Transport Limitations on Development Times of LIGA PMMA Resists

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The LIGA process, employing x-ray lithography to expose a thick PMMA resist, is capable of producing either plastic or metal structures having feature heights up to several millimeters and feature aspect ratios of 50 or more. While such structures are possible, however, the successful development of exposed resists becomes difficult and time consuming as both the resist thickness and feature aspect ratio increase. Development times for a 200 μm resist thickness are typically less than two hours for all aspect ratios, but may increase to nearly 20 hours for high aspect ratios at a resist thickness of 1 mm. The development of thick resists is particularly problematic in resists patterned with both large and small features since features of widely varying size generally develop at widely disparate rates. The resulting disparities in development times may lead to a loss of structure accuracy or, in the worst of cases, to the detachment of small posts or webs due to lateral dissolution near the PMMA substrate.

These development problems all arise from limitations on the development rate imposed by transport processes. Development of exposed PMMA requires the dissolution of PMMA fragments at the liquid-solid interface, as well as the transport of these fragments out of the feature and away from the resist. Either the dissolution kinetics or the transport rate may thus determine the local development rate and overall development time.

The transport of fragments along a feature may occur either by diffusive or convective motion, or by some combination of both. Diffusive transport rates are relatively low due to the high molecular weights typical of PMMA fragments. Convective transport rates are usually much larger, even for fluid (developer) speeds as low as 10 μm/s, but convective motion is difficult to produce deep in features of high aspect ratio. As a result, small features of high aspect ratio tend to develop slowly at a diffusion-limited rate, while larger features, having low aspect ratios, tend to develop more quickly at the kinetic-limited rate of PMMA dissolution.

To help understand and quantify these transport limitations, we have developed a one-dimensional numerical model of the development process. This model takes into account the local absorbed x-ray dose, the PMMA dissolution kinetics and PMMA fragment transport along the feature by diffusion, forced convection and acoustic agitation. Based on this model, we find that the total development time for any first-order reaction governing the dissolution kinetics can be expressed rigorously as the simple sum of the kinetic-limited development time, t_0, and the characteristic time for transport, δt. That is

$$t = t_0 + \delta t \quad \text{where} \quad t_0 = \int_0^h \frac{dh}{R} \quad \text{and} \quad \delta t = \frac{h^2}{2DSh} \tag{1}$$

where t is the total development time, h is the resist thickness, R is the kinetic-limited development rate based on the local absorbed dose, $D \sim 10^{-11}$ m^2/s is the diffusivity of PMMA fragments in the developer, and Sh is the mean Sherwood number based on the feature size, inverse-averaged over the resist thickness. The Sherwood number indicates the magnitude of the PMMA fragment transport rate relative to that by diffusion alone. Its value is Sh = 1 for diffusive transport. Sherwood numbers for forced convection and for acoustic agitation must be computed from the multi-dimensional flow field induced within the feature.

The kinetic-limited development rate depends only on the dose and development temperature, so t_0 in Eq. 1 is independent of the feature size and aspect ratio. As such, the difference in development times for two features of differing size on the same resist is given by

$$\Delta t_{1,2} = t_1 - t_2 = \delta t_1 - \delta t_2 = \frac{h^2}{2D}\left(\frac{1}{Sh_1} - \frac{1}{Sh_2}\right) \tag{2}$$

Note that this result is (nearly) independent of the absorbed dose and depends only weakly on the developer temperature through the fragment diffusivity. It does, however, depend strongly on any developer motion within the feature through the two Sherwood numbers. Also note that the maximum possible differential in development times is $\Delta t_{1,2} = h^2/2D$ based on diffusion-limited development of a very small feature ($Sh_1 \sim 1$) and kinetic-limited development of a very large feature ($Sh_2 \rightarrow \infty$).

A sample calculation illustrating development times under conditions of forced convection is shown in Figure 1. In all cases the bottom dose is fixed at 5.2 kJ/cm^3, the GG developer temperature is 25 C and the speed of the developer at the resist surface is 10 mm/s. Here we see that the development time for very small features (d ~ 0) is controlled by diffusion, while those for very large features (d >> h) are controlled by the kinetics of dissolution. These diffusion-limited and kinetic-limited values are shown by the two solid curves. As expected, the disparity in development times between these two limits grows precisely in proportion to the square of the PMMA thickness. Development times are thus similar for all aspect ratios when the resist thickness is small, less than about 200 µm. As the thickness increases, however, the diffusion-limited and kinetic-limited development times rapidly diverge. Forced convection reduces development times to roughly the kinetic-limited values only for aspect ratios up to about one, and significant reductions in the development time are obtained only for aspect ratios less than 10. For aspect ratios above 10, forced convection provides little benefit in reducing development times. The reason for this behavior is that forced convection across the resist surface produces a series of discrete counter-rotating cells within a feature. The maximum aspect ratio of each cell is about 1.4, and the speed of circulation drops by about two orders of magnitude between adjacent cells. Developer within a feature is thus nearly stagnant at all depths exceeding 3 to 4 feature widths. As a result, Sherwood numbers for forced convective transport fall rapidly when aspect ratios exceed about five.

In contrast, Sherwood numbers for acoustic agitation depend on the feature size and acoustic intensity, but are independent of the aspect ratio when the aspect ratio is large. As such, development times of thick resists are dramatically reduced by acoustic agitation for all aspect ratios, provided that the acoustic intensity is sufficiently large and the feature size is not too small. This is illustrated in Figure 2 for an acoustic intensity of I ~ 10 W/cm^2. Here we see that development times are reduced to nearly the kinetic-limited values for all feature sizes greater than about 50 µm, and this reduction is nearly independent of the resist thickness. For a feature size of 20 µm, the development time lies about midway between the kinetic-limited and diffusion-limited values. Development times approach the diffusion-limited values as the feature size is further reduced. The reason for this behavior is that the streaming velocity induced by the acoustic field is independent of the feature size when the feature size is large, but falls off inversely with the size as the size grows small.

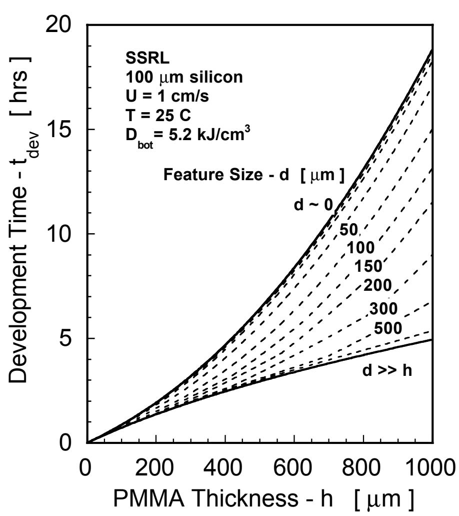

Figure 1. Development times for forced convection over PMMA surface. Time differential between small and large features grows large when the resist thickness is large and aspect ratios exceed about four.

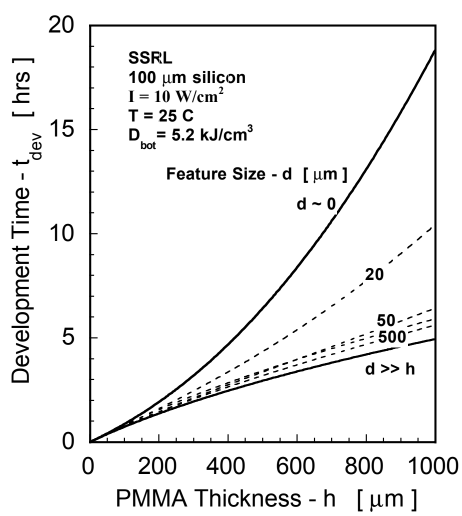

Figure 2. Development times under acoustic agitation. Development times and time differentials are dramatically reduced for all all aspect ratios when feature sizes are above about 20 µm.