

Ultrahigh resolution of calixarene negative resist in electron beam lithography

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A nonpolymer material, calixarene derivative (hexaacetate *p*-methnlycalix[6]arene) was tested as a high-resolution negative resist under an electron beam lithography process. It showed under 10-nm resolution with little side roughness and high durability to halide plasma etching. A sub-10-nm Ge quantum wire was perfectly etched off without defects. Such a performance is suitable for nanoscale device processes. © 1996 American Institute of Physics. [S0003-6951(96)00609-0]

The recent trend in device fabrication processes is toward ultimate miniaturization. In particular, reproducibility and easy process techniques for structures less than 10 nm seem to be the biggest target for quantum device applications.^{1,2} While atom manipulation by scanning tunneling microscopy STM^{3,4} seems to be a promising technique for these future requirements, there would, however, be many practical difficulties due to its long processing time.

We found the calixarene derivative, hexaacetate *p*-methylcalix[6]arene (hereafter referred to as MC6AOAc⁵), works as a negative electron resist, and shows ultrahigh resolution and high durability to halide plasma etching. Such characteristics seem to be convenient for nanodevice fabrication processes. In this letter, we present detailed techniques for handling MC6AOAc as a high-resolution negative resist, and demonstrate a fine pattern transfer to Ge films.

MC6AOAc has a cyclic structure as shown in Fig. 1. It is roughly a ring-shaped molecule with about a 1 nm diameter. The basic component of MC6AOAc is a phenol derivative which seems to have high durability and stability, originating from the strong chemical coupling of the benzene ring. As a result of this chemical structure, the melting point of MC6AOAc is about 320 °C and it is quite stable in air.

MC6AOAc powder was dissolved in *o*-dichlorobenzene. After this was filtered through a 0.2 μm Teflon mesh, a conventional spin coater was utilized to make thin resist films. Typical spin-coat conditions were as follows; a 60-nm-thick film was prepared from 2.5 wt. % of MC6AOAc solution treated with 3000 rpm for 30 s spin coating and a 30-nm-thick film was prepared from 1 wt. % of MC6AOAc solution treated with the same spin coating. These spin-coated films were then prebaked for 30 min in a N₂ gas flow oven at 170 °C.

The resist surface roughness after the prebake process was extremely smooth, the maximum roughness was measured to be less than 2 nm in a 20 μm square area using atom force microscopy. After electron beam irradiation, the MC6AOAc resist was developed by dipping it in xylene for 30 s, and then in an isopropylalcohol (IPA) rinse for 30 s. IPA alone can also develop the resist, but it took a longer time. Moreover, from our experience, quick development with strong solvent seems to give a better shape in nanostructure fabrication.

The sensitivity characteristics for the MC6AOAc resist

are shown in Fig. 2. We used the JXB-5FE (JEOL) electron beam writing system to measure the sensitivity, and a high-resolution SEM S-5000 (Hitachi) for nanopattern delineation. To measure the sensitivity, an electron beam current of 1 nA at a 50 kV acceleration voltage was used. The test pattern for sensitivity measurements was a checkerboard array with 20 μm periodicity with 5 μm squares to reduce delineation time. The threshold of sensitivity was about 0.8 mC/cm² and the required dose for practical usage was about 7 mC/cm², which is almost 20 times higher than that of polymethylmethacrylate (PMMA). The typical line dose was 20 nC/cm, when we utilized the S-5000 with a beam current of 100 pA at 30 kV acceleration voltage. Film thickness reduction by electron beam irradiation was estimated to be below 5%, which is comparable to other high sensitivity phenol-based resists.⁶

Figure 3 shows the typical dot pattern on a Si substrate delineated by the S-5000. The electron dose for each dot was about 0.2 pC. This figure shows a top view (a) and a tilted view (b) at the same place. The diameter of the dots was about 20 nm and their height was 60 nm. Such high aspect ratio in a nanosize dot pattern is one of the superior characteristics of MC6AOAc resists. The relatively smooth side wall of the pillar in Fig. 3(b) should also be noted.

The etching durability of MC6AOAc resists was tested using the DEM-451 (ANELVA) plasma dry etching system. The durability of the resist strongly depend on each etching system's setup and etching conditions; gas pressure, plasma flow style, and biasing. Figure 4 shows typical durability data for related materials obtained from the same etching system and under the same etching conditions. The typical condition was 5 Pa of CF₄ gas and an incident microwave power of 50 W with a 200 V dc electrode bias. The etching rate of MC6AOAc was estimated to be about 10 nm/s, which is almost comparable to that of Si, and the durability is about four times higher than that of PMMA. This durability seems to be sufficient to make semiconductor or metal nanostruc-

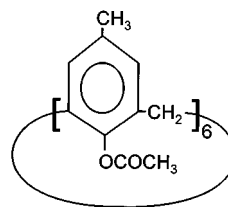


FIG. 1. Structure of MC6AOAc.

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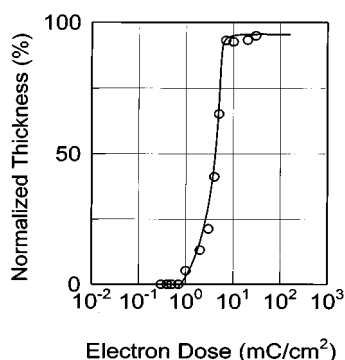


FIG. 2. Sensitivity to electron dose characteristics for MC6AOAc.

tures, since the thickness of the nanostructure is scaled down with its width. Well known highly durable novolak resist such as SAL (chemically amplified negative resist for electron beam, SHIPLEY), ZEP (positive resist for electron beam, NIPPON ZEON), and AZ (photoresist, HOECHST) are based on phenol and contain benzene rings as the frame structure, and show high durability to plasma etching. The same structure in MC6AOAc is presumably the origin for its high durability.

Germanium pattern transfer is shown in Fig. 5. The 20-nm-thick Ge layer requires at least 5-nm-thick MC6AOAc to be etched down, and the resist thickness was 30 nm. Figure 5(a) shows the line patterns of the resist on Ge film. Delineation was done using the S-5000 with a beam current of 100 pA at 30 kV acceleration voltage and the line dose was 20 nC/cm. A 10 nm line width and a smooth line edge were clearly observed. This smoothness is the key point in fabricating quantum nanowires by etching processes. Figure 5(b) shows the transferred pattern treated by 1 min of overetching, followed by oxygen plasma treatment to remove the

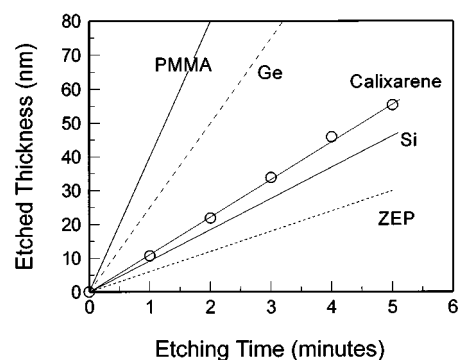


FIG. 4. Etching durability of MC6AOAc to the CF_4 plasma.

resist residues. A fine Ge line of 7 nm width was clearly observed without short cutting. Narrowing by overetching is a standard technique to obtain a fine line, however, side wall roughness limits the line width.⁷ The smoothness of the MC6AOAc side wall enables the line width to be narrowed below the 10 nm region by overetching. MC6AOAc is a single molecule and thus is monodispersed with a molecular weight of 972. In contrast, other phenol-based resists have dispersive weights from 1000 to 100 000, which set a resolution limit. We think the molecular uniformity of MC6AOAc and its small molecular size is the origin of such surface smoothness, and the resulting ultrahigh resolution.

In summary, we found MC6AOAc can be used as a high-resolution negative resist under an electron beam lithography process. It showed under 10-nm resolution with little side roughness and high durability to halide plasma etching. A sub-10-nm Ge quantum wire was etched down perfectly without defects. Such a performance is suitable for nanoscale device processes.

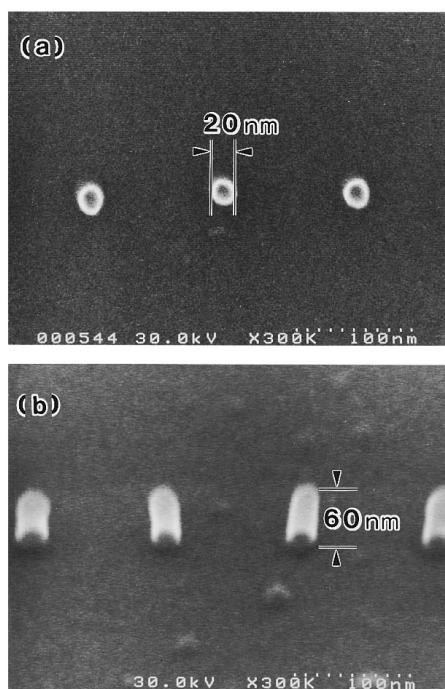


FIG. 3. Typical dot pattern on Si substrate. (a) plan view of dot array and (b) tilted view.

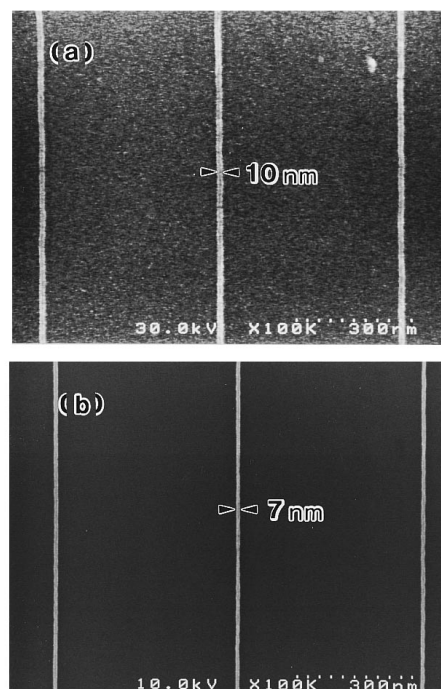


FIG. 5. Pattern transfer to Ge. (a) SEM image of resist pattern on Ge, and (b) SEM image of transferred Ge pattern.

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