PREPARATION, COMPOSITIONAL-, STRUCTURAL- AND FUNCTIONAL CHARACTERISATION OF OXIDE SEMICONDUCTORS AND INSULATOR OXIDES

PhD Theses

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1. Introduction

In the age of mass production based on automation and miniaturisation, as a consequence of the increasing market competition, the industry thrives to increase the lifetime and quality of the produced devices. From this point of view the fine structure and composition of functional materials, achieved by a series of well-designed technological steps is of special importance. In many cases the structural and compositional changes in the material, caused by some process steps or by the operation itself, are responsible for the stability and reliability of the device. That's why the investigation of the correlations between the structure, composition and functional properties is very important from the application side, however, this research has also a scientific interest. Earlier, the surface oxide of metals was regarded mostly as harmful or at best passive component in technological materials. Nowadays, however, the passivating behaviour gains increasing emphasis in the design of devices and, ever more often, oxides become functional materials. From both points of view, the stoichiometry of the oxides is of special importance.

My work focused on the surface analytical investigation of a functional (sensor), a passive (dielectrics) and a passivating oxide layer. The present Thesis summarises the new scientific results of my research on the characteristics and functional behaviour of *(i)* semiconducting SnO_2 layers planned for use as chemical gas sensors, *(ii)* insulating oxides grown on niobium for solid electrolyte capacitors, as well as *(iii)* thermal oxides formed on Ti-Al intermetallics. To study the changes in the bulk oxides and at the metal/oxide interfaces, I have prepared suitable model samples but I also investigated samples taken from the real technological process.

2. Objectives

The objective of this Thesis is – on one hand – to shed light on the mechanism and consequences of the changes in the metal-oxide systems used in the three technical fields mentioned in the introduction. On the other hand, I have also set as objective to improve or optimising the functional properties of the devices based on these metal/oxide systems. In the specific areas this can be formulated as follows:

- Preparation of SnO_2 thin films with pre-designed properties, using atomic layer deposition.

- Contribution to the development of niobium-based solid electrolyte capacitors with high stability and suitable electrical properties by basic research results.

- Description of the oxidation mechanism of Ti-Al intermetallics in case of low oxygen activity; improvement of the oxidation resistance of Ti-Al intermetallics of high Ti content.

3. Applied experimental methods

3.1. Techniques used for the preparation of oxide layers:

semiconducting SnO_2: atomic layer epitaxy (ALE) (often called atomic layer deposition,)
insulating Nb_2O_5: anodic oxidation
thermal oxides on the surface of Ti-Al intermetallics: *in situ* oxidation in the vacuum chamber of the surface analytical equipment.

3.2. Methods applied for analytic and structural characterisation, measurements of functional properties

I determined the layer-thickness by UV-VIS spectroscopy and RBS in case of planar samples, and by electron microscopy analysis of cleavage surfaces for porous bodies. The time required to sputter through the layers during depth profiling has also been used. I have established the composition (percentage of the main components) and the chemical state of the components by X-ray photoelectron spectroscopy (XPS). I determined the small amount impurities by secondary ion mass spectrometry (SIMS), and for a better comparability I gave – in the same oxides - the SIMS ion yield ratios related to the metals. To investigate the lateral homogeneity of the layers, I have recorded the electron-excited Auger electron spectrum (AES) of the surface at several points, and gave AES intensity ratios related to the metal. For depth profiling of the oxide layers, I have used XPS and AES depth analysis with Ar^+-sputtering, as well as SIMS depth profiles.

I have established the phase composition, crystallinity and texture of the layers by X-ray diffraction (XRD). I used scanning electron microscopy (SEM) as well as atomic force microscopy to investigate the morphology of the oxides.

The electrical resistance of the semiconducting oxide layers was measured by a four-point probe. The specific surface of porous bodies was measured by Kr-absorption. The bulk composition of the starting materials was measured by inductively-coupled-plasma optical emission spectroscopy (ICP-OES).

I have carried out the XPS and AES, as well as part of the SIMS investigations at the Department of Atomic Physics of the Budapest University of Technology & Economics (BUTE). In the Laboratory of Inorganic Chemistry of the Department of Chemical Technology at the Helsinki University of Technology (HUT) I carried out the SIMS, XRD, AFM, and UV-VIS and four-point probe measurements.

Some of the measurements I would like to thank the Research Institute for Technical Physics and Materials Science (XRD, RBS) and the Chemical Research Center (specific surface determination) of the Hungarian Academy of Sciences, the Department of General and Analytical Chemistry of BUTE (bulk composition determination) and the University of Karslruhe (SEM).

4. New scientific results

4.1. Preparation of homogeneous, textured SnO_2 thin films with pre-designed characteristics by atomic layer epitaxy (ALE)

1. I have experimentally shown that by an appropriate choice of the dose of the reactants ($SnCl_4$: 0.65-3 mg/cycle, H_2O: 0.2-12 mg/cycle) and of the duration of purge (200-10000 ms), as well as by the use of additives (oxygen, ozone, *n*-hexane) in the ALE process, it is possible to prepare textured polycrystalline SnO_2 layers characterised by composition near to stoichiometry and by lateral homogeneity [1, 5, 6].

   1.a. I have established that the incorporation of resistance-diminishing chlorine impurity can be suppressed by reducing the amount of $SnCl_4$, as well as by increasing the duration of the purge.

   1.b. I have established that applying a H_2O + O_3 reactant mixture – instead of water – improves the stoichiometry of the layers, but at the expense of the texture.

   1.c. I have established that the stoichiometry of the oxide improves if the carrier gas is oxygen (instead of nitrogen). The formation of oxide in such a case is also the result of the hydrolysis of $SnCl_4$ (g).

   1.d. I have established that the texture of the layer improves by the addition of hexane, without incorporation of carbon into the layer.

4.2. The anodic oxidation of niobium, annealing of the oxide and the effect of these on the composition and electric characteristics of the oxide

2. Based on the in-depth variation of the composition of anodic oxides (SIMS), as well as on the measurement and evaluation of the leakage current values, I have established [4] that:

   2.a. The in-depth homogeneity of the composition of the oxide layers depends on the forming voltage (10-40 V). The layers formed at higher voltage have less homogeneous oxygen distribution, the oxygen content is increasing continuously toward the metal/oxide interface.

   2.b. While in the constant current phase of the oxidation predominantly the thickness of the Nb_2O_5 layer increases, in the constant voltage phase the dominant process is the improvement of the stoichiometry of the oxide (by filling the oxygen vacancies), although the oxide thickness keeps increasing too.

3. I have established [4] that upon annealing in vacuum (5×10^{-5} mbar, 390°C, 30 min.) or in synthetic air (270-320°C, 60 min.) the oxygen distribution becomes more inhomogeneous. The niobium-pentoxide layer decomposes near the metal/oxide interface and its thickness diminishes. In the vicinity of the metal/oxide interface suboxides are formed, while oxygen vacancies appear in the whole depth of the layer. Due to the oxygen formed through reduction, or incorporated from the synthetic air atmosphere, the free oxygen content of the layer increases. The effect of the annealing in air below 320°C is reversible. After reanodisation of the annealed layers the suboxides can be oxidised to nearly stoichiometric pentoxide, and the oxygen content becomes more homogeneous.

4. After investigating the effect of individual technological steps on the structure and composition, I have studied the dependence of the functional parameters of the capacitors (capacity, leakage current) on the technological parameters. Based on the results in Points 2 and 3, I have set up a model for the interpretation of the results, which can be summarised as follows [7]:

   4.a. The significant capacity decrease of the anodically oxidised Nb_2O_5 layers upon positive biasing (0-6 V) can be explained by diminishing the number of polarisation charges at the Nb/Nb-oxide interface. This decrease is caused by the oxygen ions and electrons (ionisation of the oxygen vacancies) crossing the interface under the effect of the electric field.

   4.b. Upon annealing in air, the capacity of the oxide becomes practically independent on the bias, and the leakage current strongly increases. According to Point 2, the concentration of oxygen ions and oxygen vacancies increases due to the decomposition of the niobium pentoxide layer, and that leads to an increased oxygen ion transport. Due to biasing the number of polarisation charges decreases; however, this is partially compensated by the intensified oxygen ion transport towards the Nb/Nb_2O_5 interface. The ionised oxygen vacancies formed under the effect of electric field are partially neutralised and the oxygen ions passing through the interface - due to biasing - are partially recovered.

   4.c. After reanodisation of the annealed oxide layers the capacity again strongly depends on the bias, but the leakage current diminishes below the value measured after the original anodic oxidation. Corresponding to the effect of reanodisation (as described in Point 2) the intensity of oxygen transport diminishes, and the variation of the capacity with the bias corresponds to what has been described in Point 4.a.

4.3. Investigation of the oxidation mechanism of Ti-Al intermetallics at low oxygen activity

5. I have proven by XPS experiments [2], that oxidising a Ti-Al system with more than 50 at% Ti content between 5×10^{-10}-5×10^{-5} mbar oxygen partial pressure up to 900°C the formation of TiO is preferred (and the participation of Al in the oxidation is inhibited) due to the increased activity of Ti. This leads to the oxidation induced surface segregation of Ti. With increasing oxygen supply higher oxides, corresponding to higher oxidation states of Ti: Ti_2O_3 and TiO_2 also appear and TiO_2 becomes dominant. My measurements represent the extension of earlier measurements to a wider temperature range (25-1000°C).

6. In contrast to earlier statements in the literature [Mencer, 1991] my experimental results show [2], that (in the investigated temperature range) the formed amorphous Al-oxide does not transform into a crystalline Al_2O_3, if the oxidation at every temperature starts from an oxide-free surface.

7. Based on the chemical shift of the Al 2p photoelectron peak and on the quantitative analysis of the surface composition I have proven [2, 3], that around 1000°C Al_2TiO_5 appears. Detection of this compound in surface oxide layers has not been reported earlier.

[Mencer, 1991] D.E. MENCER JR., T.R. HESS, T. MEBRAHTU, D.L. COCKE, D.G. NAUGLE, J. Vac. Sci. Technol. A **9** (1991) 1610

8. During oxidation below 900°C (at $p(O_2) = 5\times10^{-10}$-5×10^{-5} mbar) no passivating oxide layer is formed. I have shown, however, that the Al_2TiO_5, appearing around 1000°C, significantly hinders the in-diffusion of oxygen into the metallic phase. This result explains why the oxidation resistance of Ti-Al intermetallics increases upon high temperature annealing in low-pressure oxygen.

5. Application of the results

As mentioned in the introduction, my work was motivated by applications, and my results contribute to the development of chemical gas sensors and that of solid electrolyte capacitors: the former in collaboration with L. Niinistö (honorary professor of BUTE), the latter in the device development program of the company EPCOS in Heidenheim. The studies on the oxidation of Ti-Al intermetallics were also carried out for EPCOS but its results may become important for the application of light weight Ti-Al alloys, e.g., in aviation.

6. Own publications related to the Thesis

Papers related closely to the Thesis in international journals

1. M. Utriainen, K. Kovács, J. M. Cambell, L. Niinistö, F. Réti: *Controlled electrical conductivity in SnO_2 thin films by oxygen or hydrocarbon assisted atomic layer epitaxy*
J. Electrochem. Soc. **146**(1), 189-193 (2000).
2. K. Kovács, I. V. Perczel, V. K. Josepovits, G. Kiss, F. Réti and P. Deák: *In situ surface analytical investigation of the thermal oxidation of Ti-Al intermetallics up to 1000 °C*
Appl. Surf. Sci. **200**, 185-195 (2002)
3. K. Kovács, V. K. Josepovits, G. Kiss, H. Zillgen and P. Deák: *Passivation of TiAl intermetallics by a mixed oxide, Al_2TiO_5*
Phys. Stat. Sol. (a) **193(1)**, R1-R3 (2002)
4. K. Kovács, G. Kiss, M. Stenzel, H. Zillgen: *Anodic oxidation of niobium sheets and porous bodies and heat-treatment of the Nb/Nb-oxide system*
J. Electrochem. Soc. **150**/8, B361-B366 (2003)

Conference contributions related closely to the Thesis

5. K. Kovács, M. Utriainen, E. B. Várhegyi, L. Niinistö, F. Réti: *Modification of the properties of tin dioxide thin films grown by atomic layer epitaxy at 500 ^oC*
Proceedings of the 5th Nexuspan Workshop On Microsystem Technology, ed. V. Snitka [Technologia, Vilnius, 1998] pp.158-161.
6. K. Kovács, M. Utriainen, Cs. Dücső, E. B. Várhegyi, M. Ádám, L. Niinistö, F. Réti: *Gas sensitive SnO_2 films by atomic layer epitaxy*
Proceedings of the 6th Nexuspan Workshop on Microsystem Technology, eds. V. Székely, K. Tarnai, I. Bársony, V. Timár-Horváth [BME, Budapest, 1999] pp. 89-91.
7. M. Stenzel, H. Zillgen, K. Kovács, G. Kiss: *Bias voltage dependence of the capacitance of anodised niobium*
Proceedings of the 16th European Passive Components Conference CARTS-Europe 2002,

Other papers in the field published in refereed journals

8. G. Kiss, K. Kovács, I. V. Perczel, V. K. Josepovits, M. Fleischer, H. Meixner, F. Réti: *Impedance spectroscopic studies of the electric conduction in polycrystalline β-Ga_2O_3*
J. Electrochem. Soc. **147**(7), 2644-46 (2000).
9. G. Kiss, E. B. Várhegyi, J. Mizsei, O. H. Krafcsik, K. Kovács, G. Négyesi, B. Ostrick, H. Meixner, F. Réti: *Examination of the CO/Pt/Cu layer structure with Kelvin probe and XPS analysis*
Sensors and Actuators B **68**, 240-43 (2000).
10. Z. Pintér, Z. Sassi, S. Kornelly, Ch. Pion, I. V. Perczel, K. Kovács, R. Bene, J. C. Bureau, F. Réti: *Thermal behaviour of WO_3 and WO_3/TiO_2 gas sensor materials*
Thin Solid Films, **391**, 243-246 **(**2001).
11. G. Kiss, O. Krafcsik, K. Kovács, V. K. Josepovits, M. Fleischer, H. Meixner, P. Deák, F. Réti: *Impedance spectroscpoic and SIMS studies of β-Ga_2O_3/O_2 interaction*
Thin Solid Films **391**, 239-242 (2001)