PROPERTIES OF Y_2O_3 THIN FILMS APPLICABLE IN MICRO–ELECTROCHEMICAL CELLS

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This work deals with selected mechanical and electrical properties of thin films prepared by planar RF diode sputtering for application in micro-electrochemical biosensors. The properties of Y_2O_3 thin films prepared by RF sputtering are comparable with published data of bulk and Y_2O_3 films. They are suitable for an insulation in the vertically arranged micro-electrochemical cell.

K e y w o r d s: sputtering, micro-electrochemical sensor, interdigitated array of electrodes, insulating yttrium oxide thin film

1 INTRODUCTION

Microelectrodes play a very important role in advanced electrochemical microsensors. Thin films are able to create "the bridge" between macrosystems and microsystems down to molecular systems, *ie*, the research and development of advanced microelectrochemical sensors cannot endure without the utilization of thin film technology. Thin film microelectrodes serve as a base array of electrochemical cells (working/auxiliary Pt, Au, C, reference Ag/AgCl electrodes in compact, microdisk or interdigitated array forms). Their use offers advantages such as diffusion-controlled currents, low charging currents, and reduced solution resistance effects.

The closely spaced interdigitated array (IDA) of electrodes (the width of microelectrode/gap is in μm/subμ-m range) has found a very favourable application in voltametric sensors. When both reduction and oxidation potential is applied to IDA pairs, the effect of redox recycling and high collection efficiency are observed. That specific electrochemical behaviour of IDA revealed a sufficient overlapping of the diffusion layers of the adjacent electrodes causing high current amplification, *ie*, a significant lowering of the detection limit of the sensor [1].

The thin-film cell consisted of vertically arranged IDA electrodes with a continuous Pt-film basis and an insulation layer, *eg*, Y_2O_3 in the middle separating the upper Pt - or Au - IDA electrodes, see Fig. 1. In this arrangement there are IDA with fingers of lengths of 400 μm, finger/gap widths of 10/10 μm, 5/5 μm, 5/3 μm. The gap between the bottom and upper microelectrodes is de-

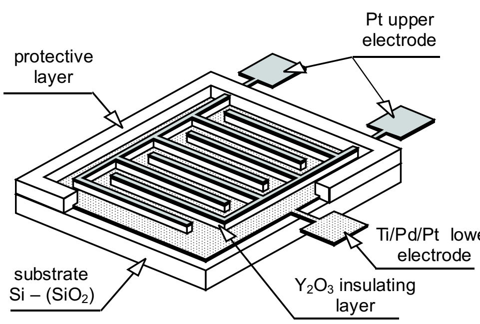

Fig. 1. The thin-film cell consisting of vertically arranged IDA electrodes

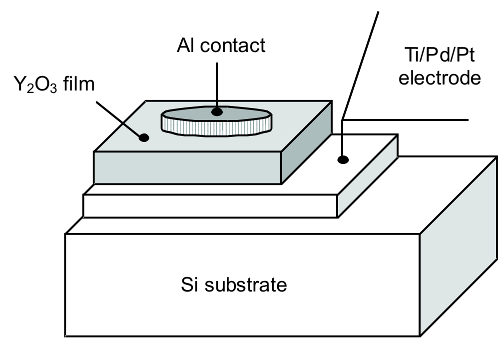

Fig. 2. Arrangement of thin film structures for electrical measurements

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termined by the thickness of the Y_2O_3 insulating layer (from 0.2 to 1 μm).

Therefore the separating insulating layer should satisfy several important requirements: high electric resistivity and strength, low leakage current and dielectric losses, good mechanical properties such as high strength and stability, low intrinsic stress and plastic deformation. Bulk Y_2O_3 has high values of electrical resistivity, dielectric permittivity, and electric strength, it also has low dielectric losses and good transparency in a wide spectral range with little light diffusion. Its mechanical strength, radiation resistance and high temperature must also be mentioned. Due to these properties, Y_2O_3 is a prospective material for antireflecting and protective coating, interference mirrors and for manufacturing passive components and dielectric layers in multilevel integrated circuits [2]. Vapour deposited and sputtered Y_2O_3 films exhibit desired properties: resistivity $10^{11} - 10^{12}\,\Omega$m, electric intensity $10^8 - 10^9$ V/m, relative dielectric permittivity 11 - 15, loss tangent $\delta = 0.01 - 0.03$, melting point 2430 K, Young modulus 150 GPa, Poisson ratio 0.298, thermal expansion coefficient 8×10^{-6}/K, [2,5,6,7,9]. The aim of this work was optimization of the sputtering technology to get Y_2O_3 films with suitable electrical and mechanical properties.

2 EXPERIMENTAL PART

A planar RF sputtering unit 2400/8L (Perkin-Elmer) was used for the preparation of all the films on Si substrates. The targets of 20 cm in diameter were utilized: metallic Ti (99.9%), Pd (99.9%), Pt (99.9%) and ceramic Y_2O_3 (99.9%). The thickness of the adhesion Ti layer was 50 nm, the barrier Pd layer 50 nm and of the Pt layer 170 nm. The sputtering chamber was pumped down to 2×10^{-5} Pa before admission of the sputtering gas Ar (99.999%), and a total gas pressure of 1.3 Pa was kept constant. Parameters of sputtering of Y_2O_3 films: RF power 800 W, mean induced target DC voltage -900 V and deposition rate 9.5 nm/min, the substrate holder was kept at room temperature. Thicknesses were measured by a TALYSTEP. Mechanical properties of Y_2O_3 were investigated on Si substrates with bottom Ti/Pt layers (Si-Ti/Pt-Y_2O_3) and electrical measurements were performed on a multilayered structure Ti/Pt-Y_2O_3-Al (with bottom Pt contact and top Al disc contact with 4 mm diameter, thickness of Y_2O_3 thin films: 100 to 1000 nm). Mechanical stresses were measured by thin film stress measurement system TENCOR FLX-2908. The Young modulus of Y_2O_3 thin films was measured using the FISHERSCOPE H-100 TESTER. Electrical resistivity and strength were evaluated from $I - V$ characteristics, dielectric permittivity was estimated by capacitance measurements (HP 4282A PRECISION LRC METER). X-ray investigations of the crystal structure of the oxide films were performed using a diffractometer SIEMENS D 5000 with the Bragg-Brentano arrangement working with monochromatic radiation Cu-K_α.

3 RESULTS AND DISCUSSION

3.1 Mechanical properties of Y_2O_3 thin films

The mechanical behaviour of thin films is quite different from that of bulk material and is very much governed by the microstructure, impurity and imperfection content which in turn governs the residual stress in the film. As the film gets thicker, the residual stress level decreases and the mechanical properties are very similar to those of thick films or bulk condensates [3].

Thin films deposited by sputtering have usually compressive stresses. This phenomenon is explained by atomic peening [4] in which high energy particles are reflected from the target and bombard the growing films. The intrinsic stress was affected by deposition conditions such as the working pressure.

The total stress δ_{total} of a film consists of two terms [5]

$$\delta_{\text{total}} = \delta_{\text{intrinsic}} + \delta_{\text{thermal}} \tag{1}$$

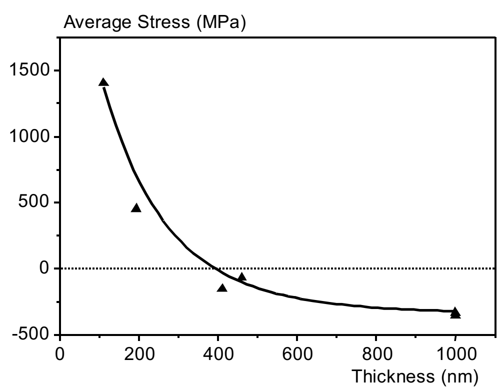

Fig. 3. Dependence of stress on thickness of Y_2O_3 film

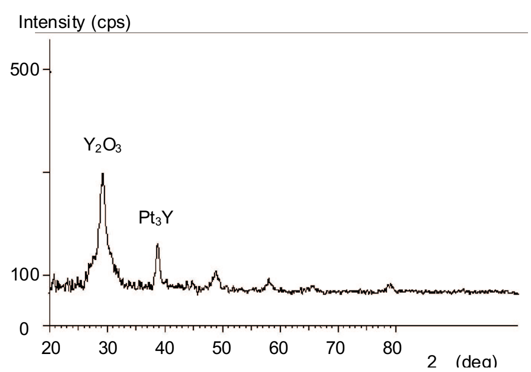

Fig. 4. X-ray investigation of the crystal structure of the samples

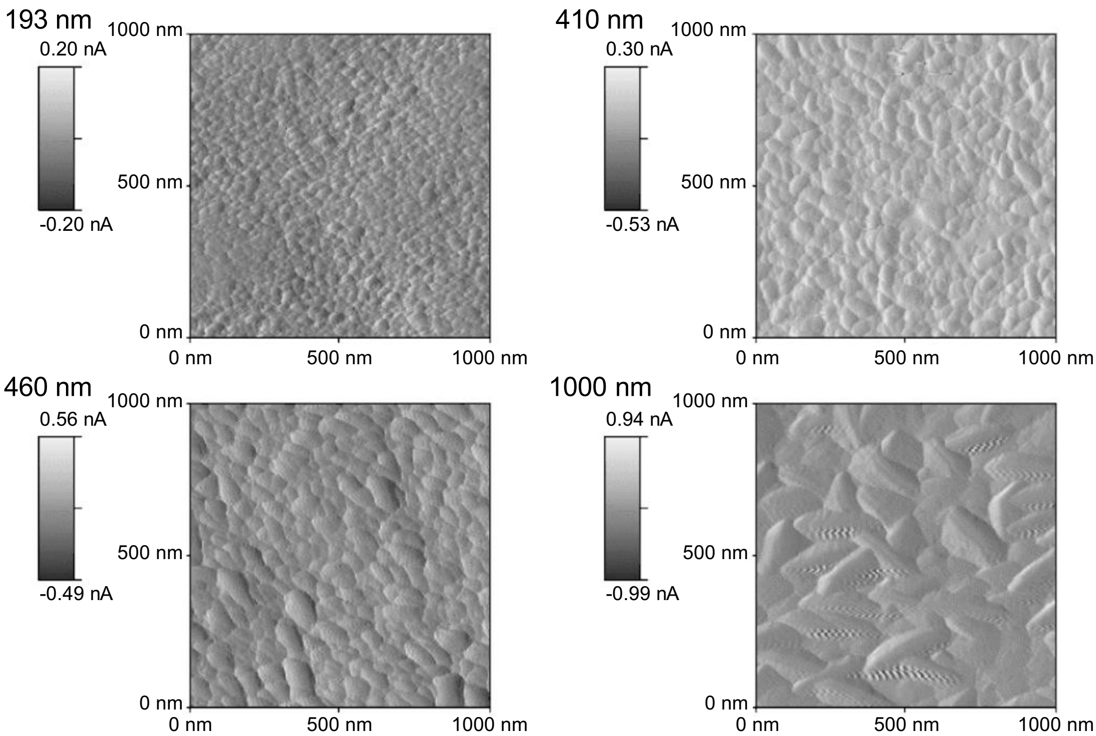

Fig. 5. Surface of Y_2O_3 thin film measured by AFM

were $\delta_{\text{intrinsic}}$ is the intrinsic stress and δ_{thermal} is the thermal stress. The measured total stress in the thin film is calculated from

$$\delta_{\text{total}} = \frac{Rh^2}{(1-\nu)6Rt} \tag{2}$$

where $E/(1-\nu)$ is the biaxial elastic modulus of the substrate, h is the substrate thickness and t is the film thickness. The effective radius is calculated from

$$\frac{1}{R} = \frac{1}{R_1} + \frac{1}{R_2} \tag{3}$$

where R_1 is the initial substrate radius of curvature (Si-Ti/Pd/Pt) and R_2 the new radius after Y_2O_3 film is deposition. The thermal stress is expressed by

$$\delta_{\text{thermal}} = \frac{E_f(\alpha_s - \alpha_f)\Delta T}{1-\nu_f} \tag{4}$$

were E_f is the Young modulus for the film, α_s and α_f are thermal expansion coefficients of the substrate and the film, respectively, ΔT is the difference between the deposition temperature and the temperature at which the stress has been measured and ν_f is the Poisson ratio of the film. The Young modulus characterizes the elastic properties of thin films. For the determination of the Young modulus of the films a method of measuring the hardness under load was used following the procedure described in [6]. The Young modulus of Y_2O_3 thin films was measured using the device FISHERSCOPE H-100. The measured values of the Young moduli are in agreement with published values [7]. The measured Young moduli were in the range of 150 to 170 GPa. The calculated thermal stress ($T_{\text{dep}} = 300\,°\text{C}$, $T_{\text{measure}} = 20\,°\text{C}$, $\nu_f = 0.298$, $\alpha_f = 8 \times 10^{-6}/\,°\text{C}$, $\alpha_s = 9 \times 10^{-6}/\,°\text{C}$ [8]) is approximately 60 MPa, which is tensile.

Table 1. The average stress of thin film structures

Si-Ti/Pd/Pt	Y_2O_3		
Measured Stress (MPa)	R (m)	Thickness (nm)	Calculated Stress (MPa)
384	34.726	110	618.20
402	61.704	193	374.94
403	−85.524	410	−126.14
405	−168.400	460	−63.74
374	−16.060	1000	−334.16
399	−15.040	1000	−256.80

Experimental and calculated data are given in Tab. 1. Figure 3 shows a plot of the average stress of Y_2O_3 wafers versus their thickness. The transition from tensile to compressive stresses takes place in Y_2O_3 films with an increase of their thickness. The absolute values of intrinsic stresses are lower (by $\approx$ 0.3 GPa) in comparison with published data [5]. These results can be explained by the

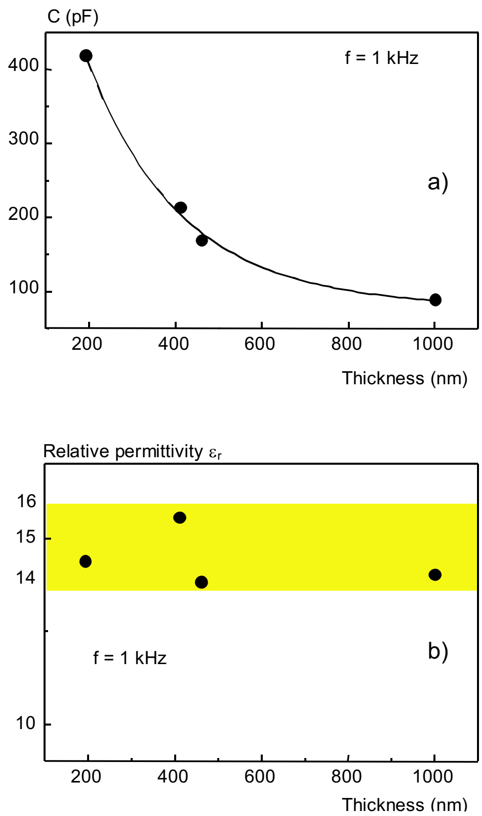

Fig. 6. Dependence of a) capacitance and b)relative dielectric permittivity on thickness of Y_2O_3 thin films

relaxation of intrinsic stress during film growth due to self-heating of the substrate caused by RF diode sputtering.

Surface morphology of Y_2O_3 thin films was observed using the Atomic Force Microscope (AFM). The AFM can image nonconducting as well as conducting surfaces. The AFM works recording the interatomic forces between its tip and surface atoms as the tip is scanned over the surfaces of the sample [4]. Y_2O_3 thin films have a polycrystalline structure (Fig. 4) and the size of grains on the whole surface is uniform and rises up with increasing of Y_2O_3 thin film thickness (Fig. 5).

3.2 Electrical properties of Y_2O_3 thin film

As we described before, electrical measurements were made using a multilayered structure Ti/Pd/Pt-Y_2O_3-Al. The relative dielectric permittivity was determined from capacitance measurements

$$\varepsilon_r = \frac{C}{\varepsilon_0}\frac{d}{S} \tag{5}$$

were C is the measured capacitance of the multilayered structure, ε_0 is the permittivity of vacuum, S is the area of the Al contact and d is the thickness of Y_2O_3 film. The initial value of capacitance (419 pF) decreased exponentially with increasing Y_2O_3 thickness (Fig. 6a). The calculated relative permittivity, $\varepsilon_r \approx 15$, was independent of the thickness (Fig. 6b) and its value is in good agreement with published data [9]. We can see from the dependence of the capacitance versus frequency (Fig. 7) that the capacitance of Y_2O_3 thin films is relatively independent of frequency up to 100 kHz. The capacitance is also independent of the applied voltage in a wide range (±20V). The independence of ε_r of thickness, frequency and applied voltage demonstrates that relatively thin Y_2O_3 films are very useful for dielectric separating layers.

Electrical cross-resistivity of Y_2O_3 thin films was estimated by $I - V$ measurements and its values are in the order of $10^{11}\Omega$m. The examined Y_2O_3 thin films have shown a low leakage current, max. 0.4 nA at 100 V, which corresponds to electrical strength of 2.5×10^8 V/m. The value of the breakdown voltage (destruction of Y_2O_3 structure) was up to 100 V in all samples.

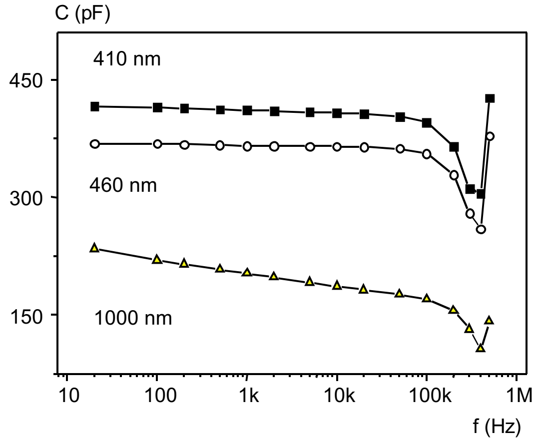

Fig. 7. Dependence of Ti/Pd/Pt-Y_2O_3-Al thin film structures capacity of frequency at different Y_2O_3 thickness

4 CONCLUSION

The presented results confirmed a possible application of RF sputtered Y_2O_3 thin films as an insulating layer in micro-electrochemical cells. Y_2O_3 thin films are polycrystalline with a homogenous surface which consists of Y_2O_3 grains. The grain sizes are different and comparable with corresponding thicknesses. In Tab. 2 the selected properties of Y_2O_3 thin films prepared by RF sputtering with published data of Y_2O_3 films are compared. Further investigations of these thin films open the way for their prospective applications in different domains of microsystem technology.

Table 2. The properties of Y_2O_3 thin film prepared by RF sputtering compared with published data [2,6,7,9]

	Published Data	Our Results
Resistivity	$10^{11} - 10^{12}\Omega$m	$\approx 10^{11}\Omega$m
Electrical intensity	$10^8 - 10^9$V/m	$\approx 10^8$V/m
Relative permittivity	$11 - 15$	≈ 15
Young modulus	150GPa	$\approx$ 150GPa
Intrinsic stress	$\approx$ 8GPa	$\approx$ 0.3GPa

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