

Nanometer-scale resolution of calixarene negative resist in electron beam lithography

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New nonpolymer materials, calixarene derivatives were tested as high-resolution negative resists for use in electron beam lithography. Arrays of 12-nm-diam dots with a 25 nm pitch were fabricated easily. The sensitivity of calixarene in terms of area dose ranged from 700 to 7000 $\mu\text{C}/\text{cm}^2$, and the required dose for dot fabrication was about 10^5 electrons/dot. The standard area dose for calixarene is almost 20 times higher than that for polymethyl methacrylate (PMMA), but the electron spot dose for dot fabrication by calixarene is almost the same as that for PMMA and other highly sensitive resists such as SAL (chemically amplified negative resist for electron beam made by Shipley). The electron spot dose for such extremely small dots does not seem to depend on standard area dose, but any resist tends to require the same dose under exposure in a 50 keV electron beam writing system. We propose a qualitative exposure model that suggests a tradeoff of dose and dot size. The calixarene seems to be promising material for nanofabrication. © 1996 American Vacuum Society.

I. INTRODUCTION

The recent trend in device fabrication processes is toward ultimate miniaturization. In particular, reproducible and easy process techniques for structures less than 10 nm seem to be the main target for quantum device applications.^{1,2} We have found that calixarene derivatives³ work as a negative electron resist,⁴ provide ultrahigh resolution, and are resistant to halide plasma etching. These characteristics seem valuable for nanodevice fabrication processes. In the work described in this article, we tested two types of calixarene: 5,11,17,23,29,35-hexamethyl-37,38,39,40,41,42-hexaacetoxycalix[6]arene (MC6AOAc), and 5,11,17,23,19,35-hexachloromethyl-37,38,39,40,41,42-hexamethoxycalix[6]arene (CMC6AOMe). In this article, we refer to these calixarene derivatives as "calixarenes."

II. FILM PREPARATION

Calixarenes have a cyclic structure (see Fig. 1) and are roughly ring-shaped molecules about 1 nm in diameter. The basic component of a calixarene is a phenol derivative which seems to have high durability to plasma etching and high stability in air, originating from the strong chemical coupling of the benzene ring. As a result of this chemical structure, calixarenes have melting points of about 300 °C and are stable in air. When calixarene powders are dissolved in o-dichlorobenzene, the MC6AOAc solution is colorless and the CMC6AOMe solution is yellow and transparent. After the solutions were filtered through a 0.2 μm Teflon mesh, a conventional spin coater was used to make thin resist films. Typical spin coat conditions were as follows: 60-nm-thick film was prepared from 2.5 wt % of calixarene solution treated with 3000 rpm for 30 s spin coating and a 30-nm-thick film was prepared from 1 wt % of calixarene solution treated with the same spin coating condition. These spin

coated films were then prebaked for 30 min under a N_2 gas flow at 170 °C. The resist surface after the prebake process was extremely smooth: the maximum roughness (peak to valley) in a 20 μm square area was measured, using atomic force microscopy, to be less than 2 nm. After electron beam irradiation, calixarene resists were developed by dipping in xylene for 30 s and then in an isopropylalcohol (IPA) rinse for 30 s. IPA alone can also develop the resist, but more slowly, and our experience indicates that a faster development with stronger solvent gives a better shape in nanostructure fabrication.

III. SENSITIVITY IN TERMS OF AREA DOSE

The sensitivity characteristics (area dose) for the calixarene resists are shown in Fig. 2. We used the JBX-5FE (JEOL) electron beam writing system to measure the sensitivity, and a high-resolution SEM S-5000 (Hitachi) to evaluate the nanopattern. To measure the sensitivity, we used an electron beam current of 1 nA at an acceleration voltage of 50 kV. As a test pattern for sensitivity measurements, a checkerboard array with 20 μm periodicity with 5 μm squares was employed to reduce delineation time. Film thickness was measured by atomic force microscopy (AFM). For MC6AOAc, the threshold of sensitivity was about 0.8 mC/cm^2 and the required dose for practical use was about 7 mC/cm^2 , which is almost 20 times higher than that for PMMA. The film thickness reduction due to electron beam irradiation was estimated to be below 5%, which is less than the reduction that occurs when other highly sensitive phenol-based resists are similarly irradiated. In general, substitution by Cl atoms in methyl groups improves the sensitivity. The sensitivity of the chloromethylated calixarene CMC6AOMe is about ten times that of MC6AOAc. The resist contrast γ is about 1.6 for each calixarene resist.

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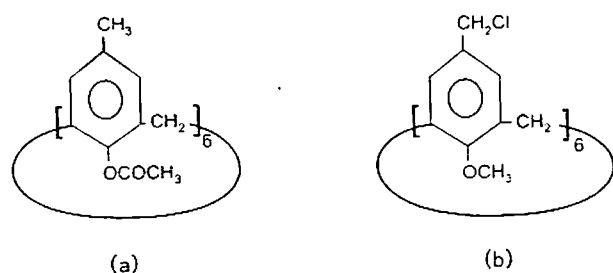


FIG. 1. Structure of calixarenes: (a) MC6AOAc and (b) CMC6AOMe.

IV. ETCHING DURABILITY

The etching durability of calixarene resists were tested using the DEM-451 (ANELVA) plasma dry-etching system, and the durability of the resist depended very much on the system setup and etching conditions: gas pressure, plasma flow style, and biasing. Figure 3 shows typical durability data obtained under the same conditions. The typical plasma condition was 5 Pa of CF_4 gas and incident microwave power of 50 W with a 200 V dc electrode bias. The etching rates for both MC6AOAc and CMC6AOMe were estimated to be about 10 nm/s, which is similar to that of Si and about one-fourth that of PMMA. This durability seems to be sufficient for making semiconductor or metal nanostructures, since the thickness of the nanostructure is scaled down with its width. Well known highly durable novolak resists such as SAL (chemically amplified negative resist for electron beam made by Shipley), ZEP (positive resist for electron beam made by Nippon Zeon), and AZ (photoresist made by

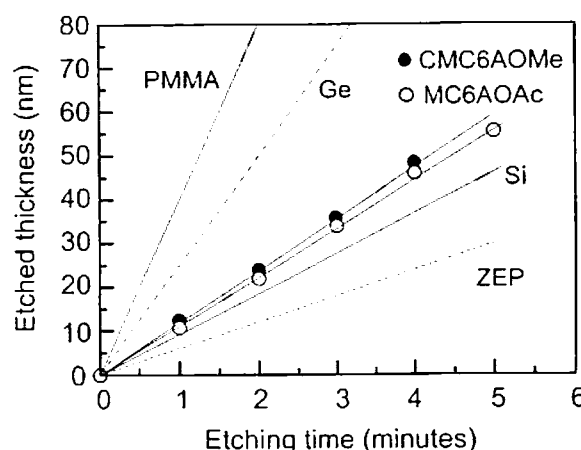


FIG. 3. Etching durability of MC6AOAc and CMC6AOMe.

Hoechst) are based on phenol and contain benzene rings as the frame structure. The high durability of these calixarenes is presumably also due to this frame structure.

V. DOT ARRAY FABRICATION AND ITS RESOLUTION LIMIT

Nanodot arrays are useful not only for quantum devices but also for studying exposure properties. In this experiment, the electron beam current was fixed to 100 pA at 50 kV accelerating voltage, for which the spot size is estimated to be about 5 nm. All the dot arrays were fabricated on Si substrates. The typical exposure dose (spot dose) was about 1×10^5 electrons/dot. If we assume the beam intensity distribution within a spot is constant, taking account of the spot size of about 25 nm^2 (5 nm square), the spot dose corresponds to an area dose of 64 mC/cm^2 . Figure 4 shows typical dot array patterns: (a) MC6AOAc dot array having a 15 nm diameter with 35 nm pitch and (b) CMC6AOMe dot array having 25 nm diameter with 50 nm pitch.

Figure 5 shows how dot diameter depends on electron dose. The larger dot size for CMC6AOMe reflects the higher sensitivity of this resist, but MC6AOAc forms smaller dots at the same electron dose. For both resists, dot diameter seems to be proportional to the spot dose. Although the dose size differs for the two resists, the minimum spot dose was in position almost in the same range for each calixarene resist. In Fig. 5, the spot dose of 1×10^5 electrons for each dot gives the average electron dose of $640 \mu\text{C/cm}^2$, taking account of the 50 nm dot pitch. This average area dose is very close to the standard area dose of CMC6AOMe, suggesting the total amount of backscattered electrons from average area dose have reached the same level of that from standard area dose. Such high contribution from the backscattering will soon limit the dot separation.

To evaluate the resolution limit for calixarene resists, we did an experiment using mainly the MC6AOAc resist. To form a high-density dot pattern, one must consider the interproximity effect: higher-density dots cause much electron backscattering. The contribution of backscattering uniformly extended in a limited small area about several microns, at

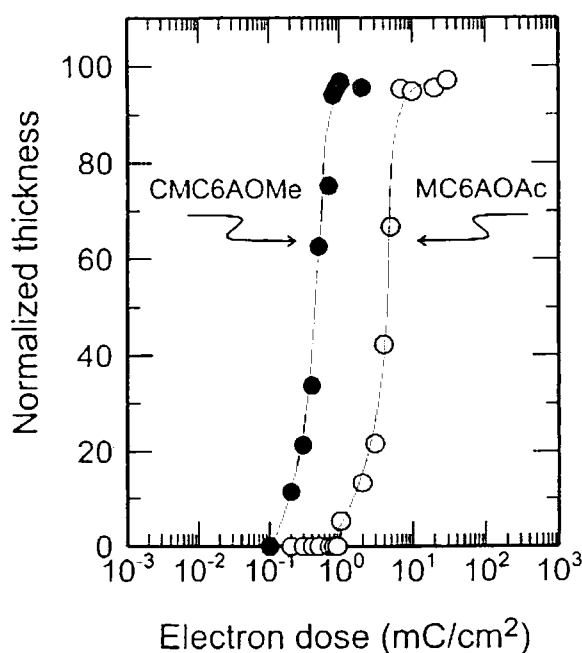
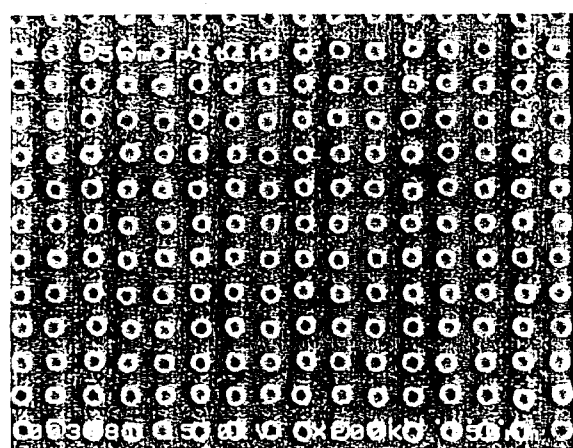
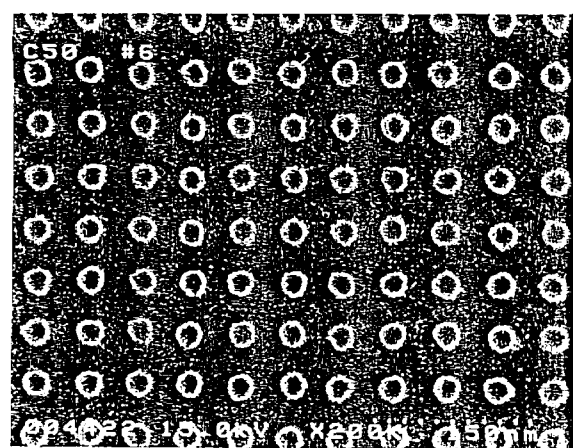


FIG. 2. Sensitivity to electron dose characteristics for MC6AOAc and CMC6AOMe.



(a)



(b)

FIG. 4. Typical dot pattern on Si substrate: (a) MC6AOAc array having dots 15 nm in diameter and 35 nm pitch and (b) CMC6AOMe array having dots 25 nm in diameter and 50 nm pitch.

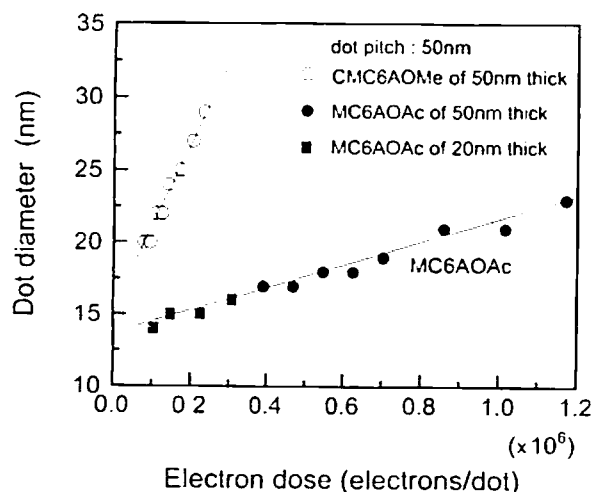


FIG. 5. Dot diameter vs electron dose for the calixarene resists.

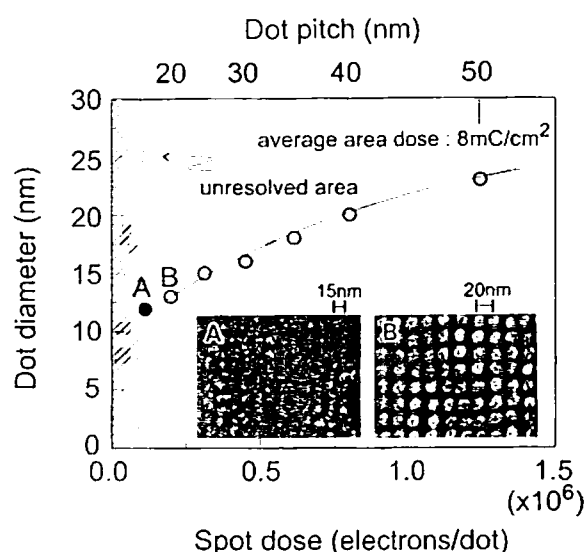


FIG. 6. Dot diameter vs electron dose. Average area dose was fixed, and the spot dose and the dot pitch were changed so as to keep average area dose constant.

least the backscattering could be uniform in the 100 nm pitched dot array. To exclude the contribution of the backscattering, experiments were done under the fixed average area dose of 8 mC/cm², which is the standard area dose for practical use with the MC6AOAc resist. Figure 6 shows dot diameter dependence on electron dose for each dot. Dot pitch and electron dose were changed so as to keep average area dose constant at 8 mC/cm². We confirmed that a dot array pitch of 20 nm can be resolved clearly as shown in the superimposed picture in Fig. 6. While there still remain traces of the dot array in the 1 nm pitched pattern, many of the dots were unresolved. These experiments revealed that the minimum gap is about 5 nm and the minimum dot size is about 12 nm.

VI. EXPOSURE MODEL

We found that the minimum spot dose for calixarenes was about 1×10^5 electrons/dot. It is very interesting that other organic resists such as PMMA⁵ and SAL⁶ required almost the same dose. Exposure parameters for different electron beam resists are listed in Table I. The standard area doses were very different for the different resists, but it is clear from the table that the spot doses for all resists are almost the

TABLE I. Exposure parameters for electron beam resists.

Resist	Type	Area dose (mC/cm ²)	Spot dose (electrons/dot)	Dot diameter (nm)	Calculated minimum pitch (nm)
SAL601 ^a	Negative	30	1×10^5	40	230
PMMA ^b	Positive	300	5×10^4	20	73
CMC6AOMe	Negative	700	1×10^5	20	49
MC6AOAc	Negative	7000	1×10^5	12	14

^aReference 6.

^bReference 5.

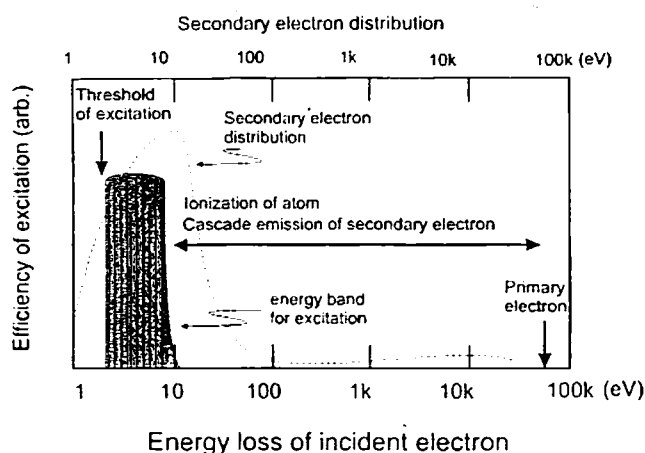


FIG. 7. Schematic diagram of exposure model.

same: 5×10^4 to 1×10^5 electrons/dot. In such an extremely small exposed region, the required minimum spot dose does not depend on the standard area dose, but tended to converge to almost the same value. Hereafter, we define this "almost converged spot dose" as the "critical spot dose."

To explain such exposure characteristics, we propose an exposure model that is qualitative and heuristic but that clearly explains those characteristics in dot array exposure. This model is based on the analogy to the elementary process of electron-molecule interaction. An exposure is a bond reaction process in which energy transferred from an incident electron excites the target bond reaction. Such excitation energy is empirically estimated to be several times larger than the binding energy, typically 4.3 eV for a C-H bond.

Now we assume that the excitation efficiency by energy transfer from a secondary and/or primary electron has a specific energy band as shown schematically in Fig. 7, where the horizontal axis is the energy loss of a primary/secondary electron. In general, the probability of electron-molecule interaction is suddenly decreased as electron energy increases. When the energy loss is more than several kiloelectron volts, shell electrons could be scattered out (cascade emission of secondary electrons). In that case, there is nothing to contribute to the bond excitation. But in many of these events, the energy transferred to molecules eventually appeared as thermal energy in the solid. An energy loss of more than ionization energy induced ionization of an atom. Only when the energy loss ranging several eV could excite the target bond reaction, was the resist exposed. Therefore the specific energy band, which could be constructed by a set of line spectra, is presumably narrow.

In an experimental electron (e)-beam condition, most of the 50 keV primary electrons pass through the resist, but a few of them generate secondary electrons having various energies. Many of the secondary electrons have energies around several tens of electron volts. These secondary electrons diffused into the resist by successive energy losses. The total efficiency of bond excitation is obtained by accumulating for the specific energy band. Even though each resist has

a different sensitivity, this only changes the position of the specific band. The obtained efficiency could be alternated to the probability of bond reaction, and then to the spot dose. On other hand, the density for each resist is almost the same. If we roughly estimate, the total number of bonds for reaction could be regarded almost the same for each resist, the integration of the efficiency for each resist could be given almost the same value. Considering both the narrow band width and the same density of the resists, probability of the bond reaction for each resist gives almost the same spot dose, as long as the primary electron energy is sufficiently higher than the specific band. Of course, there should be some deviations. Precise evaluation for such excitation energy diagram will be needed; the exposure data under low energy primary electron irradiation will help in determining the diagram.

Changes of the dot diameter are also explained well with this simple model. The lower side threshold energy of the specific band is different for each resist. Secondary electrons diffuse radially into the resist and lose energy. The circumference of the dot is defined by a boundary where the average energy loss just agrees with the threshold energy, and the lower threshold pushes the boundary far away. This explains the dot diameter dependence on the standard dose: the lower the standard area dose (the more sensitive the resist) the larger the dot. Namely, the standard area dose trades off the minimum dot size. This suggests an extrapolating guideline for electron-beam (EB)-resist used in nanofabrication. While the historical trend for resist improvement has been to increase the sensitivity (standard area dose) of resist, we should reconsider the trend from the viewpoint of the resolution. Our results indicate that high-sensitivity in terms of area dose only increases the dot size, but low sensitivity improves the resolution. From this viewpoint, calixarenes seem to be promising materials for nano-EB-resist.

These discussions have considered the fabrication of isolated dots, but the model seems to cover a wider range of exposure situations, and suggests how the resolution is limited in dot arrays for each resist. The difference between isolated dots and dot arrays is, in the context of this model, the contribution from backscattering electrons. We think the model could be adopted for dot arrays, as long as the average area dose is small enough in comparison with the standard area dose. For example, in the case of the MC6AOAc (Fig. 5) the average area dose of $640 \mu\text{C}/\text{cm}^2$ at the spot dose of 1×10^5 electrons/dot is about one order of magnitude lower than the standard area dose of MC6AOAc ($8000 \mu\text{C}/\text{cm}^2$). This situation could be suitable for application of the model. If we assume the existence of critical spot dose, the minimum dot pitch for each resist would be where the average area dose agrees with the standard area dose. The right-hand column of Table I is the minimum dot pitch calculated under the assumption that the critical spot dose is 1×10^5 electrons/dot. Smaller pitch for dot array than the minimum pitch possibly could not resolve the dot array, and the whole area could be exposed as a single pattern.

VII. CONCLUSION

We tested a new nonpolymer material, calixarene, as a high-resolution negative resist for electron beam lithography. An array of dots 12 nm in diameter and pitched at 25 nm was fabricated easily. The typical standard area dose was about 7 mC/cm² for MC6AOAc and 700 μ C/cm² for CMC6AOMe, and the spot dose was 10⁵ electrons/dot for both calixarene resists. While the sensitivity in terms of area dose for MC6AOAc is about 20 times higher than that of PMMA, the spot dose for MC6AOAc resists is almost the same value as for PMMA (as well as another high sensitive resist such as SAL). The high sensitivity tends to increase the dot size. We proposed a heuristic and qualitative model that suggests a tradeoff of dose and dot size. This suggests that we use a

highly sensitive resist for large area exposure and a lower sensitivity resist for nanolithography. The calixarene resists seem to be promising materials for nanofabrication.

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