DISSERTATIONES CHIMICAE UNIVERSITATIS TARTUENSIS
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HIGH VISCOSITY $Sn(OBu)_4$ OLIGOMERIC CONCENTRATES AND THEIR APPLICATIONS IN TECHNOLOGY

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Dissertation in organic chemistry

Dissertation is accepted for the commencement of the degree of Doctor of Philosophy in Chemistry on June 21, 2006, by the Doctoral Committee of Department of Chemistry, University of Tartu

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Commencement: August 25, 2006 at Jakobi Str. 2, 430

ISSN 1406–0299
ISBN 9949–11–409–8 (trükis)
ISBN 9949–11–410–1 (PDF)

Tartu Ülikooli Kirjastus
www.tyk.ee
Tellimuse nr 375

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Paper II Tätte T, Reedo V, Adamovich M, Avarmaa T, Lõhmus R, Mäeorg U, Pistol M-E, Subbi J and Lõhmus A 2002 Metal oxide based SPM tips prepared by sol-gel method *Phys. Low-Dim. Struct.* **5/6** 31–38

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Paper IV Tätte T, Jacobsen V, Paalo M, Branscheid R, Kreiter M, Mäeorg U, Saal K, Lõhmus A and Kink I Preparation of Sb doped SnO_2 SPM tips and their use as transparent probes in STM induced light hybrid microscopy *Proc. of NSTI Nanotech 2005 (Anaheim, CA*) May 8–12, 2005 (vol 3) 305–8

Paper V Tätte T, Paalo M, Kisand V, Reedo V, Kartushinsky A, Saal K, Mäeorg U, Lõhmus A and Kink I 2006 Pinching of alkoxide jets – a route for preparing nanometre level sharp oxide fibres *Nanotechnology* (manuscript)

Paper VI Kisand V, Shulga J, Tätte T, Visk U, Natali M, Mistura G, Paalo M, Lobjakas M and Kink I 2006Preparation of structured sol-gel films using modified tape casting *Materials Science and Engineering B*. (manuscript)

Author's contribution

As seen from the list of papers, there are very many people who have given their contribution for developing the topic of the current thesis. That is due to interdisciplinary nature of the thesis subject.

Author of this thesis carried out most of the experimental work related to preparation of oxide needle structures including construction of necessary new apparatuses. SPM measurements using oxide needles as sensor elements were performed in co-operation by Dr. M. Kreiter's group from Max Planck-Institute for Polymer Research in Mainz, Germany. Spectroscopic analyses of sol-gel materials were carried out by colleagues at Institute of Bio-organic and Organic Chemistry (University of Tartu), Institute of Physics (University of Tartu) and

National Institute of Chemical Physics and Biophysics. The results of the current thesis are the return of joint effort of many co-authors in which synergy of the group was very important.

In more detail the author is:

Paper I: responsible for preparation of nanometrically sharp oxide needle structures. Responsible for the study of sol-gel precursors. Performed the first TEM imaging of the oxide needles. Responsible for studies of optical and electric properties of the oxide fibres. Responsible for composing the manuscript.

Paper II: responsible for synthesis of different alkoxides based sol precursors. Participated in MALDI-TOF mass spectrometry analysis of alkoxides based precursors. Responsible for composing the manuscript.

Paper III: participated in testing the oxide needles as SPM sensors. Actively participated in preparation of the manuscript.

Paper IV: responsible for preparing the oxide needles. Responsible for composing the manuscript.

Paper V: responsible for needles preparation experiments and comparison of experimental formation of oxide needles with theoretical predictions. Responsible for composing the manuscript.

Paper VI: responsible for making precursors. Constructed an apparatus for dip coating experiments. Actively participated in preparation of the manuscript.

ABBREVIATIONS

NEMS	nano electromechanical systems
NFO	near-field optics
MALDI-TOF	matrix assisted laser desorption /ionization- time of flight (mass spectrometry)
ORMOCERS	organically modified ceramic compounds
ORMOSILS	organically modified silane based compounds
IR	infra red
DLVO	Derjaguin, Landau, Verwey, Overbeek (theory)
DNA	deoxyribonucleic acid
STM	scanning tunnelling microscopy
TEM	transmission electron microscopy
SPM	scanning probe microscopy
NMR	nuclear magnetic resonance spectroscopy
AFM	atomic force microscope
ITO	mixture of In_2O_3 and SnO_2
ATO	antimony doped tin oxide

1. INTRODUCTION

In the beginning of 1960's the Nobel Prize winner R. Feymann pointed to enormous opportunities of miniaturization in technology [1]. In his historical speech he intrigued the community of scientists with the question: *Why cannot we write the entire 24 volumes of the Encyclopedia Britannica on the head of a pin?* Posteriorly, it can be concluded that his lecture was the starting point of miniaturization progress in technology. In 1986 K. E. Drexler [2] proposed a word *nanotechnology* as a common definition to any technology in nanoscale [3]. The term quickly acquired enormous prestige. Nowadays it can be firmly said that realizing things in nanoscale, in some of cases also at one molecule level is the greatest challenge of technologies. In 2000 another Nobel Prize winner R. Smalley exalted nanotechnologies saying: "*The combination of high tech gee whiz, high social impact, and economic good sense gives the dream of nanotechnology the ability to inspire our nation's youth toward science unlike any event since Sputnik*" [4].

Nowadays, the structure, properties and preparation of nanomaterials are among the hottest topics in technology and science. Wires and layers minimized down to molecular size are more and more often put into practice [5] in electronics [6], optics [7, 8] and medicine [9]. It has to be pointed out that nanoscale structures are not just very little bulk systems, but have certain extraordinary properties proceeding from their dimensions. For example, Si-crystals show light emitting properties if their dimensions are less than 8 nm. Moreover, the wavelength of emitted light depends on the size of a particle [10].

To realize low-scale structuring the most widely accepted method is lithography. Conventional optical lithography methods have been put into use to enable micron scale structuring. Nowadays more complex methods enable patterning the structures down to 37 nm in width. To pattern even smaller features, photolithography requires further advances, such as decreasing the imaging wavelength to 157 nm or to even soft x-rays [11]. As these changes turn the process more expensive, most of the leading scientists believe that optical lithography will not be cost effective below 30 nm size structuring.

During the recent decade many alternative concepts have been proposed for lithography to pass the pokey spots. For example, cheap processes like soft-lithography [12], molding and embossing [11], dip-pen lithography [13,14] and others [11] are proved to enable structuring below 30 nm resolution. The most important of these methods is replica-molding, part of a large pool of chemically inspired soft-lithography fabrication techniques [15].

Several researchers believe also that bottom-up will be accepted as the main approach for nanoscale structuring [11]. Metaphorical bottom in term is labeling the level of single particles, which is origin of self-initiatives at nanoscale. It is well known that orientation, association, dissociation and organization of

nanoparticles are caused by molecular forces. Therefore, control over these processes could open the gate for potential technological applications [16].

There is no reason to wonder that oxide nanostructures have attracted much attention, being now extensively studied group of nanomaterials. Applications of bulk oxides have been mostly related to their optical and semiconducting [17], and mechanical properties. Shaping the same materials to nanosized films, fibres and particles can widen the scope of applications to nano-sensors, NEMS, NFO, etc.

For shaping silicon oxide (silica glass) into desired forms, molding of high temperature melts has been widely used technology over ages. Also sintering of powders pressed or molded to certain shapes is industrially applicable process. Still, both processes are too robust for preparing most of the nanoscale structures.

Totally new trend, which remarkably changed the situation, started around 1970's when many authors suggested novel methods for shaping the oxides. Proposed methods based on sols transformation to gels as a result of chemical hydrolysis and condensation processes. Due to the phase shift from sol to gel those technologies were called sol-gel technologies [18].

Typical sol precursors in sol-gel technology contain only some percent of solid in large amount of solvent. Therefore their physical properties do not differ significantly from the properties of pure solvents, which makes these systems easy to handle and applicable for preparing e.g. coatings. However, there are also many drawbacks that limit their applications – for instance, decrease of volumes during post treatment processes and need for large amount of solvents.

In opposite to the above-mentioned mainstream trend in sol-gel technology, a study on applicability of highly viscous and extremely moisture sensitive alkoxide based precursors and development of their application methods are the objects of the current thesis.

2. SOL-GEL TECHNOLOGY

2.1. Chemistry of sol-gel processes

Formation of sols from alkoxides and their further gelation is related to hydrolysis and condensation reactions as follows:

$$\text{Hydrolysis: M-OR} + H_2O \rightarrow \text{MOH} + \text{ROH}$$

$$\text{Condensation: MOH} + \text{ROM} \rightarrow \text{M-O-M} + \text{ROH}$$

Condensed species are formed as these reactions proceed leading to oxopolymers and then hydrous oxides MO_n, x H_2O when excess of water is added. Hydroxylated species are usually involved and sol-gel reaction can be described as the nucleophilic substitution (S_N2) of alkoxide groups [19]:

$$M(OR)_n + mXOH \rightarrow [M(OR)_{n-m}(OX)_m] + mROH$$

where X stands for hydrogen H (hydrolysis), a metal atom M (condensation) or an organic ligand L (complexation). The chemical reactivity of metal alkoxides towards hydrolysis and condensation depends mainly on the positive charge of the metal atom and its ability to increase its coordination number. Therefore the reactivity of alkoxides increases when going down the periodic table as electronegativity of M decreases and the size of M increases. For example: reactivity of the corresponding alkoxides increases if going down the periodic table: Si→Ti→Zr→Ce. If silicon alkoxides gel in several days after addition of water, then alkoxides of titanium, zirconium and cerium gel immediately due to higher coordination number [19]. High reactivity of transition metal alkoxides turn the handling of these compounds very complicated. Since precipitation of condensate appears immediately if exposed to humid atmosphere the manipulations of these material must be carried out in dry atmosphere or closed vessels.

2.2. Preparation of sol precursors

Sols are often classified as polymeric (solutions of oligomeric or polymeric particles) or colloidal types according to the shape of the particles [20].

Metal oxide colloidal sols are usually obtained by hydrolysis and condensation of alkoxides or salts (chlorides, nitrates, sulphates etc.) [20]. Stability of these sols is fairly well described by DLVO theory [21, 22].

Metal oxide polymeric sols are usually prepared from alkoxides. Success in obtaining polymeric sols depends mainly on controlling hydrolysis and

condensation rates. Processes can be often influenced by catalyst (acid, base) concentrations.

Most widely studied silica sols are usually prepared from $Si(OMe)_4$ or $Si(OEt)_4$ [18, 20]. To obtain sols, proper amount of solvent, water and acid/alkali must be added to these alkoxides. Depending on their mutual ratios either linear or branched particles are formed. If large excess of water is added or alkali catalyst is used then highly branched clusters start to grow in solution and colloidal sols are obtained. In opposite case, if solution is acidified and water is added up to molar ratio $r = H_2O / Si(OR)_4 < 4$ then mainly linear shape particles form in the solution and polymeric sol is obtained.

As relationship between particle size and viscosity is well known [23, 24], the viscosity measurements enable determination of the rate of condensation processes that occur in solutions [25]. The release of alkoxy groups due to hydrolysis and condensation is often visualized by IR spectroscopy [26].

2.3. Gelation of sols

Alkoxide sols are instable systems. Their ageing at room temperature typically results in 3-dimensional cross-linking of sol particles. Sols where particles are organized to network are called structured sols or gels. If physical properties of sols at macro scale are close to properties of liquids, then gels show elastic behaviour. As solid content of gels is very low (usually 1–2%) then they have also retained some liquid properties. For example, diffusion of solvent particles is still quite intense and similar to corresponding sols being just very slightly affected by 3-dimensional gel network [18]. Convection on the other hand does not proceed in gels due to the network of particles.

As gelation usually occurs at room temperature the sol-gel technology enables to prepare ceramics doped with organic additives like organic dyes, which are unstable at higher temperatures [27], DNA and living cells [28], etc. This makes possible to prepare such novel groups of materials like ORMOCERS and ORMOSILS [29]. In recent years many researchers are focused on ceramics and glasses doped by carbon nanotubes and fullerenes [30]. These materials often have extraordinary mechanical and sensor properties.

2.4. Shaping of gels

If the purpose is to substantiate gels in desired shape then sol precursor is let to gel in suitable shape [18]. Most common sol-gel materials are prepared in the shapes of thin films on substrate, fibres and monoliths (bulks). For preparing the films a sample surface is coated with highly diluted sols. After gelling and

evaporation of solvents thin (usually in nanoscale) amorphous films are obtained. For preparing fibres the precursor is pulled or pressed to slender jets. The solid fibres are obtained due to gelation of the jet in humid environment. To prepare the bulk monoliths, a sol is gelled in desired shape molds. After the gelation a self-standing body is released from the mold. Figure 1 explains the main paths for preparing different shape gel-bodies and their usual post treatment steps.

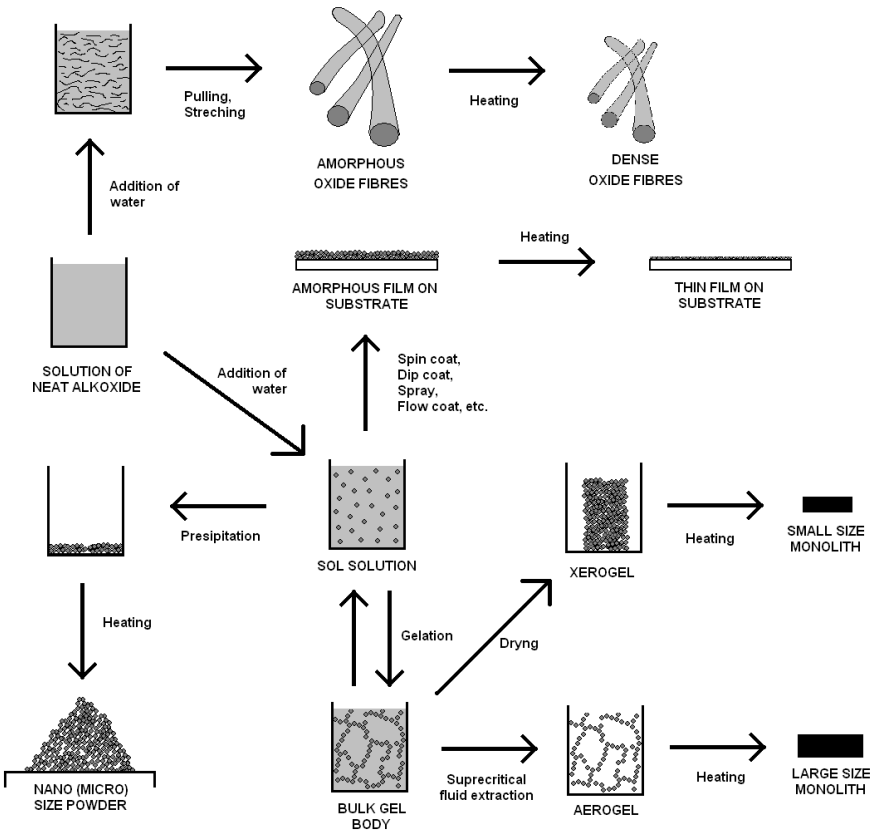

Figure 1. The main paths for preparing *sol-gel* materials.

2.5. Post treatment steps

To obtain amorphous or crystalline structure of oxides a post treatment of gels is carried out. A process called ageing is carried out for removing solvents from the gel structure. Baking is typically applied after the ageing and is required for crystallization and densification of oxide materials.

2.5.1. Ageing (drying)

Duration of the aging in air depends on the size of oxide body and can take from minutes up to several years. Careful and long-time ageing is needed to avoid cracks in gel body.

Widely accepted explanation of the formation of cracks in sol-gel structures is related to development of capillary pressures [31]. In a drying gel there are different size pores and caps (Figure 2). The liquid tends to occupy positions ensuring the minimum energy of the system as a whole. A wetting liquid forms menisci. Capillary forces act on the curved liquid-gas surface and on the three-phase liquid-solid-gas contact lines pulling and pushing apart neighbouring particles. The magnitude of the capillary forces depends on the size of the particles in system and generates stresses that may reach to considerable values. If stresses exceed the strength of gel structure then cracks appear.

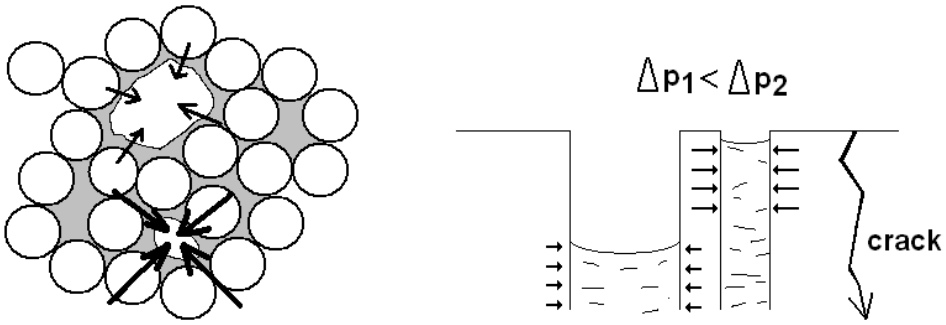

Figure 2. Formation of cracks in gel body during the drying.

To avoid cracking, organic additives are advised to add into alkoxide sols for turning structure of gels more uniform. It is showed that if formamide, glycerol or organic acids are used as drying control chemical additives, then oxide monoliths up to some tens of centimetres could be prepared [18]. The effect of these additives is related to formation of much more uniform size colloidal particles and pores, which therefore lead to lower mechanical stresses during the drying process.

An alternative and very powerful method for removing solvents out from gel bodies is supercritical fluid extraction [32]. Since at supercritical conditions no liquid-gas surface exists then the mechanical stresses cannot develop. This method has been applied for drying of bulk gels in dimensions more than tens of centimetres [33]. As a result of the process, solvent free aerogels are obtained. Silica aerogels for example are materials, which have several extraordinary properties like very low thermal conductivity, low density and refractive index (1,03–1,08), and remarkable mechanical properties [34].

2.5.2. Baking

Gels are most often densified by a baking process. For local densification, focused laser beams are also used. The principal process involved in densification is the viscous sintering. Two models have been employed to describe that process [35]. The first model is applicable at late stages of the densification when pores are closed and isolated [36]. The second, suggested for very open structures of high porosity was originally developed to describe sintering of soots produced by flame hydrolysis [37, 38].

Most critical aspect of the baking is that all solvents, organic groups and decomposition products are to be removed prior to micropores collapse due to the sintering. Oxide is formed as a result of the following processes: carbonisation of organic groups, desorption of absorbed solvents and water from the walls of micropores, polymerisation, collapse of micropores, sintering and densification.

Sintering can be observed by several analytical techniques. Probably the best apparatus for the on-line control is the termogravimetric analysis [39]. IR spectroscopy is used to study chemical bonds in the sample and also to identify gasses released from the sample during the baking. Sometimes oxide materials are analysed by NMR, but it is technically complicated [40].

3. RESULTS

3.1. Aims of the study

The aim of the study was to find new approaches for preparing nanostructured oxide materials. The particular objectives of the study were:

- Elaboration of methods for preparation of suitable precursors for preparing nanostructured oxides.
- Elaborating different methods applicable for preparation of controlled shape nanostructured oxides from the precursors.
- Theoretical analysis of the formation of oxide structures.
- Characterization of the oxide structures.

3.2. Discussion

3.2.1. Conductive and transparent oxide fibres

Our interest in technologies that are used for nanometer level shaping of transition metal oxides were initially related to an idea to use those materials as transparent and conducting SPM sensors. The most critical aspect in designing this kind of SPM sensors is sharpening the needles of these materials down to nanometer level. As a precursor we selected high viscosity (100 to some thousand poises) partially polymerized alkoxides as those materials are widely used as precursors in preparing fibres of transient metal oxides.

There are just a few solid materials known that are electrically conductive and transparent in the optical range. Widely used materials are: ITO [41, 42], ATO and ZnO. Our choice was settled on ATO, which is also mechanically stable material that is very important property of SPM sensors [43].

3.2.2. Precursors [papers I–VI]

Tin butoxide ($Sn(OBu)_4$) was synthesized as described in [44]. Due to their suitable reactivity butoxides are among widely utilized alkoxides in sol-gel fabrication of transient metal oxides [18-20]. We preferred normal butoxy compound instead of tertiary one due to it is higher viscosity caused by complexation of monomers [19]. It is also known that alkoxides, which have normal chain ligands around metal center are much more reactive in reaction with water. That is important factor as the jet, which is pulled into air is to be gelled thereafter.

In our first papers (I–II) we used thermal treatment in vacuum for partial polymerization of $Sn(OBu)_4$ similarly as described by D. C. Bradley [45]. His purpose was to distil $Sn(OBu)_4$ in high vacuum, but it resulted unexpectedly in

decomposition of the compound at 120°C. However, he did not suggest residue material for fibres pulling, which we considered having excellent properties for that. The mechanism of thermal decomposition and polymerization processes of $Sn(OBu)_4$ are discussed in detail in paper [I].

It is known that if water is added to acidified silicon alkoxides then spinnable materials (materials suitable for fibres pulling) can be obtained. In paper [II] we describe analogous reaction, which resulted in preparation of spinnable matter based on $Si(OEt)_4$. Likewise, by adding sufficient amounts of water we prepared spinnable materials from $Ti(OBu)_4$ and from $Sn(OBu)_4$. In all cases, if water was used to polymerize alkoxides, highly viscous precursors for further experiments were obtained after concentration (evaporation solvents out of material) of material in vacuum. We also tested possible thermal polymerization of $Si(OEt)_4$ and $Ti(OBu)_4$ as in the above-mentioned case of $Sn(OBu)_4$ but it resulted in distillation in the case of $Si(OEt)_4$ and in rapid precipitation of oxide at temperatures above 200 °C in the case of $Ti(OBu)_4$. We concluded that preparation of homogeneous precursors by thermal treatment of those compounds was impossible. This is in good correspondence with earlier results, which pointed out that silicon and titanium alkoxides are much more stable compounds compared to tin alkoxide [19].

In papers [III–VI] we used water treatment of alkoxides due to the simplicity compared to polymerization via thermal treatment. In these papers just some minor changes are suggested for preparing suitable precursors. The structure of precursor materials is discussed mostly in papers [I, II] and [V].

3.2.3. Sharp oxide fibres [I–V]

We described the preparation of oxide fibres first in [46]. Fibres were prepared using a glass rod method, which has been widely used for preparing fibres from sols of transient alkoxides. After aging and baking the transparent Sb doped SnO_2 fibres were sufficiently electrically conductive for STM applications. As the next step we tested variety of methods for their sharpening. The simple pinch-off of thermally treated $Sn(OBu)_4$ based precursors in air turned to be the best method since sharp and conical needles can be prepared in one-step process. All other processes included two steps, preparing and sharpening the fibres. The pinch-off also yielded the sharpest needles. TEM imaging of those fibres revealed that in some cases the needles had tip radii down to ~50 nm (paper [I]).

For more detailed studies of formation of sharp fibres an equipment was constructed that enabled to vary the pulling speed and atmospheric humidity. It was designed to enable the generation and exposure of free surface of the jets to air environment just at the moment when pulling of the material was started. Typical fibres obtained with this instrument had conical shape and length 3–10 mm (paper [V]).

In paper [IV] we present sharp fibres that were prepared at controlled pulling speeds from alkoxy precursors. Already the first results proved that the shape of the needles notably depended on pulling speed.

In paper [V] the influence of pulling speed, precursor viscosity and humidity of atmosphere on the sharpness and shape of the fibres is demonstrated. It is shown that regular needles can be pulled from precursors in range of some hundred up to one thousand poises. Experiments showed that the speed of gelation, which is determined by atmosphere humidity, was the key factor influencing the formation of the needles. Optimal gelation speed at room temperature was found to occur at 2–5% relative humidity. Different pulling speeds at this humidity range enabled reproducible preparation of needles with different cone angles.

Similarly, highly viscous $Si(OEt)_4$ and $Ti(OBu)_4$ based precursors were pinched in air to control the applicability of the method in preparing sharp SiO_2 and TiO_2 fibres. Experiments were successful in the case of $Ti(OBu)_4$ based precursors due to its sufficiently high reactivity. As $Si(OEt)_4$ precursors polymerized much more slowly in air, drops due to surface tension quickly formed at the top of the fibres, which considerably dragged down their sharpness (paper II).

Applicability of needles as STM probes was demonstrated in collaboration with M. Kreiter's group from Max Planck Institute for Polymer Research (Mainz, Germany). 1–2 nm resolution in lateral and atomic resolution in vertical direction on surface of crystalline gold test sample could be obtained (paper [III]). The result can be explained by inhomogeneous nanostructure of the fibres (paper [III]). As ATO material is both conductive and transparent the fibres were also tested as probes for local excitation of electroluminescence. The emission of light was detected and found to be non-influenced by metal sensor (paper [III]).

In paper [V] we suggest also that oxide needles can help to understand the phenomena of pinching. As jets can be solidified quickly after pinching the nanoscopic images can be obtained using e.g. TEM leading to better understanding of nanometer level dynamics of viscous liquid treads.

3.3. Tape casting of alkoxide concentrates [Paper VI]

Tape casting is a method where a material is smeared onto a surface with a structured blade (known also as a doctor blade technology). We used structured glass slide and etched monocrystalline (100) silicon pieces as the blade and smeared the precursor onto the surface of another glass slide. Thus, linearly oriented oxide structures on the glass surface were formed. After the smearing, the films were exposed to humid air, which gelled the structures. The structured surfaces were imaged with AFM, TEM and optical microscopy verifying that the smearing with structured blades enables to coat flat surfaces with well-defined linear oxide structures. We suggest that these structures can be utilized in different technological fields.

4. CONCLUSIONS

The description of and discusses about an easy method for preparing nanometer level homogeneous $Sn(OBu)_4$ based concentrates, suitable as precursors for preparing nanometer level structured oxide materials was presented in the current thesis.

Two approaches were suggested for preparing defined shape micro/nano structures from those precursors:

- **The pinching of precursor jets at room temperature in humid air** were demonstrated for the first time as reproducible way for preparing novel structures – nanometer level sharp metal oxide needles. Electron microscopy images demonstrated good quality and high sharpness of the needles. Needles shape correlated liquid jet profiles, measured and simulated in several earlier studies. The knowledge about pinching phenomenon of metal alkoxide jets may lead to better understanding of nanometer level dynamics of viscous liquid treads as needles were formed in process of quick solidification of alkoxide jets. To prove their applicability, needles were used as STM probes enabling 1–2 nm lateral and atomic vertical resolution.
- **Tape casting of precursors by structured silicon blades** was demonstrated to be suitable for preparing a few micron wide oxide lines on solid surfaces.

The formation of structures was explained by rapid solidification of used precursors in humid air that prevented destruction of the structures by surface tension.

Electrical conductivity and optical transparency of prepared ATO materials were caracterized in temperature range from 5.5 K to room temperature. Tensile strenght of prepared materials were measured on tin and titanum oxide fibres.

SUMMARY IN ESTONIAN

Kõrgviskoosssed $Sn(OBu)_4$ oligomeersed kontsentraadid ja nende tehnoloogilised rakendused

Tehnilistele probleemidele lahenduste otsimine miniaturiseerimise läbi on olnud suundumuseks alates 1960. aastatest. Kaasajaks on mitmete komponentide (näiteks transistoride) mõõtmed kahanenud alla 100 nm piiri, millest alates ei räägita kokkuleppeliselt enam mitte mikro-, vaid nanotehnoloogiatest. Jõudmine selliste suurusjärkudeni on aktualiseerinud nii otsingud uute tehnoloogiate järele kui ka tõstatanud diskussiooni molekulaartasemel tehnoloogiate võimalikkusest.

Käesolev doktoritöö on inspireeritud neist üldistest suundumustest. Uurimuse põhieesmärgina keskendutakse nanomeetrilises skaalas terava ja defineeritud kujuga oksiidsete nõelstruktuuride valmistamisele. Välja pakutakse ka uudne, sobivast lähtematerjalist ja selle vormimise metoodikast koosnev kompleks mikroskaalas defineeritud kujuga oksiidsete jadastruktuuride saamiseks. Nõel- ja jadastruktuuride saamise omavaheline seos seisneb samade lähtematerjalide – alkoksiidsete oligomeerkontsentraatide kasutamises.

Töö sissejuhatavas osas antakse ülevaade nanostruktureerimise erinevatest võimalustest, millele järgneb sügavam sool-geel tehnoloogia olemuse selgitamine. Töö diskussiooni osa seob omavahel dissertatsiooni osaks olevates teadusartiklites käsitlust leidnud temaatika ja tulemused.

Töö oluliseimad tulemused on järgmised:

- Välja on töötatud metoodika nanoskaalas homogeensete SnO_2 lähtematerjalide valmistamiseks $Sn(OBu)_4$ baasil.
- Näidatud on, et lähtematerjali joa katkestamisel niiske õhu keskonnas katkemiskoht geelistub, säilitades katkemispunkti nanomeetrilise teravuse. Vastavate struktuuride termilisel töötlusel saadud tinaoksiidseid nõelstruktuure on edukalt kasutatud STM-i sensorina lateraalse lahutuse 1–2 nm ja aatomkihi täpsusega vertikaalsuunalise lahutuse tasemel.
- Näidatud on, et laialt kasutatav määrimismetoodika (*doctor blade*; *tape casting*) on sobilik mikrojadade kandmiseks siledatele pindadele.

ACKNOWLEGEMENTS

The results of my studies have been created in joint effort of many people. Here I try to put into words my wholehearted gratitude to all of these people.
Especially I would like to thank:

- My enthusiastic and sophisticated supervisors Dr. Ants Lõhmus and Dr. Uno Mäeorg who are always ready to realize new ideas.
- Dr. Kristjan Saal for fruitful cooperation, discussions and for his skills in realizing our ideas.
- Dr. Ilmar Kink who is always enthusiastic in discussing novel ideas and realizing them. I appreciate also his efforts in increasing the productivity of our group.
- Dr. Ilmo Sildos for the optical measurements, interesting discussions about science in general and for his support in sol-gel technology related activities.
- Dr. Rünno Lõhmus for his help in solving technical problems and realizing more concrete things.
- Madis Lobjakas for his assistance in solving technical problems.
- Dr. Marco Natali (University of Padova) for providing silicon samples and interesting discussions on micro structuring.
- Dr. Volker Jacobsen, Dr. Maximilian Kreiter and Dr. Robert Brancheid (Max Planck-Institute for Polymer Research in Mainz) for SPM measurements.
- My fellow students Valter Reedo, Madis Paalo and Kaija Põhako for stimulating interest to my studies.
- All other people who have contributed to the study
- My mother Milja, my brother Tauri, my mate Kristina and my son Samuel for their support.

The work is partly supported by Estonian Nanotechnology Competence Centre, Estonian Science Foundation (grants: 5545, 6537, 5015, 6660, 6163) and European Science Foundation program *Nanotribology COST P13* program *Molsimu* for their financial support.

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