

Reprinted from

Jpn. J. Appl. Phys. Vol. 39 (2000) pp. 7075–7079

Part 1, No. 12B, December 2000

©2000 The Japan Society of Applied Physics

Imprint Characteristics by Photo-Induced Solidification of Liquid Polymer

Masanori KOMURO¹, Jun TANIGUCHI², Seiji INOUE², Naoya KIMURA²,
Yuji TOKANO², Hiroshi HIROSHIMA¹ and Shinji MATSUI³

¹*Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan*

²*Science University of Tokyo, 2541 Yamazaki, Noda, Chiba 278-8510, Japan*

³*Himeji Institute of Technology, 1479-6 Kanaji, Kamigori, Aka, Hyogo 678, Japan*

Imprint Characteristics by Photo-Induced Solidification of Liquid Polymer

Masanori KOMURO^{1,*}, Jun TANIGUCHI², Seiji INOUE², Naoya KIMURA²,

Yuji TOKANO², Hiroshi HIROSHIMA¹ and Shinji MATSUI³

¹Electrotechnical Laboratory, 1-1-4 Umezono, Tsukuba, Ibaraki 305-8568, Japan

²Science University of Tokyo, 2541 Yamazaki, Noda, Chiba 278-8510, Japan

³Himeji Institute of Technology, 1-479-6 Kanaji, Kamigori, Ako, Hyogo 678, Japan

(Received July 7, 2000; accepted for publication October 11, 2000)

Nanoimprint lithography is an attractive technology for LSIs era below 40-nm critical dimension from the viewpoints of high-throughput and low-cost equipment. In order to avoid a pattern placement error due to thermal expansion in the conventional thermal imprint process, we attempted to replicate the mold pattern onto a liquid polymer, which was solidified using ultra-violet (UV) light irradiation at room temperature. The liquid polymer used here was supplied by TEIJIN SEIKI Co., and termed TSR-820. It was spin coated on slide glass to produce approximately 1.5- μm -thick polymer film. The thickness remained after UV exposure and rinsing in acetone was observed at the dose of 10 J/cm² and it saturated about a UV exposure dose of 100 J/cm² with an increase in the exposure dose. The mold fabricated of quartz plate was first pressed onto the polymer film at about 100 kg/cm² and then the UV light was irradiated using an imprint apparatus developed for this work. After releasing the mold from the film, the substrate was rinsed in acetone to remove the residual liquid polymer. Eventually the minimum feature size of 100-nm line and 300-nm space pattern was successfully replicated in the polymer with good fidelity.

KEYWORDS: imprint, lithography, liquid polymer, photo-polymer, ultra-violet light, pattern replication

1. Introduction

Lithography performance is the core technology to promote shrinkage of silicon devices and many researchers and engineers have been making tremendous efforts to develop next generation techniques such as F₂ excimer-laser lithography, extreme-ultra-violet lithography and electron-beam projection lithography. These technologies are targeted for practical use in the size range between 70 nm and 40 nm in critical dimensions of devices. In the future scaling down of dimensions from 40 nm to 10 nm, there are several candidate technologies from the viewpoint solely of pattern resolution, such as focused electron-beam and proximal probe techniques. However these technologies may not be feasible to overcome the barrier of high-throughput requirement of mass-production lithography which should be more than 30 wafers/h for 12 inch wafers. Imprint lithography reported by Chou *et al.*^{1,2)} and Xiaoyun *et al.*³⁾ is a very simple concept, where a mold or stamper is pressed onto a substrate coated with polymer film such as polymethylmethacrylate (PMMA) while keeping the temperature up to the glass transition temperature of the polymer. After cooling lower than the glass transition temperature, the mold is removed from the substrate. Thus the fine pattern on the mold is replicated in the polymer film. By using this technique, they attempted to fabricate several kinds of devices such as field effect transistors,⁴⁾ magnetic memory disks,⁵⁾ GaAs photodetectors,⁶⁾ and zone plates.⁷⁾ They also extended this technology to roller imprint technique.⁸⁾ In addition, several groups have been investigating imprint techniques.^{9–11)} The use of this technique for LSI production which requires several layers of imprint processes, may be very promising in terms of mass-production and low-cost of equipment. However, the thermal cycle above the glass transition temperature (more than 100°C) may be a critical issue which causes poor accuracy in pattern placement and overlay. Therefore, it is a very attractive method to use for photo-induced polymerization at room temperature reported

by Haisma *et al.*¹²⁾ and Colburn *et al.*¹³⁾ Haisma *et al.* used a mold which was transparent to ultra-violet (UV) light and a spin-coated monomer film having low viscosity of about 7 cps which shrinks 5–15% in volume after solidification. This imprinting structure will allow us to align the mold position against the wafer in a similar manner to the X-ray stepper in the future. In this paper, we describe the fundamental characteristics on imprint experiments using a new liquid polymer with higher viscosity and lower volume shrinkage compared with the material used in ref. 12, which is solidified using UV light exposure.

2. Experimental

Figure 1 shows a schematic diagram of an imprint apparatus developed in this work. The vacuum chamber was fixed on the base plate which was moved up and down through a guiding pillar using a ball screw and stepping motor. This chamber was evacuated down to about 10⁻² Torr before im-

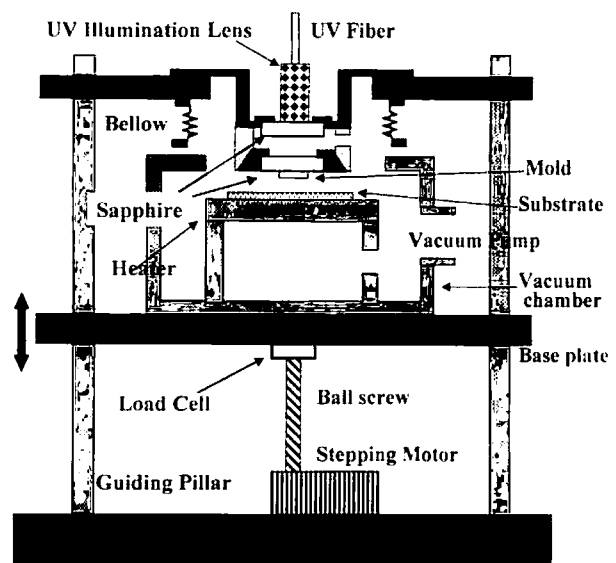


Fig. 1. Schematic diagram of imprint apparatus developed in this work.

*E-mail address: komuro@csl.go.jp

print experiments to avoid inclusion of air bubbles in the polymer. The mold fabricated of quartz plate was pasted on a sapphire plate using a small piece of carbon adhesive tape. The substrate which was covered with polymer film was also fixed as well under the mold as shown in Fig. 1. The pressure between the mold and the substrate was monitored by a load cell unit located between the ball screw and the vacuum chamber. The quartz plate mold was produced by the following process; 1) a pattern was delineated on ZEP-520 resist using an electron-beam exposure system, 2) about 100-nm-thick Al film was lifted off, 3) the quartz was etched by reactive ion etching using CHF_3 gas, 4) the remaining Al was etched off by H_3PO_4 , and finally 5) the quartz was rinsed in de-ionized water. As seen in micrographs of the molds in Figs. 5–7, we can obtain vertical side walls of protruded patterns. We used a mercury lamp of LV-7212 (Hamamatsu Photonics Co.) with a filter that can pass the wavelengths between 300 nm and 400 nm. The UV light was guided to the top surface of an upper sapphire plate through the UV fiber and an area of about 1 cm^2 was illuminated through the illumination lens. The liquid polymer used by us was TSR-820 supplied by TEIJIN SEIKI Co., which has been utilized for three-dimensional photo shaping and shrinks by 5.8% in volume after solidification. The liquid polymer has a viscosity of 225 cps and can be spin-coated on a slide glass which was used as a substrate. Since the coated polymer is still a viscous liquid film, it is readily conformable to the mold pattern when the mold is pressed onto the slide glass at room temperature. In Fig. 2, the procedure for the imprint experiment is illustrated. After imprint experiments, the slide glass was dipped in acetone to remove the liquid polymer remaining at the peripheral area where the UV light was not irradiated.

The system developed here also had a heating unit for the conventional imprint process using a thermal cycle. Figure 3 shows micrographs of the $0.5\text{-}\mu\text{m}$ -wide groove on a mold and of its replicated pattern on PMMA film produced by a conventional thermal cycle in order to check the performance of the imprinting system, where the PMMA sample was heated up to 150°C and pressed by a pressure of 80 kg/cm^2 . It is seen that the mold pattern is replicated onto PMMA with good fi-

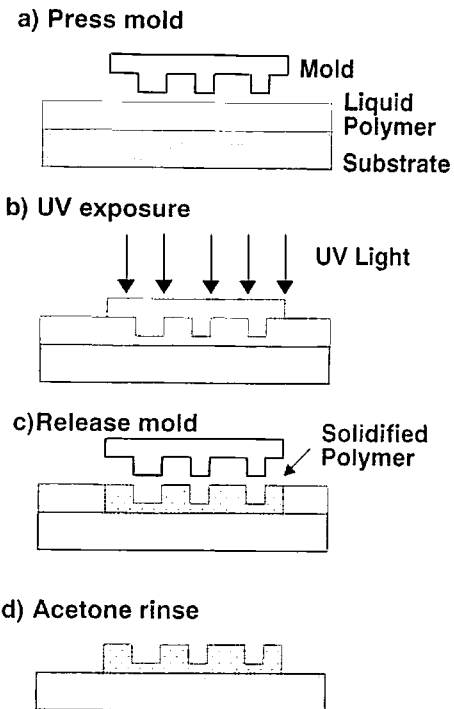


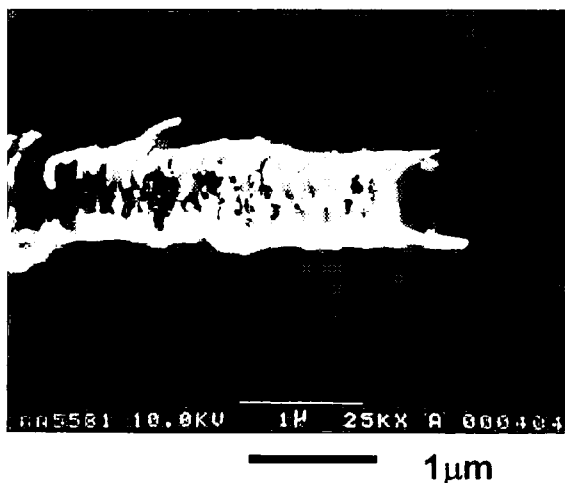
Fig. 2. Schematic procedure for UV exposure imprint experiment.

delity.

3. Results and Discussion

Figure 4 shows the dependence of thickness of solidified polymer on the UV exposure dose, where the liquid polymer was spin-coated on a slide glass with 4000 rpm for 5 min and the UV light was illuminated onto an area of about 1 cm^2 . After UV irradiation, the slide glasses were rinsed in acetone for 10 s and 30 s in order to remove the liquid polymer film from the nonirradiated area and also to investigate the solubility of solidified polymer in acetone. The remaining thickness is independent of rinse time in acetone which means that the solidified polymer has a sufficient tolerance to acetone for perfect removal of the residual liquid polymer. The remaining

a) Quartz Mold



b) Replicated pattern on PMMA

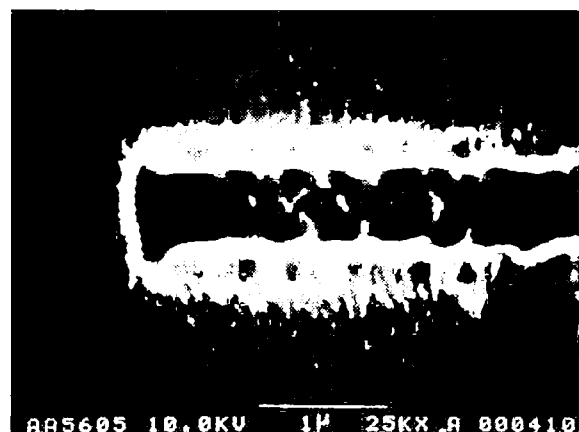


Fig. 3. Micrographs of quartz mold and its replicated pattern on PMMA by thermal cycle for $0.5\text{-}\mu\text{m}$ wide line.

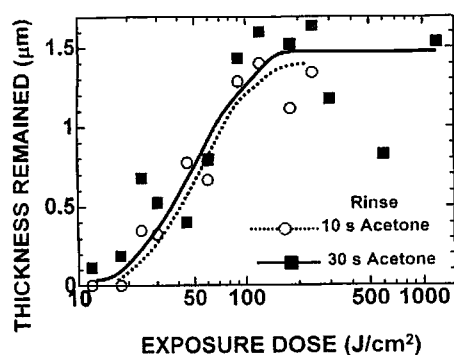
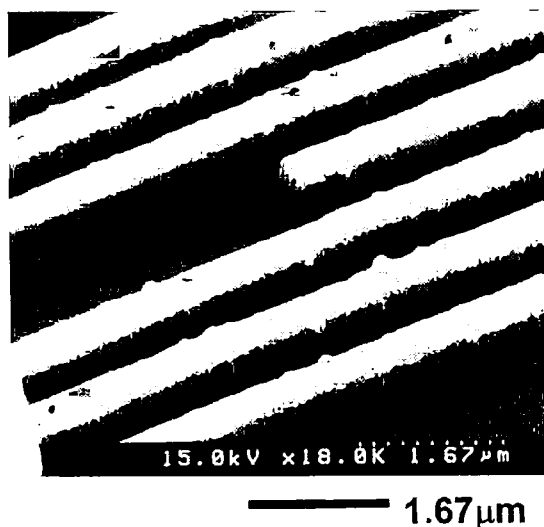


Fig. 4. Variation of remaining thickness of liquid polymer TSR-820 with UV light exposure dose for different rinse time in acetone.

thickness is observed at about 10 J/cm^2 and is seen to saturate at $1.5 \mu\text{m}$ thickness with an increase in the UV exposure dose. Since UV light illumination to liquid polymer promotes the polymerization reaction after absorption by photosensitive ingredients, the behavior illustrated in Fig. 4 can be reasonably understood. Thus UV doses of more than 120 J/cm^2 were used for pattern replication experiments.

Several kinds of replicated patterns are shown in Figs. 5, 6 and 7, where the observed mold patterns are copies of the mold actually used for the replication. The results were obtained under the conditions of UV exposure dose of 120 J/cm^2 after pressing the mold to the slide glass covered with the liquid polymer film by a pressure of 120 kg/cm^2 . Line and space patterns with $0.8 \mu\text{m}$ periodicity in Fig. 5 indicate that the replication is accomplished with good fidelity where

a) Quartz Mold



b) Replicated pattern on TSR-820

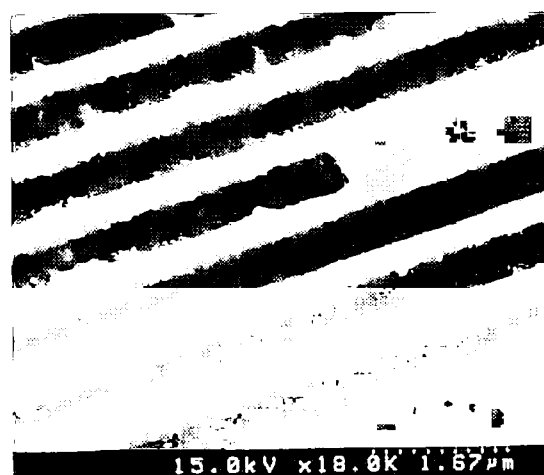
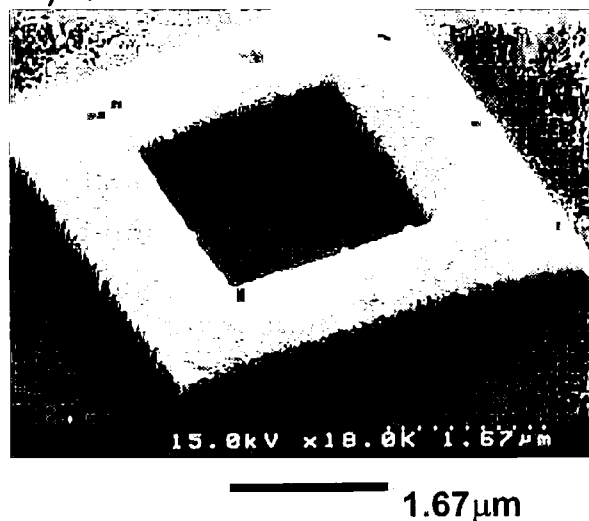


Fig. 5. Micrographs of $0.4\text{-}\mu\text{m}$ line & space pattern replicated by photo-induced solidification, where a) mold pattern and b) replicated pattern in liquid polymer.

a) Quartz Mold



b) Replicated pattern on TSR-820

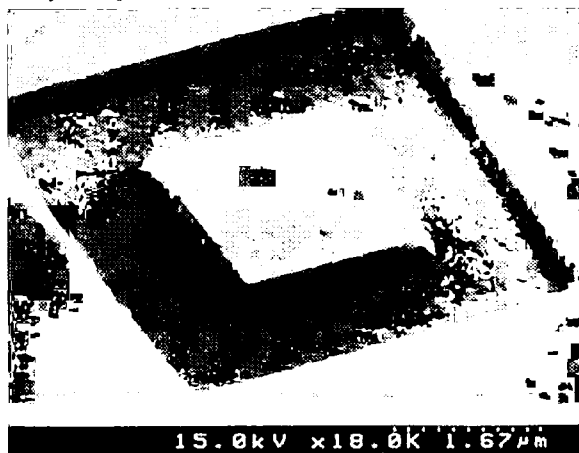


Fig. 6. Micrographs of $5\text{-}\mu\text{m}$ -square donut pattern replicated by photo-induced solidification, where a) mold pattern and b) replicated pattern in liquid polymer.

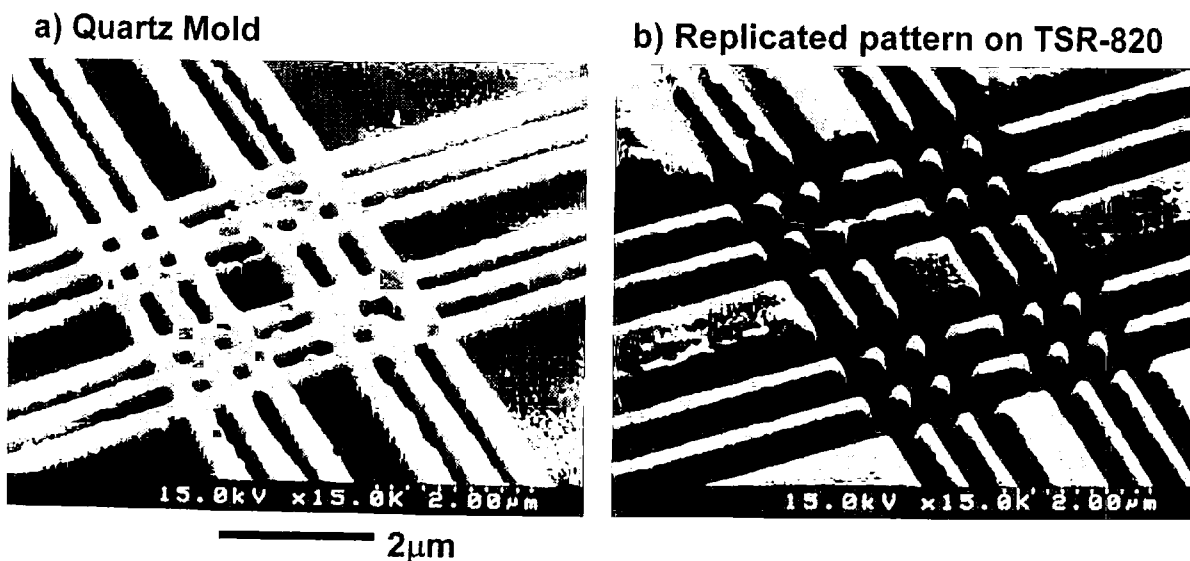


Fig. 7. Micrographs of line & space pattern with $0.6\text{-}\mu\text{m}$ periodicity and 200-nm -diameter dots replicated by photo-induced solidification.

we can see a similar surface roughness on the side wall. Figure 6 shows a $5\text{-}\mu\text{m}$ -square donut pattern and the replicated result with good fidelity indicates one of the evidences of good fluidity of the liquid polymer used here. A micrograph of a crossed area of the line-and-space patterns with $0.6\text{-}\mu\text{m}$ periodicity is illustrated in Fig. 7, where an approximately 200-nm -diameter dot pattern is replicated. These results clearly show that the replication with good fidelity is carried out at room temperature. The cross-sectional view of the replicated pattern shown in Fig. 8 where a part of the solidified film was stripped off in the release process between the mold and the slide glass, shows that an approximately $0.8\text{-}\mu\text{m}$ -thick polymer layer lying the line-and-space pattern still remains. Adopting higher pressure during the imprint process and thinner initial film thickness using liquid polymer with lower viscosity may decrease the underlying film thick-

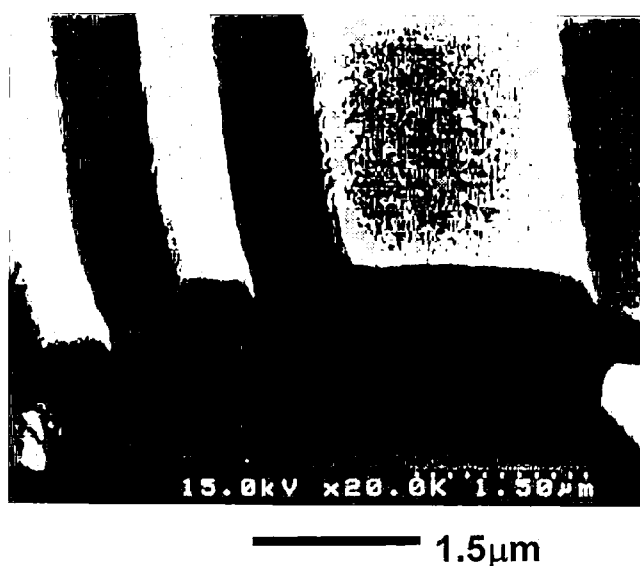


Fig. 8. Cross-sectional view of line & space pattern where a part of the solidified polymer layer was ripped away during the release process between the mold and the substrate.

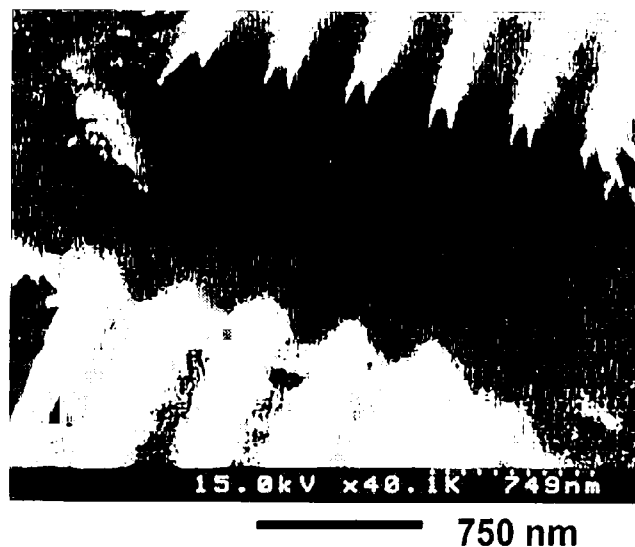


Fig. 9. The minimum feature size of 100-nm line and 300-nm space pattern obtained in this work.

ness. A large part of the solidified polymer still remains on the quartz mold in the present experiments, which means that the adhesive force between the solidified polymer and quartz mold may be stronger than that between the polymer and the slide glass. In order to avoid such an adhesion of the polymer to the quartz mold, surface treatment of the quartz mold that lowers the surface energy would be necessary. Figure 9 shows the 100-nm line and 300-nm space pattern which is the minimum feature size obtained in this experiment.

4. Conclusion

An imprint apparatus has been developed which allows us to illuminate ultra violet light onto the substrate through a quartz mold held on the sapphire block. By using a conventional thermal cycle in which the substrate and mold were heated up to the glass transition temperature of PMMA polymer, a sub-micrometer pattern is readily replicated. The liquid polymer used in this experiment showed the threshold UV

dose of about 10 J/cm^2 at which the solidified polymer was remained on the slide glass as a substrate. By increasing the UV dose, the remaining thickness was increased and saturated over the dose of about 100 J/cm^2 . Using this liquid polymer, several kinds of patterns could be replicated with very good fidelity. The minimum feature size obtained was a 100-nm line and 300-nm space pattern. It is known that the thick film layer under the fine structures still remained, but this layer may be improved by using high pressure during the imprint and small initial film thickness of the liquid polymer. The surface treatment of the quartz mold would be needed to decrease the adhesive force between the mold and the solidified polymer. In addition, the development of a photo-polymer suitable for semiconductor processes will be required in terms of wetting property to the Si wafer, dry-etching durability and low UV exposure dose.

Acknowledgements

We would like to thank TEIJIN SEIKI Co. for the supply of liquid polymer and KYOCERA Co. for the development of imprint apparatus.

- 1) S. Y. Chou, P. R. Krauss and P. J. Renstrom: *Appl. Phys. Lett.* **67** (1995) 3114.
- 2) S. Y. Chou, P. R. Krauss and P. J. Renstrom: *J. Vac. Sci. & Technol.* **B14** (1996) 4129.
- 3) S. L. Xiaoyun, W. Z. Zhuang and S. Y. Chou: *J. Vac. Sci. & Technol.* **B16** (1998) 3922.
- 4) L. Guo, P. R. Kraus and S. Y. Chou: *Appl. Phys. Lett.* **71** (1997) 1881.
- 5) P. R. Krauss and S. Y. Chou: *J. Vac. Sci. & Technol.* **B13** (1995) 2850.
- 6) Y. Zheoning, S. J. Schabitsky and S. Y. Chou: *Appl. Phys. Lett.* **74** (1999) 2381.
- 7) L. Mingtao, J. Wang and S. Y. Chou: *Appl. Phys. Lett.* **76** (2000) 673.
- 8) H. Tan, A. Gilbertson and S. Y. Chou: *J. Vac. Sci. & Technol.* **B16** (1998) 3926.
- 9) Y. Hirai, Y. Kanemaki, K. Murata and Y. Tanaka: *Jpn. J. Appl. Phys.* **38** (1999) 7272.
- 10) H. C. Scheer, H. Schulz, T. Hoffmann and C. M. S. Torres: *J. Vac. Sci. & Technol.* **B16** (1998) 3917.
- 11) B. Heidari, I. Maximov, E. L. Sarwe and L. Montelius: *J. Vac. Sci. & Technol.* **B17** (1999) 2961.
- 12) J. Haisma, M. Verheijen, K. van den Heuvel and J. van den Berg: *J. Vac. Sci. & Technol.* **B14** (1996) 4124.
- 13) M. Colburn, S. Johnson, M. Stewart, S. Damle, T. Bailey, B. Choi, M. Wedlake, T. Michaelson, S. V. Sreenivasan, J. Ekerdt and C. G. Willson: *Proc. Int. Soc. Opt. Eng.* **3676** (1999) 379.