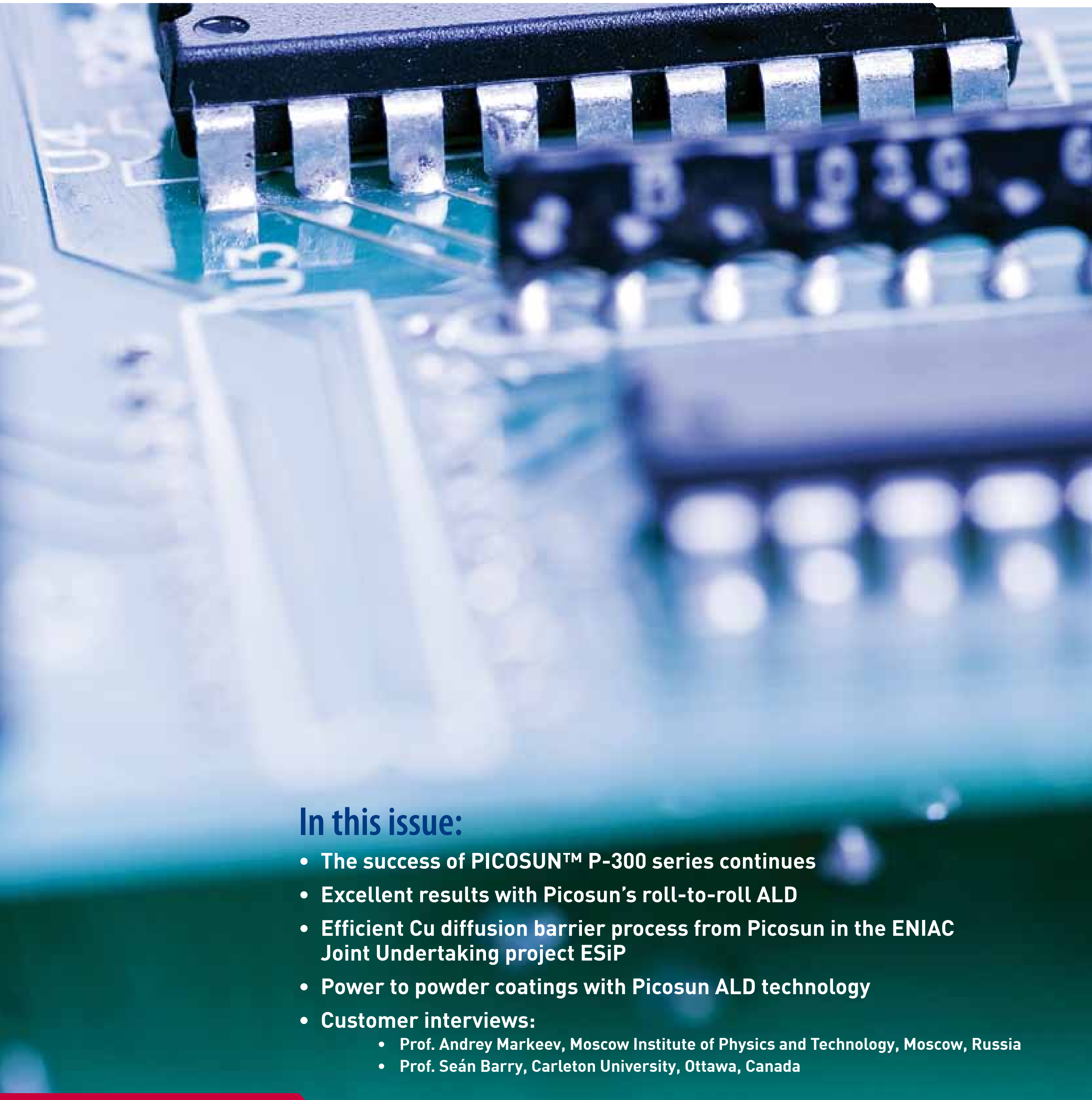
ALD - Defining the Future

Picosun News, Summer 2013



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The success of PICOSUN™ P-300 series continues

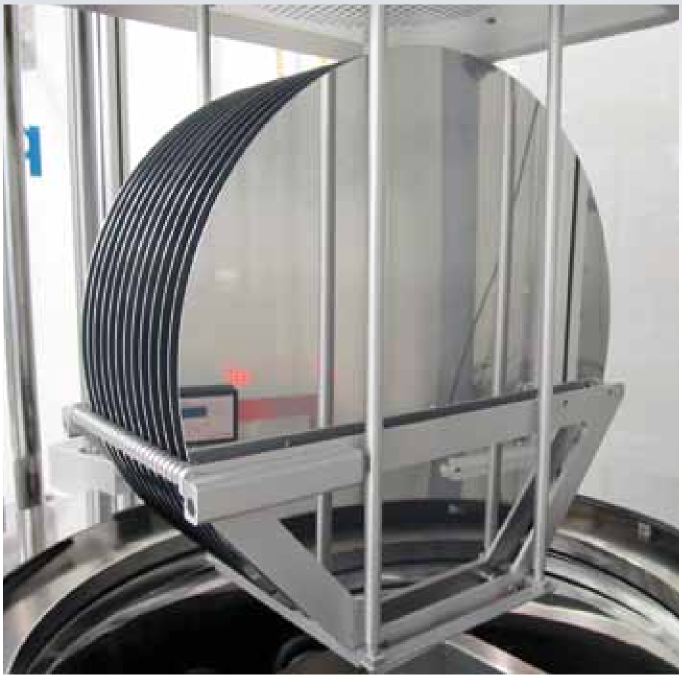
PICOSUN™ P-300 series has again proved its unparalleled process quality and efficiency with customers continuously ordering more P-300 units for production expansion. Recently, P-series ALD reactors were also combined with Picosun's high-end loading system, the Picoplatform™ ALD cluster tool.

The 300 mm cluster system, combining several P-300 ALD deposition units and an EFEM (Equipment Front End Module) with FOUP (Front Opening Unified Pod) stations will be delivered to a key customer in Asia for production of new memory devices.

The Picoplatform™ system has been on the market since 2008 and it has received lots of positive feedback from customers all around the world since its inception. The transition of this successful platform into the 300 mm era now signifies a remarkable step forward in Picosun's status as a leading provider of ALD technology for high volume manufacturing.

The Picoplatform™ 300 ALD cluster system is designed solely to fulfill the requirements of ALD. The control and automation software of the cluster unit has been optimized to guarantee the ultimate in simple, intuitive, and user-friendly operation and programming of the tool.
In addition to ALD reactors, other thin film deposition units, pre- or post-treatment equipment, or integrated substrate handling systems for complete cassette-to-cassette loading of wafers can be incorporated into the same cluster unit. Easy, cost-efficient and clean production is the key for realizing functional ALD solutions for next generation memory applications.

A 300 mm wafer coated in a P-300 single wafer reactor.



300 mm wafers coated in a
PICOSUN™ P-300 batch reactor.

The Picoplatform™ 300 ALD cluster unit comprises several individual PICOSUN™ P-300 reactors, a central vacuum wafer handling robot and an EFEM with FOUP stations.

Excellent results with Picosun's roll-to-roll ALD

ALD is the optimal technique for depositing thin inorganic coatings onto flexible materials such as plastic films, metal foils, and biomaterial sheets to enhance their barrier properties against moisture and gas penetration. These kind of ALD-treated films can be used as environmentally friendly, simple, and cost-efficient protection layers, for example on medical, food and cosmetic items and sensitive electronic components, or as ecological, fully degradable packaging materials. Recently, Picosun launched into market a roll-to-roll (R2R) ALD system in which these coatings can be realized on flexible, foil-type substrates in simple and efficient way using continuous ALD. In the R2R ALD process, a strip of the substrate material moves across the deposition zone from one reel to another in constant motion, which allows smooth ALD film formation even on long substrates with still relatively fast deposition speed.

The initial results of Picosun's R2R ALD have been very promising. Several polymer materials with poor original barrier properties, including cellophane, polylactic acid, and polyimide films, were coated both in a batch ALD chamber and in the R2R ALD chamber (which can be retrofitted into the batch chamber). The ALD film material tested was Al_2O_3, deposited from trimethyl aluminium (TMA) and water at the temperature of 100 °C. The barrier performance of the ALD films was characterized with water vapor and oxygen transmission rates (WVTR and OTR, respectively) at relative humidity of 50 % and temperature of 23 °C. The results are summarized in Table 1 below.

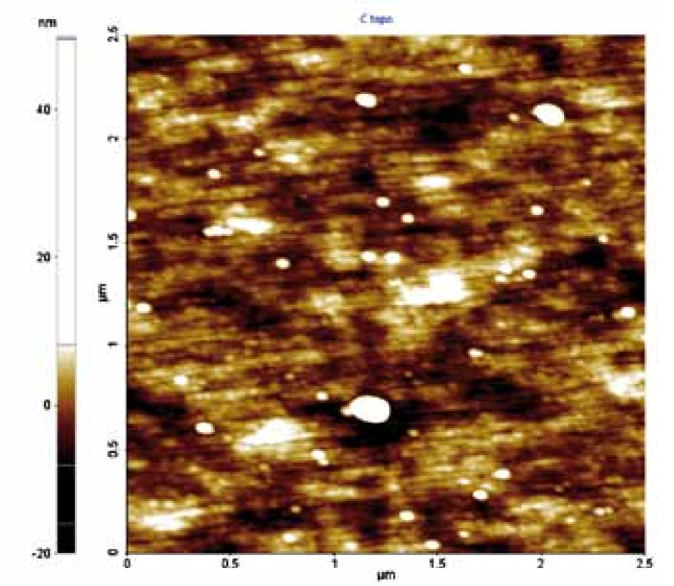
Table 1. The OTR and WVTR values of the polymer films coated with 500 cycles of Al_2O_3.

Substrate	**OTR**			**WVTR**		
	Plain polymer	**+ Al_2O_3 Batch**	**+ Al_2O_3 R2R**	**Plain polymer**	**+ Al_2O_3 Batch**	**+ Al_2O_3 R2R**
Cellophane	4.0 ± 0.1	2.6 ± 2.3	0.3 ± 0.2	144 ± 19	29 ± 16	15 ± 9
Polylactic acid	470 ± 1	0.4 ± 0.1	**47 ± 6	39 ± 5	*< 0.2 ± 0.1	**10 ± 1
Polyimide	30 ± 0.1	*< 0.01 ± 0.01	**2.2 ± 1.9	3 ± 1	*< 0.1 ± 0.1	**2 ± 1

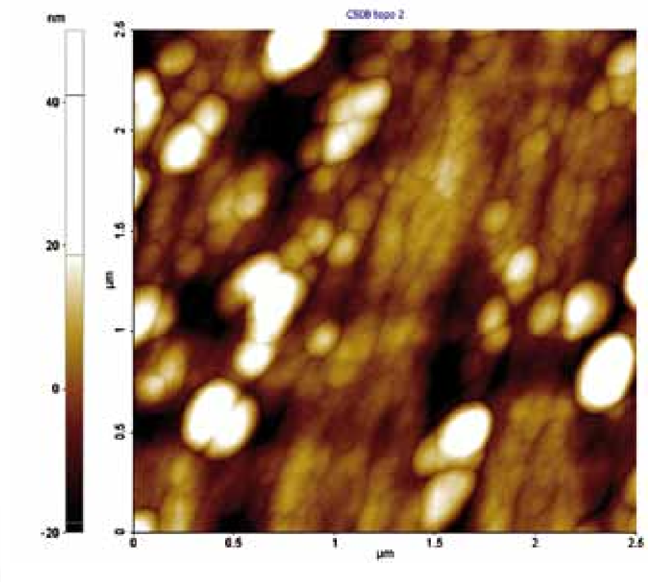
* Result was under the detection limit; **Small sample size impaired somewhat the result

The results show how both WVTR and OTR values of coated samples were 100-1000 times lower compared to uncoated sample values, and with several polymer materials even lower than the measurement equipment's detection limit. The results of the R2R-coated samples were comparable to the batch-processed samples, proving how Picosun's state-of-the-art equipment design yields top quality results no matter the deposition geometry. The R2R ALD system is currently being upscaled to high volume manufacturing which will enable Picosun's breakthrough into new, strategically important market areas.

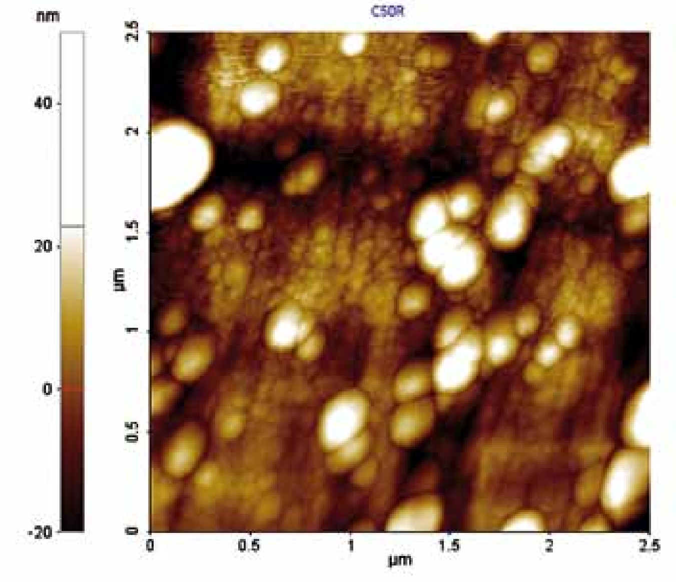
Example of metal foil coated with R2R ALD Al_2O_3 film. Uncoated metal foil as a reference under the coated piece.



Atomic Force Microscopy (AFM) graph of a plain cellophane film. The different colors represent the surface topology (areas of different height).



AFM graph of a cellophane film coated with 500 cycles of Al_2O_3 in the batch process.



AFM graph of a cellophane film coated with 500 cycles of Al_2O_3 in the R2R process. Note the similarity of the surface structure compared to the batch-coated sample.

Efficient Cu diffusion barrier process from Picosun in the ENIAC Joint Undertaking project ESiP

The project ESiP (Efficient Silicon Multi-Chip System-in-Package Integration – Reliability, Failure Analysis and Test) where Picosun was funded by the ENIAC Joint Undertaking* and the public authorities of Finland (Tekes – the Finnish Funding Agency for Technology and Innovation) ended in June 2013. This project, which started in May 2010, was the largest one Picosun has ever participated in. The project had 41 partners, bringing together the top expertise and biggest players in micro- and nanoelectronics from nine EU countries.

In ESiP, Picosun worked in close collaboration with several partners, especially VTT Technical Research Centre of Finland, developing processes for copper diffusion barriers for Through-Silicon-Via (TSV) structures. Several different barrier materials were investigated in the course of the project, e.g. tantalum oxide (Ta_2O_5), titanium nitride (TiN), titanium-aluminium carbonitride (TiAlCN), ruthenium (Ru), and tantalum nitride (TaN). Based on the studies made at VTT, TaN proved to be the best option for diffusion barrier application. With the results of the ESiP project Picosun's leading quality Atomic Layer Deposition (ALD) reactor design ensures that the TaN process can now run safely and be introduced to industrial manufacturing. The TaN films deposited in the PICOSUN™ ALD tool showed high uniformity and conformality. The process is also cost-efficient because of the low price of the precursors.

The goal of the project ESiP, which was managed by Infineon Technologies, was to strengthen Europe's competitiveness on the global micro- and nanoelectronics market and add value to its industrial activities in the field. Like in several other branches of industry, as well as in micro- and nanoelectronics, much of the mass manufacturing of end products has moved out of Europe to the Far East. However, Europe can remain a stronghold of innovation, intellectual property, and deployment of new technologies through tight cooperation between leading research institutes and companies and strong financial investments into cutting-edge R&D.

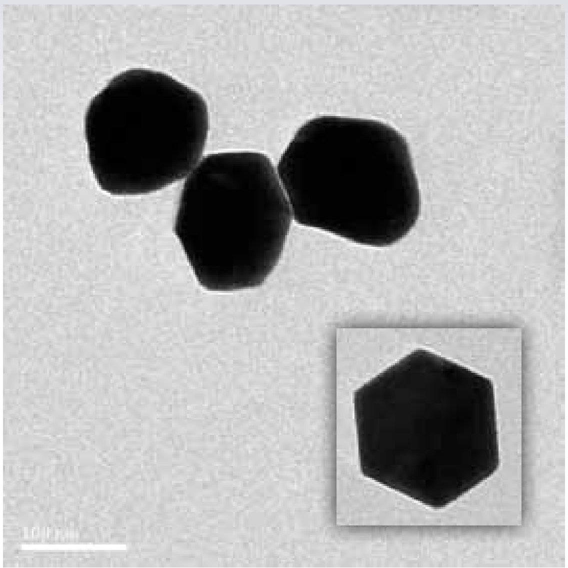
One of the technological solutions to Europe's challenges can be found from the "More than Moore" approach. This approach pushes innovation not only by the scale-down of the individual electronic component size ("More Moore"), but also by developing novel solutions for high density silicon multi-chip packaging, package stacking methods, and failure and reliability testing of the new devices – the core target of the project ESiP. In addition, System-in-Package (SiP) technology, which includes the combination of More than Moore with More Moore devices, allows realization of highly sophisticated, highly integrated, and highly miniaturized multifunctional micro- and nanoelectronic devices that require only a fraction of the physical space required by the methods of the earlier generation. Application areas for these novel devices can be found e.g. from the sensor, communication, automotive and healthcare industries.

Novel technological solutions naturally require completely new manufacturing methods and materials. When the device details can be as small as only a few nanometers, ALD is often the only method with which material layers of high enough conformality and uniformity can be deposited. In the stacking of the SiP devices, the overlapping layers often need to be connected, a requirement which is realized with TSV structures having interiors that are coated with conducting materials such as copper. Diffusion barrier layers are needed to prevent copper diffusion into underlying semiconductor materials, which could render the whole component or device nonfunctional. With TaN as the barrier material, Picosun has made a large step forward.

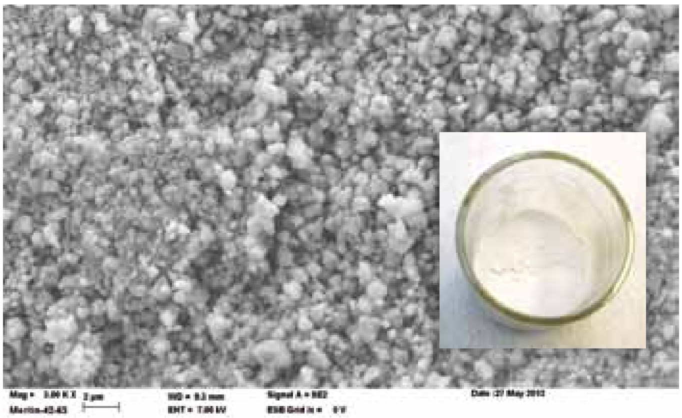
*The ENIAC Joint Undertaking (JU) is a European, public-private partnership focusing on nanoelectronics that brings together ENIAC Member/Associated States, the European Commission, and AENEAS (an association representing European R&D actors in this field). http://www.eniac.eu/web/index.php

Power to powder coatings with Picosun ALD technology

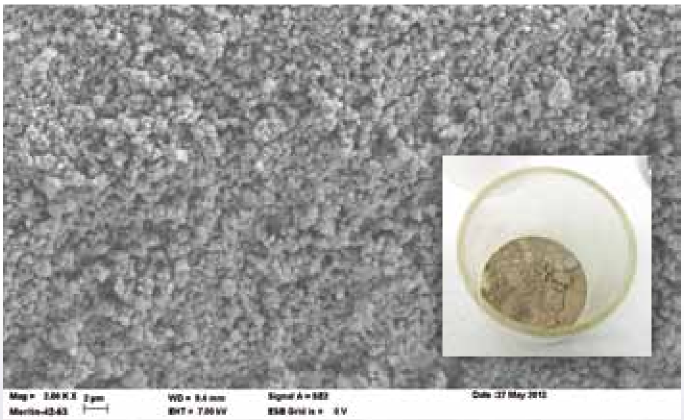
Powder and particle coatings are one of the most often requested ALD applications today. Powder materials are used everywhere in today's industry – as catalysts for chemistry and biochemistry, solid state batteries, pigments, additives, (e.g. for rubber, paper, plastic, cardboard, and food), and medical and cosmetic substances being just a few examples. ALD technology allows exact and controlled modification and tailoring of the particle surface, enabling fine-tuning of the particles' physical, chemical, electrical, or optical properties. Especially in the catalyst industry ALD offers almost unlimited possibilities to manufacture next generation materials by surface modification of the carrier particles – a method which is also much more environmentally friendly than many of the traditional techniques. Materials based on carbon nanostructures can also be effectively modified with ALD. This opens up a completely new field of a plethora of applications in e.g. tomorrow's electronics, energy storage and production.



Closer look at the coating uniformity and conformality: SEM-micrographs of 1 nm of Al_2O_3 on 100 nm diameter metal particles, deposited in a PICOSUN™ R-series ALD reactor.



SEM-micrographs of highly uniform coating of 30 nm of Al_2O_3 on TiO_2 powder, deposited in a PICOSUN™ R-series ALD reactor. Uncoated sample above, coated sample below.



Picosun is the frontrunner of this increasingly important area of ALD technology as well. Our powder coating cartridge "POCA" has already been a success for several years, and has recently been joined by two new products: a fluidized bed ALD reaction chamber and a vibrating mechanism that can be retrofitted to existing reactors to keep the coated particles in intermittent movement between the precursor pulses to ensure even more uniform and conformal formation of the ALD film. In the fluidized bed design, on the other hand, the flowing gas keeps the coated powder in constant motion to realize always optimal distribution of precursor gases in the chamber.

Currently, Picosun's powder coating ALD systems are being upscaled to high throughput industrial scale in P-series reactors.

Customer interview: Dr. Andrey M. Markeev,

Leading Research Scientist, General Chemistry Department, Moscow Institute of Physics and Technology, Moscow, Russia

Andrey M. Markeev graduated from Moscow Engineering Physics Institute (MEPhI) in 1985. In 1992 he received a Ph.D. degree at MEPhI. In 1992-2007 he worked as a senior researcher in Zelenograd Research Institute of Physical Problems. In 2007 he entered the ALD group of Moscow Institute of Physics and Technology.

Dr. Markeev's main scientific interests are atomic layer deposition of the mixed transition metal oxides, investigation of the chemical and electronic structure of thin films by *in vacuo* XPS and REELS, crystallinity characterization of ALD films by grazing incidence XRD, development of the memory devices on the alternative principles (Valency Change Resistive Switching, FeRAM), and bioactive implantable devices. Dr. Markeev is the author of more than 40 papers.

Dr. Markeev, what are the focus points and goals of your current work in your institution?

My scientific activity at Moscow Institute of Physics and Technology (MIPT) is centered on thin film deposition and characterization aimed mainly on the development of the novel functional layers for nano- and microelectronics

How did you get interested in Atomic Layer Deposition (ALD)?

In 2007 I came to MIPT and started working in the ALD group founded by Prof. A. P. Alekhin. In the 1960's, Prof. Alekhin was a Ph. D. student and worked under guidance of Prof. V. B. Aleskovskii who independently developed molecular layering (ML) methods in the same decade.

What would you see as the key advantages of ALD compared to other thin film deposition methods?

The experimental activity of the MIPT's ALD group is now mainly concentrated on the growth of multinary mixed oxide films. Largely this choice is conditioned by the possibility of ALD to grow mixed (alloyed) oxide films with very high controllability and reproducibility. So, ALD is a very convenient technique to combine the desirable properties of two or even more different oxides while eliminating the undesirable properties of each individual material.

How did you learn about Picosun?

We're in contact with many Finnish scientists – well known experts in ALD, and they mentioned Picosun as one of the leading ALD equipment manufacturers.

What made you select the PICOSUN™ ALD system?

At MIPT we are also interested in *in situ (in vacuo)* XPS-analysis of ALD-grown thin films. This is why the compatibility of PICOSUN™ ALD tool with UHV analytical equipment is very important for us. The MIPT experimental set-up combining PICOSUN™ R-100 reactor with the XPS spectrometer (Thermo Fisher Scientific) is presented in Figs. 1 and 2.

What are the benefits of PICOSUN™ products compared to other manufacturers' products?

Due to the vertical-type reactor, ALD tools from Picosun are very compact and occupy small footprint – even for the 300 mm wafer reactors.

For what kind of purposes is the PICOSUN™ ALD system used in your institution?

Recently the MIPT ALD group has developed an MIM-structure with ALD grown $Hf_xAl_{1-x}O$ with a graded Al depth profile using a PICOSUN™ ALD system. As a result, a multilevel resistive switching effect was demonstrated. The multiple states between LRS and HRS functionally emulating the biological synapse make the graded $Hf_xAl_{1-x}O_y$ oxide a promising candidate for electronic synapse device implementation.

See Fig.3 (Graphical Abstract from A. Markeev *et. al.*, Microelectron. Eng. (2013), http://dx.doi.org/10.1016/j.mee.2013.03.084).

What do you regard as being the most positive aspects of PICOSUN™ ALD systems?

The PICOSUN™ ALD system is a dual chamber hot wall reactor. As a result undesirable precursor condensation

Fig. 1

Fig. 2

is prevented in the vacuum chamber and long between maintenance periods are reached.

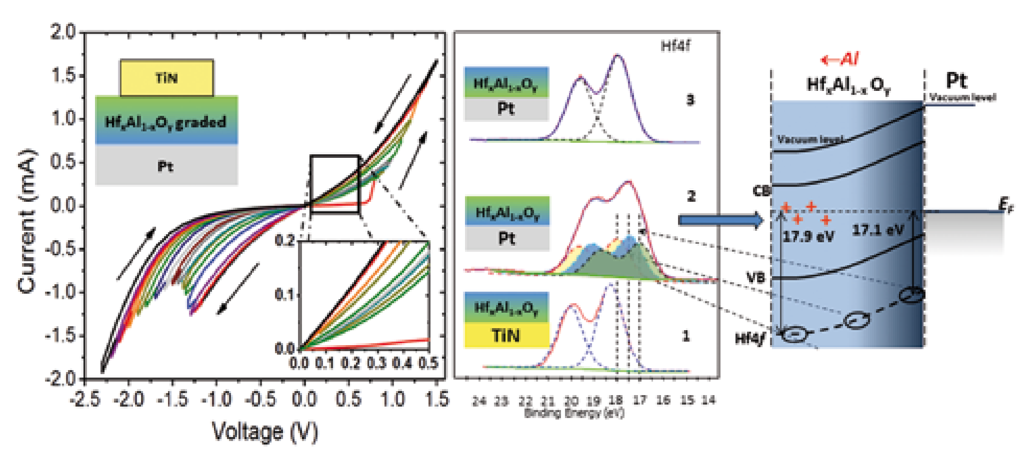
What kind of impression have you gotten about our company, products, and services in general?

In general, I have gotten a very positive impression of Picosun, especially from the rapid service and the company help in upgrading the PICOSUN™ tools even for non-standard tasks.

To whom would you recommend PICOSUN™ ALD systems?

I would like to recommend PICOSUN™ ALD systems to scientists and manufacturers interested in very uniform and reproducible thin film deposition, especially for multicomponent (alloyed) films on various types of substrates including porous, powder, and other 3-D samples.

Fig. 3



Customer interview: Prof. Seán Barry,

Department of Chemistry, Carleton University, Ottawa, Canada

Seán Barry is an Associate Professor at Carleton University, Ottawa, Canada, where he works on precursor compounds for atomic layer deposition (ALD). He was trained in inorganic synthetic chemistry by Darrin Richeson (Ph.D., University of Ottawa, 1996), and spent three years working on chemical vapour deposition (CVD) and ALD precursors in the group of Roy Gordon (post-doctoral fellow, Harvard University, 1998 – 2000, 2002 -2003). He was instrumental in the design and synthesis of the well-known copper amidinate dimers that are presently used for copper CVD/ALD.

Prof. Barry started in Carleton University in 2003 working on guanidinates of the group 13 metals (Al, Ga, In), and has recently studied guanidinates, iminopyrrolidinates and carbenes of the coinage metals (Cu, Ag, Au) for the purpose of depositing thin films of these metals. His group works mainly on the mechanisms of thermal decomposition and thin film deposition, and has invented several novel characterization methods to better understand these mechanisms.

Prof. Barry is the Founder and Senior Scientific Advisor for Precision Molecular Design, a start-up company with GreenCentre Canada to commercialize precursors for atomic layer deposition. He has also recently received a $1.9M Leader's Opportunity Fund award from the Canadian Foundation for Innovation to open a nanofabrication facility to explore nanoscience, surfaces, and sensor interfaces (FANSSI).

Prof. Barry, what are the focus points and goals of your current work in your institution?

The focus of our research is the development of novel ALD precursors. We have worked extensively on copper, and presently one of our main goals is a rugged and volatile gold-containing precursor that can be used for ALD, either with plasma, ozone, or (best of all) thermally with a standard reducing agent.

We have focused on anionic amide, amidinate, guanidinate, and iminopyrrolidinate ligands, as well as N-heterocyclic carbenes as coordination ligands. We would love to expand this ligand family to other metal centres to develop new precursors.

How did you get interested in Atomic Layer Deposition (ALD)?

I started making group 13 (Al, Ga, In) compounds in my Ph.D., mainly to further study the bonding and oligomerization of amide compounds of these metal centres. This led to employing some compounds for CVD of III-V semiconductor films. When I started a post-doc with Roy Gordon, he transitioned from CVD to ALD, and I followed him. I was instrumental in the development of the first copper amidinate precursors, and haven't strayed very far from that since.

What would you see as the key advantages of ALD compared to other thin film deposition methods?

Of course ALD is better at very thin films over very complex geometries, but I think that another (possibly underused) benefit of ALD is for the growth of nanoparticles. Since many metals undergo "island" growth before a continuous film is formed, the slow and careful growth permitted by ALD can allow control over nanoparticle size at the substrate surface.

How did you learn about Picosun?

I found out about Picosun at the ALD conference in Helsinki in 2004, and have been in contact with them ever since.

What made you select the PICOSUN™ ALD system?

I have used several commercial thermal and plasma ALD systems, and PICOSUN™ compares very favourably with any of them. I have found PICOSUN™ tools to be rugged, and not requiring very much maintenance. I also find the Picosun employees very easy to get along with, as well as being very good ALD scientists. I am always confident of the support I will get from Picosun.

What are the benefits of PICOSUN™ products compared to other manufacturers' products?

I find the range of bubblers, and the design of the precursor lines into the reactor excellent in the Picosun tools. Because we work on precursor design, we are often testing precursors with low or intermediate vapour pressure. This can mean we have quite different needs in the precursor delivery technology than some users. Having a range of solutions (like Picosun does) means we can work more easily to develop our chemistry.

For what kind of purposes will the PICOSUN™ ALD system be used in your institution?

Because we develop precursors, our main use for the ALD system we are buying will be to test these (sometimes low volatility) precursors for basic ALD processes.

What do you regard as being the most positive aspects of PICOSUN™ ALD systems?

I think we will find ourselves changing bubblers frequently to help get appropriate precursor vapour pressures, and I like the layout of the R-series tool for this purpose.

What kind of impression have you gotten about our company, products, and services in general?

I have known Picosun for about eight years, and I have always been impressed with this company. They have a real enthusiasm and commitment to ALD, and the staff is open and friendly and easy-going. I find their products hold up well in daily use and are relatively easy to maintain.

To whom would you recommend PICOSUN™ ALD systems?

I would recommend the R-series tool to any researcher in the field of ALD. It is a tool that is simple enough to be a "turn-key" solution, but sophisticated enough for very serious precursor and process development.

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