

Nanocrystalline Thin Films as a Model System for Sulfated Zirconia

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Abstract

We are presenting a model system for sulfated zirconia - a material interesting for the catalysis of light alkane isomerization - in the form of a silicon-supported nanocrystalline thin film. The goal is to obtain a conducting, non-porous material which allows the successful application of surface science techniques. The paper describes the optimization of the wet-chemical preparation method of such films, and characterization data are shown to demonstrate that these films are comparable to sulfated zirconia powders.

1. INTRODUCTION

Discovery of the extraordinary activity of sulfated zirconia for *n*-butane isomerization below 373K [1] has led to numerous efforts to investigate and correlate structure, acidity, and reactivity of this material. Although a large data set has been obtained from powdered sulfated zirconia, no consistent picture has evolved that satisfactorily describes acidity and reactivity [2]. In a new approach to better characterize sulfated zirconia we have developed a model system which consists of a nanocrystalline zirconia film supported on silicon. A preparation procedure for the deposition of various oxide films on various substrates

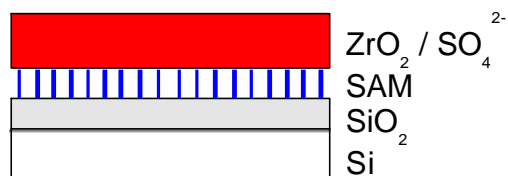


Figure 1. Schematic representation of layered model system structure.

from aqueous solution has been described in the literature [3]. A key element in this preparation is the use of a self-assembled monolayer (SAM), an ordered array of long chain surfactant molecules which are anchored to the oxidized surface of e.g. a silicon wafer. The polar

terminating groups of the monolayer are believed to play an essential role in attaching the film to the substrate. The layer structure is shown schematically in Fig. 1. Film thickness depended on deposition time, e.g. 25 nm after 4 h, and 39 nm after 24 h [3]. Calcination at 773K resulted predominantly in the tetragonal phase of zirconia [3]. For simplicity, we refer to these films as "zirconia films", although they contain additional species.

2. EXPERIMENTAL SECTION

2.1. Thin Film Preparation

Substrate preparation: Pieces 1-3 cm² of single-crystal (100) silicon wafers (CZ, 750 μm thick, p-type, polished on both sides) were cleaned sequentially with chloroform, acetone, and ethanol; and then were oxidized for 25 min with a 30:70 mixture of 30% H₂O₂ and conc. H₂SO₄ ('piranha'-solution) at 353K. The SAM was formed by immersing the wafer in a solution of 50 μl ethanethioic acid S-[16-(trichlorosilyl)hexadecyl]ester in 5 ml bicyclohexyl for 5 h under Ar atmosphere (glove bag). The desired hydrophilic sulfonic acid terminating group was introduced through oxidation of the hydrophobic thioacetate group by immersion into an oversaturated solution of KHSO₅*KHSO₄*K₂SO₄ for 5-17 hours. After this oxidative treatment the wafers were rinsed with distilled water and immediately transferred into the deposition medium.

Deposition of zirconia films: The deposition medium was a 4 mmol solution of zirconium (IV) sulfate tetrahydrate (97%, Alfa, Karlsruhe, Germany) in 0.4 N hydrochloric acid. Glass vials with the wafer and 50 ml of deposition solution were placed into a bath which was then heated to the desired temperature. Depositions were performed at two different temperatures: (i) at 343K, with deposition times from 4 to 17 h. Under these conditions, a precipitate was formed in the liquid phase after approx. 30 min. The wafers were either just rinsed with distilled water after removal from the deposition medium or they were washed by wiping the surface with lint-free tissues and distilled water. (ii) at 323K, with deposition times up to 48 h. The deposition medium remained clear for 24 h under these conditions. The specimens were only rinsed but not wiped. All samples were blown dry with Ar under ambient conditions.

Thermal treatment: Annealing was performed in stagnant air or in a flow of Ar (125 ml/min). Samples were heated at a rate of 5K/min to 773K and held at 773K for 2 h.

2.2. Characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) were performed with a Hitachi S-4000-FEG / EDAX DX4 using 5 kV acceleration voltage and secondary electron mode. Atomic force microscopy (AFM) images were taken in contact mode (Si_3N_4 tip) with a Burleigh Instruments ARIS 3300 using a small range head ARIS 3005 with a horizontal resolution of 1.0 nm and a vertical resolution of 10 pm.

X-ray and ultraviolet photoelectron spectroscopy (XPS and UPS) and ion scattering spectroscopy (ISS) were performed with a modified Leybold ESCA 100 in the FAT mode; with the following instrument settings: XPS: MgK α excitation (1253.6 eV) at 12kV/14 mA, pass energy 48 eV; UPS: He I (21.22 eV) or He II (40.82 eV) excitation, pass energy 6 eV; ISS: 1 keV He $^+$, pass energy 192 eV. Dried films were introduced into the UHV system. Thermal treatment was performed in a separate preparation chamber (base pressure $1 \cdot 10^{-8}$ mbar) adjacent to the analysis chamber (base pressure $1 \cdot 10^{-10}$ mbar) and specimens were transferred back and forth without exposure to air. The position in the analysis chamber can be well reproduced, allowing good comparison of absolute intensities within different treatment steps of a single specimen. Samples were heated in 1.013 bar of 20% O_2 in N_2 to 773K at 20K/s, held at 773K for 1 h, and cooled before evacuation.

3. RESULTS

3.1. Substrate

The surfaces of cleaned or oxidized Si-wafers appeared smooth and homogeneous in SEM and AFM images. Techniques probing the chemical rather than the morphological properties of the surface, such as streaming potential measurements [4], suggested some scattering in the isoelectric points and the hydrophilicity among different sets of wafers. SAM-coated oxidized Si-wafers

before oxidation of the terminating thioacetate group to a sulfonic acid were hydrophobic (no wetting with water) and appeared homogeneous (SEM). The oxidation of the thioacetate to the sulfonic acid group was identified as a critical step itself and may also reveal deficiencies in previous steps. Wafers with sulfonic acid terminated SAMs were characterized by an inhomogeneous appearing surface (SEM) – caused either by contaminants or by reactions other than just oxidation of the terminating group which was sometimes incomplete (C, S oxidation states, XPS). Zirconia film deposition was always possible but the quality, i.e. continuity and adherence of the zirconia films was susceptible to changes in the substrate preparation. With otherwise identical preparation conditions, an additional cleansing [5] of the Si-wafers in $\text{NH}_3/\text{H}_2\text{O}_2$ and then $\text{HCl}/\text{H}_2\text{O}_2$ (343K, 20 min each) allowed the deposition of zirconia films whose XP-spectra showed significantly less Si (sum of Si(+IV) and Si(0)), indicating fewer defects or a thicker film.

3.2. Zirconia Films from Deposition at 343K

Freshly deposited films: A SEM image of a typical fresh film after rinsing is shown in Fig. 2. The surface is characterized by the following features: (i) mainly smooth and homogeneous sections, with EDX (detection depth ca. 0.35 μm) analysis giving Zr, O, S, C, and Si, (ii) spherically

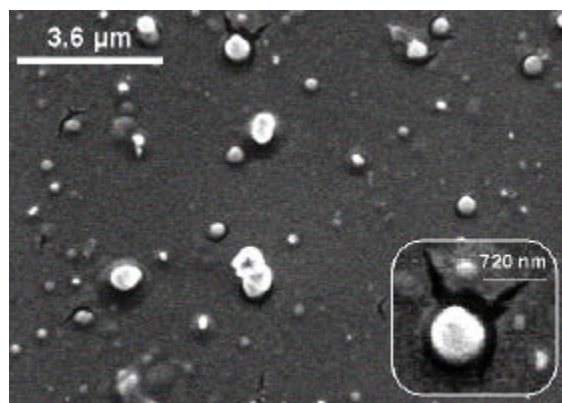


Figure 2. SEM image of a zirconia film, deposited in 4 h at 343K from 4 mmol $\text{Zr}(\text{SO}_4)_2$ in 0.4 N HCl; rinsed and dried.

shaped particles (EDX: Zr, O, S) of 200 nm size and agglomerates thereof adsorbed on the film surface or embedded into the film, and (iii) cracks of 0.5-1 μm length and 100 nm width. The deposited particles were often associated with the cracks (see inset). The surface of washed films, Fig. 3, exhibited very few, small deposited particles and numerous 0.5 – 1 μm sized circular defects [6,7]. On a scratch-marked specimen the same area could be investigated before and after washing and "holes" were found exactly in the locations where particles had been attached previously, suggesting that the film had been removed along with the particles. The roughness, R_{rms} , was about 3.5 nm in areas without holes or adsorbed particles.

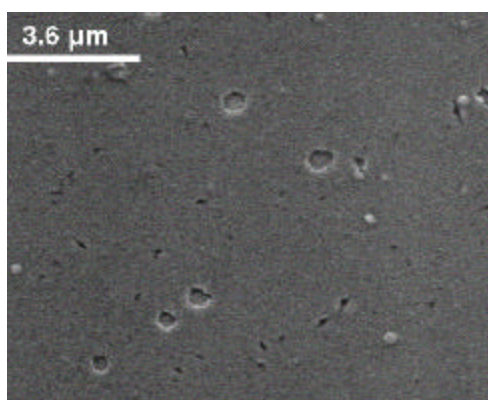


Figure 3. SEM image of a zirconia film, deposited in 4 h at 343K from 4 mmol $Zr(SO_4)_2$ in 0.4 N HCl; washed and dried.

Thermal treatment: Thermal treatment in air increased the number of cracks considerably while treatment in Ar did not change the number of cracks significantly. The films were always smoother after thermal treatment, with roughnesses (AFM) $R_{rms} \approx 2.4$ nm (air) and $R_{rms} = 1.3 - 1.9$ nm (Ar).

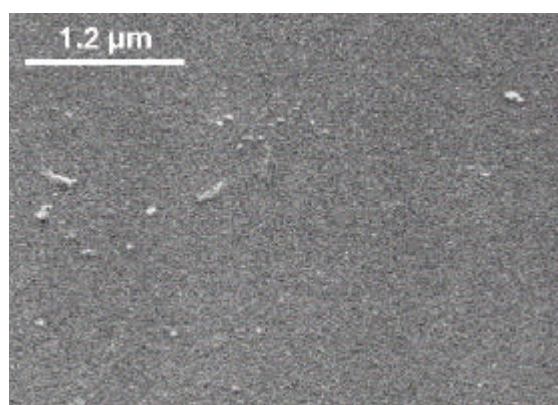


Figure 4. SEM image of a zirconia film deposited in 24 h at 323K from a 4 mmol $Zr(SO_4)_2$ in 0.4 N HCl; rinsed, dried, and calcined at 773K in air.

Deposition medium: Most of the films' defects could be associated with the presence of precipitate particles in the deposition medium. The particle growth kinetics in the deposition medium were investigated with analytical ultracentrifugation and dynamic light scattering and the rate of formation of particles with a hydrodynamic radius $r > 5$ nm was found to increase with increasing temperature, increasing zirconium concentration, and decreasing HCl-concentration [8]. At 323K, a 4 mmol $Zr(SO_4)_2$ in 0.4 N HCl solution remained clear to the eye for 24 h. Ultracentrifugation experiments indicated the presence of structures of about 1.5 nm in diameter; with the same size distribution profile at 6, 12, and 24 h.

3.3. Zirconia Films from Deposition at 323K

Film deposition: Although conditions at 323K do not favor nucleation in the liquid phase, a film is still formed on the substrate. XPS experiments showed an increasing

zirconium signal with deposition times of from 15 min to 24 h. Depositions at 323K yielded films more suitable for our purposes, i.e. free of adsorbed precipitate particles and holes, and mainly crack-free. The film surfaces were fairly smooth (AFM: $R_{rms} = 1.3$ nm). According to cross-section analysis with transmission electron microscopy (TEM) [9], the films were about 11 nm thick with 5 nm zirconia crystals after a 24 h deposition. Diffraction patterns were consistent with the presence of the tetragonal phase but not always unambiguous.

Thermal treatment: The films did not crack during thermal treatment at 773K, neither in Ar nor in air (Fig. 4). Films deposited at 323K are thinner than films deposited at 343K (≈ 25 nm [3]), and thus may be less stressed. After thermal treatment, the zirconia crystals were 5-6 nm, and R_{rms} was ≈ 0.6 nm.

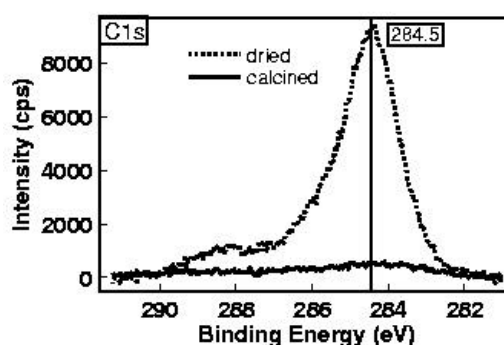


Figure 5. C1s signal of a zirconia film from 24 h deposition at 323K: dried (dotted line); calcined at 773K (solid line).

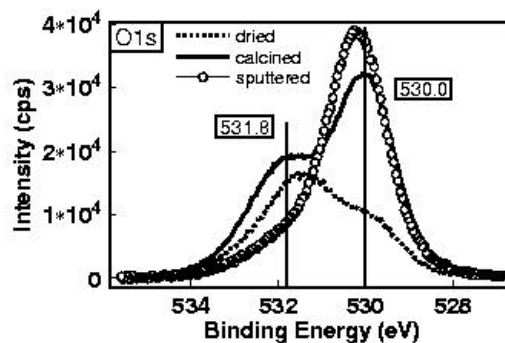


Figure 6. O 1s of a zirconia film from 24 h deposition at 323K: dried (dotted line); calcined at 773K (solid line); after He^+ sputtering (line + circles).

XPS, UPS, and ISS measurements: XP spectra of fresh films showed signals of Zr, O, S, C, often Si, and sometimes of impurities (typically N). Signals of the Si substrate were not always detectable, suggesting either a contiguous zirconia film with a thickness in/just beyond the range of the electron escape depth or a thicker film with very few flaws. The maximum of the Si 2p ($2p_{3/2} + 2p_{1/2}$) signal was detected at 99.7 eV, consistent with Si(100), and 103.4 eV, consistent with oxidized Si. Signals arising from the elements in the zirconia film were slightly shifted towards higher binding energy due to charging of the film; the shift was about 2.0 eV (dried) or 1.7 eV (calcined films) which was much less than the shift observed for sulfated

zirconia powders (almost 7 eV). Binding energies of the shifted signals were corrected using $\text{Zr } 3d_{5/2} = 182.2$ eV of ZrO_2 [10] as internal reference. Using this calibration, the main C1s signal of fresh samples was located at 284.5 eV. Calcination removed most of the carbon from the surface (Fig. 5); a concomitant increase in the intensity of Zr, O and S signals was observed. The O1s signal of the fresh film can be distinguished into at least two peaks, i.e. at about 531.5 eV and 530.0 eV (Fig. 6).

The lower binding energy species is assigned to the O^{2-} of ZrO_2 , consistent with observations on powders [11]. Heating in air reduced the fraction of high binding energy oxygen and this peak was also slightly shifted to even higher binding energy. After sputtering the sample with 1 keV He^+ (fluence: $\approx 3 \cdot 10^{16} \text{ He}^+/\text{cm}^2$), this oxygen species had almost disappeared.

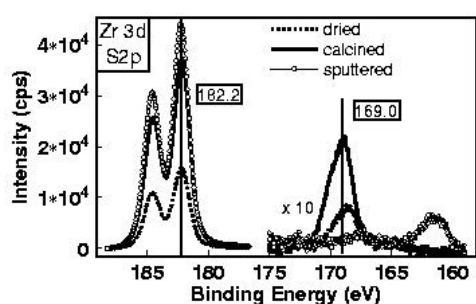


Figure 7. Zr 3d and S 2p signals (after X-ray satellite subtraction) of a zirconia film from 24 h deposition at 323K: dried (dotted line); calcined at 773K (solid line); after He^+ sputtering (line + circles).

The maximum of the S 2p ($2p_{3/2} + 2p_{1/2}$) signal was detected at a binding energy of 168.4 eV before and 169.0 eV after calcination, consistent with the presence of S(+VI). After sputtering the signal was shifted to 161.2 eV (Fig. 7, with Zr3d), consistent with S(-II) [10]. The reduction of sulfur along with the disappearance of one oxygen species strongly suggests that this particular O 1s peak at 531.8 eV belongs to the sulfate species, as has been proposed for sulfated zirconia powders [11]. ISS data showed peaks originating from O, S and Zr. In UP spectra, typically two features could be distinguished, however, their position was difficult to determine due to charging effects.

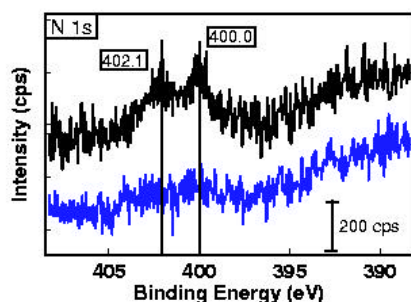


Figure 8. N 1s signal of a zirconia film from 24 h deposition at 323K; dried and calcined at 773 K (bottom); after exposure to 10000 L NH_3 (top).

XP-spectra after adsorption of ammonia: XP spectra taken of the N 1s signal after exposure to NH_3 (10000 L) at room temperature showed two peaks at 402.1 eV and 400.0 eV (Fig. 8). The higher binding energy species was significantly weakened upon heating to 473K in vacuum while the lower binding energy species remained largely unaffected.

4. DISCUSSION & SUMMARY

A consistent picture evolves when combining data from the different microscopic techniques with the information from XPS: Contiguous films with the chemical composition Zr, O, and S can be deposited on the conducting silicon substrate. Film thickness can be controlled by varying the deposition time, e.g. about 11 nm after 24 h deposition at 323K in a 4 mmol $\text{Zr}(\text{SO}_4)_2$ solution in 0.4 N HCl. The films contain zirconia crystals (≈ 5 nm), presumably the tetragonal phase. The films do not crack during calcination, and their surface is very smooth. Sulfate species are present, suggesting that the films resemble "sulfated zirconia". Ammonia can be adsorbed, and similar to what has been observed previously for the adsorption of pyridine on sulfated zirconia [11], the N 1s signal reveals two species. The two peaks are tentatively assigned to the adsorption of ammonia on two different acidic sites.

We are able to prepare sulfate-containing nanocrystalline zirconia films which appear to be a promising model system for sulfated zirconia catalysts. UP spectra which contain information on the valence levels of the catalyst could be collected. We expect the films to be suitable to acquire interpretable temperature-programmed desorption (TPD) data to further characterize acid sites.

REFERENCES

1. M. Hino, K. Arata, J. Chem. Soc. Chem. Comm., (1980) 851.
2. X. Song, A. Sayari, Catal. Rev. - Sci. Eng., 38 (1996) 329.
3. M. Agarwal, M.R. De Guire, A.H. Heuer, J. Am. Ceram. Soc., 80 (1997) 2967.
4. A. Bismarck, J. Springer, A. Fischer, F.C. Jentoft, R. Schlögl, unpublished results.
5. W. Kern, J. Electrochem. Soc., 137 (1990) 1887.
6. A. Fischer, F.C. Jentoft, G. Weinberg, R. Schlögl, T.P. Niesen, J. Bill, F. Aldinger, M.R. De Guire, M. Rühle, J. Mater. Res., accepted.
7. T.P. Niesen, M.R. De Guire, A. Fischer, F.C. Jentoft, J. Bill, R. Schlögl, F. Aldinger, M. Rühle, J. Mater. Res., accepted.
8. H. Schnablegger, H. Cölfen, M. Antonietti, A. Fischer, F.C. Jentoft, R. Schlögl, in preparation.
9. A.D. Polli, T. Wagner, M. Rühle, A. Fischer, F.C. Jentoft, R. Schlögl, unpublished results.
10. J.F. Moulder, W.F. Stickle, P.E. Sobol, K.D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer Physical Electronics Division, 1992.
11. M. Johansson, K. Klier, Topics in Catal., 4 (1997) 99.