High Resolution EB Lithography on Organic Resists: Molecular Size Effect

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The resolution of organic resists has been investigated as a function of base resin structure and molecular weight. Calixarene, which has a ring structure, and polystyrene, which has a chain structure, were used for the investigation. The polystyrene had different molecular weights. We show that a high-resolution lithography can be achieved using an organic resist with a low molecular weight, that is, a smaller molecular size. A 10-nm-level negative resist pattern is demonstrated.

Keywords: Electron Beam Lithography, Resists, Nanolithography, Calixarene, Polystyrene

1. Introduction

Nanometer lithography is becoming an important technology for sub-0.1µm MOS devices and quantum devices. Negative type organic resists are useful for structures such as gate electrodes and small junctions for single electron tunneling devices. Electron beam lithography is the most suitable technique for nanometer lithography. In fabricating nanometer patterns, the crucial factors are not only the electron beam diameter but also the resist resolution itself. Patterns under 10 nm have been reported in polymethyl metacrylate (PMMA) resist. Inorganic resists such as Li$_2$Al$_x$F show resolution under 10 nm, but it is difficult to obtain 10-nm negative resist patterns. For example, Yoshimura et al. reported that the minimum line width that can be achieved with a 30 kV EB having a diameter of 0.8 nm is 20 nm for a chain-structure negative resist, SAL601 (Shipley Co.).

In this paper, we report on the successful fabrication of a 10-nm-level negative resist pattern by using calixarene derivatives and low-
molecular-weight polystyrene as resists. Monodisperse polystyrene is well known as a negative electron beam resist. Itaya et al. reported 0.31-µm linewidth patterns using polystyrene with a molecular weight of $1.1 \times 10^5$ and a polydispersity of 1. We show that the molecular weight of the base resin is important for nanostructure lithography. In our experiments, we used the JBX-5FE electron beam lithography system (JEOL Co.). The acceleration voltage is 50 kV and the typical beam diameter is 5 nm. Both resists can be spin coated in a way similar to the conventional process. The film thickness was measured by atomic force microscopy (AFM) or by an Alpha-Step 200 (Tencor Inst.) step profiler.

2. Calixarene resist and its exposure characteristics

Calixarene, which is a general term for specific cyclic phenol resins, is a cyclic oligomer consisting of 6-phenol and having a molecular diameter of 1 nm (Figure 1(a)). The molecule shown in (a) is a calixarene derivative, hexaacetate $p$-methylcalix[6]arene (MC6AOAc), while that in (b) is hexa-chloromethoxy-hexamethoxycalix[6]arene (CMC6AOMe). Their molecular weights are respectively 972 and 996. Most calixarene derivatives have poor solubility in organic solvents, but these calixarene molecules are soluble in organic solvents such as $o$-dichlorobenzene and has high heat resistivity up to 320 °C. Therefore, making films of calixarene is easy using a spin coating method similar to that used in conventional resist processes. We found that these calixarene films work well as negative electron beam resists, and show ultrahigh resolution and high durability under halide plasma etching. The electron beam exposure characteristics of these calixarene films are shown in Fig. 2. We spin coated 1 wt% of calixarene solution on a Si wafer at 3000 rpm for 30 s to prepare a 30-nm-thick film. For MC6AOAc, the threshold sensitivity was about 0.8 mC/cm² and the practical sensitivity was about 7 mC/cm², which is almost 20 times higher than that for PMMA and almost 100 times higher than that for a SAL601 chemically amplified negative resist. The sensitivity of the chloromethylated calixarene CMC6AOMe is about ten times higher than that of MC6AOAc. Substituting Cl atoms in the methyl groups improves the sensitivity. The reason for this is that since the C-Cl bonding energy is low, the Cl bonds easily decompose. Activated Cl can affect Cl bonds at other sites and reduce their bonding energy. Their Cl bonds can then be broken by a low energy deposit. The resist contrast $γ$ is about 1.6 for each calixarene resist.

3. Polystyrene resist and its exposure characteristics

Polystyrene is a common base resin used for resist materials and has no additional functional groups for raising sensitivity such as Cl or catalyst (Fig 3). Therefore, this material is useful for studying resist resolution. We used several different types of polystyrene having a polydispersity of about 1 and different molecular weights ranging from 800 to 17500 (Pressure Chemical Co.). Polystyrene powder was dissolved in either $o$-dichlorobenzene or monochlorobenzene.
After the solution was filtered through a 0.2-µm Teflon mesh, a conventional spin-coater operating at 4000 rpm for 60 s was used to form 20- to 40-nm-thick resist films. The films were then prebaked at 120 °C for 30 min. The polystyrene films with molecular weights of less than 2000 were dried at room temperature for 1 day in a dry N2 gas flow because the baking process made the films non-uniform. After exposure to an electron beam, the resist films were dipped in xylene for 30 s and rinsed in isopropyl-alcohol for 30 s. The acceleration voltage of the electron beam was 50 kV and its beam current was 1 nA. Figure 4 shows the exposure characteristics. The area sensitivity increased with increasing molecular weight. The threshold sensitivity where the sensitivity curve rises is the "gel point," and the relation between the gel point and the inverse electron dose is shown in Fig. 5. We found that these are in proportion. The Charlesby theory explains this relation. When an electron irradiates an organic resist, organic molecules are cross-linked each other and virtual molecular weight increases, then the resist becomes a nondissolved material in a developer (organic solvent). The negative tone resist pattern is then formed by lithography. This scheme can be expressed as gel point/molecular weight = constant. According to this theory, a resist with a lower molecular weight requires high energy deposition to form resist patterns.

Figure 4 Exposure characteristics of polystyrene with various molecular weight.

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Therefore, these resists exhibit low sensitivity. This means that as a resist, polystyrene is a simple system.

4. Resolution of calixarene and polystyrene
We performed electron beam lithography using calixarene and polystyrene to evaluate resist resolution by exposing dot array. Dot arrays are also useful for quantum devices. The dot pattern is fabricated by irradiating point (pencil) electron beam on a certain site for a certain time. Figure 6 shows an SEM photograph of a dot array made by two types of calixarene on a Si substrate. Figure 6 (a) shows a MC6AOAc dot array having a 15-nm diameter with a 35-nm pitch and (b) shows a CMC6AOMe dot array having a 256-nm diameter with a 50-nm pitch, which has a higher area sensitivity than that for MC6AOAc. The electron beam used is 50 kV and 100 pA, and the beam diameter was estimated to be about 5 nm. The typical exposure spot dose was about 1 x 10^5 electrons/dot (16 fC/dot). If we assume the beam intensity distribution within a beam spot is constant, a spot dose for a 25 nm^2 (5nm square) spot size corresponds to an area dose of 64 mC/cm^2.

Figure 7 shows a polystyrene dot pattern on a Si substrate, which has a molecular weight of 800 and was exposed to an electron dose of 2.3 x 10^5 electrons/dot (37.5 fC/dot). The electron beam conditions were the same, that is, 50 kV, 100 pA, and the estimated beam diameter was 5 nm. We obtained 12-nm diameter dots which is almost the same as for the calixarene. The arrangement of arrays was wavy due to the wafer stage vibrations. The roughness of the edges was small (a few nm) for both resists. Both resists are suitable for nanolithography.
Based on the experimental results using the polystyrene resist shown in Fig. 7, we obtained the relation between the dot diameter and the electron spot dose as a function of molecular weight (Fig. 8). The polystyrene resist thickness was 25-40 nm, and dot arrays with a pitch of 100 nm were fabricated. For each molecular weight, the dot diameter increases as the electron dose increases. The increasing ratios are different due to the different area sensitivities and energy deposition profiles (electron beam profiles). For each molecular weight resist patterns are not delineated at doses less than about 1 x 10^5 electrons/dot (16 fC/dot).

For calixarene (MC6AOAc), the results are also shown in Fig. 8. For doses between 2.5 x 10^5 and 15 x 10^5 electrons/dot, the dot diameters are larger than those of the polystyrene having molecular weights of 2000 and 800. The calixarene having a molecular weight of 972 is more sensitive than polystyrene having a molecular weight of 2000 or 800. However, the minimum dot diameter for calixarene was ~12 nm, which is almost the same as that for the polystyrene having a molecular weight of 800. According to these results, the resolution (minimum dot size) of organic resist undoubtedly depends on the molecular weight of the base resin, and does not depend on the molecular structure, that is, the ring structure or chain structure.

At certain electron doses, polystyrene resists with different molecular weights show different dot diameters. This is because with a higher molecular weight, the polystyrene has a higher area sensitivity. The higher sensitivity means that the threshold energy for delineating patterns is lower. A schematic diagram for dot pattern delineation is shown in Fig. 9. The current distribution of the irradiated point electron beam is similar to a Gaussian profile. The energy deposition profile in the resist is also similar to the irradiated electron beam profile, because backscattered electrons can be disregarded due to the high incident energy. The dot diameter should be defined at the cross point between the deposited energy profile and the threshold energy, which is different for each resist. Therefore, at certain electron doses, polystyrene having different molecular weights show different dot diameters.
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The resolution of resist may also be related to its sensitivity. According to the dot array lithography experiment, for two types of calixarene having similar molecular sizes but different sensitivities, the calixarene with the higher sensitivity shows slightly larger dot diameters. One reason is that the more sensitive resist has a threshold energy for delineation. When making a dot array with short pitch, fairly large backscattered electrons, which have low incident energy compared to primary electrons, to the resist from the substrate and deposit energy by low-energy secondary electrons.

The diameter of the Calixarene (MC6AOAc) molecule is about 1 nm, and the diameter of the polystyrene molecules having a molecular weight of 800 is also 1 nm, if the chain structure molecule is packed as small as possible. These molecule have almost the same molecular size—about 1 nm. If a minimum dot with a diameter of 10 nm is assumed to be a cube with a side of 10 nm, the molecular weight of the minimum dot would be 1,000,000. In a general negative resist scheme, cross-linking occurs during electron beam irradiation and the molecules in the resist film underneath the beam irradiation area became large. In this resist process, which incorporates an organic solvent as a developer, a negative tone pattern with a molecular weight of 1 million may be the minimum possible for lithography. To find out whether the 10-nm organic negative resist pattern is the highest resolution possible, we need to conduct further experiments using electron beams with smaller diameters.

6. Summary

We investigated the resolution of organic resists using calixarene derivatives and polystyrene. Two types of calixarene were used: MC6AOAc and CMC6AOMe. The latter one has chloromethyl and is highly sensitive. Polystyrene is a commonly used base resin for various resists. In our experiment we used polystyrene resists having molecular weights ranging from 800 to 17500. We successfully fabricated 10-nm-level dot patterns in both calixarene derivatives and polystyrene having a molecular weights of 800. Both resists have almost the same molecular size—about 1 nm. We found that the resolution of the organic resist strongly depends on its molecular weight or molecular size.

References