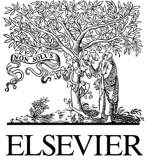

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Key issues in fabricating microstructures with high aspect ratios by using deep X-ray lithography

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Abstract

High aspect ratio microstructures are frequently made with the Lithographie, Galvanoformung, Abformung (LIGA) process. The success of this process depends critically on "deep" X-ray lithography (DXRL). This paper presents a variety of experimentally and analytically determined techniques for optimizing DXRL. These include methods for designing and fabricating high-quality X-ray masks. Methods for optimizing the exposure dosage and developing cycle are described. New methods for promoting resist adhesion and for avoiding resist film cracking are discussed. The influence of developer surface tension on the resist solvation process is quantified and new methods for controlling this surface tension are described.
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Keywords: LIGA; DXRL; High aspect ratio; Exposure and development; Microstructure

1. Introduction

The Lithographie, Galvanoformung, Abformung (LIGA) process is a micromachining method that applies deep X-ray lithography (DXRL), electroforming and micro molding techniques to fabricate microstructures of various materials, including polymers and metals. This paper considers key issues concerning DXRL. Details of the DXRL process have significant impact on the dimensional accuracy, sidewall slope and the achievable aspect ratio of developed resist structures [1,2].

In this paper, we describe the use of synchrotrons as the primary LIGA exposure source. Synchrotron radiation is applied because it is very intense and exhibits low divergence. Poly(methylmethacrylate) (PMMA) is frequently used as a photoresist material because it can yield a strong contrast when particular developers are applied. Under ideal conditions, the exposed regions of resist dissolve rapidly and the unexposed resist is unaffected. The developed microstructures have near vertical profiles with exceptionally smooth surfaces. Hence, DXRL has been shown to provide microstructures with high aspect ratio and well-controlled dimension.

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This is not to say that DXRL is problem-free. Well-controlled mask patterns are difficult to obtain due to process complexity. Thick absorbing layers are hard to pattern with good dimensional control. Such thick layers are necessary to achieve the requisite light contrast for single-exposure patterning [3,4]. In this paper, we present experimental proof that a single exposure to synchrotron radiation, without spectral filters, can produce microstructures of up to 500 μm thick within 2 h. Nevertheless, a single exposure without filters can easily cause crack defects in the PMMA photoresist, so aluminum filters are used to modify the universal power spectrum [5].

One of the important issues in DXRL concerns the effective control of processing parameters as well as incorporation of stabilizing techniques for high aspect ratio. The work described below focuses on application of these optimization approaches to problems in the fabrication of micro-column arrays with high aspect ratios.

2. Designing and fabricating an X-ray mask

2.1. Determining the thickness of the gold absorber

The X-ray mask is the most important component in DXRL. The absorber pattern of an X-ray mask is transferred into the photoresist via hard X-ray radiation. The best membrane material, beryllium, is toxic. Frequently, graphite, diamond or SiC membranes are substituted. Gold is the most frequently used absorber. It is a strong X-ray attenuator and thick-film plating techniques for gold are in widespread use.

The required thickness of the gold absorber layer must be determined before the X-ray mask is fabricated. Any technique for assigning an optimum thickness must take the spectrum of the x-radiation into account. The technique we employ here follows that proposed by Cheng and co-workers [5]. Cheng derived the following relationships, forming the basis of the method:

$$D_{\mathrm{surf}} = \sqrt{\frac{\pi}{2}} D_0 Z^{-1.5} \mathrm{e}^{-Z} (1 + 4.6892 Z^{-0.5} - 4.2386 Z^{-1}) \leqslant 3\ \mathrm{kJ/cm^3}, \quad (1)$$

$$Z = 1.599(\mu_{\mathrm{Be}} T_{\mathrm{Be}} + \mu_{\mathrm{Au}} T_{\mathrm{Au}})^{0.25} \approx 1.599(\mu_{\mathrm{Au}} T_{\mathrm{Au}})^{0.25}, \quad (2)$$

where D_0 is the nominal exposure dose, and is determined by the characteristics of the synchrotron, the exposure system, the beamline and the photoresist. T_{Be} and T_{Au} are the actual thicknesses of the beryllium window and the gold absorber layer, respectively. μ_{Be} and μ_{Au} are the coefficients of attenuation for hard X-rays, of the beryllium and gold layers, respectively. This discussion holds for other material systems, provided the relevant absorptions are used.

The dose of the X-rays that arrive upon the surface of the PMMA photoresist when obstructed by the gold absorber layer must be less than 3 kJ/cm^3 [2] to maintain full-thickness in the occluded regions. That is, $D_{\mathrm{surf}} \leqq 3$ kJ/cm^3. This criterion, Eqs. (1) and (2), determines the required thickness, T_{Au}, of the gold absorber layer. Fig. 1 indicates the required thickness of the gold/graphite mask over a range of exposure doses supplied in this experiment.

2.2. Fabricating the X-ray mask

Graphite membranes have a low atomic number and good electrical conductivity. However, commercial graphite is polycrystalline carbon with a rough surface ($R_a > 5.0$ μm). Surface roughness may generate pattern defects on the X-ray mask following electroplating with gold. Furthermore,

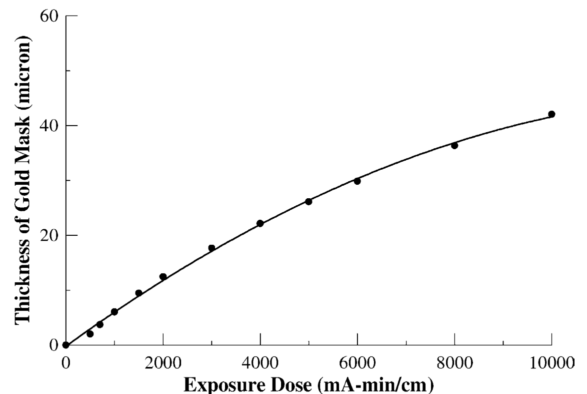


Fig. 1. Required thickness of gold absorber at various exposure doses.

the gold absorber layer is usually over 10 μm thick because an absorber with a thickness under 10 μm cannot create sufficient contrast during subsequent exposure and development. The weight of the gold absorber layer can cause the graphite membrane to bend. This bending leads to non-uniform absorption of PMMA during exposure. This effect also makes fabrication more difficult. Fig. 2 graphically illustrates the steps used in mask fabrication. The procedure for producing an X-ray mask for LIGA is summarized as follows [6,7]:

(1) An optical lithography mask (chrome on glass) was designed and fabricated.
(2) A graphite sheet was glued onto a silicon wafer. The graphite sheet was polished to $R_a < 1.0$ μm and cleaned in acetone and deionized water. It was then dried in flowing nitrogen. This step improved the coverage of the photoresist on the graphite sheet.
(3) The negative photoresist (JSR-137N or SU8-5) coated on the graphite membrane was optically exposed. Dark fields on this photomask represented the pattern that the gold absorber would make.
(4) Gold electroforming was utilized to plate gold absorber patterns to a thickness of 15 μm.
(5) After the photoresist was stripped using a remover, the graphite membrane, including the gold absorber layer, was mounted on a stainless frame, called a mask ring, to increase the mechanical strength of the X-ray mask.

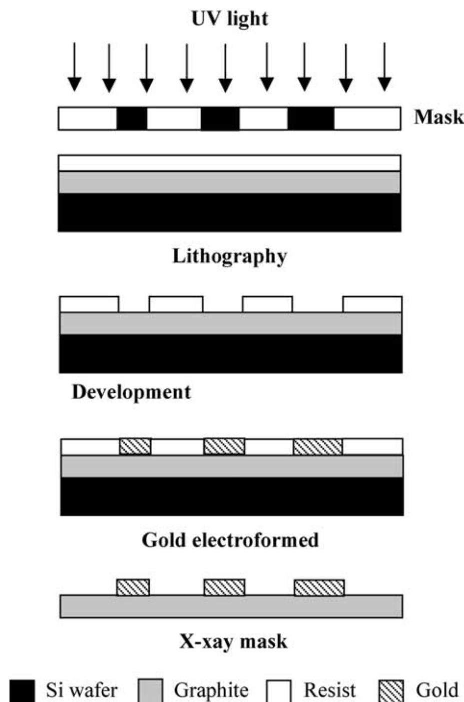


Fig. 2. Steps in fabricating a mask with gold on graphite membrane.

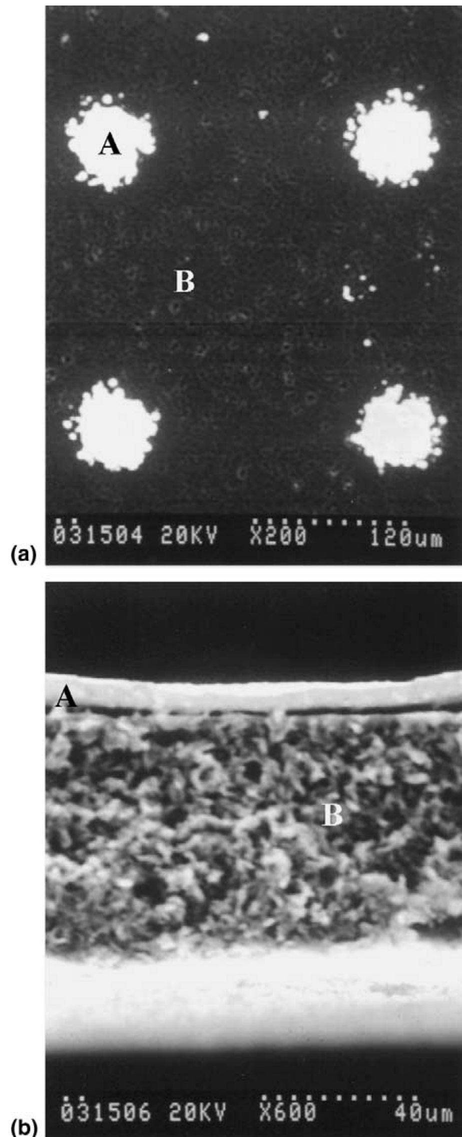


Fig. 3. (a) SEM micrograph of gold on graphite membrane. (b) Gold on warped graphite membrane at higher magnification.

Fig. 3 shows the results of this process. Fig. 3(a) focuses on the gold absorber on a graphite membrane. Fig. 3(b) clearly shows warping caused by the weight of the gold and internal stress associated with electroforming. The warping problem could be solved (to some extent) by modifying the parameters of the gold electroforming process in such a way as to minimize gold film stress.

3. Deep X-ray lithography

3.1. Exposure

The Synchrotron Radiation Research Center (SRRC) in Taiwan supplied the exposing radiation used in these experiments. The electron energy of the Taiwan Light Source (TLS) at the SRRC is 1.5 GeV. The characteristic wavelength is 0.58 nm; the stored beam current is 400 mA, and the bending radius is 3.495 m. A 17 m long micromachining beamline, without a mirror or filter, was designed because space was limited. The thickness of the beryllium end window that was joined to the X-ray scanner is 125 μm. A computer-controlled X-ray scanner (JENOPTIK) was installed to handle the four-inch standard wafers. Furthermore, helium at 100 mbar was employed to cool the exposed samples. A single exposure includes a series of pumping and venting steps.

As stated above, the dosage absorbed by the PMMA photoresist must exceed 3 kJ/cm^3, to enable the microstructure to be adequately developed. However, when the dosage absorbed at the bottom of PMMA photoresist reaches 3 kJ/cm^3, overdosing must be prevented on the surface of the PMMA photoresist to prevent the microstructures from becoming distorted. These criteria can be applied to constrain the achievable depth of the desired microstructures. A filter can be used to filter out low-energy photons, preventing dose grading normal to the resist surface. Therefore, in this work, three aluminum plates with thickness of 15, 20 and 25 mm, and a beryllium window were used as high pass filters to modify the universal power spectrum and thereby satisfy the demand for microstructures with various depths.

Although increasing the exposure dose reduces the developing time, defects are easily generated in the PMMA photoresist. Fig. 4 illustrates crack defects in the PMMA photoresist, caused by overabsorption. While the development process is carried out, these crack defects in the PMMA grow up and the whole microstructures are then destroyed. In addition to strain-induced cracking, the fluorescence emission caused by hard X-rays' interacting with the substrate introduces an uncontrollable and often undesirable source of radiation at the interface of the photoresist and substrate. In practice, a bandpass filter at the beamline and accurate control of the exposure time will reduce such fluorescent emission.

3.2. Distribution of exposure in the PMMA photoresist

The unit of dosage used in the exposure system is mA-min/cm, which must be transformed into kJ/cm^3. The transformation equation is,

$$\begin{aligned} D_0 &= 8727F\mu_R^c \int \frac{E^4 I}{\rho}\,d\tau \\ &= 8727F\mu_R^c \frac{E^4}{\rho} \int \frac{I}{H}\,d\tau \\ &= 8727F\mu_R^c \frac{E^4}{\rho}(6Q), \end{aligned} \tag{3}$$

where D_0 is the exposure dose when the X-rays do not pass through the beryllium window; τ is the

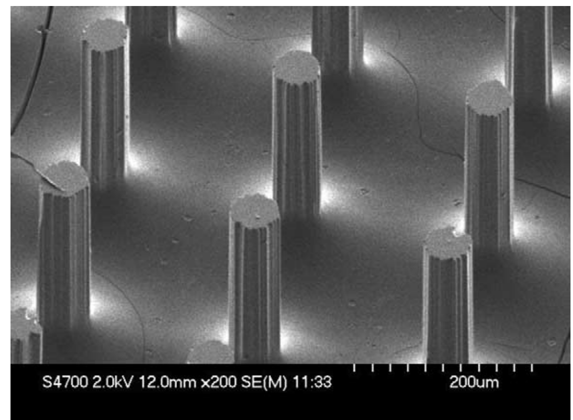


Fig. 4. Crack defects in the PMMA photoresist caused by a high exposure dose.

period of exposure; I is the stored beam current; E is the electron energy; $\mu_{\mathrm{R}}^{\mathrm{c}}$ is the attenuation coefficient of the photoresist; F is the beamline factor, and ρ is the bending radius [8].

The in-depth dose distribution from the surface of the PMMA photoresist following irradiation is also predicted using the mathematical model proposed by Cheng et al. [8]. The absorbed dose, $D(t)$, of the PMMA photoresist at a certain equivalent thickness is as follows:

$$D(t) = \sqrt{\frac{\pi}{2}} D_0 Z^{-1.5} \mathrm{e}^{-Z} \times (1 + 4.6892 Z^{-0.5} - 4.2386 Z^{-1}), \quad (4)$$

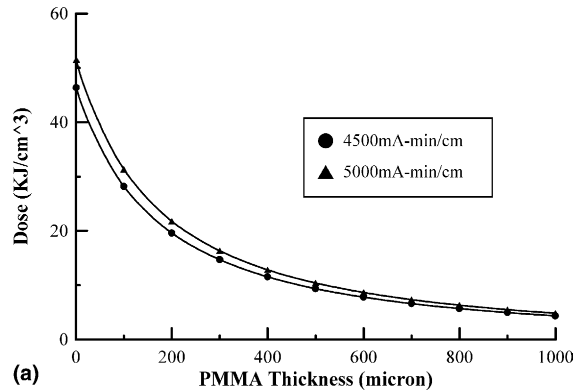
$$Z = 1.599 t^{0.25}, \quad (5)$$

$$t = \sum_x \mu_x^{\mathrm{c}} T_x, \quad (6)$$

where D_0 is the exposure dose. T_x is the actual thickness when hard X-rays pass through the absorbing materials, including the beryllium window, the graphite membrane and PMMA photoresist. t is the equivalent dimensionless thickness.

Combining Eqs. (4)–(6) yields the dose versus depth curve as measured from the surface of the PMMA photoresist following irradiation. Fig. 5(a) plots these curves for an exposure dose of 4500 mA-min/cm and 5000 mA-min/cm. The X-rays penetrate the 125 μm thick beryllium window and the 90 μm graphite membrane. Fig. 5(b) plots the in-depth dose distribution from the surface of the PMMA photoresist for an exposure dose of 4500 mA-min/cm when X-rays penetrate the 125 μm thick beryllium window and a graphite membrane with one of various thicknesses. This figure also indicates the dependence of absorbed dose on graphite thickness.

Fig. 6 indicates that an aluminum filter can reduce the surface dose on a PMMA photoresist. This effectively eliminates the generation of defects caused by over-absorption. The filters in the beamline drastically influence the power distribution. The filters readily absorbed lower energy photons with lower penetration ability. However, the filters barely affected the higher energy photons. The ratio of high to low energy photons passed by a properly designed filter is controlled by material type and thickness. Filters enable deeper penetration without burning the surface of a PMMA photoresist. The $D_{\mathrm{top}}/D_{\mathrm{bottom}}$ ratio without



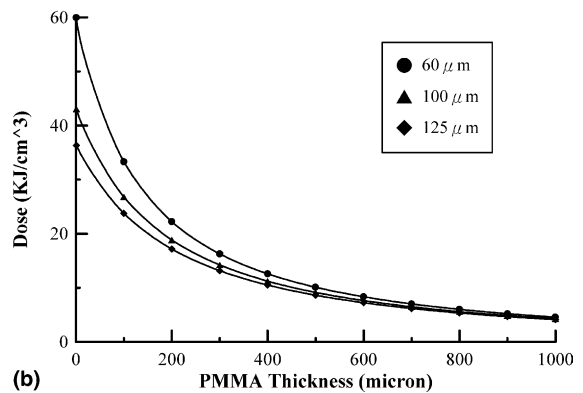


Fig. 5. In-depth dose distributions from the surface of the PMMA photoresist with various parameters: (a) exposure dose; (b) thickness of graphite membrane.

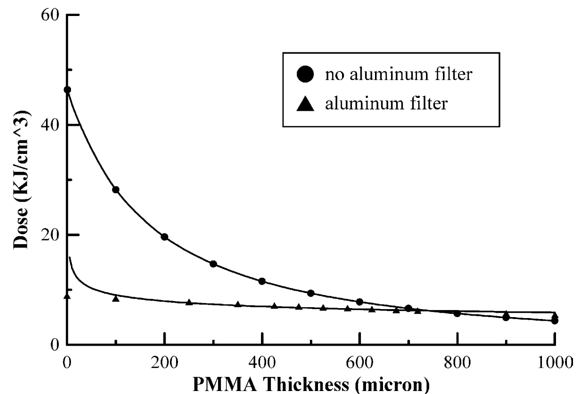


Fig. 6. Effect of aluminum filter on dose distributions with depth from the surface of the PMMA photoresist.

a filter is 10; the corresponding value with an aluminum filter is 1.5. Herein, D_{top} represents the surface dose of the PMMA photoresist and D_{bottom} represents the bottom dose of the PMMA photoresist after radiation, indicating that the aluminum filter can effectively reduce the D_{top}/D_{bottom} ratio.

4. Development

4.1. PMMA photoresist and base plate

PMMA is the most commonly used as the photoresist material in deep X-ray lithography. High energy X-rays cause a release of secondary electrons in the resist and in the substrate on which the resist sits. These secondary electrons can break the PMMA polymer bonds and reduce its molecular weight. This effectively increases the absorbed dose and makes the resist appear more sensitive.

In this study, PMMA with a high molecular weight (950 K) and a thickness of 1 mm is used. Before exposure and development, the photoresist was bound to the seed layer for plating. The preparation of the seed layer prepared in the electroforming process depends on the required electrical conduction, and, usually, a metal layer is employed. Thus, adhesion problems associated with the polymer–metal interface become important. In this work, silicon (100) wafers, 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 used to bond the 1 mm-thick PMMA sheets to the evaporated seed layer. Herein, 3-(trimethoxysilyl)propyl-methacrylate (MEMO) was added to promote adhesion [9]. Although MEMO can effectively strengthen the adhesion at PMMA photoresist–seed layer interface, the developer does not easily dissolve it.

4.2. Development process

As well as the X-ray mask fabrication and X-ray exposure, development is a critical stage of deep X-ray lithography. In a single exposure, the dose absorbed at the bottom of the PMMA photoresist is 4.3 kJ/cm^3. Following irradiation, two developing solutions, G–G developer and rinse, were applied successively to each sample. The G–G developer is a mixture of water and three different organic solvents (15 vol% water, 60 vol% butoxy-ethoxyethanol, 20 vol% tetrahydro-oxazine, and 5 vol% aminoethanol). The rinse solution, which was a combination of water and an organic solvent (20 vol% water, 80 vol% butoxy-ethoxyethanol), was applied to remove the residual G–G developer and residues in the gaps of the microstructure.

Development involved immersing the irradiated PMMA photoresist in a G–G developer. The procedure was repeated until the complete profile of the microstructures was obtained. Then, an identical procedure was applied to the rinse solution. Following development, the photoresist was rinsed with deionized (DI) water for a few minutes and dried [10]. The irradiated PMMA photoresist was developed directly using washing solution when the microstructure was highly precision but without a high aspect ratio, because the washing solution acts more smoothly on the irradiated PMMA photoresist than it does on the G–G developer.

Fig. 7 indicates that increasing the developing temperature somewhat can promote the perfusion of the G–G developer and the rinse into the gaps of the microstructures, which nevertheless remain intact. The figure also shows that using a developer with a lower surface tension has an effect on the

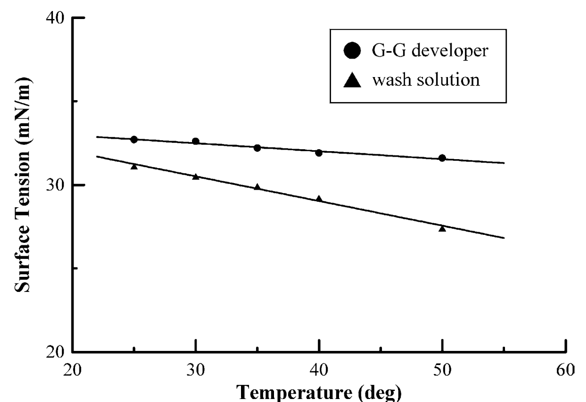


Fig. 7. Surface tension of G–G developer and washing solution at various temperatures.

mass transport of the development products that increases the rate of development, because a developer with a lower surface tension can more easily enter the gaps of the microstructures, and especially the narrow ones. Increasing the temperature of the G–G developer is more effective than using a rinse.

In deep X-ray lithography, the development behavior of PMMA, determined by irradiation dosage, the developing temperature, the rate of the chemical reaction, and the rate of mass transport of the development products, are fairly complicated. The development proceeds in three stages: (1) the G–G developer diffuses to the surface of the PMMA photoresist; (2) the irradiated zones of the PMMA photoresist chemically react with the G–G developer; (3) the products of development diffuse into the G–G developer. Two main factors drive these steps. They are the developing temperature and the concentration gradient of the G–G developer near the interface of the PMMA photoresist and the development products.

Although increasing the developing temperature can accelerate the chemical reaction between the irradiated zones of the PMMA photoresist and the G–G developer, increasing the developing temperature above 50 °C encourages the formation of defects. In step (3), whether the development products can be quickly extracted from the interface of the PMMA photoresist and the G–G developer is important, because the rate of this step strongly affects the rates of steps (1) and (2). Additionally, megasonic stirring can significantly increase the developing depth. However, the cavitations thus caused can destroy a fragile microstructure, such as a micro-column array with high aspect ratio. Hence, megasonics was not used.

A new development method, in which microstructures face downward during developing, is presented to increase the rate of development and ensure that the quality of the microstructures with high aspect ratios is satisfactory [11]. Fig. 8 depicts the effect of the process on developing quality in the upward and downward directions. Fig. 8 indicates that the residual matter easily generated when the upward-development method is used but no residual matter forms when the downward-development method is used; the latter method generates microstructures with an aspect ratio of 6.25. The downward-development process, which removes development products in a process governed by specific weight difference, was developed for application to microstructures with high aspect ratios, which are weakened by megasonics.

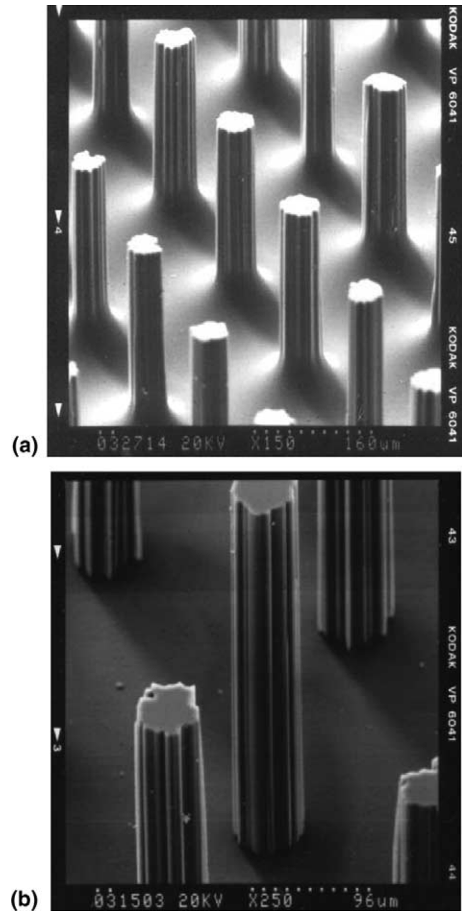


Fig. 8. Directional effects on quality of development: (a) upward-development with residual matter; (b) downward-development without residual matter.

5. Summary

This work considered processing problems associated with fabricating high-aspect-ratio microstructures using DXRL. Analytical and experimental results indicate that accurately calculating the desired

thickness of the absorber layer is important in fabricating an X-ray mask. During exposure, the exposure dose and the developing time must be determined carefully to prevent the formation of defects in the photoresist due to a higher exposure dose. An aluminum filter can be used to prevent crack defects from being generated in the PMMA photoresist and reduce fluorescent emission. It can also reduce the $D_{\mathrm{top}}/D_{\mathrm{bottom}}$ ratio from 10 to 1.5. During development, MEMO promotes the adhesion of the PMMA to the metal seed layer; however, the effect of the promoter on the subsequent electroforming process must be considered. In particular, residues from the promoter may also be difficult to remove. A lower surface tension developer increases the developing rate.

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