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Calixarene Electron Beam Resist for Nano-Lithography

Jun-ichi FUJITA, Yoshitake OHNISHI, Shoko MANAKO, Yukinori OCHIAI, Eiichi NOMURA, Toshitsugu SAKAMOTO and Shiniji MATSUI*

Fundamental Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba 305, Japan

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New electron beam (EB) resists made of calixarene resists are introduced. Typical sensitivities of calixarene resists range from 700 μC/cm^2 to 7 mC/cm^2. High-density dot arrays with 15 nm diameter constructed using calixarene resist were easily delineated using a point EB lithography system. Our results suggest that the resolution limit of calixarene resists is dominated by a development process such as adhesion to a substrate rather than by the EB profile. Calixarene resists are resistant to etching by halide plasma. We also demonstrated nanoscale devices processed by using calixarene resists. Calixarene resists are promising materials for nanofabrication.

KEYWORDS: electron-beam lithography, resist, calixarene, nanolithography

1. Introduction

The recent trend in device fabrication processes is toward miniaturization. In particular, reproducible and easy process techniques for structures of size less than 10 nm are the main targets for quantum device applications.[1,2] We have found that calixarene derivatives[3] can be used to fabricate negative electron resists,[4,5] provide ultrahigh resolution, and are resistant to halide plasma etching. These characteristics are valuable for nanodevice fabrication processes. In this paper, we report practical techniques and problems in handling calixarene resists, and discuss the resolution limit of calixarene resists by using a Monte Carlo simulation.

2. Experimental Technique

Calixarene resists have a ring-shape structure of about 1 nm diameter as shown in Fig. 1. The basic component of calixarene resists is a phenol resin, which seems to be responsible for resistance to plasma etching and high stability in air. Aside from these superior characteristics, monodispersability is another unique characteristic of calixarene resists. The uniformity of molecular weight results presumably in nm-order resolution and smooth surface of exposed patterns.

As the solvent for calixarene resists, monochlorobenzene seems to be better than *o*-dichlorobenzene, which we had used in our previous works.[4,5] The conformation and the homogeneity of MC6AOAc (commercially available from one Japanese chemical company) seem to be slightly different from those of our MC6AOAc (synthesized material in our lab.): crystallization peaks in X-ray diffraction and massspectra profiles are different. As a result of these differences, calixarene is poorly soluble in *o*-dichlorobenzene, producing a milky liquid. If this milky liquid is used after filtering through a 2-μm Teflon mesh, it can be used for EB resist, but the film thickness becomes smaller than expected. In addition, if the milky liquid is dissolved completely by heating, the suspension becomes transparent; however, poor resolution and reduced sensitivity are obtained. These problem can be solved by using monochlorobenzene.

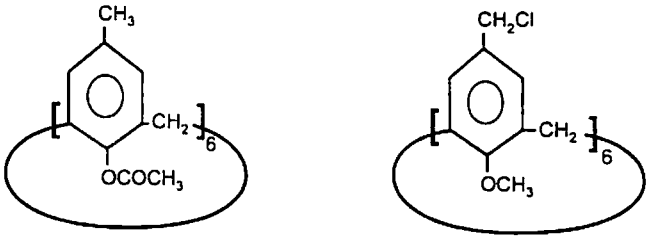


Fig. 1. Structure of calixarene resists. (a) MC6AOAc and (b) CMC6AOMe. The correct notations for calixarene resists are 5,11,17,23,29,35-hexamethyl-37,38,39,40,41,42-hexaacetoxycalixarene (MC6AOAc), and 5,11,17,23,19,35-hexachloromethyl-37,38,39,40,41,42-hexamethoxycalix[6]arene (CMC6AOMe).

Typical spin-coating conditions were as follows: A 60-nm-thick film was prepared from 2.5 wt.% calixarene solution, that was subjected to 30-s spin-coating at 3000 rpm, and a 30-nm-thick film was prepared from 1 wt.% calixarene solution subjected to the same spin-coating conditions. These spin-coated films were then prebaked for 30 minutes under N_2 gas flow at 170°C. After cooling to room temperature, the stability of calixarene resists is satisfactory. We confirmed that the resolution did not deteriorate after one-year storage in a nitrogen gas flow box.

After electron beam (EB) irradiation, calixarene resists were developed by dipping in xylene for 30-s and then rinsed by dipping in isopropyl alcohol (IPA) for 30-s. IPA alone can be used to develop the resists, but the development time is long. Our experience indicates that fastest development with a stronger solvent gives better shape in nanostructure fabrication.

3. Resist Characteristics

The sensitivity characteristics (area dose) of calixarene resists are shown in Fig. 2. We used the JBX-5FE (JEOL) EB writing system to measure the sensitivity. We used an EB current of 1 nA at an acceleration voltage of 50 kV. Sensitivities of calixarene resists were measured at about 7 mC/cm^2 for MC6AOAc, and 700 μC/cm^2 for CMC6AOMe resist. Film thickness reduction due to EB

*Present address: Semiconductor Leading Edge Technologies, Inc. 292 Yoshida-cho, Totsuka-ku, Yokohama 244, Japan.

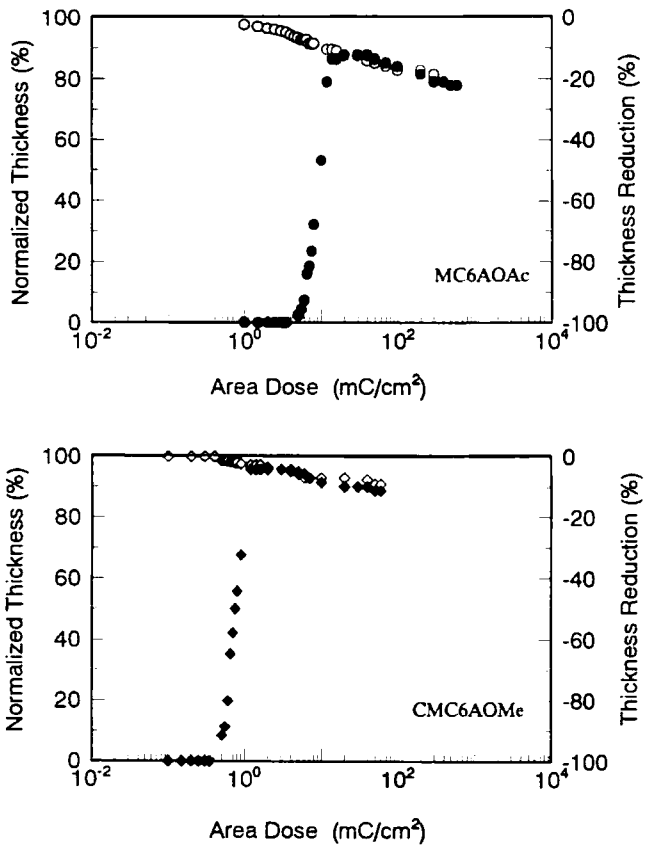
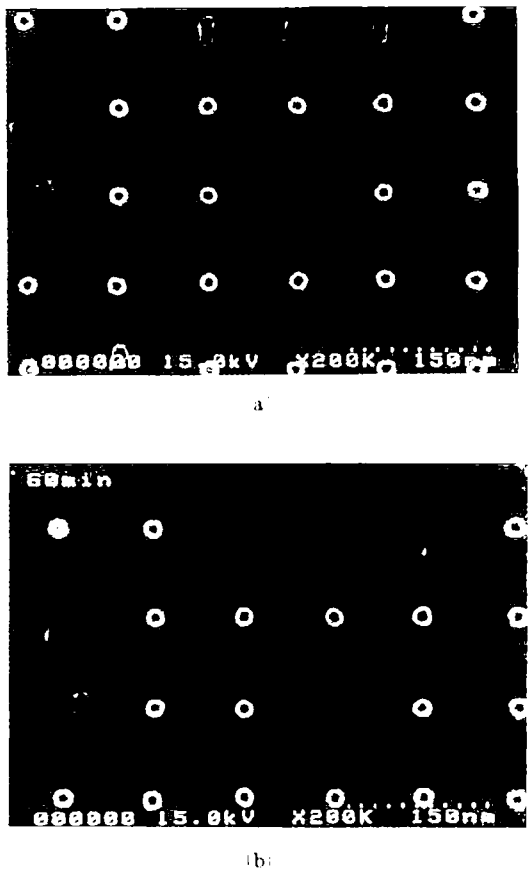


Fig. 2. Sensitivity to electron dose of MC6AOAc and CMC6AOMe. Thickness reduction is indicated by open circles (MC6AOAc) and open diamonds (CMC6AOMe), and normalized thickness is indicated by solid circles (MC6AOAc) and solid diamonds (CMC6AOMe).



(a) (b)

Fig. 3. Pattern changes after overdeveloping. (a) 30-s development. (b) 60-min. development.

irradiation was about 10% for MC6AOAc resist and less than 5% for CMC6AOMe resist. These reductions can be explained by considering chainscission by EB irradiation, which occurs simultaneously with cross-linking. Studies on the radiation-induced reaction in a molecule[6,7] have shown that a portion of the calixarene molecule could be activated by EB irradiation, e.g., hydrogen and chlorine of the methyl group, hydrogen of the methyl group of the frame structure, and the acetoxy and/or methoxygroup. In particular, desorption of the acetoxy or methoxy group causes a significant reduction in resist volume. Such volume reduction started simultaneously with EB irradiation, and increased logarithmically with increasing dose.

Another characteristic of calixarene resist is its solubility after exposure to EB. Xylene seems to be a one of the most appropriate solvents for calixarene; however, calixarene, once exposed, is difficult to dissolve. Figure 3 shows the scanning electron microscope (SEM) images taken after development, where the development times were (a) 30-s and (b) 60-min. These two photographs are taken of the same region. The 30-s development seems to be sufficient for pattern formation, and no change is observed after one hour. Such marked contrast between the soluble and the insoluble region is an attractive characteristic of calixarene resist, and oxygen plasma treatment may be the only way to remove exposed patterns.

4. Dot Array Fabrication

Nanodot arrays are useful for not only quantum devices but also other non-electronic devices such as magnetic recording media. In this experiment, the EB current was fixed at 100 pA and the accelerating voltage was 50 kV. Spot size was measured at approximately 6 nm diameter using the knife edge method. Figure 4 shows the dot diameter dependence on spot dose for each resist. All the dot arrays were fabricated on Si substrates. A comparison of the sensitivity in terms of spot dose between calixarene and SAL (chemically amplified EB resist, SHIPLEY) revealed that there is a spot dose that forms the smallest dot size for each resist, which is called the critical spot dose. While the area dose of resists is very different, the critical spot dose for SAL[8] and CMC6AOMe resist is almost the same (about 10 fC/dot, as shown in Fig. 4), and the smallest dot size for CMC6AOMe resist is much smaller. The minimum exposure dose (spot dose) to form a dot array was about 7 fC/dot for CMC6AOMe resist and 62 fC/dot for MC6AOAc resist. Taking the dot pitch of 200 nm on the Si substrate into account, the average area dose is 17 μC/cm^2, which is small enough to neglect influences from backscattered electrons. (The standard area dose for CMC6AOMe resist is 700 μC/cm^2). In addition, the pattern size of the array is about 5 μm^2, which is about one-tenth the lateral range of backscattered electrons. Therefore, we think that these dots should be regarded as

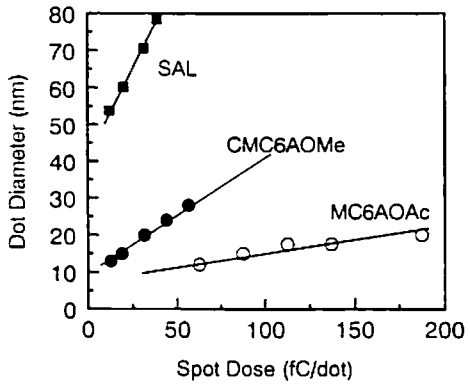


Fig. 4. Dot diameter dependence on spot dose.

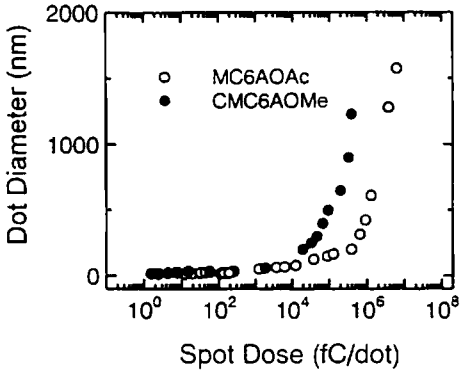


Fig. 5. Wide-area diagram of dot diameter dependence on spot dose of calixarene resists.

isolated dots. In such a dose region, dot diameter seems to be proportional to the spot dose, but the inclination is different for each resist. A small inclination represents poor sensitivity: however, one can fabricate an ultrahigh-density dot array. If one tries to fabricate a high-density dot array, the inter-proximity effect increases quickly (inversely proportional to the square of the dot pitch), and thus the effective dose increases quickly. Such a marked contribution from backscattering limits the dot separation.

5. Comparison of Experiments with Monte Carlo Simulation and Resolution Limit

From our previous experimental results.[5] we confirmed that calixarene resists have the potential to achieve 12 nm pattern formation, and that there exist a critical spot dose for each kind of calixarene resist. We are interested in the factors that influence the resolution limit. When we reduced the spot dose to below the critical dose, the dot pattern (dot pillar) fell down, maintaining a cylindrical pillar shape. Further reduction of the spot dose caused a deformation of the pillar shape, followed by the disappearance of dot pillar. This disappearance occurred at a spot dose of approximately half the critical spot dose. Monte Carlo simulation will help us understand this experimental result.

Figure 5 shows a wide-area diagram of the dot diameter dependence on spot dose of calixarene resists. Size data were obtained from absolute single dot experiments. The relationship between dot diameter and spot dose ranging from 10^0 to 10^2 in Fig. 5 is magnified in Fig. 4. The curves in Fig. 5 are easily identified as the deposited energy density (DED) curves. In the curve for MC6AOAc, the abrupt steepness of the curve beyond 10^5 fC/dot is due to backscattering and a wide exposed area. A comparison between Monte Carlo simulation and experiments gives the positional deviation of the critical spot dose from the top level (beam center) of the DED curve. In our simulation, since it is a very conventional one, we assume the elastic scattering probability according to the screened Rutherford scattering cross section, and the continuous slowing down approximation (CSDA) for inelastic scattering. The total number of electrons examined in this simulation was 1.2×10^5. The DED curve $E = f(r)$ [eV/nm^3/fC] is related to the experimental

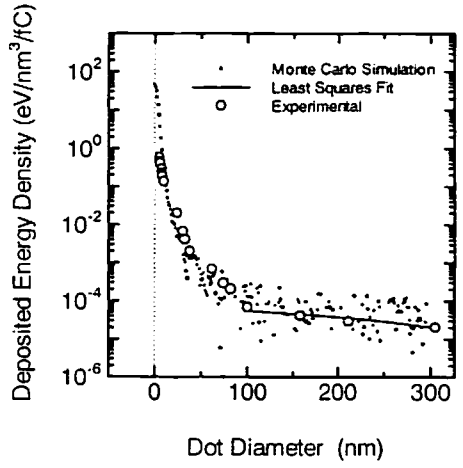


Fig. 6. Comparison of experiments with Monte Carlo simulation. Fitting parameter ε_c of 25 eV/nm^3 was used.

curve $D = g(r)$ [fC/dot] by using the critical energy density ε_c [eV/nm^3] as follows:

$$E = \varepsilon_c / D.$$

The result for MC6AOAc is shown in Fig. 6. It is very clear that our simulation closely represents the experimental results. In particular, the cross-over of forward and backscattering is fitted well by this simulation, whereas a conventional double-Gaussian approximation fails at the crossover portion. In the backscattered region, simulation results are not continuous but scattered. For convenience in data fitting, the least squares fit was utilized for the radial distance of 100 to 325 nm.

Based on the simulation, the critical spot dose was found to remain at one-hundredth of DED at the center of the EB. This means a reduction of the electron spot dose below the critical spot dose would reduce the dot diameter, although the dot disappears completely in the experiment. We think that the limited dot size is due to not the EB profiles, but a development mechanism such as adhesion to the substrate. The DED at the beam center is still sufficient for dot formation if the spot dose decreases to one-half of the critical dose. In our experiment, resist thickness was fixed at 35 nm for convenience; thus, the 10 nm dots have an aspect ratio of 3.5. If the

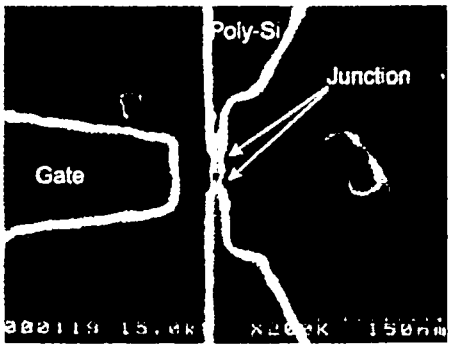


Fig. 7. SEM micrograph of poly-Si SET device.

sticking force required to fix a dot pillar to the substrate yields to the force required for dissolution in the solvent, and dot pillars exist in the solvent as a colloid, no dot patterns will be observed. To clarify our speculation, we need to conduct further experiments on very thin resists.

6. Application of Calixarene Resist

Figure 7 shows a SEM image of a poly-Si single electron tunneling (SET) device.[9] A 50-nm-thick calixarene resist was utilized for patterning the entire device structure, where the key structures are the junctions (25 nm width) placed between the central electron island and source and/or gate. The thickness of the Si electrode was 30 nm, which was formed by CF_4 plasma etching. The etching selectivity of calixarene to poly-Si is about unity and that to silicon oxide is three. This device was operated up to 15 K, and clear current oscillation was observed depending on the gate bias voltage. A similar application of calixarene is demonstrated in the fabrication of ultra-narrow gates of MOS transistors,[10] where a gate of 32 nm width controls a source current. This transistor seems to be the smallest one to date, to our knowledge. Calixarene resists can also be applied to optical devices, such as the Fresnel zone plate for X-ray optics.[11] The resolution of this device is estimated to be equal to the outer zone separation. The use of calixarene resist enables the fabrication of the zones as fine as 20 nm.

7. Conclusion

We developed new EB resists made of calixarene resists MC6AOAc and CMC6AOAc. The sensitivities are 700 μC/cm^2 for CMC6AOMe and 7 mC/cm^2 for MC6AOAc. The required spot dose for nanodot array formation, however, increases to 50–60 fC/dot which is almost the same as that for conventional highly sensitive resists such as SAL. In addition, high sensitivity tends to increase the dot diameter, but dose-independent characteristics of calixarene resists enable the formation of high-density dot arrays. We also conducted a Monte Carlo simulation in order to determine how much the critical spot dose deviated from the dose at the beam center. Comparison between simulation and experiment indicates that the critical spot dose, which has been thought to be the minimum dose for dot formation, remains at a dose of one-hundredth of the DED at the beam center. This suggests that the resolution limit of calixarene resists is not restricted by the EB profile, but by other factors during the development process such as adhesion to the substrate.

It should be noted that all arguments in this paper, in particular, the evaluation of the critical spot dose, should be distinguished from a model based on the cross-linking mechanisms[5] for nanodot formation which we had previously described, and that discussions were made from the viewpoint of electron dose level determined from the Monte Carlo simulation. For comprehensive discussion and thorough understanding of the dot size limit in negative resists, we require clear criteria for resist thickness as well as resist stiffness. Further experiments are required for a complete understanding of the resolution limit.

We also demonstrated a nanoscale quantum device processed using calixarene resists. Calixarene resists are promising materials for nanofabrication.

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