DISSERTATIONES SCIENTIAE MATERIALIS UNIVERSITATIS TARTUENSIS
I

DISSERTATIONES SCIENTIAE MATERIALIS UNIVERSITATIS TARTUENSIS
I

MARTIN JÄRVEKÜLG

Tubular microstructures by Hf-, Zr- and Ti-butoxide gel sheet rolling

TARTU UNIVERSITY PRESS

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

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

Dissertation in Materials Science

The Dissertation was admitted on May 09, 2011, in partial fulfilment of the requirements for the degree of Doctor of Philosophy in materials science, and allowed for defence by the Scientific Council on Materials Science of the Faculty of Science and Technology of the University of Tartu.

Supervisors:	Dr. Ants Lõhmus, Institute of Physics, University of Tartu
	Dr. Uno Mäeorg, Institute of Chemistry, University of Tartu
Opponents:	Dr. Marco Natali, Institute of Inorganic Chemistry and Surface Science ICIS-CNR Padova, Italy
	Dr. Mihkel Koel, Department of Chemistry, Faculty of Science, Tallinn University of Technology, Estonia
Commencement	July 4. 2011 at University of Tartu, Tartu, Estonia

Publication of thesis was supported by: Graduate School on Functional Materials and Technologies (GSFMT), University of Tartu and Tallinn University of Technology, EU Social Funds project 1.2.0401.09–0079

ISSN 2228–0928
ISBN 978–9949–19–691–3 (trükis)
ISBN 978–9949–19–692–0 (pdf)

Tartu Ülikooli Kirjastus
www.tyk.ee
Tellimus nr. 337

CONTENTS

LIST OF ORIGINAL PAPERS 6

AUTHOR'S CONTRIBUTION 7

ABBREVIATIONS 8

1. INTRODUCTION 9

2. SOL-GEL METHOD 10
   2.1. Introduction 10
   2.2. Terminology and processes 11
   2.3. Sol-gel material shaping 12

3. TUBE AND ROLL-SHAPED MICRO- AND NANO-STRUCTURES .. 15

4. MICROROLLS FROM Ti-, Zr- AND Hf-BUTOXIDES 20
   4.1. Aims of the study 20
   4.2. Formation processes [papers I–V] 20
   4.3. Structures from different metal compounds [papers I–III] 25
   4.3. Size tuning [paper III] 29
   4.4. Annealing [papers II, III, VI] 31
   4.5. Simulation of self-formation processes [paper VII] 33
   4.6. Further discussion and potential applications [papers I–VII] 35

5. CONCLUSIONS 36

SUMMARY 37

SUMMARY IN ESTONIAN 38

REFERENCES 39

ACKNOWLEDGEMENTS 42

PUBLICATIONS 43

LIST OF ORIGINAL PAPERS

I. M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus, Method for preparing oxide material, Owners: Estonian Nanotechnology Competence Center, University of Tartu, Priority number: P200700029; Priority date: 07.06.2007.

II. V. Reedo, M. Järvekülg, A. Lõhmus, U. Mäeorg, Novel route for preparation of tubular TiO_2 microstructures. *Phys. Status Solidi A* 2008 **205**(6), 1511–1514.

III. M. Järvekülg, R. Välbe, A. Salundi, V. Reedo, M. Part, U. Mäeorg, A. Lõhmus, A sol-gel approach to self-formation of microtubular structures from metal alkoxide gel films, *Appl. Phys. Lett* (manuscript).

IV. K. Saal, T. Tätte, M. Järvekülg, V. Reedo, A. Lõhmus, I. Kink, Micro- and nanoscale structures by sol-gel processing. *Int J Mater Prod Tec*, 2011 **40**(1/2), 2–14.

V. M. Järvekülg, R. Välbe, K. Utt, M. Timusk, T. Tätte, Tailoring Sol-Gel Transition Processes for the Design of Novel Shape Metal Oxide Materials. In: Functional Oxide Nanostructures and Heterostructures MRS Proceedings Volume 1256E: 2010 MRS Spring Meeting; San Francisco, USA; 5.–9. April 2010.

VI. K. Utt, S. Lange, M. Järvekülg, H. Mändar, P. Kanarjov, I. Sildos, Structure and optical properties of Sm-doped ZrO_2 microrolls. *Optical Materials* 2010 **32**(8), 823–826.

VII. J. Jõgi, M. Järvekülg, J. Kalda, A. Salundi, V. Reedo, A. Lõhmus, Simulation of cracking of metal alkoxide gel film formed on viscous precursor layer using a spring-block model*, Europhys Lett*, (submitted).

Other papers in related field:

VIII. M. Timusk, M. Järvekülg, R. Lõhmus, I. Kink, K. Saal, Sol–gel matrix dispersed liquid crystal composite: Influence of methyltriethoxysilane precursor and solvent concentration. Materials Science and Engineering B, 172(1), 1–5. (2010).

IX. M. Timusk, M. Järvekülg, K. Saal, R. Lõhmus, I. Kink, A. Lõhmus, Method of preparation of surface coating of variable transmittance and an electrooptical device including the same, Owners: Estonian Nanotechnology Competence Center, University of Tartu, Priority number: P200900022; Priority date: 25.03.2009.

AUTHOR'S CONTRIBUTION

The author has been the ideological leader in the studies of formation of tubular microstructures by metal alkoxide gel film rolling. Nevertheless, as different aspects of this research direction have been covered in listed original papers, the main contributors and first authors have been specialists in corresponding field in some publications. To be more precice in explaining the author's part:

Paper I: Experimental work leading to patented material and method as well as experimental studies of the formation processes. Responsible for background and novelty search, experimental work, writing of majority of the application.

Paper II: Creating bibliographical background, participation in experimental work and substantial part of writing of the manuscript.

Paper III: Directing and coordinating of experimental activities. Formulation of delivered message, singlehanded writing of the manuscript.

Paper IV: Participation in formulation of delivered message, participation in writing the manuscript.

Paper V: Main contributor in in formulation of delivered message and writing the manuscript.

Paper VI: Sample preparation, writing of experimental part of the manuscript.

Paper VII: Participation in formulation of delivered message, writing of experimental part of the manuscript.

ABBREVIATIONS

CVD	Chemical vapour deposition
ALD	Atomic layer deposition
3D	Three-dimensional
TEOS	Tetraethoxysilane
MEMS	Micro-electro-mechanical system
XRD	X-ray diffraction
PL	Photo-luminescence

1. INTRODUCTION

IVB group metal oxides (TiO_2, ZrO_2 and HfO_2) have several remarkable properties and are therefore used in a vast range of different applications. Oxides and oxide mixtures can generally be synthesized and shaped by employing a wide range of conventional (e.g. high temperature powder molding followed by sintering, polishing, evaporation in vacuum) and advanced techniques (CVD, ALD, various chemical methods). The main disadvantage of conventional methods is the poor control over the shapes, dimensions, homogeneity, and chemical composition (functionality) required for modern applications. Advanced techniques, on the other hand, overcome these drawbacks, yet being disproportionately costly in most cases.

The sol–gel method offers simple, flexible and low-cost technologies for producing ceramic materials from organometallic precursors. Although the method is widely considered as chemical one, it is almost always combined with modification of the shape of the substance before the gelation processes is terminated. This is the fundamental reason that makes sol-gel a very flexible technology for producing different shape materials. Sol-gel prepared oxide particles, films, fibres, different 3D structures have been studied and applied for a few decades now.

Self-formation methods of materials science exploit spontaneus processes in shaping of different structures instead of active forming approach, where pressure, mechanical (e.g. abrasion) or chemical treatment (e.g. dissolving, etching) has to be applied. By that simpler and more energy-efficient strategies can be elaborated for materials production as compared to conventional technologies (extrusion, embossing etc.) or sophisticated modern methods (lithography, high vacuum thin film technologies etc.).

Present thesis covers the research conducted on tubular microstructures obtained by an original non-template method that combines sol-gel with self-formation. Ti-, Zr- and Hf- alkoxides have been used in the synthesis that involves gelling of precursor sol surface to obtain gel film, divided to segmets by spontaneous cracking and subsequent dissolving of undelying sol to obtain freestanding gel sheets that have a tendency to roll up. Prapared microrolls with diameters ranging from a few microns to some tens of microns can be sintered to prepare oxide structures. Proposed applications of such novel structures include biomaterials, sustained release, catalysis, sensorics, high temperature and optical applications.

2. SOL-GEL METHOD

2.1. Introduction

Sol-gel is usually referred to as a method for producing ceramic materials that differs from the conventional high temperature preparation strategies (melting or sintering above 1000 °C) by being carried out at relatively low temperatures. The acid catalyzed hydrolysis-polymerization of tetraethoxysilane (TEOS) serves as an excellent example as a process by which amorphous silicon glass is obtained at temperatures below 100 °C.

Work by Ebelmann in 1846 [1] is considered to be the first publication related to sol-gel processes. Nevertheless, this method did not gain significant interest until the 1970-s, as only then its great potential was realized in the production of glass and ceramics directly from the solution of synthetic organo-metallic compunds instead of minerals. By doing so ceramic material can be synthesized directly into desired shape, excluding energy consuming melting and sintering from production process.

Organometallic compounds that can be synthesized using different methods are higher purity precursors, compared to mined oxides that are usually difficult to separate and refine. Also, precise adjusting the composition of sol-gel prepared ceramics can be easily done by mixing suitable compounds of different metals. Relatively low processing temperatures also make it possible to dope ceramics with various organic compounds or biomolecules that have low decomposing temperatures. Although sol-gel is usually used for preparing different oxides, other compounds like nitrides, carbides, fluorides, sulfides, oxynitride and -carbide glasses have also been obtained. Sol-gel materials in the shape of monoliths, fibers, films, membranes, aerogels, nanoparticles and powders can have applications that are based on their optical, thermal, electrical, mechanical, chemical or biological properties [2].

Although some precursor compounds used in sol-gel methods can also be expensive, the main difficulties are usually connected to gel drying, aging and heat treatment that are often accompanied by cracking. One possible solution against material fracture can be elongated processes at more moderate conditions but resulting longer processing times can be a serious drawback in applications. Also, since sol-gel processes are sensitive to process conditions (e.g. reaction temperature, ambient humidity) then reproducibility can also be an issue. Sol-gel materials are porous (unless post treated at temperatures close to melting temperature) and amorphous in nature and thereby somewhat restricted in the range of applications.

Overcoming these difficulties, applications of sol-gel methods have grown to be a worldwide 1 billion USD market in 2006, one third in USA. Studies have predicted that the market has grown to 1,4 billion USD by 2011 [3].

2.2. Terminology and processes

In his comprehensive „Sol-Gel Science" [4] (published in 1990), J. Brinker defined sol-gel as a method for producing ceramic materials by through the stages of sol preparation, gelation of sol and solvent removal. Sols, prepared from compounds that contain a central metal or half metal atom and surrounded by organic ligands (alkoxides) or non-metallic atoms (halides), are suspensions of ~1–1000 nm solid particles in a liquid. The particles can be polymeric clusters or have composition close to oxide material. The gravitational forces between sol particles are negligible and interactions are dominated by van der Waals attraction and electrostatic forces between surface charges. The solid particles are capable of continuously joining in larger agglomerates until gel is formed, a composite system that comprises of two continuous phases: a solid network and liquid that fills the voids. The liquid can therefore be removed without breaking the solid framework to obtain xerogel (dry gel). Aging and sintering raise the density of the material- surface energy decreases while the voids left by the solvent are filled. Brinker classifies all metal and half-metal oxides, nitrides, carbides, both crystalline and noncrystalline, pure or organically modified (e.g. Ormosil, Ceramer) as ceramics and sol-gel is suitable for producing all of these materials.

Sakka, one of the most influential authors in sol-gel research, on the other hand, defines the method solely through the transition process from sol to gel that is specific to sol-gel method [2]. That kind of definition is nor bound to the definition of sol, that can greatly vary in its nature between different works, although some authors restrict sols to being oligomeric solutions of polymerized alkoxides. As only transition metal alkoxides were used in present work then the following overview will only cover processes in to metal alkoxide systems.

The principle idea of sol-gel chemistry is rather trivial: the reaction of metal alkoxide ($M(OR)_n$) with water to produce hydrolyzed alkoxide ($M(OH)_n$) as follows [5]:

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH \quad (1)$$

Hydrolyzed alkoxide is very reactive and immediately condensates, yielding M-O-M linkage:

$$(OR)_3M\text{-}OH + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M(OR)_3 + H_2O \quad (2)$$

or

$$(OR)_3M\text{-}OR + HO\text{-}M(OR)_3 \rightarrow (OR)_3M\text{-}O\text{-}M(OR)_3 + ROH \quad (3)$$

Condensation progresses, resulting in formation of oligo- and polymeric chains $(\text{-}M\text{-}O)_n$. The mixture of these particles in a solvent is referred as polymeric or colloidal sol depending on the shape of the particles [6]. Polymeric alkoxide

molecules are less mobile than monomers and oligomers, but still reactive and continue the condensation, eventually leading the $(\text{-M-O})_n$ bonding to spread over the entire reaction medium.

The term sol usually refers to a precursor material that has properties that are suitable for material forming. Some water is in most cases added to the precursor compound(s) (the amount is usually given by R that stands for water to alkoxide molar ratio) to obtain partially hydrolyzed and polymerized material. Most authors nowadays agree that reaction processes start by formation of dense partially crystalline metal-oxo nanoparticles sterically stabilized by a shell of alkoxy groups. In later stages, the particles can form different secondary structures like gel networks, clusters, linear chains etc. [7].

Although sol-gel method is widely considered as chemical one, it is usually combined with mechanical shaping of the substance before the gelation. Such combination enables the preparation of structures with different functional shapes. Concentrated sols (containing only traces of solvent) are used for fiber pulling [8] while sols containing only some percent of oligomeric material are usually suitable for dip coating [9]. The properties of a sol also depend on pH value (both acid- and base-catalysis are possible), other catalysts (e.p. exposure tu UV), reaction time, temperature, alkoxide concentration during sol preparation and ambient humidity.

The very same polymerization reactions, accompanied by the evaporation of solvents are also responsible for gelation that follows material shaping. Final polymerization and material densification is achieved by gel aging and sintering.

2.3. Sol-gel material shaping

Sol-gel technologies based on the processes described in the previous chapter are suitable for the production of oxide structures from various oxide materials and their mixtures with different sizes and geometries by different sol-gel material shaping strategies (see Fig 2.3.1)

The earliest (for example a solution for changig the reflectivity of glass [11]) and most numerous applications of sol gel are based on thin films and coatings, dating back to 1940s. For example, windows of large buildings are sol-gel coated with titanium oxide [12]. In most cases partially hydrolyzed metal alkoxide solutions in organic solvents (e.g. hexane) are used as the sol precursor. A sol layer of suitable thickness is applied on the substrate usually by spin or dip coating. The latter is suitable for covering structures with very different shapes for example also biologic samples [13] or carbon nanotubes [14]. More recently also spray methods [15–17] and electrophoretic deposition [18] have been developed. Usually films of up to 200 nm thickness are prepared by a single coating cycle to avoid cracking. Even if the coating procedure is repeated, crack-free films with thickness exceeding 1 μm are difficult to produce without adjusting material composition [19]. Various uses of sol-gel films include reflective, anti-reflective, colouring, electrooptical, optoelectronic,

optical memory, superconductor, photo-anode, electrically conductive or insulative, anti-corrosion, surface smoothing, wear resistant, reinforcing, hydrophilic, hydrophobic, catalytic or sensor layers.

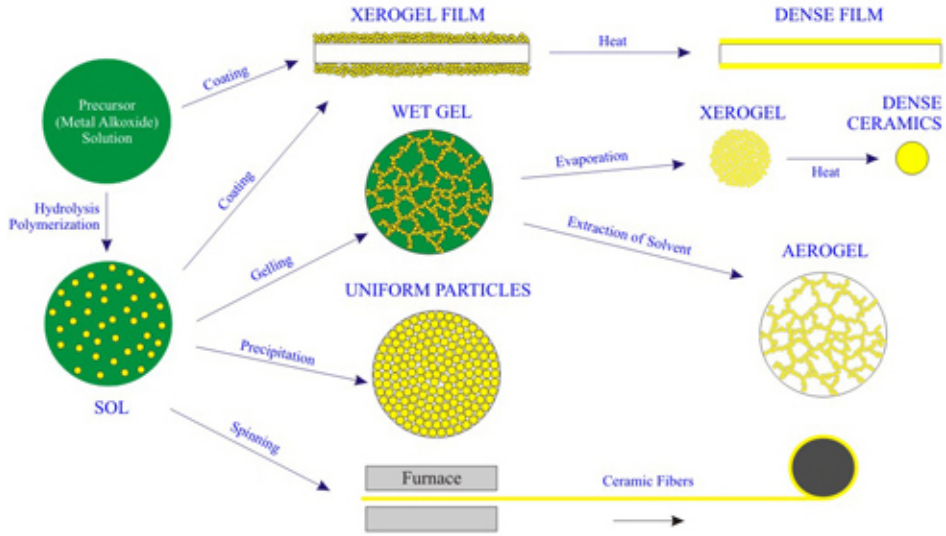

Figure 2.3.1. Main sol-gel shaping methods [10].

Liquid substrate methods have been developed in order to avoid film cracking [20]. In such case the polymerization takes place on the interface of two immiscible phases without the gelling medium being rigidly bound to a surface. That decreases the mechanical stress caused by material shrinking of the material. This ideology has been adapted for preparing silicon oxide glass [20] and Pb-Zr-Ti-oxide films [21].

Film cracking can be acceptable or even induced in some cases since it leads to increase in the specific surface area of the material [22]. Excluding the latter case, sol-gel film cracking has been treated as an unwanted process that is addressed by phenomenological [23–28] or theoretical [29] studies. Howevwe, all these works have covered films that are firmly attached to substrates and no generalized knowledge has been established.

Powders are usually the most suitable shape of oxide materials in applications, for which large specific surface area is desired. In order to obtain small gel particles, hydrolysis and polymerization of alkoxides is carried out so that many spherical particles are nucleated, grown until the suitable size and precipitated without a continuous gel phase being formed throughout the whole reaction medium. Powders are conventionally used to prepare polycrystalline ceramics by pressing and sintering, sol-gel powders are used in catalysis, pigments, abrasives and composites, electro-optical and magnetic systems [4].

Aerogels are structures specific to sol-gel method. The solvents are removed from gel material by supercritical extraction and no capillary forces are generated that would shrink the pores left by the leaving solvents. Aerogels have large specific surface area (800 m^2/g [30]), superior thermal and sound isolation properties, low refractive index and dielectric constant close to gases [31].

In order to produce monoliths (dimensions larger than 1 mm) the amount of added water needs to exceed the theoretical amount needed for complete hydrolysis of the alkoxide [32]. In such case the formation of highly branched three-dimensional polymer structures is preferred. Hydrophobic reaction vessels have to be used to minimize bonding with the gelling material, also the drying and sintering processes have to be slow. The applications of monoliths are in most cases based on their optical properties (transparency, the possibility to prepare materials with a gradient in refractive index).

Sol-gel fibers are prepared by drawing (or pulling) sol jets from viscous sols in environment with suitable humidity [8, 33] or electrospinning [34]. In addition to numerous different optical applications, sol gel fibers have also been used in composites, electrolysis or as superconductors[4].

Besides being used as the reinforcing phase in composites (for example in fiber form), sol-gel material can also serve as the matrix phase. Amongst other possible fillers or additives, organic dopants have been included to obtain organic-inorganic materials [35], added carbon nanotubes have been shown to enhance the electrical conductivity of sol-gel materials [36].

3. TUBE AND ROLL-SHAPED MICRO- AND NANO-STRUCTURES

As present thesis concentrates on a novel method of film rolling that leads to the formation of microtube stuctures, then a brief overview of some most similar structures from metal oxides and analogous shaping methods of different materials is given in present chapter. Nevertheless, it is important to stress out that the method and structures presented in present work are still clearly distinguishable and unique, as also evident from the following overview.

Tube-shaped structures in natural asbestos have been studied already 80 years ago [37]. The existence of these nanotubes was proved 20 years later with the aid of electron microscopy [38]. Some natural mined minerals with layered structure, for example kaolinite ($[Al_4Si_4O10](OH)_8$) and serpentinite ($[Mg_6Si_4O_{10}](OH)_8$) are the precursors for thin sheets (some atomic layers thick) that are peeled off due wear processes in the nature. These minerals consist of alternating layers of octahedral and tetrahedral atomic arrangement, the crystal lattice parameters of these layers are mismatched. That, in turn is the cause of mechanical stress in mineral nanosheets that causes rolling [39]. Formed tubes can be both concentric or spirally rolled [40](see figure 3.1.). This kind of materials are often reffered to as halloysite.

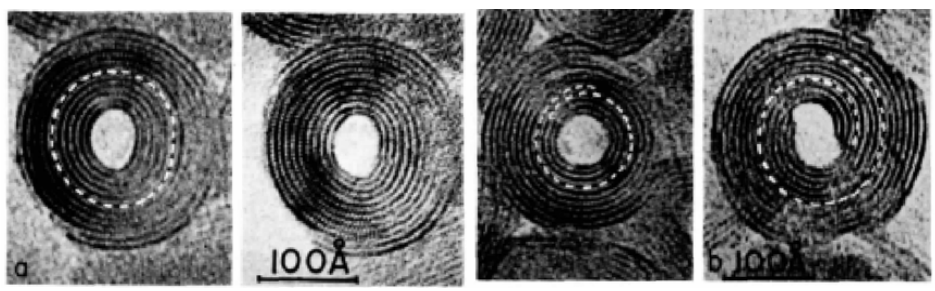

Figure 3.1. SEM images of chrysotile nanotubes with a) concentric b) spiral structure [40].

The diameter of these natural silicate nanotubes is typically 40–200 nm, length ranges from 0.5 to 10 μm (see figure 3.2.). Good electrical and thermal isolation properties, high tensile strength, chemical and thermal resistivity and large surface area make these materials make them attractive for applications like composites, absorbers, controlled (or sustained) release and high-tech ceramics.

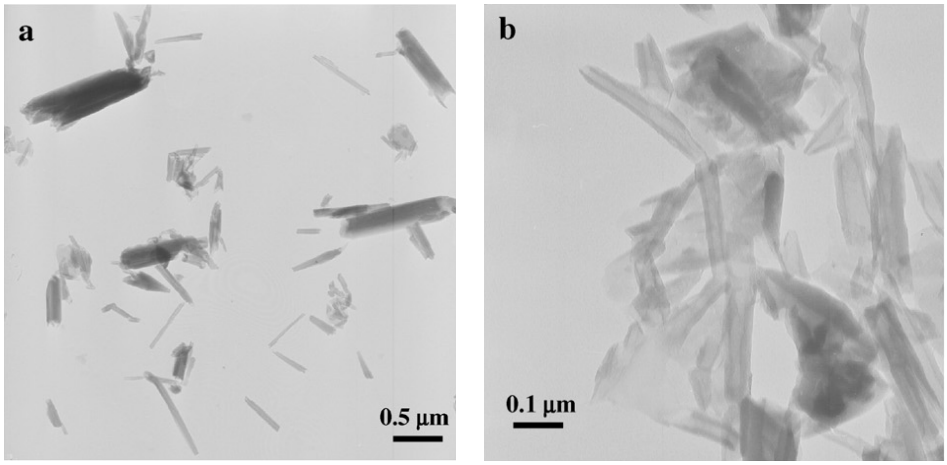

Figure 3.2. SEM images of halloysite nanotubes [41].

Since natural materials have significant variation in composition, morphology, structure and size, also synthetic analogues have been elaborated, potentially applicable in non-linear optics or isolation for nanometric conducting wires [42].

Natural silicate nanotubes are abundantly present in nature and are easy to mine. Most important factor that limits wider use is the absence of industrial purification and separation technologies [43]. However, solutions based on natural silicate nanotubes have been predicted to become more popular and hold 47% of nanocomposite plastic market in 2011 while materials based on carbon nanotubes are predicted to take up only 7,5% of the worldwide nanocomposite market [44].

Several compounds, for example dichalcogenides of some metals have layered inner structure, similar to graphite. Atoms are bonded in two-dimensional layers that are held together by van der Waals forces. Similarly with carbon, these materials also have a stable nanotube material form. The first inorganic nanotubes were prepared from WS_2 [45] (see figure 3.3.). Since then a number of different materials have been obtained in nanotube shape, including MoS_2, BN, VO_x, $NiCl_2$, $NbSe_2$, ZrS_2, HfS_2, NbS_2 ja TaS_2 [46–49]. Both gas or liquid phase growth preparation methods are possible.

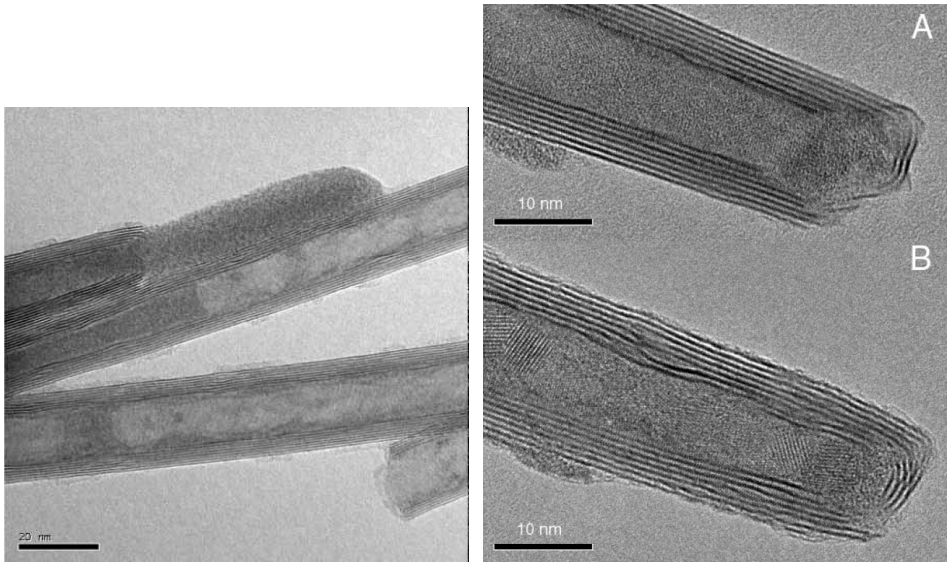

Figure 3.3. Electron microscope images of WS_2 nanotubes [50]

Such nanotubes of layered materials are usually monocrystals and and have concentric symmetry. The latter property makes these materials chemically inert and mechanically resistive, for example WS_2 and MoS_2 nanotubes and –spheres are suitable lubricants in extreme conditions [46].

Titanium oxide does not have graphite-like layered structures. However some methods have been elaborated for producing titania (or titanate) nanotubes. Crystalline powders are chemically treated to produce nanosheets of the material [51–53]. As these sheets are very thin (some atomic layers) and flexible, then they form stabile roll structures to minimize surface energy and eliminate dangling bonds [46]. 5–80 nm in diameter, up to 1 μm long nanotubes are obtained (see figure 3.4.).

Lamelles can be prepared through hydrothermal [51–54], solvothermal [55], intercalation-exfoliation [56] or sonochemical treatment [57]. As the precursor material, also sol-gel prepared oxide powders have been used [51–53]. The formation of titanium oxide nanotubes has been attempted to be explained by several theories from rolling to growth of monocrystals from the liquid phase [55–58]. Different authors have reported various material composition and crystallinity (TiO_2 [60], $Na_2Ti_2O_4(OH)_2$ [62]). Remarkable photocatalytic properties make titania nanotubes attractive materials in NO_x separation, water purification, hydrogen generation or solar panels. [63].

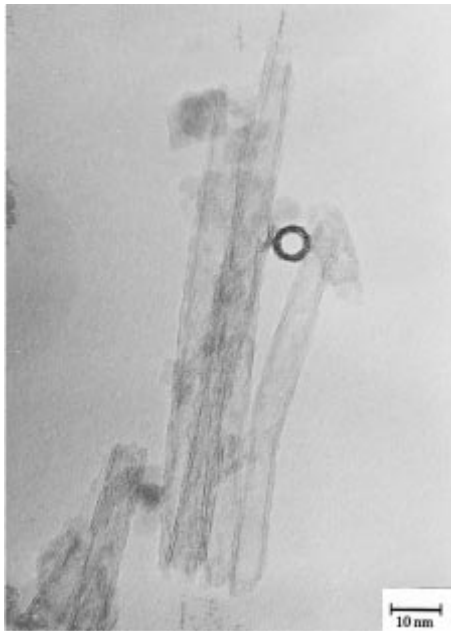

Figure 3.4. TEM images of TiO_2 nanotubes [51].

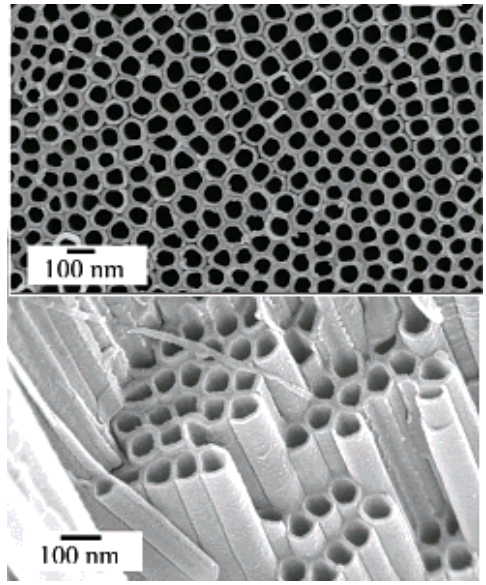

Figure 3.5. SEM images of TiO_2 nanotube arrays from anodization [64].

Oriented matrices of titanium oxide nanotubes can be prepared by anodization of titanium surfaces [64]. Dense forest of up to 360 μm high tubes with diameters from 10 to 100 nm (see figure 3.5.) is a high porosity titanium oxide material that has superior hydrogen sensing properties [65].

Perhaps the most flexible and controllable approach to micro- and nanotube production is coating templates of suitable shape and size. Among others, carbon nanotubes [66], that are burned out of the material subsequently, anodized alumina membranes [67] and different biological structures [68] have been used as templates. Coating technologies very different in their nature have been used, both chemical and physical, for example sol-gel [66] and atomic layer deposition [69]. Template structures are usually damaged or consumed and removal of the latter can often be complicated procedure.

One of the methods that relates most directly to rolling of gel films that is covered in present thesis, is rolling of stressed multilayer films. In that case layers of materials with mismach in crystal lattice parameters are deposited sequentially [70]. The film structure is then released from the substrate by etching underlying sacrificial layer. Stress is relaxed by rolling of freestanding multilayer films into tubular structures (see figure 3.6). If multilayer film structures are thin enough, then no mismatch between layers is necessary as such thin layers act the same way as the aforementioned nano-lamelles and roll to minimize surface energy [71, 80, 81]. Sacrificial layer, however, which is etched to release the film structure, is still necessary.

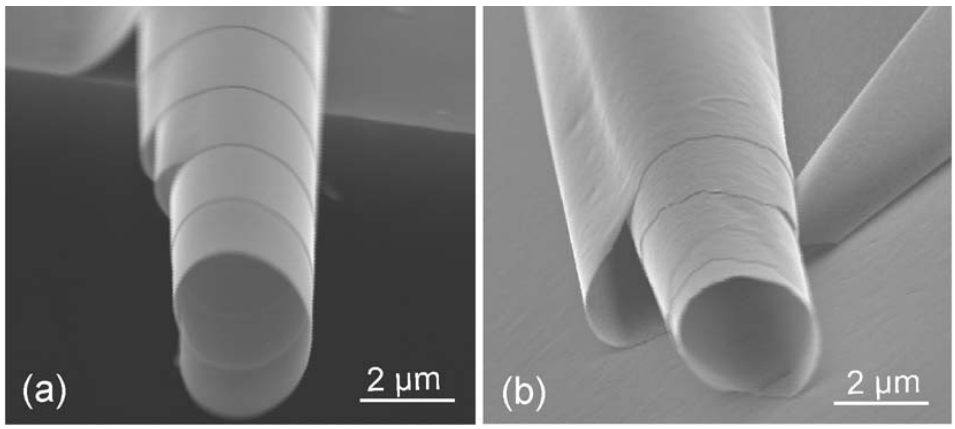

Figure 3.6. SEM images of a) Si, b)InGaAs microrolls obtained by thin film rolling [84].

The strategy of strained multilayers was originally elaborated for the production of semiconductor structures that would be compatible with already established semiconductor technologies in MEMS [70]. This method has been later adapted to metals [71–74], polymers [75, 76] and silicon oxides [77–80] while enables the preparation of tubes with inner diameters from 15 nm [81] to 6 µm [82] and up to 30 fold walls [81]. Vacuum methods as molecular beam epitaxy [70, 76, 77], electron beam sputtering [71–74,78–80] and chemical vapour deposition [82] have been used as deposition techniques. Polymeric layers are usually prepared by dip coating or spin coating [75]. Although direct deposition of films with suitable dimensions by using masks has also been realized [70,82], suitable shape and size areas are in most cases separated by nanoindentation, electron beam [70, 71–74], ion beam [75], optical or photo- [79, 80, 83] or predefined cracking-assisted lithography [70]. One paper can be pointed out specifically as being most closely related to the formation ideology covered in present thesis. Paper published by Urena in 2009 [73] (therefore after our first publications on tubular structures by rolling[Papers I, II]) includes, in addition to more directed approach, the description of the formation of microtubular structures from self-cracked strained films. However, used deposition methods, multilayer structure of the film and presence of a separately deposited sacrificial layer make it significantly different from ours.

The emerging field of strained film rolling is in its infantry, the first paper dates back to 2000 [70] and only some very promosing earliest works have been published on their applications as optical resonators [72, 79], catalysts [72], microsensors [73, 77, 87], microfluidics components [72, 86, 87] and biomaterials [78, 80, 88].

4. MICROROLLS FROM Ti-, Zr- AND Hf- BUTOXIDES

4.1. Aims of the study

The formation of roll structures from concentrated hafnium alkoxide gels by partial gelation, gel film cracking and film segment roll-up was discovered by the author of present thesis and his co-workers in 2005. The simplicity of these sol-gel processes and the cognitive potential of obtained novel shape structures from IVB group metal oxide materials with remarkable properties inspired more thorough studies.

Following research objectives were set in the direction of realizing the potential of this novel material in possible applications:

- Clarification of the nature of the processes that lead to the formation of studied microstructures.
- Characterization of the morphology and structural properties of studied rolled microstructures.
- Elaboration of repeatable and controllable methods for microroll production.
- Adaption of elaborated preparation methods to different metal oxide materials.
- Initial of evaluation of the potential of elaborated method for the production of different size roll-structures.
- Development of a theoretical model for the explanation of gelling, cracking and rolling processes through simulations.
- Identification of possible applications for microstructures prepared by metal alkoxide gel rolling.

4.2. Formation processes [papers I–V]

In general, the procedure for the preparation of rolled microstructures can be described as follows (also explained by Fig 4.1.). First a portion of moderate viscosity sol is applied on a surface and is thereafter distributed evenly on the surface. In this work different rotating surfaces were used for that purpose. Next solvents are removed from the even layer to obtain a film of viscous, non-flowing precursor. The material is then exposed to relatively high humidity causing hydrolysis in the surface layer of the metal alkoxide precursor. Thereby a gel film is obtained. The formed film cracks during gelation and is thereby spontaneously divided into segments. The film segments are thereafter released by adding a solvent that dissolves the remaining non-gelled precursor beneath the gel. Freestanding film segments have a tendency to curl and depending on the process parameters, different structures ranging from slightly arched leaflets to tubelike roll structures with ten fold walls can be obtained. Different

experimental setups were used for different precursor compositions at varied conditions to explore the possibilities of this developed method.

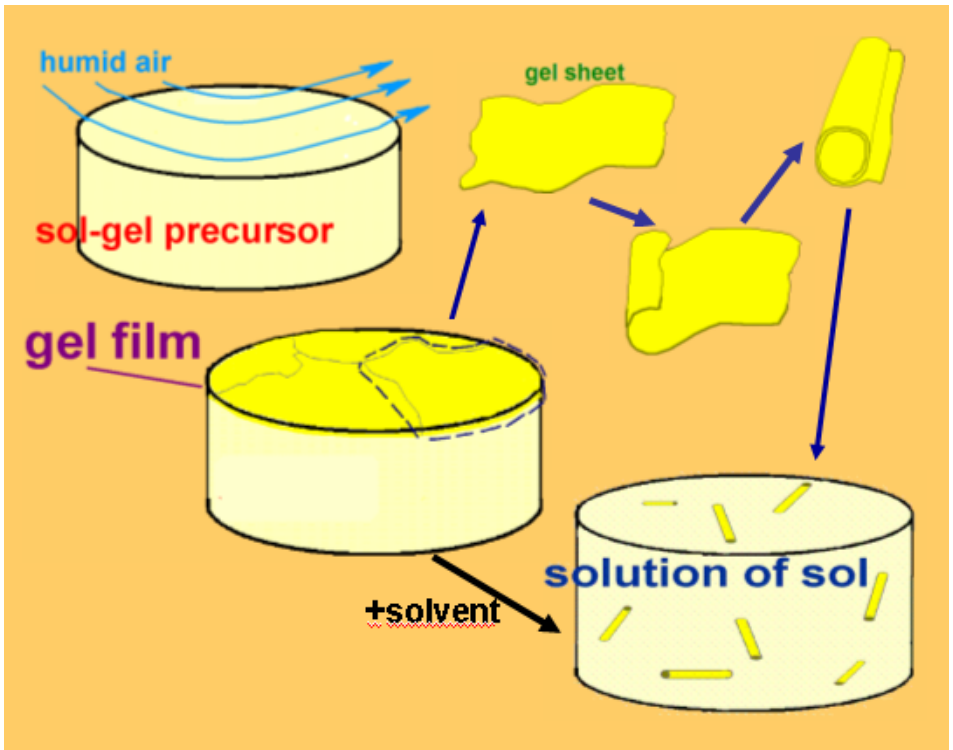

Figure 4.1. Formation of gel film and rolling of film segments

The underlying reason for self-rolling of is mechanical stress gradient in the gel film(presented schematically in figure 4.2.). The origin of differential stress can be explained by several different general reasons, or more likely a combination of these. First, as described by G. W. Scherer [89], when a gel plate dries from only one side it becomes concave towards the drying side that is accessible to water from ambient environment, causing hydrolysis and subsequent polymerization. In addition, solvents (alcohol is one of the products of hydrolysis and polymerization and is also generated in the material) also evaporate faster from the surface layers of the material.

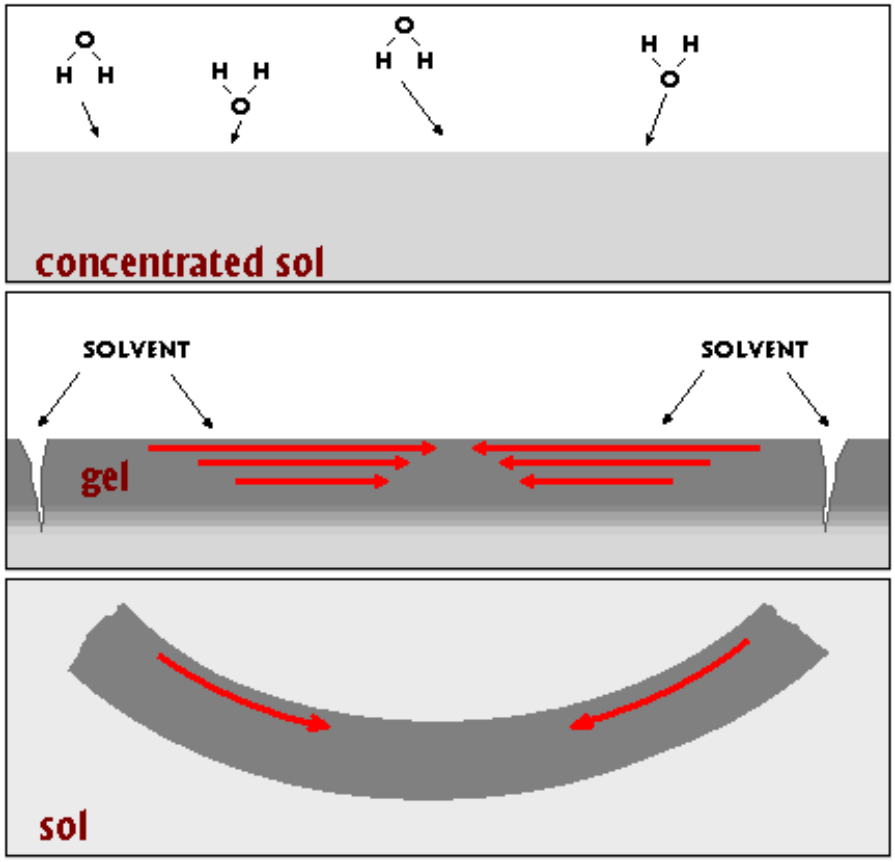

Figure 4.3. Schematical representation of gelation-induced stress and gel curling.

We use concentrated sol as the precursor in the process and the reactivity of used precursor materials ($Ti(OBu)_4$, $Zr(OBu)_4$ and $Hf(OBu)_4$) is relatively high (as compared to TEOS for example). For these reasons the diffusion depth of water molecules is expected to be short and gelation is restricted to the surface layers. As hydrolysis, polymerization and solvent evaporation processes take place in the material, it also becomes progressively denser, the diffusion of water molecules through the gel layer formed on the surface into deeper material and solvent removal from deeper layers are hindered even further. The densification speed is the highest on the surface and decrases gradually in deeper layers. We have also used relatively high humidity leading to effective gel film formation and subsequent formation of roll structures through quick surface gelation. For the aforementioned reasons, a gradient in gelation extent is expected to be established in the material.

In order to release the gel film sheets, the remaining sol under the gel layer is dissolved. Swelling of less polymerized part of gel can also be expected thereafter. This can lead to material expansion in the bottom layers of the gel

film, while the effect is considerably smaller in the upper fully gelled layer. Similar principle has been exploited in methods for obtaining micro- and nanotubes of polymer materials, whereas stress originates from physical or chemical factors having different effect on different material layers [76].

Cracking is the other (alongside rolling) spontaneous process that contributes to the formation of roll structures. Crack formation and evolution in sol-gel films has been studied in cases, where the film is firmly attached to substrate [23- 28] whereas bonding to a rigid surface has an important role in the fracture processes. In our case the film is formed on concentrated sol that can be thought as a viscous surface. To be more precise, no defined transition point between gel and sol layers exists and there is no substrate as such, each differential part of material can be considered to be homogeneous. Still, the viscosity of the sol does act in the opposite direction to the shear force originating from shrinkage. Therefore the situation can not be described as cracking of a freestanding film also. To develop a material preparation method that would have practical value, more knowledge about cracking needs to be gathered as the latter defines the dimensions (except rolling radius) of obtained microstructures.

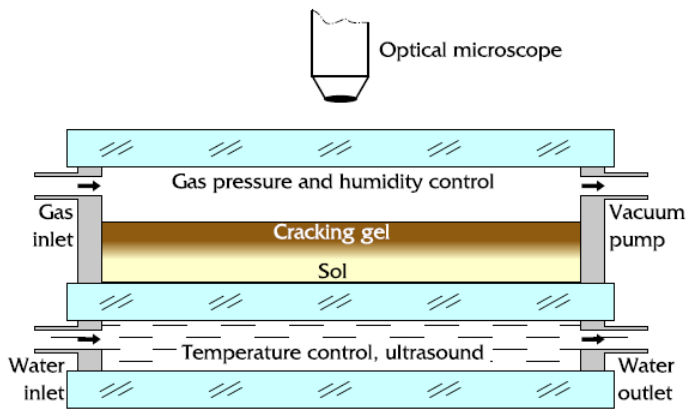

Figure 4.2.3. Experimental device for gel film cracking experiments.

A special experimental device was designed that allows controlling the temperature of gelling sol layer, gas pressure and humidity in air above the metal alkoxide based precursor layer (see figure 4.2.3.). The setup also enabled ultrasound treatment during gelling. As the result of experiments different cracking patterns were observed (see figure 4.2.4.). Generally the the cracking process sequence can be described as follows: in the first stage an initial straight crack is formed, followed by parallel cracks next to it. In the second stage, shorter cracks aligned diagonally in one direction are first formed in one direction between the initial cracks, followed by diagonal cracks in the opposite direction. Obtained rectangular segments form tube structures after dissolving the underlying sol (figure 4.2.4.c.). Experiments where ultrasound treatment was applied resulted in random patterns, curved cracks could be observed. This

can be explained by generation of disruptions that result in crack generation and non-uniform stress distribution that causes deviation from straight crack propagation.

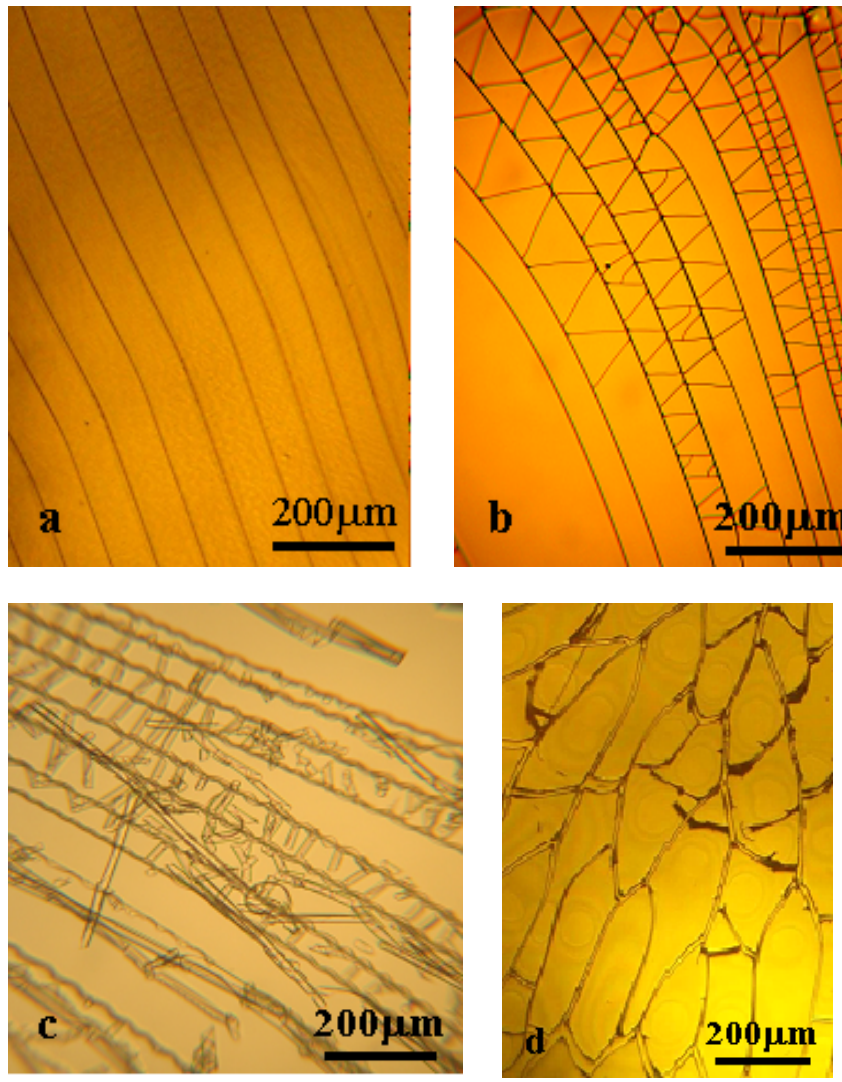

Figure 4.2.4. a)initial parallel straight cracks, b) crack patterns after the formation of secondary diagonal cracks, c) rolled structures obtained from cracked film similar to b), d) patterns formed by gelation during ultrasound exposure

Our results imply that reasonably uniform size and shape structures can be obtained at suitable conditions on small areas. Precise control over gelling processes on large surfaces can turn out to be, however, significantly more complicated.

4.3. Structures from different metal compounds [papers I–III]

Sol–gel method is suitable for obtaining a wide range of ceramic materials, although many properties of different organometallic precursors vary to some extent [6]. Thus, we expect that this introduced general route can be applied for obtaining tubular structures from a number of different compounds. As $Hf(OBu)_4$ was the precursor that was used in the first experiments that let to the formation of rolled microstructures, $Ti(OBu)_4$, $Zr(OBu)_4$ as compounds of other metals with similar chemical properties were also used in this work.

Different precursor compounds require somewhat different approach to the preparation of sol. The main considerations are:

- There should be as little mixing as possible in the precursor material when the sol layer is exposed to humid air for gelation, the mobility of molecules has to be low enough to keep gelling processes only in a thin surface layer. That can be achieved by low solvent concentration in the precursor, partial polymerization of the precursor and choosing a precursor compound that already has higher viscosity.
- For the same reason, to gelate only the surface layer, the reactivity of the precursor has to be high so that the water above the precursor layer would react with precursor molecules in the surface layer, rather than diffuse deeper in the precursor. For that precursor compounds with relatively high hydrolysis speed should be preferred and extent of precursor polymerization should be kept as low as possible, as the hydrolysis of molecules that are already partially hydrolysed and polymerized is considerably slower.

It is noteworthy that the hydrolysis/polymerization extent of used precursor has a role in both considerations, so it is preferrable to use adjustment of partial hydrolysis/ polymerization of used precursor compound as the last means for the adjustment of precursor properties.

Promising results were obtained by following a simple procedure on rotary evaporator using $Zr(OBu)_4$ with no prior hydrolysis. The butanol in 80% $Zr(OBu)_4$ was first removed and replaced with hexane, a more volatile compound to ensure removal when the layer of concentrated sol is formed. A solutuon of $Zr(OBu)_4$ in hexane with low viscosity was distributed evenly on the inner surface of roundbottom reaction flask by centrifugal forces generated due to rotation of the flask. A non-flowing film was then obtained after vacuuming and the bulb was detached from the evaporator above the water bath heated at 80 ºC before the pressure inside the bulb had decreased to normal, at approximately 730 mmHg. This causes the humid air to flow quickly over the sol surface and cause gelling in a flash. Formation of needle-like structures could be observed after adding hexane. The structures were separated from remaining sol by several cycles of diluting with hexane and decanting. SEM studies revealed roll structure of gel structures with 2–6 μm outer diameter and up to 150 μm long (see figure 4.3.1). Thickness of rolling gel film was estimated to be 200–400 nm.

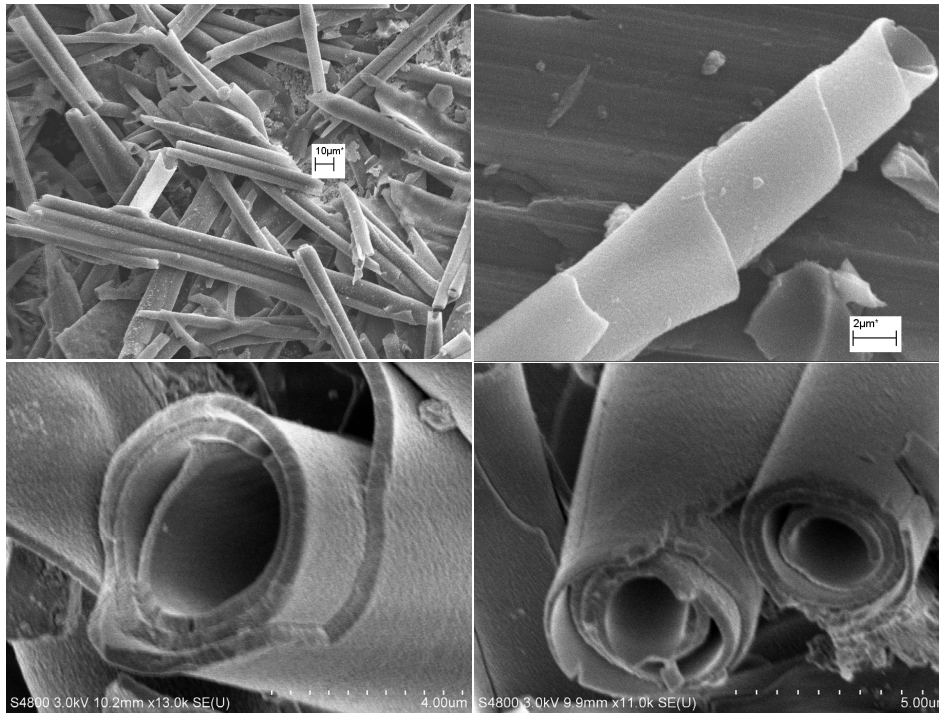

Figure 4.3.1. SEM images of showing the roll-geometry of $Zr(OBu)_4$ gel structures.

Used setup was developed in order to make the processes more repeatable. Plastic tubes were attached to the air inlet stopcock of the evaporator apparatus: one inside the device, leading to the air from the inlet to the reaction bulb and the other outside the evaporator for collecting humid air from above the water bath (see figure 4.3.2.). These small additions enabled constant flow of humid air over the sol layer over longer periods.

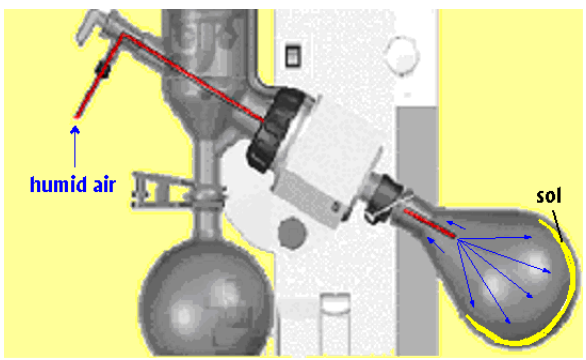

Figure 4.3.2. Rotary evaporator-based experimental setup enabling constant flow over sol surface.

Although the water bath temperatures and reaction times given for the following experiments as system parameters cannot be used as absolute or universal guidelines for reproducing the results, they are still useful for qualitative comparison between different experiments using the same setup.

$Hf(OBu)_4$ was also used as purchased, 45% solution in hexane (ABCR), as the solution has suitably low viscosity. Concentrated $Hf(OBu)_4$ that is obtained after removing the hexane is seemingly solid, high viscosity liquid. Water bath temperature was set on 60 ºC, the time of continuous ventilation with humid air was 1 minute. The product obtained after washing was characterized by optical microscopy (see figure 4.3.3.). The gel structures have predominantly tubular shape with outer diameters in the range of approximately 2–5 μm and lengths in the range of 5–100 μm. The presence of leaflets and partially curled gel sheets is also evident.

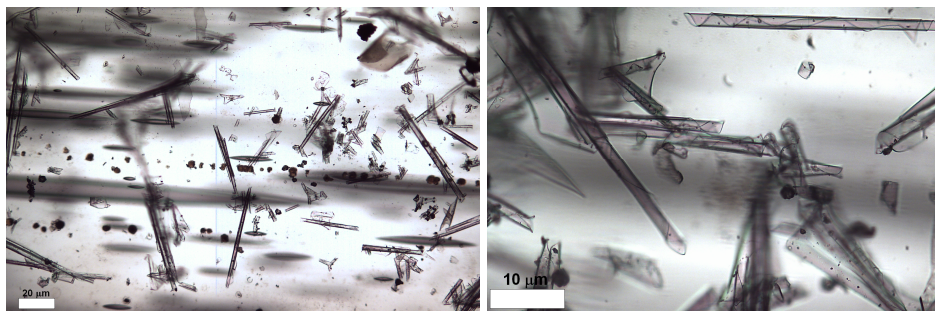

Figure 4.3.3. Optical micrographs of gel structures formed by rolling of gel film segments obtained from $Hf(OBu)_4$.

$Ti(OBu)_4$ has lower viscosity than Zr and Hf analogues. It was therefore partially hydrolysed at R=0.8 ($R=n(H_20)/n(Ti(OBu)_4$) in the presence of HCl in order to obtain a non-flowing sol layer after solvent removal. Solvents were removed from freshly prepared sol by evaporation while the flask was rotated on 80 °C water bath. Next a constant flow of air with controlled humidity was continuously directed through the reaction flask during a period of 2 minutes. Obtained structures were washed with mixture of 80% hexane and 20% butanol. Compared to the experiments with Zr- and Hf- alkoxides, the present one gave the poorest results in yield and the stability of obtained gel structures during washing. Nevertheless, the presence of rolled ubular structures in obtained material was clear (see figure 4.3.4.). Dimensions of obtained roll- structures were similar to aforementioned Hf- and Zr- butoxide gel structures.

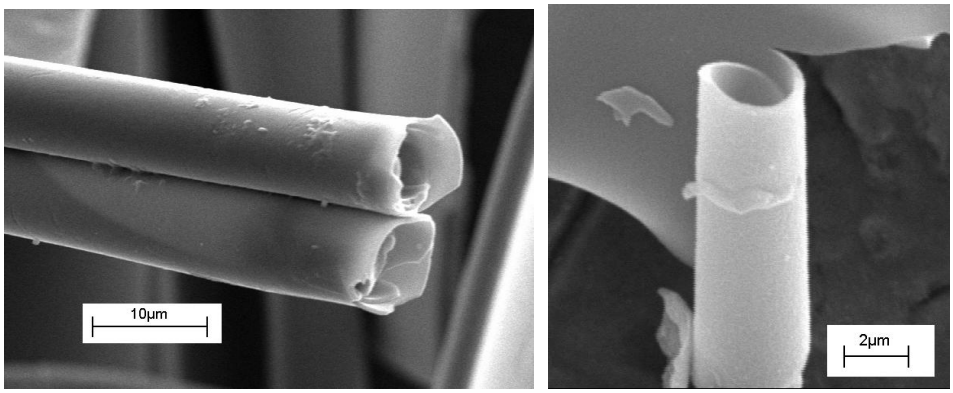

Figure 4.3.4. SEM images of obtained $Ti(OBu)_4$ gel structures.

In order to study the optical properties and crystal structure of the microrolls, Sm -doped ZrO_2 structures were prepared. For that $SmCl_3*6H_2O$ was also added with water and a small amount of catalyst HCl to prepare a sol with R≈0.6 and samarium content that would lead to 0.5 mol% concentration in the oxide obtained after sintering. 1 minute of exposure time with air from above 80 ºC was used. Obtained powder of rolled gel film segments was estimated to be of relatively poor quality, containing mostly partially rolled film segments.

After preparation the samples were annealed step by step at 500, 600, 700 and 800 ºC. After each step photoluminescence spectra of the samples were measured. In addition also Raman spectra were recorded on the surface of the microrolls. The samples were also characterized by XRD and weight fractions (mass %) of the tetragonal and monoclinic phases were determined. Optical studies revealed excellent photoluminescence properties of Sm^{3+} doped zirconia microtubular structures as PL emitters. Investigation of phase stabilisation dynamics revealed that the microrolls have good dopant stabilised tetragonal crystal structure up to 600 ºC which undergoes complete tetragonal to monoclinic phase transformation at 700 ºC. The phase transformation starting at the surface of the roll layers triggers significant volume change in nanocrystallites which leads to macroscopic scale breaking up of the microrolls.

4.3. Size tuning [paper III]

Rolling diameter is depends on gel film thickness as well as steepness and range of established gelation gradient. Both of these parameters are expected to be strongly linked to experimental parameters such as the concentration and reactivity (depends on extent of hydrolysis) of the precursor material, water content in the gaseous environment above the precursor layer during gelation, time of exposure to the humid environment and more weakly to temperature. In order to achieve sufficient control over these parameters a special device was designed based on a rotating cylinder situated in an isolated chamber. In the experiments the precursor is distributed on the outer surface of the moving cylinder as a solution of suitable viscosity. The solvents are then removed by vacuuming while the cylinder is continuously rotated to obtain a still layer, followed by gel film formation by exposure to humid air.

Several series of experiments were carried out varying the extent of initial hydrolysis/ polymerization (R) of $Zr(OBu)_4$ precursor and the time of exposure to humid air. Mean thickness of obtained gel films as well as the inner diameter was estimated by averaging over 20–30 rolled structures measured in SEM as relatively small number of roll structures could be produced in one cycle on used device. A logarithmic trend in both, the thickness and rolling diameter dependence on the exposure time was evident (see Fig 4.3.1 and 4.3.2). The shape of these curves can be explained by unisotropic processes, as the gelling starts from the surface, a increasingly thick layer of gel layer is formed that progressively inhibits the diffusion of additional water molecules to deeper material layers and removal of the solvent generated in the gelling process. Therefore the decrease in gel film thickness growth speed is expected. Similar rise in the dependence of rolling diameter and film thickness in experiments with different R values (see Fig 4.3.3.) can be taken as proof of the formation of gelling extent gradient being independent from the extent of initial hydrolysis extent of the precursor. The analysis of this kind of experimental data could provide much more valuable information about the gelling processes in general if studied more closely but further conclusions based on the estimating results described hereby would have to be considered as speculations.

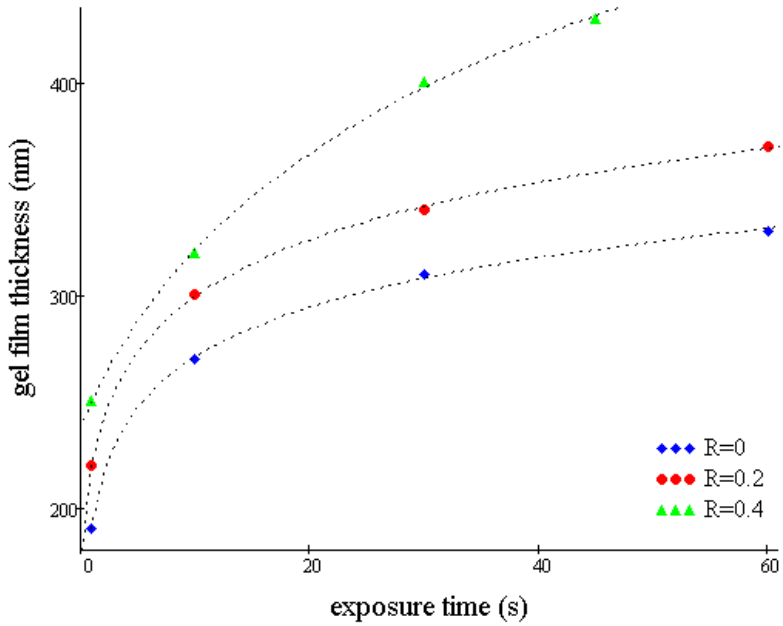

Figure 4.3.1. Dependence of gel film thickness on exposure time to humid air. Dotted lines represen logarithmic fit to experimental series.

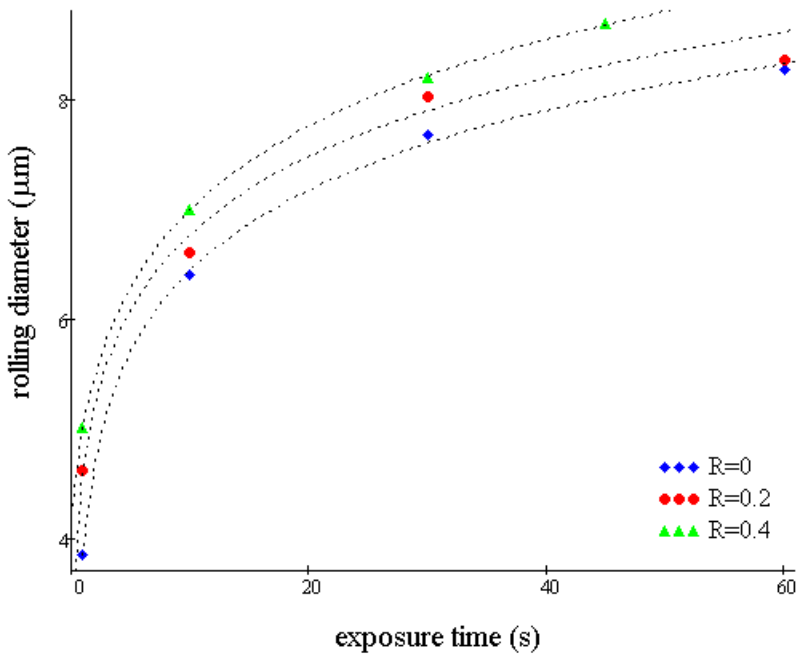

Figure 4.3.2. Dependence of gel film rolling diameter on exposure time to humid air. Dotted lines represen logarithmic fit to experimental series.

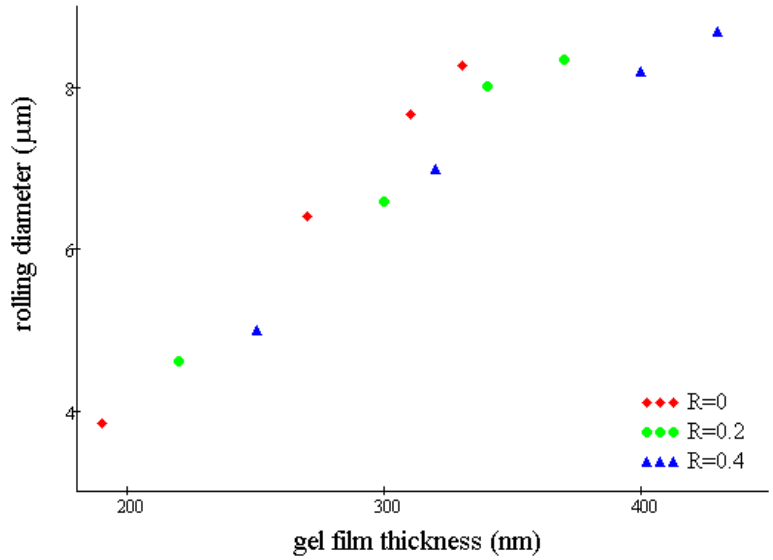

Figure 4.3.3. The relation between gel film thickness and rolling diameter.

4.4. Annealing [papers II, III, VI]

In order to observe the shrinkage of tubular structures during heat treatment, the samples were removed from the oven at certain times and photographed through optical microscope.

Total shrinkage in length was estimated to be 25–30% in case of $Ti(OBu)_4$ microrolls (see Fig 4.4.1.). The carbonization of organic species was observable at 340 ºC turning the structures black. Good optical transparency was achieved at 500 ºC.

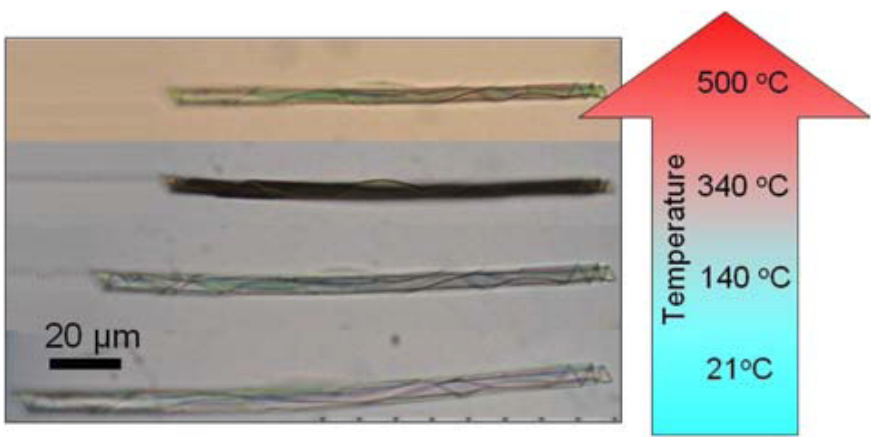

Figure 4.4.1. Shrinkage of $Ti(OBu)_4$ microrolls during annealing

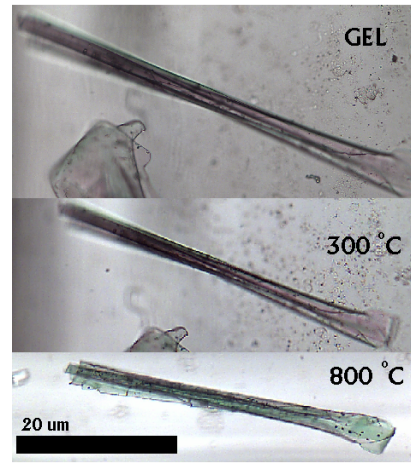

Figure 4.4.2. Optical micrographs of heated HfO_2 microroll.

Microrolls prepared from $Hf(OBu)_4$ were first heated to 300 ºC in 10 hours with a 5h dwell time, photographed and then heated to 800 ºC in 15 hours with 5 h dwell time. Shrinkage was comparable to what was seen in case of $Ti(OBu)_4$ gel structures (see Fig 4.4.2.). Temperature of 800 ºC has been shown to be sufficient for obtaining oxide material from $Hf(OBu)_4$ gels [90].

In order to overcome the problem of destructive effect of phase transformation in ZrO_2 during heat treatment, microrolls were prepared from $Zr(OBu)_4$ sols with prior hydrolysis at R=0.8 and yttrium concentration of approximately 2%. The latter was introduced as a solution of yttrium nitrate in water/butanol mixture during hydrolysis. Although obtained material contained large amount of partially rolled gel film segments and, tubular structures were also observed. The shape of microrolls was preserved after heat treatment similar to the annealing of hafnia microrolls at up to 800 ºC (see Fig 4.4.3.).

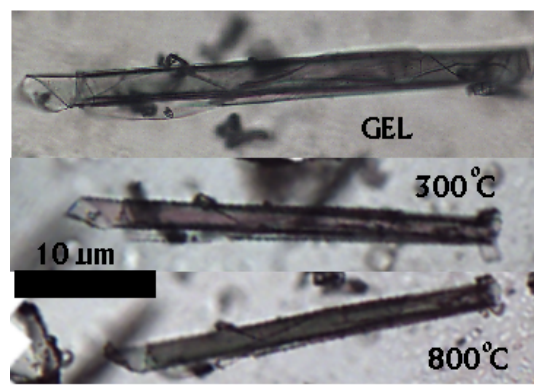

Figure 4.4.3. Optical micrographs of yttrium doped ZrO_2 microroll demonstrating material behaviour during annealing heat treatment

25–30% shrinkage can be explained by the removal of residual solvents and densification of gel network. This kind of behaviour is typical to metal-alkoxide-based sol-gel derived materials [89].

4.5. Simulation of self-formation processes [paper VII]

A discrete element method block-spring model was developed in order to simulate gelling, crack formation and evolution. Our model was aimed to mimic the features of cracking of gel films on viscous sol, the most significant of these is that the film is not fixed to a solid substrate. The formation of cracks can be only explained by the inhomogeneous contraction of the film, as in case of the film not attached to a rigid surface, no stress is generated by homogeneous contraction. This is supported by the fact that at the final stage of the experiment, the film fragments roll into tubes, which gives evidence for the stronger contraction of the upper layers of the film, as compared with the lower layers (i.e. layers closer to the liquid substrate).

The minimal model needed to describe such an inhomogeneous contraction, is provided by two layers of a triangular lattice of blocks. The springs connecting the blocks are placed between the nearest neighbours (both the same-layer neighbours, as well as the neihbours of the adjacent layer. It is implied that each block corresponds to a large number of atoms: approximately as many as corresponds to the half-width of the film. In order to describe the inhomogeneity of the stress and strain, the springs in the first layer, in the second layer and between the two layers have different force constants and relaxed spring lengths. Each spring has its own tensile breaking strength. Since the chemical bonds in the gelling material invlove a intrinsical quenched disorder, the tensile breaking strengths are obtained as random numbers in a certain range. Progressive changes in the material properties, such as the increase of force constants and decrease of relaxed spring lengths lead to instabilities in the form of spring breakages. Initially these values are set so as to ensure global stability. The configuration then evolves in discrete steps of the simulation time, according to the following rules:

(1) At each step, all the force constants are increased by a certain factor and all the relaxed spring lengths are decreased by a factor.
(2) If the tension in a spring exceeds its tensile breaking strength, the spring is broken.
(3) The spheres are moved to their new equilibrium position.
(4) The procedures 2 and 3 are repeated iteratively, until a new metastable state is achieved. This completes one simulation step.

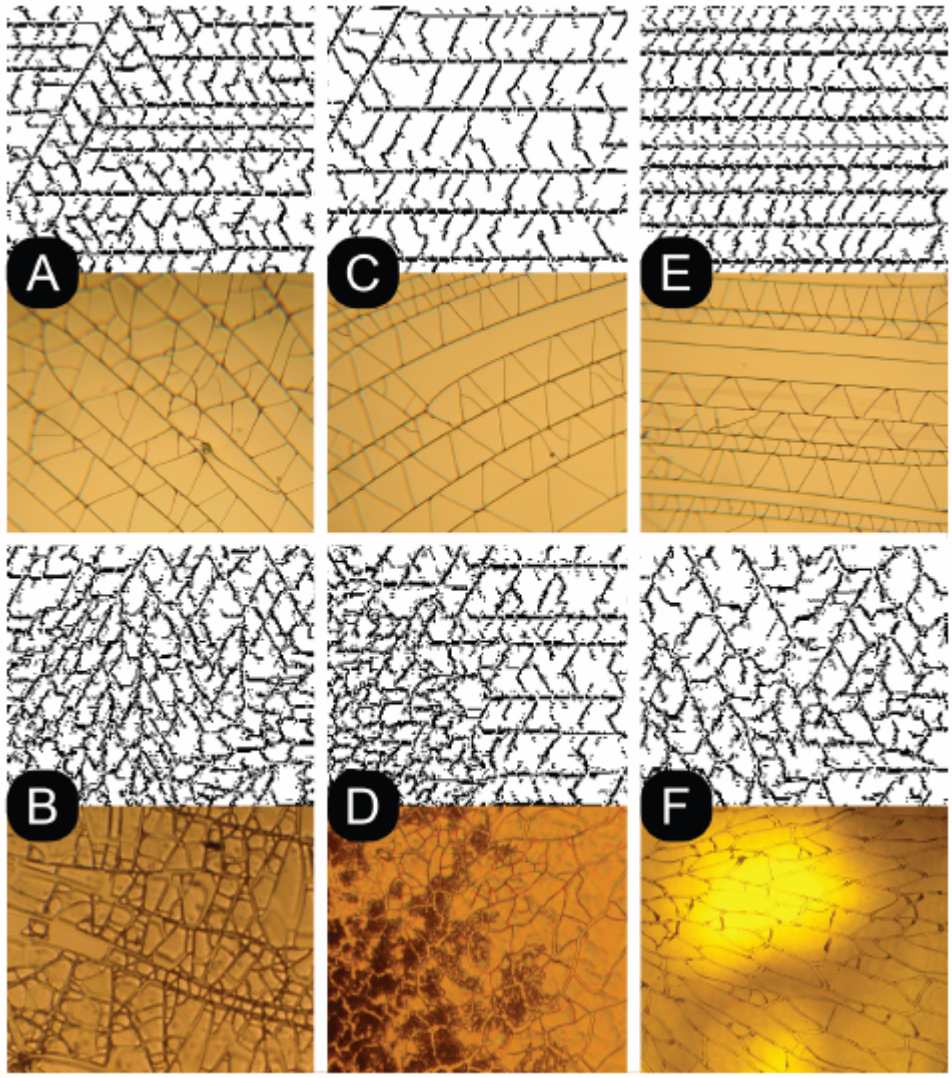

Figure 4.5.1. In the experiments, depending on the parameters, different crack patterns (A–F) are formed. All these patterns can be matched qualitatively with the spring-block model, by an appropriate choice of the model parameters (A – low R, B – high R, C – slow drying, D – fast drying, E – homogeneous, F– with inhomogeneities (caused by ultrasound).

Simulations with a wide range of the parameter values were performed, aiming to find cracking patterns similar to those seen in real experiments. As seen in the comparison (see Fig 4.5.1), relatively good agreement with the experimental crack patterns was achieved as the simulation results also display long parallel cracks and short diagonal craks between the latter

4.6. Further discussion and potential applications [papers I–VII]

The presented method is based on the very same features of sol-gel processing that are fought against in conventional technologies, namely gelling gradient leading to mechanical stress and strain, and cracking (the film is spontaneously divided into segments). These processes are universal in nature, observable in all sol-gel systems and the method based on the same processes can be considered a general one. The range of different precursors of metal oxides that can be used for preparing such rolled microstructures can be assumed to be wide. Although there have been some earlier phenomenological studies on directing the cracking processes, to the best of our knowledge no attempts have been made to exploit these conventionally unwanted phenomena in forming the material into functional shape.

Gelling is in case of this method restricted to the top layers of material and thin films on sol (rather than material gelled from top to bottom that is usually prepared in sol-gel technology) is obtained. The means for achieving that are using higher humidity for gelling the material, shorter reaction times, higher sol concentrations and precursor viscosities than considered reasonable in conventional sol-gel strategies. For the latter reason sol-gel transformation processes in such conditions have not received significant attention before. However, in addition to the elaboration of methods for the production of novel unique shape of oxide material, studies of gelling processes in such borderline conditions can give new insight into the gelling processes in metal alkoxide systems that might potentially lead to even further new applications of sol-gel methods.

However, the microtubular structures studied in present thesis have not been used or tested in any applications yet. Ti-, Zr- and Hf- oxides have high melting temperatures, chemical resistivity, in some cases catalytic activity, mechanical hardness, optical transparency, good thermal and electrical isolation properties as well as biocompatibility. Potential applications can be based on these remarkable properties, the unique shape of the roll structures or most likely the combination of the two. To name some, controlled release carriers, catalysts, filters, microcontainers or -reactors in extreme chemical or thermal environment, optical microsensors, optical resonators, insulating materials, cermet or implant composites as well as biomaterials have been suggested.

5. CONCLUSIONS

Control over speed of sol-gel transformation in Ti-, Zr- and Hf- butoxides and nature of the processes through the choice of precursor compound, its extent of hydrolysis and concentration as well as environment humidity and reaction time can lead to novel shapes of gel materials with specific shape.

As shown in present paper, exploiting phenomena that are conventionally considered unwanted (cracking and/or mechanical stress), lead to spontaneous formation of gel sheets rolled into microtubular structures. Higher concentration and reactivity of the precursor and higher humidity of the environment that is used for gelling lead to the formation of thinner gel film segments. Lower values of these parameters lead to the formation of thicker films that form rolled structures with larger diameter. Lower precursor reactivity also has affects the processes in direction of formation of less uniform rolled structures.

Spontaneous cracking processes in micro-scale define directly the dimensions of formed gel sheets and therefore also the lengths of obtained roll strucures. As seen by phenemenological studies, cracking occurs in an ordered manner and can potentially lead to uniform shape structures. General cracking evolution sequence comprises of formation of inital straight parallel cracks followed by secondary diagonal short cracks between the first. Discrete element method model of blocks and springs with increasing spring constant was developed to simulate crack evolution. Reasonably good concurrency between simulation results and observed crack patterns was achieved. Therefore it can be assumed that the patterns observed in experiments are defined by dynamic stress buildup and redistribution during gelling and cracking and are independent from the nanostructure of agglomerates that form during the hydrolysis and polymerization of metal alkoxide based precursors.

Obtained Ti-, and Hf- butoxide gel structures can be annealed to obtain oxide microrolls. Heating causes a 25–30% decrease in linear dimensions due to material densification but the morphology of roll structures is preserved. Tubular ZrO_2 structures were found to undergo destructive phase conversion from tetragonal to monoclinic at 700ºC. Such structure break down was not seen in yttrium doped microrolls heated up to 800ºC so successful yttria-stabilization mechanism can be assumed. It was also shown that rare earth-doped metal oxide microrolls can also be prepared as ZrO_2 structures proved to be excellent hosts for Sm^{3+} ions in photoluminescence studies.

The novel microroll structures can have several applications in different fields due to their size and unique shape. Similar structures obtained by other methods have been studied in connection with possible applications as optical resonators, microfluidic channels, biomaterials and microsensors. Based on the properties of Ti-, Zr- and Hf- oxides and microroll morphology applications as microcontainers, controlled release carriers, filter materials and catalysts are also suggested.

SUMMARY

Micro- and nanotubes by self-rolling of films is an exciting emerging field in materials science. As this ideology of material forming was introduced a decade ago it has been since adapted to the preparation of nano- and microrolls from different materials by vacuum deposition and lithography methods with potential applications as microfluidic channels, optical resonators, microsensors or biomaterials.

Present thesis is an overview of our studies on the formation of metal oxide microtubes by original metal alkoxide gel nanofilm rolling that opposes to previously reported approaches mainly by being simpler in its nature as no sophisticated material processing methods are required. The method is based on spontaneous gel cracking and rolling due to mechanical stress, phenomena that are conventionally considered as unwanted in sol-gel processes.

Phenomenologic studies were conducted on gel film cracking that defines the dimensions of rolled film segments. Influence of precursor composition and precursor reacting time with humid air on the diameter of obtained roll structures and thickness of gel film was also estimated. The mean diameter of microrolls obtained from zirconium(IV)butoxide was successfully varied by changing the R value of the precursor and exposure length to humid air.

The preparation method was also adapted to titanium(IV)butoxide and hafnium(IV)butoxide as starting compounds and the gel structures were successfully heat treated to achieve metal oxide composition. Roll shape was preserved despite shrinkage that is typical to sol-gel materials. Although the roll shape of structures prepared from zirconium(IV)butoxide did not withstand annealing at 700 ºC causing a transition from tetragonal to monoclinic phase they were found to be excellent hosts to Sm^{3+} ions in photoluminescence studies. As a successful solution to the problem of material fracture during heat treatment, yttrium-doped zirconia microrolls were also prepared.

Based on crack formation observation results, a discrete element method model was developed for cracking simulations. Relatively good concurrency with experimental data was achieved.

Proposed applications of microtubular metal oxide structures include optical resonators, controlled release, microcontainers, catalysis and biomaterials.

SUMMARY IN ESTONIAN

Mikrorull-struktuuride moodustumine geel-kile rullumise teel Zr-, Ti- ja Hf- butoksiididest.

Õhukeste kilede rullumine mikro- ja nanotorudeks on kümne aasta vanune aktuaalne valdkond materjaliteaduses. Selle materjali vormimise ideoloogia ellurakendamiseks on seni kasutatud kõrgvaakumis läbiviidavaid materjali sadestamise ja vormimise meetodeid. Valmistatud struktuurid on potentsiaalselt kasutatavad mikrokanalite, optiliste resonaatorite, mikrosensorite või biomaterjalidena.

Käesolev väitekiri käsitleb uudset ja originaalset sool-geel meetodit metalloksiidsete mikrorullide valmistamiseks metalli alkoksiididest saadavate geel-kilede rullumise teel. Meetod põhineb geelkile iseeneslikul jagunemisel segmentideks selle pragunemise tulemusena ja moodustunud materjali mehaanilistest pingetest tingitud spontaansel rullumisel. Tavapäraselt peetakse selliseid protsesse sool-geel meetodite puhul soovimatuteks.

Käesolevas töös uuriti geelkile pragunemise protsesse, mis määravad rulluva kilesegmendi mõõtmed ning hinnati lähteine koostise ning geelistumisreaktsioonide kestvuse mõju rullumise teel saadavate struktuuride mõõtmetele.

Meetod kohandati ka titaan- ja hafnium(IV)butoksiidist torujate mikrostruktuuride valmistamiseks, ühtlasi näidati et geelstruktuure on võimalik kuumutada oksiidmaterjali saamiseks ilma, et mikrostruktuurid laguneks. Tsirkooniumoksiidi puhul täheldati struktuuride lagunemist tetragonaalse ja monokliinse faasi vahelise siirde tõttu kuumutamisel 700 ºC kraadini. Ühtlasi näidati, et materjali lagunemist kuumutamisel on võimalik vältida üttriumi lisamise teel materjali koostisesse.

Geelkile pragunemiskatsete tulemuste põhjal konstrueeriti plokk-vedru mudel, mis võimaldab eksperimendis nähtavate pragunemismustrite suhteliselt hea kokkulangevusega simuleerimist.

Uudse kujuga metalloksiidse materjali võimalike rakendustena nähakse muuhulgas optilisi resonaatoreid, elongeeritult vabastavaid materjale, mikrokonteinereid, katalüsaatoreid ja biomaterjale.

REFERENCES

[1] M. Ebelmann, *Ann. Chem. Phys*., 16 (1846).
[2] H. Kozuka (editior), Sol-Gel Processing, Volume 1 in *Handbook of sol-gel science and technology*, S. Sakka, H. Kozuka, eds. (Kluwer Academic Publishers, Boston, Dordrecht, London, 2005).
[3] Sol-Gel Processing of Ceramics and Glass, BCC Research, 2006, http://www.the-infoshop.com/study/bc41844-ceramics.html
[4] C. J. Brinker, G. W. Scherer, Sol- Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic, San Diego 1990).
[5] J. Livage, M. Henry, C. Sanchez, *Prog. Solid State Chem.* 18 (1988).
[6] B. J. J. Zelinski, D. R. Uhlmann, *J. Phys. Chem. Solids* 45 (1984).
[7] V. G. Kessler, *J. Sol-Gel Sci. Technol*. 51(3) (2009).
[8] T. Tätte, M. Paalo, V. Kisand, V. Reedo, A. Kartushinsky, K. Saal, U. Mäeorg, A. Lõhmus, I. Kink, *Nanotechnology* 18 (2007).
[9] L. Dolgov, V. Kiisk, V. Reedo, S. Pikker, I. Sildos, J. Kikas, *Cent. Eur. J. Phys*. 9(2) (2011).
[10] Chemat Technology, www.chemat.com
[11] W. Geffcken, E. Berger (Jenaer Glaswerk Schott & Gen) „Changing the reflective capacity of optical glass", *patent* DE736411 (1943).
[12] H. Dislich, E Hussmann, *Thin Solid Films* 77 (1981).
[13] P. Greil, T. Lifka, A. Kaindl, *J. Eur. Ceram. Soc.* 18(14) (1998).
[14] T. Y. Lee, R. S. Alegaonkar, *Thin Solid Films* 515 (2007).
[15] I. Oja, A. Mere, M. Krunks, R. Nisumaa, C.-H. Solterbeck, M. Es-Souni, *Thin Solid Films* 515 (2006).
[16] P. Marage, M. Langlet, J. C. Joubert, *Thin Solid Films* 238, (1994).
[17] M. Timusk, M. Järvekülg, K. Saal, R. Lõhmus, I. Kink, A. Lõhmus (University of Tartu, Estonia; Estonian Nanotechnology Competence Centre), „Method of preparation of surface coating of variable transmittance and electro-optical appliance including the same" *patent application* WO 2010108987 (2010).
[18] H. Nishimor, M. Tatsumisago, T. Minami, *J. Ceram. Soc. Jpn*. 103 (1995).
[19] C. J. Brinker, G. W. Scherer, „Sol- gel science", (Academic Press, 1990), pp. 11–12.
[20] M. Yamame,S. Shibata, A. Yasumori, T. Yano, S. Uchihiro, *J. Sol-Gel Sci. Technol*. 2 (1994).
[21] T. Tsurumi, S. Ozawa, S. Wada, *J. Sol-Gel Sci. Technol.* 26 (2003).
[22] E. Celik, I. Keskin, I. Kayatekin, F. A. Azem, E. Özkan, *Mater. Charact*. 58 (2007).
[23] T. J. Garino, *MRS Proceedings* 180, MRS Spring Meeting; San Francisco, USA; April 16.–20. 1990.
[24] H. Kozuka*, J. Ceram. Soc. Japan.* 111(9) (2003).
[25] H. Kozuka, S. Takenaka, H. Tokita, T. Hirano, Y. Higashi, T. Hamatani*, J. Sol-Gel Sci. Techn*. 26 (2003).
[26] H. Kozuka, *J. Sol-Gel Sci. Techn*. 40 (2006).
[27] S.-Y. Chen, I-W. Chen*, J. Am. Ceram. Soc*. 78(11) (1995).
[28] M. Sendova, K. Willis, *Appl. Phys. A* 76 (2003).
[29] Z. C. Xia, J. W. Hutchinson, *J. Mech. Phys. Solids* 48 (2000).
[30] J. Fricke, *J. Non- Cryst. Solids* 100 (1988).
[31] H. Yokogawa, „Hydrophobic Silica Aerogel" in *Handbook of sol-gel science and technology, Volume 3.:Applications of sol-gel technology,* S. Sakka, ed. (Kluwer Academic Publishers, Boston, Dordrecht, London, 2005), pp. 73–84.
[32] S. Sakka, K. Kamiya, *Mat. Sci. Res*. 17, (1984).

[33] T. Tätte, A. L. Kolesnikova, M. Hussainov, R. Talviste, R. Lõhmus, A. E. Romanov, I. Hussainova, M. Part, A. Lõhmus, *J. Nanosc. Nanotech*. 10(9) (2010).
[34] H. Y. Dong, X. D. He, Y. Y. Teng, F.Y. Song, W. Ma, *Int. J. Mater. Res*. 102(2) (2011).
[35] J. Blum, D. Avnir, „Catalysis and reactivity with sol-gel entrapped organic and organometallic chemicals" in *Handbook of sol-gel science and technology, Volume 3.:Applications of sol-gel technology,* S. Sakka, ed. (Kluwer Academic Publishers, Boston, Dordrecht, London, 2005), pp. 507–526.
[36] E. Callone, J. M. Fletcher, G. Carturan, R. Raj, *J. Mater. Sci.* 43(14) (2008).
[37] L. Pauling, *Proc. Nat. Acad. Sci.* 16, 578–582 (1930).
[38] T. F. Bates, F. A. Hildebrand, A. Swineford, *American mineralogist* 35, (1950).
[39] K. A. Carrado, „Introduction: Clay Structure, Surface Acidity, and Catalysis," in *Handbook of layered materials,* S. M. Auerbach, K. A. Carrado, P. K. Dutta, eds. (Marcel Dekker, New York, Basel, 2004) pp. 4–9.
[40] K. Yada, *Acta Crystallogr. A* **27** (1971).
[41] E. Joussein, S. Petit a, B. Delvaux, *App. Clay Sci.* 35 (2007).
[42] N. Roveri, G. Falini, E. Foresti, G. Fracasso, I.G. Lesci, P. Sabatino, *J. Mat. Res*. 21 (2006).
[43] Halloysite Nanotubes, The Separation Challenge, NaturalNano,Inc. 2007., http://www.naturalnano.com/index.php?option=com_content&task=view&id=17&Itemid=45
[44] Nanocomposites, Nanoparticles, Nanoclays, and Nanotubes, BCC Research, 2006, http://www.bccresearch.com/nan/NAN021C.asp
[45] R. Tenne, L. Margulis, M. Genut, G. Hodes, *Nature* 360, (1992).
[46] R. Tenne, *Nature Nanotechn.* 1, (2006).
[47] C. N. R. Rao, M. Nath, *Dalton Trans.* (2003).
[48] Y. Xiong, B. T. Mayers, Y. Xia, *Chem. Commun*. (2005).
[49] C. N. R. Rao, A. Govindaraj, S. R. C. Vivekchand, *Annu. Rep. Prog. Chem*. A 102 (2006).
[50] A. Margolin, R. Rosentsveig, A. Albu-Yaron, R. Popovitz-Biro, R. Tenne, *J. Mat er. Chem.* 14, (2004).
[51] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekina, K. Niihara, *Langmuir* 14, (1998).
[52] T. Kasuga, M, Hiramatsu (Chubu Electric Power) „Crystalline titania and process for producing the same", *patent* EP0832847 (1998).
[53] T. Kasuga, M, Hiramatsu (Chubu Electric Power) „Crystalline titania", *patent* JP2002241129 (1998).
[54] F. Wang, J. Jiu, L. Pei, K. Nakagawa, S. Isoda, M. Adachi, *Chem. Lett.* 34 (2005).
[55] L.-R. Hou, C.-Z. Yuan, Y. Peng, *J. Hazardous Mater. B* 139 (2007).
[56] M. Wei, Y. Konishi, H. Zhou, H. Sugihara, H. Arakawa, *Solid State Comm*. 133 (2005).
[57] Y. Zhu, H. Li, Y. Koltypin, Y. Rosenfeld Hacohenb, A. Gedanken, *Chem. Commun.* (2001).
[58] A. Kukovecz, M. Hudos, E. Horvath, G. Radnoczi, Z. Konya, I. Kiricsi, *J. Phys. Chem. B*. 109 (2005).
[59] A. V. Pokropivnyi, V. V. Pokropivnyi, *Tech. Phys. Lett*. 29 (2003).
[60] B. D. Yao, Y. F. Chan, X. Y. Zhang, W. F. Zhang, Z. Y. Yang, N. Wang, *App. Phys. Lett.* 82 (2003).
[61] Y. Q. Wang, G. Q. Hu, X. F. Duan, H. L. Sun, Q. K. Xue, *Chem. Phys. Lett*. 365 (2002).

[62] J.-J. Yang, Z.-S. Jin, X.-D. Wang, W. Li, J.-W. Zhang, S.-L. Zhang, X.-Y. Guo, Z.-J. Zahang, *Dalton Trans.* 3898 (2003).
[63] T. Kasuga, *Thin Solid Films* 496 (2006).
[64] D. Gong, C. A. Grimes, O. K. Varghese, W. Hu, R. S, Singh, Z. Chen, E. C. Dickey, *J. Mater. Res.* 16 (2001).
[65] H. E. Prakasam, K. Shankar, M. Paulose, O, K. Varghese, C. A. Grimes, *J. Phys. Chem. C 111* (2007).
[66] B. C. Satishkumar, A. Govindaraj, E. M. Vogl, L. Basumallick, C. N. R. Rao, *J. Mater. Res.* 12 (1997).
[67] H. Imai, Y. Takei, K. Shimizu, M. Matsuda, H. Hirashima, *J. Mater. Chem*. 9 (1999).
[68] S. Liu, J. He, *J. Am. Ceram. Soc* 88 (2005).
[69] Q. Peng, X.-Y. Sun, J. C. Spagnola, G. K. Hyde, R. J. Spontak, G. N. Parsons, *Nano Lett*. 7 (2007).
[70] V.Y. Prinz, V.A. Seleznev, A.K. Gutakovsky, A.V. Chehovskiy, V.V.Preobrazhenskii, M.A. Putyato, T.A. Gavrilova, *Physica E* 6 (2000).
[71] Y. V. Nastaushev, V. Y. Prinz and S. N. Svitasheva, *Nanotechnology* 16 (2005).
[72] Y. Mei, G. Huang, A. A. Solovev, E. Bermúdez Ureña, I. Mönch, F. Ding, T. Reindl, R. K. Y. Fu, P. K. Chu, O. G. Schmidt, *Adv. Mater* 20 (2008).
[73] E. Bermúdez Ureña, Y. Mei, E. Coric, D. Makarov, M. Albrecht, O. G. Schmidt, *J. Phys. D: Appl. Phys.* 42 (2009).
[74] C. Müller, M. S. Khatri, C. Deneke, S. Fähler, Y. F. Mei, E. Bermúdez Ureña, O. G. Schmidt, *Appl. Phys. Lett*. 94 (2009).
[75] V. Luchnikov, M. Stamm, C. Akhmadaliev, L. Bischoff, B. Schmidt*, J. Micromech. Microeng.* 16 (2006).
[76] V. Loutchnikov, O. Sydorenko, M. Stamm (Leibniz- Institut für Polymerforshung Dresden) „ Method of manufacture of microtubes of polymeric material“, *patent* EP1557396 (2005).
[77] A. Bernardi, S. Kiravittaya, A. Rastelli, R. Songmuang, D. J. Thurmer, M. Benyoucef, O. G. Schmidt, *Appl. Phys. Lett.* 93 (2008).
[78] G. Huang, Y. Mei, D. J. Thurmer, E. Coric, O. G. Schmidt, *Lab Chip* 9 (2009).
[79] G. S. Huang, S. Kiravittaya, V. A. Bolaños Quiñones, F. Ding, M. Benyoucef, A. Rastelli, Y. F. Mei, O. G. Schmidt, *Appl. Phys. Lett*. 94 (2009).
[80] S. Schulze, G. Huang, M. Krause, D. Aubyn, V. A. Bolanos Quinones, C. K. Schmidt, Y. Mei, O. G. Schmidt, *Adv. Eng. Mater.* 12(9) (2010).
[81] O.G. Schmidt, C. Deneke, Y.M. Manz, C. Müller, *Physica E* 13 (2002).
[82] H. Paetzelt, V. Gottschalch, J. Bauer, H. Herrnberger, G. Wagner, *Phys. Stat. Sol*. 203 (2006).
[83] C. Deneke, O.G. Schmidt, *Physica E* 23 (2004).
[84] R. Songmuang, Ch. Deneke, O. G. Schmidt, *App. Phys. Lett.* 89 (2006).
[85] J. Zang, M. Huang, F. Liu, *Phys. Rev. Lett.* 98 (2007).
[86] D. J. Thurmer, C. Deneke, Y. Mei, O. G. Schmidt, *Appl. Phys. Lett.* 89(22) (2006).
[87] F. Cavallo, R. Songmuang, O. G. Schmidt, *Appl. Phys. Lett.* 93 (2008).
[88] M. Yu, Y. Huang, J. Ballweg, H. Shin, M. Huang, D. E. Savage, M. G. Lagally, E. W. Dent, R. H. Blick, J. C. Williams, ACS Nano 5(4) (2011).
[89] C. J. Brinker, and G. W. Scherer, Sol- Gel Science (Academic Press, San Diego, 1990), p. 455–513.
[90] S. Lange, V. Kiisk, V. Reedo, M. Kirm, J. Aarik, I. Sildos, Opt. Mater 11 (2006).

ACKNOWLEDGEMENTS

The autor is grateful to his scientific supervisors throughout the years, Ants Lõhmus, Uno Mäeorg and Valter Reedo, without whom the intriguing topic of this thesis would not exist.

Also, in more or less chronological sequence thanks belongs to all the other colleagues, co-workers and fellow students who have had influence or direct input to the development and advancement of the author in the stumpy field of materials science: Madis Paalo, Tanel Tätte, Ilmo Sildos, Sirje Mäeorg, Tea Avarmaa, Ilmar Kink, Vambola Kisand, Urve Kallavus, Jana Andzane, Raul Välbe, Aigi Salundi, Kristjan Saal, Rünno Lõhmus, Martin Timusk, Sven Lange, Kathriin Utt, Jakob Jõgi, Jaan Kalda, Marko Part.

Since the beginning in 2004, the scientific activities of the author have been supported by Estonian Nanotechnology Competence Center, Estonian Science Foundation SF0382149s02, ETF8377, SF0180058s07, ETF8428, ETF6163, ETF6660, ETF8420, World Federation of Scientists, Doctoral school MMTDK and Graduate School on Functional Materials and Technologies, EU Social Funds project 1.2.0401.09–0079.

PUBLICATIONS

CURRICULUM VITAE

Martin Järvekülg

General data

Date and place of birth	9. April 1983, Viljandi
Citizenship	Estonian
Maritial Status	Single
Contact	Institute of Physics, University of Tartu Riia 142, 51014 Tartu
Phone	+372 5804 6994
E-mail	martinj@fi.tartu.ee

Education

2007–2011	Tartu University, PhD Student (materials science)
2005–2007	Tartu University, MSc (materials science)
2002–2005	Tartu University, BA (materials science)
2001–2002	Military service in Estonian Defence Forces
1989–2001	C. R. Jakobson Gymnasium

Language skills

Estonian	mother tongue
English	good in speaking and writing
German	average in speaking and writing

Professional employment

2005–…	Institute of Physics, University of Tartu, laboratory assistant, engineer
2005	AS Estiko Plastar, summer employment
2006–…	Estonian Nanotechnology Competence Center

Supervised dissertations

2006	Kelli Keevend, BA in materials science
2008	Kelli Keevend, MSc in materials science; Raul Välbe, BA in materials science: Madis Umalas, BA in materials science
2010	Kadri Savi, BA in physics

Awards

2005	First student award of Institute of Physic, University of Tartu
2005	Poster award at Trends in Nanotechnology conference
2005	First award at the student competition of Estonian National Academy of Sciences
2007	First student award of Institute of Physic, University of Tartu

List of Publications

M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus, Method for preparing oxide material, Owners: Estonian Nanotechnology Competence Center, University of Tartu, Priority number: P200700029; Priority date: 07.06. 2007.

V. Reedo, M. Järvekülg, A. Lõhmus, U. Mäeorg, Novel route for preparation of tubular TiO2 microstructures. *Phys. Status Solidi A* 2008 **205**(6), 1511–1514.

M. Timusk, M. Järvekülg, K. Saal, R. Lõhmus, I. Kink, A. Lõhmus, Method of preparation of surface coating of variable transmittance and an electrooptical device including the same, Owners: Estonian Nanotechnology Competence Center, University of Tartu, Priority number: P200900022; Priority date: 25.03.2009.

M. Järvekülg, R. Välbe, K. Utt, M. Timusk, T. Tätte, Tailoring Sol-Gel Transition Processes for the Design of Novel Shape Metal Oxide Materials. In: Functional Oxide Nanostructures and Heterostructures *MRS Proceedings* **1256E**: 2010 MRS Spring Meeting; San Francisco, USA; 5.– 9. April 2010.

K. Utt, S. Lange, M. Järvekülg, H. Mändar, P. Kanarjov, I. Sildos, Structure and optical properties of Sm-doped ZrO2 microrolls. *Optical Materials* 2010 **32**(8), 823–826.

M. Timusk, M. Järvekülg, R. Lõhmus, I. Kink, K. Saal, Sol–gel matrix dispersed liquid crystal composite: Influence of methyltriethoxysilane precursor and solvent concentration. *Materials Science and Engineering B*, 2010 **172**(1), 1–5.

K. Saal, T. Tätte, M. Järvekülg, V. Reedo, A. Lõhmus, I. Kink, Micro- and nanoscale structures by sol-gel processing. *Int J Mater Prod Tec*, 2011 **40**(1/2), 2–14.

J. Jõgi, M. Järvekülg, J. Kalda, V. Reedo, A. Salundi, A. Lõhmus, Simulation of cracking of metal alkoxide gel film formed on viscous precursor layer using a spring-block model, *Europhys Lett*, (submitted).

ELULOOKIRJELDUS

Martin Järvekülg

Üldinfo

Sünniaeg ja -koht	9.aprill 1983, Viljandi
kodakondsus	Eesti
Perekonnaseis	Vallaline
Kontaktandmed	Tartu Ülikooli Füüsika Instituut Riia 142, 51014 Tartu
Telefon	+372 5804 6994
E-mail	martinj@fi.tartu.ee

Haridus

2007–2011	Tartu Ülikool, doktoriõpe (materjaliteadus)
2005–2007	Tartu Ülikool, magistriõpe (materjaliteadus)
2002–2005	Tartu Ülikool, bakalaureuseõpe (materjaliteadus)
2001–2002	ajateenistus Kuperjanovi ÜJP-s
1989–2001	C. R. Jakobsoni nimeline Gümnaasium

Keeleoskus

eesti keel	emakeel
inglise keel	hea kirjas ja kõnes
saksa keel	keskmine kirjas ja kõnes

Teenistuskäik

2005–…	Tartu Ülikooli Füüsika Instituut, laborant, insener
2005	AS Estiko Plastar, erialane suvepraktika
2006–…	Eesti Nanotehnoloogiate Arenduskeskuse AS

Juhendatud lõputööd

2006	Kelli Keevend, bakalaureusetöö materjaliteaduses
2008	Kelli Keevend, magistritöö materjaliteaduses; Raul Välbe, bakalaureusetöö materjaliteaduses: Madis Umalas, bakalaureusetöö materjaliteaduses
2010	Kadri Savi, bakalaureusetöö füüsikas

Auhinnad

2005	esimene auhind Tartu Ülikooli Füüsika Instituudi üliõpilastööde stipendiumikonkursil
2005	postriauhind konverentsil Trends in Nanotechnology
2005	esimene auhind Eesti Teaduste Akadeemia üliõpilastööde konkursil

2007 esimene auhind Tartu Ülikooli Füüsika Instituudi üliõpilastööde stipendiumikonkursil

Publikatsioonide loetelu

M. Järvekülg, V. Reedo, U. Mäeorg, I. Kink, A. Lõhmus, Meetod oksiidmaterjali valmistamiseks, Omanikud: Eesti Nanotehnoloogiate Arenduskeskus, Tartu Ülikool Prioriteedinumber: P200700029; Prioriteedikuupäev: 07.06. 2007.

V. Reedo, M. Järvekülg, A. Lõhmus, U. Mäeorg, Novel route for preparation of tubular TiO2 microstructures. *Phys. Status Solidi A* 2008 **205**(6), 1511–1514.

M. Timusk, M. Järvekülg, K. Saal, R. Lõhmus, I. Kink, A. Lõhmus, Meetod muutuva läbilaskvusega pinnakatte saamiseks ja seda sisaldav elektrooptiline seade, Omanikud: Eesti Nanotehnoloogiate Arenduskeskus, Tartu Ülikool, Prioriteedinumber: P200900022; Prioriteedikuupäev: 25.03.2009.

M. Järvekülg, R. Välbe, K. Utt, M. Timusk, T. Tätte, Tailoring Sol-Gel Transition Processes for the Design of Novel Shape Metal Oxide Materials. In: Functional Oxide Nanostructures and Heterostructures *MRS Proceedings* **1256E**: 2010 MRS Spring Meeting; San Francisco, USA; 5.–9. April 2010.

K. Utt, S. Lange, M. Järvekülg, H. Mändar, P. Kanarjov, I. Sildos, Structure and optical properties of Sm-doped ZrO2 microrolls. *Optical Materials* 2010 **32**(8), 823–826.

M. Timusk, M. Järvekülg, R. Lõhmus, I. Kink, K. Saal, Sol–gel matrix dispersed liquid crystal composite: Influence of methyltriethoxysilane precursor and solvent concentration. *Materials Science and Engineering B*, **172**(1), 1–5. (2010).

K. Saal, T. Tätte, M. Järvekülg, V. Reedo, A. Lõhmus, I. Kink, Micro- and nanoscale structures by sol-gel processing. *Int J Mater Prod Tec*, 2011 **40**(1/2), 2–14.

J. Jõgi, M. Järvekülg, J. Kalda, A. Salundi, V. Reedo, A. Lõhmus, Simulation of cracking of metal alkoxide gel film formed on viscous precursor layer using a spring-block model, *Europhys Lett*, (submitted).