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Development behaviours and microstructure quality of downward-development in deep x-ray lithography

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Abstract
This paper presents a novel development method for fabricating high aspect ratio microstructures in deep x-ray lithography. In this method, microstructures are developed downward to utilize the difference of the specific weight between the development products and the developer to efficiently remove the development products. The development behaviours of the proposed method (downward-development) are investigated and compared with the conventional method (upward-development). Experimental results indicate that the developing rate of downward-development is approximately twice that obtained by upward-development. Additionally, the development products are easily removed and a satisfactory microstructure quality is achieved via this process. The proposed method also yields accurate predictability to estimate the necessary developing time. Moreover, the elevated temperature increases the developing rate of downward-development more sensitively than for upward-development.

1. Introduction

Deep x-ray lithography significantly influences the accuracy and achievable aspect ratio for microstructures in the complete LIGA process [1, 2]. In this process, absorber patterns are transferred to a resist layer and then a suitable organic developer dissolves the irradiated zones within this resist layer. Synchrotron radiation is applied owing to its high intensity and small divergence. Poly(methylmethacrylate) (PMMA) is generally employed as a resist material because it can obtain high contrast when a specific developer is utilized. If the development process is accomplished adequately, the PMMA resist thickness of irradiated zones decreases vertically [3]. The developed microstructures can obtain a fine profile and lower surface roughness. Hence, this deep x-ray lithography process has the potential to fabricate high aspect ratio, miniature, and high precision microcomponents and devices.

Of primary concern is how to promote the developing rate and shorten the developing time in deep x-ray lithography. Although increasing the developing temperature can increase the developing rate, a crack could occur [4]. In addition, megasonics can improve the developing depth significantly. However, the cavitations that these cause can destroy the fragile microstructures [5,6]. This paper avoids the use of megasonics and tries to propose a novel development method, in which the microstructures are downward during development, to improve the developing rate and to obtain a satisfactory development quality of high aspect ratio microstructures. The influence of the proposed and conventional methods on development behaviours, including depth and rate, is investigated. Also discussed herein is the feasibility of using various developing methods to fabricate such a microstructure array.

2. Deep x-ray lithography

The x-ray mask is the most vital component of the deep x-ray lithography process. Via hard x-ray, the absorber pattern of an x-ray mask is transferred into the resist. The membrane and absorber portions of the x-ray mask employed herein are graphite and gold, respectively. The graphite membrane has a

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low atomic number and good electrical conduction. However, it should be noted that commercial graphite is a polycrystalline carbon with a rough surface, which easily results in pattern defects on the x-ray mask following gold electroplating. The gold absorber thickness is estimated according to the x-ray dose spectrum that penetrates the filter materials. An absorber with a thickness less than this estimated value cannot create enough contrast during the subsequent exposure and development processes. In this experiment, the graphite membrane and gold absorber thicknesses of the x-ray mask are 90 μm and 15 μm, respectively [7, 8].

PMMA with a high molecular weight (molecular weight 950 K) and 1 mm thickness is used as the resist material herein. During the exposure and development processes, the resist was bonded to the plating base. However, for the following electroforming process, the plating base requires electrical conduction and usually a metal layer is utilized. Thus, the adhesion problems of the polymer–metal interface become a key issue. In this work, silicon (100) wafers that were cleaned with acetone and blown dry were evaporated using Cr(20 nm)/Ti(200 nm) as a seed layer. A spun-on methylmethacrylate (MMA) monomer layer was employed to solvent bond the 1 mm thick PMMA sheets to the evaporated seed layer. Herein, 3-(trimethoxysilyl)propyl-methacrylate (MEMO) is added as an adhesion promoter. Although MEMO can promote the adhesion strength of the PMMA resist–seed layer interface effectively, it is difficult to dissolve in the developer. How this characteristic affects the subsequent electroforming process should be considered [9].

At the Synchrotron Radiation Research Center (SRRC) in Taiwan, synchrotron radiation was used to transfer the absorber patterns. The electron energy of the Taiwan Light Source (TLS) was increased to 1.5 GeV at SRRC, which has a characteristic wavelength of 0.58 nm. Due to space limitations, a 17 m long micromachining beamline without a mirror or filter was designed. The thickness of the beryllium end window that was joined to the x-ray scanner was 125 μm. A deep x-ray scanner with computer control (JENOPTIK) was installed to handle the four inch standard wafers. Furthermore, 100 mbar helium was employed to cool the exposed samples. One exposure procedure consisted of a series of pumping and ventilation steps.

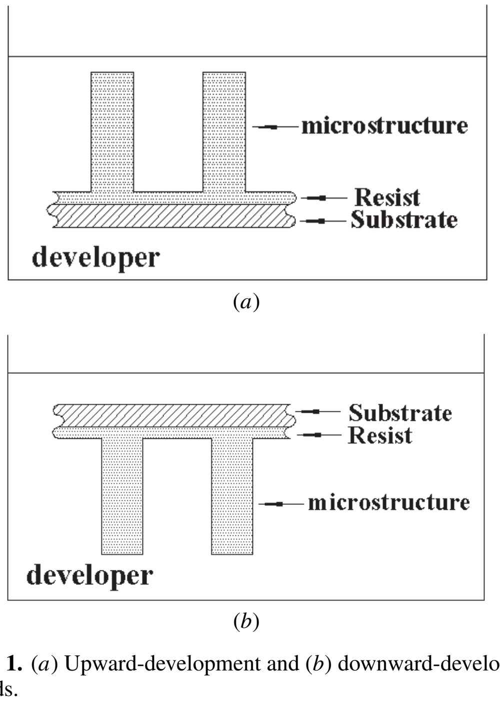
In addition to the x-ray mask fabrication and x-ray exposure, the development process is a critical issue of the deep x-ray lithography process. In this single exposure, the bottom-irradiated dose of the PMMA resist was 4.3 kJ cm^{-3}. Following irradiation, two developing solutions, a G-G developer and a washing solution, were applied successively to each sample. The G-G developer, which was a mixture of water and three different organic solvents (15 vol% water, 60 vol% butoxy-ethoxyethanol, 20 vol% tetrahydro-oxazine and 5 vol% aminoethanol) was employed to dissolve the irradiated zones of the PMMA resist. The washing solution, which was a combination of water and an organic solvent (20 vol% water and 80 vol% butoxy-ethoxyethanol) was employed to remove the residual G-G developer as well as the residual development products in the gaps of the microstructures. The washing solution had a smoother chemical action on the irradiated PMMA resist than did the G-G developer. The entire development process was introduced to immerse and develop the irradiated PMMA resist in the G-G developer. The procedure was repeated until a complete profile of the microstructures was obtained. Then, an identical procedure was applied in the washing solution. Following development, the resist was rinsed with de-ionized (DI) water for a few minutes and dried carefully [10].

3. Development experiments

In deep x-ray lithography, the development behaviours of the PMMA resist, which irradiation dose, developing temperature, chemical reaction and mass transfer of development products affect reciprocally, are fairly complex. The development action can be divided into three parts:

(1) the diffusion of the G-G developer to the surface of the PMMA resist;
(2) the chemical reaction caused by the irradiated zones of the PMMA resist and the G-G developer;
(3) the diffusion of the development products to the G-G developer.

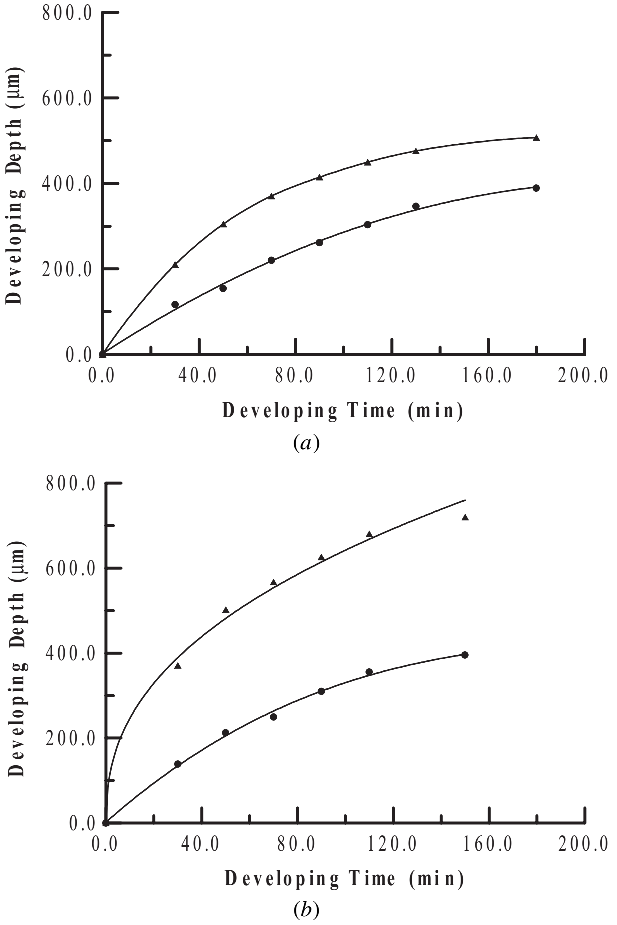
The two main accelerating forces of these reactions are the developing temperature and the concentration gradients of the G-G developer that is near the surface of PMMA resist and the development products. However, development at an elevated temperature may cause cracks within the microstructures. Consequently, it is necessary to maintain a high concentration of the G-G developer at the reacting zones to promote these development reactions. This finding implies that rapid dissipation and removal of the development products, which remain near the surface of the reacting zones, is vital to further the development effects. Notably, the current also attempts to dissipate the development products by the magnetic stirrer and megasonics. Nevertheless, they are not suited when high aspect ratio microstructures are desired, as weak microstructures are damaged easily. Thus, in this paper,



(*a*)

(*b*)

Figure 1. (*a*) Upward-development and (*b*) downward-development methods.



(*a*)

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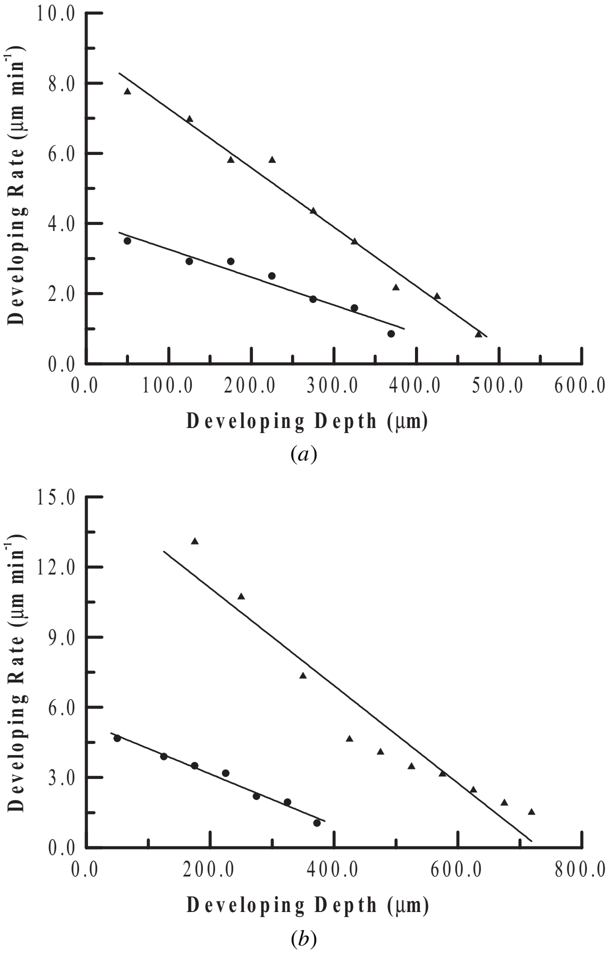
Figure 2. Developing time versus developing depth obtained for the developing methods at different temperatures: (*a*) 28 °C; (*b*) 45 °C; ●, upward-development; ▲, downward-development. The curves correspond to spline smoothing.

two different developing methods are introduced and their development properties are compared for high aspect ratio microstructures. In the development process, the developing method of upward microstructures, which is the conventional method, is dubbed upward-development; the opposite is dubbed downward-development (figure 1).

Figure 2 depicts the correlation between the developing depth and time produced by upward-development and downward-development at various temperatures. At the same developing time, the developing depth of the PMMA resist produced by downward-development is deeper than that of upward-development. The effect of temperature on the developing rate can also be observed here. Figure 3 illustrates the comparison of developing rates of different developing methods at the same developing depth. Notably, when the same developing depth is attained in the development process at various temperatures, the downward-development has a sharper developing rate than the upward-development. To explain the experimental results obtained, the mechanism of development should be considered. When the G-G developer penetrates PMMA, a gel-like layer is produced, and thus three regions can be distinguished: the pure polymer, the gel layer, and the developer. These regions are separated by the polymer–gel boundary and the gel–developer boundary, which are characterized by a sharp change in developer concentration. The development of PMMA can be described by the movement of these two boundaries [6]. Herein, the only transport mechanisms, which govern the moving speed of these boundaries, of upward-development are diffusion and natural convention caused by the local differences of temperature and concentration. However, in the downward-development process, the influence of gravity on the mechanism of transport must be considered because the specific weight of the gel-like substance is generally greater than that of the G-G developer. Gravity tends to pull apart the adhered gel-like products and causes the internal microflow of the G-G developer to enhance the conventional effect. Consequently, the fresh G-G developer could enter microstructure gaps rapidly, thus increasing the developing rate. Herein, the negative effects of gravity render upward-development unfavourable in the development of high aspect ratio microstructures. Figure 4 presents a schematic representation of the development behaviours of upward-development and downward-development.



(*a*)

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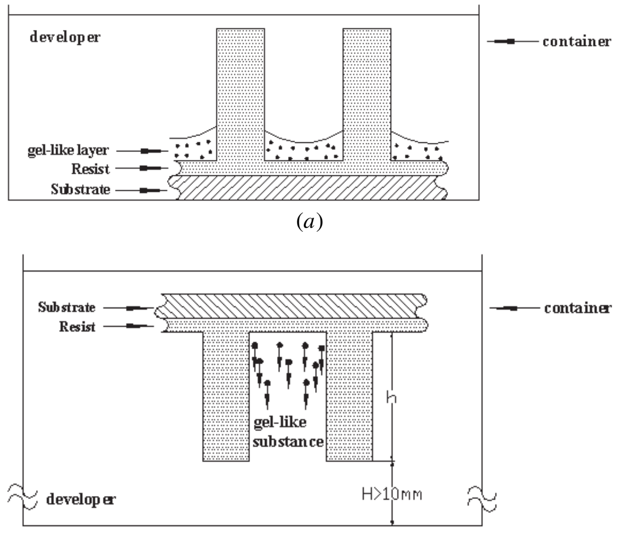
Figure 3. Developing depth versus developing rate obtained for the developing methods at different temperatures: (*a*) 28 °C; (*b*) 45 °C; ●, upward-development; ▲, downward-development. The straight lines correspond to a least-squares fit.

The decrease of the developing rate with the increase of the developing depth in both development methods (figure 3) is caused by the decrease of irradiated dose along the depth. Figure 5 presents the evaluated results of in-depth dose distribution from the surface of the PMMA resist after



(*a*)

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Figure 4. Schematic representations of (*a*) the upward-development and (*b*) the downward-development. The value of H is 10 mm in this paper.

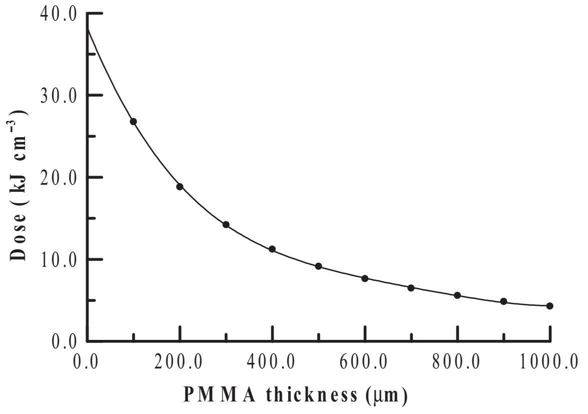
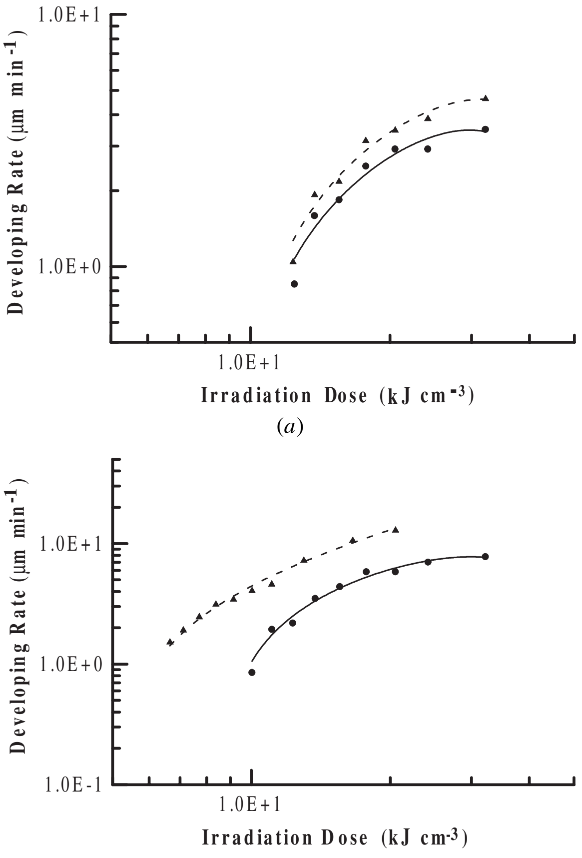


Figure 5. In-depth dose distribution in a 1 mm thick PMMA resist.

irradiation according to the model proposed by Cheng *et al* [11]. From figures 2 and 5, the minimum doses of the upward-development and the downward-development in this paper are 8–8.5 kJ cm^{-3} and 6.5–8 kJ cm^{-3}, respectively. Furthermore, the influence of irradiated dose on the developing rate of the PMMA resist were obtained, as shown in figure 6. Concerning the correlation between the irradiated dose and the developing rate, the following empirical law has been proposed [12–14]

$$R = KD^{\alpha} \qquad (1)$$

where R is the developing rate and D is the irradiated dose absorbed by the PMMA resist. K and α are constants and are related to the developing temperature. Notably, as shown in figure 6, the value of α in equation (1) varies practically with irradiated dose in both development methods. Moreover, the influence of temperature on the developing rate in upward-development is less than that in downward-development. Herein, within upward-development, the gel-like substance that is deposited on the PMMA resist surface is critical, which influences all developing rates and their stability of variation (figure 6).



(*a*)

(*b*)

Figure 6. Comparison of the developing rate versus irradiated dose for various developing temperatures: (*a*) upward-development; (*b*) downward-development; ●, 28 °C; ▲, 45 °C. The curves correspond to spline smoothing.

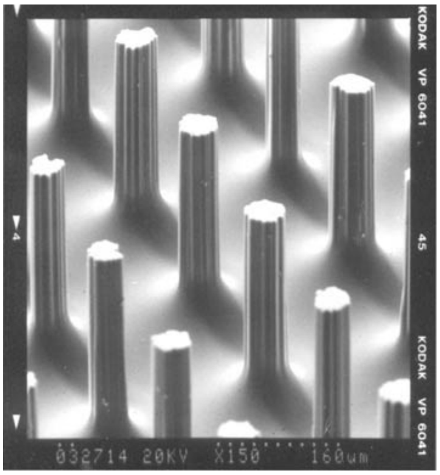
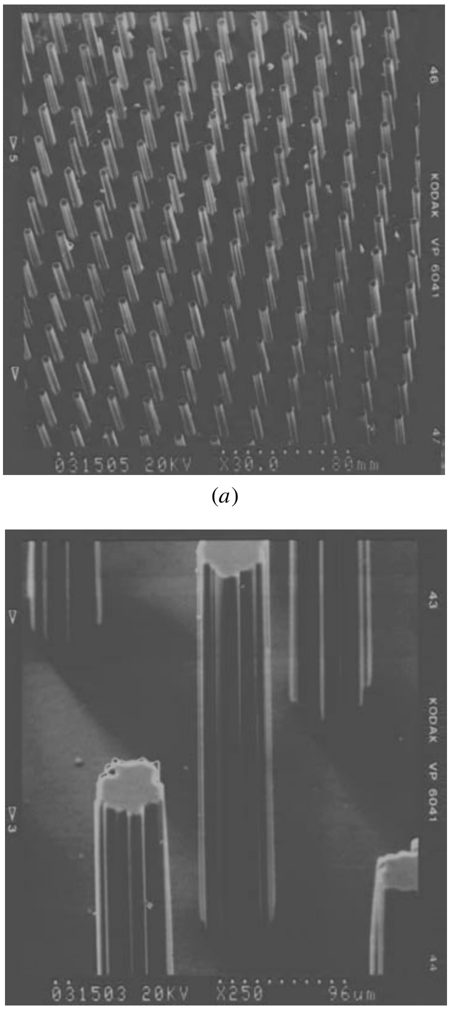


Figure 7. SEM image of the microstructures with an aspect ratio of 6.25 obtained by upward-development.

4. Influence on microstructure quality

Figure 7 displays the developed microstructures with an aspect ratio of 6.25 produced by upward-development. The residual gel-like layer surrounds the bottom of these microstructures. Figure 8 presents scanning electron microscopy (SEM) images of the resulting microstructures that downward-development



(*a*)

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Figure 8. SEM images of (*a*) the microstructure array with the dimensions of 10 mm along both edges and (*b*) a higher magnification of the development result of downward-development.

produced, with the same size and appearance as displayed in figure 7. The dimensions of this microstructure array are 1 × 1 cm^2, and it is evident that a satisfactory development quality is achieved. The residual gel-like substance that surrounds the bottom of the microstructures (figure 7) typically requires additional developing time to remove. However, this fails to produce high aspect ratio microstructures of a satisfactory condition. As extended development results in underetch of the adhesion layer between the bottom of the microstructures and substrate, or even reduces the adhesion strength, microstructures that have a high aspect ratio and dense arrangement are damaged easily.

5. Summary

Regarding the high aspect ratio microstructure array, the necessity of increasing the developing rate is indubitable in consideration of the efficiency and the cost of the whole process. Nevertheless, the negative influence of a prolonged development on the forming microstructures is the primary objective to promote efficiency. The high development efficiency depends on strong penetration ability and sharp dissolution action of the G-G developer. However, the smooth and efficient progress of the above actions is subject to satisfactory environmental conditions, which causes less obstacles and interference. Namely, immediate evacuation and exclusion of development products is essential to ideal developing conditions. The downward-development process, in which the removal of development products is accelerated via a gravity-induced pulling force and better convective transport, was developed for high aspect ratio microstructures, which megasonics weaken. A comparison of the proposed and the traditional upward-development processes has been presented. This indicates that within various exposures the developing rate of downward-development is approximately two times greater than that of upward-development. In addition, in contrast to the traditional method, the proposed method has a smooth developing rate variation that can be predicted accurately. This is a vital feature in estimating the developing time correctly. Furthermore, the effect of the elevated temperature on the increasing developing rate is obvious within the proposed method; however this effect is less within the traditional method.

Acknowledgments

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