New Self-Developing X-ray Resists Consisting of Polysilanes

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New dry-developing X-ray resists consisting of polysilanes are investigated from the viewpoints of 1) X-ray sensitivity, 2) self-development characteristics, and 3) reactive ion etching (RIE) resistance. It is found that chain scission of both backbones and side chains occurs and polysilanes behave as positive tone resists under soft X-ray exposure. Polysilane film thickness decreases with X-ray exposure, and heating during exposure enhances self-development. Heating after exposure, however, provides a reverse effect such that exposed portions are less volatile than unexposed portions. This experimental result can be explained by the oxidation of surface Si atoms which prevent inner polysilane evaporation. Finally, line and space patterns were successfully delineated by dry development in a bilayer polysilane resist, proving the feasibility of the process for X-ray lithography.

Introduction

Organic polysilanes are one-dimensional silicon polymers whose application to precursors of ceramics and nonlinear optical devices has been intensively investigated. Recently, much attention has been paid to their photosensitivity and oxygen reactive ion etching (O2-RIE) stability, which allow polysilanes to be used as photoresists.\(^1\,2\) Polysilanes have been used as both positive and negative tone photoresists and an all-dry process has been demonstrated as shown in Fig. 1.\(^3\,4\) Ultra-violet (UV) excimer laser lithography or vacuum ultra-violet (VUV) exposure excites only the valence electrons. On the other hand, X-rays have much higher energy, and therefore, excite core electrons, yielding new reactions such as localized chain scissions or crosslinking. Furthermore, X-rays produce far less thermal energy than lasers. Thus, X-ray exposure introduces a new facet to polysilane resist technology.

In this paper, we present application of polysilanes to a new self-developing resist for X-ray lithography, which is investigated from the viewpoints of 1) reaction to X-rays, 2) heating effect on sensitivity, and 3) feasibility of patterning by dry processes. This work is aimed at resists providing both high development sensitivity and high dry etch resistance, as shown in Fig. 2. By using this dry process, resist pattern degradations such as swelling and pattern fluctuation are reduced compared with wet development, because the resist is not penetrated by liquid developer. In nanometer-scale patterning, pattern size fluctuations in wet developable organic resists are significant, and can become fatal problems.\(^6\) Dry developable resists also allow full patterning in a single vacuum chamber, further reducing contamination, improving throughput, and allowing for the possibility of cluster tools.

Experimental

Poly(cyclohexylmethylsilane) (PCHMS) was synthesized using Wurtz-type coupling as described elsewhere.\(^7\) Thin films (0.1-0.3\(\mu\)m) were spin-coated on silicon wafers and quartz plates from a toluene solution and baked in a convection oven at 80°C for 20 minutes. X-ray exposure was carried out using the synchrotron radiation source at SORTEC. The source wavelength was 0.7-1nm, and the intensity was 9mW/cm\(^2\). Also, to check the feasibility of pattern replication, X-ray proximity lithography was applied to a polysilane/OFPR800 bilayer resist.

Positive Tone Resist for X-ray

UV and IR absorption spectra were observed before and after exposure to investigate the change in the structure of the polymer. The exposure dose is 16J/cm\(^2\). UV spectra are shown in Fig. 3. The absorption band around 300nm, which corresponds to excitation of \(\sigma\) electrons in the one-dimensional Si backbone, has completely disappeared after exposure. This means scission of the Si-Si bonds has occurred. In the IR absorption spectra in Fig. 4, it is shown that the peaks at 700-800cm\(^{-1}\), assigned to Si-C bonds, have also disappeared after exposure. This result suggest that Si-C side chain scission has occurred Thus PCHMS can be used as a positive tone resist (Fig. 5). A broad absorption band at 1000-1100cm\(^{-1}\) has appeared after exposure. This broad band is assigned to Si-O-Si bonds from the results of UV or VUV laser irradiation in air. X-ray exposure was carried out in a vacuum chamber, however, chain scission yields Si dangling bonds. They are reactive and oxidized when the sample comes in contact with air.

Patterning

The thicknesses of exposed polysilane films were measured. At room temperature, a decrease in film thickness was observed, as shown in Fig. 6, which levels off to around 83% of the initial thickness. This
fact implies that excitation of core electrons gives rise to chain scission as observed in UV and IR spectra, but another excitation for desorption of decomposed products is also needed. On the other hand, laser irradiation with enough intensity for chain scission causes desorption, as well as scission, resulting in a much thinner film. We suggest that thermal excitation from the pulsed laser irradiation assists desorption of decomposed products. To enhance desorption in X-ray exposure, the polysilane film was heated during exposure. At 200°C, the X-ray exposed polysilane thickness is much less than that at room temperature, as shown in Fig. 6.

Thermal desorption spectroscopy (TDS) measurement in the temperature-range from 25 to 400°C was carried out after exposure. The measurement started from 25°C, and heating and mass spectroscopy were repeated. The temperature dependence of ion counts of typical fragments in mass spectra are presented in Fig. 7. The weight of the exposed portion used for this measurement is equal to the weight of the unexposed portion. A fragment with mass number 2 (m/e=2) corresponds to H$_2$ in atmosphere. The products from substituents are 54 and 67. However, ion counts from unexposed portion decrease above 350°C. This is because almost all the polymer has evaporated. It should be noted that fragments from the unexposed portion are more volatile than those from the exposed one, that is, there is a reverse effect on volatility between heating during and after exposures. This interesting result is probably because the exposed portion has dangling surface bonds which are likely to be oxidized in atmosphere. Oxidized silicon at the surface is stable, and prevents the inner polysilane from being evaporated. Therefore, to improve desorption, heating must be carried out during exposure.

O$_2$-RIE etch rates were measured. The etch rate of PCHMS baked at 80°C is 20A/min (1.3Pa, 30sccm, 100W) and much smaller than the etch rate of OFPR800 baked at 210°C, which is 600A/min. These results indicate polysilane has enough etching selectivity to be used as an upper layer in a bilayer resist.

Fig. 8 shows 0.8μm lines which were produced by proximity X-ray exposure of 0.1μm-thick PCHMS and transferred by O$_2$-RIE (1.3Pa, 30sccm, 100W) into 1μm-thick hardbaked photoresist (OFPR800). The samples were heated to 200°C during exposure. The exposed dosage is 16J/cm$^2$ on the mask. The result shows that these bilayer resist were patterned successfully by a dry development.

**Conclusion**

We presented a new self-developing X-ray resist consisting of polysilanes. Chain scission by X-ray was observed and desorption of decomposed products was improved by heating the resist during exposure. A bilayer resist with polysilane as an upper layer was successfully patterned by dry processes (self-development+O$_2$-RIE). We will also investigate the application of the resist to 0.1μm L/S pattern in X-ray projection lithography. Such new dry processes will likely be a key technology for nanometer lithography.

**References**

Reactivity of materials

Fig. 2. Purpose of this work and conventional dry development processes.

Fig. 4. IR absorption spectra of PCHMS.

Fig. 6. Sensitivity curves of PCHMS films exposed at room temperature (O) and 200°C (●).

Fig. 7. Thermal desorption spectra of evaporated species from unexposed and exposed PCHMS films (exposed dosage is 32J/cm²).

Fig. 8. Delineated patterns of PCHMS and hardbaked novolac bilayer resist after dry development process.