A study of electron beam exposed calixarene development conditions and two application methods

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Hexaacetate p-methylcalix[6]arene was first demonstrated as a negative e-beam resist by Fujita, et. al. [1] with isolated line resolution of 10 nm, low sidewall roughness, and high etching resistance for a carbon based resist material. This material's main drawback is the low sensitivity (doses required are ~10-20 times higher than that for HSQ or PMMA resists.). Despite this, hexaacetate p-methlcalix[6]arene still exhibits one of the highest resolutions for a negative electron beam resist material; with ultrasonic development and an e-beam probe size (2-3 nm), 6 nm isolated lines have been demonstrated.[2]

There is considerable evidence that calixarene resist resolution is often limited by development conditions (due to contrast, swelling, and collapse) and not beam size. For instance, Fujita et. al. [3] demonstrated the minimum resolvable feature of 10 nm was independent of e-beam energy (varied from 10 to 50 keV) and mentioned collapse was dose dependent. Yasin, et. al. showed better line acuity is achieved with ultrasonic development. The authors demonstrated 6 nm isolated lines in calixarene (ultrasonic development and a 2-3 nm probe size).

In this paper we study application and development conditions for 100 keV electron beam exposed hexaacetate p-methylcalix[6]arene and discuss factors contributing to calixarene resolution including contrast, solvent molecule size, developer strength, swelling, and drying conditions.

For the first time, we demonstrate exposure of evaporated Hexaacetate p-methylcalix[6]arene. Evaporation allows resist application on non-planar surfaces and increases compatibility with solvent sensitive underlying films. Fig. 1 shows 30 nm thick evaporated calixarene films exposed at 10, 20, and 25 nm half-pitch.

Utilizing the Hansen solubility parameter model to determine optimal developers,[4] we test solubility of 24 solvents on spin-coated calixarene (Fig. 2). Solvents within the soluble/insoluble boundary thermodynamically favor dissolution; however, solvents positioned near the soluble/insoluble boundary swell the resist less. We use this chart to identify solvents near the boundary. We survey 6 solvents for contrast, sensitivity, and line acuity. Constrast tends to improve and sensitivity degrade as one moves towards the soluble/insoluble boundary. We find that amyl acetate provides the best contrast and sensitivity combination for the solvents surveyed (Fig. 2, table). SEM images of exposed and dense lines through dose show improved process latitude with amyl acetate over xylenes.

Finally, using critical point drying, we compared collapse using 5 sec ultrasonic and 30 sec ultrasonic development development in xylenes. Although the contrast is the same for both development conditions, collapse is significantly reduced when ultrasonic development and critical point drying are used in combination (Fig. 3).

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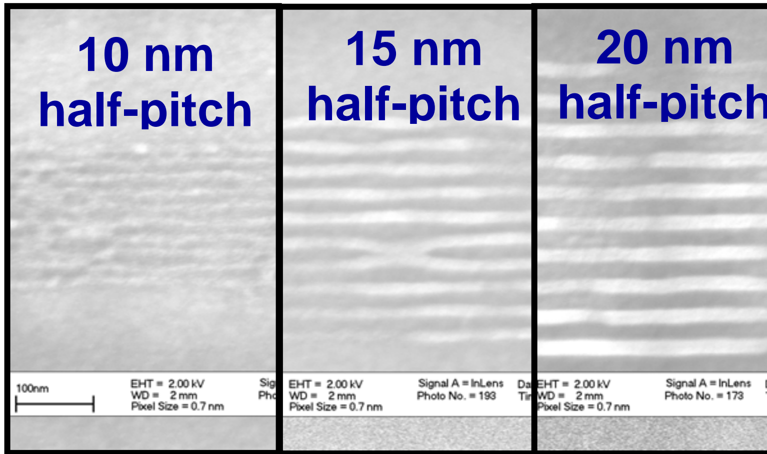

Fig. 1. E-beam exposure of evaporated calixarene (30 nm thick).

Solvent	$\sqrt{4\delta_d^2 + \delta_p^2}$	δ_h	γ	D_{50} (mC)
Xylenes	35.1	3.1	1.53	12.4
Acetonitrile	23.6	6.1	1.12	14.1
Amyl Acetate	35.5	6.1	1.95	10.5
MIBK	31.2	4.1	2.04	12.3
Benzene	36.8	2.0	1.85	13.9
Toluene	36.02	2.0	1.79	13.4

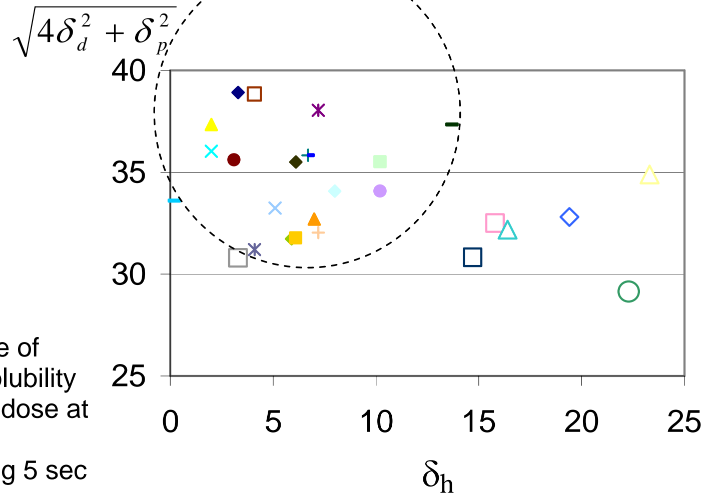

Fig. 2. Hansen Solubility plot for 24 solvents and table of select solvents. Solvents within dotted circle show solubility while solvents outside do not . Table shows contrast, dose at 50% thickness, and solubility parameters for 6 select solvents. All contrast measurements were taken using 5 sec ultrasonic development. Ultrasonic 5 sec xylenes development and 30 sec xylenes development, no agitation, produce indistinguishable contrast and sensitivity results.

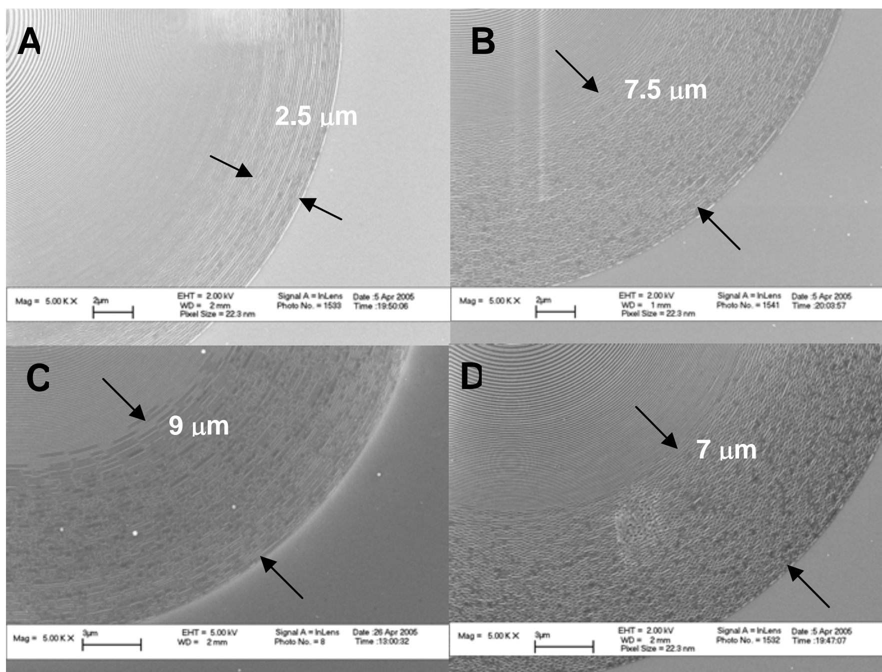

Fig. 3. Zoneplates (80 thick, 25 nm outer zone width) exposed in calixarene and developed and dried under 4 conditions. Arrows indicate approximate extent of collapsed zones. A) 5 sec ultrasonic xylenes followed by critical point drying (CPD). B) 30 sec xylenes follwed by critical point drying. C) 5 sec ultrasonic xylenes (no CPD). D) 30 sec xylenes (no CPD). Approximate linewidth where collapse occurs A) 67 nm, B) 88 nm, C) 92 nm, D) 86 nm