Comparison of EB Exposure Characteristics between HSQ and Calix Arene of High Resolution Negative Resist

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Keywords: Hydrogen silsesquioxane (HSQ), Calix Arene, Electron-beam (EB), Spaccer

1. Introduction
In present, fine processing technology is required with high functionalization in semiconductor, electro-optic device, memory and other industrials. So, the fabrication of fine patterns is an important assignment. High resolution resist is necessary for fabricating the fine patterns by electron-beam (EB) lithography. Resists widely used as high resolution negative resist are the inorganic hydrogen silsesquioxane (HSQ) and the organic Calix Arene.1,2)

In this study, we compared EB exposure characteristics of Calix Arene and HSQ. First, we present the sensitivity curves and the etching rates for the resist materials. And then, EB exposure stability has been examined.

2. Experiment
Figure 1 shows a schematic of EB writing process using HSQ and Calix Arene. First, we show fabrication process of HSQ patterns. In our experiment, HSQ (FOX-16 (Dow Corning Co.): Methyl isobutyl ketone = 1 : 5) was used. First, HSQ was spin-coated on a Si substrate at 4000 rpm for 1 min. Film thickness was 50nm. Next, HSQ coated substrate was prebaked at 120 °C for 1 min. And then, the HSQ was exposed by EB. The acceleration voltage and dose were 50 kV and 360 μC/cm², respectively. After the exposure, the HSQ was developed. The developer was a 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution. The developing time was 1 min. The rinse was water for 1 min.

Next, we show fabrication process of Calix Arene patterns. Calix Arene (TOKUYAMA Co.) was spin-coated on a Si substrate at 1000 rpm for 1 min. Film thickness was 50nm. Next, Calix Arene coated substrate was prebaked at 110 °C for 1 min. And then, the Calix Arene was exposed by EB. The acceleration voltage and dose were 50 kV and 1200 μC/cm², respectively. After the exposure, the Calix Arene was developed. The developer was an isopropyl alcohol (IPA). The developing time was 1 min.

Received April 3, 2010
Accepted May 7, 2010
3. Results and Discussion

3.1 Sensitivity

Figure 2 shows the sensitivity curves of HSQ and Calix Arene resist after EB exposure by 50kV electrons and development. The sensitivity of HSQ and Calix Arene were 360 μC/cm² and 1200 μC/cm² at 50 kV, respectively. The sensitivity of HSQ is about three times higher than that of Calix Arene.

3.2 Etching durability

Table 1 shows the etching durability. The etching rates were obtained from the measurement of the average thickness of the film before and after etching by scanning electron microscope (SEM) observation. We used commercial reactive ion etching (RIE) (RIE-10NR; Samco Co.) with CHF₃ and O₂ as etching gas. The gas flow of 50 sccm, gas pressure of 2.0 Pa and RF power of 100W were used for CHF₃ RIE. In the meanwhile, the gas flow of 50 sccm, gas pressure of 5.0 Pa and RF power of 100W were used for O₂ RIE. HSQ was hardly etched by O₂ plasma because it is an organic material that consists of repeated units of HSiO₁/₂. This indicates that HSQ is oxidized by O₂ plasma and consequently become a sufficient etching mask. In contrast, Calix Arene was superior to HSQ in case of CHF₃ RIE. The etching rate is nearly the same as that of ZEP (ZEP-520A (ZEON)). Therefore, Calix Arene can use as etching mask against CHF₃ plasma.

3.3 EB exposure stability

It has been already reported that the sensitivity of HSQ depends on preserving in the atmosphere such as air, nitrogen and vacuum before EB exposure and changes during EB exposure writing time.³

In fact, we performed the following experiment to investigate EB exposure stability using both resists. Each resist films were exposed under two different kinds of condition. Figures 3A and 3B show the HSQ and Calix Arene patterns fabricated by EB exposure, respectively. Figures 3(a) and 3(b) show each patterns of initial writing and fabricated after placed each films in air for 7 hours. Linewidth of HSQ patterns increased from 48 nm to 70 nm when the HSQ film was placed in air for 7 hours, as shown in Fig. 3A (b). On the other hand, the linewidth of Calix Arene patterns was maintained when the Calix Arene film was placed in air for 7 hours, as shown in Fig. 3B (b).

![Fig. 2. Sensitivity curves of Calix Arene and HSQ exposed with 50kV electrons.](image)

![Table 1. Etching rates of Calix Arene, HSQ and ZEP.](image)

![Fig.3 SEM images of A and B are HSQ and Calix Arene patterns, respectively. (a) Initial writing, (b) Placed in air for 7 hours later.](image)
Next, we measured EB exposure time dependence of linewidth for HSQ and Calix Arene, as shown in Fig. 4. So, HSQ and Calix Arene films were exposed over 10 hours-long EB writing time for HSQ and Calix Arene. The linewidth of Calix Arene patterns was maintained even when the Calix Arene resist were exposed over 10 hours-long EB writing time. On the other hand, the linewidth of HSQ patterns increased as EB exposure time increased. This result indicates that the sensitivity of HSQ change during EB exposure. It seems that this sensitivity changes of HSQ causes by hydrolysis and condensation reaction of HSQ which is sol-gel material with H₂O in the atmosphere.

To avoid the sensitivity change of HSQ during EB exposure writing, we proposed a new process to prevent those reactions by coating a protective thin film on HSQ surface. We used a commercial available electrification dissipating material, Espaser (Espacer300N, SHOWA DENKO Co,) as a protective thin film. HSQ film is an insulation film. It can also prevent charge by spin-coating of Espaser on HSQ film. So, we investigated EB exposure stability using HSQ without and with Espaser.

Fabrication process of HSQ patterns with Espaser is shown in Fig.5. First, HSQ was spin-coated on a Si substrate at 4000 rpm for 1 min. Film thickness was 50nm. Next, HSQ coated substrate was prebaked at 120 °C for 1 min. Following, Espaser was spin-coated on the HSQ coated Si substrate at 4000 rpm for 1 min. Film thickness was 15nm. And then, the HSQ was exposed by EB. The acceleration voltage and dose were 50 kV and 360 μC/cm², respectively. After the exposure, the HSQ was developed. The developer was a 2.38% tetramethylammonium hydroxide (TMAH) aqueous solution. The developing time was 1 min. As Espaser is water-soluble material, it was removed at the same time when HSQ was developed in TMAH aqueous solution.

We performed the following experiment to investigate whether applying Espaser on HSQ can prevent hydrolysis and condensation reaction of HSQ or not. Like the former experiment, we investigated EB exposure stability using HSQ without and with Espaser. Each HSQ films were also exposed under two different kinds of condition. Figures 6A and 6B show SEM images of the HSQ patterns fabricated without and with Espaser, respectively. Figures 6(a) and 6(b) show each HSQ patterns of initial writing and exposed over 10 hours-long EB writing time, respectively. Linewidth of HSQ patterns without Espaser increased from 48 nm to 70 nm at the conditions of Fig. 6A(b). On the other hand, the linewidth of HSQ patterns with Espaser can maintain in even both conditions by coating Espaser on HSQ, as shown in Figs. 6B(b). We demonstrated that EB exposure stability using HSQ resist has been achieved by applying a protective thin film on HSQ.
4. Summary
The comparison of EB exposure characteristics between inorganic HSQ and organic Calix Arene were carried out. The sensitivity of HSQ is about three times higher than that of Calix Arene. Linewidth of HSQ patterns increased by EB exposure writing for a long time because the sensitivity was changed by extremely chemically instability during that time. On the other hand, Calix Arene patterns maintained initial profile for chemically stability. To overcome sensitivity changes of HSQ, we have developed a new method which is Espaser coating on HSQ film. It has been demonstrated that HSQ patterns with Espaser maintained their initial profiles even over 10 hours-long EB writing time. Espaser coated on HSQ film is therefore an efficient for maintaining HSQ patterns profile.

5. Reference