Chemical Composition and Pattern Development in Inorganic Photoresist Materials Deposited from Aqueous Solution

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Metal oxide sulfates (MSOx) have recently emerged as a promising material for high resolution, high sensitivity inorganic photoresists.[1] Dense features below 10 nm can be patterned using EUV radiation or by electron beam lithography. MSOx films are deposited from aqueous solution without the use of organic ligands and yield dense, atomically smooth films. For these studies, peroxide chemistry is used to modulate film solubility and provide a mechanism for radiation-induced film condensation. To better understand the chemistry of pattern development in these inorganic resists, we investigated the solubility of hafnium oxide sulfate (HafSOx) films (10-50 nm thick) using quartz crystal microbalance (QCM) and scanning electron microscopy (SEM). In addition to radiation and peroxide chemistry, the solubility of the films is found to depend critically on ligand environment, annealing temperature, vacuum processing, and the basicity of the developer solution.

Film composition was analyzed by medium energy ion scattering (MEIS), X-ray photoelectron spectroscopy (XPS), and scanning transmission electron microscopy energy dispersive x-ray spectroscopy (STEM-EDX) mapping. The results of these studies indicate that the films are not uniform throughout their thickness, but rather surface layers form which can be significantly different from the bulk of the film. Infrared and Raman spectroscopy provided complimentary information about changes in the ligand environment within the films. Together these measurements give insight into the chemical changes in the film that lead to changes in solubility. The results of these studies advance our understanding of MSOx inorganic photoresists and will guide the development of improved materials.

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[1]A. Telecky, P. Xie, J. Stowers, A. Grenville, B. Smith, and D. A. Keszler, *J. Vac. Sci. Technol B*, **2010**, 28, C6S19