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# Behavior of the Developing Process for Ultradeep Microstructures

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The exposed portions are dissolved by an organic developer after the absorber patterns have been transferred to a polymethyl methacrylate (PMMA) resist layer. One important step in the deep X-ray lithography process to make high aspect ratio microstructures is the developing process. The accuracy and the achievable aspect ratio for microstructures are decisively determined by the development process. The developing conditions have been simplified to prevent interaction of different parameters. To identify the parameters influencing the development process, a model based on fundamental laws is created in this study to predict the developing depth. To simplify the modeling, a constant developing temperature is preset during the developing process. The results reveal that the developing rate is dependent on exposure dose and the depth of deposition. The developing rate increases as the depth of the deposition increases.

## 1. Introduction

The high demand for low weight, small volume, and high precision microcomponents and devices has proven the worth of microfabrication. Conventional precision tools might have the capability to machine soft materials to the accuracy of several microns, but they cannot machine hard materials such as nickel and ceramics due to high tool wear and low material machinability. The advanced technology of the LIGA (German abbreviation: LIthografic, Galvanoformung, and Abformung) process eliminates the problem of high tool wear and low material machinability, and can achieve submicron dimensional accu-

racy. LIGA is superior in the mass production of microstructures with extremely high aspect ratios and vertical walls and allows fabrication with a variety of materials. Industrial applications and concepts for microstructure production by LIGA are rapidly emerging.[1] This technique has the potential for fabricating high aspect ratio and accurate microsystems and microcomponents.

The deep X-ray lithography process requires a combined knowledge of mass, heat transfer and chemical reaction rate theory. There are few papers which discuss the developing process. Zanghhellini *et al.* developed the bulk diffusion model.[2,3] Only the physical dissolving process involved in PMMA development was assumed. The model also revealed that the bulk developing rate of PMMA in G-G developer is a linear function of dosage.

In deep X-ray lithography, the absorber patterns which are transferred to a resist layer and later onto the exposed portion are developed by an organic developer. High aspect ratio three-dimensional microstructures can be fabricated by LIGA. One crucial step is deep X-ray lithography. To achieve a high aspect ratio, it is necessary to understand the developing process. To have a better insight into the influence of mass transfer on developing microstructures, a diffusion model to predict the developing rate and depth is proposed.

## 2. Analysis of Theory

To investigate the development process, the influence of its parameters need to be understood. The mechanism of transport is pure diffusion and natural convection based on local differences in the concentration gradient. In this paper, a model based on Fick's Law is created to provide physical insight into the developing process.

When PMMA is developed, a gel-like layer is produced. Thus, the reacting portion can be distinguished as three regions, i.e., the pure polymer, the gel-like layer and the developer. They are distinguished by the polymer-gel boundary and the gel-developer boundary. The development of a glassy polymer like PMMA can be described by the movement of these two boundaries. The movement of the gel-developer boundary gives the dissolution course because it is here that the partition between the dissolved and undissolved polymer is likely to occur.[4] To investigate the development process independent of its essential parameters, it is necessary to simplify the development conditions as much as possible.

Considering the one-dimensional control volume in Fig. 1, species A (i.e., PMMA) flows into and out of the control volume. If the concentration of A in G-G developer (60 vol.% 2-(2 butoxyethoxy) ethanol, 20 vol.% tetrahydro-1,4-oxazine (morpholine), 5 vol.% 2-aminoethanol, 15 vol.% DI water) is less than the concentration of A at the interface between A and B (i.e., G-G developer), a driving force for mass transfer exists and species A will diffuse from the A/B interface into the G-G developer. On the other hand, the interface regresses so slowly that its movement can be neglected. Furthermore, we assume that B diffusing into solid A is negligible compared to A into B. A semi-steady state is assumed when the origin of the coordinate lies at the A/B interface. The net rate of increase

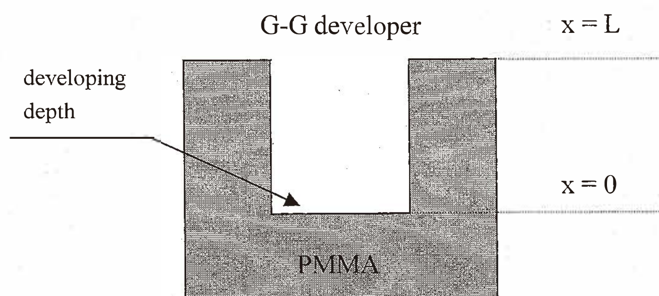



Fig. 1. Schematic illustration of diffusion boundary.

in the mass of A within the control volume relates to mass fluxes and the reaction rate as follows:

$$\dot{m}''_A = C\dot{m}''_A - \rho D\frac{dC}{dx}, \tag{1}$$

where $\dot{m}''_A$: mass flux of species A
$C$: mass fraction of A
$D$: binary diffusion coefficient
$\rho$: density.

Assuming the diffusion coefficient to be a function of concentration as follows:[5]

$$D = D_0(1 + K'_D C + K''_D C^2 + K'''_D C^3 \cdots), \tag{2}$$

where $D_0$: diffusion coefficient
$K'_D$, $K''_D$ ...: arbitrary constant,

eq. (1) can be integrated to yield

$$\frac{\dot{m}''_A}{\rho} x = D_0(\ln|C-1| + K_D C + K_D \ln|C-1|) + C_1, \tag{3}$$

where $\frac{\dot{m}''_A}{\rho}$: developing rate
$C_1$: constant of integration.

One can rearrange eq. (3) with the substitution of $V = \frac{\dot{m}''_A}{\rho}$.

$$Vx = D_0(\ln|C-1| + K_D C + K_D \ln|C-1|) + C_1, \tag{4}$$

where $V$: developing rate
$C_1$: constant of integration.

With the boundary condition, $C_1$ can be obtained as

$$C\ (x = 0) = C_i. \tag{5}$$

The above equation after rearrangement is given as

$$Vx = D_0(\ln\left|\frac{C-1}{C_i-1}\right| + K_D \ln\left|\frac{C-1}{C_i-1}\right| + K_D(C - C_i)), \tag{6}$$

where $C_1$: concentration at $x$=0.
A further assumption is made as follows:

$$\mathrm{C}\ (\mathrm{x} = \mathrm{L}) = \mathrm{C}_\infty, \tag{7}$$

where $C_\infty$: concentration at $x = L$.
After rearranging eq. (6) as

$$VL = D_0(\ln\left|\frac{C_\infty-1}{C_i-1}\right| + K_D \ln\left|\frac{C_\infty-1}{C_i-1}\right| + K_D(C_\infty - C_i)) \tag{8}$$

or

$$\frac{L^2}{t} = D_0(\ln\left|\frac{C_\infty-1}{C_i-1}\right| + K_D \ln\left|\frac{C_\infty-1}{C_i-1}\right| + K_D(C_\infty - C_i)), \tag{9}$$

where $t$: developing time,
for a certain one material system, we can assume

$$VL = \text{function}_1\ (\text{material diffusion property}) \tag{10}$$

or

$$\frac{L^2}{t} = \text{function}_2\ (\text{material diffusion property}). \tag{11}$$

## 3. Experiment

Electron energy was raised to 1.5 GeV at the Synchrotron Radiation Research Center (SRRC) of Taiwan Light Source. It provides electromagnetic radiation from UV to deep X-ray for the fields of basic research and industrial applications. Due to space limitations, a 16-m-long micromachining beamline without a mirror or filter was designed. The thickness of the beryllium end window is 125 $\mu$m.

A deep X-ray scanner with computer control (JENOPTIK) was installed to handle 4 inch standard wafers. The exposed samples are cooled by 100 mbar helium. A series of pumping and ventilation steps are executed during one exposure procedure.

In deep X-ray lithography, a 2-mm-thick PMMA photoresist is employed. The substrate must be electrically conductive for the next plating step. To reduce the number of

back-scattered electrons, the material of the plating base should have a low atomic number. The aluminum substrate has a lower density and a smaller absorption coefficient than titanium, thus producing fewer back-scattered electrons.

Rough surfaces of both materials can be created by 6 wt.% NaOH etching to increase the adhesion to PMMA. The glue for adhesion contains[6]

1. 11 wt.% PMMA and 89 wt.% methylmethacrylate (MMA).
2. 0.7 wt.% total solvent as mentioned in No.1 with benzoyl peroxide (BPO) and N,N-dimethyl aniline as starters.
3. 1.5 wt.% total solvent as mentioned in No.1 with hydroxyethyl methacrylate added to reduce stress corrosion defects and to promote adhesion.

Hot pressing was applied to bond a sandwich of copper-PMMA-aluminum. The aluminum substrate is the plating base.[6,7] The stress caused by the resin shrinkage can be released through an annealing process.

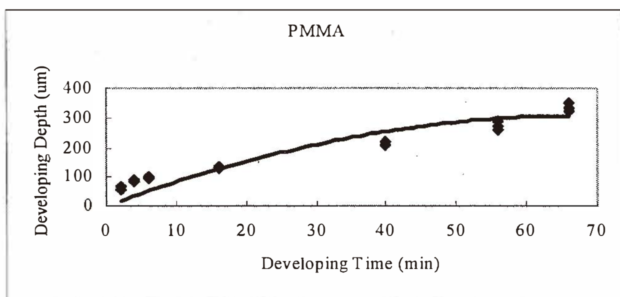
To measure the depth developed during the process, a mechanical measuring instrument with a probe tip was constructed. To avoid alignment error, this work adopts the concept of a conformal mask. A gold absorber is plated onto a copper base attached directly to the thick deep X-ray photoresist.[8] In contrast to the conventional membrane mask, the conformal mask becomes sacrificial for every die.

## 4. Results and Discussion

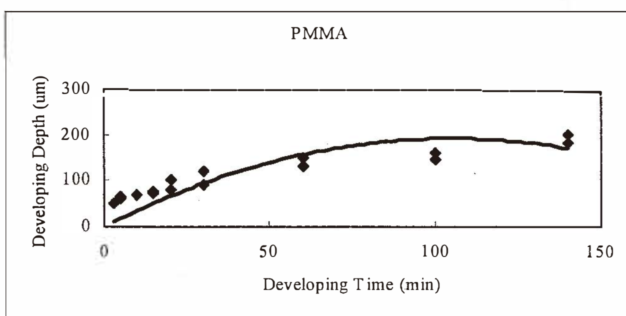
To investigate the development process independent of its essential parameters, it is necessary to simplify the development conditions as much as possible. Exposed PMMA dissolving in G-G developer is assumed not to react chemically. On the other hand, for this investigation, microstructures with a dose deposition of 4 kJ/cm$^3$ at the bottom and 20 kJ/cm$^3$ at the surface were evaluated.[9]

From eqs. (10) and (11), two effects became obvious. First, the developing rate for the same dose value is inversely proportional to the depth. The second effect is that the square root of the developing depth increases with increasing developing time. The experimental results for dose values between 4 and 20 kJ/cm$^3$ deposited in different depths are shown in Figs. 2 and 3, respectively. To simplify the problem of mass transfer, a constant diffusion coefficient is assumed in this research. Figure 2 shows that the square root of the developing depth correlates with developing time. Furthermore, as shown in Fig. 3, developing rate is inversely proportional to developing time. Both parameters show the same tendency with simulation predictions.

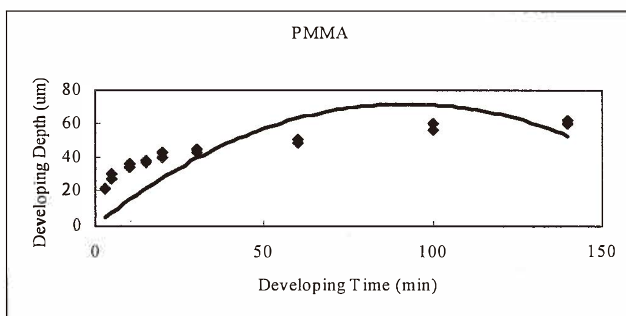
To develop exposed resist layers, a mixture of G-G developer is used at different temperatures, i.e., 36°C, 33°C and 28°C. This demonstrates the influence of temperature on the developing rate. The corresponding arithmetic developing rate is presented in Fig. 4. The developing rate increases as the developing temperature of the G-G developer increases.




(a) Developing temperature, 36°C

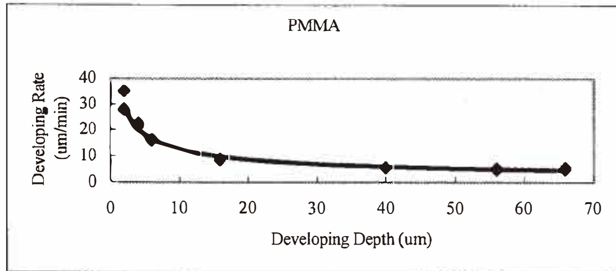



(b) Developing temperature, 33°C

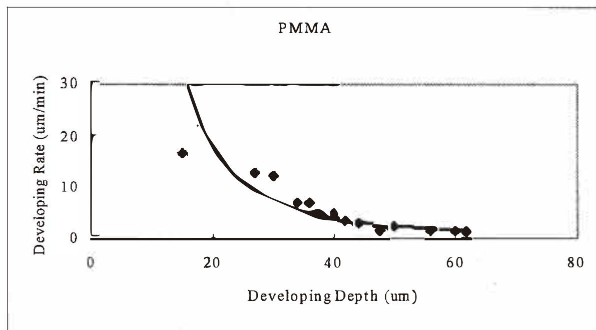



(c) Developing temperature, 28°C

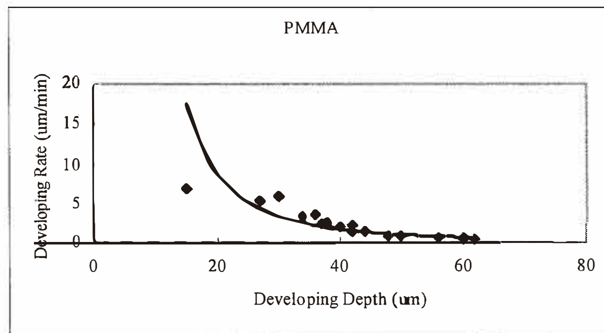
Fig. 2. Developing depth as a function of developing time. Developing temperature (a) 36°C, (b) 33°C and (c) 28°C.




(a) Developing temperature, 36°C




(b) Developing temperature, 33°C




(c) Developing temperature, 28°C

Fig. 3. Developing rate as a function of developing depth.

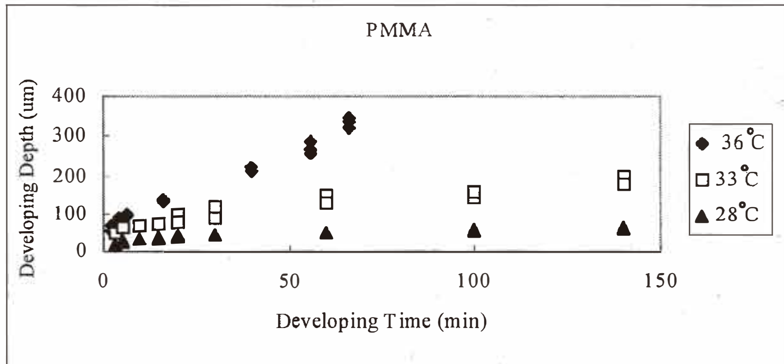



Fig. 4. Comparison between developing depth with different temperatures.

## 5. Conclusion

The observed results illustrate that the development process is determined by several different parameters. For the development rate of high aspect ratio microstructures, not only are the developing time and dosage decisive, but also the developing temperature is of great importance. In addition to the dissolution process, the coefficient for transport of the dissolved polymer out of the structure and solvent into the polymer is also decisively important.

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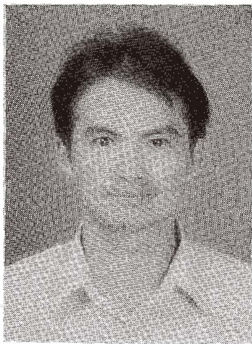

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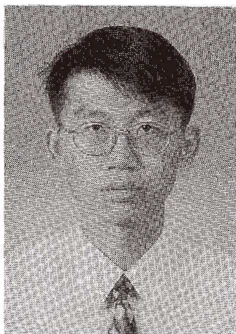

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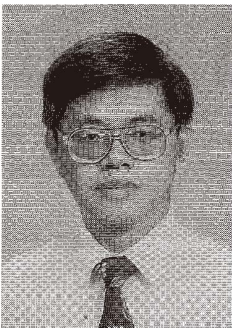

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