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Influence of master fabrication techniques on the characteristics of embossed microfluidic channels

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We describe protocols for the fabrication of microfluidic devices in plastics using a number of different embossing masters. Masters were fabricated by deep reactive ion etching (DRIE) of silicon (100), wet etching of silicon (100) and (110), and SU-8 processing. Structures embossed into a cyclo-olefin polymer were characterized in terms of the quality of pattern transfer as well as of the surface roughness. High quality pattern transfer was achieved with masters containing structures with angled sidewalls. Pattern distortions occurring during de-embossing were minimized by using masters consisting of SU-8 (which has a thermal expansion coefficient close to that of the substrates). Structures embossed with SU-8 masters also exhibited the lowest surface roughness. However, due to structural deformation, the reusability of the masters prepared for this study extended to only five embossing experiments. Masters fabricated on silicon, on the other hand, were more robust, but were subject to breakage during the de-embossing phase of the experiment. The results of this study will guide researchers in choosing master fabrication methods that will provide profile and surface characteristics of embossed microfluidic channels that are advantageous to their specific application.

Introduction

In this study, we compare the quality and characteristics of embossed microfluidic channels obtained with masters fabricated by DRIE in silicon (100), KOH wet etching in silicon (100) and (110), and SU-8 processing. These fabrication processes are commonly used to fabricate embossing masters.[1,2,3,4] They can be performed at low cost in standard semiconductor and MEMS fabrication facilities. Depending on the fabrication method, each master exhibits characteristic etch profiles as well as faceting and surface roughness. These characteristics influence the quality of pattern transfer during the embossing process and the characteristics of the embossed microfluidic devices.

In the past, several other master fabrication techniques have been employed. For the fabrication of simple, first generation devices, wire imprinting has been used. The resulting devices are limited in channel design but are readily produced at low cost.[5] More sophisticated master fabrication is achieved by utilizing electroplating of nickel or nickel alloys in processes such as LIGA (which includes synchrotron radiation lithography, galvanoforming, and plastic molding),[6,7,8] and DEEMO (which includes deep reactive ion etching of a silicon substrate, electroplating, and molding).[9] Although expensive, these approaches yield durable masters that can be used numerous times. On the other hand, silicon processing equipment is usually easier to access than high cost equipment such as synchrotron facilities.

After finishing the fabrication, researchers often apply chemical release agents to the master. These agents facilitate an easier separation of the master from the substrate after the embossing is completed.[10,11] However, release agents may transfer from the master to the polymer devices. In nano-biomedical applications, they should therefore be used with caution, because they can contaminate the samples.

In this study, we created masters with feature sizes ranging from 5 to 50 µm and aspect ratios of up to 4:1. Each of the employed fabrication methods yields a master with different sidewall angles, surface roughness, characteristic corners, and nm scale features. While silicon masters have a thermal expansion coefficient of about 2.6 ppm K^{-1},[12] that of SU-8 masters is 50 ppm K^{-1},[13] which is much closer to the values for plastic and polymer substrates (between 50 and 90 ppm K^{-1}).[6]

After optimizing the embossing parameters for polycarbonate, poly(methyl methacrylate) (PMMA), polystyrene, and poly(ethylene terephthalate glycol) (PETG), we performed the embossing under optimum conditions and evaluated the quality of pattern transfer. For this purpose, we took micrographs with SEM and AFM as well as surface profiles. Additionally, we evaluated the influence of the master's tone (negative or positive) by embossing with negative masters first and then reversing the images on the masters for the subsequent embossing experiments.

Good quality pattern transfer depends on accurate temperature and pressure control during the embossing process as well as on successful de-embossing. De-embossing, in turn, is influenced by the master characteristics that govern the interaction between the substrate and the master. For example, if a master has undercut sidewalls, it will deform the embossed features during de-embossing. Similarly, if the master and the substrate have significantly different thermal expansion coefficients, their different rates of contraction during the cooling phase will induce stress and thereby hamper the separation of master and substrate.

Besides the master's characteristics that influence the quality of pattern transfer, each fabrication method leaves micro- and nano-scale structures on the surface of the master. These structures are also imprinted into the plastic, becoming important variables in the application for which the devices are used. For example, in processes such as DNA or protein separation, rough channel surfaces may contribute to band broadening, thereby hampering low level detection. On the other hand, mixing of fluid can be achieved by modifying, with

slanted wells, the bottom of a channel.[14] Therefore, we must pay special attention to the surface characteristics of the master.

Experimental

(1) Master fabrication

Masters fabricated with deep reactive ion etching. Standard silicon (100) wafers were coated with positive resist (S1813, Shipley, Marlborough, MA) and patterned with standard contact lithography methods so that a negative image of the intended test structure was produced on the wafer. This image was transferred into silicon by etching with a protocol for deep etched structures on the Unaxis 770 (Unaxis USA Inc., St. Petersburg, FL). The final depth of the test structures was 17 µm. The die density on this master and on the masters fabricated using the following methods was 16 die per wafer, each die 10 × 12 mm in dimension.

Wet etched masters. A 200 nm low stress silicon nitride film (150 MPa) was deposited on silicon (100) and (110) wafers by low pressure chemical vapor deposition (LPCVD). The nitride film was patterned by contact g-line photolithography and dry etched using a Plasmatherm 72 (Unaxis USA Inc., St. Petersburg, FL) with CHF_3–O_2. The silicon was etched with a 50% KOH solution at 75 °C to a depth of 17 µm. To yield the desired anisotropic profile, the features were aligned to the crystal planes of the wafers by aligning the test pattern to the major wafer flat. The resulting profile was a v-groove with 54.7° angles in silicon (100) and 90° angles in silicon (110).

SU-8 masters. Masters in SU-8 were fabricated on silicon wafers by spinning NANO SU-8 photoepoxy (Microchem, Newton, MA) at a thickness of 17 µm onto the wafers. After baking the wafers for 2 min at 95 °C, the pattern was defined by proximity contact lithography followed by development with SU-8 developer (Microchem). During exposure to UV light the matrix of SU-8 is covalently cross-linked. The cross-linking is enhanced by post baking the wafers for 1.5 h at 170 °C. After this fabrication process, SU-8 exhibits glasslike mechanical properties, which makes it suitable as an embossing master.

(2) Embossing experiments

Embossing experiments were conducted using an EVG 250HE hot embosser (EV Group Inc., Cranston, RI). The polymer substrate, 4 inches square, and master, 4 inches in diameter, were positioned on the top and bottom chuck respectively. Both chucks were heated to the temperature that was established as the optimum embossing temperature for the particular substrate. Then master and substrate were pressed together *via* a piston that applied forces ranging from 0.5 kN to 40 kN to the sample stack. After 10 min, both bottom and top chuck were cooled down to the established de-embossing temperature. Then the force was released and master and substrate were manually separated.

(3) Characterization

The embossed structures were characterized by using a surface profiler (P10, KLA-Tencor Corp., San Jose, CA), atomic force microscopy (Digtal Instruments, Santa Barbara, CA), and scanning electron microscopy (LEO 982, LEO Electron Microscopy Inc., Thornwood, NY).

Results and discussion

Overall influence of temperature, force, and time

Successful embossing depends on accurate, timely control of the embossing temperature, the force with which substrate and master are pressed together, the length of time the force is applied, and the temperature at which de-embossing is initiated. The embossing and de-embossing temperatures depend strongly on the glass transition temperature of the substrate, which denotes the temperature at which the thermoplastic becomes soft and shapable.

In this study, we worked with plastics that are commonly used in biological and medical applications. Assuming that the embossing temperature has greater influence on the process than does the force with which the substrate and master are pressed together, we established optimum embossing and de-embossing temperatures for these plastics while keeping the force constant at 7 kN for 10 min (the force of 7 kN was established in a number of preliminary experiments in which forces ranging from 0.5 kN to 40 kN were tested). For these experiments, we used a master containing microfluidic channels at low die density, fabricated with the DRIE processes described above. The glass transition temperatures of polycarbonate, poly(methyl methacrylate) (PMMA), polystyrene, poly(ethylene terephthalate) glycol (PETG), and a cyclo-olefin polymer (Zeonor 1020R, Zeon Chemicals, Inc., Louisville, KY), and the optimum temperature values for embossing and de-embossing using these polymers, are summarized in Table 2. As a general rule, we found that the embossing should take place at 15 to 20 °C above the glass transition temperature and de-embossing at 10 °C below the glass transition temperature. However, because the glass transition temperatures of some substrates are given as a range of temperatures, the optimum embossing temperature needs to be established through experiments. Under optimum conditions, structures as shown in Fig. 1A were obtained. If the embossing temperature is too low, the flow of material is limited, resulting in structures shown in Fig. 1B. Furthermore, insufficient cooling results in a re-flow of material, whereas cooling to a temperature too low will result in deformation during the de-embossing process (see Fig. 1C).

The second important parameter to be controlled is pressure. In our experiments, we used the initially chosen force of 7 kN for the most successful embossings. If the pressure is too low, the material flow will be insufficient to fill the voids in the master, as shown in Fig. 1D. This figure shows a Zeonor substrate that was embossed with only 0.5 kN of force. If the pressure is too high, the master and substrate interact so strongly that de-embossing becomes difficult and masters that were fabricated in silicon break. In our experiments, we found that the embossing time is the least critical parameter. We usually successfully embossed if the force was held for 5 to 10 min.

Quality and characteristics of embossed microfluidic structures

Embossing with DRIE Master.

Quality of pattern transfer. To evaluate the quality of pattern transfer, we first performed embossing experiments under optimum temperature and pressure conditions using DRIE masters and Zeonor plastic sheets. Zeonor polymers are cyclo-olefin polymers that exhibit low outgassing properties when subjected to heat and vacuum. SEM micrographs, as well as profilometer measurements along the edges of the embossed structures, were taken. The micrographs in Fig. 2A and B show that the structures of the master, as well as its nearly vertical sidewalls, are replicated on the substrate. A magnification (50000X) of the substrate's sidewall shows that even the small

structures produced during the DRIE process on the sidewalls of the master are embossed.

However, substrate material often accumulated on the upper part of a sidewall on one side of the channels. This artifact could be due to plastic deformation that occurs during the separation of the master and the substrate. Because silicon and Zeonor have thermal expansion coefficients of 2.6 ppm K^{-1} and 70 ppm K^{-1} respectively, their rates of expansion and shrinkage during temperature shifts are different. To minimize artifacts caused by the difference in thermal properties, separation must take place when the plastic is no longer soft and deformable, but has not shrunk to a point where it mechanically interacts with the master due to contraction forces. The microstructures on the sidewalls may contribute to the accumulation of material on the top edge of the sidewalls by increasing the interaction between the master and the substrate, and pulling up material during de-embossing. Depositing a layer of Teflon or silicon dioxide may help smooth out the scalloping on the sidewalls of the DRIE master.

Surface roughness. The profiles obtained from surface roughness evaluation with AFM of the master and the embossed substrate are shown in Fig. 2D and E. The etched surface on the master had a mean surface roughness of 4.0 nm (see Table 1).

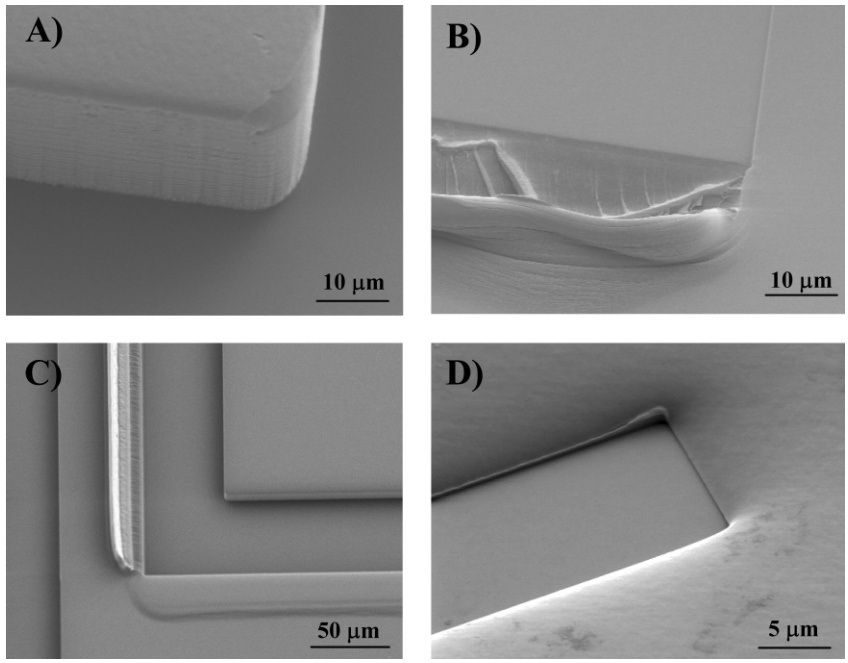

Fig. 1 SEM micrographs of sections of microfluidic channels embossed into Zeonor, using a DRIE template with 20 μm deep features. (A) The embossing was performed under optimum embossing temperature (120 °C), optimum pressure (7 kN), and optimum de-embossing temperature. (B) Embossing was performed at a temperature sub-optimum (pressure and de-embossing temperature were the same as in A). (C) De-embossing at a temperature sub-optimum caused accumulation of material at the lower portion and left top of the channel. (D) Embossing at pressures sub-optimum (0.2 kN) caused incomplete filling of the embossing master and therefore incompletely embossed channels.

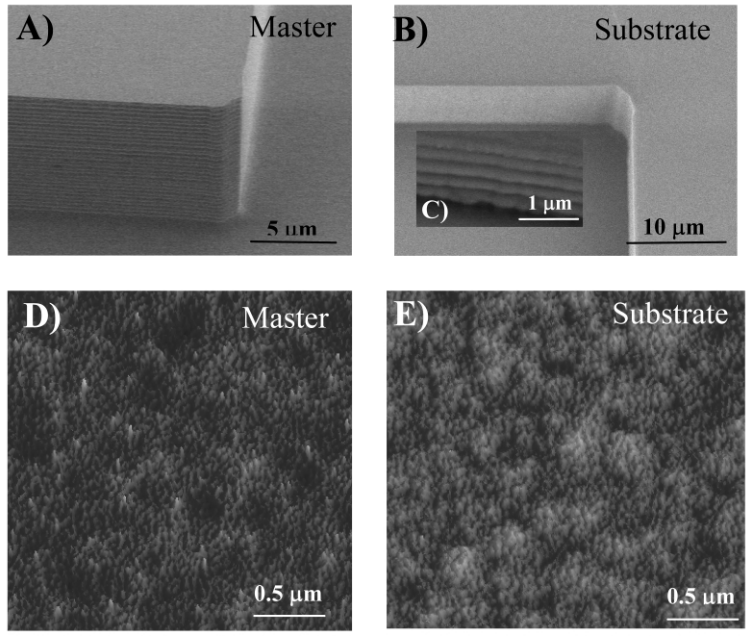

Fig. 2 SEM micrographs of a section of a DRI-etched silicon master (A) and the corresponding embossed structure on the substrate (B) (embossings were performed, under optimum conditions, into Zeonor). (C) shows a high magnification SEM micrograph of the sidewall of the structure shown in (B). AFM micrographs of the same silicon master and the corresponding embossed structures on the substrate are shown in (D) and (E) (2.5 × 2.5 μm sections shown).

Nearly the same value was obtained from the embossed structures (3.1 nm). These data provide further evidence that nm scale features on the master are completely embossed into the plastic. Table 1 summarizes the mean roughness values for all masters and substrates used in this study.

Reusability. Masters fabricated with DRIE could be used numerous times for embossing; however they were subject to breakage, especially if the de-embossing temperature was not optimized. On the masters, the structures themselves were stable and were not damaged during the embossing.

Embossing with wet etched masters.

Quality of pattern transfer. Fabricating masters by etching silicon (110) with 50% KOH solution yields smooth, 90° sidewalls if the pattern is aligned to the crystal planes of the silicon. SEM micrographs of the master and the embossed substrate are shown in Fig. 3A and B. All microstructures were faithfully replicated on the substrate. However, even though this master had smoother sidewalls than the DRIE masters, step profiles prove that accumulation of material on the top edge of some sidewalls still occurs to some degree, but to a lesser extent than as seen with the DRIE master. Furthermore, the KOH master contains artifacts such as faceting and a structured surface at the bottom of the etched feature, which also embossed into the substrate.

Fabricating masters by KOH etching of silicon (100) yielded masters with 54.7° angled sidewalls (Fig. 4A and C). Embossing with these masters led to features that did not exhibit accumulated substrate material on the top edges (Fig. 4B and D). The sloped sidewalls of these masters apparently minimize this effect. However, wet etching silicon (100) produces irregularly shaped outside corners on the master.

Surface roughness. Because of faceting at the etched surfaces, wet etched silicon (110) masters exhibited the highest surface roughness observed in this study (see Table 1). Surface roughness profiles of the master and the embossed substrate are shown in Fig. 3C and D. On the other hand, wet etched silicon (100) masters exhibited low surface roughness when measured on the microscale of 5 × 5 μm square area (see Table 1 and Fig. 4E and F).

Reusability. The reusability of wet etched masters was comparable to that of masters fabricated with DRIE. However,

Table 1 Mean surface roughness of masters and embossed substrates measured with Atomic Force Microscopy at an area 5 × 5 μm in size [DRIE, KOH etched silicon (100), and SU-8], and 20 × 20 μm in size [KOH etched silicon (110)]

	Master	Substrate
DRIE	4.0 nm	3.1 nm
KOH (110)	76.6 nm	68.3 nm
KOH (100)	1.0 nm	1.5 nm
SU-8	0.5 nm	0.7 nm

Table 2 Coefficients of thermal expansion, glass transition temperatures and optimum embossing and de-embossing temperatures for commonly used plastics

Substrate	Coefficient of thermal expansion/ ppm K^{-1}	Glass transition temperature/°C	Embossing temperature/°C	De-embossing temperature/°C
Zeonor 1020 R	70	100	120	90
polycarbonate	49.7	143–150	160	140
PMMA	55	100–105	120	90
PETG	51	79–80	95	70
polystyrene	56.7	83–100	120	90

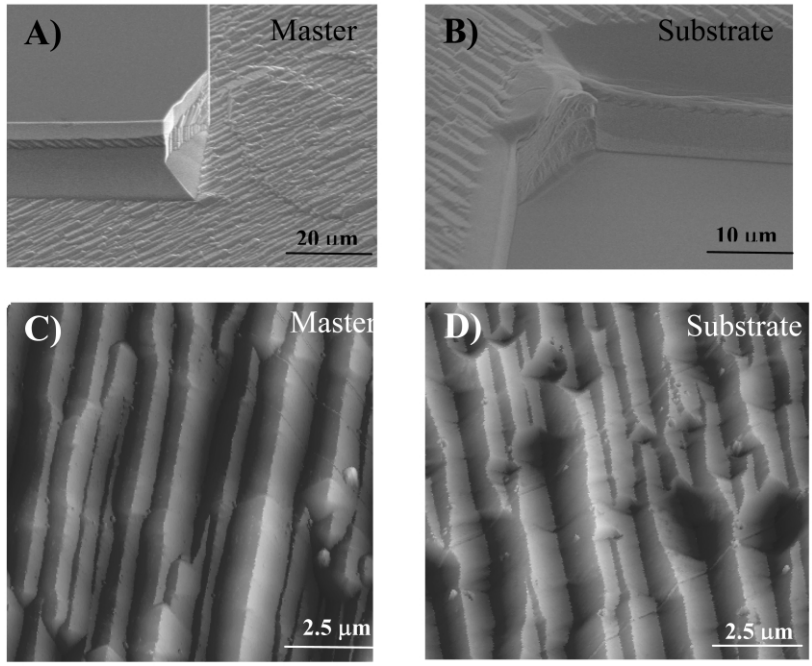

Fig. 3 SEM micrographs of a section of a wet-etched silicon (110) master (A) and the corresponding embossed structure on the substrate (B) (embossings under optimum conditions, into Zeonor), and AFM micrographs of the same silicon master (C) and the corresponding embossed structures on the substrate (D) (10 × 10 μm sections are shown).

masters with angled sidewalls were subject to less breakage than were masters with straight sidewalls. This indicates that thermal expansion plays a role in the stability of masters, since one can assume that the interaction of master and substrate is easier to overcome during de-embossing when the master's sidewalls are positively sloped.

Embossing with SU-8 Masters.

Quality of pattern transfer. Embossing with SU-8 masters led to slightly different feature characteristics than embossing with DRIE and KOH masters (see Fig. 5A and B). The sidewalls on the SU-8 masters are sloped at an angle of approximately 70° (step profile not shown). Fig. 5A shows a typical corner of the SU-8 master. The embossed structures did not exhibit accumulation of substrate material on the top edges of the microchannels. This suggests that a slightly positively sloped sidewall already eases the deformation of substrate occurring during de-embossing. Additionally, SU-8 has a thermal expansion coefficient of 52 ppm K^{-1}, which is close to that of the substrate. Therefore, during the cooldown phase, the master and substrate shrink at a similar rate, and the resulting stress is less than the stress occurring during the cooldown of a silicon/substrate stack. Another advantage of SU-8 masters is the ease with which they can be fabricated in standard laboratories and non-clean room environments. By adjusting the exposure dosage during the fabrication, the slope on the SU-8 masters can be controlled.

Surface roughness. The surfaces of SU-8 masters and the embossed substrate were by comparison with the surfaces on silicon masters and the corresponding embossed substrates the smoothest (see Table 1). Surface roughness profiles of the master and the substrate are shown in Fig. 5C and D.

Reusability. Throughout this study, SU-8 masters were the most stable in terms of breakage. We used these masters more than ten times. However, after about five embossing experiments, the SU-8 structures started to show slight damage due to mechanical forces acting on the SU-8.

Influence of stamp geometries. Stamp geometries and stamp design considerably affect the quality of the embossed features. For example, when embossing features that are smaller than 20 µm, it is easier to emboss high aspect ratio features with masters containing negative patterns rather than positive patterns (see Fig. 6A and B). The flow behavior of the substrate during the embossing and the processes occurring during de-embossing cause this effect. First, filling voids in a negative stamp with substrate material is easier than dislocating material by a positive stamp.[1] Second, because de-embossing usually occurs on one side of the wafer first, high aspect ratio features on a positive stamp dislocate substrate in the direction in which the de-embossing occurs last. Therefore, high aspect ratio features are embossed with higher quality and less pattern distortion when using a negative master. Even though large negative patterns are sometimes not completely filled with substrate, the pattern is less distorted than when using a positive stamp. However, the difference between negative and positive masters becomes less prominent when feature sizes are increased to 20 and 50 µm (see Fig. 7).

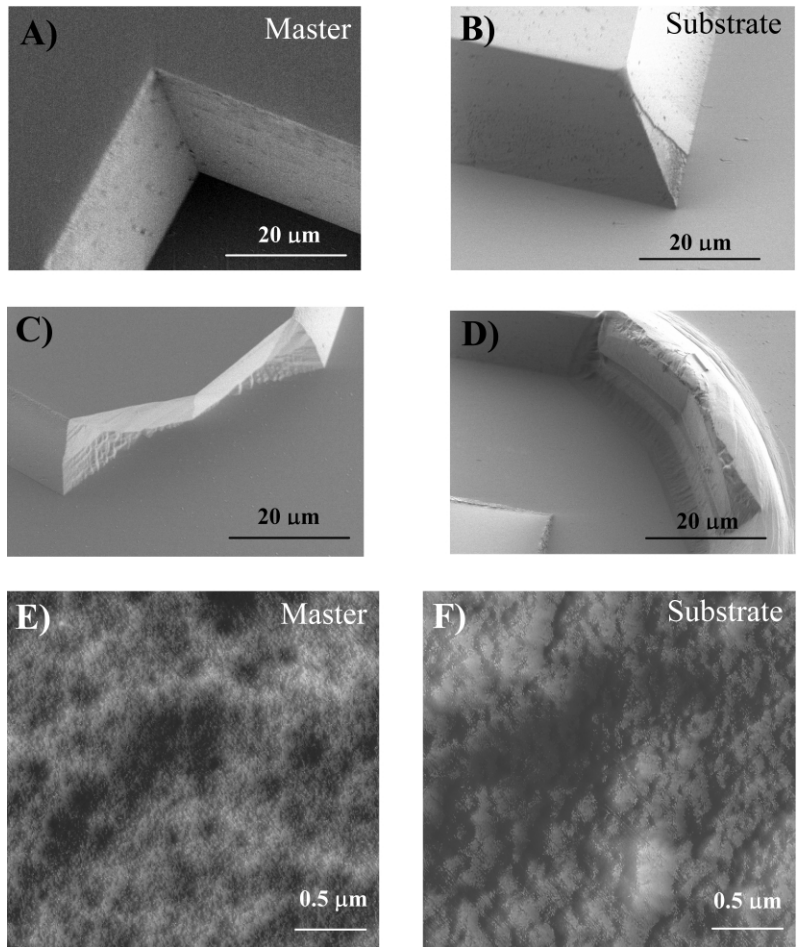

Fig. 4 SEM micrographs of sections of a wet-etched silicon (100) master (A, inside corner; C, outside corner) and the corresponding embossed structure on the substrate (B, inside corner; D, outside corner) (embossings were performed, under optimum conditions, into Zeonor), and AFM micrographs of the same silicon master (E) and the corresponding embossed structures on the substrate (F) (2.5 × 2.5 µm sections are shown).

Finally, the higher the die density on the master, the more difficult the de-embossing becomes. Masters containing only a single die fractured less often than masters containing the full set of 16 die.

Conclusion

The results from this study indicate that artifacts induced by the de-embossing process can be reduced by angling the sidewalls of the master, especially for high aspect ratio structures, and by choosing a master material with a thermal expansion coefficient close to that of the substrate. Furthermore, the fabrication method for the master should be chosen so that nm size features on the masters and corner profiles do not interfere with the goals of the application. For example, if sharp separation bands are required, a template with smooth surfaces should be chosen, whereas for mixing applications the roughness of a wet etched surface may be an advantage. All of the masters used in this study are easy to fabricate in standard semiconductor/MEMS processing facilities. However, masters created with these methods are susceptible to breakage. For more durable masters, other methods should be considered; for example, nickel LIGA

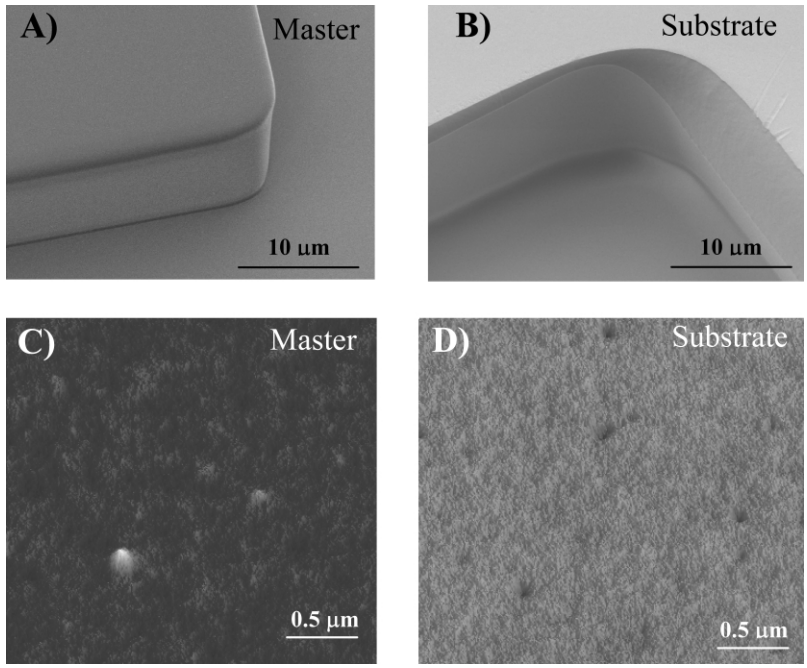

Fig. 5 SEM micrographs of a section of an SU-8 master (A) and the corresponding embossed structure on the substrate (B) (embossings were performed, under optimum conditions, into Zeonor), and AFM micrographs of the same SU-8 master (C) and the corresponding embossed structures on the substrate (D) (2.5 × 2.5 µm sections shown).

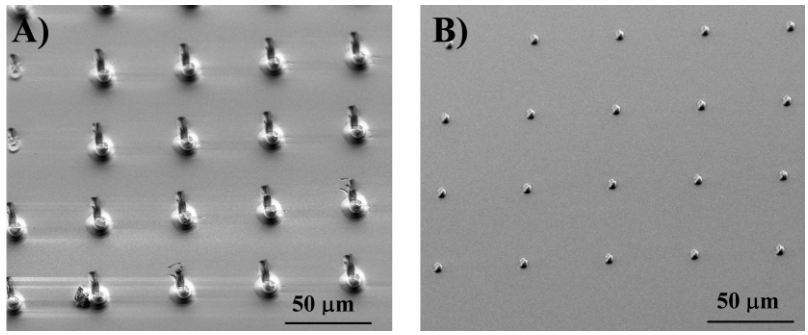

Fig. 6 SEM micrograph of 5 × 5 µm squares on a Zeonor substrate embossed, under optimum conditions, with a positive (A) and negative master (B).

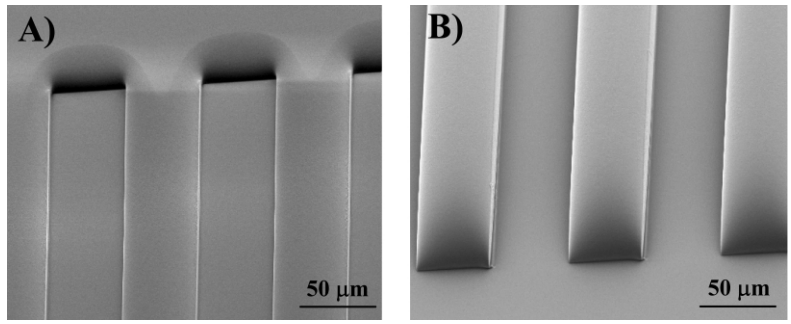

Fig. 7 SEM micrographs of a Zeonor substrate embossed, under optimum conditions, with a positive (A) and negative pattern (B) containing 50 µm lines separated by 50 µm gaps.

will yield more stable masters. The longevity of the masters discussed here can be increased by backing them with permanently attached glass wafers. When designing a master, the pattern should be adjusted so that it satisfies the requirements of a negative stamp, especially for small feature sizes. For masters with high die density, it is advisable to use antistiction layers as suggested in other publications.[10,11]

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