lowered onto the prepolymer mixture from one edge to realize continuous contact and prevent bubble formation at the interface. The master/PDMS/PTFE assembly was clamped (Figure 2) and cured at room temperature for 24 h or at 65°C for 2 h, after which the PDMS mold was peeled off from the master and was ready for the next step of replication.

Fabrication of Epoxy mold ---- The epoxy resin and its hardener were mixed thoroughly for at least 2 minutes, with a weight ratio of 25:3 as recommended by the supplier, and then degassed. The resin was carefully poured into a chamber structured with glass sheets (top and bottom), the PDMS mold, and a 2 mm PTFE spacer on the PDMS mold (Figure 3). After curing at room temperature for 24 h and peeling off the PDMS template, a microstructured Epoxy replica, which was adhered to the top glass sheet, of the master was obtained.

Electroless plating nickel on the surfaces of the epoxy mold (EN mold) ---- In general, the adhesion of metals to pristine polymers is poor, due to the inherent physical and chemical inertness of most polymers surfaces. [12], [13] In order to enhance the adhesion of metals to polymers, the technique of polymers surface graft copolymerization following the plasma treatment has been widely employed prior to metallization. [14] – [16]

In this study, the surface modification of the epoxy resin via argon plasma treatment was carried out in a March PX-500™ Cleaning System. This system uses a solid-state radio frequency generator operating at 13.56 MHz. The detailed operating conditions were as follows: the plasma treatment time at a plasma power of 100W was 60 s; the flow rate of the argon is 350 sccm (standard cubic centimeters per minute). The base pressure of the argon gas in the chamber was 50 mtorr. The plasma-pretreated epoxy mold was then exposed to the atmosphere for a few minutes to allow surface-activated species created by the plasma treatment to react with oxygen to generate surface peroxide or hydroxyl peroxide functional groups. [14] - [16] The "aged" epoxy mold was coated with a thin layer of Nitrogen-containing monomer, specifically 1-vinylimidazole, with an overlayer of Melinex® 454 film. The epoxy mold together with the monomer and Melinex® 454 film were then exposed to UV illumination for 40s at room temperature to enable graft polymerization of the monomer onto the modified epoxy surface. The UV source was a flood UV exposure system with Hg-lamp, specifically a 400W PK 102UV Lamp from I & J Fisnar Inc (NJ, USA). The measured area-averaged UV intensity at 365nm was about 110mW/cm^2. After UV grafting, the Melinex® 454 film was removed and the epoxy mold was rinsed thoroughly with deionized (DI) water to remove residual ungrafted monomer and then dried in an oven at 80°C.

The pretreated epoxy mold was activated by immersing in palladium catalyst solution, containing 1.0 mg/ml $PdCl_2$ and 10 mg/ml HCl (37wt%), for 10 minutes. After removal from the palladium catalyst solution, the mold was rinsed thoroughly with DI water before being transferred to the electroless plating bath. For electroless plating of nickel on the surfaces of epoxy mold, a commercial nickel solution PEN-99 was used. The electroless plating of nickel was carried out at 90°C for 30 min. After plating, the EN mold was gradually cooled to room temperature, rinsed thoroughly with DI water and dried in an oven at 80°C.

C. Characterization

The dimensions of the master and the replicated microstructured molds were characterized using an optical profilometer, Wkyo NT 2000. For examination using scanning electron microscopy (SEM), the replicated molds were coated with gold and examined using a Joel JSM-5600 scanning microscope at an operating voltage of 10KV; the Nickel-plated epoxy molds did not require further preparation prior to SEM.

III. Results and Discussion

A master comprising microchannels separated by walls composed of SU8 photoresist on a silicon wafer was used. Figure 4 shows the dimensions of the master measured with an optical profilometer (Wkyo NT 2000). The dimensions of the trapezoidal trenches of the master are typically 25 μm on top and 15 μm at the bottom. The average distance (z) between the tops and the bottoms of the trenches is 84 μm. Therefore, the aspect ratio of the master is about 4.

Figures 5 to 7 show the dimensions of the replicated silicone rubber mold, epoxy mold, and EN mold respectively. The corresponding dimensions of the silicone rubber mold (top: 14 μm, bottom: 25 μm, and z: 83μm) and epoxy mold (top: 23 μm, bottom: 14 μm, and z: 82μm) suggest that the 3-D channel paths on the master have been precisely replicated onto the epoxy mold using the silicone rubber mold as the intermediary. Due to the cross-linking shrinkage of silicone and epoxy, the corresponding dimensions of the replicated channel paths are slightly smaller than that of the master. Comparison of dimensions shown in Figure 6 and 7 indicates that the nickel has been homogeneously plated on the epoxy mold with a thickness of about 2 to 3 μm.

SEM micrographs of the silicone rubber mold and epoxy mold are shown in Figure 8 and 9, respectively. Though there are some spots on the surfaces of the molds, which may have been introduced by dust, lint or other debris in the non-clean-room environment of the experiment or during the preparation of samples for SEM measurement, it is observed that a complete and faithful replication has been obtained through the molding technique. This is consistent with the results of optical profilometry.

Figure 10 is the SEM micrograph of the EN mold. Although the definition of the photograph is not very good, it directly confirms that a uniform nickel film has been formed on the surface to make the EN mold conductive.

As there are many ways in which this multistep process for replicating microstructured molds can go awry, great care and attention to detail is necessary for successful implementation of this procedure. For example, only silicone rubber and epoxy resin with low shrinkage should be employed, in order to accurately replicate patterns from the master onto the 2^{nd} and 3^{rd} generation molds. The epoxy resin used to create the 3^{rd} generation mold should have a glass transition temperature (T_g) which is higher than the temperature at which the electroless plating is performed (90°C in this experiment); otherwise the EN mold may deform during plating.

By this procedure we have replicated a low-cost Nickel-coated microstructured epoxy mold from a master through the fabrication technique of replica molding combined with electroless plating. Although the EN mold produced in this study is coarse and the aspect ratio of the patterned microstructure is only 4, it does show that it is possible to rapidly replicate microstructured molds for UV embossing. Further studies are being carried out in our research group. This ongoing work shows that it is feasible to faithfully replicate microstructured molds with aspect ratios in excess of 10.

IV. Conclusion

A promising fabrication technique has been developed for replication of microstructured molds for UV embossing. A metallized epoxy mold with aspect ratio of 4 has been produced through this technique. The technique is rapid and simple, and is also economical, requiring neither "clean-room" processing conditions nor other expensive specialized facilities. Considering the advantages of UV embossing, this technique is well suited for many applications in the field of polymeric MEMS. Further studies using this technique are under way, and we believe that in the near future microstructured molds with high aspect ratio (>10) will be replicated precisely from high aspect ratio masters.

References

[1] H. Becker and U. Heim, "Hot embossing as a method for the fabrication of polymer high aspect ratio structures," *Sensors and actuators*, vol. 83, pp. 130-135, 2000.

[2] T. G. Harvey, "Replication techniques for micro-optics," in *Proceedings of SPIE-The international society for optical engineering*, 1977, pp. 76-82.

[3] M. T. Gale, Replication, In: Herzig HP (Ed), *Micro-optics*, Taylor and Francis, London, 1997.

[4] R. C. Liang, M. B. Chan-Park, S. C. J. Tseng, G. Wu and H. M. Zang, "An improved electrophoretic display and novel process for its manufacture," *US Patent Application*, filed 3/3/2000, 09/518, 488.

[5] Y. Xia and G. M. Whitesides, "Soft lithography," *Angew Chem. Int. Ed.*, vol. 37, pp. 550-575, 1998

[6] J. J. Rebecca, C. D. David, O. Emanuele, D. W. Nikolaos and M. W. George, "Fabricating large arrays of microwells with arbitrary dimensions and filling them using discontinuous dewetting," *Analytical Chemistry*, Vol. 70, pp. 2280-2287, 1998

[7] K. Hosogawa, T. Fujii, and I. Endo, "Hydrophobic microcapillary vent for pneumatic manipulation of liquid in μTAS," *μTAS'98*, Banff, Canada, pp. 307-310, 1998.

[8] H. J. Byung, M. V. L. Linda, M. M. Kathleen and J. B. David, "Three-dimensional micro-channel fabrication in polydimethylsiloxane (PDMS) elastomer", *J. Microelectromech. S.*, vol. 9, pp. 76-81,2000.

[9] W. Bacher, K. Bade, B. Matthis, M. Saumer and R. Schwarz, "Fabrication of LIGA mold inserts," *Microsyst. Tech.*, 4, pp. 117-119, 1997.

[10] R. Feng and R. J. Farris, "Thermal and mechanical properties of SU8 negative photoresist coatings," *Polym. Mat. Sci. Engr.*, Vol. 85, pp. 379-380, 2001

[11] H. Lorenz, M. Desont, N. Fahrni, J. Brugger, P. Vettiger and P. Renaud, "High-aspect-ratio, ultrathick, negtive-tone near-UV photoresist and its applications for MEMS," *Sensors and actuators A*, vol. 64, pp. 33-39, 1998.

[12] M. S. Shoichet and T. J. McCarthy, "Convenient synthesis of carboxylic acid functionalized fluoropolymer surfaces," *Macromolecules*, vol. 24, pp. 982-986, 1993.

[13] M. K. Shi, B. Lamontagne, L. Martinu and A. Selmani, "X-ray induced modification of metal/fluoropolymer interfaces," *J. Appl. Phys.*, vol. 74, pp. 1744-1746, 1933.

[14] M. B. Chan-Park, J. Zhang, J. X. Gao and E. J. Liu, "Photografting of argon plasma-treated graphite/PEEK laminate to enhance its adhesion", *J. Adhesion Sci. Technol*., in press, 2002.

[15] M. C. Zhang, E. T. Kang, K. G. Neoh and K. L. Tan, "Electroless plating of copper and nickel on surface-modified poly (tetrafluoroethylene) films," *J. Electrochem. Soc.*, vol. 148, pp. 71-80, 2001.

[16] Y. Zhang, K. L. Tan, G. H. Yang, E. T. Kang and K. G. Neoh, "Electroless plating of copper and nickel via a Sn-free process on polyimide films modified by surface graft copolymerization with 1-vinylimidazole," vol. 148, pp. 574-582, 2001.

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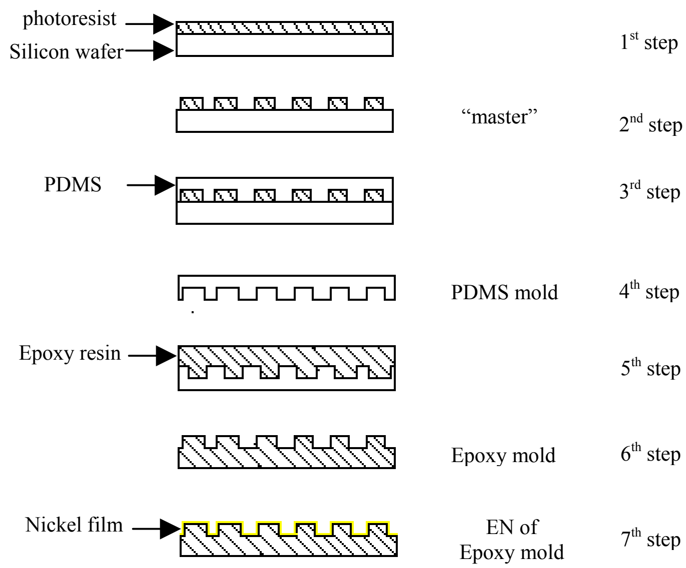


Figure 1 Procedure for the replication of microstructured molds with the aspect ratio of four

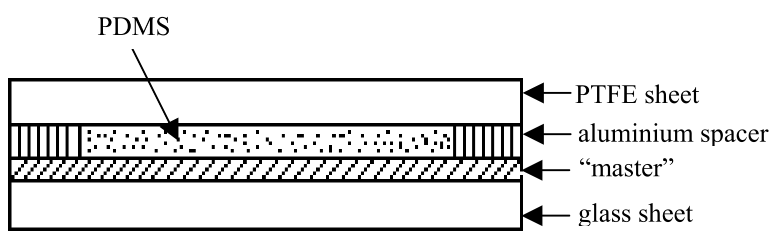


Figure 2 Scheme for replicating the PDMS mold from the master

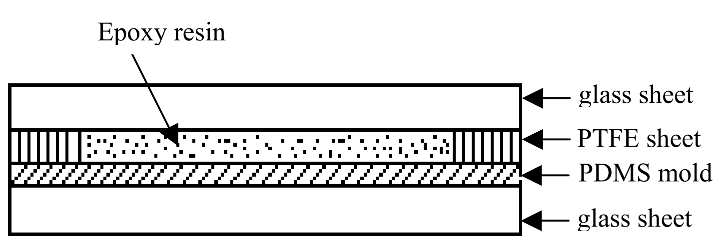
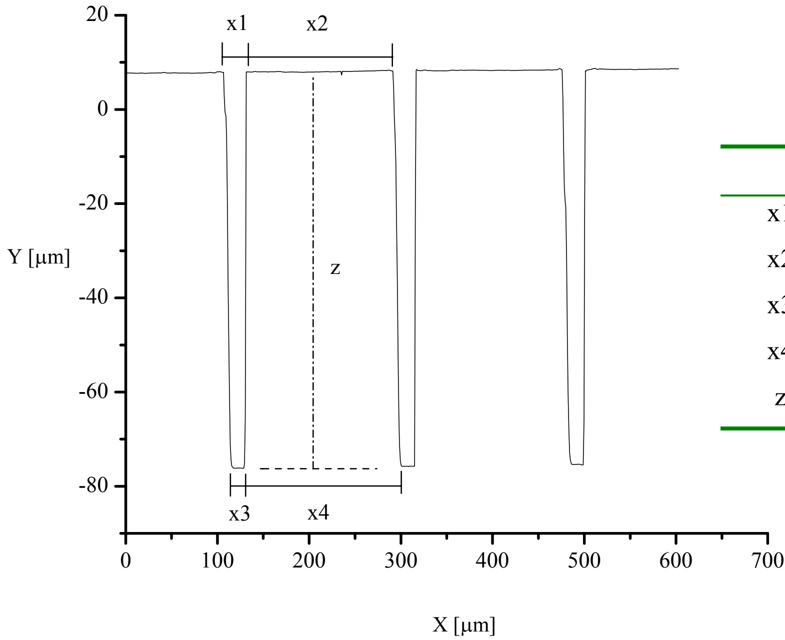
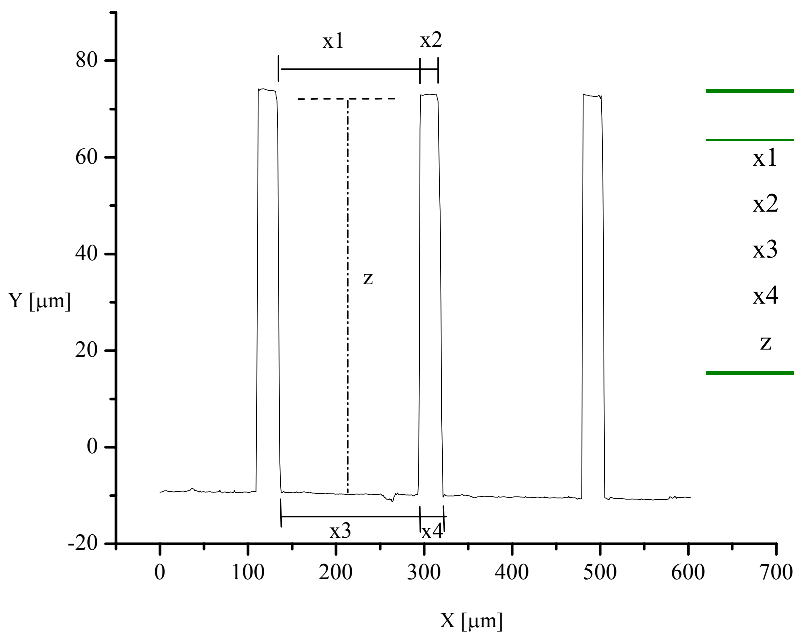


Figure 3 Scheme for replicating the epoxy mold from PDMS mold



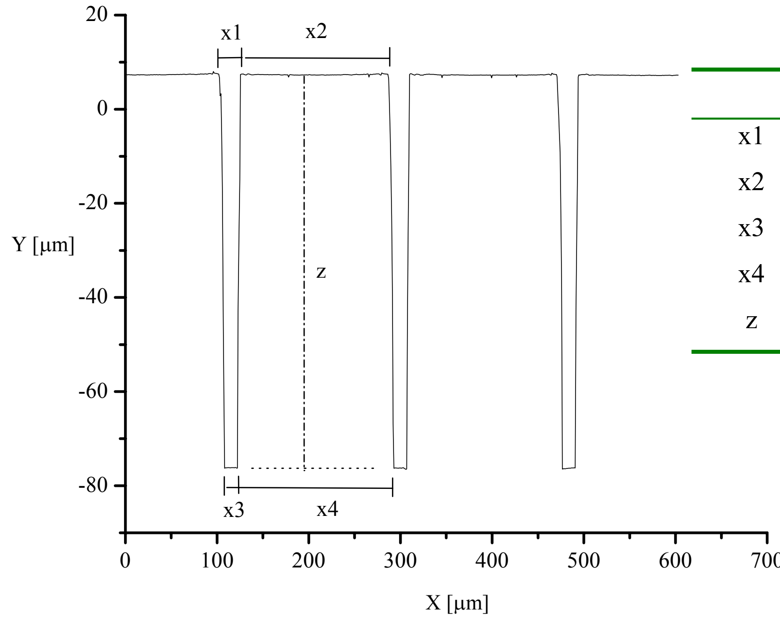
	Average (μm)
x1	25
x2	160
x3	15
x4	170
z	84

Figure 4 Dimensions of the master measured by optical profilometer



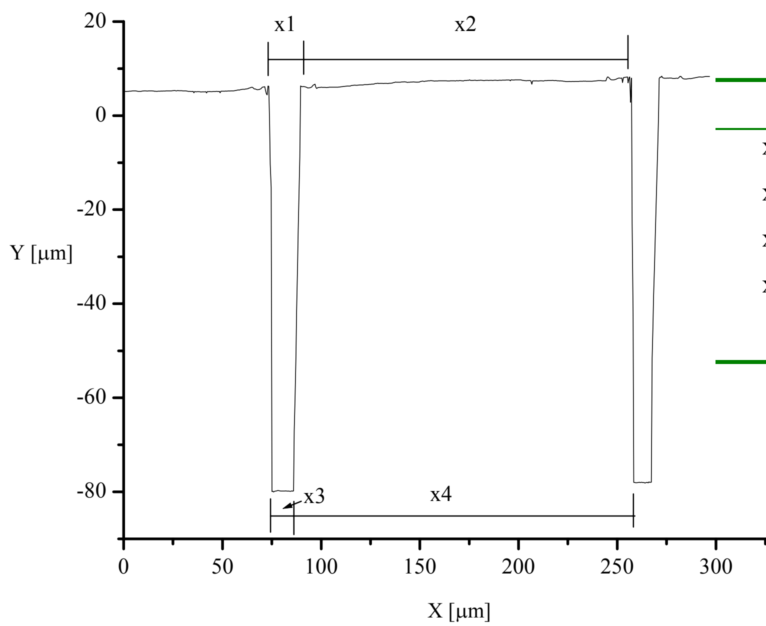
	Average (μm)
x1	169
x2	14
x3	158
x4	25
z	83

Figure 5 Dimensions of PDMS mold measured by optical profilometer



	Average (μm)
x1	23
x2	163
x3	14
x4	172
z	82

Figure 6 Dimensions of epoxy mold measured by optical profilometer



	Average (μm)
x1	18
x2	169
x3	10
x4	176
z	81

Figure 7 Dimensions of EN mold measured by optical profilometer

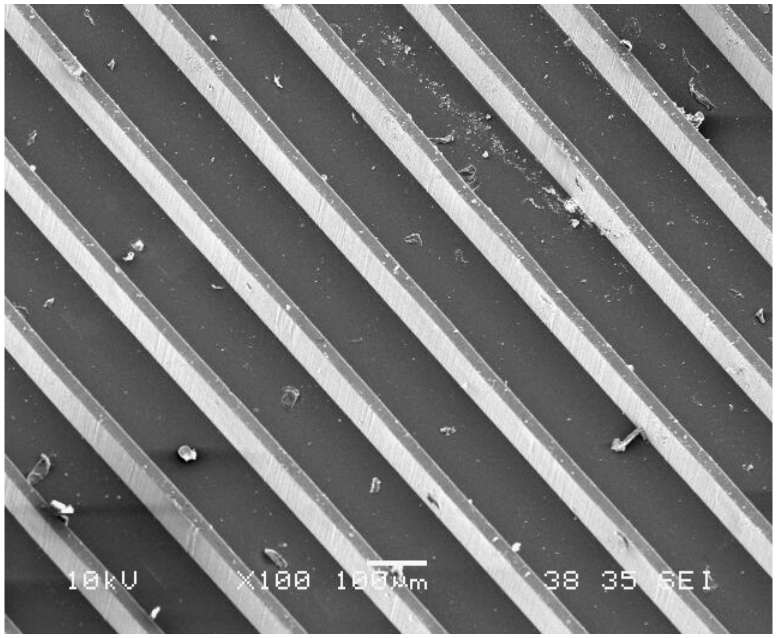


Figure 8 SEM photograph of PDMS mold replicated from the master

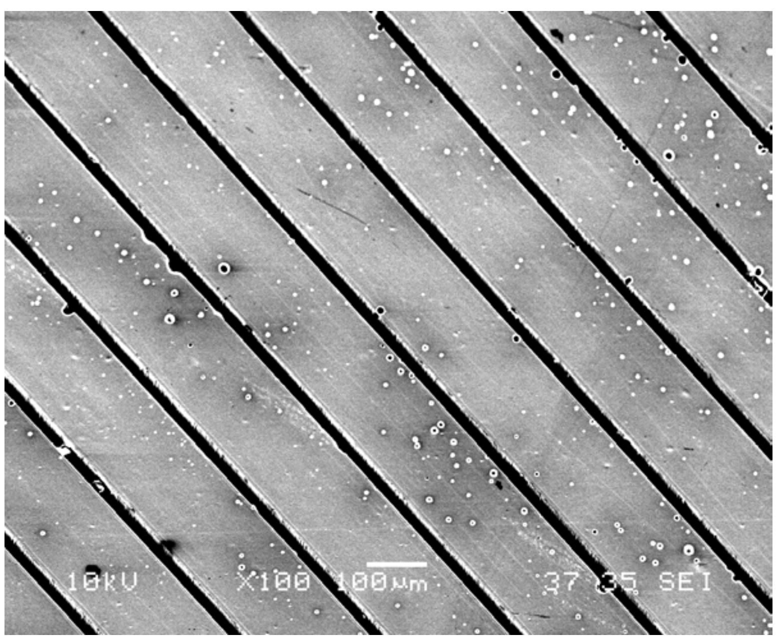


Figure 9 SEM photograph of epoxy mold replicated from PDMS mold

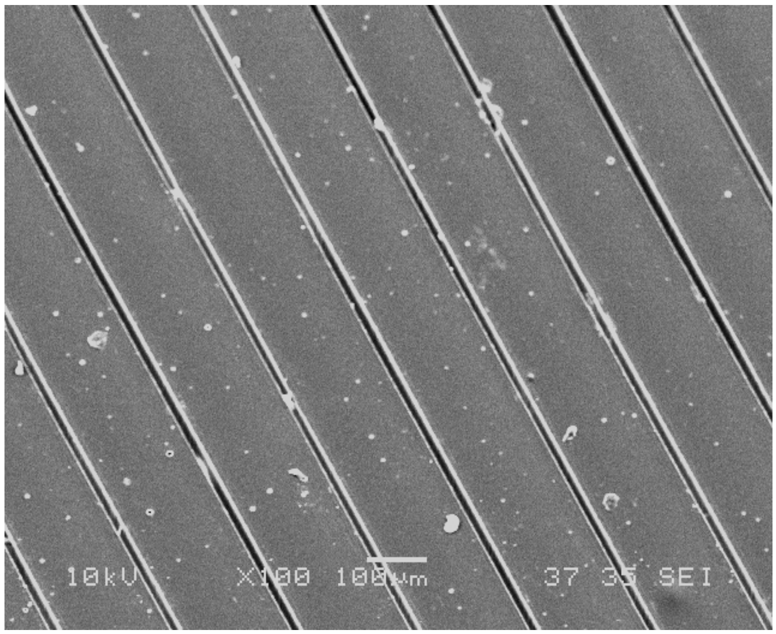


Figure 10 SEM photograph of EN mold