THE STRUCTURE OF THIN ZIRCONIA FILMS OBTAINED BY SELF-ASSEMBLED MONOLAYER MEDIATED DEPOSITION: TEM AND HREM STUDY. V.V. Roddatis, D.S. Su, E. Beckmann, F. Jentoft, U. Braun, J. Kröhnert, and R. Schlögl. Fritz-Haber-Institut der MPG, Abteilung AC, Faradayweg 4-6, D-14195, Berlin, Germany.

Thin zirconia-based films were obtained by self-assembled monolayer (SAM) mediated deposition from aqueous medium. The SAM-covered Si(100) substrate was immersed into a 4mM $Zr(SO_4)_2$ * 4 H_2O dispersion in 0.4 N HCl for 3, 12, 48, or 96 hours at 50°C. The films were annealed in Ar at different temperatures up to 600ºC for 2 hours. The structure of as-grown and annealed films was studied by means of transmission electron microscopy (TEM), EELS and EDX. Electron diffraction and high-resolution images show that as-grown films are amorphous or short-range ordered. EDX confirms the presence of sulfur in the films. Annealing at temperatures below 525ºC does not change the structure of the film, but its thickness decreases. Voids or cracks as a result of shrinking were not observed. Annealing at temperatures above 550°C causes crystallization of the films to tetragonal ZrO_2. In films annealed at 600ºC the tetragonal phase and a small amount of monoclinic phase of ZrO_2 were found to coexist. Films annealed at 550-600°C consist of grains from 10 to 50 nm in size, and, according to EDX spectra, still contain sulfur. A carbon signal from the organic monolayer between substrate surface and zirconia film was visible for all samples. Crystallization of as-grown non-annealed films was also observed under electron beam irradiation with a current density of 0.5 A/cm^2 even at liquid helium temperature.