NANO-MICRO LETTERS
Vol. 2, No. 3
197-203 (2010)

Reducing SU-8 hygroscopic swelling by ultrasonic treatment

Du Liqun[1, 2,*], Zhang Benzhuang[2] and Liu Yaping[2]

The volume expansion of SU-8 resist brings serious dimensional errors to electroformed structures. Two approaches have been proposed to reduce resist distortions during electroforming: electroforming at room temperature and adding auxiliary features for mask patterns. However, the former method induces higher internal stresses in the electroformed metal layers. And the latter method makes it difficult to predict the expansion behaviors of the resists. In the paper, the thermal expansion of the SU-8 mould is calculated by ANSYS firstly, and the lower thermal expansion value indicates that hygroscopic swelling plays a leading role in SU-8 mould distortions. An original technique is presented to reduce SU-8 hygroscopic swelling by ultrasonic treatment. The dimensional errors of the electroformed structure fabricated on the ultrasonic treatment mould are 50% lower than the one without ultrasonic treatment. Simulation of hygroscopic swelling is conducted by finite element analysis, and the results indicate that the hygroscopic strain *ε* of SU-8 after electroforming is declined from 6.8% to 3.1% because of ultrasonic. The measurements show that ultrasonic treatment increased the water contact angle of cured SU-8 from 70.8° to 74.9°. Based on these results, the mechanism of ultrasonic effect on hygroscopic swelling is proposed from the view of ultrasonic vibration decreasing the number of hydroxyl groups in SU-8. The research presents a novel method to improve the precisions of electroformed structures. It has no influence on the internal stresses of final structures and does not increase the complexities of mask layouts.

Keywords: SU-8; Hygroscopic swelling; Electroform; Ultrasonic; Hydrophilicity

Citation: Du Liqun, Zhang Benzhuang and Liu Yaping, "Reducing SU-8 hygroscopic swelling by ultrasonic treatment", Nano-Micro Lett. 2, 197-203 (2010). doi: 10.5101/nml.v2i3.p197-203

SU-8 resist has become a prevalent mould material to electroform MEMS devices because of its mechanical and chemical stability and its ability to produce high-aspect-ratio moulds by UV-LIGA technology [1,2]. However, electroforming processes based on SU-8 mould still face serious challenges. It is well known that the dimensions of electroformed structures are usually shrunk compared with the masks. This is mainly due to SU-8 mould distortions caused by thermal expansion and hygroscopic swelling during electroforming [3]. The relative dimensional errors of electroformed structures may reach 23% [4], which are unacceptable in practical applications, and the tapered structures cannot be corrected using a scaled or biased mask pattern. Furthermore, resist displacements will limit the maximum producible aspect ratio of a metal structure when the cavity of the mould will close at the top under the worst conditions [5].

Some works have been published to analyze PMMA swelling during electroforming. Two approaches have been proposed to reduce PMMA swelling. (i) Electroform at room temperature since the lower temperature may decelerate the solvent molecules diffusing rate throughout the resist thickness [6]. However, lower electroforming temperature induces higher internal stress in electroformed metal layer [7]. (ii) Improve the layout design of masks: auxiliary structures are introduced to

[1]Key Laboratory for Micro/Nano Technology and System of Liaoning Province, Dalian University of Technology, Dalian 116024, China
[2]Key Laboratory for Precision & Non-traditional Machining Technology of Ministry of Education, Dalian University of Technology, Dalian 116024, China
*Corresponding author. E-mail: duliqun@dlut.edu.cn

form trenches around the part in PMMA [8,9]. Then, the mass of the resist that swells is reduced. While auxiliary features can dramatically decrease tapers for linear structures, they increase skew for curved structures in some cases [5]. Additionally, complicated geometries pose a challenge for designing auxiliary features because the features must follow the perimeter of the part uniformly. Complex non uniform geometries of the auxiliary structures make it difficult to predict the expansion behaviors of the resists [10].

The above two methods are applicable to the processing based on SU-8, but apparently the same problems exist. Compared with PMMA, the number of publications on SU-8 swelling is very limited. Experimental and simulative studies have been taken on the thermal swelling of SU-8 [3]. And the influences of different post-exposure bake (PEB) temperatures on the thermal swelling of SU-8 were investigated [4]. However, as far as we know, no effective method which is independent of processing parameter and mask pattern has been proposed to reduce SU-8 hygroscopic swelling during electroforming.

In this paper, a novel research for the effect of ultrasonic treatment on SU-8 swelling is presented. The ultrasonic treatment was introduced to the electroformed Ni-structure fabricating process. And the dimensional errors of electroformed structures fabricated with and without ultrasonic treatment were measured respectively. The experimental results are presented and the mechanism of ultrasonic effect on SU-8 swelling is discussed.

SU-8 mould distortions

SU-8 mould distortions during electroforming

Electroformed structures based on resist moulds exhibit large dimensional errors. These errors result from thermal expansion and hygroscopic swelling of the resist since electroforming is performed in aqueous electrolyte at an elevated temperature [5,6].

Figure 1 shows the distortions of SU-8 mould during

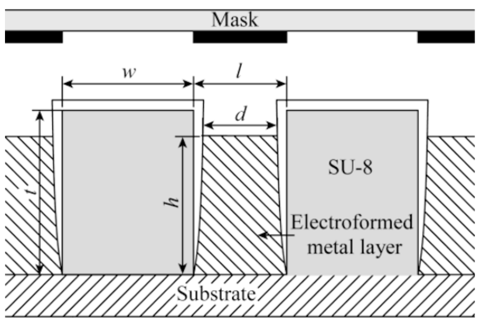

FIG. 1. Schematic of SU-8 mould distortions due to volume expansion of SU-8.

electroforming, with *t* and *w* respectively the initial thickness and width of SU-8 film, *l* the initial width of cavity in SU-8 mould, *h* and *d* respectively the height and top width of electroformed layer. Because SU-8 is confined by a rigid substrate, the distortions at the substrate interface are nearly zero. Under this condition, the top of the SU-8 structures becomes wider than the bottom, which produces a tapered metal structure with narrower top widths.

Thermal expansion

It is useful to find out which factor, thermal expansion or hygroscopic swelling, is the most important reason for SU-8 mould distortions. Thus, finite element analysis was taken by ANSYS to calculate the sole effect of thermal expansion in the total dimensional errors. For the long linear three-dimensional structure as shown in Fig. 2a, plane model (cross section with width w = 400 μm, thickness t = 56.2 μm, as shown in Fig. 2b) can be employed as an approximation to calculate the sidewall distortion. In view that the resist is confined by a substrate, zero displacement is applied on the bottom surface, and all other boundaries are free surfaces. The thermal expansion coefficient (CET) of SU-8 is 52 ppm/℃; Young's modulus is 4.02 GPa; Poission's ratio is 0.22. The temperature load is 26℃ (from room temperature 24℃ to electroforming temperature 50℃).

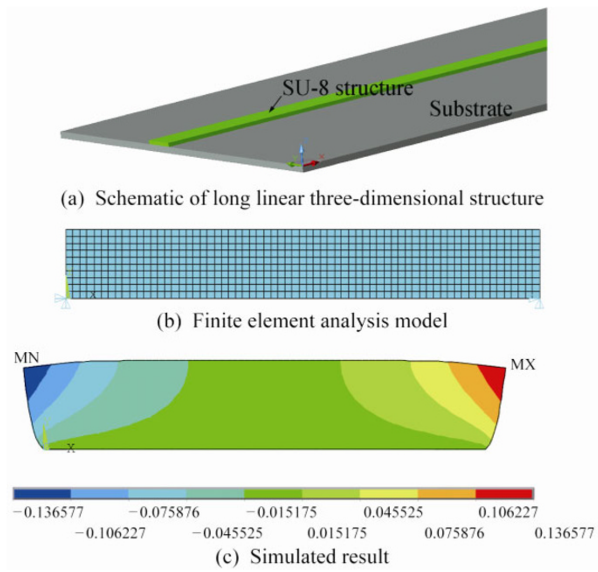

FIG. 2. Simulating of SU-8 thermal expansion.

The simulated result is shown in Fig. 2c. It is known that the top width of SU-8 only increases by 0.27 μm due to thermal expansion. In fact, moisture and thermal diffusion are two interactive processes. When the polymer absorbs external molecules its CET always changes. For SU-8, the value of CET will reduce after absorbing water molecules [11]. Thereby, the practical thermal expansion value will be smaller than 0.27 μm. On the other hand, the experimental total width increases more than 9 μm (will be shown in Fig. 6, measuring point 1). The analysis results indicate that the dimensional error produced by thermal expansion is less than 3% in the total error.

Hygroscopic swelling

From above analysis, it is known that swelling is the predominant reason for SU-8 mould distortions. The mechanism of moisture diffusion in epoxy has been widely studied. And it has been proved that the hydroxyl groups of epoxy resins play the leading role in moisture uptake process, where water molecules can form strong hydrogen bounds [12,13]. In general, each SU-8 monomer molecule contains eight reactive epoxy groups, and therefore high degree of cross linking can be obtained and form three-dimensional network after photo-thermal activation. During cross linking reaction, hydroxyl groups generated. Hydroxyl groups have significant affinity to polar molecules such as water. Consequently, SU-8 could absorb a lot of water when exposed to aqueous surroundings, which causes swelling.

The water absorption process of epoxy can generally be expressed by Fick's law [14],

$$\frac{\partial C}{\partial \tau} = D\left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2}\right) \tag{1}$$

Where C is the concentration of water; τ is time; D is water diffusion coefficient; and x, y and z are axes along the concentration gradient.

D varies with temperature, and can be described by the classic Arrhenius function [15],

$$D = D_0 \exp\left(\frac{-E_D}{RT}\right) \tag{2}$$

Where D_0 is a constant; E_D is the activation energy for diffusion; R and T represent the ideal gas constant and absolute temperature respectively.

The volume expansion with respect to the moisture content has been found to be linear to a good approximation for SU-8 [16]. Therefore, the hygroscopic strain ε induced by swelling can be related to the concentration of water according to

$$\varepsilon = \beta C \tag{3}$$

Where β stands for the coefficient of hygroscopic swelling (CHS). ε is a function of time. At a constant temperature, ε will increase up to a maximum value with stretched time.

Experiments

Processes to fabricate metal microstructures

SU-8 2015 (MicroChem Crop.) and mirror-polished Ni substrates were used in this study.

The detailed UV-LIGA processes to fabricate metal microstructures are as follows:

1) Ultrasonic wash Ni substrate for 20 min in acetone and ethanol in sequence, and then dry it after flushing with deionized water.
2) Spin coat SU-8 2015 for 18 s at 800 rpm to produce a film of approximately 60 μm thick, and then self-planarize on a level surface for 30 min.
3) Soft bake for 40 min at 65℃ followed by 40 min at 85℃, and then slow cool to room temperature.
4) Expose for 5 min, hard contact. The exposure dose is 400 mJ/cm^2.
5) Post-exposure bake for 1.5 min at 85℃, and then slowly cool to room temperature.
6) Develop for 5.5 min in SU-8 developer (MicroChem Crop.).
7) Electroform for 6.5 h at 50℃. The detailed parameters are presented in Table 1.

Table 1. Compositions of electroforming solution and process conditions

Composition		Operational condition	
$Ni(NH_2SO_3)_2 \cdot 4H_20$	550 g/L	pH	3.8~4.5
$NiCl_2 \cdot 6H_20$	10 g/L	Temperature	50℃
H_3B0_3	35 g/L	Current density	0.5~2 A/dm^2
Wetting agent	0.1~0.15 g/L	Cathode agitation speed	75 mm/s

Ultrasonic treatment

Ultrasonic treatment was performed by a self-designed ultrasonic device as shown in Fig. 3. Its vibrating frequency is 20 kHz. When the uncrosslinked regions of the resists disappear after development, SU-8 moulds become easily damaged. Therefore the ultrasonic processing was carried out before rather than after development. After PEB, the SU-8 coated Ni-substrates were bolt fixed on the worktable, and then the ultrasonic energy was imposed to the SU-8 resist for 10min at the constant input power (125 W).

Dimension measurements of SU-8 moulds and electroformed Ni-structures

In order to distinguish the different effects of ultrasonic treatment on the mould distortions before electroforming and the swelling during electroforming, the top dimensions of SU-8

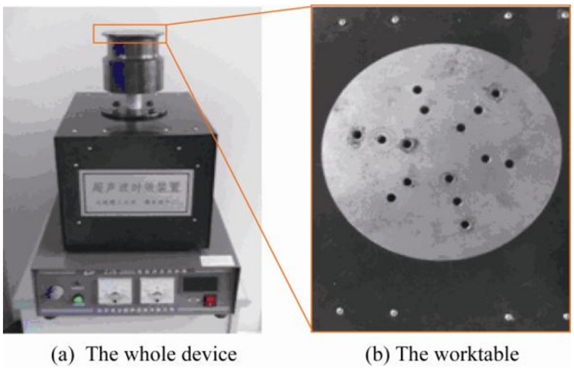

FIG. 3. Ultrasonic device

moulds were measured by stereomicroscope after development. After electroforming, the electroformed samples were manual polished until preconcerted heights (measured by inductance micrometer) were achieved. And then the lateral dimensions of Ni-structures corresponding to these heights were measured by stereomicroscope.

Results and discussion

Ultrasonic effect on development process

Figure 4 shows the photo mask used in the study. Three kinds of characteristic positions, according to different resist geometry around them, are chosen to be measuring points, and 1, 2, 3 are the serial numbers of them. The widths of all measuring points in mask are 400 μm.

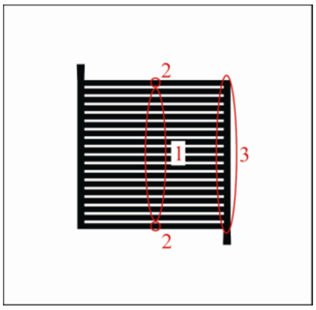

FIG. 4. The mask and measuring points

Table 2 summarizes the results of dimension measurements for SU-8 moulds before electroforming, where l means the width of cavity in SU-8 mould (shown in Fig.1), and the subscripts, “unultrasonic” and “ultrasonic”, stand for the samples fabricated by the conventional method described in section 3.1 without ultrasonic treatment and the experimental samples which were subjected to ultrasonic treatment, respectively.

Compared with the mask, the dimensions of the resist moulds are slightly shrunk. This is expected to be a combined effect of diffraction during exposure [17] and swelling due to absorbing developer during development [18]. For the same measuring points of the non ultrasonic and the ultrasonic samples in Table 2, the widths of the cavities in SU-8 moulds are almost identical. This phenomenon reveals that ultrasonic treatment has little influence on the subsequent development process.

Table 2. The widths of cavities in SU-8 moulds before electroforming

Measuring point	1	2	3
$l_{unultrasonic}$ (μm)	398.5	398.1	397.5
$l_{ultrasonic}$ (μm)	398.6	398.1	397.7

Ultrasonic effect on electroforming process

Figure 5 shows local photos of an electroformed Ni-structure and the measuring points correspond to Fig. 4 are marked. The bright area in Fig. 5 is electroformed Ni-layer while the dark area is SU-8.

The dimensional errors for both non ultrasonic and ultrasonic Ni-structures are shown in Fig. 6, where the numbers in the data labels correspond to the different measuring points (shown in Fig. 4 or Fig. 5). In ordinate, dimensional error $\delta= l\text{-}d$, where d is the width of electroformed metal structure (shown in Fig. 1).

Figure 6 clearly demonstrates that the swelling values greatly diminish when SU-8 is subjected to ultrasonic. In addition, it is visible that the larger the SU-8 mass around

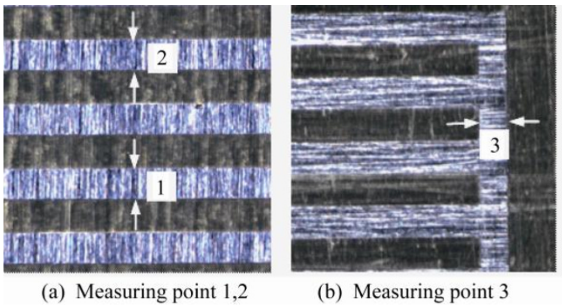

FIG. 5. Local photos of an electroformed Ni-structure.

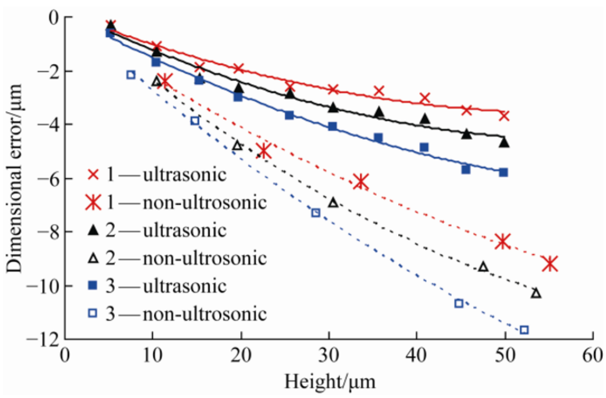

FIG. 6. Dimensional errors of electroformed Ni-structures compared with SU-8 moulds.

measuring points is, the greater the dimensional errors will be. In order to deeply illustrate the considerable effect of ultrasonic treatment on SU-8 swelling, the electroformed structure dimensional errors at 50μm height in the fitting curves (shown in Fig. 6) are listed in Table 3, where $\delta_{unultrasonic}$ and $\delta_{ultrasonic}$ are the dimensional errors of unultrasonic and ultrasonic samples respectively, and error decreasing: $\alpha=(\delta_{unultrasonic}-\delta_{ultrasonic})/\delta_{unultrasonic}$.

Table 3. The dimensional errors of electroformed Ni-structures

Measuring point	1	2	3
$\delta_{unultrasonic}$ (μm)	-8.3	-9.7	-11.4
$\delta_{ultrasonic}$ (μm)	-3.4	-4.4	-5.6
α (%)	59.0	54.6	50.9

Take measuring point 1 for example, ultrasonic treatment decreases the dimensional error of Ni-structure by 59.0%. This is a significant improvement to a MEMS device which always requires higher dimensional accuracy.

Simulation

If SU-8 is a simply freestanding film, and if the hygroscopic strain ε in SU-8 is uniform and isotropic, then all of the dimensions would simply grow by the magnitude of ε when SU-8 expands. However, the situations become complicated since the resist is bonded to a rigid substrate. Therefore, ANSYS was adopted to calculate the hygroscopic strain ω_y along the direction perpendicular to the substrate surface under a certain hygroscopic strain ε, as shown in Fig. 7, where t_0 is the initial thickness of SU-8 film; Δt is increased value of thickness due to swelling; $\omega_y=\Delta t/t_0$. The physical properties of SU-8 used in this model are introduced in section 2.2.

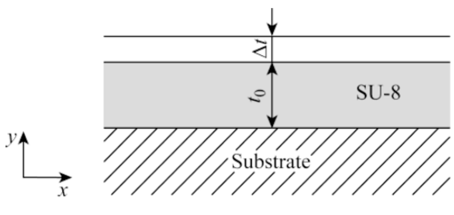

FIG. 7. Schematic of plane sheet model swelling.

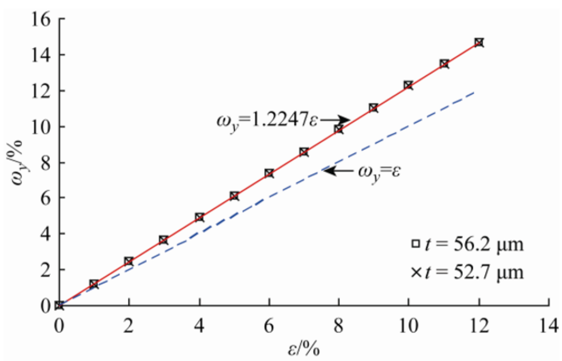

FIG. 8. Relationship between ω_y and ε.

Finite element analysis reveals the relationship between ω_y and hygroscopic strain ε of SU-8. The results are exhibited in Fig. 8.

For the large plane sheet sample which is confined by a substrate, the hygroscopic strain along the direction perpendicular to the substrate is

$$\omega_y = 1.2247\varepsilon \tag{4}$$

for both t_0=56.2 μm (for non-ultrasonic sample) and t_0=52.7 μm (for ultrasonic sample). When the resist is freestanding, $\omega_y=\varepsilon$, as shown in Fig. 8.

During experiment, the thicknesses of SU-8 resist have been measured as soon as electroforming finished, Δt =4.7 μm for non ultrasonic sample and Δt =2.0 μm for ultrasonic sample. According to equation (4), Table 4 is obtained.

As can be seen from Table 4, the hygroscopic strain ε of SU-8, after immersed in electroforming solution for 6.5 h, declined from 6.8% to 3.1% because of ultrasonic.

Table 4 ω_y and ε for non-ultrasonic and ultrasonic samples

	Unultrasonic	Ultrasonic
Δt (μm)	4.7	2.0
ω_y (%)	8.4	3.8
ε (%)	6.8	3.1

Furthermore, the hygroscopic strain ε calculated in this way can be used to predict swelling of SU-8 mould by ANSYS. The simulated results for measuring point 1 are presented in Fig.9, where "1-s-ultrasonic" and "1-s-unultrasonic" represent measuring point 1 for ultrasonic sample and non-ultrasonic sample, respectively.

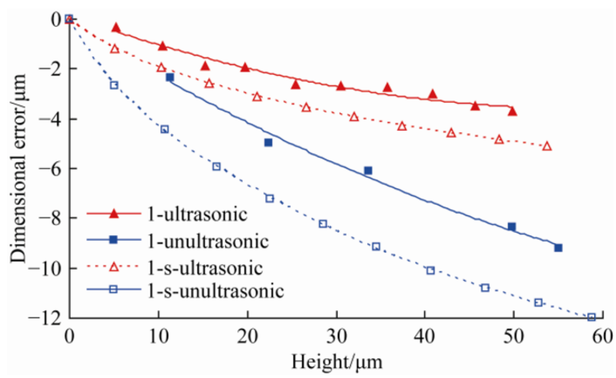

FIG. 9. Results of simulated dimensional errors and experimental dimensional errors.

Transient swelling occur throughout the electroforming process, and the convex electroformed metal layer limits lateral SU-8 swelling. Therefore, the experimental errors are lower than

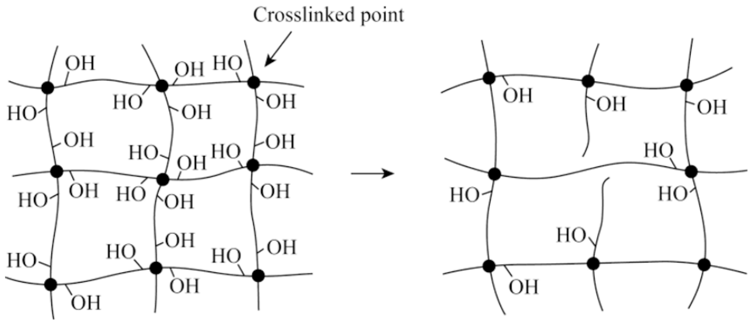

FIG. 10. Schematic of SU-8 matrix change caused by ultrasonic treatment. –OH is hydroxyl group

simulated results. Although dot not agreeing with the experiment quite well, this simulation method is useful. In a way, it can be used to improve mask design and predict electroformed structure dimensional errors. Moreover, when the processing parameters and the electroforming time are settled, the hygroscopic strain ε is certain and unrelated to the geometries of moulds. So the dimensional error simulations based on ε are applicable to arbitrary shape moulds used in electroforming.

Mechanism of ultrasonic effect on SU-8 swelling

It is known that the value of absorbed moisture in crosslinked epoxy resins is deeply depended on the quantity of hydroxyl groups, in other words, depended on the level of the hydrophilicity [12,13,19]. To deeply understand the ultrasonic effect on the hydrophilicity of SU-8, it is necessary to consider the change of contact angle after ultrasonic processing.

Therefore, the water contact angles of SU-8 were measured by Drop Shape Analysis System (DSA100, KRÜSS GmbH) at 50℃. The results show that the water contact angle of SU-8 increases from 70.8° (before ultrasonic processing) to 74.9° (after ultrasonic processing), which indicates that the hydrophilicity of SU-8 decreases while exposed to ultrasonic.

In view of water contact angle change, the mechanism of ultrasonic effect on SU-8 swelling can be explained as follows. It has been found out that ultrasonic can induce chemical bonds in polymers breaking [20]. For this study, when the samples are exposed to ultrasonic a part of hydroxyl groups may break away from the SU-8 backbones, as shown in Fig. 10. Thereby, the hydrophilicity of SU-8 reduces, which makes the amount of moisture absorbed in the same time decreases. As a result, the swelling potential of SU-8 mould declines and the dimensional errors of electroformed structures diminish. However, SU-8 still keeps three-dimensional networks and cannot be dissolved by SU-8 developer or electroforming solution.

Summary and prospect

1) The finite element analysis results indicate that the dimensional error produced by thermal expansion is less than 3% in the total error, so hygroscopic swelling is the predominant reason for SU-8 mould distortions.

2) The ultrasonic treatment was introduced to the electroformed Ni-structure fabricating process after PEB. For a 400 μm mask, ultrasonic treatment decreases the dimensional error of Ni-structure by more than 50% at 50 μm height.

3) Simulation of hygroscopic swelling is conducted by ANSYS, and the results indicate that the hygroscopic strain ε of SU-8 declined from 6.8% to 3.1% because of ultrasonic.

4) The increased water contact angles of cured SU-8 before (70.8°) and after (74.9°) ultrasonic processing indicates that the hydrophilicity of SU-8 decreases since exposed to ultrasonic.

5) The mechanism of the ultrasonic effect on SU-8 swelling is discussed. When the samples are exposed to ultrasonic a part of hydroxyl groups may break away from the SU-8 backbones, which decreases the hydrophilicity of SU-8 and in turn reduces the mould swelling.

Although this work reveals that ultrasonic treatment can reduce SU-8 hygroscopic swelling, further studies optimizing the ultrasonic process parameters such as ultrasonic frequency, acoustic power and exposure time are ongoing.

The project is supported by the National Natural Science Foundation of China (No: 50675025 and 51075057).

Received 8 September; accepted 11 October; published online 22 October 2010.

References

1. C. Ho and W. Hsu, J. Micromech. Microeng. 14, 356 (2004). doi:10.1088/0960-1317/14/3/007

2. M. Agarwal, R. A.Gunasekaran and P. Coane, et al, J. Micromech. Microeng. 15, 130-135 (2005). doi:10.1088/0960-1317/15/1/020
3. L. Du, S. Zhu and C. Liu, Piezoelect. Acoustooptic. 30, 621 (2008).
4. L. Du, S. Zhu and L. Yu, Opt. Precis. Eng. 16, 500 (2008).
5. S. K Grif, J. A. W. Crowell, B. L. Kistler, et al, J. Micromech. Microeng. 14, 1548 (2004). doi:10.1088/0960-1317/14/11/017
6. A.Ruzzu and B. Matthis, Microsyst. Technol. 8, 116 (2002). doi:10.1007/s00542-001-0138-6
7. A. Du, J. Long and H. Pei, et al, Electroplat. Finish. 27, 15 (2008).
8. G. Aigeldinger, J. T. Ceremugaj and B. E. Mills, et al, .: 'Final-Part Metrology for LIGA Springs, Build 1', Sandia Report, Sandia National Laboratories, 2004
9. C. Solf, A. Janssen and J. Mohr, et al, Microsyst. Technol. 10, 706 (2004). doi:10.1007/s00542-004-0406-3
10. G. Aigeldinger, J. T. Ceremuga and K. D. Krenz, Proceedings ASPE 2004 annual meeting (2004).
11. N. Chronis and L. P. Leel, 17th IEEE International Conference on Micro Mechanical Systems (MEMS), pp. 17-20 (2004).
12. S. Zhang, Y. Kong and Y. Ding, et al, Acta Phys. Chem. Sin. 20, 360 (2004).
13. M. J. Adamson, J. Mater. Sci. 15, 1736 (1980). doi:10.1007/BF00550593
14. S. Luo, J. Leisen and C. P. Wong, J. Appl. Polym. Sci. 85, 1 (2002). doi:10.1002/app.10473
15. S. Popineau, C. Rondeau-Mouro and C. Sulpoce-Gaillet, et al, Polymer, 46, 10733 (2005). doi:10.1016/j.polymer.2005.09.008
16. R. Feng and J. Farris, J. Micromech. Microeng.13, 80 (2003). doi:10.1088/0960-1317/13/1/312
17. Y. Hiral, Y. Inamoto and K. Sugano, et al, J. Micromech. Microeng. 17, 199 (2007). doi:10.1088/0960-1317/17/2/003
18. Z. Zhou, Q. Huang and W. Li, et al, IEEE Conf. Proc. Sensor, 325 (2007).
19. C. L. Soles, F. T. Chang and D. W. Gidley, et al, J. Polym. Sci. 38, 776 (2000).
20. J. Kost, L. Leong and R. Langer, Proc. Natl. Acad. Sci. USA 86, 7663 (1989). doi:10.1073/pnas.86.20.7663