Thermal development of calixerene resist

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Resist development in lithography is a critical step that defines the final micro or nanostructure. Dry resist development compared to typical wet development process is beneficial because of the absence of wet solvents. In this way effects such as resist swelling, increased line edge roughness (LER) and even detachment from the substrate can be avoided. One of the dry development methods is thermal development. During thermal treatment at high enough temperatures resist decomposes into gaseous products that leave the surface. In the case of negative tone resist, molecules cross-linked by the irradiation do not decay, but remain on surface to form the structure.

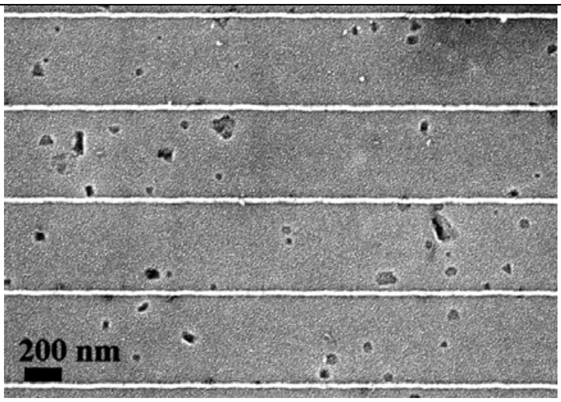
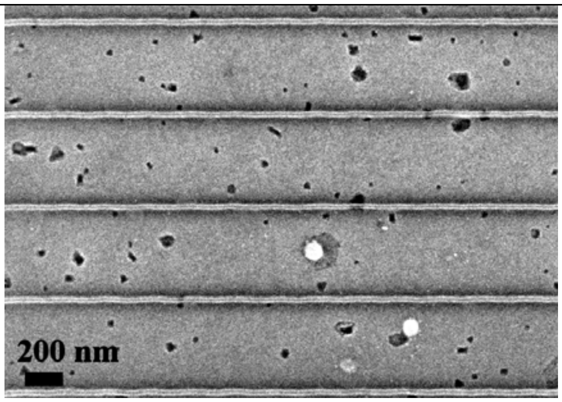
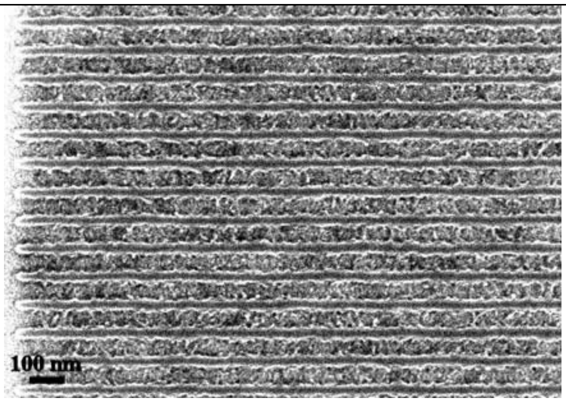
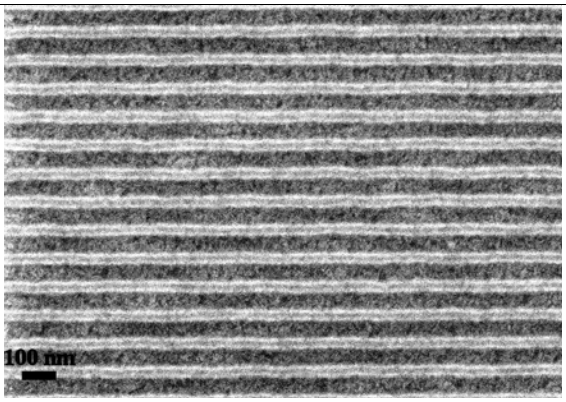
Heat treatment has previously been demonstrated for polymer resists. The full resist development with heat was done after UV irradiation of poly(4-chlorophthalaldehyde) at 100-130°C to produce sub-micrometer structures [1]. It improved the resist sensitivity and no resist flow was observed. Heat treatment of already wet-developed resist was shown to shrink the structures and improve LER [2]. Organic molecular resists are good candidates for thermal development because of a small molecular size that decomposes and evaporates much easier than polymer resists with longer polymer chains. Calixarene is a high resolution molecular resist for sub-10 nm fabrication [3]. Using heat development we are expecting to simplify the developing process and improve LER.

Development temperature is the main processing parameter. Thermo-gravimetric analysis (TGA) of unexposed calixarene resist showed that it starts to decompose at temperatures higher than 200°C. At more than 450°C all the exposed and not exposed material is lost. 30 nm thick p-chloromethyl-metoxy-calix[4]arene resist coated on silicon or Cr coated substrates was exposed using 2.5 keV electron beam. Lines with 25-250 nm half pitches have been exposed and developed at 250-430°C on a hot plate in air. The results were compared to standard development in IPA. Fig.1-4 show examples of 250 nm half pitch isolated and 40 nm half-pitch lines in calixarene developed in standard IPA developer, at 300°C and at 400°C. The thermally developed calixarene has improved LER compared to the IPA developed one. In thermally developed large area patterns of dense lines we noticed the presence of a residual film on the substrate between the lines. This residual film seems to originate from partially cross-linked molecules that are able to flow or diffuse on the surface but are not able to leave the surface. This problem was not observed for isolated features.

Thermal development technique, demonstrated here for a non-chemically amplified molecular resist, may be useful as a remedy for the notorious LER problem that is faced in nano-lithography while maintaining the sensitivity and good resolution properties of the resist.

References:

1. H. Ito, M. Ueda, R. Schwalm, J.Vac. Sci.Tecnnol. B6 (6) 1988 2259
2. S. H. Kim, H. Hiroshima and M. Komuro, Nanotechnol. 17 2006 2219
3. M. Ishida, J. Fujita, T. Ogura, Y. Ochiai, E. Ohshima and J. Momoda, Jpn. J. Appl. Phys. 42 2003 3913

 Fig.1 250 nm half pitch isolated calixarene lines on silicon developed in standard IPA developer for 30s.	 Fig.2 250 nm half pitch isolated calixarene lines on silicon developed thermally at 400°C 2s.
 Fig.3 40 nm half pitch calixarene lines on chromium developed in IPA for 30s, exposure dose was 300 $\mu C/cm^2$.	 Fig. 4 40 nm half pitch calixarene lines on chromium developed thermally at 300°C 1 min, exposure dose was 300 $\mu C/cm^2$. The grainy structure between the lines is chromium.