ORAMA news

Sep 2014

Highlights
of the ORAMA project

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Dear reader,

in the last and final edition of our Newsletter we would like to highlight the project results primarily in form of three prototypes that were developed collaboratively in order to tangibly demonstrate how the newly developed materials can be implemented in different industrial fields and products. These were:

1. Steering wheel application with displays and reconfigurable icons
2. Multifunctional glazing
3. p-type gas sensors

ORAMA ("Oxide Materials Towards a Matured Post-silicon Electronics Era") is a large-scale European materials project with a focus on simulation, material development and testing.

In the simulation part starting with modelling of electronic band-structures, doping mechanisms, optical properties and so on of crystalline or amorphous TCOs (Transparent Conductive Oxides) and ASOs (Amorphous Oxide Semiconductors) materials were done. Additionally a heuristic model for thin-film morphology prediction of thin oxide films deposited by plasma processes was developed as well as statistical Particle-in-Cell Monte-Carlo (PICMC) simulation of the growth of thin oxide films by plasma processes. Further on device modelling of electrical circuits were applied for optimized circuit layouts.

The material development has been focused on both TCOs and ASOs ranging from binary to ternary and quaternary structures with PVD, CVD processes but also non-conventional techniques like ink jet printing to overcome subtractive processes (e. g. lithography and etching) by additive processes.

Testing was conducted by utilizing the full range of established techniques along with the novel Method of 4 Coefficients (M4C) developed during the course of the project life-time serving the needs for noise bandwidth reduction by advanced AC modulation techniques, characterizing mainly very resistive/low mobility metal oxides with transport characteristics below the Johnson noise level.

However, one of the primary objectives from the beginning was to prepare post-silicon era and oxide-based materials for application in optoelectronics and chemical sensing, consequently enabling European industry prepare for next-generation products. The above-mentioned demonstrators on the one hand help in identifying the potential contained in material development and on the other function as a "show and tell" device for communicating project results to a wider community."

With best regards
Dr. Volker Sittinger
Orama Coordinator

Steering wheel application
with displays and reconfigurable icon

Steering wheel applications are particularly suited for automotive instrument panels where large displays and controls can provide a wide range of data and information with minimally distracting the driver and in turn the driver can easily and safely input data to vehicle subsystems or for communication.

Displays
Over the last decade or so, the way in which people interact with information has changed dramatically. A core element of this evolution has been the way that information is displayed to users. Flat panel displays have become ubiquitous throughout our lives, and continue to evolve into new forms and locations.

The ORAMA project has devoted a good deal of effort over the last 4 years to the development and advancement of a new generation of displays. These are focused on improved performance over traditional amorphous silicon-based panels through the use of new and improved semiconductor materials. These new materials and the performance improvements they bring also allow for innovation in other ways, such as the use of Organic Light Emitting Diode (OLED) pixels, which promise to deliver superior picture to the more traditional LCD displays.

There are a large degree of challenges along the way, of course, to guarantee entry to the market. One primary challenge is that some key traditional processes and materials used for LCD screens are not up to the challenge in terms of performance needed to drive the new generation of OLED displays. The metal oxide semiconductors that have been the focus of much of the work in the ORAMA project, both more traditional Indium containing oxides and novel materials consisting of cheaper, more abundant and sustainable materials such as Zinc and Tin.

E-readers
Early on in the project, Polymer Vision in collaboration with the Holst Centre developed an electrophoretic display (EPD) designed to be used as a next generation e-reader. This prototype used oxide semiconductor materials in the transistors making up the active matrix backplane, and provided a critical stepping stone towards the far more stringent requirements brought by the goal of active OLED driving.

Flexible OLED Displays
In the transition to OLED, we see another of the display industry's evolutions. OLEDs are inherently pliable, and bring a degree of flexibility that LCD cannot match. Future designs of displays will be flexible and can be bent and rolled. No longer relying on a static, flat surface, this new generation of displays enables new applications, form factors, and areas to continue to add useful information. The production process, however, also requires the development of flexible substrates to replace the rigid glass that is currently used. The transistors and underlying circuitry to drive these OLEDS must also not only be flexible in and of themselves, but must be processed directly on

top of these flexible substrates without harm and while retaining mechanical properties.

The Holst Centre has developed key technology in processing on top of flexible, transparent substrates, and further refined this knowledge within ORAMA. These thin plastic foils have been successfully bonded to glass carrier plates, making them easily transferrable into existing flat panel fabs, and thus have lower barriers to market entry. The debonding procedure is straightforward and relies solely on mechanical force to peel them off the glass.

Sustainable Solutions

Working closely together in the ORAMA project, a number of collaborators have developed novel solutions along the value chain to realize the incorporation of new project materials into these displays. The Holst Centre also took an active role in developing new solutions for full display development, from OLED deposition to the thin film moisture encapsulation needed to prevent degradation in air, to the driving of the completed active matrix displays. The Jožef Stefan Institute in Slovenia has produced new sputter targets for the deposition of both existing and new semiconducting materials with a variety of compositions. The Instituto de Desenvolvimento de Novas Tecnologias (UNINOVA) in Portugal has screened these materials and developed transistor solutions using these targets. TNO (in the framework of the Holst Centre) in the Netherlands worked closely with UNINOVA to transfer these transistor prototypes into an industrially compatible solution, and to integrate them into fully functional prototypes. And finally the University of Cambridge in the United Kingdom has provided detailed characterization, design and analysis of the resulting devices, with feedback helping to improve the process at all levels.

Through this collaboration, the first functional prototypes of fully flexible OLED displays on plastic foil have been produced by the ORAMA consortium utilizing a zinc- and tin-based semiconducting oxide material in lieu of the indium-based materials that the market is currently working to adopt. This provides a sustainable path forward for the next generation of displays.

Soleras Advanced Coatings, in Belgium, has been working towards this industry adoption. The upscaling process of the new materials into large-scale coaters requires a transition to new types of targets, a focus on material usage and aging, and expansion to much larger sizes used in industrial scale fabrication. The first rotary targets have already been produced, with positive feedback from industry.

Automotive applications

Given the success of the display demonstrators, additional work on use cases has been led by Centro Ricerche Fiat in Italy around automotive applications for this technology. The usage of plastic displays with their rugged nature and ability to flex and curve opens up exciting new features for incorporation into car interiors. The first such application area demonstrated within the project involves a reconfigurable icon for use in a steering wheel. Here, a small flexible active matrix display is overlaid on a flexible pressure sensor (as can be seen in the large picture). Taking input from the driver, the icon shown by the resulting button can be altered to the current operation that will be controlled. This provides an intuitive feedback to the driver and allows for quicker reaction and fewer distractions despite the ever growing information being presented in the cockpit of the car.

Reconfigurable and autonomous icon devices can be integrated into interior plastic components such as for instance the dashboard and interior trims. Industry actors have signaled great interest in this technology since it offers several benefits such as:

- Reconfigurable icon/logo to be set on-demand by customer
- Autonomous device (no cabling)
- Thin lightweight film with allowed discrete not flexible components
- Integration platform suitable for a variety of different automotive applications

Breakdown in materials (source: FIAT) used in cars (2000-2010 C segment) – 14% in weight of plastic around 40% into interiors with related impact to SMART-EC. Although up to 13 different polymers may be used in a single car model, just three "families" make up some 66 % of the total plastics used in a car: polypropylene (32 %), polyurethane (17 %) and PVC (16 %).

The plastic automotive market is an estimated 8 % of polymer production (source: EUPC)

Statement of SINGULUS TECHNOLOGIES AG,
member of the Industrial Advisory Board (IAB)

SINGULUS TECHNOLOGIES AG is a leading supplier of industrial production equipment in the fields of optical data storage, photovoltaics and semiconductors with core competencies in vacuum deposition, plasma processes, thermal treatment, nano structuring and lacquer-based processes as well as automation. Experiences in the competitive environment of mass production of high-tech devices allow us to contribute to ORAMA regarding the evaluation of technical and commercial risks of technology transfer from laboratory into industrial production.

Already in February 2013, when the ORAMA coordination asked us to join the IAB for the project, it was obvious for us that semiconducting oxide materials have a huge potential for future electronics applications on an industrial scale. The goals of this joint European research project are in line with our company's strategy to intensify the development of processes and equipment for new thin film applications. Even though ORAMA is a materials driven project, I was amazed to see how intensively and fruitfully the different project partners interact along the value chain from fundamental research to design for testing new device concepts and collaborate to build demonstrators in three different segments, i.e., optoelectronics, sensors and displays. They have proven functionality and, moreover, bear the potential to become blueprints for future industrial products. Therefore, I consider the outcome of the ORAMA project in the form of the demonstrators as industrially highly relevant.

Peter Wohlfart
SINGULUS TECHNOLOGIES AG
Kahl am Main, 6th October 2014

Multifunctional glazing

Transparent coatings offer several opportunities in automotive sector for both direct (application on glazing) and indirect (integrated in functional devices) applications. Already for several years major glass manufacturers have used functional coating on windows such as electrically conductive, IR absorbing/reflecting as well as antireflective and hydrophobic coatings with interesting results. However, one drawback was the cost. Innovative materials developed with improved functional properties need to be available at a lower cost in order to be competitive. Moreover, the introduction of plastic glazing, an aspect extremely important for reducing the weight, requires specific deposition parameters which are suitable for high performances coatings.

The reduction of weight is a very important goal for automotive companies: there is a need to reduce the vehicle's mass by 10% (3-5% FE) by 2020 both in EU and US. The use of light-weight materials such as plastic glazing is a topic of great interest.

Thus, the application of plastic to reduce weight and boost design flexibility is an interesting alternative to automotive glass. The light weight has already proven itself as a decisive factor since polycarbonate has been introduced for the rear quarter windows of FIAT 500L and 500L (Living models). The second feature of design flexibility and integration renders plastic glazing economically sustainable: designs unique to plastic can flow into the overall design and cut costs in the assembly stage by integrating functions into the injection molding step used to manufacture polycarbonate glazing.

Interesting examples have been shown at the latest K Fairs by Bayer and Sabic, as main raw material suppliers: two complete tailgates were presented including backlight and rear window. Traditional tailgate modules are designed and manufactured with a metal carrier and glass window insert, which can add weight to the vehicle. A complete, one-part tailgate with backlight module made out of polycarbonate materials has been shown by Bayer: non-transparent areas are back-printed in a dark color or back-injected with a black frame material using two-component injection moulding. The backlight is part of the polycarbonate outer skin, simplifying assembly and logistics by eliminating the need to produce separate backlite housings and covers. The result is a full plastic tailgate, which thanks to the lightness of polycarbonate also offers weight savings of roughly 30% compared to traditional tailgate structures.

Sabic's tailgate concept is optimised for an all-plastic solution from the earliest stage of the design process in order to achieve the desired stiffness and strength in addition to weight savings of up to 30% or 12.5 kg compared to tailgates of a similar size using conventional materials like steel, aluminium and various hybrid offerings. The design also provides unique levels of function integration and significant freedom to create vehicles with striking designs. Using Sabic's Lexan resin and Exatec coating technology further enhances the design freedom, function integration and weight savings made possible through this optimised tailgate design. A second shot of black out material on the glazing panel using Cycoloy XCM resin expands the possibilities for integrated functionality, such as fixing for rear lighting, antennas, and cameras.

The introduction of polycarbonate into plastic glazing application needs coating on top of the polymer to protect the surface against UV light and scratches due to the fact that the abrasion resistance and the weathering of polycarbonate are not as good as glass. Then the introduction of plastic glazing requires specific deposition parameters suitable for high performance coatings. Besides regarding the integration of lighting, antenna, camera, defrost, etc. the possibilities of conductive coatings deposition becomes necessary.

Materials and deposition techniques developed and optimized within the ORAMA project should certainly offer several opportunities on said topics. Within the ORAMA project CRF realized a prototype demonstrating the possibility to integrate lighting in the same plastic window. The component selected to realize one of the three ORAMA demonstrators is the rear quarter window of Fiat 500L Living. This rear fixed side window is made of plastic (polycarbonate) by using a two-shot injection compression molding, which allows for the seamless integration of an aerodynamic spoiler. In order to demonstrate the possibility to increase the integration of functions, CRF introduced in the same component several LEDs. In this specific prototype the holes, into LEDs are applied, were realized by milling, just to show the concept.

In the future the goal is to design a proper mould which allows for the seamless integration of all functions in one component (fixing, aerodynamic and lighting) and the results generated by ORAMA in the deposition materials and process will be exploited in the multifunctional coatings for the plastic component making it at the same time protected by UV, anti-scratchable and conductive. In conclusion the interest for plastic applications on glazing is increasing and outputs from ORAMA project will contributed to maximize the range of applications for plastic solutions to be proposed to future car models.

Low temperature gas sensors

In the past p-type gas sensors have not been explored widely, due to the fact that for p-type metal oxides the effect of surface reactions on the resistance is diminished in comparison to n-type materials. Yet there are inherent advantages related to p-type-sensors where the most important one is the reduced operation temperature. This gives some operational benefits such as

- lower power consumption, consequently potential of battery operation
- applicability on "unconventional" sensor substrates such as plastic materials

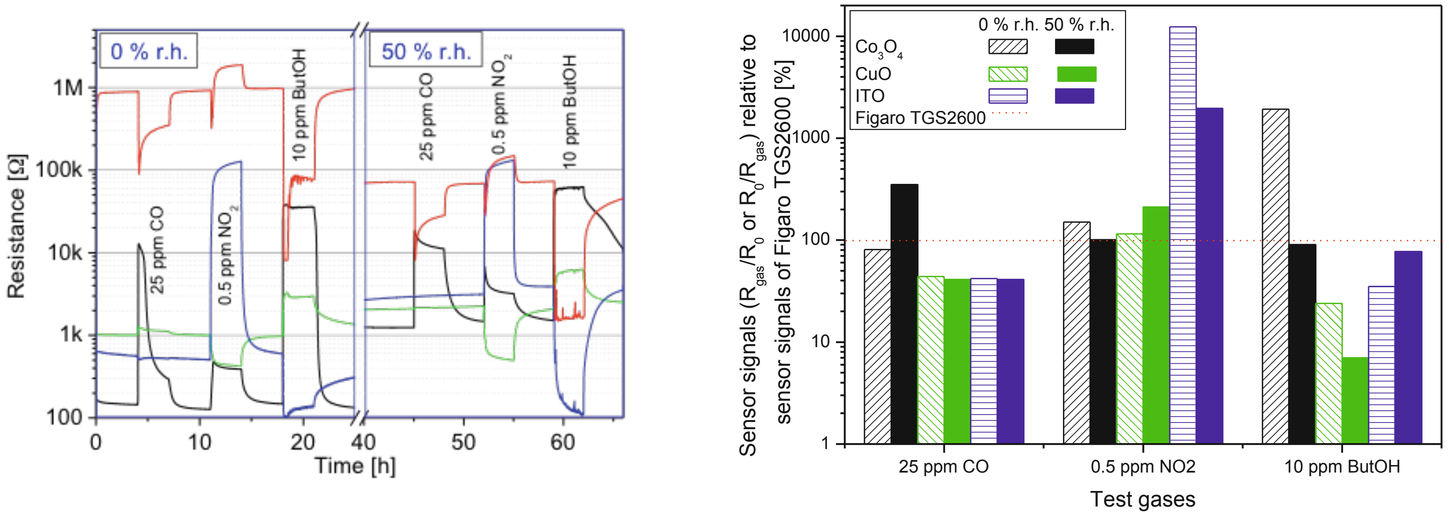
Focusing on an automotive application - monitoring of the air quality in a cabin – requires the detection of the three most relevant gases: carbon monoxide (CO), butanol (ButOH), and nitrogen dioxide (NO_2). Furthermore, to exploit the advantages of p-type oxides, the sensor array necessary for the detection of the gases shall be deposited on flexible substrates and operated below 200 °C.

Such a setup was presented at the fair "Sensor+Test 2014" in Nürnberg. For the implementation of the sensor demonstrator three materials were chosen, which displayed the best responses to the mentioned target gases: cobalt oxide (Co_3O_4; Sigma Aldrich), copper oxide (CuO; JSI), and indium tin oxide (ITO; EKUT). Those materials were drop-coated as a paste of each metal oxide mixed with 1,2-propanediol, xylene, butanol, and Tween 80 on flexible substrates (EPFL) with interdigitated electrodes and heaters of 300 µm x 300 µm size.

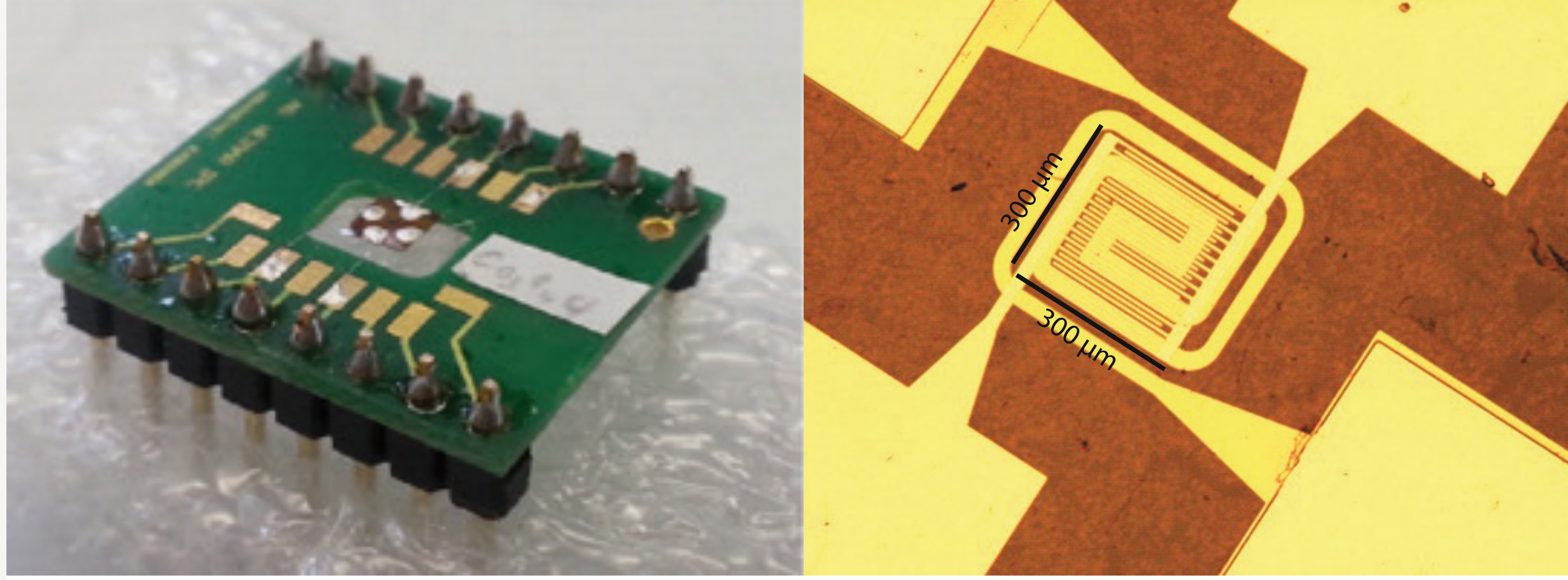
After the tempering process the sensors were fastened on a holder by welding and applying Epotek to the electrode pads (photos on the right page).

Several measurements with one of each of the sensing materials on flexible substrates under the agreed conditions were performed and are displayed in the following figures.

So, as it can be seen in Figure at yhe bottom of this page, Co_3O_4 reacts to all three test gases with a resistance increase; the best to butanol. CuO instead reacts hardly to carbon monoxide, its resistance decreases during nitrogen dioxide exposure and decreases during butanol exposure. ITO shows the highest response to nitrogen dioxide (resistance increase), no response to carbon monoxide, but a resistance decrease in the presence of butanol. To evaluate the sensors in terms of the ability to compete with sensors readily available on the market, the sensor response of a Figaro TGS2600 was set to 100%. The results are displayed on the bottom right), revealing that the sensor signals of the chosen metal oxides show at least comparable or even higher sensor signals as the reference Figaro sensor (TGS2600). All sensors within the demonstrator were operated below 200 °C; however, the Figaro TGS2600 is operated at about 380 °C.
Consequently, the prepared sensors require considerable lower temperatures, consume significantly less power, and therefore can be operated also on flexible substrates with at least comparable responses.



left: Exemplified measurement with all three target gases and all three sensing materials on flexible substrates (EPFL) @ 160-195 °C and a Figaro TGS2600 sensor as reference @ 5,0V, which corresponds to a considerable higher temperature around 380°C
right: Sensor signals (R/Rgas≥1 and Rgas/R≥1, respectively) relative to sensor signal of Figaro TGS2600.



Flexible substrate from EPFL with the drop-coated sensitive layer fastened on a holder

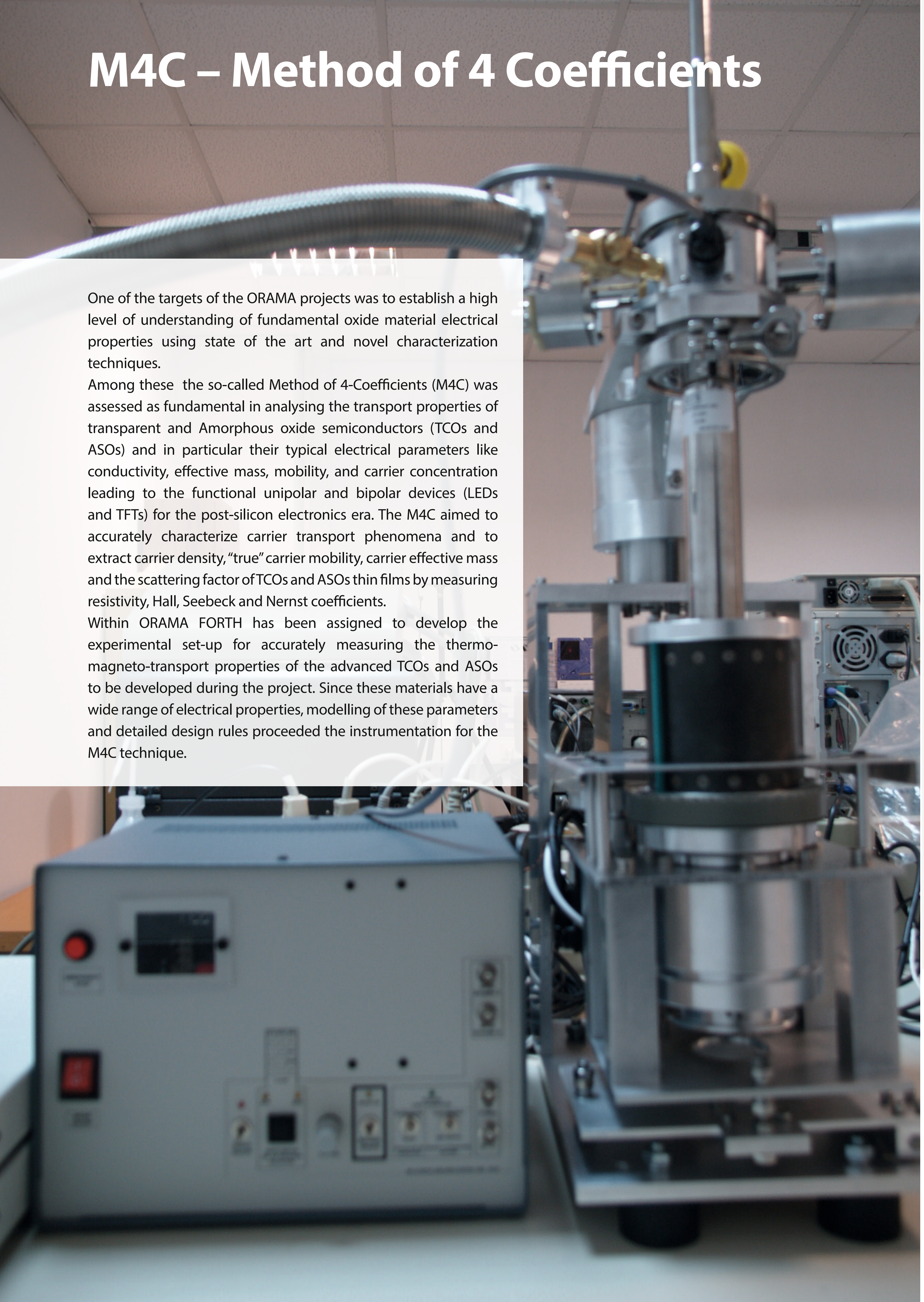
Exploitation figures / Market potential

Low power operation of gas sensors makes it possible to switch from mains operation to battery operation. If one is just looking into the classical field of gas alarms one can identify two main areas:

1. Gas alarms for burnable gases and explosion prevention
2. CO alarms for preventing from intoxication

Considering the market size it makes sense to check different sources of information. New market trends data released by Honeywell Company City Technology (UK) in August 2013 shows extensive growth in the industrial gas detection sector, which has now reached $2.2 billion in worldwide revenues. The biggest growth in the sector has been attributed to the oil and gas industry, spurred on by a surge in Shale Gas exploration and the increasing demand for energy. John Warburton, Strategic Marketing Manager at City Technology, describes this market as vibrant with many opportunities for continuing growth. "[W]e are predicting that the global demand for gas sensors will grow at 5-6% pa over the next five years with the Asia Pacific region growing at 10%. Growth in North America will remain strong, driven by the on-going development of shale gas deposits." Moreover, new trends develop in Gas Detection driven by health and safety awareness and legislation e.g. Medical and Domestic Gas Detection sensors (CO and flammable gas alarms; ~$90 million). "Furthermore, it will be an increasing demand for energy and the strengthening global economy that will shape these developments and, therefore, the future of gas detection."
One has to highlight however that the figures given there are related to whole instruments whereas the sensing element is key but from the value perspective only a fraction of the instrument price.
Looking into a report of "China Strategic Research" one will get an impression of one of the largest markets worldwide. "The market is worth about RMB 4 BN, (~ 480M€) of which will grow at a compounded average of 20% over the next five years." The market dynamics is considered to show "around 50:50 split of fixed and portable" indicating low power battery operation.
Another trend report released already in September 2010 by Global Industry Analysts, Inc. from USA was indicating the global gas detection equipment market to reach US$1.47 Billion (~ 1B€) by 2015. Considering the Chinese figure and the global figure there is a clear indication that the figures are converging. Handheld/portable gas detection equipment represents the largest and the fastest growing segment due to usage benefits, such as their compact size, simple usage pattern, and ability to provide uninterrupted monitoring services. Greater reliability and lesser false alarms are other critical factors that are influencing the growing demand for handheld/ portable gas detection equipment.
Again the handheld and portable field shows the largest growth potential. A part of this potential can be served in the future by sensors based upon p-type-materials developed within ORAMA.

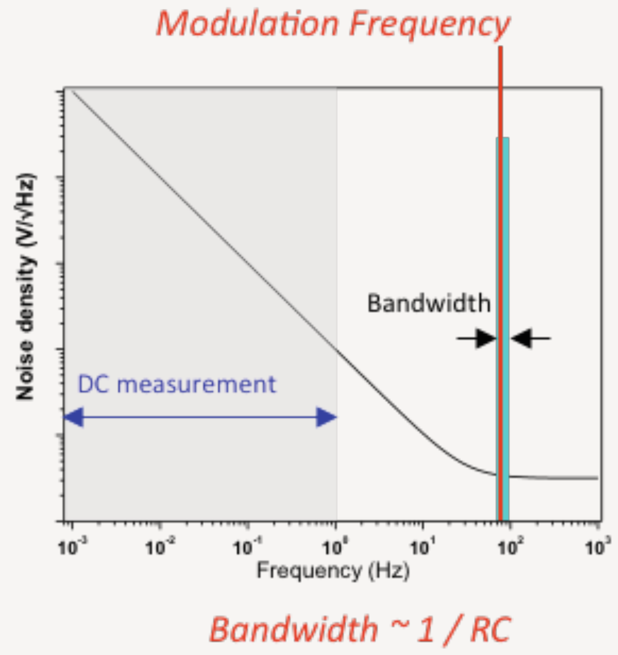
M4C – Method of 4 Coefficients



One of the targets of the ORAMA projects was to establish a high level of understanding of fundamental oxide material electrical properties using state of the art and novel characterization techniques.
Among these the so-called Method of 4-Coefficients (M4C) was assessed as fundamental in analysing the transport properties of transparent and Amorphous oxide semiconductors (TCOs and ASOs) and in particular their typical electrical parameters like conductivity, effective mass, mobility, and carrier concentration leading to the functional unipolar and bipolar devices (LEDs and TFTs) for the post-silicon electronics era. The M4C aimed to accurately characterize carrier transport phenomena and to extract carrier density, "true" carrier mobility, carrier effective mass and the scattering factor of TCOs and ASOs thin films by measuring resistivity, Hall, Seebeck and Nernst coefficients.
Within ORAMA FORTH has been assigned to develop the experimental set-up for accurately measuring the thermo-magneto-transport properties of the advanced TCOs and ASOs to be developed during the project. Since these materials have a wide range of electrical properties, modelling of these parameters and detailed design rules proceeded the instrumentation for the M4C technique.

« M4C is a novel and unique characterization platform ... »

The development of the M4C was based on the ability to measure all coefficients concerning thermo-magneto-transport effects of the specimens under study, namely by Hall, Seebeck and Nernst. Given the difficulties of the measurements associated with the nature of the TCO and ASOs samples (low mobility, relatively high resistivity) the effort was initially concentrated in modelling the expected magnitude of the quantities, to be measured experimentally, and compare them to estimated total measurement noise levels, in order to evaluate the feasibility to perform M4C measurements under different set-up approaches.



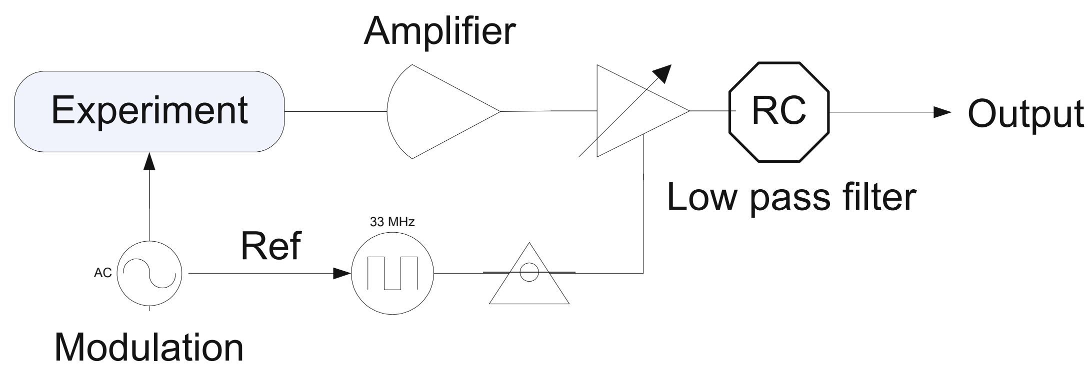
For the case of TCOs and ASOs characterized by high resistivity material and small voltage signals a direct application of the method is not possible due to the fact that the voltage signals levels are below the intrinsic Johnson (thermal) noise levels. To address this, a modulation set-up for M4C measurements has been design and implemented. The basic underlying principle in modulated measurements, permitting to overcome the Johnson noise limit, is depicted in the graphs on this page.

By applying a modulated excitation and employing synchronous amplification methods, the measurement bandwidth can be reduced, thus permitting the extraction of voltage signals of interest. The setup implemented in FORTH has the ability to achieve all three relevant modulations to this method:

(a) Current modulation
(b) Magnetic field modulation
(c) Thermal gradient modulation

Additionally this setup is capable to perform double modulation experiments, for example to perform Hall coefficient measurement applying both current and magnetic field modulations at different frequencies at the same time, to further reduce interfering noise contributions and artifacts. It is also equipped with a cryostat to permit temperature dependent measurements in the range of 4 to 300K. On the left side is a photo of the new M4C measurement system.

M4C is a novel and unique characterization platform that facilitates the detailed analysis of the electro-thermal-magnetic properties of ANY metal oxide that has very high resistance and extremely low mobility. It is a technique that can measure i.e. transport properties at a level below the Jonson noise, thus at a range that all other conventional techniques measure "noise" signals!



further Highlights ORAMA

In addition to the demonstrators which are featured in the newsletter at hand, we would like to provide some space for the other highlights of the project. Here they are:

- Soft growth methods for TCOs were established to avoid damaging LED devices as a result of the high energy species by RF superimposed DC sputtering when using PICMC simulation.
- A large area rotatable target for industrial use was developed with an indium free ASO material:
  - Optimised properties of In-free n-type oxides were obtained by fine tuning the composition within the ZnO-SnO_2-Ga_2O_3 system.
  - Phase pure p-type delafossite $CuAlO_2$ ceramic research-grade sputtering targets were prepared by an optimised solid-state synthesis route.
- established a model based evaluation of oxide materials for advanced mirror layer stacks, which paves the way for a new type of LED using the concept of an omnidirectional mirror, thus increasing overall electro optical performance of the devices.

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SEVENTH FRAMEWORK PROGRAMME

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