Transfer Printing by use of Delayed UV Cure Resin for Fabricating Multilayer Structures

Takenori Yamamoto, Masaaki Yasuda, Yoshihiko Hirai, and Hiroaki Kawata*

*Physics and Electronics, Graduate School of Engineering,
Osaka Prefecture University, Sakai 599-8531, Japan
kawata@pe.osakafu-u.ac.jp

Two processes, the PVA (polyvinyl alcohol) /PET (polyethylene terephthalate) bilayer-film process and the delayed UV cure resin process, are proposed in order to improve the transfer printing process for multilayer structure fabrication. In the PVA/PET bilayer-film process, a commercial PVA/PET bilayer-film is used. The water soluble PVA pattern is used as the temporal mold for the PMMA pattern fabrication. Since the PVA temporal mold is dissolved in water, the demolding process, which often becomes serious issue for the transfer printing, can be eliminated. Although two layer structure by stacking PMMA films with 2 μm half pitch LS pattern can be fabricated by the thermal press bonding, the press conditions for the successful transfer is restricted. The delayed UV cure resin process is developed instead of the thermal press bonding. The delayed UV cure resin is used as the adhesive layer for the press bonding. Since its UV cure gradually proceeds after UV exposure, the press bonding can be started after the UV exposure. Two layer structure by stacking PMMA films with 2 μm half pitch LS pattern can be successfully fabricated by combination of the PVA/PET bilayer-film process and the delayed UV cure resin process.

Keywords: Transfer printing, Multilayer structure, Polyvinyl alcohol, Delayed UV cure

1. Introduction

Three dimensional multilayer structures with micro- and/or nano- air space patterns such as nano-channels can be used as micro fluidic devices [1] and micro electromechanical systems [2]. Although these devices can be fabricated by conventional IC processes [3], the fabrication process is often complicated, because the IC process is well defined for two dimensional pattern fabrication. The additive manufacturing processes are very powerful techniques for the fabrication of three dimensional structures [4,5]. However, their throughput and resolution may be insufficient.

Nano imprint lithography (NIL) is one of the most important techniques for nano pattern fabrication. Both micro- and nano-patterns can be fabricated at high resolution, high throughput, and low cost [6,7]. Nanochannels for fluidic devices has been also fabricated by NIL [8]. However, it is difficult to fabricate three dimensional structures by a conventional NIL process, because fine patterns are usually fabricated to a resin film on a flat substrate.

Huang et al. have developed reversal-imprint technique [9]. In reversal imprint, nano-patterns can be fabricated and two modes, inking and whole-transfer modes, are available. The reversal imprint is considered as the sophisticated transfer printing (TP) [10]. The process sequence of conventional TP is shown in Fig. 1. TP consists of two main processes, which are film coating ((a) and (b) of Fig.1) and film transfer ((c) and (d) of Fig. 1). A liquid resin is spin-coated on a patterned mold (Fig. 1(a)) and the patterned resin film is fabricated on the mold (Fig. 1(b)). The patterned resin film is pressed to the substrate and bonded to the substrate (Fig. 1(c)). After demolding, the patterned resin film is obtained on the substrate, that is, the patterned resin film is transferred to the substrate from the mold (Fig. 1(d)). Since the patterned films can be stacked from the bottom, three dimensional structures can be obtained by a relatively simple process [11-14]. However, TP process has the following serious issue. In the film coating process, the mold surface energy should be large in order to obtain good thin resin

Fig. 1. Process sequence of conventional transfer printing.

film. In the transfer process, low mold surface energy is required in order to avoid the pattern defects by large sticking force between the mold and the resin film (demolding problem). For satisfying these contradictory requirements, the control of the mold surface energy is very important [15].

When the mold is fabricated by water soluble resin such as polyvinyl alcohol (PVA), the mold can be dissolved in water instead of the demolding. Then, the demolding problem can be avoided. PVA film is often used as a temporal mold and/or a sacrificial layer [16-19]. In this paper, modified TP process is proposed by use of a commercial bilayer film of PVA/PET (polyethylene terephthalate) as a temporal mold and delayed UV cure resin as an adhesive layer. Multi-layer structures are also fabricated by the modified TP process.

2. Experimental

2.1. PVA/PET bilayer-film process

For preparation of water soluble PVA mold, the commercial PVA film laminated on PET film (SO sheet supplied by Aicello [20]) is used. The bilayer film is termed as PVA/PET in this paper. The thicknesses of PVA and PET films are 30 and 75 μm , respectively. The thin PVA film, whose mechanical strength is insufficient, is supported by the PET film. The PET film can be easily removed by hand. The schematic view of the TP process by use of PVA/PET is shown in Fig. 2. In this paper, Poly (methyl methacrylate) (PMMA, $M_w=350$ kg/mol)

resin is used as resin film. The PVA film of PVA/PET is patterned by T-NIL (Fig. 2(a)). The silicon mold is used for T-NIL. The mold has the line and space pattern (LS pattern) of which both the line width and height are 2 μm . The pressure and temperature are 10 MPa and 150 $^{\circ}\text{C}$, respectively. The PVA pattern is used as temporal mold for PMMA pattern fabrication. The PMMA resin is spin-coated on the patterned PVA film (Fig. 2(b)). When the PMMA resin is spin-coated on a flat Si wafer, its thickness is about 3 μm . The Si wafer with thin PMMA film of 200 nm thick is prepared as the substrate. The thin PMMA film on the substrate is required for the successful transfer process. The PMMA film on the temporal PVA mold is stuck to the substrate by the thermal bonding (Fig. 2(c)). The bonding conditions, where the bonding pressure, p_b , temperature, T_b , and bonding time, t_b , are varied in order to find good transfer conditions. The value of T_b is limited below 120 $^{\circ}\text{C}$ in order to avoid the pattern degradation of PVA and PMMA. After bonding, the PET film is peeled off from PVA/PET by hand. Then, the PVA film appears. The substrate is put into hot water of 75~80 $^{\circ}\text{C}$ in order to remove the temporal PVA mold (Fig. 2(d)). The PMMA pattern is fabricated on the Si substrate (Fig. 2(e)). By repeating this procedure, multilayer PMMA films with the LS pattern can be obtained. Then, capped microchannel is fabricated between the layer interfaces when the PT process is successfully

Fig. 2. Process sequence of PVA/PET bilayer-film process.

Fig. 3. Process sequence of delayed UV cure resin process.

carried out. The shape of the capped microchannel is important criterion for the estimation of TP process in our experiments.

2.2. Delayed UV cure resin process

When the stacking structures are fabricated by the thermal bonding, the control of the bonding pressure and temperature is very important. The lower layer patterns must be damaged when the bonding pressure and/or temperature are high. On the other hand, the patterned film bonding must be difficult when the bonding pressure and/or temperature are low. The process window for the successful bonding is usually narrow [13]. UV cure resin is often used as the adhesive layer for the transfer process [21,22]. Successful transfer can be achieved by relative low pressure at room temperature. However, the UV cure adhesive layer cannot be used when both the patterned film and the substrate are opaque. For example, patterned metal film cannot be transferred on Si substrate. In order to exclude the limitation, the process by use of commercial UV triggered command cure resin (SX-UV200 supplied by CEMEDINE Co. Ltd) is developed. The UV cure of this resin gradually proceed after UV exposure. Therefore, the film bonding can be started after the UV exposure. This unique resin is named as the delayed UV cure resin in this paper. Figure 3 shows the schematic view of TP process by use of the delayed UV cure resin adhesive layer. The PMMA film is fabricated on the patterned PVA/PET by the same processes as shown in Figs. 2(a) and (b). The delayed UV cure resin for the adhesive layer is prepared by adding 4 parts of butyl acetate to one part of the original SX-UV200 resin. When the delayed UV cure resin is spin-coated on a flat Si wafer, its thickness is about 1 μm . The delayed UV cure resin is spin-coated on the PMMA film (Fig. 3(a)). The UV light is exposed to the delayed UV cure resin (Fig. 3(b)). A commercial UV-O₃ surface treatment device (PL-160, SEN LIGHTS Corp.) is

used for the UV exposure, where a low pressure mercury lamp of 110 W is used. The exposure time is fixed for 1 min. The press is started after finishing the UV exposure. The time between the UV exposure finish and the press start is defined as the setting time t_{set} . The setting time is an important parameter in this process. The PMMA film is pressed to a Si substrate (Fig. 3(c)). The press conditions are defined by the bonding pressure, p_b , and bonding time, t_b . The bonding temperature, T_b , is fixed at the room temperature. The PET film of PVA/PET is peeled off by hand, and the substrate is put into hot water of 75~80 °C (Fig. 3(d)). The PMMA pattern is fabricated on the Si substrate (Fig. 3(e)).

3. Results and discussion

3.1. PVA/PET bilayer-film process

First, single layer PMMA film with the LS pattern is fabricated on the Si wafer with thin PMMA film. The bonding pressure and temperature are $p_b=4$ MPa and $T_b=90$ °C, respectively. The bonding time is fixed for $t_b=10$ min. A good LS pattern can be successfully obtained on the Si substrate. Next, the second layer of the patterned PMMA film is stacked on the first layer PMMA pattern. When the same

Fig. 4. Fabricated two layer PMMA pattern by use of PVA/PET bilayer-film process and hot press bonding.

Fig. 5. Mechanical property of delayed UV cure resin.

press conditions for the single layer transfer are used, the LS pattern in the first layer PMMA film is seriously damaged. The bonding time, t_b , is varied in order to reduce the damage of the LS pattern in the first layer. The fabricated PMMA patterns are shown in Fig. 4. The serious damage for the first layer LS pattern is observed even for $t_b=6$ min (Fig. 4(a)). On the other hand, LS patterns in both the first and second layers are successfully fabricated for $t_b=4$ min (Fig. 4(b)). A good capped microchannel is obtained. However, when the bonding time t_b is shortened to 2 min, the second layer PMMA film bonding is unsuccessful. It is clear that the successful transfer can be obtained only in the limited press conditions, that is, process window for the successful transfer is narrow. Note that the serious LS pattern damage is induced even when the bonding temperature is lower than the glass transition temperature of PMMA (110 ~ 120 °C) [23].

Fig. 6. Single layer PMMA pattern by delayed UV cure resin process.

3.2. Delayed UV cure resin process

The narrow process window for the thermal press bonding is caused by the LS pattern degradation in the first layer which is induced by the hot press for the second layer transfer. Therefore, it is considered that the damage must be reduced when the bonding process is carried out at the room temperature such as the delayed UV cure resin process. Since the mechanical property of the delayed UV cure resin is important, its mechanical property is measured by rheometer (Anton Parr, MCR-310). Figure 5 shows the relation between the elapse time after the UV exposure, τ_e , and the storage modulus, G . The hardness of the resin always increases as τ_e increases in the experimental range. The increasing rate of the resin hardness is relatively high for the short τ_e , and its rate gradually decreases as τ_e increases. Since the increasing rate of the resin hardness becomes small after $\tau_e=10$ min, the bonding time, t_b , is fixed for 10 min in our experiments.

First, single layer PMMA film with the LS pattern is fabricated on the Si wafer. No thin PMMA film on the Si wafer is necessary, because the delayed UV cure resin works as the adhesive layer. The setting time is $t_{set}=3$ min, and the bonding pressure is $p_b=10$ MPa. The fabricated PMMA pattern is shown in Fig. 6. The LS pattern can be fabricated on Si wafer although many particles are found because of poor sample handling. It is confirmed that the delayed UV cure resin works well for the patterned PMMA film transfer. Next, the second layer of the patterned PMMA film is fabricated on the PMMA pattern. Figure 7 shows the fabricated PMMA pattern, when the same transfer conditions for the single layer PMMA transfer ($t_{set}=3$ min, $p_b=10$ MPa) are used. The space of the LS pattern in the first

Fig. 7. Two layer PMMA pattern for $t_{set}=3$ min and $p_b=10$ MPa by delayed UV cure resin process.

Fig. 8. Two layer PMMA pattern for $t_{\text{set}}=3$ min and $p_b=5$ MPa by delayed UV cure resin process.

PMMA film is filled by the delayed UV cure resin and the capped microchannel cannot be obtained. Since the delayed UV cure resin is soft for the short elapse time as shown in Fig. 5, the soft resin pushed by the PMMA line flows into the space. The bonding pressure is decreased in order to reduce the resin flow. Figure 8 shows the fabricated PMMA pattern when the bonding pressure is decreased to 5 MPa by keeping $t_{\text{set}}=3$ min. The resin flow into the space of the first layer LS pattern is suppressed and the capped microchannel can be obtained. However, since the top of the microchannel is $0.6\ \mu\text{m}$ below the top of the PMMA line, the delayed UV cure resin penetrates into the space of the LS pattern. It is expected that the resin penetration into the space can be suppressed by decreasing the bonding pressure. However, it is difficult for us to reduce the bonding pressure because of the limitation of the used press machine. Therefore, the setting time, t_{set} , is changed instead of decreasing the bonding pressure. When t_{set} is increased, the resin hardness at the press start

Fig. 9. Two layer PMMA pattern for $t_{\text{set}}=6$ min and $p_b=5$ MPa by delayed UV cure resin process.

becomes large as shown in Fig. 5 and the resin penetration into the space must be suppressed. Figure 9 shows the fabricated PMMA pattern when the setting time is increased to $t_{\text{set}}=6$ min by keeping $p_b=5$ MPa. The capped microchannel is obtained and the delayed UV cure resin penetration can be reduced to $0.2\ \mu\text{m}$.

4. Conclusion

Two processes, the PVA/PET bilayer-film process and the delayed UV cure resin process, are proposed in order to improve the transfer printing (TP) process for multilayer structure fabrication. In the PVA/PET bilayer-film process, a commercial PVA/PET bilayer-film is used. The water soluble PVA pattern is fabricated by the thermal imprint process. The PVA pattern is used as the temporal mold for the PMMA pattern fabrication. Since the PVA temporal mold is dissolved in water, the demolding process, which often becomes serious issue for the TP process, can be eliminated. Moreover, the commercial PVA/PET film is used, the PVA pattern can be obtained only by Si mold press. Two layer structure by stacking PMMA films with $2\ \mu\text{m}$ half pitch LS pattern can be fabricated by the thermal press bonding. However, the process window for the thermal press bonding is narrow. Then, the delayed UV cure resin process is developed. The UV cure of this resin gradually proceeds, the press bonding after UV exposure is possible. Then, opaque film and mold can be used. Moreover, the resin hardness can be controlled by changing t_{set} . when the delayed UV cure resin is used. Two layer structure by stacking PMMA films with $2\ \mu\text{m}$ half pitch LS pattern can be successfully fabricated by combination of the PVA/PET bilayer-film process and the delayed UV cure resin process.

References

1. G. M. Whitesides, *Nature*, **442** (2006) 368.
2. J. W. Judy, *Smart Mater. Struct.*, **10** (2001) 1115.
3. Y. Xu, N. Matsumoto, Q. Wu, Y. Shimatani, and H. Kawata, *Lab Chip*, **15** (2015) 1989.
4. M. Vaezi, H. Seitz, and S. Yang, *Int. J. Adv. Manuf. Technol.*, **67** (2013) 1721.
5. S. Maruo, O. Nakamura, and S. Kawata, *Opt. Lett.*, **22** (1997) 132.
6. S. Y. Chou, P. R. Krauss, and P. J. Renstrom, *Appl. Phys. Lett.*, **67** (1995) 3114.
7. S. Y. Chou, P. R. Krauss, W. Zhang, L. Guo, and L. Zhuang, *J. Vac. Sci. Technol. B*, **15** (1997) 2897.
8. I. Fernandez-Cuesta, A. L. Palmarelli, X. Liang,

- J. Zhang, S. Dhuey, D. Olynick, and S. Cabrini, *J. Vac. Sci. Technol. B*, **29** (2011) 06F801.
9. X. D. Huang, L.-R. Bao, X. Cheng, L. J. Guo, S. W. Pang, and A. F. Yee, *J. Vac. Sci. Technol. B*, **20** (2002) 2872.
10. A. Carlson, A. M. Bowen, Y. Huang, R. G. Nuzzo, and J. A. Rogers, *Adv. Mater.*, **24** (2012) 5284.
11. A. Mata, E. J. Kim, C. A. Boehm, A. J. Fleischman, G. F. Muschler, and S. Roy, *Biomaterials*, **30** (2009) 4610.
12. H. Ooe, M. Morimatsu, T. Yoshikawa, H. Kawata, and Y. Hirai, *J. Vac. Sci. Technol. B*, **23** (2005) 375.
13. M. Nakajima, T. Yoshikawa, K. Sogo and Y. Hirai, *Microelectron. Eng.*, **83** (2006) 876.
14. K. Nagato, S. Sugimoto, T. Hamaguchi, and M. Nakao, *Microelectron. Eng.*, **87** (2010) 1543.
15. T.-H. Kim, A. Carlson, J.-H. Ahn, S. M. Won. S. Wang, Y. Huang, and J. A. Rogers, *Appl. Phys. Lett.*, **94** (2009) 113502.
16. C. D. Schaper and A. Miahnahri, *J. Vac. Sci. Technol. B*, **22** (2004) 3323.
17. C. D. Schaper, *Proc. SPIE*, **5374** (2004) 325.
18. K. Nakamatsu, K. Tonei, and S. Matsui, *Jpn. J. Appl. Phys.*, **44** (2005) 8186.
19. K.-S. Han, S.-H. Hong, J.-H. Jeong, and H. Lee, *Microelectron. Eng.*, **87**, (2010) 610.
20. AICELLO corporation, [http:// www. aicello. com/](http://www.aicello.com/).
21. Y. Hirai, T. Yoshikawa, M. Morimatsu, M. Nakajima, and H. Kawata, *Microelectron. Eng.*, **78-79** (2005) 641.
22. R. Wakamatsu and J. Taniguchi, *Microelectron. Eng.*, **123** (2014) 94.
23. Y. Hirai, T. Yoshikawa, N. Takagi, S. Yoshida, and K. Yamamoto, *J. Photopolym. Sci, Technol.*, **16** (2003) 615.