Editors: Volodymyr Khranovskyy and Rositza Yakimova

# **Book of Abstracts**



# 1<sup>st</sup> International Workshop on Functional Oxide (FOX) Materials

organized within the frame of **VR Swedish Research Links** program, bilateral Sweden – Egypt collaborative research project 2013-2016 "Elaboration of transparent electronic materials for renewable energy technologies" *and* **EU FP-7 IRSES** Grant "Development of Nanotechnology based Biosensors for Agriculture (BiosensorsAgricult)".

Linköping University, Sweden October 1-2, 2015

Series: Linköping University Electronic Press Workshop and Conference Collection, No. 5

# Organized by Volodymyr Khranovskyy and Rositsa Yakimova

Oxide semiconductors are an important part of the functional materials field. Technological accessibility (physical & chemical synthesis), diversity of geometrical shapes (bulk, films, nanostructures) and environmental stability combined with ambience sensitivity makes them promising materials for plenty of future applications. Among other, ZnO, Al<sub>2</sub>O<sub>3</sub>, GaO, NiO, TiO<sub>x</sub>, Gd<sub>2</sub>O<sub>3</sub>, Fe<sub>3</sub>O<sub>4</sub> and graphene oxide are considered as materials for both active and passive components in many applications: transparent conductive coatings, gas sensors, biosensors, tomography markers, light emitters, thermoelectric materials, catalysts and many others. We expect the experts to present their latest results on fabrication, characterization and application of the oxide materials.

Topics of the workshop are focused, but not limited to:

# **Material Science**

- Synthesis and fabrication of FOX
- Characterization of the structural, optical and electrical properties
- QDs, 2D materials and nanocomposites of FOX

#### **Applications**

- Gas and biosensors
- ❖ Solar Cells
- ❖ LEDs & LDs
- Detectors
- Nanoelectronics

# **Invited speakers:**

- Prof. Rositza Yakimova (Linkoping University, Sweden)
- Asst. Prof. Mustafa Boshta (Kairo University, Egypt)
- Prof. Omer Nour (Linkoping University, Sweden)
- Sen. Lec., Doc. Per Eklund (Linkoping University, Sweden)
- Asst. Prof. J. Eriksson (Linkoping University, Sweden)
- Asst. Prof. Gholam Reza Yazdi (Linkoping University, Sweden)
- Jerry Eriksson, (Glafo Glass Research Institute, Sweden)

#### **FOX Workshop agenda**

Thursday, Oct., 1st. Chair: R. Yakimova

# 13.00-13.30 Opening and Introductory talk (R. Yakimova)

- 13.30 14.00 M. Boshta "Preparation of oxides thin films by spray pyrolysis technique"
- 14.00 14.20 Muhammed Gomla "Preparation and characterization of NiO thin films"
- 14.20 14.40 Alla Tereshchenko "Immune Biosensors Based on Photoluminescence From TiO<sub>2</sub> Nanostructures"

# 14.40 – 15.00 Coffee Break.

- 15.00 15.30 Omer Nour "Zinc oxide: from nano material to nano-systems"
- 15.30 16.00 Per Eklund "Oxide for thermoelectrics, fuel cells and hard coatings"
- 16.00 16.20 Biplab Paul "Mechanism of formation of thermometric misfit layered Ca3Co4O9 by annealing CaO-CoO thin films"
- 16.20 17.20 Free discussion

Friday, 2<sup>nd</sup> of Oct. Chair: V. Khranovskyy

- 9.15 9.45 Gholam Reza Yazdi "Graphene layer a template with different local properties"
- 9.45 10.05 Martin Eriksson "Influence of the annealing on the recombination dynamics of ZnO"

# <u>10.05 – 10.30 Coffee Break</u>

- 10.30 10.50 Jerry Eriksson "Transparent Intelligence"
- 10.50 -11.10 Volodymyr Khranovskyy "Transparent multifunctional coatings based on metal oxides nanocomposites"
- 11.10 11.40 Jens Eriksson "Graphene Metal-oxide hybrids for gas sensor tuning"
- 11.40 12.00 Donatella Puglisi "Exploring the gas sensing performance of catalytic metal oxides on gas sensitive SiC-FETs".

Closing remarks

12.30 Lunch

# Preparation of Oxides by Spray pyrolysis technique

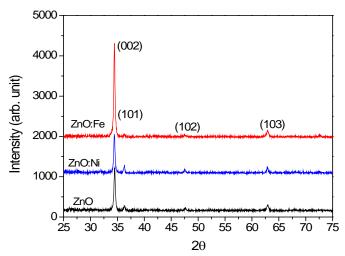
#### M. Boshta

Solid State Physics Dept., National research Centre, El-Behooth st., 12311 Dokki, Giza – Egypt boshta2000@yahoo.com

The increasing need for high-quality, large-area electronic thin films in the recent ten years has led to the development of a new class of electronic materials namely metal oxide semiconductors. It is now accepted that metal oxide semiconductors are strong candidates for application in next generation of electronic thin films since they offer numerous advantages over competing technologies such as organics, and amorphous silicon [1].

Metal oxide semiconductors are usually deposited by vacuum based techniques such as molecular beam epitaxy (MBE) [2], sputtering[3], chemical vapor deposition[4], ion-assisted deposition[5] and pulsed laser deposition[6]. However, vacuum-based deposition techniques are still suffering from the high cost of manufacturing and limited large area. In order to overcome the vacuum technology limitation the researchers focused on the development of alternative deposition methods such as spin casting, dip coating and spray pyrolysis [7].

Using Spray pyrolysis technique to deposit metal oxide compounds in form of n-type and p-type. The n-type metal oxides such as (zinc oxide (ZnO) with different dopant, tin oxide dopped fluorine (SnO<sub>2</sub>:F),WO<sub>3</sub>,TiO<sub>2</sub>) and p-type (NiO, CuAlO<sub>2</sub>, CuCrMgO<sub>2</sub>) have been deposited by spray to be used in different applications.



- [1] G. Adamopoulos, A. Bashir, W. P. Gillin, S. Georgakopoulos, M. Shkunov, M. A. Baklar, N. Stingelin, D. D.C. Bradley, and T. D. Anthopoulos, Adv. Funct. Mater. 21 (2011)525
- [2] Y. Chen, N. T. Tuan, Y. Segawa, H-J Ko, S-K Hong, T. Yao, Appl. Phys. Lett. 78 (2001) 1469
- [3] T. Miyasako, M. Senoo, E. Tokumitsu, Appl. Phys. Lett. 86 (2005)162902
- [4] J. Jo, O. Seo, H. Choi, B. Lee, Appl. Phys. Express 1(2008)041202
- [5] L. Wang, M. H. Yoon, G. Lu, Y. Yang, A. Facchetti, T. J. Marks, Nat. Mater. 5 (2006)893
- [6] J. Nishii, F. M. Hossain, A. Takagi, T. Aita, K. Saikusa, Y. Ohmaki, I. Ohkubo, S. Kishimoto, A. Ohtomo, T. Fukumura, F. Matsukura, Y. Ohno, H. Koinuma, H. Ohno, M. Kawasaki, Jpn. J. Appl. Phys. 42(2003)L347 L349
- [7] M. Boshta, M.O. Abou-Helal, D. Ghoneim, N.A. Mohsen, R.A. Zaghlool, Surface & Coatings Technology 205 (2010) 271

# Preparation and characterization of NiO thin films

M. M. Gomla and M. Boshta

Solid State Physics Dept., National Research Center, El-Behouth st., 12311, Dokki, Giza, Egypt E-mail: m\_metwaly2006@yahoo.com

Transparent conducting oxides (TCO) are well known and have been widely used for a long time in optoelectronics industries as well as in research fields. The most traditional TCOs show n-type conductivity. But the corresponding p-type transparent conducting oxides (p-TCO) are essential for junction devices.

The lack of p-type transparent conducting oxides with optimum transparency and conductive properties is the main motivation of our work. NiO is a promising candidate for p-type transparent conducting oxide films with a simple cubic structure and band gap energy from 3.6 to 4.0 eV [1]. The most attracting features of NiO due to its high chemical stability, excellent durability, low material cost. The Chemical spray pyrolysis (CSP) and chemical bath deposition (CBD) are convenient, low cost, and large-area thin films deposition with good uniformity. In the present work, the NiO films were synthesized by (CBD) and by chemical spray pyrolysis (CSP) [2]. The complete characterization of structural and optical properties of the NiO will be performed in order to understand their dependence of fundamental properties to preparation technique parameters. Where the CSP process is performed at relatively high temperature for very short time and the annealing process is canceled.

The final stage of the work will be fabricated of a transparent hetero p-n junction as UV photo-detector based on p-NiO /n-ZnO [3]. This work will open the pathway towards the realization of transparent systems "Transparent Electronics".

- [1] Xinman Chen, Lingzhizhao, and Qiaoliniu, J. Electron. Mater. 41, 12 (2012)
- [2] Wang, X., Wei, Z., Journal of Advanced Microscopy Research, 10, 24(2015)
- [3] A. Echresh, C. O. Chey, M. Z. Shoushtari, V. Khranovskyy et al. J. Alloys Compd, 632, 165 (2015).

# Immune Biosensors Based on Photoluminescence From TiO<sub>2</sub> Nanoparticles

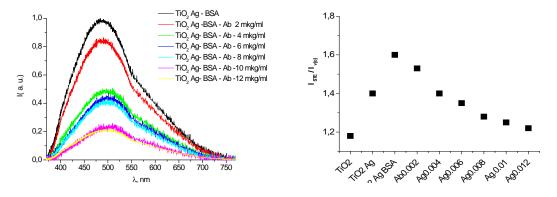
# Alla Tereshchenko and Valentyn Smyntyna

Experimental Physics Department, Odesa National I.I. Mechnikov University, Ukraine

Immune biosensors, based on  $TiO_2$  photoluminescence nanoparticles, for the detection of *Bovine leucosis* and *Salmonella spp.* bio-targets have been developed. The  $TiO_2$  substrates, used as a biosensor platform, were deposited from colloidal suspension of  $TiO_2$  nanoparticles solved in water. Structural and surface properties showed that obtained substrates formed high surface area porous structure that is suitable for immobilization of biological species. The photoluminescence (PL) from  $TiO_2$  nanoparticles (anatase modification) was used as a signal of biosensor response. PL spectra of  $TiO_2$  nanostructures were excited by solid state laser with  $\lambda_{ex}$  = 355 nm and were measured in the range of 370-800 nm. The sensitive layer was formed by immobilization of biorecognition layer (antibodies of *Salmonella spp.* and antigens in the case of *Bovine leucosis*) on  $TiO_2$  surface. After forming of biosensitive layer BSA was used as a blocking agent for non-specifically bounded proteins.

The photoluminescence spectrum of pure  $TiO_2$  nanostructures is characterized by broad peak centered at 505 nm. In both cases, the immobilization of sensitive layer on  $TiO_2$  surface led to the increase of PL intensity and UV-shift of PL maximum. Increase of PL intensity could result from charge transfer between proteins and conductance band of  $TiO_2$ . UV-shift of PL maximum can be caused by additional dipole-dipole interaction that can change energetic position of recombination centers in  $TiO_2$ . The BSA deposition resulted in increase of PL in all cases. Analyte deposition with increasing concentration led to the decrease of PL intensity and shift of peak position to higher wavelengths. Thus, the biosensor response to analyte concentration can be a function of two parameters: PL intensity and PL peak position. To analyze the possible mechanisms of interaction between  $TiO_2$  and proteins the fitting of PL spectra of  $TiO_2$  nanostructures before and after interaction with biological molecules was performed and plotted the ratio of PL intensities related to STE and oxygen vacancies.

The sensitivity of biosensor, based on  $TiO_2$  nanoparticles, for *Bovine leucosis* antibodies was in the range of 2 – 10 mkg/ml [1]. The sensitivity of biosensor, based on  $TiO_2$  nanoparticles for *Salmonella spp*. antigens was in the range of  $10^3$  to  $10^6$  cl/ml.



**Figure 1**. a) PL spectra of  $TiO_2$ -Ag-BSA layer under different concentrations of Bovine leucosis Ab b) Ratio of  $I_{STE}/I_{V[O]}$  before and after interaction with biomolecules.

#### References

[1] R. Viter et al. Procedia Engineering 47. – 2012. P. 338 – 341.

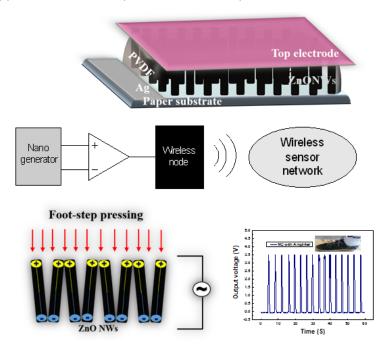
# **Zinc Oxide: From Nanomaterial to Nano-systems**

#### Omer Nur

Department of Science and Technology (ITN), Linköping University, 601 74 Norrköping, Sweden

Zinc oxide (ZnO) well aligned nanorods (NRs) possessing high piezoelectric coefficients were synthesized on flexible substrates using the low temperature hydrothermal route [1]. These ZnO NRs were then used in different configurations to demonstrate different low frequency energy harvesting devices. Generally the demonstrated piezoelectric devices were tested under the influence of low frequencies and under different weights. The results show relatively high sensitivity for a frequency as low as 5 Hz and relatively low weights down to 10 g. The first application to be demonstrated is handwriting enabled energy harvesters, where we have managed to design a configuration capable of generating up to 4.8 V from handwriting [2]. We further demonstrate a self-powered an anisotropic direction sensor processed on flexible plastic [3]. We will also show that doping ZnO NRs with impurities like e.g. Ag, will lead to loss of crystal symmetry and hence reduce the output harvested electrical energy [4]. Finally we will show our first results from wire-less communication of our ZnO NRs piezoelectric harvesters with application for security and surveillance systems.

**Figure 1:** The configuration of the nano-generator, (middle) wireless circuit schematic diagram, and (bottom) left schematic diagram showing the voltage developed up the exerting foot pressure, and right showing the voltage developed pressure from foot steps.



# References

[1] E. S. Nour, Azam Khan, Omer Nur, and Magnus Willander, Nanotechnology and Nanomaterials (2014). DOI: 10.5772/59068.

[2] E. Nour, M. Sandberg, M. Willander, O. Nur, Nanoenergy 9, 221-228 (2014). Also highlighted by the Wissenschaft aktuell in Germany:

http://www.wissenschaft-aktuell.de/artikel/Elektrisierende\_Handschrift\_1771015589640.html [3] E. S. Nour, C. O. Chey, M. Willander, and O. Nur, Nanotechnology 26, 095502 (2015). Also highlighted in Nanotech Web: http://nanotechweb.org/cws/article/lab/60281.

[4] E. S. Nour, A. Echresh, Xianjie Liu, E. Broitman, M. Willander and O. Nur, AIP Advances *5*, 077163 (2015).

# Oxides for hard coatings, fuel cells, and thermoelectrics

#### Per Eklund

Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183, Sweden

In this invited talk, I will give an overview of our activities on oxide thin-film materials for applications as hard coatings, fuel cells, and thermoelectrics.

For hard coatings, the chromium-aluminum oxide is of interest to make wear- and corrosion-resistant coating with enhanced stability compared to pure alumina. I will discuss results from arc-deposited Cr-Al-O film synthesized in an industrial setup. X-ray diffraction and transmission electron microscopy show the predominance of the metastable cubic-(Cr,Al)<sub>2</sub>O<sub>3</sub> solid solutions and secondary hexagonal corundum-structured  $\alpha$ -(Cr,Al)<sub>2</sub>O<sub>3</sub> [1]. Phase-stability calculations by density-functional theory [2] of fcc with ordered and disordered metal site vacancies are studied for fcc-(Cr,Al)<sub>2</sub>O<sub>3</sub> and found to a have cubic lattice spacing close to experimental values [3,4] in contrast to potentially competing fluorite and perovskite structures. The fcc structures are higher in energy than corundum for all compositions, but with an energy offset similar to other metastable systems possible to synthesize with physical vapor deposition techniques, explaining their preferential growth relative to the corundum structure.

For fuel cell electrolytes, there is a growing trend of implement thin-film plasma-deposited electrolytes  $Y_2O_3$ - $ZrO_2$  (YSZ) and  $Gd_2O_3$ - $CeO_2$  (CGO) where nanostructuring can increase ionic conductivity and reduced thickness compared to bulk can minimize losses thereby reducing the operating temperature [5,6]. We have deposited YSZ/CGO solid electrolytes in an industrial coating unit applicable for medium scale production onto fuel-cell anode substrates and demonstrated homogenous deposition over large areas on substrates of sizes greater than 10cm x 10cm to satisfy industrial requirements [7] and developed barrier layers [8,9].

I will also give a brief introduction to growth of misfit layered thermoelectric cobalt oxide Ca3Co4O9 thin films prepared by reactive rf-magnetron sputtering followed by post-annealing [10].

- [1] A. Khatibi et al Acta Mater 60, 6494 (2012); ibid. 61, 4811 (2013)
- [2] B. Alling et al J. Vac Sci. Technol A 31, 030602 (2013)
- [3] A. Khatibi et al Thin Solid Films 519, 2426 (2011)
- [4] A. Khatibi et al Surf Coat Technol 206, 3216 (2012)
- [5] M. Sillassen, P. Eklund, et al, Journal of Applied Physics 105, 104907 (2009)
- [6] M. Sillassen, P. Eklund, et al, Advanced Functional Materials 20, 2071 (2010)
- [7] S. Sønderby, ..., P. Eklund, Surface and Coatings Technology 206, 4126 (2012)
- [8] S. Sønderby, ..., P.Eklund, Advanced Energy Materials 3, 923 (2013)
- [9] S. Sønderby, ..., P. Eklund Journal of Power Sources 267, 452 (2014)
- [10] B. Paul,...,P. Eklund Advanced Electronic Materials 1, 1400022 (2015)

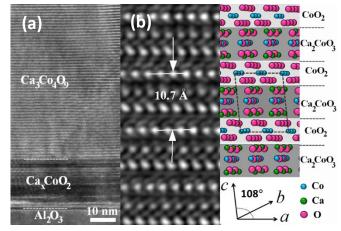
# Mechanism of formation of thermometric misfit layered Ca₃Co₄O₂ by annealing CaO-CoO thin films

<u>Biplab Paul</u>\*, Jeremy L. Schroeder\*, Sit Kerdsongpanya\*, Ngo Van Nong\*\*, Norbert Schell\*\*\*, Daniel Ostach\*\*\*, Jun Lu\*, Jens Birch\*, Per Eklund\*

\*Thin Film Physics Division, Department of Physics, Chemistry, and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden, \*\*Dept. of Energy Conversion and Storage, Technical University of Denmark, Risø Campus, Frederiksborgvej 399, Building 779, 4000 Roskilde, Denmark, \*\*\*Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Institute for Materials Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany

Grain-aligned bulk  $Ca_3Co_4O_9$  ceramics exhibit higher thermoelectric performance than randomly oriented  $Ca_3Co_4O_9$  ceramics due to the anisotropic transport properties of  $Ca_3Co_4O_9$ , which is attributed to the inherent layered structure of  $Ca_3Co_4O_9$ . Several approaches have been reported to improve the texture quality of bulk polycrystalline  $Ca_3Co_4O_9$  [1, 2]. However, it is difficult to produce perfectly textured  $Ca_3Co_4O_9$  ceramics. One promising approach for improving thermoelectric performance is texturing  $Ca_3Co_4O_9$  in the form of thin films. We present the growth of  $Ca_3Co_4O_9$  thin films by a two-step sputtering/annealing method. First, CaO-CoO thin films were deposited on 0001-sapphire ( $Al_2O_3$ ) substrates by reactive co-sputtering from Ca and Co targets. Second, the CaO-CoO thin films were annealed at 720 °C under CoO-gas flow in order to form the final phase of  $Ca_3Co_4O_9$ . The thermal-induced phase transformation was investigated by ex-situ x-ray diffraction and in-situ time-resolved synchrotron annealing experiments. The two-step sputtering/annealing method produced a highly textured  $Ca_3Co_4O_9$  thin film with an electrical resistivity of CaO (CaO) and CaO of CaO and CaO phases during film deposition

**Figure 1.** a) A typical TEM image showing the layered  $Ca_3Co_4O_9$  structure with a 17 nm region from the interface comprised of  $Ca_xCoO_2$ . b) Lattice-resolved TEM image and schematic of the atomic arrangement of the layers.



- [1] E. Guilmeau et al. Synthesis and thermoelectric properties of  $Bi_{2.5}Ca_{2.5}Co_2O_x$  layered cobaltites, J. Mter. Res., 20, 1002 (2005).
- [2] J. Noudem A new process for lamellar texturing of thermoelectric Ca3Co4O9 oxides by spark plasma sintering, J. Eur. Ceram. Soc. 29, 2659 (2009).
- [3] B. Paul et al. Adv. Electron. Mater. 1, 1400022 (2015).

# **Graphene layer - a template with different local properties**

<u>G. Reza Yazdi</u>, <sup>1</sup> T. lakimov, <sup>1,3</sup> F. Akhtar, <sup>1</sup> Ivan. G. Ivanov, <sup>1</sup> S. Schmidt, <sup>1</sup> A. Zakharov, <sup>2</sup> M. Syväjärvi<sup>1,3</sup> and R. Yakimova<sup>1,3</sup>

<sup>1</sup> Department of Physics, Chemistry and Biology, Linköping University, SE-58183 Linköping, Sweden

<sup>2</sup> MaxLab, Lund University, S-22100 Lund, Sweden

<sup>3</sup> Graphensic AB

yazdi@ifm.liu.se

Epitaxial graphene growth on Si face of SiC substrates was carried out in an inductively heated furnace at a temperature of 2000°C and an ambient argon pressure of 1 atm. Graphene surface morphology, thickness, structure and electronic properties have been assessed by using AFM, LEEM, Raman, STM, STS, XPS and EFM.

Graphene formation and its thickness uniformity have been analyzed in respect to step bunching and surface decomposition energy differences on different SiC polytypes. The uniformity of silicon sublimation is an important factor for obtaining large area homogenous graphene. We have demonstrated a monolayer (ML) graphene growth on all SiC polytypes, but larger area, over  $50\times50~\mu m^2$ , on 3C-SiC substrates. 6H-SiC shows close quality of graphene to that on the 3C-SiC, because half of the unit cell contains three Si-C bilayers. The results on 4H-SiC show that graphene formation process has narrower window of growth parameters.

Graphene wrinkles form by compressive strain due to the thermal mismatch of graphene and SiC induced during sample cooling. Wrinkles are linear defects which can cause carrier scattering and decrease mobility. Deep understanding and control of wrinkle appearance are central to our current research. By modifying substrate conditions we have been able to change the wrinkle orientation from a random network to a full alignment in a particular direction or radial. We will present effect of thermal cycling, cooling down to 4 K, and ambient conditions on graphene layer and wrinkles.

Adsorption of ambience species was observed to be more pronounced on a ML graphene. The second monolayer was distinguished by phase contrast mode and EFM and it is confirmed by the LEEM images as well. On 2ML adsorption occurs on the edge of steps and wrinkles due to the geometry of the  $\pi$  bonds. The mechanism of this effect and dependency of their density on surface morphology will be elucidated. Strain differences between one and two monolayer graphene have been studied by Raman spectroscopy. To clean the graphene surfaces we have performed a series of annealing at different temperatures to find out the optimal regimes. The complete study will help to develop proper conditions for graphene maintenance before subsequent device process.

All different features on graphene surface which mentioned above changing the properties of graphene layer and make it a suitable template with different local properties for different applications.

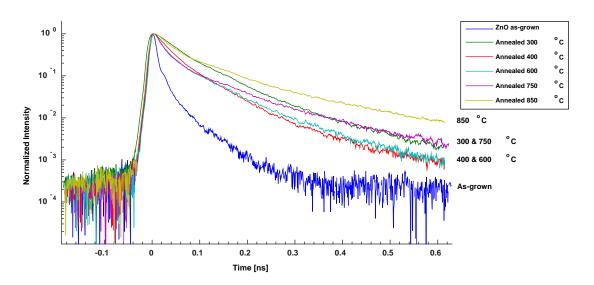
# The Effect of Annealing Temperature on the Recombination Dynamics in ZnO Nanorods

Z.N Urgessa<sup>1</sup>, J.R Botha<sup>1</sup>, <u>M. O. Eriksson</u>\* <sup>2</sup>, K Talla<sup>1</sup>, S.R Dobson<sup>1</sup>, S.R. Tankio Djiokap<sup>1</sup>, F. Karlsson<sup>2</sup>, V. Khranovskyy<sup>2</sup>, R. Yakimova<sup>2</sup>, P.O. Holtz<sup>2</sup>.

South Africa

The metal oxide semiconductor ZnO has optical properties that make it a promising material for light emitting diodes working in the ultraviolet and visible region of the electromagnetic spectrum. The high exciton binding energy enables radiative recombination of excitons at room temperature, which is crucial for many applications. We have studied the optical properties of ZnO nanorods grown by chemical bath deposition and the effect of annealing temperature on the recombination dynamics of near band edge excitons and basal plane stacking fault (BSF) related recombination events.

The neutral donor bound exciton D<sup>0</sup>X and the BSF related emissions are visible for all annealing temperatures. For the as-grown sample, there is a fast recombination channel present for both the D<sup>0</sup>X and the BSF related emission, attributed to surface traps yielding non-radiative recombination. The surface traps are largely considered to originate from adsorbed impurities on the rods, which cause near surface band bending. As the samples were annealed, ranging from 300 °C to 850 °C, the short recombination channels for the BSF related recombination and for the D<sup>0</sup>X recombination became less pronounced, indicating the removal of surface adsorbed impurities. Furthermore, for samples annealed at 400 °C and above, free exciton (FX) recombination could be observed, with a very short lifetime and weak intensity. The photoluminescence lifetime for the D<sup>0</sup>X and FX states increase with annealing temperature. Our investigation on the recombination dynamics of near band edge excitons in ZnO has important implications for the understanding of the optical properties of these structures and in the construction of more efficient light emitting diodes. [1]



**Figure 1.** Time-dependent PL intensity (normalized and background corrected) of the D<sup>0</sup>X emission line from the samples annealed at different temperatures.

#### References

[1] Z. N. Urgessa et al., Journal of Applied Physics 116, 123506 (2014)

<sup>&</sup>lt;sup>1</sup> Department of Physics, P.O Box 77000, Nelson Mandela Metropolitan University, Port Elizabeth 6031,

<sup>&</sup>lt;sup>2</sup> Department of Physics, Chemistry, and Biology (IFM), Linköping University, 58183 Linköping, Sweden

# **Transparent Intelligence**

# J. Eriksson

Glafo – the Glass Research Institute, Växjö, Sweden

Transparent materials are a prerequisite for future technology where invisible functions are placed on, or under, the surface of interactive devices. Within the concept "Transparent Intelligence", transparent functions such as sun protection, solar electricity, load-bearing capability, antenna, self-cleaning surface, electrochromic foil, touch function etc. are gathered and studied for the creation of new multidisciplinary applications.

Historically the first flat glass application was to cover a hole in the wall, serving as an environmental shield, at the same time as daylight was led into the room. Already here glass provided a multifunctional solution. Moving into modern times, as transparent metallic coatings were developed supplementary functions as infrared reflection could be added. The continuous development of selective multi-functional coatings today brings us a multitude of possibilities for new flat glass applications in buildings, vehicles and display uses etc. (Fig. 1).

Glafo actively looks for collaborations where new technologies and solutions can be developed and implemented in industrial processes. Our aim is to help the industry develop new products that is at the cutting edge of the current technology. The concept "Transparent Intelligence" was developed as part of our work to promote and encourage the application of new technologies in the somewhat conservative glass industry.



**Figure 1.** An example of Transparent Intelligence where a regular low energy coating on glass has been used to integrate a transparent antenna in a window.

# Transparent multifunctional coatings based on metal oxides nanocomposites

Yi-Chieh Chung, Thomas Ederth, Per Eklund, Jerry Eriksson, Rositza Yakimova and Volodymyr Khranovskyy

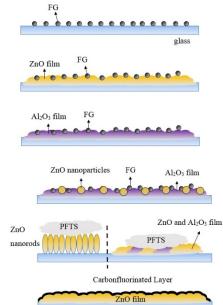
Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183, Sweden

Different types of touch-screens are widely used nowadays — in personal smartphones, public information access points and industrial monitoring and control processes. Apart from touch-screens performance and design there is another serious problem — their contamination. Human's fingers are the main contamination agents, bringing the different types of organic contamination on the front surface of the touch-screen. Development of the transparent, hard and fingerprint-proof coating is the ambitious challenge, enabling a shiny and stain-free future.

At nowadays, most touch-screens that are produced are coated by thin organic film of the fluor-containing organic solution. Organic coatings, however, does not satisfy the hardness issue and are easily worn out. In contrast, inorganic materials, being the same transparent, usually possess higher hardness, are more thermally, mechanically and environmentally stable.

In this project, we focus on development of the oleo- and hydro- phobic coatings, mainly based on *inorganic* materials. For this purpose we have studied both oil and water wettability of transparent inorganic coating, such as nanocrystalline thin films of zinc oxide (ZnO) and sapphire (Al $_2$ O $_3$ ) as well as their nanocomposites with fluorinated graphite particles (FG). The results are compared to the organic coating with perfluordecyltrichlorosilane (PFTS).

The fabricated coatings were investigated in terms of their wettability to water and hexadecane (as a model oleo-liquid) as well as their optical transparency for the visible range (300 – 800 nm). Coating of the surface by FG was found to be efficient for improving the hydro-and oleo-phobicity of the surface, keeping the high optical transmittance. The water and hexadecane contact angles were 165° and 38° respectively at the optical transparency ≈90%. However, the weak mechanical bonding of the nanoparticles to the surface is the main drawback of this type of coating. This can be overcame via fabrication of the nanocomposite coating, consisting of crystalline phases of ZnO, Al<sub>2</sub>O<sub>3</sub> and FG. However, the technological parameters (films thickness, grain size, roughness, FG particles size and concentration) still has to be optimized. Adding the ZnO nanoparticles into the matrix of Al<sub>2</sub>O<sub>3</sub> influence positively the results and increase the oleophobicity of coating due to



increased roughness. Coating of the surface by carbonfluor containing film allows increase of the hydrophobic and oleophobic behaviour – up to CA =  $115^{\circ}$  and  $20^{\circ}$ , respectively. While the organic coating (PFTS) of nanocomposite films of ZnO and Al<sub>2</sub>O<sub>3</sub> demonstrate the best performance for both water and oil repellence (CA of  $150^{\circ}$  and  $112^{\circ}$  respectively).

# Graphene metal-oxide hybrids for gas sensor tuning

J. Eriksson<sup>1</sup>, D. Puglisi<sup>1</sup>, C. Strandqvist<sup>1</sup>, R. Yakimova<sup>1</sup>, A. Lloyd-Spetz<sup>1</sup>

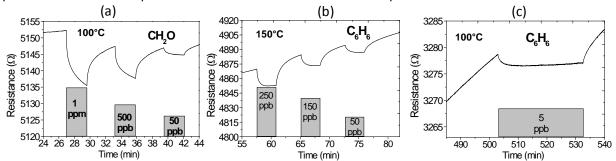
<sup>1</sup>Department of Physics, Chemistry and Biology, Linköping University, SE-58183, Linköping, Sweden; jenser@ifm.liu.se

We report on surface modifications of epitaxial graphene on SiC (EG/SIC) with metal-oxide (MOx) nanoparticles (NPs) and monolayers, formed by reproducible thin film deposition techniques, and their effect on the electronic properties of the graphene and on gas interactions at the graphene surface. The scope is to exploit the sensing properties of MOx materials for selectivity tuning while utilizing the unique electronic properties of graphene as an ultra-sensitive transducer.

We have previously found that monolayer graphene is crucial for optimum gas sensitivity [1]. This highlights the importance of achieving well-controlled uniform single-layer graphene growth. To that end, we have recently shown [2] that the graphene thickness uniformity can be significantly tuned by careful control of the EG/SiC morphology.

Chemiresistor sensors based on EG/SiC, decorated with Au, Pt, TiO<sub>2</sub> and Fe<sub>3</sub>O<sub>4</sub> core-shell NPs (Fe core surrounded by Fe<sub>3</sub>O<sub>4</sub> shell), were tested towards parts per million (ppm) down to low parts per billion (ppb) concentrations of hazardous volatile organic compounds (VOCs), e.g.  $CH_2O$  and  $C_6H_6$ , as well as common pollutants like NO, NO<sub>2</sub>, CO, and NH<sub>3</sub>. While pristine EG/SiC showed no response to the tested VOCs, it was found that decoration with TiO<sub>2</sub> or Fe<sub>3</sub>O<sub>4</sub> NPs can yield selective detection of both  $CH_2O$  and  $C_6H_6$ . The effect of decoration on the sensor performance strongly depends on the choice, thickness, surface coverage, and size of the NPs. Decoration with nanoporous (2-3 nm) Au improved the detection limit and selectivity for NO<sub>2</sub> [3]. Decoration with TiO<sub>2</sub> NPs allowed detecting low ppb levels of formaldehyde and benzene, where the effect on the sensor performance depends on the diameter and surface coverage of the deposited TiO<sub>2</sub> NPs. Graphene decorated with monodispersed Fe<sub>3</sub>O<sub>4</sub> NPs showed an even larger sensitivity to formaldehyde (Fig. 1a) and benzene (Figs. 1b and 1c) compared to EG-TiO<sub>2</sub> NP hybrids.

The results show that graphene decoration can be an effective strategy for tuning the sensor performance in the scope of ultra-sensitive detection of toxic air pollutants.



**Figure 1**. Response of a EG/SiC sensor decorated with FeO core-shell NPs ( $\approx$  60 nm in diameter) to CH<sub>2</sub>O concentrations from 1 ppm to 50 ppb (a) and to C<sub>6</sub>H<sub>6</sub> concentrations in the range 250-50 ppb (b) and 5 ppb (c).

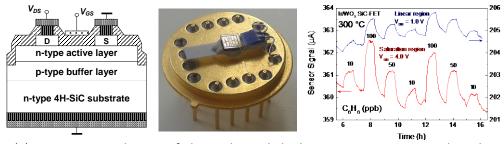
- R. Pearce J. Eriksson et al., "On the differing sensitivity to chemical gating of single and double layer epitaxial graphene explored using Scanning Kelvin Probe Microscopy", ACS Nano 7 (5) (2013), 4647-4656
- 2. J. Eriksson, R. Pearce et al., "The Influence of Substrate Morphology on Thickness Uniformity and Unintentional Doping of Epitaxial Graphene on SiC", *Appl. Phys. Lett.* 100 (2012), 241607
- 3. J. Eriksson D. Puglisi et al., "Adjusting the electronic properties and gas reactivity of epitaxial graphene by thin surface metallizations", *Physica B* 439 (2014), 105–108

D. Puglisi<sup>1</sup>, J. Eriksson<sup>1</sup>, J. Huotari<sup>2</sup>, M. Bastuck<sup>1,3</sup>, M. Andersson<sup>1,2</sup>, and A. Lloyd Spetz<sup>1,2</sup>

<sup>1</sup>Department of Physics, Chemistry and Biology (IFM), Linköping University, 58183 Linköping, Sweden <sup>2</sup>Microelectronics and Materials Physics Laboratories, University of Oulu, 90014 Oulu, Finland <sup>3</sup>Lab for Measurement Technology, Saarland University, 66123 Saarbruecken, Germany In the last 15 years, gas sensitive field effect transistors based on silicon carbide (SiC-FETs) have been extensively studied as reliable, high-performance, and cost-efficient chemical sensors for high- and room-temperature applications [1-3]. The choice of the catalytic materials for the sensing layer (gate contact) is crucial for optimizing the electrical and sensing performance of the FET sensor device. Metal oxides play an important role in many areas of chemistry, physics, and material science. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites [4]. Unfortunately, the majority of metal oxide based gas sensors suffer from low sensitivity and lack of selectivity due to the wide band gap, high resistivity, and low reactivity of the metal oxide. To solve these problems, the addition of a noble metal, such as iridium (Ir), to a semiconducting oxide is an effective mean to enhance detection of specific gas molecules.

In this work, we employ a combination of iridium and tungsten trioxide (Ir/WO<sub>3</sub>) as a new sensing layer of gas sensitive SiC-FETs to enable monitoring and control of hazardous gas molecules at ultra-low concentrations with high sensitivity and selectivity. The metal/metal oxide gate contact was deposited by combining pulsed laser deposition and DC magnetron sputtering. For the gas tests, benzene ( $C_6H_6$ ), which is the only aromatic hydrocarbon to be classified as known human carcinogen at any level of exposure, was used as the target gas at the low parts per billion (ppb) concentration range. The sensor performance was studied as a function of the operating temperature from 180 to 300 °C as well as of the electrical operating point of the device, i.e., linear, onset of saturation, and saturation mode. High sensitivity to 10 ppb  $C_6H_6$  was demonstrated during several repeated measurements. Measurements performed in saturation mode gave a sensor response up to 52 % higher than those performed in linear mode.

The demonstrated high sensitivity to benzene together with good stability and lifetime of the sensor device confirms  $Ir/WO_3$  SiC-FETs as a promising candidate for indoor and outdoor air quality monitoring and control applications. Further investigation will be done to investigate detection limit and selectivity.



**Figure 1**. (a) Cross sectional view of the n-channel depletion type SiC-FET used in this work, (b) Mounted sensor chip, (c) Sensor response to 10, 50, and 100 ppb of benzene ( $C_6H_6$ ) at 300 °C, in dry air, under operation at the linear (upp. signal) and saturation (bott. signal) regions of the transistor [5].

- [1] A. Lloyd Spetz et al., Sensor. Actuat. B-Chem. 70, 67-76 (2000).
- [2] D. Puglisi et al., J. Sens. Sens. Syst. 4, 1-8 (2015).
- [3] C. Bur et al., Sensor. Actuat. B-Chem. 214, 225-233 (2015).
- [4] S. Phanichphant, Proc. Eng. 87, 795-802 (2014).
- [5] D. Puglisi et al., ICSCRM 2015, Mat. Sci. Forum (submitted on 25 September 2015).