TEM and EELS Characterisation of ZrO_2 Thin Films Obtained by Self-Assembled Monolayer-Mediated Deposition.

V.V. Roddatis, D.S. Su, E. Beckmann, F.C. Jentoft, A. Fischer, J. Kröhnert and R. Schlögl.

Fritz-Haber-Institut der Max-Planck-Gesellschaft, Abteilung Anorganische Chemie, Faradayweg 4-6, D-14195, Berlin, Germany.

Zirconia coatings are of great importance because of their physical properties and their use in numerous applications [1-3]. This work presents the results of high-resolution transmission electron microscopy (HRTEM) as well as electron energy loss spectroscopy (EELS) investigations on the structure of thin ZrO_2-based films obtained by self-assembled monolayer (SAM) mediated deposition from aqueous dispersion on a Si (100) substrate. The aqueous deposition medium was prepared by dissolving $Zr(SO_4)_2$ * 4 H_2O in 0.4 N HCl to give a Zr concentration of 4 mmol/L; this solution was heated to 323 K. Films grown on Si substrate were obtained by immersing SAM-functionalized Si-wafers in solutions for 3, 12, 48 or 96 hours. The specimens were rinsed with distilled water after removal from the deposition medium. HRTEM investigations were performed using a Phillips CM20FEG SOPHIE electron microscop [4] equipped with helium-cooled superconducting objective lense and a CM200 FEG electron microscop equipped with Gatan imaging energy-filter GIF100. The microscopes were operated at 160kV and 200kV, respectively.

HRTEM of films after 3h of growth revealed a thin dark band along the surface of the Si substrate. This indicates the appearance of the first monolayers of the zirconia film. The thickness of film increases proportionally to the growth time. As grown films did not contain crystalline grains and have light rounded areas (Figs. 1a). Fast Fourier transform (FFT) analysis (Fig. 1b) shows the presence of short-range ordered structure. The SiO_x layer and self-assembled monolayer was observed between the Si surface and the zirconia film in all samples. During electron beam irradiation the crystallization of the films took place. For instance, after 1 minute irradiation with current density of 0.5A/cm^2 at 4.2K the small crystallites were found in the film. After 20minutes the film was completely crystallized (Figs. 2a). Grains are 15-20nm in size. Using Si lattice fringes as a reference, FFT analysis confirmed that these grains can be attributed to the tetragonal phase of ZrO_2 (Fig. 2b). In some grains twins were observed. It can be seen that film thickness decreases by 6-10% after crystallization (compare Fig. 1a and Fig. 2a). This may indicate that the growth of zirconia film in the solution occurred only through precipitation. No rearrangement of precipitating clusters at this time took place. Without cooling the samples in electron microscope, this beam induced crystallization process proceeds much more quickly (duration less than 1min). Probably, electron beam irradiation causes the diffusion of Zr atoms along the illuminated surface of the film. A local heating gives rise to the formation of small ZrO_2 grains and their following growth.

The Spectra of oxygen *K*-edge of one sample (48h) taken at the very beginning of the illumination and after 20 min irradiation are displayed in Fig. 1c and Fig. 2c. The spectral features of Fig. 2c are identical with those from a bulk tetragonal ZrO_2 sample. No noticeable loss of oxygen during the electron irradiation could be observed. Since the whole shape of the edges in Fig. 1c and 2c is similar, we may conclude that Zr atoms in the as grown films have the same coordination with oxygen as in tetragonal ZrO_2. The fine difference in both spectra can be due to the loss of the long-rang order in the as grown films mentioned above.

References:

[1]. M. Shane and M.L. Mecartney, J. Mater. Sci. 25, 1537 (1990).
[2]. M. Atik, J. Zarzycki, and C. R'Kha, J. Mater. Sci. Lett. 13, 266 (1994).
[3]. R. Di Maggio, L. Fedrizzi, S. Rossi, and P. Scardi, Thin Solid Films 286, 127 (1996).
[4]. F. Zemlin, E. Beckmann, K.D. van der Mast, Ultramicroscopy 63: (3-4), 227 (1996).

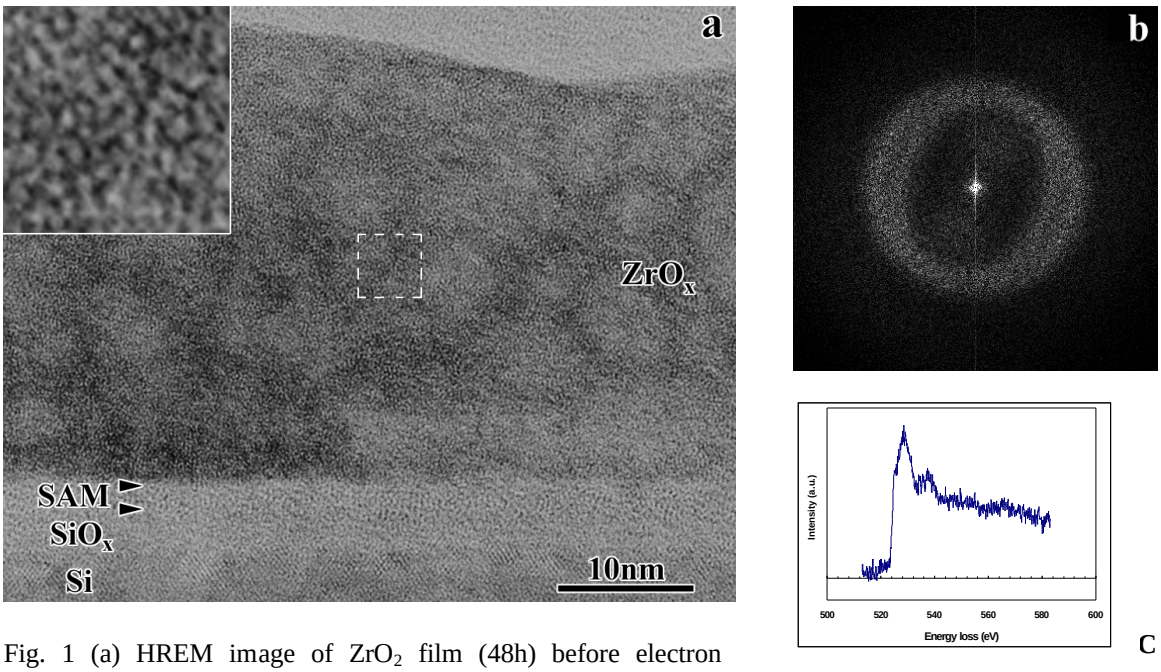

Fig. 1 (a) HREM image of ZrO_2 film (48h) before electron irradiation, an enlarged part is shown in inset; (b) FFT image; (c) Corresponding EELS spectra.

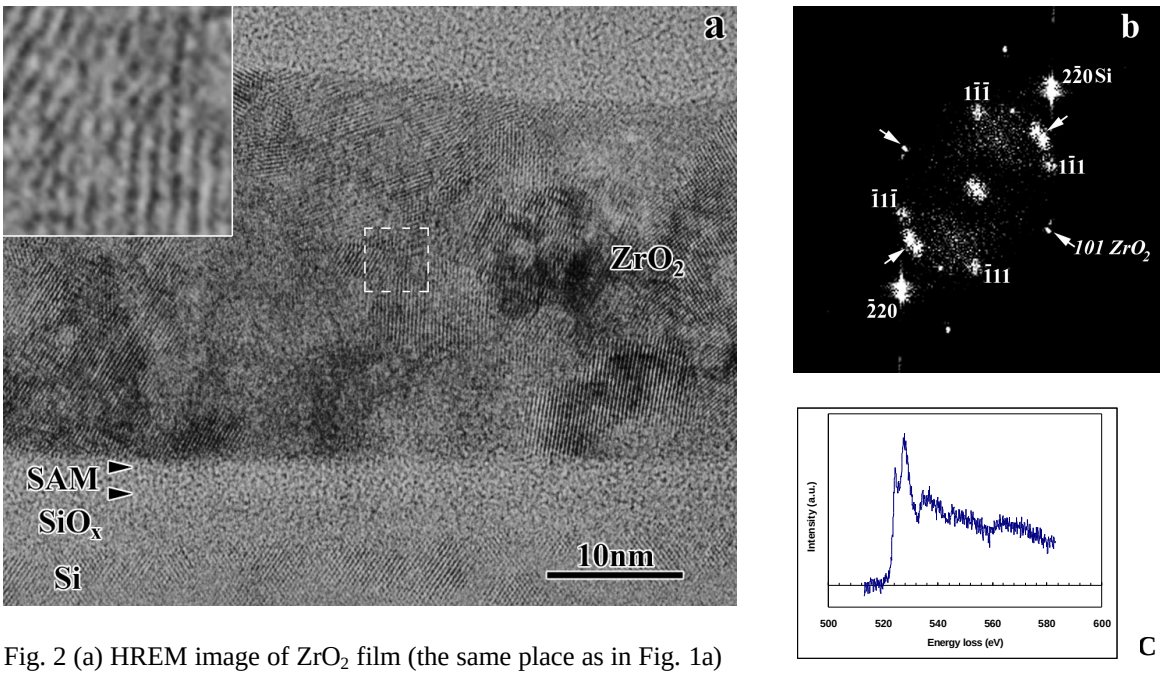

Fig. 2 (a) HREM image of ZrO_2 film (the same place as in Fig. 1a) after 20 min of electron irradiation, an enlarged part is shown in inset; (b) FFT image; (c) Corresponding EELS spectra.