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Creation of Micro-Resinoid Siloxane and Its Optimization for High T_g E-Beam Resist

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A newly designed micro-resinoid siloxane resist for use in electron beam lithography was presented. This resist exhibits high resolution, excellent thermal stability, and high dry etch resistance against O_2 RIE and Cl_2 RIE. Resist patterns of under 0.1 um for point-beams and 0.2 um for variable-shaped electron beams were obtained by optimizing the resist structure and its molecular weight, and by selecting a suitable developer. Bilayer resist patterning by O_2 RIE and undoped polysilicon patterning by Cl_2 were demonstrated as applications.

1. Introduction

Ever since efforts began toward the development of 16 Mbit DRAMs, a requirement for the practical use of lithography has been a resolution of 0.5 um or less. Electron beam lithography and excimer laser lithography are thought to have the potential to become key technologies in these development. For high resolution, resist thickness must be reduced for both of these technologies. Electron beam lithography has a problem with foward scatter, and excimer laser lithography has a problem with narrow depth of focus. The bilayer resist process helps solve these lithography problems and helps preserve dry-etch resistance. However, until recently few organosilicone resists were provided for production use because of the difficulty of their synthesis and because of their low Tg. In this report, we describe and apply to E-beam lithography a newly designed siloxane resist with both simplicity of synthesis and a variety of applications.

2. Resist Characterization

The chemical composition of the newly designed negaive tone siloxane resist is shown in Figure 1. It consists of an $SiO_{4/2}$ core with methyl and another functional group, R, around that core. It is easily synthesized from alcoxysilane and chlorosilane, which contains the functional group R. The siloxane structure is $SiO_{4/2}$ and is different from that of such siloxanes as the linear-chain $(R_2SiO_{2/2})n$ or ladder-type $(RSiO_{3/2})n$. The total concentration of Si and O is more than 70 wt%. This resist

$$[(CH_3)_3SiO_{1/2}]_m[(CH_3)_2\overset{R}{\overset{|}{Si}}O_{1/2}]_n[SiO_{4/2}]$$

Fig.1 Chemical composition of the newly designed siloxane resist.

shows excellent O_2 RIE resistance and thermal stability because of its $SiO_{4/2}$ structure. High resolution is expected because the volume per one molecule is the smallest of all other siloxanes of the same molecular weight, and swelling is suppressed as a result of crosslinking between closely-packed molecules which have an advanced three dimensional mesh structure. Various functional groups (R) may be introduced into the resist by making the starting material RR'R"SiCl. That is, the $SiO_{4/2}$ frame determines such fundamental properties as O_2 RIE resistance and thermal stability, and the functional group R determines a specific application. For example, chloromethyl, vinyl, and p-chloromethylphenetyl were used as R, and UV absorption spectra were observed (Fig.2). Transmittance in the deep UV region changed, and these changes depended upon the functional group, which suggests the possibility of application to excimer laser lithography. For electron beam lithography, chloromethyl was selected as R because of its step reaction mechanism.

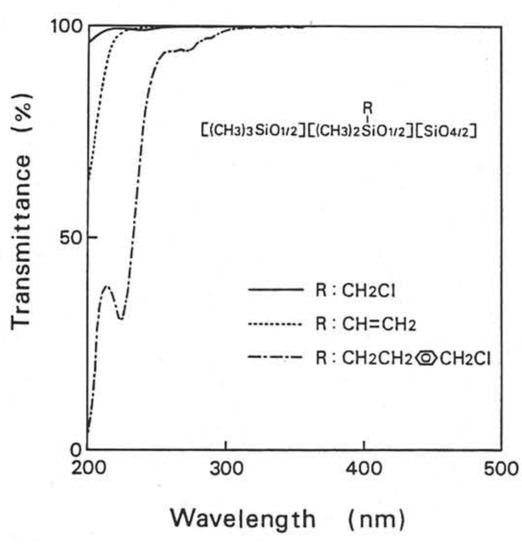


Fig.2 UV absorption spectra of the siloxane resists with different functional groups, R.

3. Optimization as an E-beam Resist

Resolution depends upon both the contrast of the resist and swelling of the resist pattern during the development, especially for negative tone resist using organic solvent as a developer. High contrast is achieved by resists with uniform molecular weight distribution and by avoidance of chain reaction propagation during exposure.[1] On the other hand, sensitivity depends upon the molecular weight of the resist, in the relationship described in the gel formation theory for negative tone resist.[2]

For this siloxane resist, the molecular weight was set at Mw=20000 in order to get a balance between contrast and sensitivity. Futhermore, the crosslinking reaction of the chloromethyl group takes place at random without any chain reaction, so high contrast was expected in comparison with resists produced with such functional groups as vinyl or allyl, which lead to a chain reaction.

As for swelling, the solubility of this resist in many kinds of organic solvents was examined. While the resist was highly soluble in both polar and non-polar solvents. we discovered that pattern flow, not swelling, was a problem. An alcohol-based organic solvent was chosen as a developer because it helped keep the pattern flow to a minimum.

A sensitivity curve is shown in Fig.3. The resist contrast obtained from the sensitivity curve was about 3.2. Resolution of less than 0.1 um was confirmed by point-beam exposure, and lines and spaces of 0.2 um

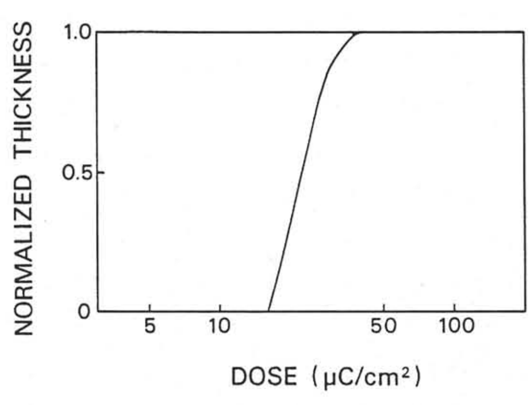
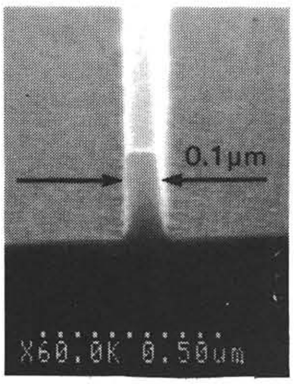


Fig.3 Sensitivity curve of the siloxane resist.

each were obtained by using a variable-shaped electron beam exposure system (Fig.4). The proximity effect, which is particulary noticeable in electron beam exposure of organic resists, such as chloromethylated polystyrene(CMS), was not a serious problem here.



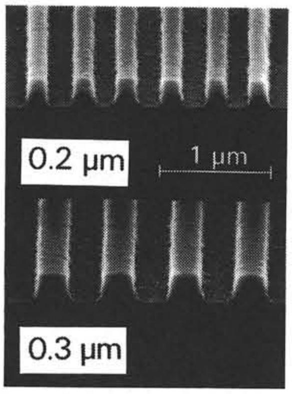


Fig.4 Siloxane resist patterns obtained by point-beam (left) and variable-shaped beam (right).

The heat resistance of this resist was examined by annealing in air for 30 minutes at 400°C, 600°C, and 800°C. Up to 400°C, the resist profile did not change. IR spectra showed that the absorption originating from

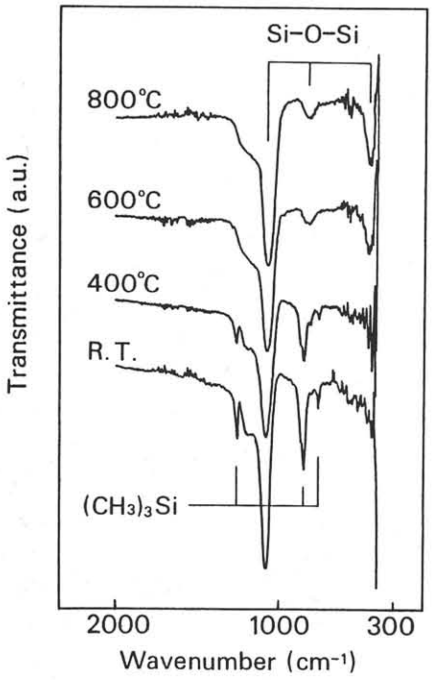


Fig.5 IR spectra of siloxane resist after annealing.

$(CH_3)_3$-Si decreased and the Si-O-Si structure grew as the annealing temperature increased (Fig.5). The chemical structure of the patterned resist after annealing above 600°C is thought to be similar to that of SiO_2.[3]

4. Applications

A bilayer resist system was constructed with a top imaging layer of this siloxane resist and a bottom layer of 1.5 um-thick Microposit-1400 for planarization. Fig.6 shows bilayer resist patterns formed by O_2 RIE. 0.3 um lines with a high aspect ratio were produced above the steps. Further, an application for Cl_2 RIE was tried expecting high dry etch resistance of this siloxane

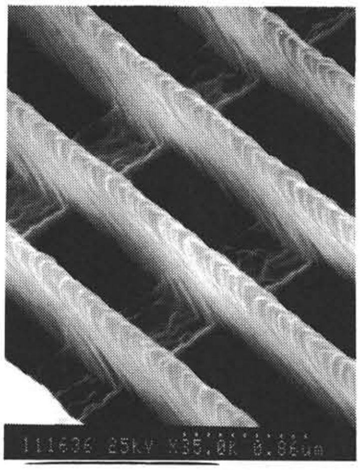


Fig.6 Bilayer resist patterns formed by O_2 RIE.

resist against Cl_2 RIE because of structural analogy between $SiO_{4/2}$ siloxane core and such SiO_2 as thermaly grown or CVD. Fig.7 shows the Cl_2 gas pressure dependence of etching rates for various materials. In these etching conditions, the selectivity ratio of the undoped polysilicon to the novolac-based photoresist was about 1.2, whereas the etching rate of the siloxane resist less than half of that of novolac-based photoresist. This resist has the potential, then, to be used as a single layer. Fig.8 shows the

0.2 um undoped polysilicon patterns formed by Cl_2 RIE with the siloxane resist mask, which had been patterned by e-beam exposure.

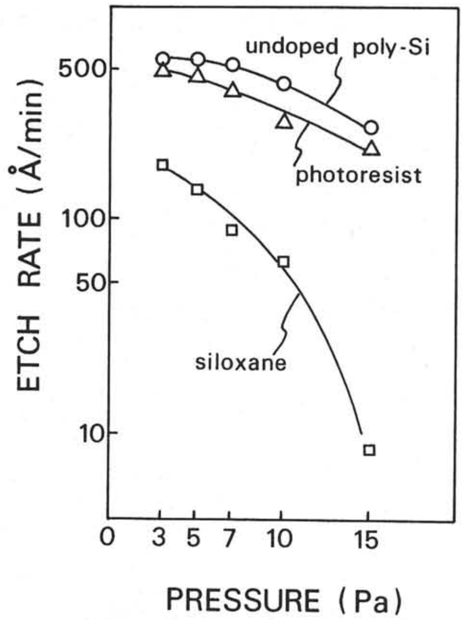


Fig.7 Cl_2 gas pressure dependence of etching rates for various materials.

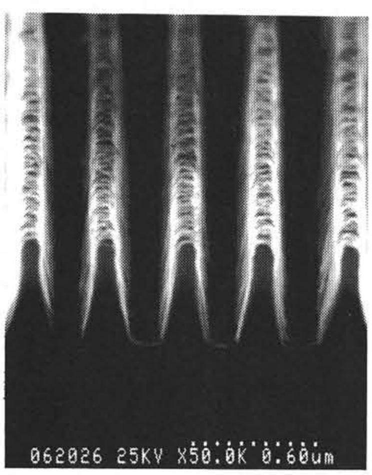


Fig.8 Undoped polysilicon patterns formed by Cl_2 RIE.

5. Conclusion

We have presented here a newly designed micro-resinoid siloxane resist for use in electron beam lithography. This resist exhibits high resolution, excellent thermal stability, and high dry etch resistance against O_2 RIE and Cl_2 RIE. Resist patterns of under 0.1 um for point-beams and 0.2 um for variable-shaped electron beams were obtained by optimizing the resist structure and its molecular weight, and by selecting a suitable developer. Bilayer resist patterning by O_2 RIE and undoped polysilicon patterning by Cl_2 RIE were demonstrated as applications.

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