



Fabrication of ultrathin films of Ta₂O₅ by a sol–gel method

M.J. Wolf^{a,*}, S. Roitsch^b, J. Mayer^b, A. Nijmeijer^a, H.J.M. Bouwmeester^a

^a Inorganic Membranes, University of Twente, P.O. Box 217, 7500 AE Enschede, The Netherlands

^b Ernst-Ruska-Centre for Microscopy and Spectroscopy with Electrons, Research Centre Jülich, 52425 Jülich, Germany

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ABSTRACT

Tantalum oxide (Ta₂O₅) is widely known for its high chemical, thermal and hydrothermal stability. In this study, a sol–gel method has been developed to produce homogenous, i.e., defect and pin-hole free, ultrathin films of Ta₂O₅. These were coated onto a porous substrate by means of dip-coating, and subsequently fired at 400 °C. Despite their small thickness of only 30–40 nm, the films showed very low gas permeation.

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1. Introduction

The chemical inertness of tantalum pentoxide (Ta₂O₅) [1], combined with several distinct physical properties, enables its potential use in, for example, corrosion protection coatings for biomedical implants [2], surgical instruments [3] and evanescent optical sensors with high surface sensitivity [4]. Ta₂O₅ is also used as catalyst for the photolysis of water to yield hydrogen [5]. Furthermore, it exhibits a high refractive index, and therefore holds promise for use as anti-reflective coating for lenses and solar panels [6]. As a piezoelectric material, it can be applied in surface acoustic wave devices such as band-pass filters [7], and various types of mechanical sensors [8]. Because of its high dielectric constant and compatibility with silicon, thin films of Ta₂O₅ are used in transistors [9,10], ion-sensors [11], and storage capacitors for dynamic random-access memory [12–14]. Recently, thin sheets of tantala have been applied as dielectric spacers between metal electrodes for fabricating negative refractive index materials, also known as metamaterials [15,16]. All of these promises have resulted in an increased interest in the growth of Ta₂O₅-films.

In this study, a sol–gel method has been developed for the fabrication of continuous thin films of Ta₂O₅. Though the initial aim of the work was for use as membranes in size selective gas separation, during testing the thin films were found to be not suitable for the intended application.

2. Experimental part

Tantalum(V)ethoxide (Ta(OC₂H₅)₅, 99% pure, ABCR) was dissolved together with diethanolamine (DEA, 99.5% pure, Fluka) in absolute ethanol (dried, Emsure®, Merck) under dry nitrogen to prevent premature hydrolysis. After adding deionized water, the solution was stirred for 30 min at room temperature. The solution had a final molar ratio of Ta(OC₂H₅)₅:ethanol:H₂O:DEA of 1:210:22:4. If not applied immediately after synthesis the sol was stored at –28 °C.

Dried tantala powders were obtained by drying the sols in Petri dishes overnight. Calcined powders were obtained via thermal treatment for 3 h in air at temperatures between 300 and 700 °C using constant heating/cooling rates of 1.0 °C min^{–1}. Tantala thin films were prepared by dip-coating (substrate speed 10 mm s^{–1}, dip-time 5 s) the sol onto homemade α-alumina supported mesoporous γ-alumina supports [17] under cleanroom class 1000 and flow cupboard class 100 conditions. The thin films were then thermally treated at 400 °C in air atmosphere using constant heating/cooling rates of 1.0 °C min^{–1}. The coating step was repeated once, to end with two coated layers of tantala.

Particle size distributions of the tantala sols were measured by dynamic light scattering (DLS), using a Zetasizer NanoZS (Malvern Instruments). Measurements were performed using 1.0–1.5 ml of the sol in a disposable sizing cuvette (Type DTS0012, Malvern Instruments). Dried powders were analyzed using combined thermogravimetry–differential scanning calorimetry (TG–DSC). Measurements were carried out on an STA 449 F3 Jupiter® (Netzsch) instrument in synthetic air (50 ml min^{–1}) with nitrogen as protective gas (20 ml min^{–1}). Brunauer–Emmett–Teller (BET) surface area measurements of calcined tantala powders were made by nitrogen sorption, at 77 K (TriStar 3000,

* Corresponding author at: Research Centre Jülich, IEK-1, 52425 Jülich, Germany. Tel.: +49 2461 612877; fax: +49 2461 619120.

E-mail address: m.wolf@fz-juelich.de (M.J. Wolf).

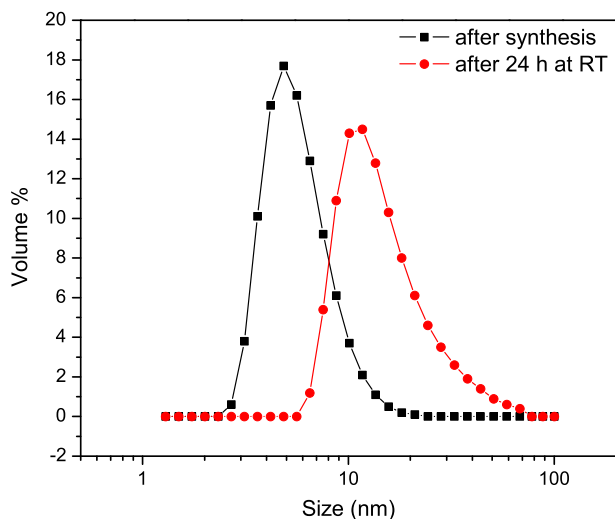


Fig. 1. Particle size distributions of the tantalum sol after synthesis and after 24 h of storage at room temperature.

Micromeritics). Before the measurements, the powders were degassed at 200 °C under vacuum for 2.5–24 h. X-ray powder diffraction data were recorded at room temperature using a Philips Panalytical PW 1830 diffractometer.

Single gas permeation measurements were conducted in the dead-end mode, using H₂, CO₂, N₂, CH₄ and SF₆ as test gases. The membranes were sealed in a home-made stainless steel module with Viton® O-rings with the top layer exposed to the feed side. The pressure difference across the coated thin film was varied between 180 and 300 kPa. The permeate side of the membrane was kept at atmospheric pressure. The gas flow was measured using a thermal mass flow meter (EL-FLOW®, Bronckhorst High-Tech Nederland BV). Before the measurements, the membranes were dried at 200 °C for at least 5 h under flowing helium in the module.

The microstructure of the powders and membranes was investigated by means of transmission electron microscopy (TEM), using a Tecnai G² F20 (FEI) instrument operated at an acceleration voltage of 200 kV. The TEM specimens were produced by means of a focused-ion beam process (Helios Nanolab 400s, FEI) with subsequent argon-ion milling.

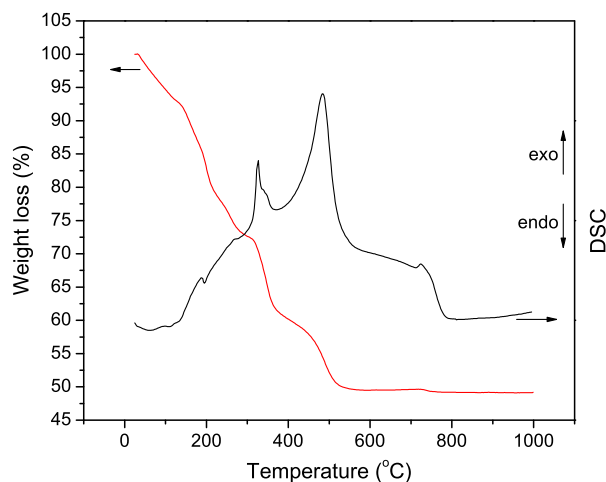


Fig. 2. TGA/DSC data of tantalum powder recorded under flowing synthetic air at a heating rate of 5 °C min⁻¹.

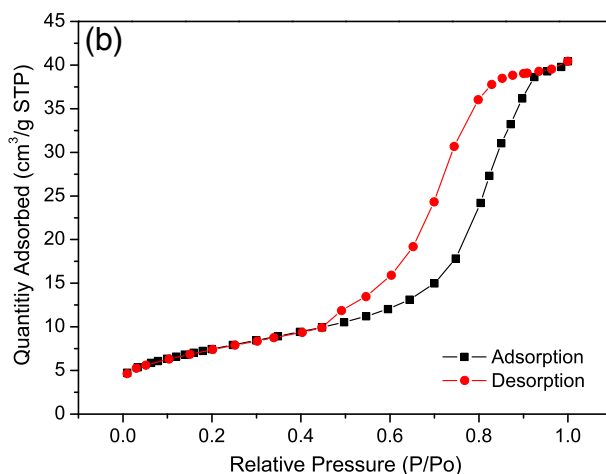
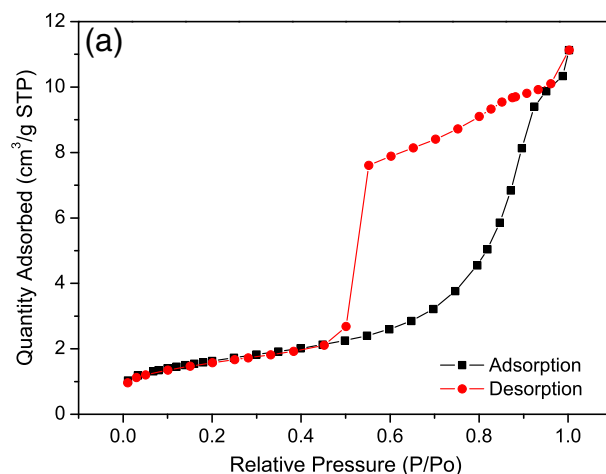


Fig. 3. Nitrogen sorption isotherms of tantalum powder calcined for 3 h at (a) 600 °C and (b) 700 °C.

3. Results and discussion

In general, sols can be stabilized via two routes. Firstly, the particles in the sols can be stabilized electrostatically by preparation via an acid–base-catalyzed sol–gel route. Secondly, the sol particles can be stabilized by the use of chelating/complexing agents to avoid fast condensation and rapid particle growth [18]. In this study, the latter method was employed, utilizing diethanolamine (DEA) as sol-stabilizer. Fig. 1 shows

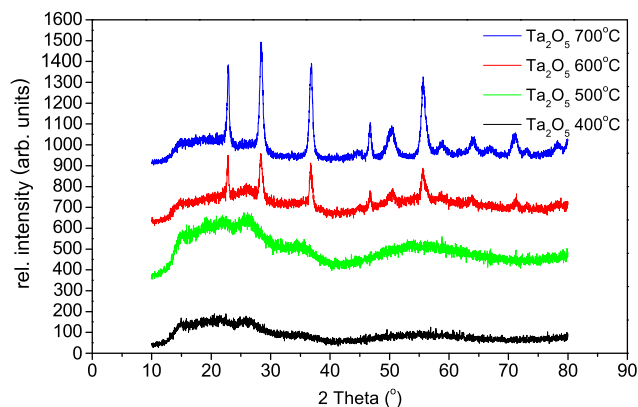


Fig. 4. X-Ray diffraction patterns of tantalum powders calcined for 3 h at different temperatures.

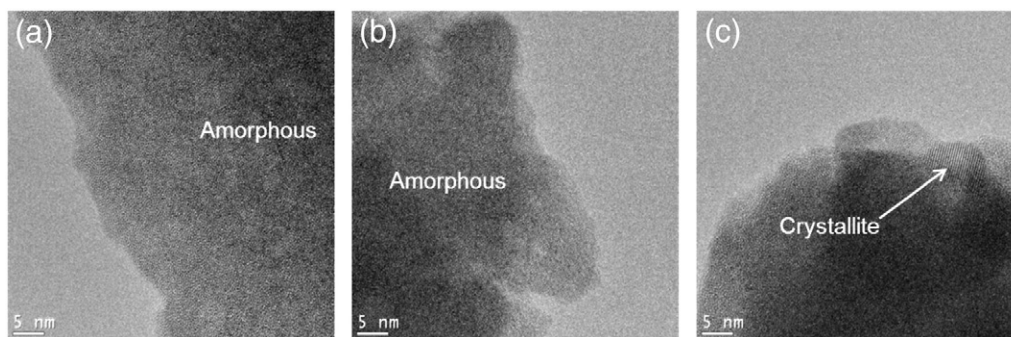


Fig. 5. TEM pictures of tantalum powders calcined for 3 h at (a) 300, (b) 400 and (c) 500 °C. Amorphous and crystalline regions are indicated.

particle size distributions of the tantalum sol. Immediately after synthesis the size of the sol particles is in the range of 3–21 nm, with an average size of 8 nm. Particle growth was experienced to be very fast. As seen from Fig. 1, within 24 h at room temperature the particles grew to a size range of 6–70 nm.

Shown in Fig. 2 are data of thermal analysis of a dried tantalum gel. Several weight loss steps are observed. A continuous weight loss is observed up to 280 °C, which can be assigned to the evaporation of residual water and ethanol. This is followed by distinct weight losses between 310 and 380 °C and between 450 and 520 °C, which are accompanied by pronounced exothermic effects at approximately ~340 and ~480 °C. The peak at ~340 °C may be ascribed to evaporation and/or decomposition of DEA. The peak at ~480 °C is very broad, which suggests a slow kinetic process. A possible explanation may be the crystallization of amorphous Ta₂O₅ into the low-temperature orthorhombic structure of β-Ta₂O₅ [19]. Ling et al. [20] observed crystallization of tantalum from its amorphous form to be a nucleation and growth process and, hence, to be rather slow. Tantalum is highly acidic, especially in its hydrated form [21]. Another contribution to the weight loss at ~480 °C may arise from the evaporation of strongly bound water. The small exothermic peak at 725 °C may be linked to either crystallization or another structural rearrangement of the material. The small weight loss at that temperature may be due to associated oxygen release.

No nitrogen sorption was found for the powders obtained from calcination at 300–500 °C, which suggests that the material is either dense or microporous with pores smaller than the kinetic diameter of nitrogen. Samples calcined at 600 and 700 °C showed a BET surface area of 9 m² g⁻¹ and 27 m² g⁻¹, respectively. The observed type II isotherms (see Fig. 3) are characteristic for mesoporous materials, and the type of hysteresis indicates the presence of bottlenecked pores [22].

Results of X-ray diffraction and TEM analysis on tantalum powders calcined at different temperatures are shown in Figs. 4 and 5, respectively. The observations from TEM show that the material after calcination at

300 and 400 °C is highly amorphous, which for the powder calcined at 400 °C is confirmed by the data from X-ray diffraction. The very broad non-Bragg reflection observed at 14–30° in the diffraction pattern of the sample calcined at 500 °C suggests that nanocrystals (<10 nm) are embedded in an amorphous matrix. This is confirmed by the corresponding TEM image in Fig. 5c. The X-ray diffraction pattern of the sample calcined at 600 °C shows clear evidence of crystalline Ta₂O₅. Diffraction peaks at 2θ values of 22.9, 28.4, 36.9 and 55.7° can be assigned to orthorhombic β-Ta₂O₅ [23,24], which is the low-temperature form of Ta₂O₅.

Sol-gel deposition of thin films of tantalum on glass supports has been reported previously by several authors [25–28]. In the cited studies, the thickness ranged from 75 to 327 nm. In the present study, continuous thin films of Ta₂O₅ of thickness of only 30–40 nm were coated on mesoporous γ-alumina layers (supported by α-alumina). These showed good adhesion to the γ-alumina interlayers. Despite the small thickness of the films (see Fig. 6), a hydrogen permeance was measured, at 200 °C, of only 5 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹. This value is extremely low, slightly above the detection limit of the apparatus used (~1 × 10⁻¹⁰ mol m⁻² s⁻¹ Pa⁻¹), and more than 3 orders of magnitude lower than found for microporous silica membranes [29]. The permeances of the gases with larger kinetic diameters, i.e., CO₂, N₂, CH₄ and SF₆, were found to be at, or below, the detection limit, which confirms that the films obtained in this work are defect and pin-hole free.

4. Conclusions

Continuous ultrathin films of tantalum, with a thickness of 30–40 nm, were coated on porous supported γ-alumina layers by a sol-gel method. Evaluation by permeance testing, at 200 °C, showed that the deposited thin films are defect free and demonstrate a gas permeance below the detection limit. Only for hydrogen, having the smallest kinetic diameter in the present study, the measured permeance was found to be slightly above the detection limit. The low thickness and the

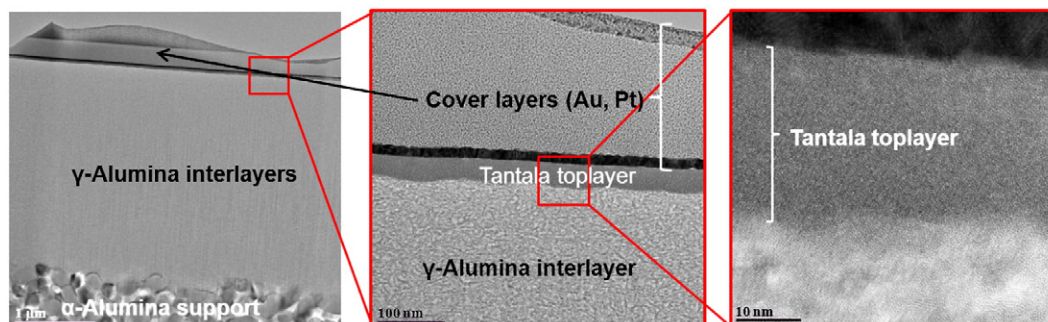


Fig. 6. TEM cross-sectional images of the tantalum thin film, calcined at 400 °C in air. Also visible are the α-alumina support and γ-alumina interlayer.

straightforward processability of the tantalum thin films to gases may open perspectives towards a number of the earlier mentioned applications.

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