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Fabrication of ultrathin films of Ta_2O_5 by a sol–gel method

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ABSTRACT

Tantalum oxide (Ta_2O_5) 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 Ta_2O_5. 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.

1. Introduction

The chemical inertness of tantalum pentoxide (Ta_2O_5) [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]. Ta_2O_5 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 Ta_2O_5 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 Ta_2O_5-films.

In this study, a sol–gel method has been developed for the fabrication of continuous thin films of Ta_2O_5. 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 ($Ta(OC_2H_5)_5$, 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 $Ta(OC_2H_5)_5$:ethanol:H_2O: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,

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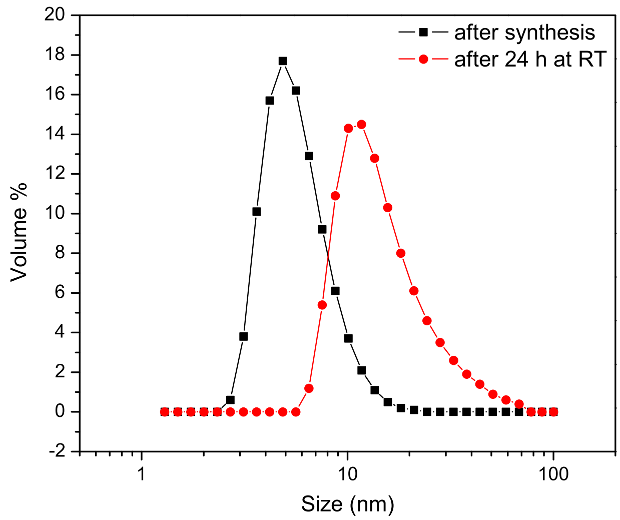

Fig. 1. Particle size distributions of the tantala sol after synthesis and after 24 h of storage at room temperature.

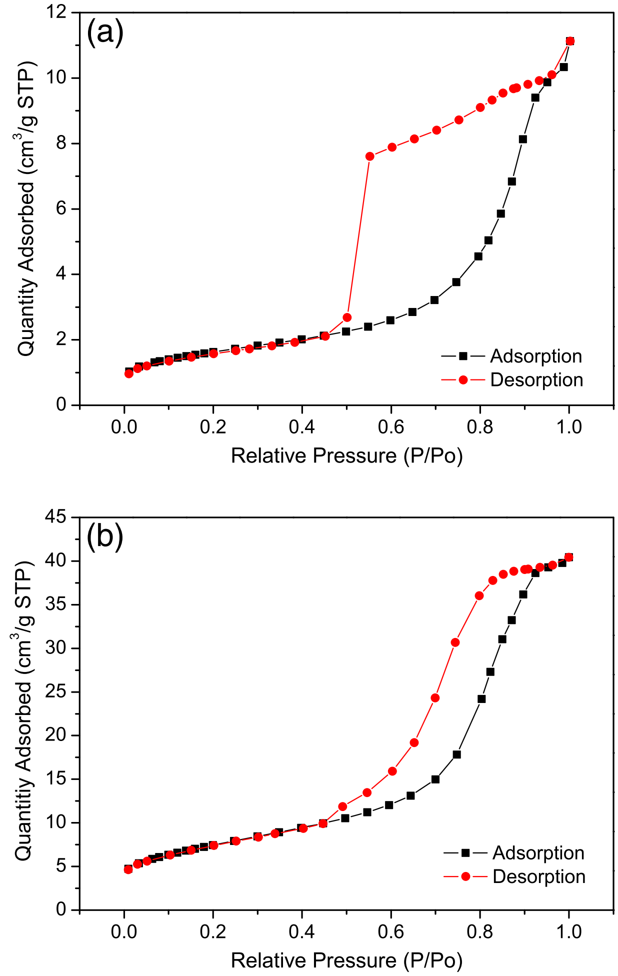

Fig. 3. Nitrogen sorption isotherms of tantala powder calcined for 3 h at (a) 600 °C and (b) 700 °C.

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 H_2, CO_2, N_2, CH_4 and SF_6 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 G^2 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.

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

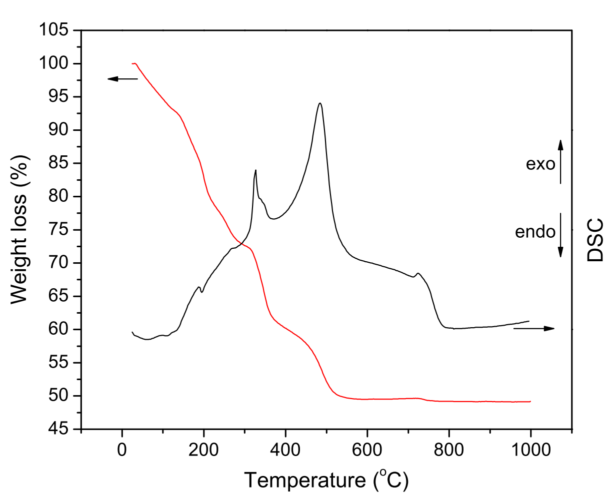

Fig. 2. TGA/DSC data of tantala powder recorded under flowing synthetic air at a heating rate of 5 °C min^{-1}.

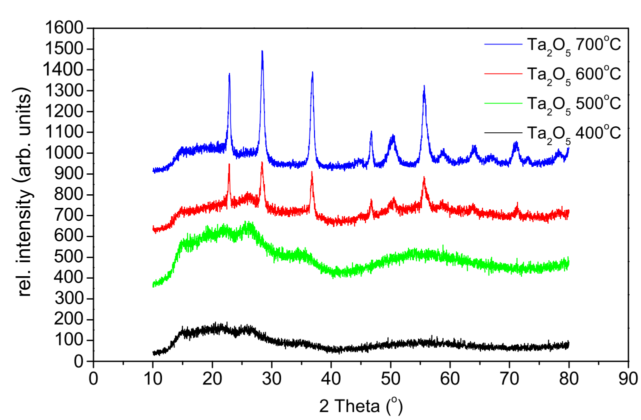

Fig. 4. X-Ray diffraction patterns of tantala powders calcined for 3 h at different temperatures.