The Structure of Thin Zirconia Films Obtained by Self-Assembled Monolayer Mediated Deposition: TEM and HREM study.

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-Introduction

Sulfated zirconia is a promising catalyst for low temperature alkane isomerization [1]. Despite numerous efforts [2], the active sites have not yet been identified and the mechanism of alkane activation on sulfated zirconia remains unknown. Product distributions suggest catalysis by acid sites but results from acidity characterization fail to explain the extraordinary activity. In order to facilitate the characterization of surface sites we are developping a model system in the form of a Si-supported thin film of sulfated zirconia [3]. The structure of as grown and annealed films was studied by means of transmission electron microscopy (TEM).

-Experimental

The zirconia films were prepared through wet-chemical deposition with subsequent annealing. The substrate, a Si(100) wafer, was first functionalized with a self-assembled monolayer (SAM). 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 50ºC. The SAM-functionalized Si-wafers were immersed into the deposition solution for 3, 12, 48, or 96 hours. The films were annealed at temperatures ranging from 100°C to 600ºC for 2 hours. TEM investigations were performed using a Phillips CM200 FEG electron microscope, operated at 200 kV and equipped with a DX-4 detector for energy dispersive X-ray spectroscopy.

-Summary of results

Electron diffraction and high-resolution images show that the as-grown films are amorphous or short-range ordered (Fig. 1a and Fig. 3a). 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 the crystallization of films in tetragonal ZrO_2 (Fig. 1b and 1c). In films annealed at 600ºC, the tetragonal phase and a small amount of monoclinic phase of ZrO_2 were found to coexist (Fig. 2). Annealed films consist of grains from 10 to 50 nm in size (Fig. 3). The sulfur signal was still visible in EDX spectra obtained from films annealed at 600ºC.

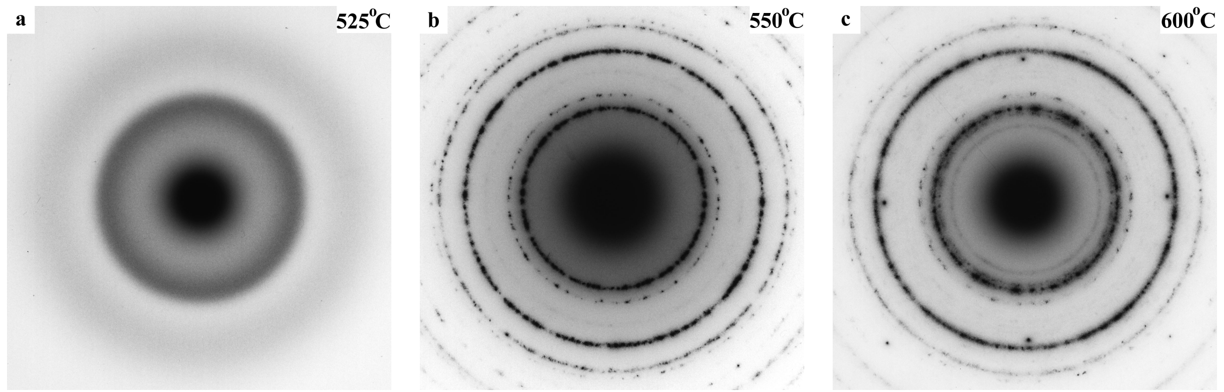


Fig.1. Diffraction patterns obtained from zirconia films annealed at 525ºC (a), 550ºC (b) and 600ºC (c)

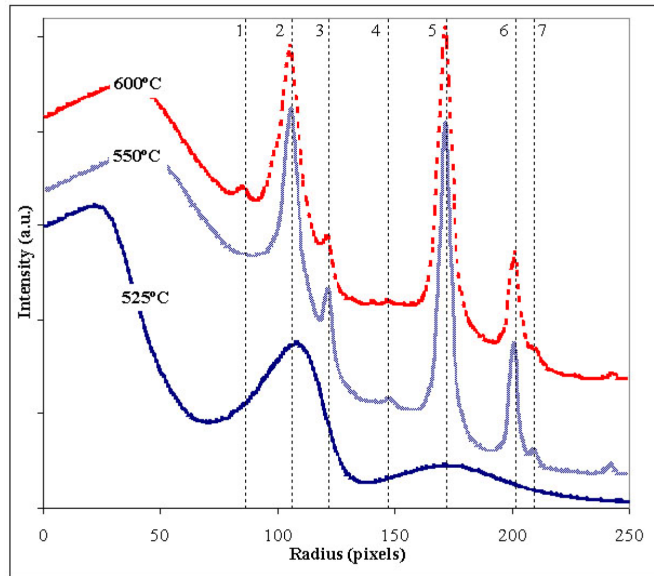
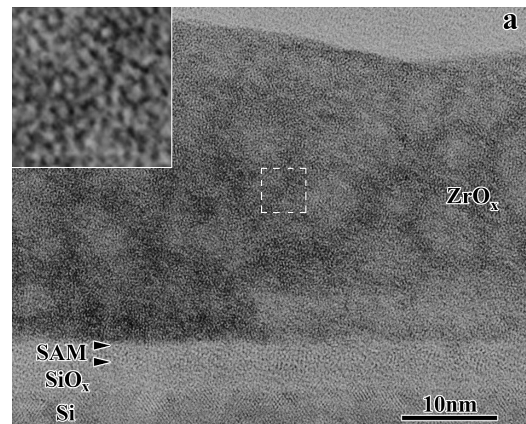


Fig. 2. Radial profiles of diffraction patterns shown in Fig.1a, b, c. Peaks marked with 1 to 7 are: 1. (011)/(110) Monoclinic; 2. (11-1)/(111) Monoclinic +(101) Tetragonal; 3. (002)/(110) Tetragonal + (020)/(020)/(200) Monoclinic; 4. (102) Tetragonal; 5. (112) Tetragonal + (220) Monoclinic; 6. (121) Tetragonal; 7.(202 Tetragonal.)



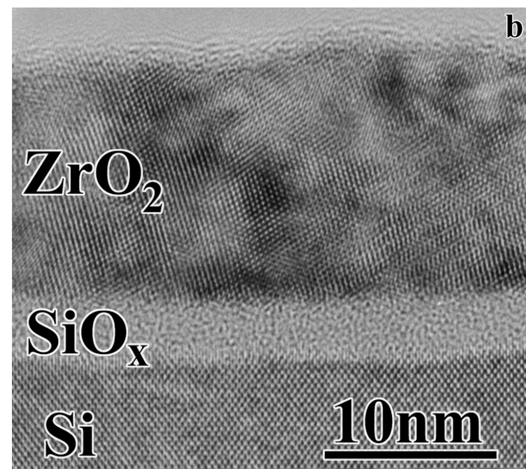


Fig.3 (a) HREM image of as grown ZrO_2 film (48h); (b) HREM image of ZrO_2 film annealed at 550ºC.

References

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