High-purity, ultrahigh-resolution calixarene electron-beam negative resist

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Calixarene is a promising high-resolution negative electron-beam resist having a resolution of the order of 10 nm because of its low molecular weight. We have made a purified calixarene resist containing metal contaminants whose concentrations are measured in parts per billion and which therefore do not degrade the performance of silicon-based electron devices. The purity of the calixarene itself was also improved and we obtained high-purity calix[6]arene and high-purity calix[7]arene, both of which contain the main component, which is more than 95% of all the calixarene present. The resolution of both purified calixarene resists is almost the same as that of the unpurified calixarene, but the sensitivity of calix[7]arene is higher than that of calix[6]arene because its molecular weight is higher. © *2000 American Vacuum Society.*
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I. INTRODUCTION

Electron-beam (e-beam) nanolithography is the only lithographic technology currently used to fabricate working nanometer size devices.[1] Nanometer resolution lithography has been achieved by using e-beam spot sizes below 5 nm,[2] and high-resolution positive resists such as poly(methylmethacrylate) (PMMA) and ZEP520.[3] But no high-resolution negative resist has been available. Minute devices such as single-electron devices have therefore been fabricated by using PMMA and a lift-off process. In the development of silicon metal–oxide–semiconductor (MOS) devices, conventional negative resists have been used for the gate fabrication.[4] The reason for the use of a negative resist is that a gate electrode is fabricated by dry etching a polysilicon layer, or a multilayer consisting of metal and polysilicon. A negative resist is therefore useful for reducing e-beam exposure time and increasing process latitude, which improves throughput and yield.

We have reported a high-resolution calixarene resist[5] and have used it to obtain a high-density dot array with dots about 10 nm in diameter.[6] We have also used it in the fabrication of minute silicon devices and have obtained a 8 nm gate-length electrically variable *EJ* MOS field effect transistor shallow junction with trimming technology.[7] Our calixarene resists, however, contains calixarenes with various numbers of benzene rings and also a significant amount of metal contamination. A low-purity calixarene resist is not suitable for use when investigating its characteristics, nor for the fabrication of silicon MOS devices.

In this article we report the purification of calix[6]arene

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and calix[7]arene resists, their e-beam exposure characteristics, and the high-resolution patterning that can be obtained with these resists.
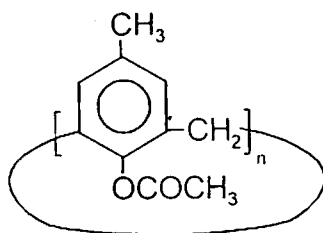
II. EXPERIMENTS

We used the JBX-5FE (JEOL Ltd.) electron-beam lithography system operating at 50 kV acceleration voltage and with a Gaussian spot size of 5 nm in diameter. The calixarenes were dissolved in mono chlorobenzene, and 1.5 wt % solutions were spin-coated in a way similar to that used in conventional semiconductor processes. Resist films 40 nm thick were formed on Si wafers when spin coated at 3000 rpm for 30 s and were baked at 170 °C for 30 min under a nitrogen flow to dry sufficiently and to prevent them from oxidization; however, this prebake condition has not been optimized. After e-beam exposure, the wafers were developed by dipping them in xylene for 1 min. After they were then dried in an oven at 170 °C for 30 min, the film thickness was measured by an atomic force microscope (AFM) or by using an Alpha-Step 200 (Tencor Inst.) step profiler. Resist patterns were observed with a S-5000 (Hitachi) high-resolution scanning electron microscope (SEM).

III. PURIFICATION OF CALIXARENE RESISTS

The chemical structure of calixarene[8] is shown in Fig. 1. Calixarene is a cyclic oligomer consisting of a number (shown by "*n*") of phenol groups. The number of phenol groups in a typical calixarene high-resolution resist is 6, and the molecular weight of such a calixarene is 972. The mo-

FIG. 1. Chemical structure of calix[n]arene.

lecular diameter is about 1 nm.[9] When the number of phenols is 6, we call the calixarene hexaacetate p-methylcalix[6] arene (MC6AOAc). Most calixarene derivatives have poor solubility in organic solvents, but our calixarene is soluble in organic solvents such as o-dichlorobenzene or mono-chlorobenzene and can withstand temperatures of up to 220 °C.[10] Films of calixarene can therefore be easily made .. ng a spin-coating method similar to that used in conventional resist processes. We previously found that calixarene films work well as negative electron-beam resists, providing both ultrahigh resolution and extreme durability during halide plasma etching.[11]

In this article the word "purity" has two meanings. One refers to the homogeneity of the calixarene itself, and the second refers to the absence of metal contaminants, such as Na, Mg, K, and Fe. Some of these metals are catalysts when synthesizing calixarenes and are from the environment, but all are considered contaminants in silicon-based electron device fabrication.

The components of calixarene resists are listed in Table 1. What we call unpurified calix[6]arene is the low-purity calix[6]arene which we have already shown can produce high-resolution patterns. The purity of samples was evaluated by using high-pressure liquid chromatography (HPLC: silica-chloroform/hexane) and size-exclusion chromatogra-▲ (TSK gel/G2000H-chloroform). After most of the metal n.. purities were removed, the trace amounts remaining were measured by inductively coupled plasma–atomic emission spectrometry (ICP-AES) for Ca and by ICP mass spectrometry (ICP-MS) for other metals. As shown in Table 1, the

unpurified calix[6]arene resist was found to contain a lot of metal impurities and macromolecules and a lot of calixarenes with phenolcount different from the number in the main calixarene component. The term macromolecule used here implies other types of organic chain polymers.

Calix[6]arene was synthesized as described in our previous article[9] and was further purified by filtration from ethyl acetate. Calix[7]arene was obtained as a byproduct of the calix[6]arene synthesis: it was extracted from the acetone-soluble portion of the reaction mixture by column chromatography. The crude product was then purified by precipitation from ether to give a white solid. The precipitate was identified using several analytical techniques including proton-nuclear magnetic resonance (^{1}H), infrared spectroscopy and secondary ion mass spectroscopy. With these processes high-purity calixarenes were obtained (Table I). In the process for calix[6]arene, the main calixarene composition was 96.8% and for calix[7]arene it was 95.0%. In both cases the metal contamination was reduced by three orders of magnitude.

IV. SURFACE ROUGHNESS

Resist film roughness is one of the important characteristics for obtaining high-resolution patterns. The surface roughness of spin-coated calix[n]arene resist was observed using AFM. Figure 2 shows the AFM image of an area of 2 by 2 μm of calix[7]arene resist before e-beam exposure. No significant irregularity was observed for all calix[n]arenes. The summary of surface roughness of both high-purity calix[6,7]arene and unpurified calix[6]arene is shown in Table II. The measurement repeatability is less than 0.1 nm. The roughness shown by peak-to-valley and by rms for high-purity calix[6]arene and unpurified calix[6]arene is almost the same: about 3.5 and 0.38 nm, respectively. On the other hand, the roughness for high-purity calix[7]arene is smaller than that for both calix[6]arene. This may be due to the deference in molecular structure of calix[6]arene and calix[7] arene. Calix[7]arene has poorer symmetrical structure compared with that of calix[6]arene, so this unsymmetrical struc-

TABLE 1. Composition of calix[n]arene resists.

Resist components		High-purity calix[6]arene resist	High-purity calix[7]arene resist	Former calix[6]arene resist (wt.%)	Quantitative analysis method
calix[6]arene		96.8	1.5	59.0	HPLC
calix[7]arene		0.2	95.0	29.0	
calix[8]arene		0.3	0.7		
Macromolecules		2.7	2.8	12.0	SEC
Metal impurity (ppb)	Na	27	<10	9.6 ppm	
	Mg	6	<8	4.2 ppm	
	K	15.5	395	5.8 ppm	
	Fe	<6	45	2.0 ppm	ICP-MS
	Al, Ca, Cr, Mn, Ni, Cu, Sn	2–70	20–200	0.04–12ppm	ICP-AES

FIG. 2. Surface roughness of calix[7]arene resist observed by AFM before e-beam exposure.

FIG. 3. E-beam exposure characteristics of high purity and unpurified calix-arenes.

—ure may affect the binding structure of amorphous hydrocar-_on caused by exposure of the electron beam.

V. E-BEAM EXPOSURE CHARACTERISTICS

Resist films were exposed by 50 kV e-beam lithography with a 5 nm spot size and address grid of 1.25 nm. The threshold dose for large area exposure for the unpurified calix[6]arene was about 0.5 mC/cm^2 and the dose needed for full film retention was about 20 mC/cm^2. The sensitivity is almost 40 times lower than that for a PMMA positive resist and almost 200 times lower than that for the chemically amplified negative resist NEB22 (Sumitomo chemical Co., Ltd.). The threshold doses for the high-purity calix[6]arene and calix[7]arene were 6 and 5 mC/cm^2, respectively, but the full film retention doses for these calix[n]arenes were the same as that of the unpurified calix[6]arene, about 20 mC/cm^2. The contrasts of high-purity calix[n]arenes were better than that of the unpurified calix[6]arene. The contrast values of calix[6]arene and calix[7]arene were 4.7 and 5.6, respec-ively, while that of the unpurified calix[6]arene was 2.5. This improvement in contrast is due to the purification process of the calixarene itself. Components with different molecular weights have different sensitivities, thus lowering the contrast of the unpurified calix[6]arene. The high-purity calixarene, on the other hand, shows high contrast. A high-contrast resist can be used for high-resolution patterning and thus is useful when we want to make a high-aspect-ratio pattern. We have not, however, actually measured the resolution differences between these calixarenes (see Fig. 3).

The residual resist thickness after development was greatest for the high-purity calix[7]arene and least for the unpuri-

fied calix[6]arene. This is because the unpurified calixarene contains more components, such as chain polymers with high molecular weight. These chain polymers are more easily decomposed by electron-beam irradiation compared with calixarene. The resultant molecules such as hydrocarbons and carbon–oxides evaporate, causing the volume and thickness of the resist to decrease.

For a given negative resist, the sensitivity increases with increasing molecular weight. Negative resists function by crosslinking in regions which are irradiated. This causes the molecular weight to increase above the level where a developer cannot dissolve the resist. This threshold molecular weight is known as the gel point. The gel point dose is proportional to the reciprocal of molecular weight. This is known as the Charlesby theory.[12] "Gel point" dose refers to the electron dose at which resist pattern formation begins. Figure 4 shows that the relation between gel point dose and the inverse of molecular weight for high-purity calix[6]arene and high-purity calix[7]arene agrees well with the model proposed by Charlesby. This implies that the resist sensitivity increases with molecular weight and that the exposure mechanism of calix[n]arenes is due to crosslinking similar to that of chain polymers.[13] The specific molecular functional groups, which contribute to crosslinking, are not clear.

TABLE II. Comparison of surface roughness among high-purity calix[6 and 7]arene and unpurified calix[6]arene.

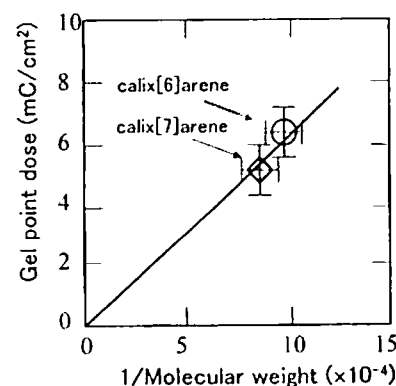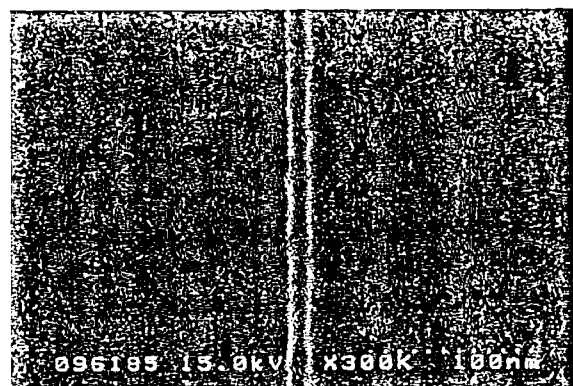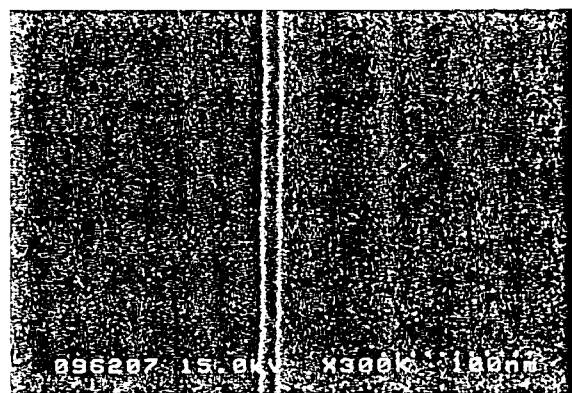|	High-purity calix[6]arene	High-purity calix[7]arene	Unpurified calix[6]arene
Peak to valley (2 μm long)	3.4	2.6	3.7
rms	0.38	0.31	0.38

FIG. 4. Gel point dose vs the reciprocal of the molecular weight of high-purity calixarene resists.

(a)

(b)

FiG. 5. SEM micrographs of: (a) high-purity calix[6]arene and (b) high-purity calix[7]arene exposed by using a 50 kV electron beam. Line dose was 40 nC/cm.

We speculate that the linkages are mainly between acetyl and methyl groups.

VI. HIGH RESOLUTION PATTERNING

Figures 5(a) and 5(b) show SEM micrographs of resist patterns produced by single-line-scan e-beam exposure, with a dose of 40 nC/cm^2, of calix[6]arene and calix[7]arene. The resolution obtained was 14 and 14 nm, respectively. The line-edge roughness seems to differ somewhat between the two resists, but we have not yet obtained consistent results.

For e-beam exposure using a point electron beam, the linewidth increases with increasing line doses because of the beam tail and the forward scattering. The relation between linewidth and line dose is shown in Fig. 6. Linewidth increased with increasing line dose and the difference between the high-purity calix[6,7]arene and unpurified calix[6]arene was indistinguishable. The minimum linewidth for these calixarenes is also essentially the same: 12 nm. Although these calixarenes have different sensitivity characteristics, their linewidth dependences on the line dose are almost the same.
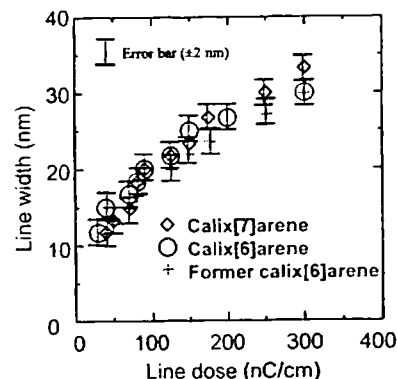

FiG. 6. Relation between linewidth and line dose for calix[n]arenes.

VII. SUMMARY

We have succeeded in making extremely pure electron-beam negative resists, 4-methyl-1-acetoxycalix[n]arene; calix[n]arene ($n = 6,7$). The main component of each of these calixe[n]arenes constitutes at least 95% of the resist, and the concentrations of metal contaminants in these resists are three orders of magnitude lower than those in our unpurified calix[6]arene. These new calix[n]arene resists can therefore be used in silicon device processes. The higher sensitivity of high-purity calix[7]arene agrees with that predicted by the Charlesby theory. The contrast of the high-purity calix[n]arenes was greater than that of the unpurified calix[6]arene, without loss of resolution. High purity calix[n]arene retains more resist thickness after development than the unpurified calix[6]arene. All these improvements make high purity calix[n]arenes suitable for use in nanostructure fabrication of silicon devices.

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