2nd International workshop

Atomic Layer Deposition: Russia 2017
(ALD Russia - 2017)

Book of Abstracts

September 24 – 30, 2017

Saint-Petersburg
Russia
The workshop is organized by:

The Ministry of Education and Science of the Russian Federation
Hooking together European Research in Atomic Layer Deposition - HERALD (COST action MP1402)
St.Petersburg State Institute of Technology
St.Petersburg branch of Mendeleev Russian Chemical Society

Sponsored by:

Picosun Oy (Finland)
Eurointech Ltd. (Russia)
Chemical Assembly of Nanomaterials, Ltd. (Russia)

Supported by:

Rustour LLC (Russia)
ORGANIZING COMMITTEE

Anatoly A. Malygin – Prof., Dr., St.Petersburg SIT(TU), St.Petersburg, Russia (Chairman)
Eugene A. Sosnov – Ph.D., St.Petersburg SIT(TU), St.Petersburg, Russia (Secretary)
Sean T. Barry – Prof., Dr., Carleton University, Ottawa, ON, Canada
Victor A. Bykov – Prof., Dr., NT-MDT-Spectral Instruments Companies Group, Moscow, Russia
Victor E. Drozd – Prof., Dr., St.Petersburg State University, St.Petersburg, Russia
Simon D. Elliott – Prof., Dr., Tyndall National Institute, University College Cork, Cork, Ireland
Steven M. George – Prof., Dr., University of Colorado, Boulder, CO, USA
Nikolay A. Kulikov – Ph.D., Svetlana-Roentgen Ltd., St.Petersburg, Russia
Markku Leskelä – Prof., Dr., University of Helsinki, Helsinki, Finland
Andrey M. Markeev – Ph.D., Moscow Institute of Physics and Technology, Dolgoprudny, Russia
Gregory N. Parsons – Prof., Dr., North Carolina State University, Raleigh, NC, USA
Riikka L. Puurunen – Prof., Dr., Aalto University, Aalto, Finland
Anatoly I. Rusanov – Full Member of Russian Academy of Sciences, Prof., Dr., St.Petersburg State University, St.Petersburg, Russia
Vladimir M. Smirnov – Prof., Dr., St.Petersburg State University, St.Petersburg, Russia
Jonas Sundqvist – Dr., Fraunhofer IKTS, Dresden, Germany

PROGRAM COMMITTEE

Sergey E. Alexandrov – Peter the Great St.Petersburg Polytechnic University, St.Petersburg, Russia
Anatoly A. Malkov – St.Petersburg SIT(TU), St.Petersburg, Russia
Anatoly A. Malygin – St.Petersburg SIT(TU), St.Petersburg, Russia
Andrey M. Markeev – Moscow Institute of Physics and Technology, Dolgoprudny, Russia
Vladimir M. Smirnov – St.Petersburg State University, St.Petersburg, Russia
Eugene A. Sosnov – St.Petersburg SIT(TU), St.Petersburg, Russia
Valentin B. Aleskovsky was born June 3, 1912 in Merv (since 1937 - Mary), Turkmenistan.
1931 – entered the Chemical Faculty of Leningrad Institute of Technology (LIT)
1937 – Researcher in Navy Scientific Research Chemical Institute
1938 – entered the graduate school of Leningrad Institute of Technology
1940 – defended his Ph.D. "Active silica"
1940 – Senior Researcher of the Department of Sorption Technology of LIT
June 1941-1945 – volunteered to the front of Great Patriotic War; fought on the Leningrad front, was wounded, took part in the battles near Pskov, in Baltic region, in the Balkans, in Hungary, Austria, Czechoslovakia; Awarded with orders and medals.
1945 – Senior Researcher of the Department of Sorption Technology of LIT
1949 – Head of the Analytical Chemistry Department of LIT
1952 – defended Doctoral of Chemical Sciences dissertation "Framework hypothesis and way of synthesis of some active solid compounds"
March 1960 – was sent to Great Britain for lecturing
November 1962 – was sent to German Democratic Republic for lecturing
1965-1975 – Rector of the Leningrad Institute of Technology
February 1967 – was sent to Finland for lecturing
1967 – founded and headed the Department of Chemistry of Solids LIT (now – Department of Chemical Nanotechnology and Materials for Electronic Devices)
May 1971 – was sent to CSSR for lecturing
1972 – elected Corresponding Member of the USSR Academy of Sciences
1975-1986 – Rector of the Leningrad State University
1977 – founded and headed (until 1986) the Department of Solid State Chemistry at the Chemical Faculty of Leningrad State University.
1986-2006 – Professor of the Department of Solid State Chemistry in Leningrad State University
Valentin B. Aleskovskii is a well-known expert in the field of hydrochemical prospecting of non-ferrous metals deposits, automatic analysis of microimpurities, physical chemistry and materials technology. However, the main area of V.B. Aliskovskii's scientific interests was the study of the nature and chemical transformations of solids and the development of a technology for the creation of inorganic materials that have precisely specified composition and structure.

On the basis of the "framework" hypothesis formulated in doctoral dissertation (1952), V.B. Aleskovskii and his disciples more than 60 years developing new ideas about solids and the ways of their physical and chemical transformations.

At the first stage of research (1960-1970s) the development (on the base of the "framework" hypothesis) of the fundamentals of the synthesis of individual solid compounds and materials with the specified structure and properties and simultaneously - specific methods for the purposeful synthesis of multicomponent solids of a reproducible composition were held. In the works of VB.Aleskovskii and his collaborators formulated a fundamentally new concept reflecting the most general regularities in the chemistry of solids and developed (by some analogy with DNA replication) an original and largely unique process of Molecular Layering (ML), consisting in the chemical assembly of solids in a pre-planned program.

In the 1990s, this method was elaborated abroad and now widely known as Atomic Layer Epitaxy (ALE) or Atomic Layer Deposition (ALD) and is currently one of the main methods for synthesizing layered nanomaterials for microelectronics.

The final stage of the Molecular Layering method creation was the doctoral dissertation of S.I. Kol'tsov (Synthesis of Solids by Molecular Layering Method, 1971), in which the principles of the ML method were formulated and its synthetic possibilities were illustrated.

Later (1980-1990s) V.B. Aleskovskii developed the concept of chemistry of supramolecular compounds, revised in the 1990s, taking into account his own data and supramolecular chemistry data (J.-M. Lehn, Nobel Prize in 1987) and elaborated the concept of chemistry of highly-organized substances (1993).

V.B. Aleskovskii was a talented teacher who prepared a pleiad of specialists in solid state chemistry who work both in our country and abroad. Among his students there are 30 doctors of science and more than 100 Ph.D. In the USSR-Russia formed the leading scientific school "Chemistry of highly organized substances", the organizer and the permanent leader until the last days of his life was Valentin B. Aleskovskii.

V.B. Aleskovskii was an author of more than 450 scientific publications, including 12 monographs and textbooks and more than 150 inventions. Many results of developments and inventions of V.B. Aleskovskii and his students are realized in practice.

Some works of V.B. Aleskovskii, which form the basis of chemistry of highly organized substances


Monographs and textbooks for students


Valentin B. Aleskovskii's Scientific School
Picosun is the leading supplier of high quality Atomic Layer Deposition (ALD) thin film coating solutions for industrial production and R&D.

The agile design of Picosun™ systems enables the highest quality ALD film depositions together with the ultimate system flexibility to fit future needs and applications. The patented hot-wall design with fully separate inlets and instrumentation enables particle-free processing adaptable on a wide range of materials on wafers, 3D objects, and all nanoscale features. Picosun™ equipment creates the highest quality ALD films with excellent yield, low particle levels, and superior electrical and optical performance. Excellent uniformity even on the most challenging through-porous, ultra-high aspect ratio, and nanoparticle samples is achieved thanks to our proprietary Picoflow™ technology. The PICOSUN™ systems are equipped with highly functional and easily exchangeable precursor sources for liquid, gaseous, and solid chemicals. Highly efficient and patented remote plasma option enables deposition of metals without the risk of short-circuiting or plasma damage. Integration with glove boxes, UHV systems, manual and automated loaders, cluster tools, powder chambers, roll-to-roll chambers, and various in situ analytics systems enable efficient and flexible research with good results no matter what your research area is now or might become later on.

PICOSUN™ ALD product portfolio ranges from fully automated, SEMI compliant batch and cluster systems for high volume manufacturing to smaller scale R&D and pre-pilot production tools. Production-proven coating solutions for IC, MEMS, LED, sensor, and 3D component processing are mastered with world-class process quality, the leading equipment design, the most comprehensive process support, and the best customer care.

PICOSUN Oy Main Headquarters
Tietotie 3, FI-02150, Espoo, Finland
Tel. +358 50 321 1955
e-mail: info@picosun.com
www.picosun.com
Eurointech Ltd. is supplier of equipment, materials and CAD software for universities, research institutes and production companies in the sphere of microelectronic industry from 2007 year.

Eurotech Ltd. is committed to basic principle to supply the best equipment, well tried and reliable, cooperating with many manufacturers over the world in following areas: wafer processing, including deposition of thin films, micro assembling, testing and visual control, automatization of processes etc.

In the area of Atomic Layer Deposition, Eurointech Ltd. is the official representative of the company Picosun Oy (Finland) from 2014 year. In frames of this cooperation, Eurointech Ltd. can provide preliminary consultation of customers, delivery and service support.

Making special emphasis on service, Eurointech Ltd. has own technical department. Engineering staff has been trained on the side of Picosun Oy and continues to improve their skills.

Being in contact with a lot of potential customers, Eurointech Ltd. continuously finds new opportunities for application of ALD technology in practical purposes. Customers meetings in format of seminars regularly take place in demo facility of Eurointech Ltd.

**Eurointech Ltd.**
26 Yubileinaya str., office 016
Lyubertsy, Moscow reg., 140011, Russia
Tel./Fax: +7-(495)-228-72-04
e-mail: sales@eurointech.ru
www.eurointech.ru
The team of Chemical Assembly of Nanomaterials, Ltd. is engaged in the development of precision methods for the synthesis and investigation of solids and materials in a low-dimensional state, as well as technologies and equipment for the production of nanostructured solid-phase materials of various functional purposes.

At the Chemical Assembly of Nanomaterials, Ltd. is organized the production of:
- Indicator-sorbent modified IVS-1 (TU 6-10-1971-84),
- Sorbent modified FS-1-3 (TU 6-10-1970-84),

Chemical Assembly of Nanomaterials, Ltd.
26 Moskovsky prosp., St.Petersburg,
190013, Russia
Tel.: +7-(911)-931-98-61
Tel./Fax: +7-(812)-316-74-83
e-mail: malygin@lti-gti.ru
PLENARY LECTURES

PERSPECTIVES OF FUNDAMENTAL AND APPLIED RESEARCHES IN RUSSIA, WITH USING OF THE METHOD OF MOLECULAR LAYERING

Anatoly A. Malygin

St. Petersburg State Institute of Technology, St. Petersburg, Russia

In 2017 it will be celebrated 65th anniversary of formulated by V.B. Aleskovskii "framework" hypothesis, which formed the basis of the proposed chemical model of solids [1]. From the standpoint of "framework" hypothesis has been the development of new approaches in the field of chemistry and chemical transformations of solids. V.B. Aleskovskii's ideas were formed as a result of the deep analysis of achievements in the field of chemistry in the 18th to 20th centuries [2]. V.B. Aleskovskii introduced the concept of a solid body as "supermolecule" [3], chemical interaction that is subject to known stoichiometric laws [2, 3]. Hypothesis required experimental validation. And in the middle of the sixties of the last century under the leadership of V.B. Aleskovskii his disciples were developed the principles of chemical assembly of solids and materials using precision techniques of synthesis, one of which was the method of molecular layering (ML) established by S.I. Kol'tsov in conjunction with his supervisor in the mid-sixties of the last century [4, 5]. The classification of solids from the standpoint of the "framework" hypothesis was proposed, the principles of ML, the synthetic capabilities of this process were formulated and real experiments were carried out of the chemical assembly of the surface of solids.

The purpose of the present communication is to evaluate not so much the results achieved how to identify the most interesting and important questions, tasks, problems that require solutions or study in subsequent years.

It should be noted that the fundamental principles of the ML, which were formulated in the first papers of V.B. Aleskovskii, S.I. Kol'tsov and their students are not in doubt and was confirmed not only our research, but also the works of foreign colleagues. At the same time, given the more modern research methods, expanding the range of the used reagents, substrates, instructional techniques were able to identify some new features in this synthesis.

The report from the standpoint of structural-size effects and synthetic possibilities of the method ML (table) describes the main achievements and some of the issues of interest for deeper study.

The effect of the monolayer

The use of the different reactivity of halides allows synthesizing multi-component monolayer system. The use of the different reactivity of halides allows synthesizing multi-component monolayer system. Important are the stability of the chemical bond with the matrix of formed groups when exposed to water vapor at the stage of surface preparation for the second cycle of ML. It also needs to consider the impact of side product of the reaction of hydrogen chloride on the composition of the produced functional groups. Of interest more in-depth study of the influence of structure and concentration of centers in a monolayer on the composition and structure of emerging layer of a given thickness of in the ML process. Not only theoretical but also practical importance is the formation of surface centers in the processing of the matrix by a mixture of reagents. When synthesizing such complex systems,
Table - Structurally-dimensional effects in the products of molecular layering

<table>
<thead>
<tr>
<th>2-D and 3-D structures that synthesized on the surface of solid matrix in ML process and also chemical transformations in system &quot;matrix - surface structure&quot;</th>
<th>Structurally-dimensional effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>A single-component monolayer (from 1 to 4 ML cycles)</td>
<td>The effect of monolayer - sharp change in the properties of material (after 1-4 ML cycles)</td>
</tr>
<tr>
<td>A single-component nanolayers (from 4-6 etc. ML cycles)</td>
<td>The effect of physical overlap of substrate surface (after at least 4-6 etc. ML cycles)</td>
</tr>
<tr>
<td>A multi-component layers (mono- and nanolayers)</td>
<td>Effects related to multi-component systems</td>
</tr>
<tr>
<td>3-D structure that connected with the surface of matrix by chemical bonds and is in a certain phase state depending on the structure of the substrate surface</td>
<td>Effects related to the mutual coordination between of structural of a substrate surface and thin film formed in ML process</td>
</tr>
</tbody>
</table>

it is useful to involve quantum-chemical and thermodynamic modeling. The main thing is to identify the relationship between concentration and ratio of reagents in the gas and solid phases. A large number of publications related to modify the surface of polymeric materials. But the work is mainly concerned with the regulation of functional properties of such materials (flammability, thermal resistance, water vapor permeability, wettabiliy, electrical characteristics). At the same time, almost no significant results in the study of the functional composition of the surface of polymer, the ways of its regulation, the structure and distribution on the surface new functional groups formed during the ML's.

The effect of the overlapping substrate
When implementation of the key tasks are: identifying the beginning of the formation of phase of the substance in the formed layer depending on the number of cycles ML; regularities of phase transformations on the surface with the use of different thermal regimes on the stages of chemisorption, vapor-phase hydrolysis; changes in the properties of the coating with increasing number of cycles of ML.

The effect of a multicomponent system
It is important to assess the boundaries between layers of different composition and the possibility of interdiffusion.

The effect of the mutual harmonization of the structure of the substrate surface and building up layers
This effect has already found a practical application for reducing the temperature of sintering of ceramic materials, acceleration of solid-phase chemical reactions. But, in fact, no one of an overview paper on the study of the mechanism of such interactions.

All the structural-size effects in the products obtained by the ML, has received experimental confirmation. A number of developments introduced to the industry: electroluminescent coatings, sorbents, modified ceramics, protective coatings [6-10]. Assessing modern trends in the development of solid-phase materials and products for high-tech industries, the report discusses some of the promising applications of nanotechnology. These include the creation of functional systems of kind "core – shell", thin-film materials as
components products alternative energy (solar, hydrogen, electrochemical, etc.), sensory instrumentation, membrane, catalytic and sorption processes, components of nanoelectronics.

Studies of molecular layering processes are supported by the Ministry of Education and Science of Russia (project 16.1798.2017/4.6) and Russian Foundation for Basic Research (project 16-03-00214).


PLASMA SOURCE OF ATOMIC NITROGEN FOR ACTIVATED ALD

Sergey E. Alexandrov

Peter the Great St.Petersburg Polytechnic University, St.Petersburg, Russia

The fact that participation of atomic nitrogen in surface reactions during PEALD of various nitride layers can lead to improved material properties has been demonstrated experimentally [1]. The use of molecular nitrogen as an initial source for formation of atomic nitrogen is of particular interest comparing to ammonia NH$_3$, dimethyl hydrazine (N$_2$H$_2$Me$_2$) or hydrazine (N$_2$H$_4$) not only because of simplicity of the technological equipment required and safety but sufficient decrease of amount of reaction pathways also.

In this report we describe the effect of argon dilution of the nitrogen passed through the RF discharge region on plasma composition and particularly relative concentration of atomic nitrogen.

Analysis of typical emission spectra for nitrogen and nitrogen-argon plasmas, obtained from a region about 5 cm below the inductor coil allowed several groups of bands mainly belonging to nitrogen to be distinguished. In each group, line intensity varied symbiotically with the total pressure and RF power. The emission lines in the region 290-400 nm were the most intense and they constituted the second positive system of emission lines of nitrogen, corresponding to the transitions of molecular nitrogen from the C$_3^3$Π$_u$ excited electronic state ($v'$ = 0 - 4) with 11.18 eV energy ($v'' = 0$), to the low-lying B$_3^3$Π$_g$ excited state ($v'' = 0$ - 7) with 7.5 eV energy ($v'' = 0$). The breaking of the sequence of bands corresponding to the second positive system of nitrogen at $v' > 4$ of the C$_3^3$Π$_u$ state is caused by predissociation.

A group of lines in the region 200-270 nm constitutes the fourth positive system of bands attributed to the transitions of molecular nitrogen from the D$_3^3$Σ$_u^+$ excited state (13 eV for $v' = 0$) to the B$_3^3$Π$_g$ excited state.

The regularities found in the variation of line intensity with pressure for the second and fourth positive systems of nitrogen can be explained in terms of direct participation of argon atoms, in metastable states, in excitation of nitrogen to vibrational levels of the C$_3^3$Π$_u$ state, characterized by $v' = 2$, and probably $v' = 3$. However, the energy of metastable argon atoms is not sufficient for pumping of the vibrational state with $v' = 4$ of the C$_3^3$Π$_u$ electronic state of molecular nitrogen (12 eV). The anomalous population density of the vibrational state with $v' = 4$ is most likely to be caused by reverse predissociation of nitrogen.

\[ \text{N}(^4S) + \text{N}(^2D) + M^0 = C^5\Pi_u + M^1 = C^3\Pi_u (v'=4,3,2) + M^2, \]  

where M$^0$ - “third body” particles with different energies.

Metastable argon atoms are close in energy to vibrational states belonging to the C$_3^3$Π$_u$ state of N$_2$. Hence, it seems likely that inelastic collisions of nitrogen molecules with metastable argon atoms increase the probability of predissociation of molecular nitrogen both from the C$_3^3$Π$_u$ state directly and through the C$^5\Sigma_u^+$ electronic state of N$_2$, resulting in the formation of nitrogen atoms in $^4S$ and $^2D$ states. This should be accompanied, however, by an increase of the probability of the reverse predissociation, when a fraction of excited molecules descend to the closest low-lying vibrational levels of the C$_3^3$Π$_u$ electronic state. This is related to the level with $v' = 4$ and explains its anomalous population density.

The regular trends mentioned above in the intensity growth with increasing amount of argon added, as shown for the 4→3 and 3→2 lines, correlate very well with the simultaneous increase of the Lewis-Rayleigh glow. If the similar sizes of a nitrogen molecule and an argon atom are taken into account, the increase in glow intensity caused by substituting a portion of nitrogen for argon cannot be attributed to an increased probability of recombination of atomic nitrogen, which involves a “third body”. The greater glow intensity is likely to be caused only
by the higher concentration of nitrogen atoms in the gas phase. Considering all of the facts, there is very strong evidence that the dilution of nitrogen with argon leads to an increase in concentration of atomic nitrogen in the gas phase and this effect becomes more significant with an increasing argon fraction in the gas mixture.

It was shown that the intensity of lines of the fourth positive system is increased with the addition of argon compared to nitrogen plasma. Since the transition of argon to a metastable state is most likely to proceed via an electronic state with excitation energies not less than 13 eV, it can be concluded that the increased intensity of lines of this system, which are attributed to transitions from the D$^3\Sigma_u^+$ state with 12.98 eV energy, is caused by an increased population density of these states of molecular nitrogen, arising from inelastic collisions of the nitrogen with metastable argon. It is known that the potential well of the D$^3\Sigma_u^+$ state is fairly shallow and predissociation in this state already occurs at $v^\prime > 1$. Consequently, the transition of molecular nitrogen to the D$^3\Sigma_u^+$ state increases the probability of predissociation and therefore the concentration of atomic nitrogen in $^4S$ and $^2D$ states.

The long lived argon atoms in metastable states have a considerable influence on the length of the plasma column which extends along the reaction chamber downstream from the RF discharge generation region. The total pressure in the reactor did not affect this area under the conditions studied. Also, it was found that the Lewis-Rayleigh glow intensity stayed approximately the same along the plasma column section. This shows the constancy of the concentration of atomic nitrogen because of the lower rate of recombination in an argon-nitrogen mixture as compared to that in a pure nitrogen plasma.

Thus, it has been found experimentally that the addition of argon to nitrogen passing through the discharge generation region leads to a significant increase in the atomic nitrogen concentration because of selective excitation of molecular nitrogen by argon atoms in metastable states.

“PINNING” COINAGE METAL NANOSTRUCTURES TO PRESERVE PLASMONIC EFFECTS: NEW COLOURS FOR GOLD AND SILVER

S.T. Barry¹, P.G. Gordon¹, F.A. Monteiro¹, J.-M. Guay², A. Cala’Lesina², J. Baxter², L. Ramunno², P. Berini², W. Weck²

¹ Department of Chemistry, Carleton University, Canada
² Centre for Research in Photonics, University of Ottawa, Canada

Nanostructured coinage metals have the attractive ability to generate a surface plasmon resonance in the visible and infrared range of the electromagnetic spectrum. This allows metal nanofeatures to act as sensors when interrogated with light, and even to generate colour in the visible range. These nanoscale effects can be exploited for both decorative and sensing effects on metal surfaces.

One drawback to these effects is the high surface mobility of coinage metals under standard conditions. As the metal shows more noble behaviour, it also shows higher surface mobility on oxide and metal substrates. This can allow redistribution of metal atoms among nanofeatures (akin to Ostwald ripening) that change the size distribution of nanofeatures, and ultimately leads to a shift in plasmon wavelength and apparent colour.

With the advent of atomic layer deposition (ALD) processes for the fabrication of all coinage metals as nanostructures, the ability to generate in-tool stacks of metals and dielectrics has become straightforward. We have recently discovered that alumina can be used in conjunction with silver and gold metal nanofeatures to “pin” nanostructures in place, and preserve plasmon activity.

Silver metal can be patterned by laser ablation to give angle-independent colour, arising from periodic nanostructure formation on the bulk silver surface (Figure 1). This impressive effect can generate decorative elements to coinage metal objects without the introduction of paints or patinas. However, these colours have been seen to fade over several weeks due to mobility of silver metal at the nanostructured surface.

Gold metal nanoparticles and nanostructures have been formed by two different methods: co-evaporation of silver and gold, followed by the chemical etch of silver in nitric acid has produced a variety of colours, while plasma ALD deposited gold on silica and alumina have shown a detectable plasmon absorbance in the near IR. In both cases, the gold plasmonic response has faded rapidly (sometimes over just hours) due to the facile mobility of gold metal atoms.

We have shown in a variety of cases that these plasmonic coinage metal structures can be preserved with as little as 5 cycles of alumina deposition using TMA and water. This overlayer can shift the observed colour of the developed plasmon (likely through optical interference from the high index of refraction of alumina), but a full range of colour can be preserved.

This presentation will cover the different methods of developing silver and gold nanostructures to produce plasmonic responses and observable colours, as well as the preservation of these effects by alumina overcoating. Applications in “collector” coinage preservation and sensing will be discussed.

Figure 1. Photos of (a) full colour palette on silver, (b, c, d) various designs on collectors coins
MODERN POSSIBILITIES OF SCANNING PROBE MICROSCOPY AND SPECTROSCOPY FOR INVESTIGATION OF PHYSICAL PROPERTIES AND SPECTRAL FEATURES OF SURFACE STRUCTURES

Victor A. Bykov¹,², Arseny Kalinin¹,², Vyatcheslav Polyakov¹, Artem Shelaev¹,²

¹ NT-MDT-Spectral Instruments Companies Group, Moscow, Russia
(www.ntmdt-si.com, spm@ntmdt-si.ru)
² Moscow Institute of Physics and Technology, Russia

During last years the development of SPM technology was transformed to the side of specialization. The application field was increased very wide – from one side micro- and nanoelectronics with extra high-level the metrology requirements and up to material science, biology, ecology with requirements to the side of simplification in operation procedures, possibility of the materials and molecules recognitions.

Scanning Probe Microscopy gives an opportunity to carry out studies of spatial, physical and chemical properties of objects with the typical dimensions of less than a few nanometers. Owing to its multifunctionality, availability and simplicity, Atomic-Force Microscope (AFM) has become one of the most prevailing “tools for nanotechnology” nowadays. NTEGRA platform has been designed as the special base for the constantly developing options of Scanning Probe Microscopy that combines them with various other modern research methods. Integration of SPM and confocal microscopy / luminescence / Raman scattering spectroscopy / Infrared Apertureless Nearfield Spectroscopy and Microscopy. Owing to the effect of giant amplification of Raman scattering (TERS – Tip Enhances Raman Scattering) it allows carrying out spectroscopy studies and obtaining images with 10 nm resolution.

New generation of AFM control electronics now allows a real-time cantilever deflection tracking and analyzing. Based on a fast force-distance measurement we developed a new group of non-resonant atomic force microscopy methods of scanning probe spectroscopy - called Hybrid mode. Hybrid mode is the most proposal AFM mode since it summarizes all advantages of amplitude modulation and contact modes allowing simultaneously: free of share force topography measurement with direct tip-sample interaction control, real-time quantitative nanomechanical measurements [1], conductivity [2], piezoresponse and electroscatic imaging, all with conventional scanning speed. Hybrid mode is also very helpful for liquid measurements because it utilizes the issue with cantilever eigenfrequency detection.

Progress in micromechanics manufacturing resulted in significant increase of the cantilever yield rate (to practically 100%) with repeatability of resonant characteristics at 10% level, thus preconditioning implementation of the concept of multi-probe cartridges for AFM.

A cartridge of this type is a multi-probe contour-type sensor with 38 cantilevers. The cantilevers can be either of the same type or "colored" with predefined coverings and rigidities. Depending on AFM system type the cartridge rotation to select working cantilever can be manual or software-controlled and takes only a few seconds.

A whole cartridge can be exchanged manually through a simple procedure without the risk to damage cantilevers. The cartridges operate in dedicated measuring heads, which are designed for integration in the latest instruments by the Company (Titanium, NEXT, SOLVER-NANO, VEGA-SPM).

For fully software-controlled AFMs Titanium and NEXT the cantilever setup procedure was motorized and automated including: precise cartridge rotation to the user-selected cantilever, optical beam deflection (OBD) system adjustment, lock-in amplifier tuning and sample positioning. This approaches us to the concept of ease-of-use AFM where routine system adjustment before scanning is proceeded automatically in a few tens of seconds.
Ease-of-use is not the only feature of automated multi-probe cartridge. One of the most demanding application of modern AFM is routine and repeatable atomic and molecular resolution. This requires extra-low tip-sample thermal drift assumed us lower than 1 Å/min. Development of thermally stabilized cabinet with 0.01°C temperature control accuracy and drift-minimized mechanical design of Titanium AFM helped us to achieve mentioned drift level and repeatable atomic/molecular resolution imaging [3]. But conventional cantilever exchange procedure requires opening the cabinet and manipulating with AFM therefore destabilizing perfect temperature conditions. So the concept of automated multi-probe cartridge together with active thermal stabilization and drift-minimized mechanical design can be a perfect tool for routine high-resolution AFM imaging.

AFM is a candidate to solve some of “Metrology Difficult Challenges” proposed by The International Technology Roadmap for Semiconductors like: “Structural and elemental analysis at device dimensions and measurements for beyond CMOS”, “Nondestructive, production worthy wafer and mask-level microscopy for critical dimension measurement for 3D structures, overlay, defect detection, and analysis”. A rapid development of polymer [4] and single-molecular electronics [5] also requires AFM to measure and control the topography, nanomechanical, conductivity, temperature and other properties at the nanoscale.

To summarize, future electronics development and manufacturing can be a wide field for AFM application, especially for large-sample AFMs. But the biggest drawback of AFM technology to overcome is low throughput. Throughput of AFM is limited by: system adjustment time before scanning (OBD system and lock-in adjustment, area of interest searching time etc.), scanning parameters adjustment time, scanning speed and amount of data gathered after one scanning session. So to develop the next-generation AFM all these limits should be overcome.

To minimize system adjustment and scanning parameters tuning time we develop and improve new software algorithms allowing fully automated topography imaging. New high-speed control electronics together with Hybrid mode allow more data points and different properties to be recorded per one scanning session. We also develop new AFM-scanner control algorithms to increase a topography imaging speed noticeably.

These developments implemented to the fully motorized large-sample AFM is a promising tool for nanotechnology industry.

To use AFM-cluster technology in the portable SPM, such as Solver-NANO (http://www.ntmdt.com/practical-afm/solver-nano) can open the road for the using of this unit right on the Space Stations for material quality control in the Space and Space Station conditions.

Development of modes for scanning spectroscopy combined with SPM in the instruments NTEGRA-SPECTRA-II provides new options of confocal laser luminescence spectroscopy and Raman spectroscopy as well as higher reliability of detection for TERS and high-resolution scanning probe-optical microscopy and spectroscopy. Probes with diamond nanocrystals containing N-V defects are capable to detect magnetic states as microscopic as single spins and so they are promising for studies of surface catalytic activity and for detection of free radicals, including applications in biology and medicine.

Apertureless scanning nearfield optical microscope (ASNOM) probe induce light scattering give the possibility to investigate infrared as chemical nature of surface functional gropes and to measure the doped impurity implantations in microelectronic structures [6] that it impossible to observed in electron microscopy (Fig.1).
Figure 1. Silicon semiconductor structure chip in SEM (left) and ASNOM images (D. Kazantsev, ITEF RAS & NT-MDT-SI)

QUANTUM CHEMISTRY AS A TECHNOLOGICAL TOOL FOR ALD DEVELOPMENT

Stanislav D. Dubrovensky
St.Petersburg State Institute of Technology, St.Petersburg, Russia

The possibility of a search of optimum choice of conditions of synthesis by ML/ALD technology of titanium, vanadium and chromium oxide coatings on the surface of silica using chloride (XClₙ) and alkoxide (X(OR)ₙ) precursors based on quantum-chemical analysis is shown (X = Ti, VO, CrO₂).

The results of the analysis of the composition and structure of the products of structural-chemical transformations as a function of temperature and concentration factors are presented. The dentisity (a number of covalent bonds between modifier X and matrix surface) strongly depends on the reaction temperature: the less the temperature the less dentisity. The growths of partial pressure of reagent vapors, as well as the total gas pressure in the reaction space lead to decrease dentisity. Such regularities correspond well with experimental data.

The conditions leading to uncontrolled growth of the coating as a result of chlorination or esterification of OH groups of the silica surface are studied, the probability of such processes increasing in the Cr-V-Ti series.

Using two-component systems it has been shown that, according with model predictions, it is possible to select optimal synthesis conditions that provide products with a specified ratio of components in the coating composition.

The simulation results predict that the subsequent evacuation stage can, in addition to removing of physically sorbed molecular products, also may lead to a significant (up to 30%) decrease in the content of grafted surface sites.

It is shown that the contact of element-oxide and element-chloride sites with water vapor has a high probability in low-temperature area (T <450 K) hydrolytic destruction with complete breakage of the =SiO-El (El = Ti, V, Cr, P) bonds and the formation of bulk hydrated oxides of the corresponding elements. The stability of surface centers to the action of water vapor decreases in the series of Cr-V-Ti species and sharply increases with increasing denticity of surface sites.

The analysis of the processes of cyclic synthesis by the ML/ALD method demonstrates the possibility of a significant deviation of the mechanisms of coating growth from a layer-by-layer scheme to a complete cessation.

Such results indicate a lack of chemical analysis to control the surface composition during ALD and require independent means of spectral identification. Fortunately quantum chemistry provides wide opportunities to use for this purpose the calculated transition energies in optical and vibrational spectra, which make it possible to determine not only the presence of =Si-O-El and El-O-El bonds, but also to estimate the local structure of the surface centers. Examples of the correspondence between the calculated and experimental spectra of ALD products are given.

The developed theoretical technique can be used for a priori analysis of other chemical systems based on ALD method. Thus, quantum-chemical modeling can act not only as a means of theoretical analysis, but also as a tool for design of the processes of synthesis of low-dimensional systems by the ALD technology.

This work was financial support from the Ministry of Education and Science of Russia (project 16.1798.2017/4.6)
Atomic layer deposition is unusual in that it is defined through its chemical mechanism: self-limiting reactions of a gaseous precursor with the solid substrate. Understanding ALD growth thus requires a detailed understanding of reactivity and inertness, and thus of the mechanism of gas-surface reactions [1]. To design, analyse or improve an ALD process in a rational way therefore requires knowledge of the underlying chemical mechanism. Quantum chemical modelling using density functional theory (DFT) has been successfully applied to determining a variety of chemical mechanisms at the atomic scale [1]. DFT is a reliable, accurate, parameter-free approach to computing electronic structure and hence chemical structure and bonding, leading eventually to thermodynamics and kinetics. This talk discusses three recent examples.

We start with Al$_2$O$_3$: although it is the most widely-studied ALD process, new insights about the mechanism are still coming to light. We present DFT calculations that demonstrate how the reactions of the precursors self-limit, comparing the H$_2$O [2] and O-plasma processes. The recent experimental observation of persistent surface-CH$_3$ [3] has confirmed some of our predictions. The second topic is area-selective deposition, where we explain the surprising finding that even plasma-based deposition of silicon can be selective to different types of surface preparation. Finally, we give some examples of how theory and experiment can be combined to design and characterise a novel molecular layer deposition process for hybrid organic/inorganic films. We discuss the challenges in modelling the complex structure of the growing polymer.

Transparent conductive oxides (TCOs) based on doped ZnO and In$_2$O$_3$ are ubiquitous in many of today’s electronic devices, most prominently in displays and solar cells. There has been a growing interest in preparing such TCO films by atomic layer deposition (ALD). This interest is triggered by the acclaimed key merits provided by ALD but also by the fact that ALD is a soft deposition technique. This means that damage to the underlying substrate/device, as often caused by sputtering, can be avoided. Moreover, the TCO films can be deposited quite easily by spatial ALD (especially ZnO) such that industrial application can be economically viable. Finally, the ALD method is also well suited to study and precisely control the properties of the TCO films; hence it can provide a better understanding of aspects that are important to improve the performance of the TCOs.

In this contribution, ALD of ZnO:X (X = Al, B, H) and In$_2$O$_3$:H will be considered [1-4]. The ALD processes will be described and the possibilities provided by the use of supercycles for doping will be addressed. The surface chemistry will be discussed and a correlation will be made between the ALD process parameters and the resulting properties. It will be shown that films with very good TCO properties can be obtained. Aspects related to the scale up of the processes by spatial ALD will also be discussed [5].

TCOs combine a low absorption with a high conductivity. These figures show the absorption coefficient of various TCO films prepared by ALD (ZnO:Al, ZnO:B, ZnO:H, and In$_2$O$_3$:H) in a comparison with the most commonly applied TCO of In$_2$O$_3$:Sn (ITO). As one prominent application of TCOs is in solar cells, the solar irradiance spectrum (AM1.5g) is shown for reference.

HYBRID MATERIALS BY ALD-DERIVED METHODS: OPPORTUNITIES FOR NOVEL MATERIAL DESIGN

Mato Knez\textsuperscript{1,2}

\textsuperscript{1} CIC nanoGUNE, E-20018 Donostia – San Sebastián, Spain
\textsuperscript{2} Ikerbasque, Basque Foundation For Science, E-48013 Bilbao, Spain
(m.knez@nanogune.eu)

Atomic layer deposition (ALD) has become the method-of-choice for solving many technical issues that occurred on the way towards designing current and future electronics. Serious effort has been invested in order to optimize the materials, processes and processing instrumentation, which eventually resulted in the success story of this processing technique.

The ALD process can be seen from various perspectives. On the one hand, it allows controlled deposition of thin films on a variety of substrates and in this way enables a modification of a given functionality of a surface or even introduction of a new functionality. On the other hand, it may be seen as a chemical reactor that allows precise dosing of a chemical, allowing for chemical interaction and modification of the substrate. Considering both points of view, the process opens large variation possibilities for a design of novel functional materials for emerging applications and devices. Among those functional materials hybrid materials play an increasingly important role. Hybrid materials are in most cases blends of inorganic and organic materials and are considered to be key for the next generation of materials research. The main goal while fabricating such materials is to bridge the worlds of polymers and ceramics, ideally uniting the most desirable properties within a singular material. Furthermore, in a well performing hybrid material the individual components will add value to their counterpart in a synergistic way.

In this talk, some approaches will be discussed that show great promise for establishing ALD as the method-of-choice for innovation in technological fields beyond the microelectronics industry. Rather than growing thin conformal films, the ALD process technology is applied to controllably grow nanoparticles on functional substrates adding value to their chemical or electrochemical properties. In an adapted processing mode, the ALD processing technology also allows infusing metals into polymeric substrates, which leads to novel material blends that cannot easily be obtained in other ways. In either of those cases the chemical or physical properties of the initial substrate are improved or new functionalities added. With some showcases, this talk will discuss approaches towards non-traditional application of ALD to fabricate novel materials with great promise in energy storage, catalysis, personal protection or flexible electronics.
RECENT ADVANCES IN ATOMIC LAYER DEPOSITION
M. Leskelä, T. Hatanpää, J. Hämäläinen, M. Mattinen, M. Mäkelä, K. Väyrynen, M. Ritala
Department of Chemistry, University of Helsinki, PO Box 55, FI-00014 Helsinki, Finland

During the last 15 years Atomic Layer Deposition (ALD) has grown rapidly and has established its position as one of the major thin film technologies. In microelectronics ALD is the fastest growing thin film processing technology but its importance is increasing in several emerging areas such as solar cells and other energy technology sectors, optics, protective coatings, and catalysis. The selection of ALD materials has increased rapidly and at the moment more than 1000 processes have been reported in the literature [1, 2]. It should be noted that the amount of ALD processes applied industrially is limited to a few tens of processes. In the applications the beneficial properties of ALD – high conformality and precise control of thickness and composition – are appreciated.

Thermal ALD of metal films is challenging. Good processes have been developed for platinum group metals and these processes rely on the oxidation of organometallic or metal organic compounds [3]. The oxidation processes do not work for other metals and for them finding a suitable reducing agent is the key for successful thermal ALD. In the presentation the recent achievements in deposition of Cu, Ag, Au and Re are highlighted.

Thin films or monolayers of transition metal dichalcogenide (TMDC) 2D materials have received enormous amount of attention due to their unique properties, which are not seen in their bulk form. This is due to quantum confinement effects and the weakness of interlayer interactions in TMDCs. Molybdenum disulfide (MoS2) is the most extensively studied TMDC material and it has been studied as a channel material in field-effect transistors as well as phototransistors and other optoelectronic devices. MoS2 has also shown promise in catalysis, batteries, photovoltaics, and sensors. In the presentation the ALD of transition metal dichalcogenides is highlighted.

ATOMIC LAYER DEPOSITION OF DIELECTRICS FOR RESISTIVE SWITCHING AND FERROELECTRIC MEMORY APPLICATIONS


Moscow Institute of Physics and Technology, 141700, Dolgoprudny, Moscow region, Russia

Atomic layer deposition (ALD) is a powerful technique for fabrication of atomically precise coatings on a variety of surfaces, with atomic level accuracy in both film thickness and composition. Due to the self-limiting surface chemistry of ALD, one can conformally coat ultrahigh aspect ratio surfaces including three-dimensional 3D-structures. As a result an ALD technique has become the most in demand in semiconductor industry and it was adopted for production of high-κ gate dielectrics for transistors, diffusion barriers for metal interconnects, and high aspect-ratio memory devices.

Recently some novel trends arise in microelectronics: among them - new generation non-volatile emerging memories as redox-based Resistive Random Access Memory (ReRAM) and hafnium oxide based Ferroelectric Random Access Memory (FeRAM). ReRAM with transition metal oxides (HfO₂, Ta₂O₅ and TiO₂) [1-3] and HfO₂-based FeRAM [4-6] are the most promising emerging non-volatile memory due to their unique properties as ultra-low power consumption, high speed, good scalability and compatibility with CMOS fabrication technology. Thus, it is of interest to employ the advantages of ALD for obtainment of the ReRAM and FeRAM memory stacks.

According to the general point of view it is favorable for ReRAM functional oxide layer to contain oxygen deficiency [7], that is a rather complicated task for ALD. Therefore, it is of a great interest to find a way to control oxygen content in metal oxide ALD films. A few attempts to achieve oxygen-deficient TiOₓ and TaOₓ have been made in previous works [8, 9] through using Plasma Enhanced ALD (PEALD) with plasma-activated oxygen as a reactant by varying its partial pressure and/or pulse duration. During such deposition processes, the active oxygen has to perform rather contradictory tasks: (1) remove the organic ligands and (2) achieve oxygen deficiency in the growing film, which make the precise process control tricky.

In this work a robust ALD process of oxygen-deficient TaOₓ film was developed basing on plasma-activated hydrogen as the reactant and alkoxide compound Ta(OC₂H₅)₅ as Ta precursor, which already has a Ta–O bond. In this approach, the critical idea is to remove the C₂H₅ by forming volatile C₂H₆ or C₂H₅(OH) molecules via reaction with plasma-activated hydrogen (H*) without breaking Ta–O bond in the chemisorbed Ta precursor molecules, whereby the oxide film can be grown even when hydrogen is adopted as the reactant for oxide ALD. Another critical feature is a novel reaction pathway of partial reduction of the growing oxide in a controllable manner due to the attack of H* on Ta–O bonds, whereby the TaOₓ film can be grown even when hydrogen is adopted as the reactant for oxide ALD. Another critical feature is a novel reaction pathway of partial reduction of the growing oxide in a controllable manner due to the attack of H* on Ta–O bonds, whereby the TaOₓ film can be grown in a well-controlled manner. As a result, the new way to control the oxygen vacancy concentration in PEALD TaOₓ films was confirmed by the in situ X-ray Photoelectron Spectroscopy (XPS) measurements of Ta 4f core and the valence band (VB) photoelectron lines. The comparison of the XPS-measured Ta⁴⁺ content (~5%) and the time-of-flight secondary ion mass spectrometry (TOF-SIMS)-estimated H-containing species allowed us to conclude that nonstoichiometry is largely related to the formation of oxygen vacancies rather than Ta–H ones. The oxygen-deficient TaOₓ layer played a fluent role as the oxygen vacancy source for the resistance switching. Thus, the PEALD TaOₓ based ReRAM stack performance up to 1.3×10⁶ switching cycles was demonstrated.

The recent discovery of ferroelectricity in HfO₂ films, precisely doped with various elements including Si, Al, Zr, Gd, Sr, Y [4-6, 10], creates the possibility of implementation of novel FeRAM stacks, which overcome crucial technological challenges, related to the
The key point in the ferroelectricity achievement in HfO$_2$ is its precise doping which allows to stabilize metastable non-centrosymmetric orthorombic phase possessing ferroelectric properties. An ALD is a really appropriate instrument for such precise and reproducible doping.

Our approach to ferroelectric (FE) HfO$_2$ obtainment is to use dopants with large atomic radius which allow to stabilize various metastable phases through the proper oxygen vacancies concentration obtainment [11]. Among the 3+ dopants La poseses the highest atomic radius (~190 pm). Our studies showed that ALD La doping of HfO$_2$ in conjunction with the proper rapid thermal treatment (650°C) lead to effective FE stabilization. In particular, we found, that La:HfO$_2$ is practically free from fatigue effect (up to $5\times10^8$ switching cycles) in comparing with high fatigue demonstrated by another extensively used FE system based on Hf$_{0.5}$Zr$_{0.5}$O$_y$.

Moreover, in this work, the ALD was employed for La doping of Hf$_{0.5}$Zr$_{0.5}$O$_y$ system: the strategy was to combine the advantages of La doping with lower temperature of FE transition in Hf$_{0.5}$Zr$_{0.5}$O$_y$. As a result the La: Hf$_{0.5}$Zr$_{0.5}$O$_y$ based FE structures were obtained revealing both low FE phase transition temperature (~450°C) and high endurance of $\approx10^{11}$ switching cycles.

This work was supported by Russian Science Foundation (Project No 14-19-01645-P).

Emerging electronic materials and device designs require new capabilities for nanoscale localized material placement and lateral position control that are currently not well developed. While steady-state ALD reactions are well explored for many metal oxides and metals, the specific chemical sequences involved in growth initiation, i.e. the first few ALD cycles, are often less studied. Moreover, while it is well known that many ALD processes show a propensity to nucleation preferentially on some substrates versus others, emerging studies show that these differences can be exploited to achieve well-controlled inherent selective deposition, without the need for integrated blocking layers. To better classify and understand mechanisms for lateral-scale control of thin film growth, our group explores how surface composition affects initial nucleation reactions during metal and metal oxide ALD. We find for example, that tungsten nucleation during ALD using WF₆ and SiH₄ is strongly affected by the density and local bonding structure of surface OH groups on SiO₂. For example, as shown in the Figure, removing clustered OH groups by annealing before ALD tends to promote nucleation, whereas, removing vicinal OH groups tends to delay nucleation, indicating that vicinal OH groups are more reactive with WF₆. Other studies of nucleation reactions during TiO₂ ALD on Si-H and SiO₂ surfaces show that nucleation proceeds rapidly on silicon oxide, but the rate of nucleation on Si-H depends strongly on the surface preparation and initial wetting contact angle. Our group has also begun to explore novel atomic layer etching and atomic-scale passivation reactions that can be further used to enhance substrate selectivity during ALD. The impact of understanding nucleation reactions will be discussed as it relates to challenges for selective-area ALD.

**Figure.** (a) IR data of SiO₂ as prepared, and after annealing to remove clustered and vicinal surface OH groups; (b) ellipsometry results showing the onset of nucleation (up arrows) is delayed upon removal of vicinal Si-OH groups; (c) schematic showing the propensity for WF₆ to preferentially react at vicinal Si-OH sites.
INCREASING INTEREST IN ALD HfO$_2$ AND ZrO$_2$ BASED SEMICONDUCTOR DEVICES: FROM DRAM CAPACITOR TO NEGATIVE CAPACITANCE DEVICES

Uwe Schroeder
NaMLab/TU Dresden, Noethnitzer Strasse 64, 01187 Dresden, Germany

ALD was first introduced into semiconductor production as a dielectric material in dynamic random access memory (DRAM) devices. Starting with aluminum oxide as a ‘high-k’ material for high aspect ratio DRAM capacitor dielectrics in 2004 [1], industry quickly shifted to ‘higher-k’ materials like HfO$_2$ [2] and ZrO$_2$ [3]. 15 years later, ZrO$_2$ is still in production as the capacitor dielectric, even though, a longer list of dielectrics with enhanced dielectric constants was suggested (e.g. Al doped TiO$_2$, SrTiO). Furthermore, the interest in ferroelectric (FE) HfO$_2$ and ZrO$_2$ based devices is growing with the recent discovery of FE and field induced FE properties in both materials. The continuously increasing list of devices is ranging from non-volatile memory applications in FeRAM or FeFET cells [4], ferroelectric tunnel junctions, and steep slope negative capacitance transistors to energy harvesting devices. Even, a FE enhancement of the current ZrO$_2$ based DRAM capacitor was proposed [5].

In order to improve structural and electrical properties of the simple binary ALD based ferroelectric layer, research is ongoing to understand the root cause of this so far unknown phase. Accordingly, the ferroelectric properties and crystal structure of these thin ALD films are investigated for different ALD process conditions. Piezoresponse force microscopy (PFM) in conjunction with transmission electron microscopy (TEM) measurements revealed a domain size in the order of single grains with a grain diameter of ~20-30 nm for 10 nm thick films. Layers are only slightly textured, which caused a modulation of the polarization orientation within the layer. Electrical characterization of the defects and charges confirmed the influence of oxygen vacancies on the phase stability of ferroelectric HfO$_2$. Finally, different HfO$_2$ based device approaches are discussed and their performance compared. A non-volatile DRAM concept based on the field induced ferroelectric properties of ZrO$_2$ is presented. Detailed electrical characterization show high endurance and retention values that can be extrapolated to 10 years while providing the speed of FE memories during stable and low power operation.

SURFACE AND TOPOCHEMICAL REACTIONS IN THE ATOMIC LAYER DEPOSITION OF TITANIUM DIOXIDE ON A SUBSTRATE CONTAINING STRUCTURAL HYDROXYL GROUPS

I.S. Bodalyov\textsuperscript{1}, A.A. Malkov\textsuperscript{1}, T.P. Maslennikova\textsuperscript{2}, A.A. Krasilin\textsuperscript{3}, A.A. Malygin\textsuperscript{1}

\textsuperscript{1} St.Petersburg State Institute of Technology, St.Petersburg, Russia
\textsuperscript{2} Institute of Silicate Chemistry RAS, St.Petersburg, Russia
\textsuperscript{3} Ioffe Physical-Technical Institute RAS, St.Petersburg, Russia

The chemisorption of a gas on a hydroxylated surface at the first half-cycle of atomic layer deposition (ALD) is usually described by the following idealised reaction:

\[
H + EL_n \rightarrow (||O)_nEL_{n-m} + mLH, \quad (1)
\]

where E is the element whose oxide is deposited, L is a ligand and || is a monovalent surface site. Equation (1) emphasises the key features of ALD, namely irreversibility, self-saturation and confinement to the surface. However, in practice it is often violated because of the gaseous by-product reactivity, other side reactions or the diffusion of any involved species to the bulk of the solid substrate. Side reactions occur with aggressive precursors, such as halides, and produce particulate matter instead of a uniform monomolecular layer \cite{1, 2}. Signs of the precursor diffusion to the substrate bulk were observed on polymers, which consist of individual macromolecules and lack a continuous framework of covalently bound atoms \cite{3}.

When a thin conformal layer is needed, the cited side processes play a negative role, complicating the process design. On the other hand, if controlled appropriately, they might be exploited to produce composite materials of complex morphology and expand the pool of ALD substrates beyond traditional elementary substances and binary compounds.

From this perspective, a promising object of study is the nanotubular magnesium hydroxysilicate \( \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \), a synthetic analogue of natural chrysotile asbestos. Its nanotube consists of 10–30 serpentine layers rolled into cylinders and put concentrically into each other. Each layer is composed of a sheet of corner-sharing silicon–oxygen tetrahedra (from the concave side) and a sheet of edge-sharing magnesium–hydroxyl octahedra (from the convex side) joined by common oxygen atoms. Hydroxyl groups located on the surface can be employed in traditional ALD to grow a thin shell on a nanotubular core, while those residing deep in the nanotube wall may engage in diffusion-complicated topochemical reactions.

Reported herein are the results of an experimental investigation of the two mentioned synthesis routes in the ALD of a titanium–oxygen compound on synthetic chrysotile from titanium tetrachloride and water vapours. To explore different reaction paths possible at the first half-cycle, its temperature was varied between 150 and 400°C, while the temperatures of the second half-cycle and of the preliminary heat treatment were fixed at 400°C. All reactions were carried out in inert gas flow under atmospheric pressure.

At 150°C the chemisorption reaction is confined to the surface. The areas of the initial surface per chemisorbed titanium–chlorine group and per chlorine atom are 0.30 and 0.13 \( \text{nm}^2 \) (0.27 and 0.11 \( \text{nm}^2 \) if the micropore area is excluded), which corresponds to a rather dense random packing, given the titanium tetrachloride landing area of 0.29 \( \text{nm}^2 \) and the chlorine cross-section of 0.10 \( \text{nm}^2 \). The infrared diffuse reflectance spectra show a drop by 40 \% in the
intensity of all chrysotile absorbance bands after one full ALD cycle and a further decrease after three more cycles. This effect is attributed to high reflectance of optically dense titanium–oxygen shells formed around nanotubes (compare with an increase in the hiding power of an ALD-coated white pigment [4]). X-ray diffractometry reveals a gradual decrease in the intensity of the (004) reflection of chrysotile as the number of ALD cycles grows, part of which results from changes in the elemental composition of the sample, while the rest is ascribed to chrysotile structure perturbation. The extent of the latter is 10 % after one cycle, corresponding to the innermost and the outermost serpentine layers of the nanotube. No further alteration is observed after four cycles, consistent with purely surface ALD reactions.

At 300–400°C the fixation of titanium–chlorine groups on the nanotube’s surface is followed by a topochemical reaction that proceeds from the outer surface towards the central void of the nanotube and leads to progressive chlorination, amorphisation and dehydroxylation of serpentine layers and formation of titania (mostly rutile) crystallites in free space between nanotubes, whose morphology is preserved. The initial surface reaction is confirmed by the same rise in infrared reflectance as that observed at 150°C. Morphology preservation is illustrated by transmission electron microscopy. Amorphisation is most evident at 400°C from x-ray diffraction data and from a partial coalescence of the infrared bands of chrysotile skeletal vibrations at 900–1100 cm⁻¹. The direction of the reaction front advance is deduced from the preservation of an infrared band at 1025 cm⁻¹ ascribed [5] to Si–O–Si bonds close to the central void. The siloxane surface of the void blocks the front advance, as shown in syntheses at on talc, a similar substrate with almost exclusively siloxane surface.

The diminution of the infrared band of hydroxyls after the synthesis at 400°C suggests that amorphisation of the substrate is accompanied by its dehydroxylation. The latter is caused by the by-product of reaction (1), hydrogen chloride, whose potency to amorphise and dehydroxylate chrysotile at 400°C was confirmed in a separate experiment by infrared spectroscopy and diffractometry. Chloride determination coupled with in situ gravimetry showed that dehydroxylation proceeds not only by substitution of chlorine atoms for hydroxyls but also by pairwise condensation of hydroxyls. The latter is probably caused by a decrease in the thermal stability of affected layers resulting from an increased misfit between the tetrahedral and the chlorinated octahedral sheets. Water evolved during dehydroxylation at the first half-cycle of an actual ALD process is able to react with titanium tetrachloride to form titania (mostly rutile) crystallites detectable by diffractometry and visible in scanning electron micrographs as spheres 50–300 nm in diameter.

To sum up, by adjusting temperature at the first ALD half-cycle it is possible to produce either pure core–shell particles of crystalline chrysotile and disordered titania or a mixture of titania-encapsulated partly amorphous hydrosilicate nanotubes and rutile nanoparticles.

*The study was supported by the Ministry of Education and Science of Russia (project 16.1798.2017/4.6).*

MOLECULAR LAYER DEPOSITION OF VANADIUM-TITANIUM ALLOY HYBRID ORGANIC-INORGANIC THIN FILMS AND THEIR POST-PROCESSING

Ka.N. Ashurbekova1, Kr.N. Ashurbekova1, I.M. Abdulagatov1, M.Kh. Rabadanov2, A.I. Abdulagatov2

1 Dagestan State University, Department of Chemistry, Makhachkala, Russia
2 Dagestan State University, Department of Physics, Makhachkala, Russia

Molecular layer deposition (MLD) is a gas phase deposition technique to grow organic or hybrid organic-inorganic thin films [1]. MLD films can be useful in number important applications such as energy storage [2], gas separation [3], flexible barrier coatings [4] and others. In this work, MLD vanadium-titanium alloy hybrid organic-inorganic thin films, called “vanticones”, deposited by alternating doses of vanadium oxytrichloride (VOCl₃), ethylene glycol (C₂H₆O₂) and titanium tetrachloride (TiCl₄). In situ quartz crystal microbalance (QCM) monitor showed that the vanticone had linear growth with number of MLD cycles and that the surface reactions during MLD process proceed in self-limiting manner. QCM confirmed. Ex situ characterization techniques, revealed that the films deposited at 115°C with 1:1 cycle ratio were amorphous, had a growth rate of 5.8 Å/ cycle, density of ~1.75 g/cm³ and RMS roughness of 3.97 Å. X-ray photoelectron spectroscopy (XPS) survey scan showed that the 1:1 film consist of Ti (5.81 at.%), V (0.92 at.%), C (58.20 at.%), O (31.80 at.%) and Cl (3.27 at.%). With 4:1 vanadicone to titanicone cycle ratio concentration of vanadium in the film can be increased to 3.3 at.%.

By post-deposition heat treatment of the hybrid films, in the oxidizing or inert atmosphere, organic constituency can be either removed, with formation of porous metal oxide thin film, or retained in the form of graphitic carbon. Heat-treated films can have new useful properties. The results of post-processing of the hybrid MLD films are shown in Fig. 1. SEM image of air annealed (450°C, 2 h) 4:1 vanticone MLD film shown in Fig. 1 a). This image shows that the surface consists of nanoparticles uniformly permeated with nanocrystals. TEM analysis showed that crystals in Fig. 1a) were single crystal V₂O₅ nanorods. Vanadium oxide nanowires can find potential application in electrochromics [5] advanced lithium ion batteries [6] and porous thin TiO₂-V₂O₅ films can be used in heterogeneous or photo-activated catalysis [7]. We found that by changing annealing condition or Ti:V atomic ratio surface morphology of resulting films can be manipulated.

Figure 1. SEM images of a) air annealed and b) pyrolysed in argon 4:1 Vanticone films
Different surface morphology was discovered for the samples pyrolysed in argon (900°C, 1 h). Figure 1b) shows SEM image of the surface of the vaniccone film after pyrolysis. The surface evenly covered with nanosize particles and no nanocrystals were observed. Raman spectra of the pyrolysed samples contained signature D and G peaks for graphitic carbon. These materials can find potential application in Li⁺ batteries as well [8, 9].


**ATOMIC LAYER DEPOSITION OF TITANIUM AND TITANIUM-ALUMINUM NITRIDES USING TITANIUM TETRACHLORIDE, HYDRAZINE AND TRIMETHYLALUMINUM**

Aziz I. Abdulagatov¹,²

¹ Department of Chemistry and Biochemistry, University of Colorado at Boulder, CO 80305, U.S.A. (Aziz.Abdulagatov@Colorado.edu)

² Department of Physics, Dagestan State University, Makhachkala, Russia

Titanium and titanium-aluminum nitrides are technologically important materials. Despite many years of scientific study, the growth of these films by thermal ALD process remain challenging. In this work thermal atomic layer deposition (ALD) of titanium nitride (TiN) was researched at temperatures ranging from 150 to 350°C using titanium tetrachloride (TiCl₄) and hydrazine (N₂H₄). *In situ* quartz crystal microbalance (QCM) study of the surface processes performed at 200°C and 225°C showed that surface reactions between TiCl₄ and N₂H₄ proceed in a self-limiting manner. *Ex situ* X-ray reflectivity (XRR) measurements showed that ALD TiN has a growth rate of ~0.3 Å/Cycle and ~0.36 Å/Cycle at 200°C and 275°C deposition temperatures respectively. XRR also revealed that the density of TiN films gradually increases with the deposition temperature reaching its maximum value of 4.6 g/cm³ (85% of bulk density) at 275°C. X-ray photoelectron spectroscopy (XPS) analyses of TiN films deposited at 200°C and 275°C showed that Cl impurities were below detection limit of the instrument (< 0.2 at.%). XPS depth profile also displayed that TiN films deposited at 275°C contained oxygen impurities at ~14 at.% in the bulk of the film. Most of the film oxidation is believed to occur after exposure in air. Grazing incidence X-ray diffraction (GIXRD) measurements showed that the deposited TiOₓNᵧ film had crystalline structure. Infrared spectroscopy was employed to study ALD TiN surface chemistry at 200°C and 275°C. In addition, feasibility of ALD TiAlN at 275°C was also demonstrated where trimethylaluminum (Al(CH₃)₃) is used as an aluminum precursor. XPS depth profile of ALD TiAlN deposited at 275°C revealed the presence of about 40 at.% of Al, 15 at.% of Ti, 3 at.% of O, 4 at.% of Cl and carbon below detection limit. Overall, TiCl₄/N₂H₄ and TiCl₄/N₂H₄/TMA showed very favorable surface chemistries to grow ALD TiN and TiAlN compare to other thermal ALD processes.
Molecular layer deposition (MLD) is a gas phase technique to grow purely organic or hybrid organic-inorganic thin films [1]. MLD films can be useful in making advanced electrode materials for Li+ batteries [2], thin film membranes for gas separation [3], or to stabilize catalysts [4] etc. In this work, the growth of a MLD aluminum-titanium alkoxide type polymer, we called “alticone”, is demonstrated using sequential exposures of titanium tetrachloride (TiCl4), ethylene glycol ((CH2OH)2) and trimethylaluminum (TMA, Al2(CH3)6). Previously, MLD of titanium (titanicone) and aluminum (alucone) alkoxides was demonstrated using TiCl4, TMA and EG [5,6]. One deposition cycle of alticone consisted of sequential exposures TMA/EG/TiCl4/EG (1:1 ratio) with purge times in between. This film may have hybrid properties of alucone and titanicone films.

Alticone depositions carried out at reactor temperatures varying from 90 to 115°C. In situ quartz crystal microbalance (QCM) confirmed linear growth with number of MLD cycles. QCM signal profile observed during alticone deposition was similar to previously published for alucone and titanicone (Fig. 1) [5, 6]. Optimal deposition temperature for MLD found to be 115°C. X-ray reflectivity showed alticone growth rate of 6.63 Å/cycle and density of ~1.76 g/cm3, RMS roughness 6.43 Å, for the film deposited at 115°C. X-ray photoelectron spectroscopy (XPS) compositional analysis of 1:1 films deposited at 115°C revealed content of C (50.66 at.%), O (31.59 at.%), Cl (3.09 at.%), Al (12.51 at.%), and only 2.15 at.% of Ti. Concentration of titanium was less than expected which suggested that this MLD process has a unique growth mechanism.

**Figure 1.** QCM signal during alticone MLD at 115°C.

**Figure 2.** Nucleation of MLD Alucone on Titanicone

We believe that the observed low concentration of titanium might be result of partial substitution of titanium atoms with aluminum after TMA dose. We suggest that the alticone growth is the result of competing deposition and partial removal of titanium-alkoxide constituency. This growth mechanism is indirectly confirmed by our QCM experimental observations and thermochemical calculations. Figure 2 presents a case of nucleation of MLD alucone on MLD titanicone. This picture shows that first dose of TMA on titanicone results in sharp mass loss.
with removal of the underlying material. The results of this work can potentially allow to predict the composition of other similar two or more component MLD systems.


IMPROVEMENT OF THE MCP TECHNOLOGY BY THE USE OF ALD FILMS
A.V. Drozd, V.E. Drozd, S.A. Kesaev, A.M. Yafyasov
Saint-Petersburg State University, St.Petersburg, 198504, Russia

Atomic Layer Deposition thin films revolutionizing microchannel plates, channel electron multipliers, photomultiplier tubes and other devices, such as image intensifier tubes used in night vision. ALD film properties improve the functionality devices by significantly improving efficiency and lifetime performance. Films developed for MCP application have been optimized for resistance and secondary electron emission in order to replicate and improve upon the behavior of the lead glass films technology unchanged from the early 1970s. The functionality of the MCP relies upon an elevated temperature hydrogen reduction of the surface film to simultaneously form the electrically active resistive and secondary electron emission layers. The unreduced lead based glass MCP was used as substrate for development of resistive and emissive films and demonstrate substrate independence and MCP performance improvements in gain and lifetime as a direct result of the ability to tailor all elements to maximize MCP performance.

The aim of this work is to study the properties of conducting AZO layers on the surface of unreduced lead glass MCP. Thickness and composition dependences of conductivity of final MCP structures were investigated. Experimental results were compared with theoretical model. Substrate functionalization as a component of the layers synthesis was studied.

The object of the study was composition of multilayers structures. MO precursors were used for the synthesis of conducting and secondary electron emission layers. For better SEE layers of aluminum oxide and magnesium oxide were synthesized with different position on the glass MCP substrates. Films of different thicknesses were deposited in a travelling wave flow type device “Nanoserf” at a temperature of about 200ºC. The thickness of the dielectric layers was determined on cleaved structures with the scanning helium ion microscope Zeiss ORION and monitored by ellipsometry at the wavelength of 632.8 nm.

The quality of the synthesized structures was controlled by a scanning electron microscopy (SEM), a scanning ion microscope (SIM) and X-ray microanalysis. It was established for all the films the thickness uniformity better than 0.3 nm across the wafer.

Presented study have used the equipment of interdisciplinary resource center "Nanotechnology" and resource center "Innovative technologies of composite nanomaterials" of St.Petersburg State University.
THE EFFECT OF TEMPERATURE ON THE MOLECULAR LAYERING SYNTHESIS AND ON STRUCTURAL-CHEMICAL TRANSFORMATIONS OF "CORE (ALUMINUM OXIDE) – SHELL (PHOSPHORUS OXIDE)" COMPOSITION

N.V. Chernyakova¹, A.A. Malkov¹, N.V. Zakharova¹, T.S. Belorukova¹, A.A. Malygin¹, M.V. Chislov²

¹ St.Petersburg State Institute of Technology, St.Petersburg, Russia
² St.Petersburg State University, St.Petersburg, Russia

Phosphorus oxide and aluminophosphates find wide application as high-efficiency gas-drying agents, active adsorbents, catalyst supports and catalysts as such. Of importance for creating the P₂O₅/Al₂O₃ system is the choice of a method for deposition of the phosphorus oxide component onto the substrate surface. This method should provide a uniform distribution of the additive over the pore surface, its firm binding to the matrix, and its strictly prescribed concentration. The above requirements are fully satisfied by the molecular layering (ML) method [1].

Using the principles of the molecular-layering method, a core–shell nanocomposite can be created via formation of phosphorus oxide structures with varied composition and structure at an atomic molecular precision on the surface of porous alumina by varying the number of alternating treatment cycles of an aluminum oxide matrix with POCl₃ and H₂O vapors.

In present work we examine the effect of temperature on the aspects of synthesis by the molecular layering method of phosphorus oxide compounds on the γ-Al₂O₃ surface and on subsequent structural-chemical transformations under high temperature treatment of obtained products.

By using an integrated in situ monitoring and chemical analysis of solid and gas phase products in temperature range of 200-600ºC the aspects of synthesis of phosphorus oxide nanostructures on the surface of γ-Al₂O₃ were studied. Comprehensive examination of the nature of chemical transformations has shown that they highly depend on temperature of the preliminary annealing of aluminum oxide due to the changes on the surface of the initial material when heated [2].

The impact of the degree of chloride groups' substitution by hydroxyl groups on changes of acid-base properties of the surface of the material was also analyzed in present work. Based upon combined data from gravimetric measurements, IR- spectroscopy, XRD, and chemical analysis the formation of phosphorus oxide amorphous structures chemically bound to the surface has been established.

The nature of formation of a double-phase core–shell system was studied by carrying out 1-4 modification cycles of ML on initial γ-Al₂O₃ matrix. Chemical analysis of obtained products has shown that the concentration of phosphorus in the samples steadily rises with increasing treatment rate (from 1 to 4) of the solid-phase matrix with halide and water vapors, confirming the growth of phosphorous oxide shell on the surface.

The regular decrease in the volume of the mesoporous space, pore diameter, and specific surface area of the samples is due to the growth of a phosphorus oxide nanolayer within the pores in the course of synthesis. This indicates that not only the nature of a functional additive being introduced, but also the transport characteristics in double-phase system constituted by a core (gamma alumina) and a shell (phosphorus oxide layer) can be finely adjusted by using the ML method.

It has been shown that changes in mole ratio of phosphorus to aluminum from 0 to 0.14 influence on general acidity of the surface. While initial γ-Al₂O₃ matrix demonstrates mainly basic properties, modified samples exhibit incensement in acidity of water solutions after undergoing through additional treatment cycle of POCl₃ and H₂O vapors.
Dispersed aluminophosphates, which are of high interest as catalysts, and catalyst supports, may be obtained by high temperature treatment of given double-phase systems $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$. To thoroughly study such process in present work, we closely examined the nature of structural-chemical transformations of earlier mentioned nanocomposites under temperature treatment.

The results of thermal analysis and differential scanning calorimetry have shown, that initial and modified samples loose about 10% of their mass when heated up to 1530°C. The loss of mass is attributed to removal of different types of water: physically adsorbed water evaporates from the surface under temperature up to 380°C, coordination-bound water is removing in temperature range of 380–550°C, and structural water removes in successive heating [3].

With growing phosphorous concentration in synthesized nanocomposites, rate of weight loss seemingly increases from 0.5 to 1.0 %/min. This fact shows agreement with value of endothermal effects: with growth of phosphorous concentration in the sample increases the value of corresponding endothermal effects.

The opposite trend is observed on DSC and DTG graphs for smaller endothermal effect in temperature range of 400-650°C, which corresponds to removal of coordination-bound water from the surface of $\gamma$-$\text{Al}_2\text{O}_3$. Distinctive trend of shifting in high temperature area of mentioned endothermal effect is noted, from 446°C for initial alumina the maximum for modified samples shifts to 496°C after four cycles of ML. Furthermore, weight loss in considered temperature range decreases from 5.19% to 2.56% of overall weight loss, and the rate of weight loss of corresponding type of water also decreases from 0.40 to 0.18 %/min. Such correlation is considered to be due to diffusion difficulties of this type of water in escaping the surface, which became covered in phosphorous oxide nanolayer after modification.

Differential thermal analysis has shown the shift of exothermal effect corresponding to transformation of alumina into $\alpha$ phase in high temperature area after modification. Moreover, the maximum of mentioned exothermal effect continues to shift with increase in thickness of phosphorous oxide shell, which proves to stabilize transitional phases of alumina.

There are additional exothermal effects that appear on DTA curves at about 1165°C for modified samples, which are attributed to crystallization of aluminophosphates. Presence of aluminophosphates on the surface of modified nanocomposites is also confirmed by IR–spectroscopy and X-ray diffraction analysis.

Previously discussed results, which were obtained by linear heating of system $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$, were supplemented by stage heating of the same materials in certain temperature ranges with equalized heating for 4 hours. Structural characteristics of obtained products were also subjected to IR – spectroscopy and X-ray diffraction analysis.

The results obtained during the study are of interest for the development of functional materials such as core-shell, the chemical composition, the structure and properties of which can be precisely regulated.

The studies have a financial support from the Ministry of Education and Science of Russia (project 16.1798.2017/4.6) and Russian Foundation for Basic Research (grant 16-03-00214).

LONG-ENDURANCE FERROELECTRICITY IN MULTICOMPONENT HAFNIUM OXIDE-BASED ALD GROWN THIN FILMS

A.G. Chernikova, M.G. Kozodaev, D.V. Negrov, A.M. Markeev

Moscow Institute of Physics and Technology, 141700, Dolgoprudny, Moscow region, Russia

Ferroelectricity of HfO$_2$ thin films discovered recently inspired the progressive development of the concepts related to this phenomenon. In [1] it was particularly firstly proposed that the stabilization of non-centrosymmetric polar o-phase (Pca$_{21}$) is responsible for ferroelectricity in such films, which was exhaustively confirmed both theoretically and experimentally [2, 3] despite the difficulties of distinguishing different phases in polymorphic HfO$_2$. This discovery attracted much attention because HfO$_2$ provides numerous advantages over perovskites, including CMOS and BEOL compatibility. As a result the new ferroelectric materials were proposed to replace perovskites in the conventional and emerging ferroelectric memory concepts. Among them 1 transistor – 1 capacitor (1T-1C) FeRAM which cell is quit alike to the DRAM is rather promising if new HfO$_2$ based ferroelectrics become the materials of choice. Indeed, first of all, although the ferroelectricity of HfO$_2$ thin films was initially found after the doping with Si it became immediately clear that other dopants not only can lead to the more preferable stabilization of o-phase over centrosymmetric ones, but also change the crystallization temperature making such films more suitable for the BEOL process of FeRAM [4-6]. Secondly, the ferroelectric capacitor area in this case can be routinely extended to the third direction by utilization of ALD, which can be successfully applied both for ferroelectric HfO$_2$-based film and TiN electrodes, proved to be well suitable for HfO$_2$-based ferroelectrics [7]. As a result the scaling challenge of FeRAM can be potentially solved. Moreover metal–ferroelectric–metal (MFM) structures were proved to possess higher endurance in comparison to metal-ferroelectric-semiconductor structures. In support of 1T-1C FeRAM approach recently TiN/Hf$_{0.5}$Zr$_{0.5}$O$_2$/TiN MFM capacitors were successfully integrated with CMOS transistors in 1T-1C cells and, importantly, provided preeminent endurance reported so far following 10$^{10}$ switching cycles [8]. It worth to notice, however, that drastic decrease of remnant polarization P$_r$ (so called fatigue effect) was observed in the result of such amount of ferroelectric switches, which means, that further investigations directed toward improving the voltage cycling behavior are still required. This work was particularly aimed to find the possible ways to increase reported endurance in such MFM capacitors, which are suitable to 1T-1C approach. It was shown that decrease of voltage amplitude as well as pulse duration significantly effect the maximum number of the switches (N$_s$) and P$_r$ vs. N$_s$ behavior, making it possible to obtain 10$^{11}$ and even beyond endurance. The minimal pulse duration that can be applied for the cells operations (i.e. the time of switching) is also discussed.

It worth to notice, that the choice of Hf$_{0.5}$Zr$_{0.5}$O$_2$ is explained by the lowest crystallization temperature in comparison to the doped HfO$_2$, which varies with thickness but generally does not exceed BEOL-desired 400°C. On the other hand, introduction of the dopants, which differ significantly from Hf in terms of atomic radius, could allow receiving more promising results, particularly higher P$_r$ [8]. Indeed, recently we found that low-level doping of HfO$_2$ with La resulted in the effective inhibition of formation of undesired monoclinic phase and consequently relatively high P$_r$ as well as the absence of the fatigue during more than 10$^{8}$ switches [9]. However, P$_r$ decreased with decrease of the annealing temperature, so that after annealing at temperatures 550°C La doped HfO$_2$ dielectric (with the lowest doping level) remained amorphous. In this work we also explored the possibilities to further increase P$_r$ while maintaining relatively low crystallization temperature and long endurance. The strategy was to dope Hf$_{0.5}$Zr$_{0.5}$O$_2$ with low amount of La by utilization of ALD. The detailed structural and electrical measurements were carried out to investigate such films. As a result rather promising ferroelectric
response and long endurance following $10^{11}$ cycles were obtained after annealing of MFM structures at relatively low temperatures. The possibility of decreasing crystallization temperature of ferroelectric La doped HfO$_2$ films just by further decrease of La content, which can be also achieved by ALD, was analyzed in this work too.

This work was supported by Russian Science Foundation (Project No 14-19-01645-P).


OXIDE STRUCTURES SYNTHESIZED BY THE METHOD OF MOLECULAR LAYERING ON THE SURFACE OF POLYMERIC FILMS AND THEIR INFLUENCE ON THE ELECTRET PROPERTIES OF OBTAINED COMPOSITES

N.Yu. Efimov$^1$, A.A. Malygin$^1$, A.A. Rychkov$^2$

$^1$ St.Petersburg State Institute of Technology, St.Petersburg, Russia (efimov@technolog.edu.ru)
$^2$ Herzen State Pedagogical University, 48, Moiki str., St.Petersburg, 191186, Russia

Polytetrafluoroethylene (PTFE) films with low-dimensional titanium oxide structures on the surface are shown to have promising applications as electret materials. In this paper, we try to estimate the correlation between electret properties and hydrophobicity of polymeric films surface, modified by ALD (ML) [1, 2].

PTFE films were modified using Molecular Layering method by sequential treatment with titanium tetrachloride and water vapor. To increase a number of reactive centers and create titanium oxide structures with different hydrophobicity, a part of polymer samples was subjected to plasma treatment in the water vapor prior to gas-phase modification. To investigate surface structure and properties of treated film samples, X-ray photoelectron spectroscopy, scanning electron and atomic force microscopy were used.

Figure 1. X-ray photoelectron spectra of titanium 2p electrons for the specimens prepared (a) without and (b) with plasma activation.
Table 1 – XPS data

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atomic concentration, %</th>
<th>Concentration ratio</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>F</td>
<td>O</td>
<td>Ti</td>
</tr>
<tr>
<td>PTFE</td>
<td>32.4</td>
<td>67.1</td>
<td>0.5</td>
<td>-</td>
</tr>
<tr>
<td>PTFE+TiCl₄</td>
<td>40.0</td>
<td>48.7</td>
<td>8.5</td>
<td>2.8</td>
</tr>
<tr>
<td>PTFE+HF discharge+TiCl₄</td>
<td>49.8</td>
<td>32.7</td>
<td>13.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

The analysis of XPS spectra suggests that plasma treatment before gas-phase modification not only leads to an increase in the content of the titanium in the sample, but also to the formation of titanium oxide structures where titanium is in lower oxidation level.

Atomic force microscopy and scanning electron microscopy indicate the formation of island-like structures (~50 nm in diameter) on the surface.

Film samples were rendered electret by poling in a positive corona discharge. The charge stability was then studied by means of thermally stimulated surface potential decay. It was found that the onset of surface potential decay in modified PTFE films begins at higher temperatures (100°C, 200°C and 260°C for plasma treated, gas-phase and plasma plus gas-phase modified materials, respectively) as opposed to 70°C observed for non-treated material. This effect is due to the formation of titanium-oxide nanostructures on the surface of PTFE films. Since the most significant increase in charge stability was observed after plasma and chemical modification, it is probably due to the presence of titanium in lower oxidation states on the surface of the film. Surface titanium-containing structures can act as energetically deep traps that can retain charge and prevent the discharge of the electret.

Contact angle was measured for each sample.

Table 2 – Wettability and Temperatures of the beginning of the decline in potential of synthesized electret materials

<table>
<thead>
<tr>
<th>Sample</th>
<th>Contact angle θ, °</th>
<th>Surface Free Energy, mN/m</th>
<th>Temperature of the beginning of the decline in potential, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water Decane</td>
<td>γₜ, mN/m</td>
<td>γₜ, mN/m</td>
</tr>
<tr>
<td>PTFE</td>
<td>91.4</td>
<td>8</td>
<td>28.0</td>
</tr>
<tr>
<td>PTFE +HF discharge</td>
<td>68.9</td>
<td>10</td>
<td>37.46</td>
</tr>
<tr>
<td>PTFE +TiCl₄</td>
<td>84.6</td>
<td>9</td>
<td>30.37</td>
</tr>
<tr>
<td>PTFE +HF discharge+TiCl₄</td>
<td>99.2</td>
<td>8</td>
<td>24.77</td>
</tr>
</tbody>
</table>

It was found for treated samples that the temperature of the beginning of the decay of the charge increases, the higher the hydrophobicity of their surface.

As a result of the study, it was expected that the temperature of the onset of electret relaxation could correlate with the hydrophobicity of the titanium oxide structures on the surface of the polymeric material.

Research was partly financed from Ministry of Education and Science of Russian Federation (project No 16.1798.2017/4.6)

INSTALLATION FOR MOLECULAR LAYERING
WITH A PULSATIING ACTION OF A GASEOUS MEDIUM
ON A LAYER OF DISPERSE MATERIAL

V.F. Dergachyov, A.A. Malkov, A.A. Malygin

St.Petersburg State Institute of Technology, St.Petersburg, Russia

Chemical modification of solid materials from vapour or gas phase by the molecular layering (ML) method is a way to create functional nanostructures on their surface for the production of catalysts, sorbents, fillers, pigments etc [1]. Various hardware designs are known for this method. For the surface modification of disperse materials, flow-type installations seem most effective. To intensify the process, the disperse phase is often fluidised in a gas flow of high linear velocity. However, the nature of the ML process is such that the efficiency of gaseous reactant consumption declines substantially in fluidised-bed reactors. Besides that, the disperse phase itself is subject to a number of limitations and strict requirements. As a solution to this problem, the fluidised phase may be created by application of pulsations to the layer of disperse material through a gaseous medium [2, 3]. A substantial advantage of this approach is the ability to create a fluidised layer while maintaining minimal gas flow and keeping the reactor fixed in space.

Described in this communication is an experimental installation designed according to the above-stated principles. Its main unit is a newly developed controller of the frequency of vibrations of a membrane or bellows. The installation was used to investigate the effect of technological parameters on the character of fluidisation.

The figure 1 displays a principal scheme of the installation. Pulsating action is transmitted to the solid material from bellows actuated by an electromagnetic vibrodrive 13 and a frequency regulator 14, which provide an ability to set the amplitude and the frequency of vibrations in the ranges of 0.5–2.5 mm and 1–30 Hz respectively.

Figure 1. Principal scheme of the installation.

1, flow booster; 2, gas preliminary drying unit; 3, gas final drying unit; 4, rotameter; 5, ampoules with reactants; 6, reactor discharge fitting; 7, furnace; 8, reactor; 9, on/off temperature controller TRM-202; 10, phase–impulse power controller; 11, bellows; 12, bubble absorber; 13, electromagnetic vibrodrive; 14, frequency regulator.
To maintain the required temperature in the reactor and in the ampoules with reactants, a system was created on the base of an on/off temperature controller TRM-202. To reduce temperature oscillations, TRM-202 was equipped with two phase–impulse power controllers (PIPCs), which made it possible to vary consumed power from 0 to 100 % at currents up to 10 A (up to 16 A during an impulse). PIPCs set two levels of applied voltage for temperatures above and below the specified one, and the temperature controller switches between these voltage levels, thereby minimising temperature oscillations. Operating voltages were determined experimentally depending on the desired temperature and the power of the resistance furnace.

The designed experimental installation was used to determine resonance frequencies at membrane vibration amplitudes of 0.5, 1.0 and 2.0 mm, disperse silica layer thickness of 100 mm (particles 100–200 μm in diameter) and constant air flow of 4 ml/s. The resonance effect was fixed by maximal relative expansion of the layer thickness, ΔH/ΔH₀. At all three amplitudes, a homogeneous fluidised layer was observed at resonance frequency. However, at the amplitudes of 1.0 and 2.0 mm two marked resonances were fixed: one at a lower frequency characterised by a higher ΔH/ΔH₀ value, and another one with a significantly lower value at a higher frequency. It is also noteworthy that the greater was the amplitude of the membrane oscillations; the lower was the resonance frequency, which may result from the oscillations being not sinusoidal. Also considered is the effect of airflow in the range of 1–5 ml/s on the resonance frequency. At the studied flow rates all the resonance frequencies were approximately equal to 16 Hz.

The selected regimes were applied to modify silica gel with phosphorus oxychloride and titanium tetrachloride vapours. The results obtained were compared with those of experiments conducted earlier with a fixed layer of disperse material.

Studies in the reported direction are carried out as a part of state task from the Ministry of Education and Science of the Russian Federation under project no 16.1798.2017/4.6.


CATHODOLUMINESCENCE SPECTROSCOPY OF Si-TiO₂ AND Si-SiO₂-TiO₂ STRUCTURES

A.P. Baraban, V.A. Dmitriev, V.E. Drozd, A.A. Selivanov
Saint-Petersburg State University, St.Petersburg, 198504, Russia

Among the many candidates for next-generation non-volatile memory based on a non-charge mechanism, resistance-switching random access memory has attracted attention. Among the various contenders the transitional metal oxides appears to be one of the most promising switching materials. The titanium oxide is considered as the most promising switching material due to existence of a continuous homologous series of oxides of TiO to TiO₂, a good mobility of the oxygen ions, the existence of thermal-chemical switching mode and minimum value of switching time (5 ns) [1]. Note that to provide a switching control of such elements it is necessary to create defects in materials, either during or after fabrication of the element through electric field effect on the pristine structure (electroforming process – EF) [1].

The aim of this work is to study the properties of TiO₂ films on a silicon and silicon-SiO₂ substrates using cathodoluminescence spectroscopy (CLS). A comparison of the luminescence spectra recorded on the individual layers of the layered structure, with the luminescence spectrum of the whole structure is the way to reach this aim.
The objects of the study were Si-TiO$_2$ and Si-SiO$_2$-TiO$_2$ structures. For the synthesis of TiO$_2$ layers we used mainly the method of molecular layer deposition that was well established earlier, for example, in the synthesis of structures of Si-Al$_2$O$_3$ [2]. The TiO$_2$ film was grown on a single-crystal silicon wafer of $p$-type ($N_A = 8 \times 10^{14}$ cm$^{-3}$) and on the wafers with thermal SiO$_2$ ("dry" oxidation at 1000°C, oxide thickness of 32 and 40 nm). In both cases the TiO$_2$ films of 18, 20 and 28 nm thickness were deposited in a cross-flow "Nanoserf" reactor at a temperature of 200°C using Ti(OCH(CH$_3$)$_2$)$_4$ and H$_2$O precursors. The thickness of the dielectric layers was determined on cleaved structures with the scanning helium ion microscope Zeiss ORION and monitored by ellipsometry at the wavelength of 632.8 nm.

The quality of the synthesized structures was controlled by a scanning electron microscopy (SEM), a scanning ion microscope (SIM) and X-ray microanalysis. It was established for all the films the thickness uniformity better than 0.3 nm across the wafer.

To implement the CLS method we used the scanning electron microscope Zeiss SUPRA 40VP with the Gatan MonoCL3+ recording system. The CL spectra were recorded in the range of 250-800 nm while continuously scanning an electron beam over the sample surface. Each spectrum was recorded at a new location of the sample. The width of the scanning area was 30 microns, the acquisition time of one point of the spectrum was 1 s, the spectral resolution was 2 nm, incident electron energy was 5 keV, the beam current was 2 nA.

A comparison of the luminescence spectra of single dielectric layers with the spectrum of the double-layer structure fabricated of these layers (fig.1) allowed us to gain the following information: i) absorption coefficient of the TiO$_2$ layer as a function of the photon energy (fig.2), ii) band gap of the TiO$_2$ films ($\approx 3.2$ eV for the used technology of formation of the oxide layer), and iii) draw a conclusion on the electroforming process of the TiO$_2$ films. It is established that the process of electroforming led to significant modifications of the electronic structure of the outer part of the TiO$_2$ layer ($< 10$ nm), which is manifested in the appearance of luminescence in the spectral region 250-350 nm. The TiO$_2$ layer adjacent to the silicon or SiO$_2$ layer almost did not change its optical properties (transmittance) and hence its electronic structure.

![Figure 1. CL spectra of Si-TiO$_2$ (1), Si-SiO$_2$-TiO$_2$ (2), Si-SiO$_2$ (3), Si-TiO$_2$ after the electroforming (4) and Si-SiO$_2$-TiO$_2$ after the electroforming (5).](image1)

![Figure 2. Transmission coefficient of TiO$_2$ layer with thickness of 20 nm.](image2)

The work performed using equipment of interdisciplinary resource center for "Nanotechnology" and resource center "Innovative technologies of composite nanomaterials" of St.Petersburg State University.

SYNTHESIS OF TWO-COMPONENT PHOSPHORUS-TITANIUM-
CONTAINING COATINGS ON SILICA SURFACE BY MOLECULAR
LAYERING METHOD

E.O. Drozdov, S.D. Dubrovensky

St.Petersburg State Institute of Technology, St.Petersburg, Russia (xdeox88@gmail.com)

Two-component coatings containing low-dimensional phosphorus- and titanium-
containing structures on the silica surface are shown to have promising applications in areas
of catalysis and sorption. Traditionally, their deposition is carried out by sol-gel methods. In
this paper, we estimate the feasibility of synthesizing such systems by molecular layering
method (ML) [1], also known as ALD, which provides covalent bonding between the coating
and the substrate.

Two variants of phosphorus-titanium-containing coatings synthesis in a flow system are
considered. The first is carried out by the interaction of a part of the silanol groups of the
silica surface with gaseous POCl3,

\[ 2n(\equiv\text{Si-OH}) + \text{POCl}_3 \rightarrow (\equiv\text{Si-O}-)_n\text{POCl}_3-n + n\text{HCl} + n(\equiv\text{Si-OH}), \]

with consecutive treatment by TiCl4 vapors

\[ n(\equiv\text{Si-OH}) + \text{TiCl}_4 \rightarrow (\equiv\text{Si-O}-)_n\text{TiCl}_4-n + n\text{HCl} \]

As a result, local centers with different number of covalent bonds to the substrate
(referred to as functionality, \(n \leq 3\)) are formed. It was shown by methods of chemical analysis,
Fourier-IR and EDR spectroscopy that the phosphorus- and titanium-containing sites formed
in this case do not interact with each other. So, the elements are distributed unevenly on the
surface and, probably, form single-component regions.

In the second way, the surface of silica surface is treated with a mixture of POCl3 and
TiCl4 vapors.

\[
(m + n)(\equiv\text{Si-OH}) + \text{POCl}_3 + \text{TiCl}_4 \rightarrow
\rightarrow (\equiv\text{Si-O}-)_m\text{POCl}_3-m + (\equiv\text{Si-O}-)_n\text{TiCl}_4-n + (m + n)\text{HCl} \]

The last implementation requires controlling the ratio of reagent concentrations in the
gas phase. Quantum chemical calculations of the thermodynamics of the synthesis process
were carried out to estimate the range of operating concentrations and select the synthesis
conditions. Spectral analysis of products synthesized with the use of calculated prognosis
made it possible to detect the presence of donor-acceptor interactions of phosphorus and
titanium-containing groups. It indicates the formation of a mixed system and a more even
distribution of modifier elements over the substrate surface as compared to sequential treatment.
The chemical composition of such coatings demonstrates the presence of mostly monofunctional
\((n = 1)\) titanium-containing groups in full accordance with quantum chemical calculations.

Thus, the research shows the possibility of synthesizing phosphorus-titanium-containing
structures on the surface of silica, an estimation of their mutual arrangement and interfunctional
interactions by means of a combination of experimental methods and quantum-chemical calculations.

This study was financially supported by the Ministry of Education and Science of the Russian
Federation (grant no. 16.1798.2017/4.6).

SYNTHESIS OF NANOLAYERS OF CHROMIUM OXIDE ON GALLIUM ARSENIDE AND THE CHARACTERISTICS OF THE INTERFACE

Yurii K. Ezhovskii
St.Petersburg State Institute of Technology, St.Petersburg, Russia

The design of microelectronic and nanoelectronic devices has been determined in many respects by the considerable advances made in research into the mechanism of formation and the properties of low-dimensional systems, which, in turn, has given impetus to the development of nanotechnology for these systems. Among the large variety of methods used in the chemical nanotechnology of low-dimensional systems, the atomic layer deposition, or the so-called ALD technology, has enjoyed the widest application [1, 2].

Ultrathin dielectric layers of chromium oxides are very promising for use as components of metal–insulator–semiconductor structures, as well as adhesive and diffusion barrier layers, in silicon and gallium arsenide integrated devices [3].

Chromium oxide nanolayers were synthesized in a vacuum–flow-type reactor (the residual pressure was no higher than $10^{-2}$ Pa) at temperatures in the range $T_s=373–473$ K by using alternate treatment of the surfaces of gallium arsenide with the (110) orientation and (110) orientation in vapors of chromium oxochloride $\text{CrO}_2\text{Cl}_2$ with different hydroxylating reagents according to the following technological schemes.

1). Alternate treatment of the surface in $\text{CrO}_2\text{Cl}_2$ and $\text{H}_2\text{O}$ (the neutral hydroxylating reagent) vapors.

2). Alternate treatment of the surface in $\text{CrO}_2\text{Cl}_2$ and $\text{CH}_3\text{OH}$ (or $\text{CH}_3\text{OH} + \text{H}_2\text{O}$) (the reducing hydroxylating reagent) vapors.

3). Alternate treatment of the surface in $\text{CrO}_2\text{Cl}_2$ and $\text{H}_2\text{O}_2$ (or $\text{H}_2\text{O}_2 + \text{H}_2\text{O}$) (the oxidizing hydroxylating reagent) vapors.

In all cases, the reagent vapor pressure was approximately equal to 1.3 Pa.

The examination of the composition of the synthesized products with the use of the X-ray photoelectron spectra showed that all layers prepared at temperatures $T_s>400$ K contained $\text{Cr(III)}$ and $\text{Cr(VI)}$ ions. The presence of $\text{Cr(III)}$ ions in the products prepared upon hydrolysis in the oxidizing medium indicates that pyrolytic processes play an important role in the formation of the oxide layers.

The conductivity of the chromium oxide layers depends on the synthesis temperature and is governed by the layer composition [the $\text{Cr(III)} / \text{Cr(VI)}$ ratio]. The lowest conductivity ($\sigma <10^{11}$ $\text{Ω cm}^{-1}$) is observed for the layers prepared at temperatures of 373–423 K with ratios $[\text{Cr(III)}]/[\text{Cr(VI)}] \approx 2$. The low conductivity of these chromium oxide nanolayers is associated with their structure, i.e., the layered distribution of supramolecular clusters formed by the $\text{Cr}_2\text{O}_3$ and $\text{CrO}_3$ oxides over the layer thickness [4].

Examination of the characteristics of the semiconductor–dielectric interface with the chromium oxide layers prepared under different conditions revealed that the minimum density of surface states $N_{ss}$ is observed in the structures synthesized through alternate treatment of the etched GaAs surface in $\text{CrO}_2\text{Cl}_2$ and $\text{CH}_3\text{OH}$ vapors.

As follows from our results, the lowest density of states at the interface ($N_{ss}<10^{12}$ $\text{eV}^{-1} \text{ cm}^{-2}$) is observed for the chromium oxide dielectric layers prepared at low temperatures. It seems likely that this circumstance is primarily explained by the formation of ordered chemical bonds with the matrix surface and the more favorable layer mechanism of nanostructure growth at low synthesis temperatures.

Silicon carbide is an excellent semiconductor material due to its ability to carry high currents and operate at higher temperatures compared to silicon. Due to its low wet etch rate compared to conventional silicon oxide it can be used for barrier applications, such as low-k spacers/liners and air gap liners for interlayer dielectric.

Using silicon carbide for spacers/liners requires the ability to deposit thin films of material on a high-aspect ratio surface at low temperatures (<400°C). Currently, silicon carbide thin films are deposited by chemical vapor deposition (CVD) at evaluated temperatures (1500-1600°C), commonly using silane (SiH₄) as a silicon precursor and propane (C₃H₈) or ethylene (C₂H₄) as a carbon precursor. This technique is well established; however, thin films may suffer from non-uniformity. Several plasma-enhanced (PE) CVD processes at somewhat lower temperature (>750°C) are reported using silane plasma. Atomic layer deposition (ALD) or PE-ALD at even lower temperature would be the ideal solution, as it would give atomic-level precision, and PE-ALD is widely used for depositing Si-based dielectrics. However, there is no known high-volume manufacturing ALD process for SiC films.

**Figure 1.** Reaction pathway of SiH₂ stripping H from (a) C-H bond, (b) Si-H of the H-SiC 3C (011) surface producing SiH₃ group on the surface.

R=reactants, where SiH₂ is (a) 3.10 Å, (b) 2.74 Å from the C/Si of the surface; P=products, where SiH₃ group is produced; TS=transition state.

Color scheme: white=hydrogen, grey=carbon, yellow=silicon, red=spin density.

Isosurface for spin density plot = 0.022.
Figure 2. Reaction pathway of SiH$_3$ stripping H from (a) C-H bond, (b) Si-H of the H-SiC 3C (011) surface producing SiH$_4$.

R=reactants, where SiH$_3$ is 3.81 Å from the H of the surface, P=products, yielding SiH$_4$; TS=transition state.

Color scheme: white=hydrogen, grey=carbon, yellow=silicon, red=spin density.

Isosurface for spin density plot = 0.008.

We are using ab initio modeling to investigate the potential reaction mechanism of silicon carbide ALD. Through performing thermodynamical screening for the CVD-like reactions of the possible silicon and carbon precursors, we predict that the precursors silane, disilane or monochlorosilane with ethyne, carbon tetra chloride or trichloromethane are the most favorable for ALD of silicon carbide at 400°C [1]. Indeed we compute that these Si and C precursors react spontaneously with a bare SiC surface. However, none of these precursors react spontaneously with the H-terminated SiC surface that is likely to exist during growth.

In order to understand how H can be stripped from the H-terminated SiC surface, we compute the reaction mechanism and activation energies of silane plasma species (silyl, SiH$_3$, and silylene, SiH$_2$) reacting with the H-terminated SiC surface (see Figures 1 and 2). Silane plasma is known to be highly reactive in the PE-CVD SiC process and the primary and secondary reactive species are SiH$_3$ and SiH$_2$. SiH$_3$ is a long-lived species and less reactive than SiH$_2$, while SiH$_2$ is a reactive, short-lived species [2]. We find that both silyl and silylene show selectivity towards insertion into the Si-H surface bond, rather than the C-H bond. In fact, silyl is computed to show no barrier in its insertion reaction into the Si-H bond.

These results on the reactivity of Si and C precursors give insight into why high temperature and/or plasma conditions are needed for existing SiC growth processes, and give pointers for why low-temperature ALD processes are proving so difficult to find.

EFFECT OF Al2O3 AND SnO2 COATINGS SYNTHESIZED BY ATOMIC LAYER DEPOSITION ON THE POSITIVE ELECTRODE OF LITHIUM-ION CELL CONTAINING Li1.2Mn0.54Co0.13Ni0.13O2

Y.M. Koshtyal¹, A.M. Rumyantsev¹, M.Yu. Maximov², N.A. Kalinin³, V.V. Zhdanov¹

¹ Ioffe Physical-Technical Institute RAS, St.Petersburg, Russia
² Peter the Great Saint-Petersburg Polytechnic University, St.Petersburg, Russia
³ St.Petersburg State Institute of Technology, St.Petersburg, Russia

Lithium-ion cells because of their high energy density and cycle life are widely used as power sources for portable electronics (laptop, tablet, smartphone, cell-phone), hand power tools, hybrid and electric vehicles. The further increase of energy density of lithium-ion cells improves the operational characteristics (autonomous use time, decrease of weight, path length etc.) of powered devices. The increase of energy density can be achieved by the use of better technology of production, active materials (cathode, anode) with higher capacity (storage of lithium ions) and increase of operational voltage.

Augmentation of lithium ion cell voltage (higher charge, more lithium deintercalated from cathode material) can lead to reduction of cycle life (cathode materials are less stable, the extent of electrolyte decomposition increases etc.) and safety of lithium-ion cells. Most of lithium-ion cells used for powering of portable electronics contain LiCoO2 as a cathode material. Application of various protective films known as artificial SEI allowed increasing voltage (energy density) with small or without drop in cycle life.

Atomic layer deposition (ALD, molecular layering method) can be applied in order to deposit protective films on the powder cathode material as well as on positive electrode. Since the first works [1, 2] appeared in 2010 many research articles were dedicated to application of ALD in order to improve performance of various cathode materials. The literature review of published articles cited in system Web of Science revealed the following positive effects of films synthesized on positive electrodes and cathode materials: improvement of capacity retention, cycle life during cycle at higher potentials, Coulomb efficiency, high-rate performance, high-temperature performance, thermostability in charged state. The diminution of self-discharge and increment of resistance during cycling are observed.

The summarized data of the effect of Al2O3, TiO2, ZnO2, ZrO2, LiAlO2 and other types of coatings is communicated in present work. Furthermore we discuss the influence of SnO2 coatings on the electrochemical performance of lithium-rich cathode material (Li1.2Mn0.54Ni0.13O0.13O2), which to our knowledge hasn’t been reported in literature earlier.

The research was conducted with financial support of RFBR, project № 16-33-01030 mol_a.

CHEMICAL CONSTRUCTION OF IRON-CONTAINING NANOCOMPOSITE FERROMAGNETIC MATERIALS BY ML–ALD – THE EXPERIMENTAL JUSTIFICATION

E.G. Zemtsova, O.Yu. Kurapova, P.E. Morozov, V.M. Smirnov

St.Petersburg State University, Institute of chemistry, St. Petersburg, Russia (vms11@yandex.ru)

It is known that there are not so many natural magnetic materials. In general, only transition metals and their oxides demonstrate magnetism. Therefore, an important fundamental and practical problem is the development of new techniques suitable for production of artificial ferromagnetic materials and determination of the correlation between structure and magnetism. Designing of the new ferromagnetic materials significantly increases the number of magnetic substances and ferromagnetic materials.

In fact, we say here about the objects of new scientific direction – spintronics. Traditional objects of spintronics are molecular magnetic materials. Usually, these are either organic paramagnetic molecules or paramagnetic complexes where magnetic metal ions are coated by organic ligand shell. Such molecular magnetic materials with various structures and spin densities can be readily synthesized. However, they have serious disadvantages due to specificity of organic structures. Namely, there is a low spin density and a lot of non-magnetic ballast. As a result, exchange interactions in such structures are weak; ferro-paramagnetic transition temperatures are low (3–30 K).

The more promising alternative here is to get high spin density by means of the directed chemical construction of high-spin nanostructures on the inorganic matrices.

Iron-propargyl and iron-oxygen nanostructures on the silica surface. Synthesis, structure and magnetic properties

The technique included the attachment of organic brush-like chains to the silica surface with the subsequent study of their magnetic properties. Namely, iron-propargyl (Fe-Pr), including –Fe⁺³–O groups formed ≡Si–(R–Fe–R)n chains, where R = propargyl [–C≡C–CH₂–O–] and n is the number of attached chain fragments (R–Fe–R). Iron-organic groups were synthesized on the silica or silicon substrates by means of Molecular Layering method (ML or ALD, atomic layer deposition) that was developed by the St.Petersburg scientific school. The synthesis was carried out using gas phase equipment that provides surface chemical reactions (1-5) in the He stream. All the reactions were performed at 200°C with helium as the carrier gas (consumption of 1-2 ml/s).

As a support, dispersed silica (Silochrom, SH-120, the specific surface area of S=120 m²/g, pore diameter of dₜₚₒʳ=35.0 nm, the magnetic susceptibility of -0.348·10⁻⁶ cm³/g) was used. In some cases, monocrystal silicon KDV-10 (100) was used. Magnetic susceptibility (χ) of the iron-organic structures attached to the silica surface was studied using Faraday method at filed strength values of H₁ = 4100, H₂ = 5820, H₃ = 7190, H₄ = 8280 Oe.

It was found that Fe-Pr nanostructures on silica in the temperature range 70-293 K demonstrate dependence of χₛₚ on the magnetic field strength. This means the presence of non-compensated room-temperature antiferromagnetism of iron-organic groups on silica. Such behavior is established for the first time.

This effect can be related to the redistribution of electron density in the surface organic groups due to the presence of triple bonds. Further analysis demonstrates the strong dependence of χₛₚ on the number of coated layers and on the size of the terminal organic groups. As the layers’ amount increases, χₛₚ is also increases and depends now on the field strength H. Effective magnetic moment was calculated based on the values of χₛₚ and the data of chemical analysis. This parameter increases while temperature increasing that suggests antiferromagnetic interactions within the layer and between layers.
Possibly, these effects are related to the specific distribution of spin density of organic groups in the nanostructures. The difference of 2- and 4-layers samples is evident. In the first case the interactions are antiferromagnetic. In the second case non-compensated antiferromagnetism is observed that is characterized by the significant dependence of $\chi_{sp}$ on the direction of the magnetic field. Such effect can be related to the different value of exchange interactions within one layer and between the layers. However, this dependence of $\chi_{sp}$ on H suggests the presence of the non-compensated antiferromagnetism for Fe-Pr groups on silica surface. The effect is established for the first time. Room-temperature data indicate the prospects of the study of nanostructures fixed on the substrate, for spin electronics.

ALD-based technique of the synthesis is developed of magnetic composite materials built of the iron-propargyl nanostructures layers of the various thicknesses together with coated iron-oxygen groups. The highest coercive strength up to 3640 Oe was found in the sample with two Fe$^{3+}$-O groups monolayers. These results indicate the possibility of the fabrication of magnetically hard materials based on the composite nanolayers on the surface of disperse substance (usual members of this class of magnetic materials are metallic alloys).

Fabrication of metallic clusters (Fe$^0$/Si) by means of the reduction of Fe-Pr nanostructure on the silicon surface

The technique of synthesis of iron-based nanostructures on silicon [Fe$^0$/Si] is developed. This is based on the reduction of pre-synthesized iron-organic nanostructures (number of treatment cycles $n = 20$) on the silicon surface with promising parameters – [Fe$^0$] nanoclusters size: average cluster height of ca. 3 nm, width ca. 10 nm, density of the order of $10^9$-$10^{10}$ cm$^2$, area of the fields with the uniform distribution $\geq 1 \mu m^2$.

It is found that the produced samples have paramagnetic properties with magnetization of 61 A/m. This means new opportunities for the utilization of such structures for the fabrication of the magnetic materials for information storage.

This work is supported by the Russian Foundation for Basic Research grant No. 17-03-01331a.

ATOMIC LAYER DEPOSITION PROCESS FOR FORMING LAYERS OF A HIGH-K METAL GATE STACK WITH 32 NM TOPOLOGICAL SIZE

V.A. Gvozdev$^1$, O.P. Gutshin$^1$, E.S. Gornev$^1$, K.V. Rudenko$^2$, A.V. Miakonkikh$^2$, A.E. Rogozhin$^2$

$^1$ Molecular Electronics Research Institute, Zelenograd
$^2$ Institute of Physics and Technology of Russian Academy of Sciences, Moscow

The plasma enhanced atomic-layer deposition (ALD) of the HkMG stack of MOS nanotransistors was studied, including the layers of the gate dielectric HfO$_2$, the ultrathin (1-3 nm) metal stabilizing layer of hafnium nitride HfN, as well as the main layer of the metal gate of tantalum nitride TaN, on wafers with a diameter of 200 mm. Using the spectral ellipsometry, the thickness uniformly of the deposited films was measured over the wafer. The dielectric constant of the gate dielectric and the breakdown voltages are investigated. By four point probe the resistivity of tantalum nitride deposited by the ALD. The dependences of the homogeneity of the deposited films on the duration of the purging and pumping stages in the ALD process are investigated. In addition, the dependence of the resistivity of the TaN metal layer on the composition and plasma discharge parameters was studied.
Sc₂O₃ THIN FILMS: PRECURSOR SYNTHESIS, ALD-GROWTH, CHEMICAL STRUCTURE AND OPTICAL PROPERTIES

M.S. Lebedev¹, M.Yu. Afonin¹, S.V. Trubin¹, V.N. Kruchinin²

¹ Nikolaev Institute of inorganic chemistry SB RAS, Novosibirsk, Russia
² Rzhanov Institute of semiconductors physics SB RAS, Novosibirsk, Russia

Scandium oxide is known as heat resistant, transparent and wide gap dielectric. The material is interesting for many applications: W:Sc₂O₃ thermionic cathodes, laser active medium, solid electrolytes, high-k dielectrics. Ferroelectric properties of Sc-doped HfO₂ thin films are expected [1]. Atomic layer deposition (ALD) is good decision for similar challenges. But ALD-technologies of scandium oxide are much less developed yet.

In this work scandium (III) tris(methylcyclopentadienyl) Sc(CH₃C₅H₄)₃ and water vapors were used as precursors for ALD-growth of Sc₂O₃ thin films. This precursor system was recently suggested and described in literature [2, 3]. Here we enlarge data about this subject by using wider ranges of ALD-process parameters and films thicknesses. Also complementary techniques were applied for the films study.

Sc(CH₃C₅H₄)₃ was synthesized as result of KCH₃C₅H₄ + ScCl₃ reaction in diethyl ether with further solvent evaporation and sublimation at 110°C [4]. Successfully of the synthesis and purification was confirmed by CHN-analysis and mass-spectrometry investigations.

ALD-growth was performed on Si(100) substrates by using hot-wall Picosun Oy Sunale R-200 ALD reactor (Finland). Nitrogen N₂ (99.999% purity) was used as carrier and purging gas. The Sc₂O₃ films with thickness d = 20-80 nm were deposited at temperature range T = 200-400°C. ALD-window has been observed at range T = 230-370°C. Growth-per-cycle values were found to be Δh = 0.80-0.84 Å/cycle that is somewhat higher than has been reported [3]. Dependence of thickness on number of cycles is linear that typically for ALD.

The films were shown to be carbon-free (XPS). Sc/O ratio was found to be 38/62. The characteristic doublet Sc₂p₃/₂ and Sc₂p₁/₂ with binding energies E_{BE} = 401.7 and 406.1 eV respectively corresponds for Sc in Sc³⁺ state in Sc₂O₃. The O1s main peak with E_{BE} = 529.8 eV is also in good agreement with known data for scandium oxide [5]. The films are polycrystalline as was shown by SEM. The crystallinity is more apparent for higher growth temperature films. The grain size increases with the thickness. Cubic Sc₂O₃ phase has been determined by FTIR, Raman spectroscopy and XR-diffraction. The optical properties were investigated by spectroellipsometry. The refractive index n(λ) follows Cauchy’s dispersion relation that indicates transparency of the films (extinction coefficient k(λ)=0). The optical properties were shown to be same for the films (d=40-42 nm) deposited at ALD-window temperatures. The refractive index of these films lies in narrow range 1.954-1.962 at λ = 632.8 nm. This parameter significantly increases with the thickness (at T = 300°C). The annealing influence (T_{ann} = 700°C, inert atmosphere) on the ALD-films microstructure and optical properties should be recognized as negligible.

The data obtained confirm convenient ALD-behavior of Sc(CH₃C₅H₄)₃-H₂O precursor system. It gives possibilities of the wide applied usage this system for production of Sc₂O₃-containing thin films by ALD.

RECENT DEVELOPMENTS IN ATOMIC LAYER DEPOSITION: HfO₂ PROCESS IMPROVEMENTS, AND RF SUBSTRATE BIASING FOR IN-SITU PRE-TREATMENT

Aileen O’Mahony¹, Agnieszka Kurek¹, Thomas Miller¹, Harm Knoops¹,², Owain Thomas¹, Robert Gunn¹

¹ Oxford Instruments Plasma Technology, North End, Yatton, Bristol, BS49 4AP, UK
² Eindhoven University of Technology, 5612 AZ Eindhoven, Netherlands

RF substrate biasing can be applied during thin film deposition to increase the ion energy and influence film properties such as stress [1], crystallinity [2], and density [3]. In this work, the use of an Atomic Layer Deposition (ALD) system for in-situ etching of material using radio frequency (RF) substrate biasing in combination with an Ar plasma is reported [4].

Four different thin film materials; Al₂O₃, HfO₂, SiO₂, and Si₃N₄ were exposed to Ar plasma for 20 minutes under the following conditions: 60 sccm Ar, 15 mTorr chamber pressure, and 400 W inductively-coupled plasma RF (13.56 MHz) power, in an Oxford Instruments FlexAL ALD tool equipped with an RF-biased table (0-100 W). Figure 1 shows that the thickness of the material etched increases monotonically with applied DC bias with SiO₂ etched the fastest and Al₂O₃ etched about five times slower. The pre-treatment time and DC bias can be tuned to remove unwanted surface oxides or nitrides of a known thickness in just a few minutes before plasma ALD process proceeds.

![Figure 1. Etch rate of Al₂O₃, HfO₂, SiO₂ and Si₃N₄ versus DC bias at the substrate.](image)

In addition, improvements in the HfO₂ ALD process are outlined. HfO₂ is used in high volume manufacturing as a high-k dielectric layer deposited by ALD [5], in memory devices such as DRAM [6], and also ferroelectric-RAM technology due to the ferroelectric properties of both pure HfO₂ [7] and doped HfO₂ layers [7,8] (e.g. HfO₂ doped with SiO₂, Al₂O₃, ZrO₂, La₂O₃).

A process optimisation study was undertaken with HfO₂ films deposited using tetrakis(dimethylamido)hafnium (Hf(NMe₂)₄, (TDMAH)) as a comparison to the existing HfO₂ process of record which uses tetrakis(ethylmethylamido)hafnium (Hf(ETMe)₄, (TEMAH)). It has a higher vapour pressure compared to TEMAH [9,10] which allowed the TDMAH to be delivered by vapour draw rather than requiring delivery assistance by argon bubbling (as required for TEMAH). A 0.4 s TDMAH dose was required for surface saturation (Figure 2(a)) with significantly improved HfO₂ film uniformity across a 200 mm substrate (2.7%) for the TDMAH PEALD process compared to the TEMAH PEALD process.
A wide ALD window of 150-325°C resulted for both the thermal ALD and PEALD of HfO₂ ALD processes (Figure 2(b)). The higher GPC for the PEALD process (~1.2 Å/cycle) was attributed to the highly reactive plasma species. Linear ALD growth was observed for both the thermal and plasma ALD HfO₂ processes (Figure 2(c)). HfO₂ films deposited with TDMAH yielded analogous electrical performance to metal-insulator-metal structures fabricated with an HfO₂ layer deposited by TEMAH/O₂ plasma.

RF substrate biasing could be implemented to remove material in-situ from substrate surfaces (e.g. Si, GaN, GaAs) to form a “cleaner” interface prior to deposition of high-k layers, for example HfO₂ or passivation layers for semiconductor applications such as MOSFETs or GaN HEMT devices.

REGULATION OF THE PHASE COMPOSITION AND DISTRIBUTION OF TITANOXIDE STRUCTURES IN THE VOLUME OF A POROUS MATRIX IN THE PROCESS OF MOLECULAR LAYERING ON γ-Al2O3

A.A. Malkov1, A.S. Chernov1, S.N. Petrov2, A.A. Malygin1

1 St.Petersburg State Institute of Technology, St.Petersburg, Russia
2 Central Research Institute of Structural Materials “Prometey”, St.Petersburg, Russia

Titanium oxide structures deposited on various porous matrices are of practical interest as solid-phase carriers, catalysts, sorbents, fillers of composite materials, etc. For such systems, an important condition for their effective use in various physicochemical processes is not only the chemical and phase composition, but also Uniformity of the distribution of the deposited structures in the inner space. One of the ways to ensure the ability to meet these requirements is the molecular layering method, based on the flow of chemical interactions between the functional groups of the solid body and the reagents supplied to them.

In the present work, the influence of temperature - time regimes of synthesis by molecular layering on the phase formation and chemical composition of titanium oxide structures deposited on the dispersed and granular gamma alumina is considered, as well as their distribution over the cross section of the alumina matrix.

Synthesis was carried out on preliminary heat-treated samples of γ-Al2O3 at various degrees of dispersion by 500°C samples by successive 1-4-fold treatment with TiCl4 and H2O vapors at 200, 350 and 500°C (Tch) under flow conditions both in a reactor with a septum and with the weights of McBen. The obtained samples were studied with the help of SEM, XRF, ESD, the content of titanium was determined by the results of chemical analysis and X-ray spectral analysis (PCMA).

For all the temperatures under consideration, according to gravimetric measurements, the completion of individual stages of synthesis is observed and the monotonous increase in the mass of the build-up layer and the content of titanium in the composition of the modified products are observed.

It is established that the temperature of the synthesis makes a significant impact on the phase formation of titanium oxide structures. At 200°C, only the X-ray amorphous thianoxide phase is realized on the γ-Al2O3 surface. At 350°C, in addition to the X-ray amorphous phase, anatase and rutile phases are simultaneously formed, and at 500°C anatase modifications of titanium dioxide.

Based on the analysis of the first derivatives of diffuse reflection spectra, the influence of the synthesis temperature on the coordination state of titanium in the supported titanium oxide structures was established. The appearance of an additional peak on the first spectrum derivatives of the modified samples in the region of 32,000 cm⁻¹, which is observed in the spectra of aluminum titanate is interpreted as evidence of the formation of Al-O-Ti bonds. In the spectra of samples obtained at 350 and 500°C, the main edge of the absorption band increases with the number of conducted cycles, the ML shifts to values characteristic of rutile and anatase, respectively. On the hardware differentiation curves for all series after the first processing cycle, there are two maxima at 32,000 and 25,000 cm⁻¹. If the first maximum, as already noted, corresponds, apparently, to the formation of Al-O-Ti bonds, then the second indicates the presence of titanium in the octahedral polyhedron TiO6 of the bulk phase of anatase-like type. In the course of further synthesis, there is a decrease in the area under the first and an increase under the second peak. For samples obtained at 350 and 500°C, a shift of the second maximum to values characteristic of the rutile and anatase phase, respectively, is observed. The position of the sample maxima in after 4 cycles of ML at 350°C indicates the presence on the surface of titanium atoms with coordination polyhedra characteristic of rutile
and anatase. In a sample with Tch 500 °C, the position of the maximum of the anatase characteristic for titanium atoms with a coordination oxygen polyhedron is fixed.

With the help of scanning electron microscopy and X-ray microprobe analysis, the distribution of the titanium content along the granule cross section is determined as a function of the time of the TiCl₄ chemisorption step. The effect of the chemisorption time of titanium tetrachloride on the nature of the titanium distribution was carried out at 200°C by feeding TiCl₄ to the reactor for 10, 20, 40, 80, 120 and 220 minutes, and controlling the flow of all stages in situ using the McBen weights. The results of the RSMA cleavage indicate a gradual shift of the reaction front from the surface to the center of the granules. And at times of chemisorption (τ_ch = 10 ÷ 80 min) the presence of titanium is fixed mainly in the near-surface layer. And only with the increase of chemisorption time up to 120 min is the presence of titanium in the center of the pellet (figure 1).

A similar character of the distribution of titanium oxide structures is apparently due to the process in the porous space of alumina pellets in the intradiffusion region.

![Figure 1. Change in the concentration of Ti along the γ-Al₂O₃ granule cross-section from the time of chemisorption of TiCl₄](image)

For all the temperatures considered, a decrease in the concentration of titanium is observed in the modified samples as they move away from the surface toward the center of the granule. The greatest difference in titanium concentrations at the center and at the surface is fixed in products synthesized at T_ch = 200 and 350°C. At 500°C there is a significant decrease in the concentration gradient over the cross section.

*The studies have a financial support from the Ministry of Education and Science of Russia (project 16.1798.2017/4.6).*
HIGH SPECIFIC SURFACE AREA CATALYTIC SYSTEMS CONTAINING TRANSITION METAL (Ti, V, Mo, Nb) OXIDES PREPARED USING ALD

S.V. Mikhailovskii¹, A.O. Koryagina¹, A.A. Obletsova¹, N.V. Zhilyaeva², M.M. Ermilova², N.V. Orekhova², A.A. Malygin¹, A.B. Yaroslavtsev²

¹ St.Petersburg State Institute of Technology, St.Petersburg, Russia
(Mikhailovsky83@mail.ru)
² A.V. Topchiev Institute of Petrochemical Synthesis RAS, Moscow, Russia

It is well known that a transition metal oxides are catalysts for many organic and inorganic processes. These oxides used in a mixture with each other or other compounds often. The catalytically properties of such mixtures are dependent not only on their chemically composition and relation of components, but also on a structures of this components and whole catalytic systems, and on the catalytic surface species, their quantity and activity. These factors, in its turn, dependent highly on the methods of preparing the catalysts and on values of their specific area.

Conventional methods such as evaporation of solutions, hydrothermal synthesis, slurry method for bulk catalysts, and impregnation for supported catalysts prepare catalysts containing transition metal oxides usually. The presence of catalyst support can be increase significantly specific surface area and improve other properties of catalytic systems. The molecular layering method (the name of atomic layer deposition in Russia) allows to obtain more reproducible results than impregnation and other methods. Moreover, this method allows to regulate precisely the position of supported structures relative to each other.

Previously, we investigated the catalytic properties of the VOₓ/TiOᵧ/γ-Al₂O₃ systems (obtained by ALD with using vapors of TiCl₄ and VOCl₃) in the reactions of oxidative dehydrogenation of methanol to formaldehyde [1], and ethane to ethylene [2]. It was shown that the yield of the desired products increases significantly with the increment of the number of ALD cycles not only for the VOₓ structures, but also for TiOᵧ structures, although the TiOᵧ structures are nonselective themselves for these reactions. It should be noted that the specific surface area of these catalytic systems decreases with the increment of the number of ALD cycles, mainly due to a decrease in the proportion of the matrix in the samples, rather than blocking matrix pores. At the present time we also obtained by ALD and investigated multicomponent systems, such as Mo(Nb)Oₓ/TiOᵧ/γ-Al₂O₃; VOₓ/Mo(Nb)Oᵧ/Nb(Mo)Oₓ/SiO₂; NbOₓ/VOₓ/SiO₂ and others. The chemosorption stage of synthesis of molybdenum (niobium) oxides structures was carried out both from the solution of MoCl₅ (NbCl₅) in acetonitrile and using of the vapors of these chlorides due to their heating. It should be noted that titanium oxide sublayers can not only fulfill the role of cocatalyst, but also regulate the pore size of the matrix, which makes it easy to obtain membrane catalysts by using ALD [3].

The study was in part financially supported by the Ministry of Education and Science of the Russian Federation (project 16.1798.2017/4.6), and the Russian Foundation for Basic Research (agreement no. 16-03-00214).

REGULATION OF THE ROUGHNESS OF A TiO$_2$ NANOLAYER ON A SILICON SUBSTRATE BY THE ALD METHOD AS A PROMISING MATERIAL FOR BIOSENSORS

V.S. Mironov, V.M. Smirnov

Institute of Chemistry, St.Petersburg State University, St.Petersburg, Russia

Since the properties of the material are determined both by the nature of the constituent components and by their spatial arrangement, the study of the structuring processes at the micro and nano level is an effective modern tool for solving the problem of synthesizing materials with controlled functional properties. In this regard, research in the field of chemical design of more complex systems (composite systems) in the field of creating electrochemical biosensors is relevant [1].

At present, biosensors are used in numerous fields from environmental protection, medical diagnostics and bioengineering. The main characteristics of biosensors are sensitivity and selectivity, as well as speed.

Despite the considerable success achieved over the last 10 years in the field of synthesis and application of biosensors, their widespread use in medicine is hampered by many unsolved problems, mainly in the field of the creation of new composite nanomaterials for biosensors of the third generation [2].

It should be noted that the most difficult task in developing a third generation of biosensors that can have sharply improved analytical properties (for example, sensitivity can be increased by several orders of magnitude) is the problem of creating an interface between the electrode (silicon / nanostructured titanium oxide) and protein.

In fact, it is a controlled chemical synthesis on the surface of silicon taken as an electrode matrix. To create the necessary nanoscale (nanorelief) of the silicon surface on silicon, TiO$_2$ nanostructures are applied. To obtain such a material, it is proposed to use the gas-phase method of molecular layering (ML-ALD), the size of the nanostructures obtained lies in the range 1-100 nm.

As a result, a new functional material with improved sensor properties is obtained based on the system: (silicon / nanostructured titanium oxide / bioreceptor). The purpose of this work was to study the effect of the algorithm for the synthesis of titanium dioxide film by the ALD method on its electroactive surface area.

We proposed an algorithm for the synthesis of nanoscrubbed titanium dioxide, which allowed us to increase the surface area of the film.

The nanosheet titanium dioxide synthesized by the MH method was studied by SEM, EDX, XRD, and AFM methods. Electrochemical properties were studied by cyclic voltammetry. The electroactive surface area of a nanoscale titanium dioxide film synthesized by the proposed algorithm is 1.1 times higher than the reference film and 1.2 times as compared to the reference silicon electrode.

Titanium and its alloys have a unique combination of excellent mechanical properties and biocompatibility that allows it to be widely used as a material for medical implants. Nevertheless, titanium materials, which currently used in medical practice, require improvement of both mechanical properties and bioactivity for reliability and accelerating of engraftment.

In this study, we used an integrated approach for the preparation of a bioactive coating on the surface of ultra-fine grained titanium. The integrated approach combined three methods: severe plastic deformation (SPD), chemical etching and atomic layer deposition (ALD) [1]. SPD method improved mechanical properties of the material. Chemical etching in basic or acidic Piranha solutions (NH₄OH/H₂O₂ or H₂SO₄/H₂O₂) produced a topography and morphology of the surface that is necessary for the rapid engraftment of the implant. Finally, ALD method served for deposition of biocompatible and bioactive crystalline titania coating that protects implant from biological corrosion keeps the topography of etched titanium surface and favors the growth of bone tissue.

Earlier we investigated in detail the features of the etching of ultrafine grain (UFG) and coarse grain (CG) titanium in Piranha solutions [2]. Based on this information, we selected 4 types of samples for titania ALD. Precursors were titanium isopropoxide and water. Titania coatings were successfully deposited at 250°C. The samples were characterized by ellipsometry, contact angle measurements, scanning electron microscopy, atomic force microscopy, X-ray diffraction, X-ray photoelectron microscopy. The “in vitro” study of adhesion, viability, proliferation and differentiation of MC3T3-E1 osteoblasts showed that integrated approach can significantly improve bioactivity of the UFG titanium. But the variations of viability, proliferation, and differentiation depend noticeably on the nature of etchant and etching conditions. The samples with ALD coatings revealed the significant improvement of proliferation and differentiation of osteoblast cells.

The authors would like to acknowledge the Russian Ministry of Science and Education for financial support through megagrant No. 14.B25.31.0017.

This research was conducted using the equipment of the resource centers of the Research Park of the St. Petersburg State University «Innovative Technologies of Composite Nanomaterials», «Physical Methods of Surface Investigation», «X-ray Diffraction Studies», «Nanotechnology Interdisciplinary Centre» and «Nanophotonics».

DISCRETE VACUUM PULSE MO CVD PROCESS: THE FEATURES OF FILM DEPOSITION IN THE SYSTEMS WITH A HIGH ASPECT RATIO

Yu.V. Shevtsov, B.M. Kuchumov, S.V. Trubin, E.S. Vikulova, I.K. Igumenov
Nikolaev Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russia

Earlier, we have revealed an effect of a thickness-modulated growth of metal oxide layers in slot systems with an aspect ratio ranging from 5 to 50. On studying the processes of hafnium and magnesium oxide growth via PULSE MO CVD, when one of the substrates with metal pattern used in the slot structure, the film on the other substrate was thickness-modulated according to this pattern. The oxide film is visible in the optical range in the form of a corresponding pattern that repeats the shape of the metal pattern.

The features of metal oxide layer deposition are studied for a system with a high aspect ratio. The deposition of hafnium (HfO$_2$) and magnesium (MgO) oxide layers was carried out using a pulse MO CVD reactor with a discrete dosing of reagents with no use of any carrier gas. The following volatile organometallic compounds were used as precursors: Hf(thd)$_4$ for hafnium, Mg(thd)$_2$, Mg(thd)$_2$(TMEDA), Mg(tfac)$_2$(TMEDA) for magnesium, where thd =Me$_3$CCOCHCOCMe$_3$, TMEDA=Me$_2$NCH$_2$CH$_2$NMe$_2$, tfac = CF$_3$COCHCOMe. Oxygen was used as the reactant gas, and water vapor was also used in a number of experiments.

Polished silicon [100] was used as the substrate in the slot structure. The modulating substrate represented a 25 × 25 mm glass wafer, 2 mm thick with a deposited chromium pattern (Cr layer 0.25 μm thick) was placed parallel to the silicon substrate at a distance of 200 μm. A gap of 25 μm between the chrome strips appeared on the opposite surface of Si after the deposition of HfO$_2$ film onto the slot structure.

Additional studies of temperature dependences for a multi-tier slot structure were carried out. Temperature changes of the samples have been registered in the course of the in situ deposition experiment. It is established that when the precursor and the reactant gas in the slot structures are inflated into the evacuated reaction chamber, an increase in the temperature is observed, and when the reaction chamber is evacuated, the temperature exhibits a decrease. The change in temperature in the course of a single film deposition cycle (filling with the precursor, with the reactant gas, and pumping-out the organic ligand products) amounts to about 20° at a constant temperature of the reaction chamber furnace. Heat exchange mechanisms that result in the observed effects of temperature fluctuations within a single cycle are discussed.

The investigation of optical parameters for the thickness-modulated films was carried out using a scanning laser ellipsometry technique. The effect resolution under these experimental conditions amounts to 25 μm.

It is established that the effect of image transfer is realized in 2 - 3 tiers of the used structure. The only limitation is presented by the substrate temperature. It has been shown that changing the "top - bottom" position of the system with respect to the heated furnace does not result in disappearing the observed effect. An additional effect is observed that could be interpreted as positive-negative one.

It has been found that changing the material of the modulating substrate to silicon and glass-ceramics with the conservation of chromium metallization results in the absence of the image transfer effect. Changing the metallization material (gold instead of chromium) when silicon and glass-ceramic substrates are used results in renewing the effect observed earlier. In the case of using fluorinated magnesium precursors, the image transfer effect is observed, whereas the deposited layers are presented by magnesium fluoride.

The growth mechanism of a thickness-modulated film is under discussion.
APPLICATIONS OF THE ATOMIC LAYER DEPOSITION METHOD IN PHOTONIC SENSORS MANUFACTURING

G.Ya. Buymistriuk

Intel-Systems LLC, St.Petersburg, Russia (gy@isi.spb.ru)

The method ALD for maximum adhesion of the functional coatings to the substrate, has an expanding application in the photonic sensing, including technologies of fiber optic sensors [1] for practical applications in various industries [2].

Considered the application of the method ALD for deposition of functional oxide coatings of TiO₂, ZrO₂, SiO₂ and Al₂O₃ in the manufacture of fiber optic sensors for extreme conditions. The examples of fiber optic sensors based on fiber Fabry-Perot micro- and nano-interferometers and diffraction Bragg gratings with functional nano-coatings: protective, reflective and spectrally selective on silica and sapphire optical fibers.

Experimental results stability of nano-coatings created through the method ALD for external influencing factors – vibration, temperature and ionizing radiation – relevant extreme conditions. The comparison of the characteristics of nano-coatings to optical micro- and nano-fibers, made by ALD, by magnetron sputtering and by ion sputtering, confirming the maximum adhesion of ALD coatings on substrates.


APPLICATION OF ALD FOR OBTAINING THE SENSITIVE LAYER OF GAS SENSOR

K.T. Akkuleva, V.V. Antipov, N.V. Zakharova

St.Petersburg State Institute of Technology, St.Petersburg, Russia

Currently gas sensors, which work on different physical principles, are widely used in security systems. Among air control sensitive devices there are visual indicators, which change their color when saturated with certain component [1].

A lot of attention is currently given to Semiconductor gas sensors based on metal oxides (SnO₂, ZnO, In₂O₃, TiO₂). They spark such interest because of their undoubtful advantages, such as high sensitivity in detection of small gas concentrations, reversibility, wide range of gas components that could potentially be detected with such indicators and their low cost.

It is of high importance to conduct investigations aimed on increasing selectivity and shortening response time of semiconductor gas sensors. To solve these problems different approaches can be taken, including not only search for brand new materials, but also application of already existing methods of modification on the surface of sensor’s active elements [2, 3].

In present study, by using the Atomic Layer Deposition (ALD) method vacuum chamber under the temperature of 200°C titanium oxide structures has been synthesised on the surface of aluminum oxide ceramic elements of gas sensors.

In order to analyze the structure and the morphology of the surface of obtained films the investigation has been conducted by using atomic force microscope Solver P47 Pro (NT-MDT, Russia) in two different modes: topography and phase contrast, which allowed to detect areas with different physical and chemical properties on the surface.
600 cycles of Atomic layer deposition create on the surface of ceramic plate TiOx cover, which consists of spherical structures with diameter about 50 nm. Average surface roughness Rₐ of synthesized samples increased up to 5.2 nm, comparing to previous 3.6 nm.

We plan to continue our research by evaluating functional characteristics of new samples, ones that are modified by the ALD method, and ones synthesized by sol-gel technology, regarding its interactions with CO, CO₂, NO₂, etc.

Preliminary tests performed at the N.S. Kurnakov Institute of General and inorganic chemistry and refers to the theses of sensory fusion [4].

The work was supported by the Russian Foundation for Basic Research (project no. 16-03-00214).


ATOMIC FORCE MICROSCOPY POSSIBILITIES FOR INVESTIGATING THE MORPHOLOGY OF PRODUCTS OF ATOMIC LAYER DEPOSITION

Eugene A. Sosnov

St.Petersburg State Institute of Technology, St.Petersburg, Russia

The directed synthesis of solids technologies, which actively developed with the 1960s, based on V.B.Aleskovskii's "framework" hypothesis, allow to create on the surface of materials with different composition and spatial structure the nanostructures and nanoscale coatings with specified physicochemical and performance properties. At the same time, the introduction of such processes into production requires the provision of instrumental control of the dimensions and characteristics of the nanosized 0D-2D structures.

One of the methods allowing to control as the passing of Molecular Layering (ML) (or ALD) with the necessary (nanometer) accuracy, as the characteristics of synthesized nanomaterials (including distribution uniformity and continuity of nanostructures formed by coating) is an atomic force microscopy (AFM) with unique sensitivity, resolution, and a wide range of physicochemical characteristics studied, combined with simple work of the instruments.

At the same time, the real possibilities for estimating the size and distribution of the formed by ML (ALD) structures are determined by three factors:

- shape and geometric dimensions (radius of curvature) of used AFM probe;
- morphology of surface used as a matrix for ML (ALD);
- chemical affinity (proximity of physicochemical and adhesive properties) of the matrix and the structures built up during the ML (ALD).

This report shows the possibilities of AFM for analyzing results of synthesis by ML method of different element-oxide structures on the surface of matrices with various genesis (flat, highly disperse, highly porous materials with different forms and ordering of pores).

This work was financial support from the Ministry of Education and Science of Russia (project 16.1798.2017/4.6)
COMPARATIVE ANALYSIS OF PLATINUM GROUP METALS THIN FILMS ALD/CVD FEATURES

Vladislav Yu. Vasilyev

Novosibirsk State Technical University, Russian Federation

Last years, platinum group metals (PGMs: Ru, Rh, Pd, Os, Ir, Pt) of The Periodic Table of Elements reveal increasing interest as perspective materials in the form of thin films. These films are considered for the use in modern precision technologies, chemistry, medicine, etc. Some research summaries on Atomic Layer Deposition/Chemical Vapor Deposition (ALD/CVD) of PGMs thin films were published since the beginning of this century [1, 2]. Currently, the number of research publications and individual summaries on PGMs thin films differs substantially. The largest number of research reports performed with the use of wide range of chemicals and deposition conditions seems to be devoted to the Ru and Ir metal thin films, see detailed reviews [3-5]. In contrast, just a few reports have been published on Rh and Os thin films deposited using CVD and ALD, as summarized in references [1, 2].

PGMs thin films are deposited using a number of complex chemical compounds (precursors), such as carbonyls, cyclopentadienyls, β-diketonates, allyl derivatives, nitrogen-containing compounds with oxidizers or reducing agents. It has been shown that depending on conditions the PGMs thin films grow with significant nucleation delay at low temperatures and form polycrystalline materials with carbon and oxygen as undesirable impurities [2]. However, till recently there have been no comprehensive summary on the topic, particularly explaining on comparative basis the advantages and drawbacks of precursors used for PGMs thin film synthesis.

In this work, an attempt of comparative analysis of PGMs ALD/CVD features is presented. Using a set of selected criteria, a large amount of published research materials with the depth of publications of about 20 years (including experimental data and summaries made by the author), are summarized and analyzed comparatively, focusing on the following aspects:
- nucleation and the first steps of the films growth on substrate surfaces;
- deposition kinetics and deposition features of the films on 3D objects;
- correlations of the precursors types with the film deposition rates;
- effects of the second reaction compounds (oxidizers, reductants), etc.

As a result of performed comparison, a number of discovered ALD/CVD features and film commonalities are selected and compared. Based on this analysis, some conclusions on the PGMs thin film growth features and the films growth schemes are presented.

SURFACE MORPHOLOGY, CRYSTALLINITY AND ELECTRICAL PROPERTIES OF SOME RARE-EARTH OXIDE ALD FILMS

Satu Ek¹, Riina Ritasalo¹, Tiina Sarnet¹, Jesse Kalliomäki¹, Erik Østreng¹, Alexey Veselov¹, Silvia Vangelista², Alessio Lamperti², Sabina Spiga², Rossella Piagge³, Gabriella Ghidini³

¹ Picosun Oy, Tietotie 3, 02150 Espoo, Finland (alexey.veselov@picosun.com)
² CNR-IMM - MDM Laboratory, Via C. Olivetti 2, Agrate Brianza (MB), 20864 Italy
³ STMicroelectronics, Via C. Olivetti 2, Agrate Brianza (MB), 20864 Italy

Rare-earth oxides (REOs) have interesting optical and electrical properties that make them useful for several applications. Many REOs have high dielectric constant (k), which can easily reach values k>20. Therefore, they are relevant for the microelectronics industry. At present, there is a growing need for thinner gate dielectrics of current materials, such as SiO₂, which might lead high leakage currents, subsequently leading to increased power dissipation, reliability problems and unaccepted electrical breakdown [1, 2]. The implementation of high-k gate dielectrics is one of several strategies developed to allow further miniaturization of microelectronic components. A possible gate dielectric material needs to fulfill certain requirements [1]: (i) k-value high enough to fulfill the roadmap of components scaling, (ii) thermodynamically stable with Si, (iii) kinetically stable, and compatible with processing to 1000°C for few seconds, (iv) act as an insulator, by having band offsets with Si of over 1 eV to minimize carrier injection into its bands, (v) form a good electrical interface with Si, and (vi) have few bulk electrically active defects.

In this work, we have succeeded in the deposition of various REOs, such as CeO₂, La₂O₃, Y₂O₃, and Y₂O₃-doped Al₂O₃ (Y:Al₂O₃), in a uniform manner on 200 mm Si wafers using a Picosun R-200 Advanced atomic layer deposition (ALD) reactor. REO films were deposited using Ce(thd)₄, La(thd)₃ and Y(thd)₃ as metal-containing precursors, and ozone as oxidizer.

Figure 1. Conformality, crystallinity and roughness of Y₂O₃ and Y:Al₂O₃ films. Y₂O₃ has 1σ non-uniformity of 1.9% and Y:Al₂O₃ of 1.4%. GIXRD patterns demonstrate the crystallinity of Y₂O₃. When mixed with amorphous Al₂O₃ to obtain Y:Al₂O₃, the resulting film is amorphous.

63
The surface morphology, crystallinity and grain size of the deposited layers were studied. Conformality maps, AFM surface morphology and XRD analysis of Y2O3 and Y:Al2O3 films are presented in Fig. 1 as an example. The results show that uniform ALD layers were deposited, i.e. 1.4-2.5% (1σ non-uniformity), with a very smooth surface, with 0.5 nm roughness. Additionally, electrical measurements of the REO films were studied. Fig. 2 shows an example of the effect of Y2O3 content in Al2O3 on the breakdown field and leakage current. The Y2O3 films exhibit a high dielectric breakdown field (>6 MV/cm), a relatively high k value (~11), and a low-leakage current density (<10^-8 A/cm² at 3 MV/cm) with 100 nm layer deposited at 300°C, well-comparable to the values obtained by de Rouffignac et al. [2]. By adjusting the amount of Y2O3 in Al2O3 a good compromise can be reached with relatively high growth rate, low leakage and high breakdown together with relatively high k-value.

**Figure 2.** Electrical properties of Y2O3 in comparison with Y2O3-Al2O3.

*This work has received funding from TEKES and ECSEL-JU R2POWER300.*


**ATOMIC LAYER DEPOSITION OF TIN OXIDE THIN FILMS USING TETRAETHYL TIN TO PRODUCE HIGH-PERFORMANCE ELECTRODES FOR LI-ION BATTERIES**

D.V. Nazarov¹, M.Yu. Maximov¹, P.A. Novikov¹, A.O. Silin¹, A.A. Popovich¹, A.M. Rumyantsev², V.M. Smirnov³

¹ Peter the Great Saint-Petersburg Polytechnic University, St.Petersburg, Russia
² Ioffe Physical-Technical Institute RAS, St.Petersburg, Russia
³ Saint-Petersburg State University, St.Petersburg, Russia

SnO2 has been considered a promising anode material and alternative to commonly used commercial Li-ion power sources because of its high theoretical capacity. Recently, its importance has increased because of its excellent performance in sodium-ion batteries and solid-state batteries.

In this study, thin films of tin dioxide have been synthesized on substrates of silicon and stainless steel by atomic layer deposition (ALD) with tetraethyl tin and a series of coreactants such as remote oxygen plasma, hydrogen peroxide, and ozone. The optimal conditions for growth and “ALD windows” have been determined earlier [1]. The films growth rates in this ranges have been found to be 0.025, 0.045 and 0.07 nm per cycle for H2O2, O3, and O2 plasma coreactants. The samples were characterized by ellipsometry, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray diffraction and X-ray reflectometry (XRD and XRR), X-ray photoelectron microscopy (XPS). The films deposited at temperatures
below 300°C were amorphous irrespective of the nature of coreactant. According to XPS, the samples mainly contained tin in oxidation state +4. Electrochemical properties of the films deposited on stainless steel substrates were studied in detail. During electrochemical cycling in the voltage range of 0.01-0.8 V, it was shown that tin oxide deposited with oxygen plasma oxidizer has a stable discharge capacity of approximately 650 mAh/g during 400 charge/discharge cycles with an efficiency of approximately 99.5%. The decrease in capacity after 400 charge/discharge cycles was around 5-7%. Samples deposited with ozone have the higher reversible capacity (above 900 mAh/g), exceptional cyclability and good electrochemical performance as an anode material for lithium ion batteries. Results obtained in this work with respect to the specific capacity and cyclic stability of thin films of SnO2 synthesized by ALD exceed the values mentioned in the literature for pure tin dioxide thin films. All deposited thin films of SnO2 have fast kinetics and excellent discharge efficiency at high C-rates, up to 40°C, with a small decrease in capacity of less than 20%.

This research was conducted using the equipment of the resource centers of the Research Park of the St. Petersburg State University «Innovative Technologies of Composite Nanomaterials», «Centre for Physical Methods of Surface Investigation», «Centre for X-ray Diffraction Studies», «Nanotechnology Interdisciplinary Centre».


EVALUATION OF DIFFERENT NANOIMPRINT RESISTS FOR A USE IN AREA-SELECTIVE ATOMIC LAYER DEPOSITION OF SELECTED MATERIALS

Riina Ritasalo1, Satu Ek1, Erik Østreng1, Alexey Veselov1, Martin Messerschmidt2, Kestutis Grigoras3, Mika Prunnila3

1 Picosun Oy, Tietotie 3, 02150 Espoo, Finland (alexey.veselov@picosun.com)
2 Micro Resist Technology GmbH, Köpenicker Str. 325, 12555 Berlin, Germany
3 VTT, Tietotie 3, 02150 Espoo, Finland

Nanopatterns of diverse materials are of much interest and have great relevance as a means of enhancing performance, enabling miniaturization, or as determining components of functional devices or interfaces. Several top-down and bottom-up techniques have been attempted to meet these goals, however with varying degrees of success [1]. In this study we employ a combination of nanoimprint lithography (NIL) and area-selective atomic-layer deposition (ALD); in which NIL is used to produce suitable patterned polymeric templates for area-selective ALD enabling thus a patterned ALD growth.

ALD requires typically the presence of OH-groups on the sample surface in order to get growth initiated. The lack of active surface sites e.g. in the case of hydrophobic polymer layers inhibits the nucleation process. This method would enable growth of patterned ALD wafers and would therefore eliminate one costly mask layer step in the fabrication process.

The main goal of this study is to evaluate and to identify those NIL resists that feature effective ALD growth inhibition properties and to test the concept with NIL-patterned templates and using PICOSON™ ALD technology. For these investigations in total four NIL resists with different chemical compositions were chosen. The selection of ALD materials included oxides of ZnO, HfO2, ZrO2, Ta2O5, TiO2 and Al2O3, as well as Pt as a metallic candidate. After the ALD step the samples were treated by oxygen plasma to evaluate their performance in terms of the area selectivity. Examples of this empirical approach are presented in Fig 1. In those cases in which a compact ALD coating layer is formed onto the organic NIL resist, the oxide layer acts as an etch barrier for the oxygen plasma, so that no
NIL resist is removed while in those cases where no compact oxide layer is deposited, the oxygen plasma will attack and remove the organic NIL resist.

Figure 1. Example of test setup and ALD area selectivity of ZnO. (a) There is no (compact) ALD coating layer on top of NIL resist thus oxygen plasma removes the polymer and (b, c) The organic NIL resist (mr-NIL210) is not removed completely due to ALD coating on top of it.

The results revealed that the type of applied NIL resist, the type of investigated ALD material and also the applied ALD parameters had all significant effects on the ALD growth inhibition capability. Usually the selectivity was few tens of cycles but at best it reached over 200 cycles. The most promising candidates for a use in area-selective materials by ALD were ZnO, HfO$_2$, ZrO$_2$ and one of the two TiO$_2$ and Al$_2$O$_3$ processes. We also found, that in such cases where only a limited area-selectivity of the NIL resist toward the ALD process is observed, nanopatterns can also be effectively fabricated (Fig. 2).

Figure 2. AFM topographical image of ZnO ring-patterns made by a combination of imprinted cavities applying the organic photo-curable mr-NIL210 resist, area-selective ALD and subsequent oxygen plasma treatment to remove the NIL resist.

The research has received funding from the EU FP7 project QUANTIHEAT (604668).

TIN DIOXIDE NANOTUBE ARRAYS IN ALUMINA MEMBRANES FOR EFFICIENT GAS-SENSING

O. Yurkevich\textsuperscript{1}, K. Maksimova\textsuperscript{1}, A. Goikhman\textsuperscript{1}, A. Chuvilin\textsuperscript{2,3}, M. Knez\textsuperscript{2,3}

\textsuperscript{1}Immanuel Kant Baltic Federal University, Nevskogo 14, Kaliningrad, 236041, Russia
\textsuperscript{2}CIC nanoGUNE, Tolosa Hiribidea 76, Donostia-San Sebastián E-20018, Spain
\textsuperscript{3}IKERBASQUE, Basque Foundation for Science, Maria Diaz de Haro 3, Bilbao E-48013, Spain

Tin dioxide has been the material-of-choice for gas sensor industry in the past decades for its n-type semiconducting properties and the wide band gap ($E_g=3.6$ eV, at 300K). Over that time various configurations of sensors have been developed aiming at increasing their surface area, thus enhancing the response upon gas adsorption. Anodic alumina oxide (AAO) membranes can be used as tunable templates with a high surface area, suitable for functionalization with SnO\textsubscript{2}. As the optimal sensitivity of a sensor is achieved when thickness of the active material is in the range of the Debye length, only $\sim 3$ nm of tin dioxide are needed for the formation of an effective sensor \cite{Xu1991}. Since conformal deposition in high aspect ratio structures as well as thickness control in the nanometer range is challenging for most deposition methods, we opted for atomic layer deposition (ALD). In contrast to SnO\textsubscript{2} electrodeposited in AAO \cite{Kolmakov2003}, structures obtained by ALD can be used for sensing without removal of the supporting substrate, simplifying the fabrication process.

![Scanning electron microscopy (SEM) images of SnO\textsubscript{2} deposited in an AAO membrane: a) 45 degree cut b) top view](image)

Figure 1. Scanning electron microscopy (SEM) images of SnO\textsubscript{2} deposited in an AAO membrane: a) 45 degree cut b) top view

This initial study opts for optimizing the SnO\textsubscript{2} process for a later development of gas sensors. For conformal deposition of SnO\textsubscript{2} throughout the whole pore length with an initial aspect ratio of 1:500, an exposure step was added subsequent to precursor dosing. Taking into account that the aspect ratio of the pores increases with the thickness of the deposit, the exposure times were dynamically varied to ensure best possible conformality. The uniformity of the coatings was proven with high resolution SEM (Fig.1). The lateral face of the membrane was cut by a focused ion beam at 45 degree angle and the resulting images show a deposition throughout the whole pore length (Fig.1a). Furthermore, 3D tomography data of the tin dioxide arrays were recorded, which helps to study the evolution of the pore diameter along the pore depth.

PULSE MOCVD FILMS DEPOSITION IN MCP CHANNELS. SECONDARY ELECTRON EMISSION CHARACTERISTICS OF MULTICOMPONENT STRUCTURES

S.V. Zabuslayev\textsuperscript{1}, Yu.V. Shevtsov\textsuperscript{2}, B.M. Kuchumov\textsuperscript{2}, S.A. Kesaev\textsuperscript{1}, S.V. Trubin\textsuperscript{2}, Yu.V. Shubin\textsuperscript{2}, E.S. Vikulova\textsuperscript{2}, I.K. Igumenov\textsuperscript{2}

\textsuperscript{1} JSC «Katod», 3, Padunskaya St., Novosibirsk, Russia
\textsuperscript{2} Nikolaev Institute of inorganic chemistry SB RAS, Novosibirsk, Russia

Studies are carried out concerning the modification of an internal channel surface of microchannel plates (MCPs) used as an electronic brightness amplifier in night vision devices. An inch-sized glass MCP thick of 300 $\mu$m in thickness has through channels of 6 $\mu$m in diameter being a three-dimensional object with an aspect ratio of 50. As the emitting layer, magnesia (MgO) thin films being a rather efficient secondary emitter to provide an increase in the MCP common gain have been chosen. Ruthenium oxide (RuO\textsubscript{2}) films provide a resistive conduction in the near-surface layer of the channels necessary for the charge drain. Hafnium oxide (HfO\textsubscript{2}) films have been chosen as the barrier layer to hinder the ionic emission from the near-surface layer of the channels.

The deposition of oxide layers was carried out using a vacuum pulsed MOCVD technique (chemical vapor deposition from an organometallic precursor) with a discrete dosing of reagents with no use of carrier gas (DP MOCVD). The experiments were performed using an original Pulse MOCVD unit equipped with "hot" vacuum valves with a pneumatic control. This unit can operate in an ALD mode with the use of precursors that exhibit chemisorption relative to substrate materials.

In this work, the following deposition mode was used: introducing a portion of the precursor vapor into the evacuated and isolated reaction chamber, mixing it with a known amount of reactant gas, and exposing for a sufficiently long time (about 30 seconds). At the end of the single cycle of layer deposition, the reaction chamber has been pumped out. The process was cyclic, and the number of deposition cycles varied from 25 to 200. The substrate temperature and the precursor exposure time in the reaction chamber were chosen basing on mass spectrometric studies on the in-situ precursor decomposition. The thickness of the film grown per one deposition cycle ranged from 1 to 20 Å. Hf(thd)\textsubscript{4}, Ru(acac)\textsubscript{3} and Mg(thd)\textsubscript{2} were used as precursors.

In order to study deposition processes in three-dimensional systems with a high aspect ratio, a slot structure has been developed that allows one to study film deposition processes of films in systems with an aspect ratio from 5 to 500. This technique provides studying on film formation in the systems with different geometric dimensions and aspect ratios, for different substrate materials.

Nanodimensional multicomponent MgO/RuO\textsubscript{2}/HfO\textsubscript{2} films on the internal surfaces of MCP channels, as well as mono- and multicomponent films on the satellites (Si substrates) have been obtained. The mono- and multilayered MgO/RuO\textsubscript{2}/HfO\textsubscript{2} oxide coatings on the silicon substrate were characterized using the methods of X-ray diffractometry and scanning electron microscopy. Secondary electron emission coefficients of the obtained mono- and multicomponent layers on Si substrates were measured. The componential distribution in the composite coatings over the depth of MCP channels was analyzed using an EDS technique.

Experimental samples with the modified surface of the channels being in the structure of an electron-optical converter showed an increase in the MCP amplification coefficient by an order of magnitude.

The work was supported by the the RAS Presidium Program No.1.31.2.6.15
FERROELECTRIC PROPERTIES OF ALD-GROWN La:HfO$_2$ THIN FILMS

M.G. Kozodaev, A.G. Chernikova, A.M. Markeev

Moscow Institute of Physics and Technology, 141700, Dolgoprudny, Moscow region, Russia
(kzdmaks@gmail.com)

The recent discovery of ferroelectric effect in thin HfO$_2$-based films revealed their prospects of various applications. It’s considered, that the observed ferroelectric effect may be explained by the stabilization of non-centrosymmetric polar o-phase ($Pbc2_1$), which presence was predicted theoretically [1] and confirmed experimentally [2]. Such phenomenon aroused much interest to its implementation into ferroelectric memory due to HfO$_2$ CMOS compatibility and possible scaling potential. It was reported earlier that many different dopants can stabilize ferroelectric phase in hafnium oxide [3], but precise doping control was highly desired. Thereby, ALD seems to be the most effective way for this task due to its excellent thickness and composition control. Moreover, ALD can be successfully utilized not only for FE layer formation but also for electrodes, especially TiN, proved to be well-suitable for such FE materials [4]. Unfortunately, ferroelectric properties of the proposed films are not completely stable due to the so-called wake-up and fatigue effects, characterized by remnant polarization change, which is a major concern on the way of further memory production. Hence, our approach was a La$^{3+}$ dopant utilization, which allowed to overcome fatigue problem up to $5 \times 10^8$ switching cycles [5]. Unfortunately, optimal La concentration was not found and relatively high annealing temperature (650°C) was required for best ferroelectric properties achievement. Therefore, the main purpose of this work was to investigate ferroelectric properties of La-doped (~1 mol. %) HfO$_2$ films, annealed at different temperatures (400-650°C). The detailed structural and electrical investigations of such films were carried out. As a result rather promising ferroelectric response (remnant polarization up to 30 $\mu$C/cm$^2$) and long endurance (up to $10^{10}$ switching cycles) were obtained after annealing of MFM structures at relatively low temperatures.

AUTHOR'S INDEX

Abdulagatov A.I. 32, 33, 34  Filatova E.A. 22, 46
Abdulagatov I.M. 32, 34  Fomengia G.N. 22
Ablat H. 22  
Afonin M.Yu. 51  Ghidini G. 63
Akkuleva K.T. 60  Goikhman A. 67
Alexandrov S.E. 15  Gordon P.G. 17
Amashaev R.R. 34  Gornev E.S. 50
Antipov V.V. 60  Grigoras K. 65
Ashurbekova Ka.N. 32, 34  Guay J.-M. 17
Ashurbekova Kr.N. 32, 34  Gunn R. 52
Baraban A.P. 42  Gutshin O.P. 50
Barry S.T. 17  Gvozdev V.A. 50
Baxter J. 17  
Belorukova T.S. 36  Hämäläinen J. 25
Berini P. 17  Hatanpää T. 25
Bodalyov I.S. 30  Hausmann D. 46
Buymistriuk G.Ya. 60  
Bykov V.A. 18  Igumenov I.K. 59, 68

Cal'a Lesina A. 17  Kalinin A. 18
Chernikova A.G. 26, 38, 69  Kalinin N.A. 48
Chernov A.S. 54  Kalliomäki J. 63
Chernyakova N.V. 36  Kesaev S.A. 35, 68
Chislov M.V. 36  Kessels W.M.M. 23
Chuvinil A. 67  Knez M. 24, 67

Dergachyov V.F. 41  Knoops H. 52
Dmitriev V.A. 42  Koryagina A.O. 56
Drozd A.V. 35  Koshtyal Y.M. 48
Drozd V.E. 35, 42  Kozodaev M.G. 26, 38, 69
Drozdov E.O. 44  Krasilin A.A. 30
Dubrovensky S.D. 21, 44  Kruchinin V.N. 51

Efimov N.Yu. 39  Kuchumov B.M. 59, 68
Egorov K.V. 26  Kurapova O.Yu. 49
Ek S. 63, 65  Kurek A. 52
Elliott S.D. 22, 46  Kuzmichev D.S. 26
Ermilova M.M. 56  
Ezhovskii Yu.K. 45  Lamperti A. 63

Lebedev M.S. 51
Leskelä M. 25
<table>
<thead>
<tr>
<th>Name</th>
<th>Pages</th>
<th>Name</th>
<th>Pages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macco B.</td>
<td>23</td>
<td>Ritasalo R.</td>
<td>63, 65</td>
</tr>
<tr>
<td>Mäkelä M.</td>
<td>25</td>
<td>Rogozhin A.E.</td>
<td>50</td>
</tr>
<tr>
<td>Maksimova K.</td>
<td>67</td>
<td>Rudenko K.V.</td>
<td>50</td>
</tr>
<tr>
<td>Malkov A.A.</td>
<td>30, 36, 41, 54</td>
<td>Rumyantsev A.M.</td>
<td>48, 64</td>
</tr>
<tr>
<td>Malygin A.A.</td>
<td>12, 30, 36, 41, 54, 56</td>
<td>Rychkov A.A.</td>
<td>39</td>
</tr>
<tr>
<td>Markeev A.M.</td>
<td>26, 38, 69</td>
<td>Sarnet T.</td>
<td>63</td>
</tr>
<tr>
<td>Maslennikova T.P.</td>
<td>30</td>
<td>Schroeder U.</td>
<td>29</td>
</tr>
<tr>
<td>Mattinen M.</td>
<td>25</td>
<td>Selivanov A.A.</td>
<td>42</td>
</tr>
<tr>
<td>Maximov M.Yu.</td>
<td>48, 64</td>
<td>Shelaev A.</td>
<td>18</td>
</tr>
<tr>
<td>Messerschmidt M.</td>
<td>65</td>
<td>Shevtsov Yu.V.</td>
<td>59, 68</td>
</tr>
<tr>
<td>Miakonkikh A.V.</td>
<td>50</td>
<td>Shubin Yu.V.</td>
<td>68</td>
</tr>
<tr>
<td>Mikhailovskii S.V.</td>
<td>56</td>
<td>Silin A.O.</td>
<td>64</td>
</tr>
<tr>
<td>Miller Th.</td>
<td>52</td>
<td>Smirnov V.M.</td>
<td>49, 57, 58, 64</td>
</tr>
<tr>
<td>Mironov V.S.</td>
<td>57</td>
<td>Solokhin A.Yu.</td>
<td>58</td>
</tr>
<tr>
<td>Monteiro F.A.</td>
<td>17</td>
<td>Sosnov E.A.</td>
<td>61</td>
</tr>
<tr>
<td>Morozov P.E.</td>
<td>49</td>
<td>Spiga S.</td>
<td>63</td>
</tr>
<tr>
<td>Mykota D.I.</td>
<td>26</td>
<td>Thomas O.</td>
<td>52</td>
</tr>
<tr>
<td>Nazarov D.V.</td>
<td>58, 64</td>
<td>Trubin S.V.</td>
<td>51, 59, 68</td>
</tr>
<tr>
<td>Negrov D.V.</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Novikov P.A.</td>
<td>64</td>
<td>Vangelista S.</td>
<td>63</td>
</tr>
<tr>
<td>O’Mahony A.</td>
<td>52</td>
<td>Vasilyev V.Yu.</td>
<td>62</td>
</tr>
<tr>
<td>Obletsova A.A.</td>
<td>56</td>
<td>Väyrynen K.</td>
<td>25</td>
</tr>
<tr>
<td>Orekhova N.V.</td>
<td>56</td>
<td>Veselov A.</td>
<td>63, 65</td>
</tr>
<tr>
<td>Østreng E.</td>
<td>63, 65</td>
<td>Vikulova E.S.</td>
<td>59, 68</td>
</tr>
<tr>
<td>Parsons G.N.</td>
<td>28</td>
<td>Week W.</td>
<td>17</td>
</tr>
<tr>
<td>Petrov S.N.</td>
<td>54</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Piagge R.</td>
<td>63</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polysakov V.</td>
<td>18</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Popovich A.A.</td>
<td>64</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Prunnila M.</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rabadanov M.Kh.</td>
<td>32, 34</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ramunno L.</td>
<td>17</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ritala M.</td>
<td>25</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CONTENT

Organizing Committee 4
Valentin B. Aleskovskii 5

Sponsors
Picosun Oy 9
Eurointech Ltd. 10
Chemical Assembly of Nanomaterials, Ltd. 11

Plenary Lectures

Perspectives of fundamental and applied researches in Russia, with using of the method of Molecular Layering
Malygin A.A. 12

Plasma source of atomic nitrogen for activated ALD
Alexandrov S.E. 15

“Pinning” coinage metal nanostructures to preserve plasmonic effects: new colours for gold and silver

Modern possibilities of Scanning Probe Microscopy and Spectroscopy for investigation of physical properties and spectral features of surface structures
Bykov V.A., Kalinin A., Polyakov V., Shelaev A. 18

Quantum chemistry as a technological tool for ALD development
Dubrovensky S.D. 21

Quantum chemical modelling of the mechanism of Atomic Layer Deposition: new insights and future challenges
Elliott S.D., Filatova E.A., Fomengia G.N., Ablat H. 22

ALD of transparent conductive oxides
Macco B., Kessels W.M.M. 23

Hybrid materials by ALD-derived methods: opportunities for novel material design
Knez M. 24

Recent advances in Atomic Layer Deposition
Leskelä M., Hatanpää T., Hämäläinen J., Mattinen M., Mäkelä M., Väyrynen K., Ritala M. 25

Atomic Layer Deposition of dielectrics for resistive switching and ferroelectric memory applications

Area-selective Atomic Layer Deposition of metals and dielectrics
Parsons G.N. 28

Increasing interest in ALD HfO₂ and ZrO₂ based semiconductor devices: from DRAM capacitor to negative capacitance devices
Schroeder U. 29
Oral Reports

Surface and topochemical reactions in the Atomic Layer Deposition of Titanium Dioxide on a substrate containing structural hydroxyl groups
Bodalyov I.S., Malkov A.A., Maslennikova T.P., Krasilin A.A., Malygin A.A.

Molecular Layer Deposition of vanadium-titanium alloy hybrid organic-inorganic thin films and their post-processing
Ashurbekova Ka.N., Ashurbekova Kr.N., Abdulagatov I.M., Rabadanov M.Kh., Abdulagatov A.I.

Atomic Layer Deposition of Titanium and Titanium-Aluminum Nitrides using Titanium Tetrachloride, Hydrazine and Trimethylaluminum
Abdulagatov A.I.

Molecular Layer Deposition of aluminum-titanium alloy hybrid organic-inorganic thin films

Improvement of the MCP technology by the use of ALD films
Drozd A.V., Drozd V.E., Kesaev S.A., Yafyasov A.M.

The effect of temperature on the Molecular Layering synthesis and on structural-chemical transformations of "Core (Aluminum Oxide) – Shell (Phosphorus Oxide)" composition
Chernyakova N.V., Malkov A.A., Zakharova N.V., Belorukova T.S., Malygin A.A., Chislov M.V.

Long-endurance ferroelectricity in multicomponent Hafnium Oxide-based ALD grown thin films
Chernikova A.G., Kozodaev M.G., Negrov D.V., Markeev A.M.

Oxide structures synthesized by the method of Molecular Layering on the surface of polymeric films and their influence on the electret properties of obtained composites
Efimov N.Yu., Malygin A.A., Rychkov A.A.

Installation for Molecular Layering with a pulsating action of a gaseous medium on a layer of disperse material
Dergachyov V.F., Malkov A.A., Malygin A.A.

Cathodoluminescence spectroscopy of Si-TiO₂ and Si-SiO₂-TiO₂ structures
Baraban A.P., Dmitriev V.A., Drozd V.E., Selivanov A.A.

Synthesis of two-component phosphorus-titanium-containing coatings on Silica surface by Molecular Layering method
Drozdov E.O., Dubrovensky S.D.

Synthesis of nanolayers of Chromium Oxide on Gallium Arsenide and the characteristics of the interface
Ezhovskii Yu.K.

Ab initio modelling for understanding PECVD of Silicon Carbide and the routes towards ALD
Filatova E.A., Elliott S.D., Hausmann D.

Effect of Al₂O₃ and SnO₂ coatings synthesized by Atomic Layer Deposition on the positive electrode of Lithium-Ion cell containing Li₁₂Mn₀.₅₄Co₀.₁₃Ni₀.₁₃O₂
Koshtyal Y.M., Rumyantsev A.M., Maximov M.Yu., Kalinin N.A., Zhdanov V.V.
Chemical construction of iron-containing nanocomposite ferromagnetic materials by ML–ALD – the experimental justification
Zemtsova E.G., Kurapova O.Yu., Morozov P.E., Smirnov V.M. 49

Atomic Layer Deposition process for forming layers of a high-k metal gate stack with 32 nm topological size
Gvozdev V.A., Gutshin O.P., Gornev E.S., Rudenko K.V., Miakonkikh A.V., Rogozhin A.E. 50

Sc2O3 thin films: precursor synthesis, ALD-growth, chemical structure and optical properties
Lebedev M.S., Afonin M.Yu., Trubin S.V., Kruchinin V.N. 51

Recent developments in Atomic Layer Deposition: HfO2 process improvements, and RF substrate biasing for in-situ pre-treatment
O’Mahony A., Kurek A., Miller Th., Knoops H., Thomas O., Gunn R. 52

Regulation of the phase composition and distribution of titanoxide structures in the volume of a porous matrix in the process of Molecular Layering on γ-Al2O3
Malkov A.A., Chernov A.S., Petrov S.N., Malygin A.A. 54

High specific surface area catalytic systems containing transition metal (Ti, V, Mo, Nb) oxides prepared using ALD

Regulation of the roughness of a TiO2 nanolayer on a silicon substrate by the ALD method as a promising material for biosensors
Mironov V.S., Smirnov V.M. 57

Surface modification of the coarse and ultra-fine grained titanium by Chemical Etching and Atomic Layer Deposition to produce bioactive coatings
Nazarov D.V., Zemtsova E.G., Solokhin A.Yu., Smirnov V.M. 58

Discrete vacuum pulse MO CVD process: the features of film deposition in the systems with a high aspect ratio
Shevtsov Yu.V., Kuchumov B.M., Trubin S.V., Vikulova E.S., Igumenov I.K. 59

Applications of the Atomic Layer Deposition metod in photonic sensors manufacturing
Buymistriuk G.Ya. 60

Application of ALD for obtaining the sensibilitive layer of gas sensor
Akkuleva K.T., Antipov V.V., Zakharova N.V. 60

Atomic Force Microscopy possibilities for investigating the morphology of products of Atomic Layer Deposition
Sosnov E.A. 61

Comparative analysis of platinum group metals thin films ALD/CVD features
Vaslyyev V.Yu. 62

Surface morphology, crystallinity and electrical properties of some rare-earth oxide ALD films

Atomic Layer Deposition of Tin Oxide thin films using Tetraethyl Tin to produce high-performance electrodes for Li-Ion batteries
Evaluation of different nanoimprint resists for a use in area-selective Atomic Layer Deposition of selected materials
Ritasalo R., Ek S., Østreng E., Veselov A., Messerschmidt M., Grigoras K., Prunnila M. 65

Tin Dioxide nanotube arrays in Alumina membranes for efficient gas-sensing
Yurkevich O., Maksimova K., Goikhman A., Chuivilin A., Knez M. 67

Pulse MOCVD films deposition in MCP channels. Secondary electron emission characteristics of multicomponent structures

Ferroelectric properties of ALD-grown La:HfO₂ thin films
Kozodaev M.G., Chernikova A.G., Markeev A.M. 69

Author's Index 70