Evaluation of calixarene—derivatives as high-resolution negative tone electron-beam resists

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We present a systematic evaluation of calixarene derivatives as high-resolution negative tone resists for electron-beam lithography with a focus on their sensitivities. We studied the effect of a modification of the calixarene molecules to trimethysilyl ethers as well as the effect of an introduction of an allyl group and showed that the introduction of double bonds into the molecules can improve the sensitivity of the resists while their position does not seem to be important. The high-resolution capability of tetraallylcalix[4]arene was confirmed by fabricating an 18 nm dot array. © 2002 American Vacuum Society. [DOI: 10.1116/1.1521737]

I. INTRODUCTION

In electron-beam (e-beam) lithography, there is a continual need for high-resolution negative tone resists. It has been shown previously that calixarenes and their derivatives can be used as negative tone electron-beam resists.1,2

Calixarenes are a group of macrocyclic molecules in which phenolic units are linked via methylene bridges in ortho-position to the phenolic hydroxyl groups. They acquired their name because of the resemblance of the shape of one conformer (cone) of the smallest member of the family (calix[4]arene) to a type of Greek vase called (a) calix crater. Calixarenes are available in large quantities by an easy one-pot condensation of p-tert-butylphenol and formaldehyde under alkaline conditions. This reaction leads to a calix[n]arene consisting of n phenolic units (n = 4–20) in a cyclic arrangement. Procedures have been elaborated that make the cyclic tetra-, hexa-, and octamer selectively available in high yields. Compared to most organic compounds, calix[n]arenes have extremely high melting points and a high chemical stability. Chemical modifications are possible at both, the so-called “upper rim” and the “lower rim”. Therefore, a large variety of derivatives are available by chemical modification.3 In Fig. 1, the cavity structure of tert-butylcalix[4]arene is shown. It is very analogous to the polymeric structure of the well-known novolak resins.

Due to their small molecular size ∼1 nm calixarene e-beam resists have the potential of enabling patterning down to the regime of 10 nm or even below.3,4 The area dose, however, lies in the regime of several mC/cm² which is almost three orders of magnitude worse than that of a standard chemically amplified resist. Many calixarene derivatives have very bad solubility in organic solvents and tend to form microcrystals which results in very inhomogeneous films.

It has been shown previously2 that both the solubility and sensitivity can be improved by the introduction of functional groups in the “upper rim” and “lower rim” of the molecules. Hexachloromethyl–hexaacetoxycalix[6]arene with a practi-cal area dose of about 0.7 mC/cm² at 50 kV has become a commonly used calixarene derivative for high-resolution e-beam exposures.1,2,4

In order to further improve sensitivity and to learn something about the crosslinking mechanism, which has not been fully resolved up to now, we have started systematic studies on different calixarene derivatives with a focus on their sensitivities. Issues like etching resistance and high-resolution capabilities have also been examined.

II. SYNTHESIS

All used calixarene derivatives were synthesized according to literature procedures5–7 and characterized by common analytical techniques. The formation of the cycles out of p-tert-butylphenol and formaldehyde in one reaction step [Fig. 2(a)] is based on a complex mechanism. The reaction conditions, like the temperature and the amount and kind of base involved, determine which ring sizes are formed.5

To get a better starting material for further modifications on the upper rim and to increase the solubility of the calixarene-cycles, the tert-butyl groups were removed via a so-called retro-Friedel–Crafts reaction [Fig. 2(b)]. This Lewis-acid catalyzed transalkylation is a useful tool to obtain calix[n]arenes containing unsubstituted para-positions.6 The lower rim of the calix[n]arenes is already functionalized with the phenolic hydroxyl groups. These groups provide an excellent starting point for derivatizations via esterifications and etherifications.

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Fig. 1. Structure of a calix[4]arene in cone conformation. R = –C(CH3)3.
The trimethylsilyl ethers of the calix[n]arenes provide useful derivatives for use as e-beam resist materials because of the anticipated increase of the etch resistance. To get a complete functionalization of all hydroxyl groups of the calix[n]arenes, especially reactive silylating reagents such as N,O-bis(trimethylsilyl)acetamide, are required [Fig. 3(a)].

A useful method for preparing alkyl ethers involves treatment of the calix[n]arenes with the respective alkyl halide in alkaline conditions.

Fig. 2. (a) One-pot procedure to synthesize tert.-butylcalix[n]arenes. (b) Dealkylation of the tert.-butylcalix[n]arenes via a retro Friedel–Crafts reaction.

Fig. 3. (a) Formation of the trimethylsilyl ethers of the calix[n]arenes. (n=4, 6, and 8). (b) Preparation of allyl derivatives at the lower rim and the upper rim of the calix[4]arene, respectively.
a tetrahydrofuran–dimethyl formamide solution in the presence of sodium hydride. First, an allyl ether was generated [Fig. 3(b)] in an ether formation reaction to introduce a double bond in the calix[4]arene molecule. The product of this reaction step (tetraallyloxy calix[4]arene) was then converted into the upper rim derivative (tetraallyl calix[4]arene) via a so-called Claisen rearrangement reaction. Because of difficulties encountered with the electrophilic substitution reactions of calix[n]arenes, this alternative synthesis pathway permitted higher yields of the tetraallyl calix[4]arene. The tetraallyl ether was heated in refluxing $N,N$-diethylaniline to obtain a rearrangement of all allylic groups in the calixarene molecule.6,7

III. FILM PREPARATION AND EXPOSURE

The calix[n]arenes ($n=4$, 6, and 8) and their derivatives were dissolved in dichloromethane with varying concentrations up to 5 wt % under reflux conditions. The solutions were filtered through 0.45 μm filters and spun on silicon wafers with film thicknesses ranging from 25 to 500 nm. The samples were prebaked at 80 °C for 3 min.

To estimate the sensitivity we used a 25 kV e-beam lithography system. High-resolution exposures were performed at 30 kV using a Philips XL30 FEG scanning electron microscope together with a digital pattern generator.8 The samples were developed in methylisobutylketone (MIBK) and rinsed in isopropyl alcohol (IPA) before drying.

IV. SENSITIVITY

In order to study the dependence of the sensitivity on the number of phenolic units, we exposed films of tert.-butylcalix[4,6]arenes to 25 keV electrons. These materials showed poor solubility in dichloromethane and also other organic solvents and the spun films were inhomogeneous. In the case of tert.-butylcalix[8]arene, no resist layer with sufficient quality and thickness could be obtained.

Figure 4(a) shows the contrast curves of the tert.-butylcalix[4,6]arenes. The sensitivity seems to increase with increasing number of phenolic units. This fact has been reported before9 and can be explained by the increasing size and weight of the molecules.

In a next experiment, we tested the sensitivity of calix[4,6]arene where the tert.-butyl groups had been removed. These materials showed improved solubility and film quality. Figure 4(b) shows the same dependency on the molecular size. The sensitivity was slightly decreased compared to Fig. 4(a).

In order to improve solubility and resist adhesion, we tested calixarene derivatives which were converted into trimethylsilyl ethers by etherification of the hydroxyl groups at the lower rim. These trimethylsilyloxy-tert.-butylcalix[n]arenes could be easily dissolved in dichloromethane in sufficient concentrations for $n=4$, 6, and 8. Homogeneous films with thicknesses up to 500 nm could be spun. In the case of $n=4$, sensitivity was improved by a factor of 2 compared with the unmodified materials [Fig. 5(a)]. The derivative with eight phenolic units had a threshold dose of ~1.5 mC/cm² at 25 kV beam voltage and a practical dose of ~3 mC/cm².

Tetraallyloxy calix[4]arene and tetraallylcalix[4]arene both showed good solubility and film quality. Compared to calix[4]arene, the practical dose at 25 kV was about one order of magnitude lower [see Fig. 5(b)]. The position of the allyl group (upper or lower rim) does not seem to have a strong influence on the resist behavior.

The fact that an introduction of double bonds into the molecules improves sensitivity indicates that chemical amplification techniques which are well known from novolak resists can also be applied to calixarene derivatives. This will be the issue of our further investigations.

V. ETCHING RESISTANCE

Preliminary etching experiments were performed using an Oxford Plasmalab 80 reactive ion etching tool. First, we
transferred structures of tetrakis(trimethylsilyloxy)-tert.-butylcalix[n]arene and tetraallylcalix[4]arene into silicon. For that experiment, we used a mixture of 45 sccm CHF₃ and 6 sccm O₂ at a pressure of 75 mTorr and a power density of 0.5 W/cm². We estimated a selectivity for both derivatives to silicon of 2:1.

We anticipated an improved resistance of the trimethylsilyl ether toward etching in an oxide plasma due to the silicon atoms in the molecules. Therefore, we spun both derivatives on a 500 nm thick crosslinked novolak layer and tried to transfer resist patterns into the bottom resist at 75 mTorr and 0.25 W/cm². The selectivity however was 1:1 for both materials. Further investigations of this finding and of ways to improve selectivity are underway.

VI. HIGH-RESOLUTION PATTERNS USING TETRAALLYLCALIX[4]ARENE

As the main interest for this negative tone resist is its potential for high-resolution e-beam lithography, we exposed dot patterns in a 25 nm thick tetraallylcalix[4]arene layer on a silicon wafer which had been primed with hexamethyldisilazane using a beam energy of 30 kV and a beam current of 65 pA. After exposure, the sample was developed in MIBK for 12 s and rinsed in IPA (isopropyl alcohol). We obtained dot patterns with a diameter of 18 nm in a period of 40 nm. The dose in Fig. 6 was 65 fC/dot.

VII. CONCLUSION AND OUTLOOK

We have investigated the behavior of different calixarene derivatives as e-beam resists and found that the resist sensitivity can be improved by the introduction of allyl groups into the molecules while the etching resistance and high-resolution capabilities remain sufficient. Further research will address the application of techniques which are generally used to enhance the sensitivity of novolak resins for sensitivity improvements with calixarene derivatives.

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