Synthesis, characterization, and investigation of a conformationally immobile calix[6]arene as a negative electron beam resist

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Calixarenes of a variety of molecular weights and with several different functional attachments have been studied as high resolution, high contrast negative electron beam resists. In this article, results are presented for a new type of calixarene molecule to be used as an electron beam resist. The molecule differs from previous calixarene resists through the use of bridging groups to limit its conformational mobility and by having only a partial functionalization of the available phenol units with allyl groups to enhance the resist sensitivity. Both the sensitivity and contrast of the calixarene were measured. The measured contrast was found to be 4, while the sensitivity was 3.6 mC/cm^2 which is comparable to other fully functionalized calix[6]arene resists. A closer comparison of this calixarene with similar calixarenes indicates that the measured sensitivity is better than would be expected for this partially functionalized molecule and that full functionalization might not be necessary to obtain a significant benefit from the functional groups. © *2005 American Vacuum Society.* [DOI: 10.1116/1.2038027]

I. INTRODUCTION

Calixarenes form a group of macrocyclic compounds that have been studied as high resolution, high contrast, negative electron beam resists for some time.[1–3] They have demonstrated very high resolution, having patterned features down to 10 nm or less. Their high resolution capability is due in part to the small size of the monomer, roughly 1 nm, in comparison to more standard polymeric e-beam resists like poly(methylmethacrylate) (PMMA). While the ultimate resolution may be limited by the size of the molecule, other resist patterning issues such as contrast and sensitivity help to determine the operational resolution during an exposure. Both high contrast and sensitivity are important to improve the dimensional control of the smallest features during electron beam exposure.[4]

Calix[n]arenes are cyclicized, oligomeric products of the base-induced condensation of p-*tert*-butylphenol and formaldehyde where *n* indicates the number of repeating phenolic/methylene units in the molecule, as shown in Fig. 1(a).[5] A three-dimensional depiction of a calix[6]arene is shown in Fig. 1(b). When all of the phenolic units point in the same direction as in Fig. 1(b), the molecule obtains the vase-like appearance known as the cone conformation. Depending on the size of the calixarene, many other conformations are possible. Besides the cone conformation, the most frequently encountered conformation is the 1,2,3-alternate in which three contiguous phenols point in one direction while the remaining three (in the calix[6]arene) point in the opposite direction. A significant synthetic advantage of the calixarene structure over other types of resists is realized because both the upper and lower rims of the molecular annulus may be

tailored with specific functional groups to enhance the stability and performance of the resist. This methodology has been exploited to improve both the calixarene resist sensitivity and its etch resistance in earlier work.[2] While functionalization of all of the rings in the calixarene annulus has been used most extensively, it is possible (and even desirable) to employ selective functionalization techniques in which different types of groups may be placed on either the upper or lower rims of specific rings in the annulus.

Besides being synthetically versatile, most calixarenes are highly flexible molecules due to through-the-annulus rotation [shown in Fig. 1(c)] occurring about the C–C bonds of the Ar–CH$_2$–Ar units (where Ar=aromatic ring). As a consequence of the rotations of individual aromatic rings, different conformations arise, and often coexist with each other resulting in a structurally ill-defined mixture. In this way, partial or complete inversion of the functional groups on the upper and lower rims may occur. To date, all of the calixarene electron beam resists reported have possessed some degree of this conformational mobility. This prompted our interest in investigating a conformationally rigid calixarene compound, to see whether removing this mobility would influence its resist behavior for better or worse. In a similar vein, previous calixarene studies have employed functional groups to enhance the resist sensitivity. But in all cases those works functionalized every available phenol unit in the ring on either the upper or lower rim. Since no work has been reported on the behavior of partially functionalized compounds, the compounds studied here were given functional groups only on selected locations of the calixarene molecule.

A variety of conformationally mobile calix[n]arene compounds have demonstrated high resolution as electron beam resists into the nanometer size scale. One of the earliest experiments[1] used hexaacetate p-methylcalix[6]arene (abbre-
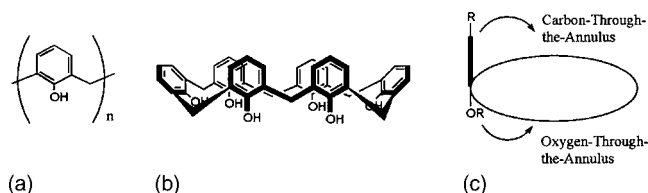

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FIG. 1. (a) Schematic of the generic calix[n]arene structure; (b) a three-dimensional representation of a calix[6]arene cone conformer; (c) possible rotation modes due to conformational mobility.
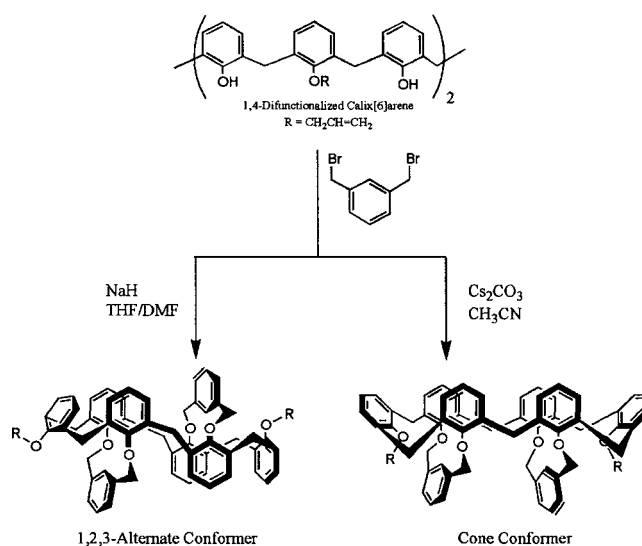

FIG. 2. Stereoselective syntheses of the 1,2,3-alternate and cone conformers. The 1,2,3-alternate conformer was studied as a negative electron beam resist.

viated as MC6AOAc by those authors) to pattern fine lines to 10 nm. In subsequent work,[2] this resist was determined to have a sensitivity 8.0 mC/cm^2 and a contrast of 2.4. This was considerably less sensitive than PMMA (~0.1 mC/cm^2), but the MC6AOAc did display a similar contrast. By chlorinating all the methyl groups on the upper rim, new chloromethylated calixarene resists (CMC[n]AOMe) were made. The addition of the chlorine was found to increase the sensitivity of the resist, CMC[6]AOMe, by an order of magnitude over the original MC6AOAc, approaching that of PMMA. Additionally, it was found that the sensitivity could be further enhanced simply by increasing the molecular weight of the resist by increasing the number of phenol units (calix[n]arenes with $n=5,6,7$ were studied). A similar dependence on the number of phenolic units n and on the functional groups was found by silylating the hydroxyl groups on the lower rim.[3] Extensive purification of the calixarene resist also resulted in improved contrast for both calix[6]arene and calix[7]arene compared to the less-purified calix[6]arene results.[6]

In this article, we report on the use of a conformationally immobile calix[6]arene as an electron beam resist. Conformational flexibility was greatly reduced by appending two rigid tethering units (*m*-xylenyl) to the lower rim in a transannular fashion. Additionally, the molecule was selectively functionalized, rather than fully functionalized, to enhance the electron beam sensitivity beyond that of the basic monomer. This leaves open the possibility of further resist enhancements by the addition of other functional groups. Although the ultimate resolution of the resist was not measured here, the resulting resist displayed a high contrast, which will favor the resolution capability. In addition, the resist displayed a sensitivity similar to the fully functionalized CMC[6]AOMe discussed previously.

II. CALIXARENE PREPARATION

The conformationally immobile calixarene monomer used in this study was diallyloxy bis-*m*-xylenyloxycalix[6]arene (hereafter abbreviated as DXC6). The monomer was prepared in both the usual cone conformer and in the asymmetric 1,2,3-alternate conformer. These conformers are depicted schematically in Fig. 2. We previously demonstrated our strategy for constructing intramolecularly bis-bridged calix[6]arenes in syntheses of two cesium-selective calix[6]-bis-crown-4 stereoisomeric ionophores.[7] The principle starting materials utilized in the syntheses of the bis-bridged

calix[6]arenes are also shown in Fig. 2. When the diallyl calixarene was reacted with α,α-dibromomethyl-*m*-xylene in the presence of Cs$_2$CO$_3$ and CH$_3$CN, analysis via thin layer chromatography indicated that the crude reaction mixture was comprised of one major component with some smaller amounts of more polar components. The major fraction was isolated (at 56% yield) via preparative liquid chromatography. The solid-state structure was studied by both x-ray diffraction and nuclear magnetic resonance (NMR) (^{1}H and ^{13}C) and found to be that of the cone isomer shown in Fig. 2. Changing of the base and solvent to NaH and THF/DMF (90/10), respectively, resulted in the formation of a different calixarene structure that was isolated with 65% yield. Subsequently, x-ray diffraction and NMR verified that this product was the 1,2,3-alternate bis-bridged isomer also shown in Fig. 2. Most of the resist studies were performed on the 1,2,3-alternate conformer as this represented the most significant structural departure from standard calixarene resists.

The presence of these bridges reduces the ability of the aromatic residues to rotate thereby creating semirigid compounds.[8] A number of linkers that immobilize the members of the calix annulus have been reported.[8,9] While the primary function of the xylene bridges in our compound is to provide conformational integrity, we presume that they may contribute to the overall sensitivity as well due to their aromatic nature. The inclusion of substituents with aromatic functionalities has previously demonstrated a higher degree of plasma etch resistance due to the aryl groups.[4] It has also been demonstrated that the calixarene resist sensitivity can be improved by an order of magnitude without degrading etch resistance by introducing allyl groups on the upper or lower rim.[10] In previous studies, the calixarene annulus has been fully functionalized. In the current work, the calix[6]arene has been selectively functionalized with only

two allyl groups strategically positioned on opposite sides of the annulus. This leaves the other phenol units available for functionalization for other purposes.

To create the resists, chlorobenzene was used as the solvent. The solids were dissolved by stirring and heat until a homogeneous mixture was prepared. The solutions were filtered through millipore filters and dispensed into vials for later use. All formulations were based on the weight percentage of the monomer relative to the solvent. In some solutions recrystallized benzoyl peroxide (BPO) was included in the mixture to act as a radical initiator to determine whether the BPO had any affect on the cross-linking behavior of the resist.

III. ELECTRON BEAM EXPOSURE SAMPLE PREPARATIONS

To characterize the film-forming capability of the calixarene and prepare samples for electron beam exposure, clean 100 mm Si(100) wafers were used. The DXC6 formulations (of the 1,2,3-alternate monomer) were manually applied to the sample wafers using a 0.2 μm polytetrafluoroethylene filtered glass syringe and a dynamic dispense method was employed for the coating. Samples were spun on a programmable spinner for a total spin time of 60 s. After spinning, the samples were soft baked at 170 °C for 120 s on a hot plate in a laminar flow hood.

These coated 100 mm samples were examined as is to measure the resist thickness. Samples for electron beam exposure were cleaved along the crystal axes of the (100) wafers into square samples of approximately 2.5 cm on a side.

IV. RESULTS AND DISCUSSION

To determine film thicknesses of the samples, three-angle null ellipsometry at a wavelength of 632.8 nm was performed. The measurements were analyzed using a Marquardt-Levenberg algorithm[11] for a best fit. To provide a calibration check, thermally oxidized wafers with a known oxide thickness were first checked with the procedure. Measurement of clean, bare wafers gave a native oxide thickness of 2.05 nm. This value was used in the subsequent measurement and analysis of the calixarene-coated wafers using a three-layer model of the calixarene/native oxide/Si substrate samples.

Spin curves for a variety of concentrations of resists were measured. Spin curves for the 1,2,3-alternate conformer of DXC6 with weight percentages 0.5% and 1.0% are shown in Fig. 3. Uniform, continuous films down to at least 8 nm were formed using the lowest concentration resists. Checks of film uniformity were made on some samples, giving values of about 3% of the film thickness for the lower concentrations. Film uniformity was more difficult to maintain for higher concentration resists ($\geq 5\%$) and was more sensitive to the precise spin conditions. For comparison, the inset of Fig. 3 presents film thicknesses for four different concentrations (weight percentages of 0.5%, 1.0%, 1.5%, and 5.0%) all spun at 3000 rpm and soft baked as noted. Spin curves for the cone conformer of the DXC6 calixarene were also ob-
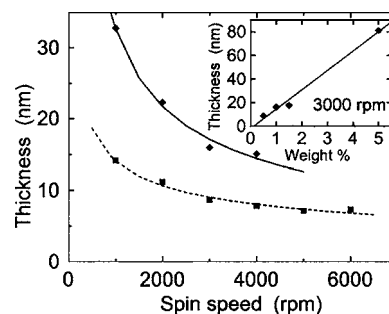

FIG. 3. Spin curves for 1, 2, 3-alternate calixarenes at concentrations (weight percentages) of 0.5% (square symbols) and 1.0% (diamond symbols). The lines are best fits to the data using a power law relation. The inset shows thicknesses of several different weight % calixarene solutions at 3000 rpm.

tained. The cone conformer films were found to be thicker than the alternate conformer at each spin speed. Additionally the refractive index of the both DXC6 conformers was found to be $n = 1.56 \pm 0.01$.

In a separate experiment, the dispersion of the DXC6 alternate conformer was measured between 600 and 1100 nm using a rotating analyzer ellipsometer. The measured ellipsometric angles Δ and Ψ were then used to model the wavelength dependence of the refractive index by fitting the Cauchy coefficients from $n = A_n + B_n/\lambda^2$. For the DXC6 alternate conformer sample used in the electron beam exposures, the Cauchy coefficients were found to be $A_n = 1.54$ and $B_n = 0.016$ μm^2.

Electron beam exposures were performed in a JEOL JSM IC848 scanning electron microscope. All the exposures were performed at an acceleration voltage of 20 kV. For contrast and sensitivity measurements of the resist, a large area exposure was used to create a rectangular pattern 30 μm $\times 40$ μm in size. Exposures of the DXC6 alternate conformer were made of samples up to 7%. The contrast reported here was measured using 1% samples. Exposed samples were developed by manual agitation in xylene for 30 s, a 30 s rinse in isopropyl alcohol, followed by drying with nitrogen gas.

After inspection in an optical microscope, patterned samples were measured with an atomic force microscope (AFM) to determine film thickness and develop a contrast curve. The results of the exposure measurements are shown in Fig. 4 using solid data points. Extrapolation of the curve from the linear regime was used to determine both the threshold dose and the insolubation (or gel) dose needed to retain the full resist thickness. The threshold sensitivity for the DXC6 alternate conformer was $D_{th} = 2.0$ mC/cm^2, while the gel dose was $D_g = 3.6$ mC/cm^2. From these values, the resulting resist contrast was found to be 4.0. A best fit to our data was also obtained and is displayed in the plot.

In order to compare contrast and sensitivity of the DXC6 alternate conformer, exposure data from other calix[6]arene formulations have been added to Fig. 4 as lines. The contrast curve from Ref. 2 for the unfunctionalized MC6AOAc is shown as a dotted line while the sensitivity-enhanced chloromethylated CMC[6]AOMe is shown as a dashed line.[2] The
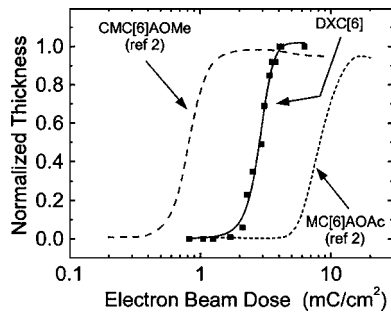
FIG. 4. Measurement of the sensitivity and contrast from threshold exposure through to a fully exposed resist thickness for the DXC6 alternate conformer (solid symbols). The DXC6 alternate had a gel dose D_g of 3.6 mC/cm^2 and a contrast of 4. The solid line through the data is a best fit to our data. Also shown are data from Ref. 2; the dashed line is CMC[6]AOMe with a D_g $\sim$1 mC/cm^2 and the dotted line is MC[6]AOAc with $D_g \sim$8 mC/cm^2. The contrast for each of these was reported to be 2.4.

sensitivity of our DXC6 alternate conformer, which is only partially functionalized with two allyl groups, falls between these on the log graph. Results from a number of calix[6]arene experiments are tabulated in Table I with the current results presented first. Although the ultimate resolution of the DXC6 alternate calixarene was not probed in the current work (the smallest structures that have been patterned so far for device applications are about 200 nm), its exposure parameters compare very favorably with the other calix[6]arene formulations. (In this table, results from other works were collected, but when a particular value was not reported it has been measured from their published data and entered with brackets to indicate that it is an estimated value.) The contrast of the DXC6 alternate was higher than the others presented in the table while its gel dose was among the lowest. Of the calix[6]arene resists in the table, only the fully functionalized, CMC[6]AOMe at 50 kV displayed a higher sensitivity.[2] (Of course, one must be careful when comparing exposure sensitivities between different groups.) Both of these characteristics, high contrast and low D_g, will contribute to high resolution patterning for the DXC6 calixarene conformer.

A question that arises is whether the resist behavior can be significantly enhanced with less than a fully functionalized monomer, by intentional manipulation of the number of attached functional groups. Previous resist studies have demonstrated clearly that attaching functional groups on the calix annulus does improve resist characteristics (such as sensitivity or etch resistance). But those earlier studies only examined either unfunctionalized calix[n]arene resists (i.e., not deliberately functionalized to enhance behavior) or they have attached functional groups to *every* available site on one of the molecular rims, creating fully functionalized molecules. If the resist improvement is simply proportional to the number of functional groups, then fully functionalizing the molecule with the appropriate group would yield the best possible result. On the other hand, if the resist behavior is more complex than this, it might be possible to optimize a given property by employing only partial functionalization with a specific group. Then the remaining, unused sites on the ring could be used for other purposes or optimization of other traits. Since our calix[6]arene is only partially functionalized, comparison with other results may help to answer this question.

In comparing these results with others, one must account both for differences in calixarene size or molecular weight (since larger rings are known to be more sensitive) as well as functionalization differences between monomers. In the current work, the DXC6 alternate conformer is partially functionalized with only two allyl groups (out of six sites on a given rim). The work presented in Ref. 3 experimented with calix[4]arenes that either were unfunctionalized or fully functionalized, also with allyl groups. Comparison with their results removes the possible effects of different chemical amplification paths. One of their molecules was fully functionalized with allyl groups either on the upper or lower rims (100% functionalized with four allyls on an upper or lower rim), while another had no functional groups attached (0% functionalized). For the 100% functionalized calix[4]arenes (tetraallylcalix[4]arene), the authors reported seeing no significant sensitivity differences between attachment on the upper or lower rims, although the two contrast curve results were not identical. Since these are mobile conformers, this might not be unexpected. However, comparison between functionalized and unfunctionalized calix[4]arenes did show an improvement of about one order of magnitude in sensitivity. These results are given in Table II along with our partially functionalized DXC6 result. If the sensitivity varies with the number of attached allyl groups, then one could interpolate its value to different numbers of allyls using their

TABLE I. Comparison of the exposure results for the DXC6 alternate (conformationally immobile) and a number of conformationally mobile calix[6]arene conformers with different functional groups. Bracketed values are estimated from the data plots of that reference. (α=4-tert-butyl-calix[6]arene.)

Calix[6]arene	V_{acc} (kV)	Sensitivity D_{th} (mC/cm^2)	D_g (mC/cm^2)	Contrast	Ultimate resolution (nm)
DXC6 alternate (this work)	20	2.0	3.6	4	Not measured
MC[6]AOAc (Ref. 1)	50	0.8	7	1.6	12
CMC[6]AOMe (Ref. 2)	50	[$\sim$0.6]	[$\sim$1.1]	2.4	12
TBC[6]$^\alpha$ (Ref. 3)	25	[$\sim$3.5]	[$\sim$7]	[2.9]	Not reported

TABLE II. Comparison of the exposure sensitivities of the DXC6 alternate calix[6]arene of the current work partially functionalized with two allyl groups to calix[4]arenes with and without attached allyl groups. (α = tetraallylcalix[4]arene.)

Calix[n]arene n	Name	No. of attached allyl groups	% allyl group functionalization	Gel dose D_g (mC/cm^2)	Data source
4	calix[4]	0	0%	30	Ref. 3
4	TAC[4]$^\alpha$	4	100%	3	Ref. 3
6	DXC6	2	33%	3.6	This work

two results. Assuming a simple linear relationship of the sensitivity D_g on the degree of functionalization using the calix[4] data, then we can interpolate a sensitivity at the 33% DXC6 functionalization giving $D_g \sim 21$ mC/cm^2. This is compared to the actual DXC6 sensitivity of 3.6 mC/cm^2. To complete the comparison, it is still necessary to account for the larger DXC6 monomer which should be more sensitive than the calix[4]arenes. Several authors have measured the sensitivity difference between different monomers.[3,6] The linear relationship between D_g and the inverse molecular weight for calixarene resists is understood as a cross-linking mechanism using the Charlesby theory.[12,13] In going from the more sensitive calix[6]arenes to the less-sensitive calix[4]arenes, the molecular weight decreases roughly by 33% to $\sim$50% (depending on whether the DXC6 bridging units are also counted). This would increase the DXC6 gel dose by the same percentage, giving a range from $\sim$4.8 to $\sim$5.4 mC/cm^2. However, this is still a factor of $\sim$4 better than that predicted using the linear relation for D_g vs % functionalization. This rough comparison suggests that our partially functionalized resist is more sensitive than would be expected from a linear dependence on functionalization. One possible explanation is that the cross-linking mechanism might be a strong, nonlinear function of the number of allyl groups and that the presence of any such groups provides a sensitivity enhancement. This implies that full functionalization may not be necessary to get a significant benefit compared to an unfunctionalized, native calixarene. We are currently investigating the chemical synthesis pathways needed to produce other partial functionalizations in our calix[6]arenes in order to test these ideas in a single set of exposure experiments on a single calixarene monomer.

In conclusion, data have been presented on the use of a partially functionalized, conformationally rigid calix[6]arene as a negative electron beam resist. Although the ultimate resolution capability of the DXC6 resist was not measured, the resist did display both high sensitivity and high contrast. The values of each parameter were comparable to those found in other calix[6]arenes that were fully functionalized, even though the DXC6 was only partially functionalized. A comparison of the current work with calixarenes that used the same functional groups suggests that full functionalization may not be necessary to obtain a significant benefit of functional group attachment. This result is undergoing further study.

ACKNOWLEDGMENTS

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