1. Introduction

The tremendous progress in semiconductor fabrication technology has made it possible to fabricate Si nanodevices, such as one-dimensional Si nanowires [1,2] and Si single-electron transistors [3], that are only a few tens of nanometers in size. It is indispensable for nanodevice fabrication to make resist patterns with high accuracy. However, line-edge roughness (LER) generated in the resist patterns prevented its formation. This is because most LER are reported to have a magnitude of 3 nm or more [4-9] and the major cause is by polymer aggregates in resist films. The size of the polymer aggregates normally contained in resist films are 20 to 30 nm [4,10]. The polymer aggregates embedded on the pattern sidewall after development generate the LER [11,12]. Therefore, in order to reduce LER, the appearance of the large polymer aggregates on the pattern sidewall need to be suppressed. There are two approaches to doing this. One is reducing the aggregate size. The appearance of small aggregates on the pattern sidewall minimizes the amount of LER. We have already proposed a resist that contains small aggregates and have confirmed the effectiveness of this approach by using a single electron Transistor[5,12]. The other approach is suppressing the appearance of the aggregates themselves, which is expected to extremely reduce the LER.

In this article, we introduce a new cross-linked positive-tone resist based on the above approach of suppressing the appearance of aggregates on the pattern sidewall. Here, we focus on LER as well as patterning characteristics obtained by electron-beam lithography in order to evaluate the performance of this resist.

2. Approach to Reducing LER

Figure 1(a) shows a schematic diagram of the LER generation process in a positive-tone resist. It has been confirmed that polymer aggregates are normally contained in resist films by observing cross-sections of resist films with a scanning electron microscope (SEM) [10] and also by observing the exposed resist surface after development with an atomic force microscope (AFM) [4,5,10-12]. When such a resist film containing the polymer aggregates is developed after exposure, the developer molecules diffuse faster between aggregates and then the polymers...
surrounding the aggregates dissolve faster than the aggregates themselves. This is because the polymer density of the aggregates is higher than that of the surrounding polymers [11]. As a result, the polymer aggregates, whose surrounding polymers have been completely dissolved, can be extracted from the resist surface even if the aggregates themselves can not be fully dissolved in the developer. We refer to this as the aggregate extraction development [11]. However, many aggregates remain embedded on the pattern sidewall because their surrounding polymers have been not sufficiently dissolved due to insufficient exposure doses and this is responsible for LER.

To suppress such aggregate extraction development, it is necessary to reduce the difference in the dissolution rate between the aggregates themselves and their surrounding polymers. Therefore, the dissolution rate of the surrounding polymers needs to be reduced to the same level as that of the aggregates. The best way to achieve this is by cross-linking just the surrounding polymers, and in this way we were able to obtain a cross-linked positive-tone resist. We call this type of resist a Suppressed Aggregate Extraction Development Resist (SAGEX). Figure 1(b) shows the suppression process of the LER in the SAGEX resist. After the entire resist film is cross-linked by baking, it is exposed to an electron beam. In the exposed regions of the SAGEX resist, the resist dissolves uniformly over the whole surface because the dissolution rate of the surrounding polymers is reduced. As a result, the appearance of the aggregates on the pattern sidewall is suppressed and the resulting patterns have smaller LER.

3. Experiments

In order to form the SAGEX resist, we used a chemical amplification technique. An electron-beam positive-tone resist ZEP520 (Nippon Zeon Co., Ltd.), which is a chain-scission type of resist, was used as a base polymer. The base polymers were purified by precipitation in ethanol after heating the resist solution and then dried. We used 1,3,5-trimethyl-2,4,6-(triacetoxymethyl) benzene as a cross-linker, and cyclohexylmethyl (2-oxocyclohexyl) sulfonium trifluoromethane-sulfonate (CMS-105, Midori Kagaku Co., Ltd.) as a thermal acid generator (TAG). Resist solutions were prepared by adding cross-linkers and TAG in various ratios to the base polymers dissolved in 2-methoxyethyl acetate.

The cross-linking reaction was investigated by Fourier transform infrared (FT-IR) spectroscopy and solid-state $^{13}$C nuclear magnetic resonance (NMR) spectroscopy. In the NMR study, the spectra were taken by two pulse sequences: one was a normal cross-polarization (CP) sequences with high-power $^1$H decoupling and magic-angle spinning (CP/MAS) and the other was a normal CP sequence with a short delay inserted between the CP contact period and data acquisition (dipolar dephasing (DD)/MAS). In the DD/MAS experiment, the magnetization of those carbons with no attached protons were relatively unaffected, whereas those carbons with attached protons were rapidly destroyed due to the large proton-carbon dipolar interaction.

Resists were spin-coated on a Si wafer to a
thickness of 50 nm. Unless otherwise specified, resist films were cross-linked by baking on a hot plate at 200°C for 2 min. After cross-linking, an electron beam exposure was performed at a beam voltage of 70 kV. Then, resists were developed in n-hexyl acetate for 90 sec and rinsed in 2-propanol for 30 sec. Film thicknesses were measured with an interferometer (Nanospec 210XP, Nanometrics, Co., Ltd.). The resist pattern profiles were observed with a scanning electron microscope (SEM) (ELS-7300, Elionix Co., Ltd). Surface roughness of the exposed resists after development and linewidth fluctuations were measured with AFM. Linewidth fluctuation was defined as the standard deviation of the linewidth from AFM data at a depth of 5 nm and a sampling length of 800 nm. AFM measurements were performed with the SPI3700/SPA3500 system (Seiko Instruments Co., Ltd.) in the dynamic-force mode.

4. Results and Discussion
4.1. Cross-linking reaction

There are two requirements for the SAGEX resist. One is that only surrounding polymers should be cross-linked. The other is that cross-linking should occur at sites unrelated to electron-beam reactivity. We satisfied these requirements with a three-component resist composed of the base polymer, cross-linker, and thermal acid generator (TAG).

When we make the base polymer solution, aggregates form naturally. And as the cross-linker and TAG are added to it, they should disperse mainly outside of the aggregates in resist films because the polymer density inside the aggregates is higher than that outside of the aggregates [8]. This is precisely the reason why the base polymers can be more highly cross-linked in the surroundings than in the polymer aggregates in our three-component resist system.

We used a ZEP520 polymer, which is an alternating copolymer of methyl (α-chloroacrylate) and α-methylstyrene, as the base polymer [13]. Aromatic rings in the base polymer, which are independent of the electron-beam reactivity, were used as the cross-linking site. We applied an electrophilic aromatic substitution reaction [14] for a cross-linking reaction between aromatic rings. In this reaction, it is expected that acetoxymethyl groups of benzyl acetate are cleaved through acid-catalyzed reactions, resulting in the formation of benzylic carbocationic species. These carbocationic species react rapidly with other aromatic rings. Thus, we selected 1,3,5-trimethyl-2,4,6-(triacetoxymethyl) benzene as a cross-linker. Three acetoxymethyl groups in the cross-linker are introduced for high cross-linking efficiency and three methyl groups are introduced in order to prevent self-condensation. As a thermal acid generator, cyclohexylmethyl (2-oxocyclohexyl) sulfonium trifluoromethanesulfonate was selected because this material is a non-aromatic compound, which can not be attacked by carbocationic species, and since it decomposes and generates acids at a relatively low temperature of 142°C [15].

Figure 2 shows FT-IR spectra of SAGEX resists before and after baking, and the conventional ZEP resist. All peaks related to the ester group in the cross-linker, C=O (1734 cm⁻¹), CH₃ (1377 cm⁻¹), and C-O (1240 cm⁻¹), decreased after baking. This indicates that the acetoxymethyl groups in the cross-linker were cleaved by baking and benzylic carbocationic species were formed, although the cross-linking sites were not clearly observed.

Figure 3(a) shows ¹³C CP/MAS NMR spectra of SAGEX resists before and after baking in an oven at 200°C for 5 min. The assignment of all peaks due to carbons of the base polymer and cross-linker are shown in the Fig. 3. Peaks Zₙ and Xₙ (n=1-10) correspond to carbons in the base polymer and the cross-linker, respectively. The main changes in the spectrum of Fig.3 (a) are the appearance of two new peaks at 134 ppm (peak A) and 35 ppm (peak B), and the marked decrease in the relative intensity of peak Xₙ (128ppm) and peak X₁ (60ppm), which are
assigned to the unsubstituted carbons of the aromatic ring in the base polymer and the methylene carbons in the cross-linker, respectively. In order to clarify the origins of peak A and B, $^{13}$C DD/MAS spectra was investigated to distinguish those carbons having directly attached protons from those having no directly attached protons. Figure 3(b) shows $^{13}$C DD/MAS spectra of SAGEX resists corresponding to samples in Fig. 3(a). As clearly seen in the figure, peak A remarkably increases while peak B can not be observed after baking. Therefore, peak A is due to those carbons with no attached protons and peak B is due to the methylene carbons or the methine carbons. It is well known that the alkylated aromatic carbons appear at 130-140 ppm and the methylene bridge carbons appear at 35-40 ppm in the structure of two benzene rings that are bridged by methylene linkage. Therefore, peak A and B can be assigned to the alkylated aromatic carbons and the methylene bridge carbons in the structure of the methylene linkage connecting two benzene rings, respectively. This assignment gives a good account for the change in the spectra of SAGEX resists before and after baking. The increase in peak A and the decrease in peak $Z_{4,5,6}$ result from the conversion from the unsubstituted carbons of the aromatic rings in the base polymer to the aromatic carbons substituted by the methylene bridge carbons. The decrease in peak $X_1$ and the increase in peak B result from the conversion from the methylene carbons in the cross-linker into the methylene bridge carbons connecting two benzene rings. Consequently, the result of the NMR study definitely indicates that the aromatic ring of the base polymer is cross-linked with the aromatic ring of the cross-linker by means of the methylene bridge carbon. It is unclear which carbons of the aromatic ring of the base polymer cross-linked with the cross-linker from these spectra. However, it is expected that the carbon in the “para” position ($Z_6$) of the aromatic ring of the base polymer predominantly cross-linked because the aromatic ring of the base polymer has ortho-para orientation and since alklylation at the ortho position is suppressed due to steric hindrance. The cross-linking reaction can be schematized, as shown in Fig. 4. TAG generates acids by baking at temperatures higher than 140°C. Then, the cross-linker supplies benzylic carbocationic species through acid-catalyzed reactions. These carbocationic species react rapidly with aromatic rings of the base polymers. And then, base polymers are cross-linked to each other by the cross-linker.

4.2. Lithographic performance

When the cross-linked SAGEX resist is exposed to an electron beam, the fragmentation
of main chain of the base polymers occurs by means of Norrish type I reaction because the carbonyl groups in the base polymers are independent of the cross-linking reaction. As a result, the SAGEX resist works as a positive-tone resist. Figure 5 shows sensitivity curves of SAGEX resists after baking at various temperatures. The composition ratio (ZEP/cross-linker/TAG) is 100/30/10. This figure clearly shows that the SAGEX resist works as a positive-tone resist. The clearing dose of SAGEX resist films formed at 130°C is about the same as that of the conventional ZEP film after baking at 130°C (not shown here). At temperatures higher than 150°C, the clearing dose of SAGEX resist films decreases with increasing baking temperature. This behavior is consistent with the behavior of the cross-linking reaction accompanied by the decomposition of TAG. Sensitivity curves of SAGEX resist with various amounts of cross-linker and TAG are also obtained. The clearing dose increased by increasing the amount of cross-linker or TAG. For example, clearing doses of SAGEX resists with the composition ratios (ZEP/Cross-linker/TAG) of 100/15/10, 100/30/10, and 100/30/15 after baking at 200°C were 400, 800, and 1200 μC/cm², respectively. This indicates that the degree of cross-linking increased by increasing the amount of the cross-linker and TAG. The increase in molecular weight due to cross-linking makes the dissolution rate lower, which in turn raises the clearing dose.

Figure 6 shows an SEM image of SAGEX resist patterns with a linewidth of 20 nm. Although the clearing dose increases, it was confirmed that the SAGEX resist does not greatly influence the electron-beam reactivity. This low...
sensitivity will be solved with a strong developer because the unexposed region of SAGEX resist film hardly dissolves even when the good solvent for the base polymer is used.

Figure 7 shows AFM images of the surface of ZEP and SAGEX resist films remaining after exposure with various doses and subsequent development. For conventional ZEP resists, the surface morphology changes as the remaining resist thickness decreases. It is obvious that this morphology change is induced by the appearance of polymer aggregates on the surface. This behavior of the surface roughness can be explained in terms of aggregate extraction development. In ZEP resist, as previously explained, the developer molecules diffuse faster between aggregates than within them, so the polymers surrounding aggregates dissolve faster. This is why aggregates appear on the surface, as can be seen in Fig. 7(e). As the dissolution of surrounding polymers proceeds, the aggregates are extracted one by one when they become dislodged. Therefore, the surface becomes rougher because the aggregate extraction occurs randomly, as is shown in Fig. 7(f).

On the other hand, for SAGEX resists, the surface morphology does not change and shows a very flat surface without polymer aggregates as the remaining resist thickness decreases. The fact that the surface maintains very small roughness during development means that the resist film dissolves uniformly over the whole surface. It is noteworthy that the magnitude of surface roughness of SAGEX resist films is drastically suppressed to less than one-third compared to ZEP resist films at the remaining thickness of 60%. As we expected, these results clearly demonstrate that aggregate extraction development is actually suppressed in the SAGEX resist.

To determine the LER quantitatively, linewidth fluctuations of isolated patterns with the linewidth of 100 nm formed in the SAGEX resist and the conventional ZEP were measured with AFM. As expected from results of the surface roughness, it is confirmed that the linewidth fluctuation was reduced to about 2 nm in the SAGEX resist, whereas the linewidth fluctuation is more than 3 nm in the conventional ZEP resist.

5. Conclusion
We have developed a cross-linked positive-tone resist called the SAGEX resist to
reduce the LER. Our key approach is the suppression of aggregate extraction development by cross-linking. We have achieved this by reducing the dissolution rate in the surrounding regions by cross-linking the surrounding polymers. The cross-linking reaction between the base polymers in the SAGEX resist was actually confirmed by FT-IR spectroscopy and solid-state $^{13}$C NMR spectroscopy. AFM measurements indicate that the LER, as well as surface roughness of the exposed film, is successfully reduced in the SAGEX resist.

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References