Contrast Enhancement Behavior of Hydrogen Silsesquioxane (HSQ) in a Salty Developer

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Hydrogen silsesquioxane(HSQ) is known as one of the widely utilized negative-type ebeam resist materials. Several development systems, such as high temperature and high concentration alkali developers, have been suggested to improve the e-beam resist performances including contrast (γ) and sensitivity (D_o).¹ Recently, a novel development system was reported by adding salt in alkali developer, which offers an outstanding γ value for high resolution and high density patterning of HSQ.² However, the role of salt in contrast enhancement of alkali developer was not clear. It is known that pure alkali developers usually cause the HSQ surface to be covered with an insoluble layer which retards the further development process.³

We have investigated the γ enhancement behavior of HSO when salt is incorporated in a conventional alkali developer, by observing the time-resolved thickness variations during development process. We made sets of HSQ blanket patterns by utilizing 100 keV e-beam and developing them for various times with respect to both salty (NaCl 4 wt%/NaOH 1 wt%) and non-salty (pure NaOH 1 wt%) developer solutions. We obtained contrast curves for different developing times, as shown in Fig. 1, demonstrating the difference between salty and non-salty developers. Figure 2 describes the variations of γ and D_0 for different developing times. In the case of salty developer, the contrast enhancement behavior ($\gamma > 10$) is seen after ~4 min developing time (Fig.2a), which is attributed to the continuous development process as shown in Fig.2b. On the other hand, development with the non-salty developer stops after ~ 4 min, which saturates both γ and D_0 to ~4 and ~1.7 mC/cm², respectively (Fig.2a and b). This development stopping behavior is expected to prohibit the improvement of γ . Figure 3 shows the plot of thickness variations as the developments are going on. Interestingly, at the early stage of development process, both salty and non-salty developers show similar behaviors such as a sharp decrease of thickness followed by a gradual saturation. However, as the developing time is further increased, the salty developer continues to thin the resist film, whereas the non-salty developer does not lead any significant changes in resist thickness. The thinning process is a unique step of the salty development system, which enhances the γ of HSQ.

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Figure 1. Time-resolved contrast curve variations for salty(NaOH/NaCl) and non-salty(NaOH) developers.



Figure 2. The variations of contrast (γ) and sensitivity (D_o) for both salty and non-salty development processes. Contrast enhancement behavior is clearly shown in salty developer. On the other hand, non-salty developer causes the development process to stop after ~ 4 min.



Figure 3.The thickness variations as the function of developing time. At the early stage of development, both developers show similar behaviors such as a sharp decrease of thickness followed by a gradual saturation. However, as developing time is further increased, the salty developer leads the collapse of HSQ, which is a unique step enhancing the γ of HSQ.