

# **Elaboration of IVB group metal oxide structures and their possible applications**

**Valter Reedo**

Faculty of Science and Technology, Institute of Chemistry, University of Tartu,  
Estonia

Faculty of Science and Technology, Institute of Physics, University of Tartu,  
Estonia

Dissertation in organic chemistry

Dissertation is accepted for the commencement of the degree of Doctor of  
Philosophy in Chemistry on September 25, 2008, by the Council of Institute of  
Chemistry, University of Tartu

Supervisors: Dr. Ants Lõhmus (University of Tartu, Institute of Physic)  
Dr. Uno Mäeorg (University of Tartu, Institute of Chemistry)

Opponent: Dr. Chem. Donats Erts, (Institute of Chemical Physics, University of  
Latvia, Riga)

Commencement: October 31, 2008, at Ülikooli Str. 18, Tartu University Council  
Hall

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## List of original publications

- Paper I P. Kanarjov, V. Reedo, I. Oja-Acik, L. Matisen, A. Vorobjov, V. Kiisk, M. Krunk, I. Sildos, Luminescence materials based on thin metal oxide films doped with rare earth ions. *Phys. Solid State* 2008, **50**, 9, 1661 – 1663.
- Paper II S. Lange, V. Kiisk, V. Reedo, M. Kirm, J. Aarik, I. Sildos, Luminescence of RE-ions in HfO<sub>2</sub> thin films and some possible applications. *Opt. Mater.* 2006, 28, 1238-1242.
- Paper III V. Kiisk, I. Sildos, S. Lange, V. Reedo, T. Tätte, M. Kirm, J. Aarik, Photoluminescence characterization of pure and Sm<sup>3+</sup>-doped thin metal oxide films. *Appl. Surf. Sci.* 2005, **247**, 1-4, 412-417.
- Paper IV V. Reedo, S. Lange, V. Kiisk, T. Tätte, A. Lukner, I. Sildos, Influence of ambient gas on the photoluminescence of sol-gel derived TiO<sub>2</sub>:Sm<sup>3+</sup> films. *In: Optical materials and applications: (A. Rosental, ed.), Proc. SPIE 5946, 59460F (2005)*
- Paper V V. Reedo, M. Järvekülg, A. Lõhmus ja U. Mäeorg, Novel route for preparation of tubular TiO<sub>2</sub> microstructures. *Phys. Status Solidi A* 2008, **205**, 6, 1511-1514.
- Paper VI Invention: Meetod oksiidmaterjali valmistamiseks (Method for preparation of an oxide material); Owner: Tartu Ülikool and Estonian Nanotechnology Competence Centre; Authors: M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus; Priority number: P200700029; Priority date: 07.06.2007, PCT/EE2008/000016 09.06.2008

### **Author's contribution**

As seen from the list of authors of included papers there were many people involved in the research, which was because of the interdisciplinary nature of the work. During the research we had a good synergetic relationship among experts in different areas of expertise and with students. The author of this thesis performed or actively supervised all sol-gel syntheses and in many cases sample preparation for different analyses. The spectroscopic measurements of prepared samples were performed and interpreted by coauthors. The results of current thesis are return of joint effort of many co-authors and with great importance for different groups.

Paper I: Participated in sample preparation and supervision of graduate student A. Vorobjov in sol-gel synthesis. Participated in preparation of the manuscript.

Paper II: Responsible for sol-gel synthesis and sample preparation. Participated in preparation of the manuscript.

Paper III: Responsible for sol-gel synthesis, film-making and sample preparation for spectroscopic analyses. Participated in preparation of the manuscript.

Paper IV: Responsible for sol-gel synthesis, film-making and sample preparation for spectroscopic analyses.

Paper V: Responsible for sol-gel synthesis, development of theory for formation of tubular structures, supervision of graduate student M. Järvekülg. Responsible for composing final version of the manuscript.

Paper VI: Involved in development of sol-gel synthesis and supervision of M. Järvekülg. The contribution to patent is nominated to be 25%.

## **Abbreviations**

AcAc – Acetylacetone  
ALD – Atomic layer deposition  
CRT – Cathode ray tube  
CVD – Chemical vapor deposition  
EAcAc – Ethyl acetoacetate  
ICCD – intensified charge-coupled device  
IR – Infrared electromagnetic radiation  
PL – Photoluminescence  
RE – Rare earth metals (Lanthanoids)  
SEM – Scanning electron microscope  
TTIP – Titanium iso-propoxide  
UV – Ultra violet electromagnetic radiation

## Preface

Improvement of the available techniques and finding new approaches for synthesis and shaping of oxide materials in desired dimensions and application determined composition is essential in the development of many scientific and technical fields such as optics, electronics, optoelectronics, telecommunication, data storage, medicine and biology.

Oxides and oxide mixtures can generally be synthesized and shaped by employing a wide range of conventional (melt-processing of oxides at temperatures over 1000 °C, polishing, and evaporation in vacuum) and advanced techniques (CVD, ALD, various chemical methods). The main disadvantages in conventional methods are poor control over shape, size, chemical composition and functionality required for modern applications.

In the recent decade, sol-gel techniques in conjugation with materials chemistry have extensively been investigated and employed to explore new approaches in obtaining low-dimensional oxide materials with improved properties and functionality. Due to its simplicity and high flexibility, the sol-gel method exhibits huge potential for the preparation of micro- and nano-dimensional oxide structures in the form of particles, films, fibers and 3D matrices.

In current thesis the main attention is focused on elaboration of IVB group metal oxide ( $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ ) thin films by means of sol-gel process and development. In addition, group's invention of new technique for oxide material manipulation (formation of metal oxide micro-tubes) is discussed.

The thesis is divided into five chapters. The first chapter gives overview about the physical properties and technological significance of IVB group metal oxides and their preparation possibilities. The second chapter takes a brief look at sol-gel processing and development opportunities for elaboration of  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ , giving explanation to the motivations behind this work. The third chapter will give reasoned overview of used experimental techniques, materials and installations. The fourth chapter defines the aim of this study and in fifth chapter a summary of results is given.

## 1. IVB group metal oxide materials

Titanium dioxide (titania or  $\text{TiO}_2$ ), zirconium dioxide (zirconia or  $\text{ZrO}_2$ ) and hafnium dioxide (hafnia or  $\text{HfO}_2$ ) belong to the IVB group of transition metal oxides.  $\text{TiO}_2$  also occurs as a mineral in the nature [1]. Pure mineral of  $\text{ZrO}_2$  is rare in nature and most of zirconium occurs as zircon ( $\text{ZrSiO}_4$ ). Hafnium is received as by product of zirconium production from corresponding minerals.

IVB group metal oxides have received a great deal of attention due to their chemical stability, low-toxicity, and other advantageous properties. They can be applied in numerous electronic [2,3] as well as optical devices [4,5] where dielectric materials with a relatively wide band gap and/or high refractive index [6] are needed. Due to low phonon frequencies [7] the oxide matrices are expected to be suitable hosts for rare earth activators. Because of their high density, rare-earth-activated  $\text{ZrO}_2$  and  $\text{HfO}_2$  are also attractive as scintillating materials.

During the last decade, titanium, zirconium and hafnium oxides have been suggested as good promoters in catalytic reactions [8].  $\text{TiO}_2$  is also successfully used as gas sensor [9] photocatalyst [1] and as a window layer in photovoltaic solar cells [10].

### 1.1. Properties of $\text{TiO}_2$ , $\text{ZrO}_2$ and $\text{HfO}_2$

$\text{TiO}_2$  occurs in three crystalline modifications – brookite (orthorhombic), anatase (tetragonal) and rutile (tetragonal) all containing the  $\text{TiO}_6$  octahedra (Fig. 1.1).

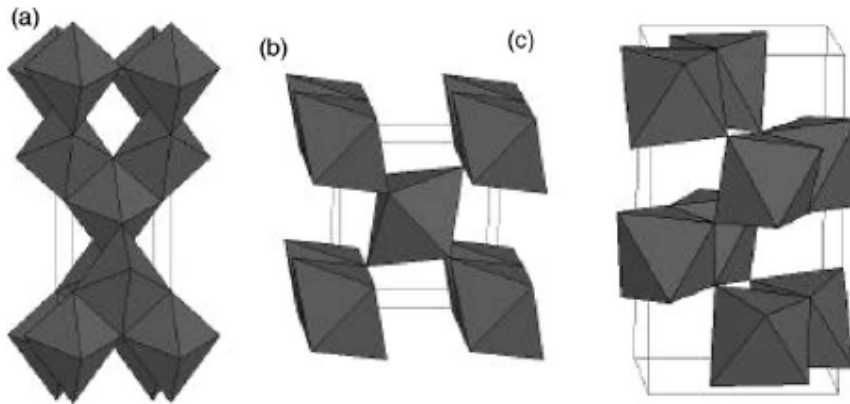


Figure 1.1. Crystal structures of anatase (a), rutile (b), and brookite (c) [1].

The most common form is rutile, which is also most stable form. Anatase and brookite both convert to rutile upon heating. The optical band gap of  $\text{TiO}_2$  is determined by the crystal modification and defect in crystal matrices. Experimentally measured values vary: 3.5 eV for amorphous films, 3.2-3,5 eV for



crystalline films in the anatase phase, 2,95-3,2 eV for crystalline films in the rutile phase and 3,15-3,29 for crystalline films in the brookite phase [1,11-15].

ZrO<sub>2</sub> and HfO<sub>2</sub> could be called twin oxides as they exhibit remarkably similar physical and chemical properties. Both oxides exist in three crystalline modifications – monoclinic, tetragonal and cubic. The experimentally measured optical band-gap of ZrO<sub>2</sub> can vary from 4,37-5,8 eV [16-19] and optical band-gap of HfO<sub>2</sub> can vary from 5,5-6 eV [18-22].

## 1.2. Synthesis methods of TiO<sub>2</sub>, ZrO<sub>2</sub> and HfO<sub>2</sub>

IVB group metal oxides can be prepared mostly in the form of thin films, powders and crystals. There are two different routes for synthesis of Ti, Zr and Hf oxides – gas phase methods and solution routes.

For some applications, especially the synthesis of thin films, liquid-phase processing is one of the most convenient and utilized methods of synthesis. This method has the advantage of control over the stoichiometry, producing homogeneous materials, allowing formation of complex shapes, and preparation of composite materials. Most common solution routes are described as follows:

- Solvothermal methods. These methods employ chemical reactions in aqueous (hydrothermal method) or organic media (solvothermal method). Generally, but not always, a subsequent thermal treatment is required to crystallize the final material.
- Precipitation(co-) methods. These involve precipitation of hydroxides by the addition of a basic solution (NaOH, NH<sub>4</sub>OH, urea) to a raw material followed by calcination to crystallize the oxide. The disadvantage is the tedious control of particle size and size distribution, as fast (uncontrolled) precipitation often causes formation of larger particles instead of nanoparticles.
- Sol–gel methods. These methods are used for the synthesis of thin films, powders, and membranes. Two types are known: the non-alkoxide and the alkoxide route. Depending on the synthetic approach used, oxides with different physical and chemical properties can be obtained.
- Electrochemical synthesis. Electrochemical synthesis may be used to prepare advanced thin films such as epitaxial, superlattice, quantum dot and nanoporous ones. Also, varying electrolysis parameters like potential, current density, temperature, and pH can easily control the characteristic states of the films.

For thin films, most synthesis routes are performed from the gas phase. These can be chemical or physical by nature. Most of these techniques can also synthesize powder, if a method to collect the produced particles is employed. The main techniques are:

- Chemical vapour deposition. CVD is a widely used versatile technique to coat large surface areas in a short span of time. In a typical CVD process, the wafer (substrate) is exposed to one or more volatile precursors, which react and/or decompose on the substrate surface to produce the desired deposit. Frequently, volatile by-products are also produced, which are removed by gas flow through the reaction chamber. In industry, this technique is often employed in a continuous process to produce ceramic and semiconductor films.
- Physical vapour deposition (PVD). PVD is another class of thin-film deposition techniques. Films are formed from the gas phase, but here without a chemical transition from precursor to product. This is, therefore, only possible with substances that are stable in the gas phase and can be directed towards the substrate. The most commonly employed PVD technique is thermal evaporation, in which a material is evaporated from a crucible and deposited onto a substrate.
- Spray pyrolysis deposition (SPD). SPD is an aerosol deposition technique for thin films and powders related to CVD. The main differences are that in spray pyrolysis: (1) an aerosol (a mist of small droplets) is formed from a precursor solution instead of a vapour in CVD. (2) The aerosol is directly focussed onto the sample in most cases, whereas diffusion is a dominant process in CVD. (3) The heated substrates are at ambient pressure, while in CVD, the set-up commonly is under reduced pressure. The size of the particles formed and the morphology of the resulting film are strongly dependent on deposition parameters like substrate temperature, composition and concentration of the precursor, gas flow, and substrate–nozzle distance. Some of these parameters are mutually dependent on each other.

## 2. Overview of sol-gel method and its applications

### 2.1. Introduction to “sol-gel processing”

Traditional ceramic and glass technology has always been high temperature chemistry. A ceramist has mixed batches, used variety of methods to produce a shape and allowed a furnace to serve as chemical laboratory. In the case of glass, a three dimensional oxide network is formed during high-temperature melting and is preserved without crystallization by super-cooling of the melt [23].

“Sol-gel processing” as a new approach for the preparation of glasses and ceramics expanded from mid-1970. In case of “sol-gel processing”, an oxide network is obtained via organic polymerization by starting from molecular precursors. These reactions occur in solutions (generally near room temperature) and the term “sol-gel processing” is often broadly used to describe the synthesis of inorganic oxide by “wet chemistry” methods. These processes offer many advantages as compared to the conventional route, such as:

- Homogeneous multi-component systems can be easily obtained by mixing the molecular precursor solutions [24].
- Temperatures required for material processing can be noticeably lower leading to unusual glasses or ceramics.
- The rheological properties of sols or gels allow the formation of fibers [25], films or composites by such techniques as, dip-coating, impregnation or printing [26].

Sol-gel processing started from synthesis of silica glass from silicon tetraethoxides and metal nitrate salts [27]. Most of the studies on processing and synthesis principles have been done on silica. Today there are wide varieties of materials (majority of transition metal oxides) that can be synthesized and shaped by sol-gel processing.

Synthesis of oxide product by sol-gel processing can be divided mostly in to three general steps which are:

- Sol synthesis and gelation (includes shaping of gel in to fibers, films, bulk objects or other shapes)
- Drying of prepared gel (formation of xerogel)
- Baking of xerogel and crystallization of amorphous oxide network.

The chemistry of sol synthesis and gelation is based on hydroxylation and condensation of molecular precursors. Two different routes are usually described in the literature depending on whether the precursor is a metal alkoxide or an aqueous solution of an inorganic salt [28]. In current thesis we concentrate on sol-

gel synthesis of metal oxides from metal alkoxide. More detailed overview of chemistry involved in sol and gel formation from metal alkoxides is given in the second section of this chapter.

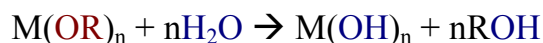
For obtaining of amorphous oxide structure from sol-gel processed gel, a drying is carried out for removing of solvents (desiccation) from the gel structure. Principles and problems during drying process are covered in the third section of this chapter.

Baking is typically applied after the drying and it is required for densification and crystallization of synthesized oxide materials. Overview of baking process is given in the fourth section of this chapter.

In the last section we will give an overview of shaping opportunities and about variety of materials which can be manipulated by sol gel processing.

## 2.2. Chemistry of “sol-gel processing” from metal organic compounds

The most versatile precursors for the sol-gel synthesis of metal oxides are metal alkoxides. Metal alkoxides are compounds, which have an organic moiety (-OR) attached to a metal (M) or metalloid atom through oxygen atom. Electronegative alkoxy groups (-OR) make the metal atom highly attractive to nucleophilic attack. Metal alkoxides are therefore extremely reactive with water leading to the formation of hydroxides or hydrous oxides. The overall reaction can be written as follows:



Hydrolysis of the alkoxide is described in the literature as a nucleophilic addition of a water molecule to the positively charged metal atom M and the departure of the better leaving group which should be the alcohol (figure 2.2.).

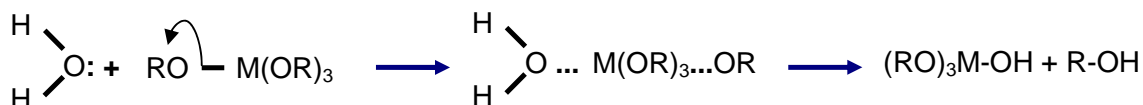
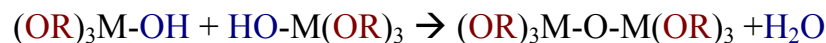
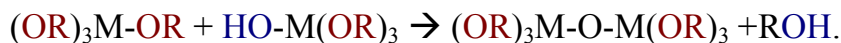


Figure 2.2. S<sub>N</sub>2 type hydrolysis mechanism of metal alkoxide.

Two partially hydrolyzed molecules can link together in condensation reaction, such as:



or



Above described hydrolysis and condensation reactions can proceed simultaneously and larger molecules (strongly branched or linear chains) by the process of polymerization can form.

Reaction kinetic of hydrolysis and condensation is strongly influenced by the electronegativity of metal atom involved in reactions. It is well known that silicon alkoxides are not very reactive with water. On the other hand, transition metal alkoxides react vigorously as soon as the alkoxide is brought in to contact with water. A rough estimation of the partial charge distribution (table 1) in metal alkoxides show that partial positive charge is much higher for transition metals than that of silicon. This explains why transition metal alkoxides are very unstable toward hydrolysis. They must be handled very carefully in a dry environment and stabilizing agents (for example EAcAc [29]) are often added in the sol-gel processing of transition metal alkoxides [30].

Table 2.2. Positive partial charge of M for some metal ethoxides [31].

Alkoxide	Zr(OEt) <sub>4</sub>	Ti(OEt) <sub>4</sub>	Nb(OEt) <sub>4</sub>	Ta(OEt) <sub>4</sub>	W(OEt) <sub>4</sub>	Si(OEt) <sub>4</sub>
$\delta(M)$	+0.65	+0,63	+0,53	+0,49	+0,43	+0,32

If monomer of metal alkoxide can form by hydrolysis more than two bonds, then there is no limit on the size of the molecule that can form. If one molecule reaches macroscopic dimensions so that it extends throughout solution, the substance is said to be a gel.

Gelation can occur after a sol is cast in to a mold, in which case it is possible to make objects of a desired shape. If the smallest dimension of the gel is greater than a few millimeters the object is generally called monolith. For obtaining of amorphous oxide structure from sol-gel processed gel, a drying is carried out for removing solvents from the gel structure.

### 2.3. Drying of gels (formation of xerogel)

After the desirably shaped gel has been formed it must be dried to remove the solvent phase. By increasing the thickness of formed gel body, there arise problems of cracking during evaporation of solvent. In obtaining monoliths from gels, the drying procedures are largely determined by the need to minimize internal stress associated with the volume changes during drying and the capillary forces in the gel pores.

Overview of the development of stress within drying gels is given by Zarzycki et al. [24]. During the initial stages of drying, the volume change of the gel is equal to the volume of evaporated liquid. The gel network is still flexible and can rearrange to accommodate the decreasing volume. All pores are filled with solvent and liquid-air interface is not present. As drying proceeds, the gel

network becomes more restricted, and the removal of liquid leads to the formation of such interface and the development of capillary stress.

The development of cracks in a drying gel can be illustrated by figure 2.3. Evaporation leads to the formation of menisci, the different radii of pores cause unequal capillary pressures to generate differential stresses. If the stress difference locally exceeds the strength of gel network, a crack will result. The tendency toward fragmentation is determined by both average pore size and the pore size distribution.

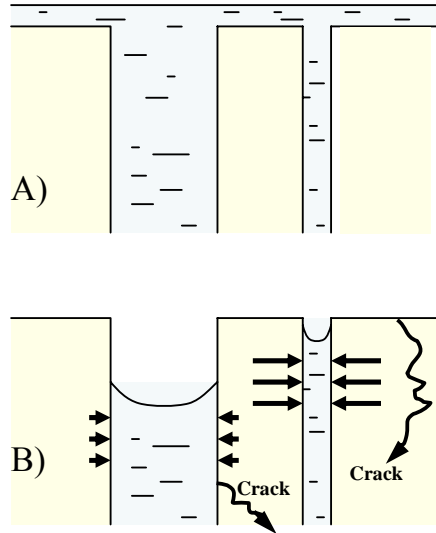


Figure 2.3. Formation of differential strains at the pores during drying: A) before and B) after the onset of capillary forces.

To decrease fragmentation of prepared gel structures we need to increase the size of pores, uniform size distribution of pores or stronger gel structures. This can be achieved by introducing organic additives into alkoxide sols. It is shown that if formamide, glycerol or organic acids are used as drying control chemical additives, then oxide monoliths up to some tens of centimeters could be synthesized [24,25].

Since shrinkage and cracking are produced by capillary forces, Kistler [32] reasoned that those problems could be avoided by removing liquid from the pores above the critical temperature ( $T_c$ ) and critical pressure ( $P_c$ ) of the liquid. In the process of supercritical (or hydrophercal) drying, a sol or wet gel is placed into an autoclave and heated. The pressure and temperature are increased in such way that the phase boundary is not crossed; once the critical point is passed, the solvent is vented at a constant temperature ( $>T_c$ ). The resulting gel, called aerogel, has a volume similar to that of original sol. The process makes it possible to produce monolithic gel large as the volume of autoclave.

After removing solvent from prepared gel structure and depending on application, there can be carried out a heat treatment to convert xerogel to dense oxide.

#### **2.4. Heat treatment of xerogel**

Once a gel has been obtained in dry state, it must be heated treated to convert it to dense ceramic. The most obvious physical change that occurs when amorphous gel is heated above room temperature is shrinkage and weight loss. Average shrinkage proportion for metal-alkoxide-based and sol-gel derived gels is typically around 25% [30]. Weight loss is mostly influenced by selection of synthesis route (acid or base catalyzed) or starting compounds [25]. Weight loss and shrinkage are attributed to the number of physical, chemical and structural changes that occur during the heat treatment of xerogel. These processes can be viewed as desorption of physically adsorbed water; carbonization and combustion and removal of residual organic groups and solvents; polymerization (condensation) and structural relaxation (a process by which excess free volume is removed); densification, crystallization and phase transformation (in temperatures greater than  $\sim 400$  °C).

#### **2.5. Micro- and nano-scale shaping of sol-gel synthesized materials**

Flexibility of sol-gel processing on synthesis of materials with different chemical composition and geometrical shape has been lead to elaboration of various shaping methods and applications. Brief overview of main possibilities for shaping of metal alkoxide based sol-gel materials has been presented on figure 2.5.

A large number of sol-gel based applications (reflective or antireflective layers etc.) are using thin oxide films prepared by number of coating techniques (dip coating, spin coating, spraying). In micropatterning methods (embossing, molding) desired structures are embossed in the soft gel films on various substrates using a stamp or an initially fluid sol-gel precursor is allowed to acquire its final geometry by solidifying in a mold. For preparing fibers the precursor is pulled or pressed to slender jets. The solid fibers are obtained due to gelation of the jet in humid environment. Nano or micropowders are obtained by controlled hydrolysis of metal alkoxide in water containing solutions and precipitation. To obtain the bulk monoliths, a sol is gelled in desired shape molds. Cracking and collapsing of large monoliths ( $\sim 10$  cm diameter cylinders) is avoided by controlling pore sizes and drying conditions.

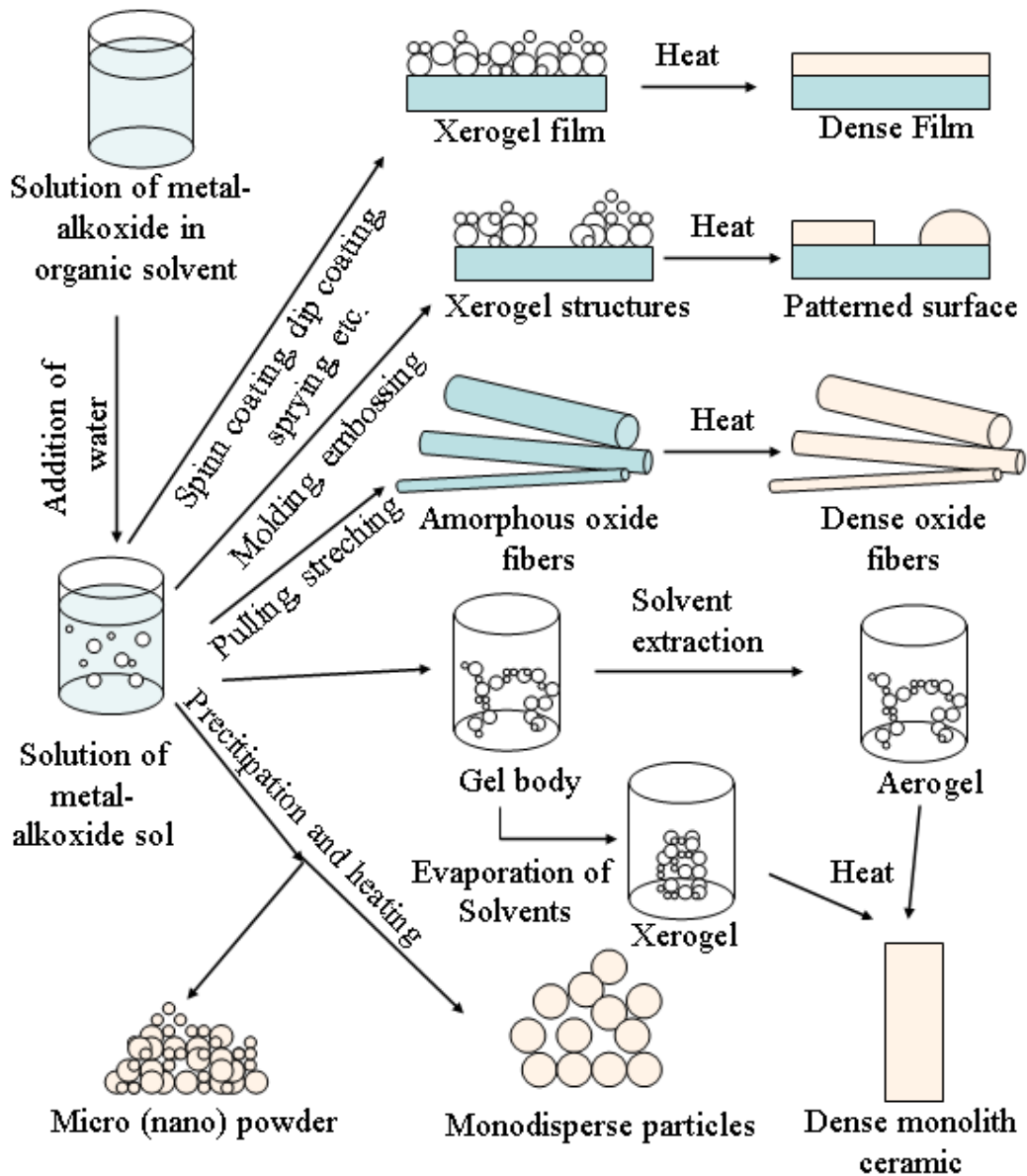


Figure 2.5. Main possibilities for shaping of metal alkoxide based sol-gel materials.



### **3. Results**

#### **3.1. Aim of the study**

The aim of the study is elaboration of IVB group metal oxide structures and their possible applications. In present work we have concentrated on preparation and characterization of non-doped and rare-earth-doped ( $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ ) thin metal oxide films ( $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ ). My contribution has been a development, synthesis and preparation of thin metal oxide films and dealing with problems concerning incorporation of dopants in these films.

In addition, under collaboration with supervised student we have taken under consideration phenomenon of rolling up thin alkoxide gel-sheets as they have tendency to form tubular metal oxide structures. The work has been divided in to two closely related subjects where one half is concentrated on preparation of thin films and other is about rolling up thin gel sheets.

#### **3.2. Results and discussion**

##### **3.2.1. Synthesis and deposition of non-doped and RE-doped thin IVB group metal oxide films [Papers I-IV]**

RE-doped IVB group metal oxide films, prepared by a variety of deposition techniques, have attracted wide interest as dielectric, photocatalytic, photovoltaic, scintillating and luminescence (CRT and lamp phosphours) materials. Atomic layer deposition appears to be a promising technique for producing pure crystalline films with precisely controllable thickness [33]. Yet, an intentional incorporation of impurities appears to be complicated. A versatile but expensive doping method is ion implantation. In addition, high concentrations of ion implanted impurities destroy significantly the crystalline structure. In the case of sol-gel method one can point out excellent compositional control, homogeneity on the molecular level due to the mixing of liquid precursors, and low preparation temperature (close to room temperature). Sol-gel based film processing routes such as dip-coating, spray pyrolysis and spin-coating are usually applied because they are versatile and cost-effective.

For synthesis of precursors we were using our knowledge from previously conducted work where we have been elaborate method for preparation of metal alkoxide (Sn, Ti) concentrates for preparation of sharp oxide jets [34][35]. In current work we have adapted and elaborated previously matured techniques and extended synthesis for incorporation of RE-dopants in precursors for thin film deposition.

### 3.2.1.1. Synthesis of RE-doped TiO<sub>2</sub> precursors for spray pyrolysis [Paper I]

For widening our capabilities in obtaining rare-earth-activated metal-oxide films as luminescent materials and providing possibility for applying these materials on complex surfaces we have developed spray pyrolysis technique in collaboration with M. Krunko et al.

For synthesis of luminescence material by spray pyrolysis processing and incorporation of rare-earth-dopant in TiO<sub>2</sub> films the precursors were prepared analogously by previously described work [36]. The precursor solution contained titanium(IV)isopropoxide (TTIP), acetylacetonate and ethanol with TTIP concentration of 6 vol% at TTIP:AcAc molar ratio of 1:2. To introduce Sm<sup>3+</sup> ions to precursor solution certain amount of SmCl<sub>3</sub>·6H<sub>2</sub>O was added. The Sm concentration in the resulting films was calculated to be ~0.5 to 5 at %.

The basic annealing was performed at 500 °C for 2 h in air. This treatment results in development of an anatase structure free of organic residues. We successfully used pyrolysis technique to prepare rare earths activated TiO<sub>2</sub> films with controllable and uniform thickness and quite high refractive index (2.16). An intense Sm<sup>3+</sup> emission was observed under a photoexcitation of host matrix.

### 3.2.1.2. Synthesis of RE-doped HfO<sub>2</sub> precursors [Paper II]

For synthesis of luminescence material based on HfO<sub>2</sub> we have proceeded from Hf(OBu)<sub>4</sub>. For a sol-gel (dip-coating) processing and incorporation of rare-earth-dopant in HfO<sub>2</sub> films the precursors were prepared by polymerising Hf(OBu)<sub>4</sub> in 45 % hexane solution and by subsequently adding water at molar ratios 1:1.6. For Re-doping 0.5–1 % corresponding metal chloride was dissolved into the obtained sol solution. The estimated Sm<sup>3+</sup>, Eu<sup>3+</sup> and Tb<sup>3+</sup> concentrations were 0.3–0.4 at. % in the HfO<sub>2</sub> films obtained. In order to remove organic ligands and crystalline the films the final thermal treatment was carried out at 800 °C for 1 hour.

For comparison HfO<sub>2</sub> films were deposited by (ALD) process and doping was carried through by an ion-implantation.

We successfully used sol-gel dip-coating processing to prepare rare earths activated HfO<sub>2</sub> films with controllable and uniform thickness. We have shown that the Sm-, Eu- and Tb-doped samples prepared by using the sol-gel method emitted an emission specific to inner 4f-shell transitions of corresponding rare earth ions when excited with the 6,4 eV photons. Also we have observed that compared to pure ALD grown samples sol-gel derived films have a lower structural quality. This is probably because of the higher porosity which is characteristic for materials prepared by sol-gel processing. We suggest the possibility of using synthesized RE doped HfO<sub>2</sub> as scintillator material (e.g. in medicine) as it has high density and atomic number combined with luminescent properties for that application.

### 3.2.1.3. Synthesis of RE-doped TiO<sub>2</sub> precursors [Papers III-IV]

For obtaining information about possibility for synthesis of luminescence material based on TiO<sub>2</sub> we have proceeded from Ti(OBu)<sub>4</sub>. For a sol-gel (spin-coating) processing of TiO<sub>2</sub> films proper metal-oxane sol precursors were obtained by adding water to the mixture of Ti(OBu)<sub>4</sub> and ethyl acetoacetate in buthanol (molar ratio 2:1:1). For doping with Sm, 1% of SmCl<sub>3</sub>·6H<sub>2</sub>O was dissolved in the mixture of neat titanium butoxide before adding water. The Sm concentration in the resulting films was calculated to be ~0.1 at %. In order to remove organic ligands and crystalline the films the final thermal treatment was carried out at 520 °C for 1-2 hours.

A Sm<sup>3+</sup>-specific emission was observed in the samarium doped titanium dioxide thin film. This is good indication for showing that rare-earth-impurities' has been successfully incorporated into host oxide matrix. In collaboration with A. Lukner we have observed that intensity of the emission was found to be sensitive to the chemical composition of the ambient atmosphere. In the oxygen-containing environment the laser irradiation of the sample placed into the intensity of the Sm<sup>3+</sup> emission increased substantially. The existing experimental evidence does not allow any unambiguous identification of the physical processes responsible for the PL oxygen sensing. It is clear that for the enhancement of the PL intensity, the presence of the oxygen containing ambient and the stimulation of the band-to-band transitions by the laser irradiation is necessary. Most likely PL intensity response is determined by the reaction of the Sm<sup>3+</sup> ions to the change of the oxygen content in the ambient atmosphere due to the recharge of the surface and the subsurface (within the space charge region) happening due to a changed amount of the chemisorbed oxygen species. We propose that thin porous TiO<sub>2</sub>:Sm<sup>3+</sup> films can be considered as photoluminescence-based oxygen sensing material

### 3.2.1.4. Synthesis of RE-doped ZrO<sub>2</sub> precursors

For obtaining information about possibility for using zirconiumtetrabutoxide as precursor for luminescence material, we have synthesized sol analogously and with some modifications as described in section 3.2.1.3.

For a sol-gel (dip-coating) processing of ZrO<sub>2</sub> films the precursors were prepared by adding water to the mixture of Zr(OBu)<sub>4</sub> and ethyl acetoacetate in buthanol (molar ratio 2:1:1). For RE doping 0.5–1 % SmCl<sub>3</sub> or EuCl<sub>3</sub> was dissolved in the obtained sol solution. The estimated Sm<sup>3+</sup> and Eu<sup>3+</sup> concentrations were calculated to be 0.3–0.4 at. % in the ZrO<sub>2</sub> films obtained. In order to remove organic ligands and crystalline the films the final thermal treatment was carried out at 620 °C for 2 hour and 30 min.

We were modified synthesis by adding ethyl acetoacetate as stabilization agent for preventing rapid hydrolysis and condensation of precursor in to powder.

### 3.2.1.5. Dip-coating technique

For deposition of thin metal oxide films we have used dip-coating and spin-coating methods and modified these to mach with our precursors. Dip-coating represents method where the substrate to be coated is immersed in a liquid and then withdrawn with a well-defined withdrawal speed (see figure 3.2.1.5.1.).

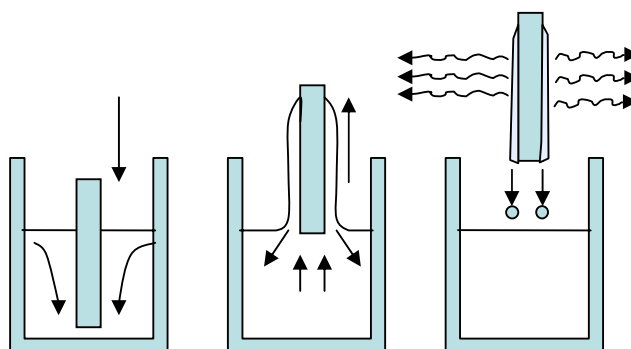


Figure 3.2.1.5.1. Scheme of the dip-coating procedure.

In our work we were used dip coater where withdrawing speed of sample holder was controlled by electrical motor and varied using gearbox. In optimization of dip-coating we were used dipping speeds ( $0.0375$ ,  $0.15$ ,  $0.6$ ,  $2.4$ ,  $9.6 \times 10^{-3}$  m/s). We found that most optimal dipping speed for our precursor is  $2,4 \times 10^{-3}$  m/s. The coating thickness is mainly defined by the withdrawal speed and the viscosity of the liquid. In our work we where using  $\sim 5\%$  metal alkoxide undoped and  $\text{Re}^{3+}$  doped sol solutions in hexane. The viscosity of described solution in our laboratory was hard to measure due to relatively low viscosity (close to hexane) and chemical reactivity (exposure to humid atmosphere cause gelation of mixture). The thickness of the films was measured in collaboration with V. Kiisk by ellipsometrical measurements. The average coating thickness for titaniumterabutoxide based films after annealing at 1 h and  $520^\circ\text{C}$  was  $\sim 3$  nm. The thicker films can be obtained by applying multiple coating on substrate. We have demonstrated that multiple coating will yield films with well defined thickness. Coating thickness dependence on number of dips for  $\text{Sm}^{3+}$  doped  $\text{TiO}_2$  after annealing has been presented on figure 3.2.1.5.2.

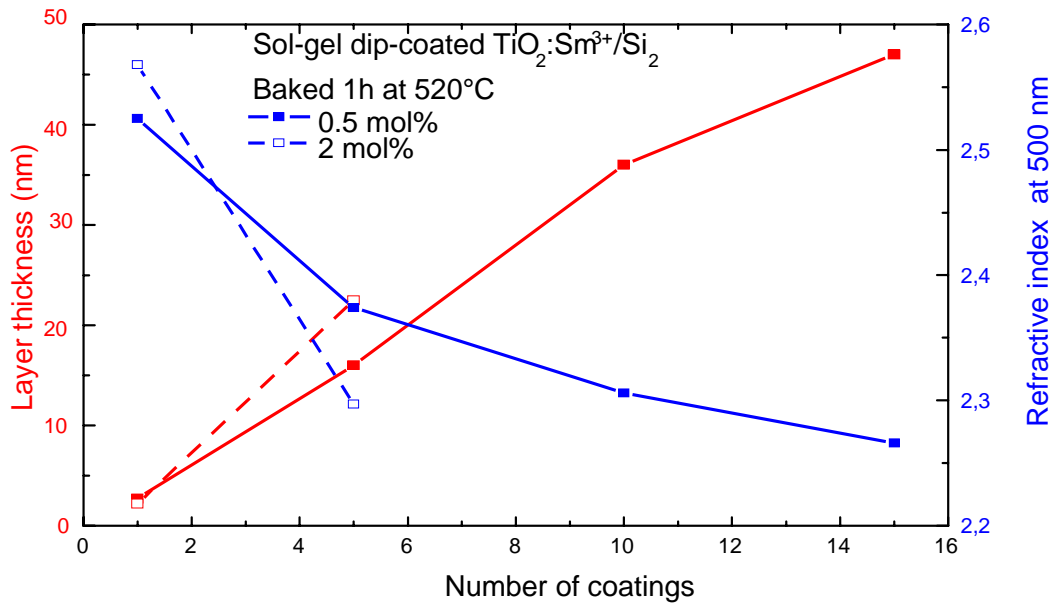


Figure 3.2.1.5.2. Coating thickness dependence on number of coatings (Figure is created by V. Kiisk).

### 3.2.1.6. Spin-coating technique

Alternative method for applying sol coatings on substrate is to use spin-coating technique. This method is schematically described on figure 3.2.1.6.

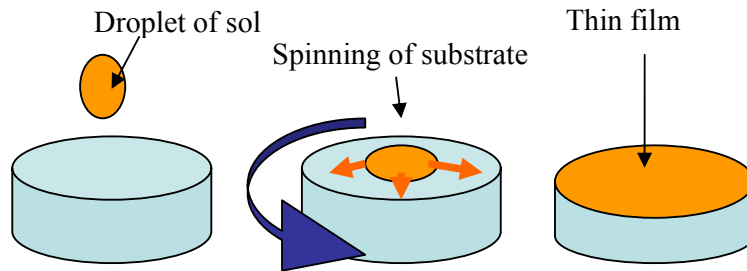


Figure 3.2.1.6. Schematically represented spin-coating procedure

Advantage of spin-coating over dip-coating is that film is formed only on side of the surface. Thicknesses of spin coated thin films were measured using Swanepoel method [37]. Transmittance spectrum of films was measured by spectrophotometer JASCO-570 in range 200-500 nm. Measured film thicknesses varied from 50 to 200 nm.

### 3.2.1.8. Measurement of luminescence characteristic

Luminescence characteristics of prepared films were measured at Institute of Physics of the University of Tartu. For the registration of photoluminescence an ICCD camera (ANDOR) was used. For excitation of  $\text{TiO}_2$  the third harmonic 3,49 eV (355 nm) of Nd:YAG impulse laser was used. Monochromator LOMO MDR-23 with resolution of 0,5 nm was used for spectral separation. Schematic setup is presented in figure 3.2.1.8. For excitation of  $\text{HfO}_2$  and  $\text{ZrO}_2$  ArF gas eximer laser 6,4 eV (193 nm) was used. For measurements of luminescence characteristics at low temperature (down to 5 K), cryostat UTERUS was used. Luminescence radiation intensity dependence from surrounding gas content was observed using a vacuum chamber.

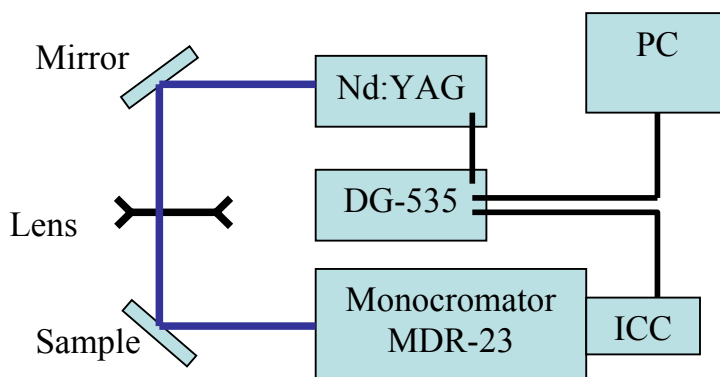


Figure 3.2.1.8. Setup for measuring luminescent characteristics of prepared films.

### **3.2.2. Method for rolling up thin titanium alkoxide gel sheets [Papers V-VI]**

During synthesis of precursor for preparation of thin films we have discovered in collaboration with M. Järvekülg the formation of tubular structures. We shown that obtained tubular gel structures can be baked at up to 500 °C to crystalline the material. Obtained metal oxide micro-tubes are transparent in visible light and have outer diameter of 20-30 µm. Detailed synthesis procedure is described in papers V and VI. We propose that tubular structures are formed by rolling up of gel sheet from the inner surface of flask where concentrated sol has been deposited as the result of continuous spinning of flask in rotavapor. The moisture was introduced during ventilation of the system before removing of flask from the system. After adding of hexane to the mixture the needle like sediment was formed. After observing sediment under optical microscope we saw fiber like object with hollow inner core. We have also used SEM for scrutinize formed object and that confirmed formation of tubular like objects.

We suggest that self-rolling of gel sheets is caused by mechanical stress imbalance between the material layers. The origin of differential stress can be described by several different general scenarios, or a combination of these. Firstly, as described by G. W. Scherer [38], when a gel plate dries from only one side it becomes concave toward the drying side. In addition, the material shrinks during gelation due to polymerization. In this case the polymerization starts from one side of the gel layer. Since hydrolysis and polymerization take place in sol material that is densified through solvent removal, the diffusion speed of water molecules in deeper material layers can be assumed to be low. Therefore, formation of gelation extent gradient is expected to be established in upper layer of the material that is directly exposed to humid air. In the case considered drying and polymerization processes both start from one side of the sol material and lead to differential densification of material. Stress is released when the remaining sol under the gel layer is dissolved and the gel sheets are released. Furthermore, swelling of less polymerized layers is to be expected upon adding hexane. This leads to material expansion in the bottom layers of the gel film, while the same effect is considerably smaller in the upper layer that is completely gelled. Similar principle has been exploited in methods for obtaining micro- and nano-tubes of polymer materials, whereas stress originates from physical or chemical factors having different effect on different material layers [39].

Sol-gel method is suitable for obtaining wide range of ceramic materials, although many properties of different metal alkoxide precursors vary to some extent [24]. Thus we expect that presently introduced synthesis route can be applied for obtaining tubular structures from a number of different materials.

Technical solution of above described method has been patented. We propose that obtained oxide materials can be used in the production of catalysts,

gas-sensors, stationary phases in chromatography, composite materials, MEMS or NEMS components, heat insulators etc.

### 3.2.2.1. Equipment elaborated for synthesis of tubular micro-structures

In collaboration with supervised student R. Vålbe we have elaborated equipment for synthesis of tubular micro-structures. The main motivation for preparation of this equipment was to create the reactor where it was possible to control environment and observed key parameters for controlled synthesis of tubular structures. The idea was to use a silindrical body for stable and with well defined flat surface for contrast to previously used inner surface of spherical flask. Also this will simplify theoretical calculations (starting layer thickness calculation taking into account the amount of added precursor material) and sol flow control on surface. We have also improved the air flow mechanism for better control of polymerazion and film growth on surface by introducing air through the needle over the rolling surface. On this apparatus we managed to show diameter growth of tubular structures as a function of the amount of added moistured air.

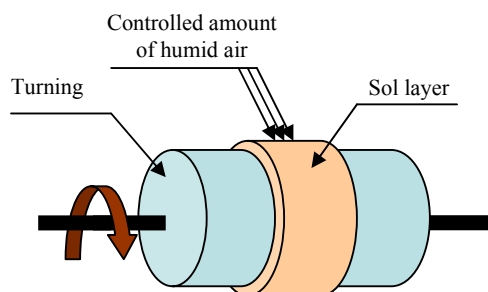


Figure 3.2.2.1. Schematic representation of constructed reactor.



### 3.3. Conclusions

We have successfully elaborated methods for preparation of IVB group metal oxide thin films, tubular microstructures and incorporation of rare-earth-ions in to these materials.

We have shown that spray pyrolysis, dip-coating and spin-coating techniques can be used to prepare rare earths activated  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  films with controllable and uniform thickness.

We have demonstrated that metal alkoxide based synthesis of thin  $\text{Sm}^{3+}$  doped titania and hafnia films will yield materials which after band-to-band optical excitation give  $\text{Sm}^{3+}$ -specific emission with a well-resolved fine structure. The latter indicates that the samarium ions are fitted in to quite regular positions in the host lattices.

We suggest the possibility of using synthesized RE doped  $\text{HfO}_2$  as scintillator material (e.g. in medicine) as it has high density and atomic number combined with luminescent properties for that application. Also we propose that thin porous  $\text{TiO}_2:\text{Sm}^{3+}$  films can be considered as photoluminescence-based oxygen sensing material as intensity of the  $\text{Sm}^{3+}$ -specific emission was found to be sensitive to the chemical composition of the ambient atmosphere.

We have demonstrated for the first time that gelation of the surface of a metal-alkoxide precursor, spontaneous cracking of obtained gel film, subsequent dissolving the non-gelled layer of precursor will lead to self-rolling of gel film segments. Obtained metal oxide micro-tubes are transparent in visible light and have outer diameter of 20-30  $\mu\text{m}$ . We have also shown that obtained tubular gel structures can be baked at up to 500  $^\circ\text{C}$  to crystalline the material. We propose that obtained oxide materials can be used in the production of catalysts, gas-sensors, stationary phases in chromatography, composite materials, MEMS or NEMS components, heat insulators etc.

## **Elaboration of IVB group metal oxide structures and their possible applications**

### Summary

The description and discussion about an easy and flexible method for preparing of nanometer level homogeneous  $\text{Ti}(\text{OBU})_4$ ,  $\text{Zr}(\text{OBU})_4$ ,  $\text{Hf}(\text{OBU})_4$  based sols and concentrates, suitable as precursors for preparing metal oxide thin (RE doped and undoped) films and tubular microstructures were presented in the current thesis.

The main results presented in current thesis can be summarized as follows:

- We have shown that spray pyrolysis, dip-coating and spin-coating techniques can be used to prepare rare earths activated  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  films with controllable and uniform thickness.
- We have demonstrated that metal alkoxide based synthesis of thin  $\text{Sm}^{3+}$  doped titania and hafnia films will yield materials which after band-to-band optical excitation give  $\text{Sm}^{3+}$ -specific emission with a well-resolved fine structure. The latter indicates that the samarium ions are fitted in to quite regular positions in the host lattices.
- We suggest the possibility of using synthesized RE doped  $\text{HfO}_2$  as scintillator material (e.g. in medicine) as it has high density and atomic number combined with luminescent properties for that application. Also we propose that thin porous  $\text{TiO}_2:\text{Sm}^{3+}$  films can be considered as photoluminescence-based oxygen sensing material as intensity of the  $\text{Sm}^{3+}$ -specific emission was found to be sensitive to the chemical composition of the ambient atmosphere.
- We have demonstrated for the first time that gelation of the surface of a metal-alkoxide precursor, spontaneous cracking of obtained gel film, subsequent dissolving the non-gelled layer of precursor will lead to self-rolling of gel film segments. Obtained metal oxide micro-tubes are transparent in visible light and have outer diameter of 20-30  $\mu\text{m}$ . We have also shown that obtained tubular gel structures can be baked at up to 500  $^\circ\text{C}$  to crystalline the material. We propose that obtained oxide materials can be used in the production of catalysts, gas-sensors, stationary phases in chromatography, composite materials, MEMS or NEMS components, heat insulators etc. Patent pending.

## Summary in Estonian

### IVB grupi metallide oksiidstruktuuride väljatöötamine ja nende võimalikud rakendused

Käesolevas väitekirjas käsitletakse dopeerimatta ja haruldaste muldmetallide ioonidega dopeeritud õhukeste oksiidkilede ja torukujuliste mikrostruktuuride valmistamismeetodeid ja sünteesitud materjalide mõningaid omadusi. Materjalide valmistamisel kasutatakse lähtematerjalidena metallide (Ti, Zr, Hf) alkoksiidide ja nendest sünteesitud homogeeniseid soole ja kontsentrante.

Tööst lähtuvad tulemused on järgmised:

- Näidati, et pihustus-pürolüüsi-, vurr-katmis- ja sukelduspindamistehnikat, kasutades on võimalik valmistada kontrollitava ja ühtlase paksusega ja haruldaste muldmetallide ioonidega dopeeritud õhukesi  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$  kilesid.
- Näidati, et metallide alkoksiididel baseeruv  $\text{Sm}^{3+}$  dopeeritud titaan-, ja hafniumoksiidkilede süntees annab materjali, mis tsoon-tsoon ergastuse tulemusel kiirgab samaariumi 3+ ioonile iseloomuliku hästi eristatava struktuuriga spektriga. Viimane näitab, et samaariumi ioonid on asetunud regulaarselt põhioksiidi kristallvõresse.
- Pakume välja võimaluse, et sünteesitud haruldaste muldmetalli ioonidega lisandatud  $\text{HfO}_2$  on potentsiaalselt rakendatav sintillaatormaterjalina, sest sellises materjalis on ühendatud vastava rakenduse jaoks olulised omadused nagu raske aatom, suur tihedus ja luminescentskiirguse eraldumine kõrge energiaga osakesega vastasmõjust. Samuti pakume välja, et  $\text{Sm}^{3+}$  ioonidega dopeeritud  $\text{TiO}_2$  on rakendatav fotoluminesentsil põhineva hapniku sensori väljatöötamiseks, sest täheldati, et sünteesitud materjalist lähtuv luminescentskiirguse intensiivsus on tundlik ümbritseva atmosfääri keemilisele koostisele.
- Näidati esmakordselt, et metallalkoksiidi kontsentreeritud sooli pinna geelistamisel ja selle spontaanse pragunemise tulemusena saadud geelkile fragmentide geelistumatta materjali lahustamine viib geel-segmentide rullumiseni. Saadud metalloksiid mikro-torud on nähtavas valguses läbipaistvad ja omavad välisdiameetrit 20-30  $\mu\text{m}$ . Samuti näitasime, et saadud struktuure on võimalik kuumutada vähemalt 500 °C, mis on vajalik materjali viimiseks oksiidsele keemilisele koostisele. Sünteesitud materjalide võimalikeks rakendusteks näeme nende kasutamist näiteks katalüsaatorite, gaasisensorite, kromotograafia kolonnide seisvate faaside, komposiitmaterjalide, mikro- või nanoelektromehaaniliste süsteemide (MEMS või NEMS) komponentide, soojusisolatsioonimaterjalide valmistamiseks. Väljatöötatud meetodi tehniline lahendus on patenteeritud.

## Acknowledgment

First of all, I would like to express my sincere gratitude to all the people in Institute of Chemistry and Institute of Physics of University of Tartu and Department of Material Science of Tallinn University of Technology who had one way or another contributed to my thesis.

Especially I would like to thank:

- My supervisors Dr. Ants Lõhmus and Dr. Uno Mäeorg for their knowledge, guidance and patience.
- Dr. Ilmar Kink for many useful discussions and support in sol-gel technology related activities.
- Dr. Ilmo Sildos for interesting discussions and fruitful collaboration in a field of optic.
- Dr. Malle Krunk and Dr. Ilona Oja Açıık for their knowledge and collaboration in a field of material science.
- Dr. Valter Kiisk, Argo Lukner, Sven Lange, P. Karanjov, A. Vorobjov for being very important ally's in the field of optical measurements, interpretation of results and giving long discussions and argumentations about optical effects and problems concerning photoluminescence radiation many more.
- Martin Järvekülg and Raul Välbe for comprehensive collaboration and discussion in preparation of tubular oxide structures.
- Tanel Tätte for guidance, discussions and stimulating the creation of novel ideas.
- All the other people who have contributed to the study.
- My parents, brother and my mate Eve for their support and being wit me.

This work has been supported by the Estonian Science Foundation (Grants No. 6163, 6537, 6660, 6706, 6954, 6999, 7456), Estonian targeted project SF0180058s07 the Estonian Nanotechnology Competence Center and the European Science Foundation program Nanotribo and COST program Molsimu.

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## **Publications**



## Curriculum vitae (CV)

Valter Reedo

### General Data

Date of birth 17.05.1980  
Citizenship Estonian  
Marital status cohabitation  
Contacts Institute of Physics University of Tartu (IPUT)  
124 Riia Str, 51014  
Tel.: (+372) 5206421  
Fax.: (+372) 7383033  
E-mail: valterre@fi.tartu.ee

### Education

1988 – Rakvere Realgümnaasium  
2002 – University of Tartu, Materials science, Bachelor's studies  
2004 – University of Tartu, Organic chemistry, Master's studies

### Work experience

2006 – 2007 Engineer (IPUT)  
2005 – 2008 University of Tartu, Faculty of Science and Technology,  
Materjaliteaduse ja materjalide tehnoloogia doktorikool;  
Extraordinary Researcher  
2007 – Extraordinary Researcher (IPUT)

### Awards

2004 – Estonian Ministry of Education and Research, diploma for the scientific work of student contest

### Dissertations supervised

2008 – Kelli Hanschmidt, Master's Degree, (sup) Martin Järvekülg, Valter Reedo, Ants Lõhmus, Elaboration of precursors for carbide materials with timber structures, University of Tartu, Faculty of Science and Technology.

2007 – Martin Järvekülg, Master's Degree, (sup) Valter Reedo, U. Mäeorg, Formation of novel HfO<sub>2</sub>, ZrO<sub>2</sub> and TiO<sub>2</sub> tubular microstructures, University of Tartu, Faculty of Science and Technology.

## Publications

1. V. Reedo, M. Järvekülg, A. Lõhmus ja U. Mäeorg, Novel route for preparation of tubular TiO<sub>2</sub> microstructures. *Phys. Status Solidi A*, **205**, 6, 1511-1514.
2. P. Kanarjov, V. Reedo, I. Oja-Acik, L. Matisen, A. Vorobjov, V. Kiisk, M. Krunk, I. Sildos, Luminescence materials based on thin metal oxide films doped with rare earth ions. *Phys. Solid State+* 2008, **50**, 9, 1661 – 1663.
3. J. Shulga, V. Kisand, I. Kink, V. Reedo, L. Matisen, and A. Saar, Formation of nickel oxide nanostructures on TiO<sub>2</sub>. *J. Phys.: Conference Series* 2007, **93**, 012006.
4. Tätte, Tanel; Paalo, Madis; Kisand, Vambola; Reedo, Valter; Kartushinsky, Alexander; Saal, Kristjan; Mäeorg, Uno; Lõhmus, Ants; Kink, Ilmar. Pinching of alkoxide jets – a route for preparing nanometre level sharp oxide fibres. *Nanotechnology*, 2007,**18**, 2, 125301.
5. S. Lange, V. Kiisk, V. Reedo, M. Kirm, J. Aarik, I. Sildos, Luminescence of RE-ions in HfO<sub>2</sub> thin films and some possible applications. *Opt. Mater.* 2006, **28**, 11, 1238 - 1242.
6. V. Kiisk, I. Sildos, S. Lange, V. Reedo, T. Tätte, M. Kirm, J. Aarik, Photoluminescence characterization of pure and Sm<sup>3+</sup>-doped thin metaloxide films. *Appl. Surf. Sci.* 2005, **247**, 1-4, 412 – 417.
7. V. Reedo, S. Lange, V. Kiisk, T. Tätte, A. Lukner, I. Sildos, Influence of ambient gas on the photoluminescence of sol-gel derived TiO<sub>2</sub>:Sm<sup>3+</sup> films. *In: Optical materials and applications: (A. Rosental, ed.), Proc. SPIE* 5946, 59460F (2005)
8. T. Tätte, V. Reedo, T. Avarmaa, R. Lõhmus, U. Mäeorg, ME. Pistol, J. Subbi, A. Lõhmus, Metal oxide based SPM tips prepared by sol-gel method. *Phys. Low-Dimens. Str.* 2002, 5-6, 31-37.
9. Invention: Meetod oksiidmaterjali valmistamiseks (Method for preparation of an oxide material); Owner: Tartu Ülikool and Estonian Nanotechnology Competence Centre; Authors: M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus; Priority number: P200700029; Priority date: 07.06.2007, PCT/EE2008/000016 09.06.2008.

## Curriculum vitae (CV)

Valter Reedo

### Üldandmed

Sünniaeg 17.05.1980  
Kodakondsus Eesti  
Perekonna seis vabaabieliu  
Kontaktandmed Tartu Ülikool Füüsika Instituut  
124 Riia Str, 51014  
Tel.: (+372) 5206421  
Fax.: (+372) 7383033  
E-mail: valterre@fi.tartu.ee

### Haridus

1988 – Rakvere Reaalgümnaasium  
2002 – magistrikraad keemias, Tartu Ülikool  
2004 – bakalaureuse kraad materjaliteaduses, Tartu Ülikool

### Teenistuskäik

2006 – 2007 Insener, Tartu Ülikool Füüsika Instituut  
2005 – 2008 Erakorraline Teadur, Materjaliteaduse ja materjalide tehnoloogia doktorikool, Tartu Ülikool  
2007 – Erakorraline teadur, Tartu Ülikool Füüsika Instituut

### Tunnustused

2004 – Diplom, Eesti Haridus ja teadusministeerium, üliõpilastööde konkurs

### Dissertations supervised

2008 – Kelli Hanschmidt, Magistrikraad, (juh) Martin Järvekülg, Valter Reedo, Ants Lõhmus, Biomorfsete karbiidsete komposiitmaterjalide lähtestruktuuride väljatöötamine, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.

2007 – Martin Järvekülg, Magistrikraad, (juh) Valter Reedo, U. Mäeorg, HfO<sub>2</sub>, ZrO<sub>2</sub> ja TiO<sub>2</sub> torujate mikrostruktuuride moodustumise mehhanismi selgitamine tööstuslike materjalide väljatöötamiseks, Tartu Ülikool, Loodus- ja tehnoloogiateaduskond.

## Publikatsioonid

- 10.V. Reedo, M. Järvekülg, A. Lõhmus ja U. Mäeorg, Novel route for preparation of tubular TiO<sub>2</sub> microstructures. *Phys. Status Solidi A*, **205**, 6, 1511-1514.
- 11.P. Kanarjov, V. Reedo, I. Oja-Acik, L. Matisen, A. Vorobjov, V. Kiisk, M. Krunk, I. Sildos, Luminescence materials based on thin metal oxide films doped with rare earth ions. *Phys. Solid State+* 2008, **50**, 9, 1661 – 1663.
- 12.J. Shulga, V. Kisand, I. Kink, V. Reedo, L. Matisen, and A. Saar, Formation of nickel oxide nanostructures on TiO<sub>2</sub>. *J. Phys.: Conference Series* 2007, **93**, 012006.
- 13.Tätte, Tanel; Paalo, Madis; Kisand, Vambola; Reedo, Valter; Kartushinsky, Alexander; Saal, Kristjan; Mäeorg, Uno; Lõhmus, Ants; Kink, Ilmar. Pinching of alkoxide jets – a route for preparing nanometre level sharp oxide fibres. *Nanotechnology*, 2007,**18**, 2, 125301.
- 14.S. Lange, V. Kiisk, V. Reedo, M. Kirm, J. Aarik, I. Sildos, Luminescence of RE-ions in HfO<sub>2</sub> thin films and some possible applications. *Opt. Mater.* 2006, **28**, 11, 1238 - 1242.
- 15.V. Kiisk, I. Sildos, S. Lange, V. Reedo, T. Tätte, M. Kirm, J. Aarik, Photoluminescence characterization of pure and Sm<sup>3+</sup>-doped thin metaloxide films. *Appl. Surf. Sci.* 2005, **247**, 1-4, 412 – 417.
- 16.V. Reedo, S. Lange, V. Kiisk, T. Tätte, A. Lukner, I. Sildos, Influence of ambient gas on the photoluminescence of sol-gel derived TiO<sub>2</sub>:Sm<sup>3+</sup> films. *In: Optical materials and applications:* (A. Rosental, ed.), Proc. SPIE 5946, 59460F (2005)
- 17.T. Tätte, V. Reedo, T. Avarmaa, R. Lõhmus, U. Mäeorg, ME. Pistol, J. Subbi, A. Lõhmus, Metal oxide based SPM tips prepared by sol-gel method. *Phys. Low-Dimens. Str.* 2002, 5-6, 31-37.
- 18.Invention: Meetod oksiidmaterjali valmistamiseks (Method for preparation of an oxide material); Owner: Tartu Ülikool and Estonian Nanotechnology Competence Centre; Authors: M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus; Priority number: P200700029; Priority date: 07.06.2007, PCT/EE2008/000016 09.06.2008.