New method of EB exposure stability using HSQ high-resolution negative resist

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Hydrogen silsesquioxane (HSQ) is used as a high-resolution, electron-beam (EB) negative-tone resist.¹⁾ However, 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.²⁾ It seems that the sensitivity changes causes by hydrolysis and condensation reaction of HSQ with H₂O in the atmosphere. In this paper, 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, Espacer (Espacer300N, SHOWA DENKO.Co.) as a protective thin film.

Figure 1 shows a schematic of EB writing process using HSQ proposed here. (1) First, HSQ (FOX-16, Dow Corning Co.) was spin-coated on a Si substrate at 4000 rpm for 1 min.. Film thickness was 50nm. (2) Next, HSQ coated substrate was prebaked at 120 °C for 1 min.. (3) Following, Espacer was spin-coated on the HSQ coated Si substrate at 4000 rpm for 1 min.. Film thickness was 15nm. (4) And then, the HSQ was exposed by EB. The acceleration voltage and dose were 50 kV and 360 μ C/cm², respectively. (5) 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 Espacer is water-soluble material, it was removed at the same time when HSQ was developed in TMAH aqueous solution.

We investigated EB exposure stability using HSQ without and with Espacer. Each HSQ films were exposed under three different kinds of condition. Figures 2A and 2B show SEM images of the HSQ patterns fabricated without and with Espacer, respectively. Figures 2(a), 2(b) and 2(c) show HSQ patterns of initial writing, fabricated after placed HSQ film in air for 7 hours and exposed over 10 hours-long EB writing time, respectively. Linewidth of HSQ patterns without Espacer increased from 46nm to 70nm and 73nm at the conditions of Figs. 2A (b) and 2A (c). On the other hand, the linewidth of HSQ patterns with Espaser was maintained when the HSQ film was placed in air for 7 hours and exposed over 10 hours-long EB writing time, as shown in Figs. 2B (b) and 2B (c). Figure 3 shows changes of several HSQ patterns size when the HSQ films without Espacer and with Espacer were exposed over 10 hours-long EB writing time. The result indicates that feature size of HSQ didn't change even at 10 hours-long EB writing time by coating Espacer on HSQ. We demonstrated that EB exposure stability using HSQ resist has been achieved by applying a protective thin film on HSQ.

Reference

1) H. Namatsu et al., J. Vac. Sci. Technol. B 16 (1998) 69.

2) N. Clark, et al., J. Vac. Sci. Technol. B 24 (2006) 3073.



Fig.1 Schematic of EB exposure using HSQ.

(A) Without Espacer



- (a) Initial writing. Linewidth; 46nm
- (B) With Espacer



(a) Initial writing. Linewidth; 48nm



EB writing time.

(b) Placed in air for 7 hours later. Linewidth; 70nm



Espacer and without Espacer over 10 hours-long

(c) 10 hours passed writing. Linewidth; 73nm



(b) Placed in air for 7 hours later. Linewidth; 48nm



(c) 10 hours passed writing. Linewidth; 48nm

Fig.2 SEM images of HSQ patterns.

Comparison of HSQ feature sizes between without and with Espacer.