The interplay between kinetics and thermodynamics during development of calixarene, a negative resist.

Deirdre L. Olynick [a], Weilun Chao [b] , Mark Lewis [a], Timothy Jen [a], Stefano Cabrini [a]
[a] *Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720 USA*
e-mail: dlolynick@lbl.gov
[b] *Center for X-ray Optics, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720 USA*

There is considerable evidence that resist resolution is often limited by development conditions (due to contrast, swelling, and collapse) and not beam size. For instance, Fujita et. al. [1] demonstrated the minimum resolvable feature of 10 nm in calixarene was independent of e-beam energy (varied from 10 to 50 keV) and found collapse was dose dependent. Yasin, et. al. [2] showed better line acuity is achieved with ultrasonic development. Here we present a study of the thermodynamics and kinetics of development for hexaacetate p-methylcalix[6]arene (calixarene), first demonstrated as a negative resist by Fujita, et. al. This material's main drawback is the low sensitivity (doses required are ~10-20 times higher than that for HSQ or PMMA resists) and propensity to collapse. However, hexaacetate p-methlcalix[6]arene still exhibits one of the highest resolutions for a negative electron beam resist material; 6 nm isolated lines have been demonstrated.[2]

Previously, we presented a study where we determined a 3-dimensional Hansen solubility sphere for calixarene and discussed how it could be used to optimize solvent choice for spinning, rinsing, and development of a negative resist.[3] We used this sphere to find the Flory-Huggins interaction parameter, χ, for calixarene-solvent pairs. Furthermore, we showed that contrast can be correlated to the χ parameter Low χ parameters, (stronger solvent/resist interaction) showed higher contrast, but more swelling, resulting in better overall pattern resolution. Furthermore, we discussed how ultrasonic development reduces pattern collapse because of the thermodynamic of swelling and kinetics of development.[4]

In this work, we expand upon this study to create a picture of development thermodynamics and kinetics in this negative system. We evaluated contrast and high resolution pattern quality for 11 solvents interacting with calixarene. Fig. 1 (top) shows contrast curves for development times of 30 sec. We found normalized thickness (at constant dose and time) correlates with χ/V_s where V_s is the molar volume of the solvent (Fig. 1, bottom), indicating the importance of both mixing energetics and solvent size during development. Fig. 2 shows time dependent contrast curves for calixarene development by xylenes. Long development was investigated to elucidate kinetically versus thermodynamically controlled behavior. Contrast is higher at lower development times because removal of the higher dose material is kinetically limited. Other developers tested show the same trend. Implications for developer and development time selection in the context of nanofeature pattern quality will be discussed.

1 J. Fujita, Y. Ohnishi, S. Manako et al., Microelectronic Engineering **41/42**, 323 (1998).
2 Shazia Yasin, D. G. Hasko, and F. Carecenac, J. Vac. Sci. Technol. B **19** (1), 311 (2001).
3 D. L. Olynick, W. L. Chao, M. K. Lewis et al., 2008 submitted to Journal of Polymer Physics..
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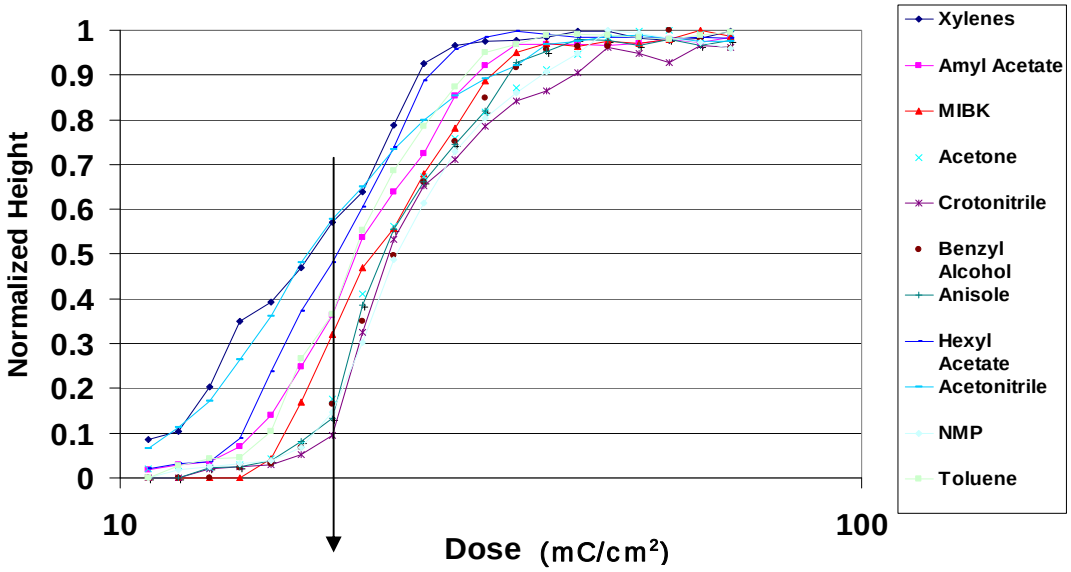

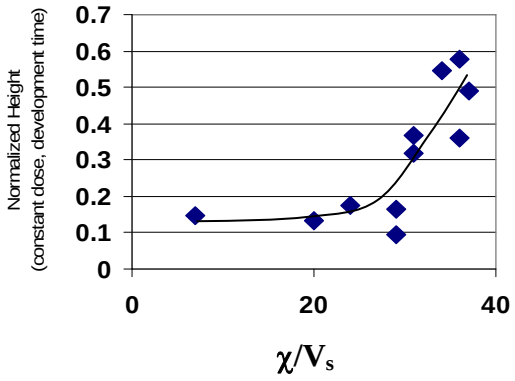

Fig. 1. Top: Contrast curves for 11 solvents with calixarene for 30 seconds of development time. Bottom: Normalized thickness at constant dose (dose noted by arrow on top curve) as a function of χ/V_s for each solvent. The trend is as for the thickness to decrease as χ/V_s decreases until all the unnetworked material is removed from the matrix (~.15 on the chart).

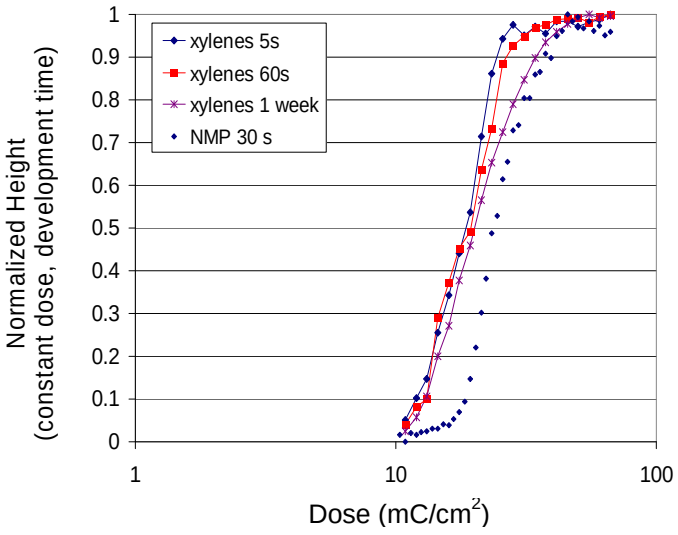

Fig. 2. Contrast curves as a function of time for xylenes. For xylenes, development is kinetically limited for the higher dosed material. Hence, shorter development times give better contrast. For comparison, NMP, a strong developer very effective at removing networked material, is shown.