Nano and Photonics Mauterndorf 2017

22th – 25th March 2017

Mauterndorf/Salzburg
Austria

www.nanoandphotonics.at

AIT

HUMBOLDT-UNIVERSITÄT ZU BERLIN

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Unverkäufliches Exemplar,
hergestellt in der Druckerei der Humboldt-Universität zu Berlin.

Scope of Nano and Photonics:

The purpose of this event is to organize an informal meeting for those who are interested in photonic applications of modern nanotechnology.

One goal of this event is to create an European wide discussion platform for state of the art work in basic research done at the various universities as well as industrial based research and development. The location, Castle Mauterndorf, provides an ideal environment to discuss the entire range of topics without any pressure of time, particulary between the morning and afternoon sessions as well as in the evening.

Another goal is to give young students the possibility to present their work in the form of talks or poster presentations. With this orientation, the Nano and Photonics Seminar tries to continue with the long tradition of the Mauterndorf LASERSEMINARS.

Nanotechnology as a crossover technology enables application based product and system innovations in different industries and obtains worldwide importance in driving the economy. Nanophotonics is an area of nanotechnology of growing importance where breakthrough results in the development of devices and material systems are reported on a day-to-day basis. The seminars are spanning their topics from light emitting devices based on inorganic and organic semiconductors, over theoretical aspects of photonics to the point of photonic structures and structuring techniques.

Information and Registration

Mauterndorf

Mauterndorf is a little village about 100 km south of the city of Salzburg close to a well known ski resort (sea level 1100 m).

The closest train station is Radstadt
(on the Track Bischofshofen – Graz).

Conference Location

The sessions will take place in the festival room of the Castle Mauterndorf.

Program

The program will be in a way so that there will be enough free time for you to have informal chats and time for all kinds of winter sports (skiing, cross country skiing, hiking, ...).

Accomodation

There are several hotels, bed and breakfast pensions available for you (about 5 to 10 minutes from the castle). Please book your accomodation by yourself or via the local tourism agency:

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Registration

We would like to keep the costs for the organization as low as possible so that all costs will be covered by subsidies and sponsors and therefore we can refrain from charging fees for participants. For this reason, we ask all potential participants for a binding registration on the homepage (www.nanoandphotonics.at). If a participant would like to present a poster, he or she needs to submit an English abstract on the homepage after the registration process. Before the poster session, the poster will be presented in front of the plenum by the authors or presenters (1 slide and 1 min).

Program and Time Table

Wednesday, 22.3.2017 – Afternoon

13:30 – 14:00	**Registration**
14:00 – 14:10	**Opening by W. Knoll, F. Aussenegg, and E. List-Kratochvil and greetings by Mayor Wolfgang Eder**
14:15 – 15:00	**N. Halas** (Rice University, Houston/USA) *“Merging light with nanoparticles: artificial molecules, photocatalysis, cancer therapy, and solar steam”*
15:00 – 15:30	**U. Kreibig** (Rheinisch-Westfälische Technische Hochschule, Aachen/GER) *“Self-assembly of nano-bio-matter: The example of tobacco mosaic virus”*
15:30 – 16:00	**A. Trifonova** (AIT Austrian Institute of Technology, Wien/AUT) *“How nanotechnology changes the lithium battery developments”*
16:00 – 16:30	**Coffee**
16:30 – 17:00	**M. Wilkening** (Technische Universität Graz, Graz/AUT) *“A Microbattery with 3D patterned monocrystalline silicon”*
17:30 – 18:00	**S. Koller** (Montanuniversität Leoben, Leoben/AUT) *“New materials for advanced lithium ion batteries”*
18:00 – 18:30	**A. Pogany** (Bundesministerium für Verkehr, Innovation und Technologie, *Wien/AUT)* *“Forschungspolitik im Bereich Nanotechnologie und Photonik: Neues aus dem BMVIT”*

Thursday, 23. 3. 2017 – Morning (Plasmonic and Photonics)

09:00 – 09:30 **G. Strasser** (Technische Universität Wien, Wien/AUT)
“Remote gas sensing with quantum cascade systems”

09:30 – 10:00 **A. Hohenau** (Karl-Franzens-Universität Graz, Graz/AUT)
“Imaging localized surface plasmons with electron- and dielectric probes”

10:30 – 10:30 **T. Klar** (Johannes Kepler Universität Linz, Linz/AUT)
“Fluorescence from plasmonic nanoparticles”

Thursday, 23. 3. 2017 – Afternoon

16:00 – 17:45 **Poster presentation and poster session**

17:45 – 18:30 **O. Martin** (EPF Lausanne, Lausanne/CH)
“Using the phase of individual plasmonic nanostructures and metasurfaces to mold the flow of light”

Program and Time Line

Friday, 24. 3. 2017 – Morning (Plasmonic Sensing)

09:00 – 09:30 **G. Spoto** (University of Catania, Catania/IT)
“Nanoparticle-enhanced surface plasmon resonance imaging for the detection of genomic DNA: properties and role of functionalized gold nanoparticles”

09:30 – 10:00 **R. Hainberger** (AIT Austrian Institute of Technology, Wien/AUT)
“Silicon nitride waveguide based integrated photonic devices for medical diagnostics and other sensing applications”

10:00 – 10:30 **E. Maillart** (HORIBA Jobin-Yvon, Paris/FRA)
“Plasmonic in biosensing: principles, use, evaluation and coupling to other techniques”

10:30 – 11:00 **F. Wenzl** (JOANNEUM RESEARCH Forschungsgesellschaft mbH, Weiz/AUT)
“Micro- and nanotechnological approaches for performance improvements of phosphor converted LEDs”

Friday, 24. 3. 2017 – Afternoon (IR and Raman Spectroscopy)

16:00 – 16:30 **Coffee**

16:30 – 17:00 **S. Boujday** (Université Pièrre & Marie Curie, Paris/FRA)
“Gold nanoparticles as transducing and/or nanostructuration agents for Biosensors”

17:00 – 17:30 **M. L. de la Chapelle** (University Paris 13, Bobigny/FRA)
“Detection, identification and structural study of proteins by Surface Enhanced Raman Spectroscopy”

17:30 – 18:00 **B. Lendl,** (Technische Universität Wien, Wien/AUT)
“Advances in chemical sensing concept for gases and liquids basedon mid-IR Laser spectroscopy”

18:00 – 18:30 **Closing remarks**

Oral Presentation Abstracts

MERGING LIGHT WITH NANOPARTICLES: ARTIFICIAL MOLECULES, PHOTOCATALYSIS, CANCER THERAPY, AND SOLAR STEAM

N.J. Halas

Rice University, Houston/USA

Metallic nanoparticles, used since antiquity to impart intense and vibrant color into materials, have more recently become a central tool in the nanoscale manipulation of light. This interest has led to a virtual explosion of new types of metal-based nanoparticles and nanostructures of various shapes and compositions, and has given rise to new strategies to harvest, control, and manipulate light based on metallic nanostructures and their properties. As one begins to assemble metallic nanoparticles into useful building blocks, a striking parallel between the plasmons- the collective electronic oscillations- of these structures and wave functions of simple quantum systems is universally observed. Plasmon hybridization, the electromagnetic analog of molecular orbital theory, enables us to envision these structures as "artificial molecules". These nanoscale principles apply as we move from noble metals to more sustainable materials, such as Aluminum or carbon, that also support plasmon resonances. The inherently large optical absorption and scattering cross sections of these materials enable strong light-matter interactions and new functionalities: hot electron generation for photo-activated processes, and strong photothermal effects that can be used successfully for cancer therapy. Just as the principles of optics span a universe of applications, we find that the same photothermal effects responsible for nanoparticle-based cancer therapy can also be exploited for generating steam without the need to boil water. This effect provides a direct method for harnessing sunlight to drive physicochemical processes, such as distillation, without the need for conventional power sources.

SELF-ASSEMBLY OF NANO-BIO-MATTER: THE EXAMPLE OF TOBACCO MOSAIC VIRUS

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[1] Physical Institute I A, RWTH Aachen/GER
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Tobacco mosaic viruses (TMV) settle parasitically in many kinds of plants. They have very regular and uniform shapes of nano - rods, about 300 nm long and 18 nm wide. After proper preparation they can be extracted ex situ into special aqueous electrolytes and can be manipulated there.

In situ, i.e. in the cell (in their active, „living“ state) regular hexagonal crystals of TMV can be observed. After proper treatment, different kinds of well-ordered liquid-crystal structures of TMV can also be generated ex-situ in the electrolyte. They can grow larger than the natural crystals, but with random shapes. Most spectacular is the creation of Smectic B crystals. Due to the fact that the virus length amounts to about half of the wavelengths of the typical VIS range, these crystals exhibit strong lattice diffraction of visible light (in first diffraction order), and as a consequence, they show brilliant diffraction colours. In analogy to X-ray diffraction of inorganic crystals, optical diffraction experiments yield information about lattice parameters, crystallite sizes, etc. of the crystallites, which can be interpreted to learn about the underlying binding mechanisms and binding forces leading to the spontaneous formation of crystalline order, i.e. to spontaneous self-organization. Such crystals differ strongly from regular inorganic crystals. Irrespective of the extremely complex chemical structure of the single TMV, the mains of the process of self-arrangement can be described by the very simplifying physical model of the Derjaguin-Landau-Vervey-Overbeek-(DLVO) theory, i.e. by electric forces due to the surface charges, the virus can store in the electrolyte. They cause static Debye-Hückel repulsion which fights against the omnipresent Van der Waals attraction. If virus concentrations are sufficiently high, also entropic ordering contributes.

Two kinds of experiments will be presented in this report, concerning (i) the lyotropic behaviour (i.e. influences of the TMV concentration) and (ii) the thermotropic behaviour (i.e. dynamic relaxation).Both will demonstrate the dramatic differences of bio-matter compared to the inorganic solid state.However, there are close similarities to classical „soft-matter“ and liquid-crystal- systems.

HOW NANOTECHNOLOGY CHANGES THE LITHIUM BATTERY DEVELOPMENTS

A. Trifonova

AIT Austrian Institute of Technology, Wien/AUT

Energy storage is more important today than it has ever been before in our history. Future generations of rechargeable lithium batteries are required to power portable electronic devices, store electricity from renewable sources, and as a vital component in electric vehicles. To achieve the increase in energy and power density demand to meet the future challenges of energy storage, new nanomaterial chemistry is essential. Producing smaller particles, coating the particles or film surfaces, mixing the electrode material with e.g. conducting fibres, nanostructuring for short diffusion distances, or doping with various additives are some of the methods of improving the attributes of battery electrodes and electrolytes. Scientists must find appropriate ways for designing new nanomaterials with certain properties or combinations of properties that are required for use in lithium batteries.

In the last two decades, there has been much interest in the application of nanostructures (<100nm) to Li-ion battery design, e.g., A123 Systems has developed a lithium-iron-phosphate battery, and Altair Nanotechnologies implemented lithium-titanate as an electrode material. However, the use of nanotechnology in this field has some advantages and disadvantages. This work will show how “nano” can help/ add value in lithium-battery technology development by demonstrating appropriate examples.

A Microbattery with 3D Patterned Monocrystalline Silicon

M. Wilkening

Technische Universität Graz, Graz/AUT

Silicon is known as a negative electrode material for lithium-based batteries guaranteeing an outstanding high storage capaci-ty. In many cases nanostructured Si in various forms is used to buffer the extreme changes in volume upon lithiation. Therefore, monocrystalline Si, as it is omnipresent in semiconductor industry, is anticipated to be excluded from any usage in modern energy storage systems. We will show, however, that 3D structured monocrystalline wafer grade Si is excellently suited to be used in Si-based microbatteries that can directly implemented on the chip [1]. Besides electrochemical characterization of the device we used time-domain and high-resolution Li(7) and Li(6) nuclear magnetic resonance (NMR) spectroscopy to study local structures and the underlying lithium-ion dynamics [2]. The latter crucially determines overall performance of the device. The rechargea-ble microbattery developed benefits from its 3D patterned Si electrode and takes advantage of a remarkable cycling stability with high charge capacities. It allows for unexpectedly high peak currents considerably widen the field of applications. This field may include mobile devices, such as wireless sensors, that require an on-board power supply.

[1] M. Sternad, et al., Sci. Rep. 6 (2016) 31712

[2] A. Dunst, et al., J. Phys. Chem. C 119 (2015) 12183

NEW MATERIALS FOR ADVANCED LITHIUM ION BATTERIES

H. Kren, B. Fuchsbichler and S. Koller

Varta Micro Innovation, Graz/AUT

Since the large automotive companies go ahead with the electrification of the power train, also the demand for more powerful electrochemical energy storage systems is growing. However not only the automotive industry requires more powerful accumulators. In the area of mobile consumer electronics the proceedings of the last years are compensated by the rising energy demand of the devices., Accordingly the doubling of the energy density of lithium ion batteries, since they were commercialized by Sony in 1991, increased only imperceptibly the operating time.

The key to enter new application fields like the storage of solar energy, or wind power is the development of new materials. The specific energy of a lithium ion battery is given by the product of specific charge - more precisely the lithium storage ability per mass and the voltage difference of negative and positive electrode. As far as the negative electrode is concerned lithium and lithium compounds already represent the most reductive species of the electrochemical series. However carbonaceous materials that are used in state of the art lithium ion batteries are only able to store up to 1 lithium ion per 6 carbon atoms [1] in the case of fully crystalline graphite, which results in a quite low specific charge of 372 Ah·kg^{-1}. The application of metals or semi metalloids, which are able to store lithium under formation of an intermetallic phase represents a very promising alternative, whereat especially silicon is able to store up to 4.4 [2] lithium ions per silicon atom. Unfortunately the high capacity of the Si/Li-intermetallic phases is accompanied by large volume changes during lithium insertion and deinsertion, which leads to cracking and disintegration of particles and a fast capacity decay [3]. This, and of course also the mechanical instability of the SEI during the volume changes are problems that need to be solved for a successful implementation of this materials. An overview on possible strategies and approaches to overcome these

[1] Martin Winter, et al., Advanced Materials, 1998, 10, No. 10

[2] B.A. Boukamp, et al., Soc. Vol.128 No. 4, 1981, 725-729

[3] J.O. Besenhard et.al., Journal of Power Sources, 1997, 68, 87-90

RESEARCH POLICY IN NANOTECHNOLOGY AND PHOTONICS: NEW DEVELOPMENTS AT THE BMVIT

A. Pogány

Bundesministerium für Verkehr, Innovation und Technologie, Wien/AUT

Photonics and Nanotechnology can contribute to solve the major societal challenges of Europe with regard to energy efficiency, the ageing society, safety and security as well as the European knowledge society. These technologies are Key enabling technologies and the EC makes strong efforts to address these topics under H2020. Austria is well positioned in the photonics and nanotech area. The BMVIT has initiated plattforms with stakeholders from Research and Industry to network and to establish R&D-roadmaps. The BMVT runs a big Research programme called "Production of the Future" which includes Nanotechnology and Photonics. Within this programm R&D-projects between research and Industry can be funded. Austria is also taking part in several ERA-Nets in photonics and nanotechnology in order to help research and industry to cooperate with partners abroad. Additionally the BMVIT has established a strong cooperation with China with the goal to fund R&D-Projects between Austrian counterparts and the Chinese Academy of Science and the University of Shanghai.

REMOTE GAS SENSING WITH QUANTUM CASCADE SYSTEMS

R. Szedlak[1], A. Harrer[1], B. Schwarz[1], M. Holzbauer[1], J.P. Waclawek[1], D. MacFarland[1], T. Zederbauer[1], H. Detz[2], A.M. Andrews[1], W. Schrenk[1], B. Lendl[1] and G. Strasser[1]

[1] Technische Universität Wien, Wien/AUT
[2]Österreichische Akademie der Wissenschaften, Wien/AUT

Optical sensors for mid-infrared spectroscopy are widely used in industrial and environmental monitoring as well as medical and biochemical diagnostics. Conventional optical sensing setups include a light source, a light-analyte interaction region and a separate detector. We present a sensor concept, based on a bi-functional quantum cascade heterostructure, for which the differentiation between laser and detector is eliminated. This enables mutual commutation of laser and detector, simplifies remote sensing setups and facilitates a crucial miniaturization of sensing devices.

Liquid sensing utilizing bi-functional quantum cascade lasers/detectors (QCLDs) can be realized on a single chip [1]. Typical analyte interaction lengths for gas sensing are in the range of tens of centimeters or more and exceed the common semiconductor chip sizes. Our gas sensing approach incorporates surface-active lasers and detectors [2]. The latest demonstrator consists of two concentric ring QCLDs with second order distributed feedback (DFB) gratings on top of the waveguides. These DFB gratings facilitate vertical light emission [3] and detection in the biased lasing and unbiased detector configuration, respectively. The two rings emit at two different wavelength, which provides room temperature lasing and detection of two wavelengths monolithically integrated on the same chip.

[1] B. Schwarz, et al., Appl. Phys. Lett. 107 (2015) 071104
[2] A. Harrer, et al., Scientific Reports 6 (2016) 21795
[3] R. Szedlak, et al., ACS Photonics 3 (2016)1794

IMAGING LOCALIZED SURFACE PLASMONS WITH ELECTRON- AND DIELECTRIC PROBES

A. Hohenau[1], F.P. Schmidt[1], M. Krug[1], G. Schaffernak[1], V. Leitgeb[3], A. Trügler[1], H. Ditlbacher[1], U. Hohenester[1], F. Hofer[2] and J.R. Krenn[1]

[1] Karl-Franzes-Universität Graz, Graz/AUT
[2] Technische Universität Graz, Graz/AUT
[3] Materials Center Leoben Forschung GmbH, Leoben/AUT

Localized surface plasmons (LSP) - the optical resonances occuring on metallic nanoparticles - lead to surface confined enhancement of the electromagnetic light fields. This property makes them important for applications and research on bio-chemical sensing or sub-wavelength photonics. Imaging of LSPs with high spectral and spatial resolution is therefore crucial, but remains a challenge for nanometric resolution and probe influence. Electron energy-loss spectroscopy (EELS) in a transmission electron microscope is now able to offer the most detailed view to the optical properties of metal nanoparticles, which we demonstrate for an individual plasmonic nanoparticle [1].

Although the unperturbed LSP properties are best imaged by TEM-EELS, for biochemical sensing applications the influence of the probe itself has to be considered. Imaging techniques based on lithography [2] or a scanning probe [3] are the method of choice for this purpose. We will demonstrate this on two simple examples of induced LSP resonance shifts.

[1] F.P. Scmidt et al., Nano Lett. 16 (2016) 5152
[2] V. Leitgeb et al., Nanoscale 8 (2016) 2974
[3] M. Krug et al., Nanoscale 8 (2016) 16449

FLUORESCENCE FROM PLASMONIC NANOPARTICLES

T.A. Klar

Johannes Kepler Universität Linz, Linz/AUT

Plasmons are apt to substantially improve the quantum efficiency of the intrinsic luminescence from gold stemming from the recombination of d-band holes with sp electrons [1]. We have observed an anticorrelation of the intensity of the gold luminescence with the intensity of the hot spots between two gold nanoparticles [2]. Further, we found that three dimensionally percolated gold nanosponges, while showing highly polarized scattering spectra [3], produce much less polarized luminescence spectra [4].

[1] E. Dulkeith, et al., Phys. Rev. B 70 (2004) 205424
[2] D. Sivun, et al., Nano Lett. (2016)
[3] C. Vidal,et al., ACS Photonics 2 (2015) 1436
[4] C. Vidal, et al., in preparation.

USING THE PHASE OF INDIVIDUAL PLASMONIC NANOSTRUCTURES AND METASURFACES

O.J.F. Martin

Swiss Federal Institute of Technology Lausanne, Lausanne/CH

Plasmonic nanostructures are very well known for the strong optical field they provide, which is instrumental to techniques such as surface enhanced Raman spectroscopy. It is however often overseen that at the plasmon resonance, the phase of the electromagnetic field experiences extremely rapid variations. In this presentation, I will first review this phenomenon and show how plasmonic nanostructures and metasurfaces can be engineered in order to produce very significant phase shifts, much larger than the $\pi/2$ phase shift associated with a classical harmonic oscillator. The spectral variation of this phase shift can be extremely rapid, leading to the phenomenon of phase bifurcation. This is the case for example in Fano-resonant plasmonic nanostructures, which can be incorporated into metasurfaces to design a system that can route different colors into different directions, as will be demonstrated experimentally. I will then study the case when a plasmonic nanostructure supports several optical resonances and show that the phase between these different modes determines the overall response of the structure. In the case of a T-shaped antenna, that supports both dipolar and quadrupolar resonances, it is possible to engineer the antenna response in a way such that it twists the emission pattern from fluorescent molecules placed at the vicinity of the antenna, resulting into multipolar circularly polarized fluorescence, in spite of the fact that fluorescence is normally dipolar and linearly polarized. Remarkably, this achiral metasurface is able to split fluorescence light into opposite handedness, as can be measured in back-focal plane of an optical microscope.

NANOPARTICLE-ENHANCED SURFACE PLASMON RESONANCE IMAGING FOR THE DETECTION OF GENOMIC DNA: PROPERTIES AND ROLE OF FUNCTIONALIZED GOLD NANOPARTICLES

R. D'Agata, M.C . Giuffrida, N. Bellassai,
A.M. Aura, M. Calcagno, C. Valenti and G. Spoto

Università di Catania, Catania/IT

Standard methods for the detection of nucleic acids exploit the enzymatic amplification of sequences to be identified to achieve a high level of sensitivity. The amplification step introduces constraints and drawbacks in the assays. For instance, PCR suffer from artifacts generated by sample contamination and recombination between homologous regions of DNA.

Advanced methods for genomic DNA and RNA detection are requested to operate with high selectivity, multiplexed capability and ultrasensitivity. In this context, efforts have been made to identify innovative PCR-free protocols for DNA detection [1]. Most of such protocols exploit strategies for signal amplification based on the use of enzymes or metallic nanostructures. In particular, gold nanoparticles have been used to achieve the ultrasensitive detection of DNA [2].

Possibilities offered by nanoparticle-enhanced surface plasmon resonance imaging (SPRI) [3, 4] in the detection of non-amplified human genomic DNA [5, 6] will be discussed in the context of applications to cancer early diagnosis, oncology follow-up and prenatal non-invasive diagnosis [7]. The characteristics of functionalized nanoparticles useful for the effective nanoparticle-enhahnced SPRI detection of genomic DNA will be discussed with specific attention to streptavidin-coated gold nanoparticles. In particular, emphasys will be given to the role played by biotinilated oligonucleotides in the stabilization/destabilization of the streptavidin-capped nanoparticle dispersions.

[1] G. Spoto, Detection of Non-Amplified Genomic DNA, Springer, 2012.
[2] L. M. Zanoli, et al., Anal. Bioanal. Chem. 402 (2012) 1759
[3] G. Spoto, et al., J. Phys. Chem. Lett. 3 (2012) 2682
[4] R. D'Agata, et al., Anal. Bioanal. Chem. 405 (2013) 573
[5] R. D'Agata, et al., Biosens. Bioelectron. 25 (2010) 2095
[6] R. D'Agata, et al., Anal. Chem. 83 (2011) 8711
[7] N. Bellassai, et al., Anal. Bioanal. Chem. 408 (2016) 7255

SILICON NITRIDE WAVEGUIDE BASED INTEGRATED PHOTONIC DEVICES FOR MEDICAL DIAGNOSTICS AND OTHER SENSING APPLICATIONS

R. Hainberger

AIT Austrian Institute of Technology, Wien/AUT

During the past two decades research and development on silicon photonic components has been primarily driven by optical data- and telecommunication. Activities therefore have been focused on the telecom wavelength regions of 1.55 µm and 1.31 µm with silicon-on-insulator (SOI) material forming the waveguide layer. Recently, there is an increasing interest to apply silicon photonic devices also to sensing applications in a wide range of fields. Among these fields, medical diagnostics represents a particularly relevant topic in view of ever increasing health care costs in an aging society. This opens up a strong potential for integrated silicon photonic sensing devices operating in the visible and < 1.1 µm near infrared region. We present our research activities on the development of CMOS-compatible photonic integrated circuits using silicon nitride waveguides fabricated by low-temperature plasma enhanced chemical vapor deposition (PECVD). CMOS compatibility allows for monolithic co-integration with silicon photodiodes and CMOS based electronic read-out circuitry. We will show the design and practical implementation of various photonic building blocks required for the implementation of sensing devices. We will show results of optical biosensing experiments based on integrated Mach-Zehnder interferometers and demonstrate how inkjet material printing technology can be effectively used to locally deposit sensitive biomaterials and polymers onto the optical waveguide transducer components. Moreover, we will discuss the potential of this silicon nitride based photonic integration platform for the miniaturization of optical coherence tomography systems.

PLASMONIC IN BIOSENSING: PRINCIPLES, USE, EVALUATION AND COUPLING TO OTHER TECHNIQUES

E. Maillart

HORIBA Jobin Yvon S.A.S., Palaiseau/FR

In this talk, the principles of the Surface Plasmon Resonance (SPR) technique, the different ways of exciting plasmons, of measuring SPR shifts and the differents kind of plasmons will be briefly described. I will then describe the principle of biosensing with SPR, illustrating its advantages and its limitations based on the example of Horiba's XelPleX instrument. Knowing what we want to measure, it can be important to know how to evaluate the performances of instruments and to compare them, using sensitivity, LoD (Limit of Detection), FoMs (Figure of Merit) and other more or less useful quantities and units. Then, it's time to try to push a little bit further the performances of plasmonic biosensing with coupling to other techniques: propagating or localized plasmons coupled to fluorescence for lower concentration detection, or coupling detection with identification (MS, Raman,...) in order to get a fingerprint of the captured molecules are some possibilities. These various coupling will be illustrated by results from founded collaborative projects.

Finally, if there is still some time, the role of a company transforming technologies into solutions for the customer and all that this assertion is involving will be explained.

MICRO- AND NANOTECHNOLOGICAL APPROACHES FOR PERFORMANCE IMPROVEMENTS

F.P. Wenzl

JOANNEUM RESEARCH Forschungsgesm, Weiz/AUT

Even though the last years have witnessed an increasing market penetration of solid state lighting sources, light-emitting diode (LED) based lighting solutions have by far not reached all their potentials yet.

In this contribution two examples will be given to highlight the potentials of micro-and nanotechnologies to improve the performance of LED based lighting solutions, one example with respect to white light quality and the other one with respect to system integration. Common LED light sources rely on phosphor conversion, which is based on the combination of typically blue LED light and the excited emission from one or more phosphor materials embedded in a matrix material such as silicone. While the phosphor materials determine the spectral power distribution and the color rendering index, also the composition and arrangement of the CCEs within the LED package strongly influence the white light quality and the lumen output. For instance, a geometrical mismatch between CCE and LED die may result in an anisotropic color distribution, like a bluish center and a yellowish halo or vice-versa. The related concerns with respect to an LED's quality of white light still impede the replacement of traditional lighting sources with LED-based luminaires. In this contribution the use of nanophosphors in combination with printing technologies is shown to improve the preciseness in the deposition of phosphor layers with desired geometries.

The second example concerns the fabrication of ultrathin and lightweight direct-lit luminaires. These luminaries rely on the use of ultrathin freeform micro-optical elements with heights of below 100 µm, for which both design as well as fabrication strategies by UV-imprinting on plastic foils will be discussed.

GOLD NANOPARTICLES AS TRANSDUCING AND/OR NANOSTRUCTURATION AGENTS FOR BIOSENSORS

S. Boujday

Sorbonne Universités, Paris/FR

Biosensors enable rapid and fast monitoring of specific targets in numerous media among them body fluids, environmental matrixes, and food. The use of gold nanoparticles (AuNPs) in biosensors, either as transducers or as nanostructuration agents, has expanded during the last decade; the unique optical properties of AuNPs associated to their biocompatibility, ease of preparation, and cheap cost, make them indeed optimal candidates for signal transduction and/or enhancement.

We use gold nanoparticles to generate nanostructured substrates on planar surfaces and to read the molecular recognition phenomena by Localized Plasmon Resonance and/or color change. The first strategy requires mastering the assembly of gold nanoparticles on surfaces which is not a trivial task as the application necessitates a perfect control of coverage, dispersion and stability. We therefore explore the parameters governing the mechanism of assembly on Gold and Silicon substrates with a special focus on the nature of the terminal chemical function, the surface charge, the flexibility of the organic layer, and the protocol of deposition. Our optimizations allow us to adapt the final nanostructured substrates to the applications needs. In the second strategy, the modification of the environment of AuNPs by target adsorption leads to a change in the plasmonic band, which in extreme cases can generate a color change from red to blue making the molecular recognition detectable by naked eyes. Finally, we combine surface chemistry and nanoparticles color change to detect the presence of toxin in complex media.

DETECTION, IDENTIFICATION AND STRUCTURAL STUDY OF PROTEINS BY SURFACE ENHANCED RAMAN SPECTROSCOPY

M. Cottat[1], C. D'Andrea[2], R. Yasukuni[1], N. Malashikhina[3],
R. Grinyte[3], N.L. Guigui[1], B. Fazio[2], A. Sutton[1], O. Oudar[4],
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The development of reliable, sensitive and specific biosensors is a very active research field. Among all the technique, the Surface Enhance Raman Scaterring (SERS) is one of most sensitive and has been widely used for ultrasensitive chemical analysis down to single molecule detection [1]. Its field of applications now includes chemical-biochemical analysis, nanostructure characterization and biomedical applications. SERS is based on the exploitation of the optical properties of metallic nanoparticles and on the electromagnetic field enhancement localised at the vicinity of the nanostructures and created by the excitation of the Localized Surface Plasmon (LSP).

In order to control the LSP resonance position and to optimise the SERS signal, we have used some arrays of metallic nanoparticles, made by electron-beam lithography (EBL) [2-3]. The nanoparticles were in gold with different shapes: cylinders and rods. The optimization of the plasmonic nanostructures to improve their sensing properties such as their sensitivity and their easy manipulation is of first importance in order to develop a highly sensitive detection system. Several aspects can be considered in order to optimise the sensing performances: size and shape of the nanoparticles, nanoparticle coupling, molecular adhesion layer between gold nanostructures and glass [4].

First, by controlling all these aspects, we are able to produce a highly sensitive sensor. We have determined the sensor characteristics such as its detection limit and its selectivity. We have determined that such sensor could be highly sensitive by reaching some detection limits lowest than the pico-molar. In this work, we have applied this sensor to the detection and the identification of specific proteins and we have been able to detect some specific disease biomarkers in body fluids (serum, saliva) paving the way to the potential disease diagnosis.[5]

Second, a clear connection is established between a specific structure *of a protein and its function. In a given biological system, a protein exists as multiple modified forms and plays various roles, suggesting numerous conformations. In the present work, we studied the Syk protein, a kinase protein involves in the phosphorylation of others proteins and we established a link between its activation status and its conformation.*

Using SERS technique, we are able to detect and identify proteins even in complex fluids. Moreover, the spectral analysis allows a clear observation of the conformation modifications of the proteins due to their biological activity.

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ADVANCES IN CHEMICAL SENSING CONCEPT FOR GASES AND LIQUIDS BASED ON MID-IR LASER SPECTROSCOPY

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Mid-IR quantum cascade lasers have enabled the development of a set of new sensing schemes for liquids and gases which outperform established FTIR spectroscopy in many aspects, mainly due to their high power and the coherent nature of the emitted radiation.

This presentation will report on most recent advances in the measurement of proteins in aqueous solution as well as temperature and reaction induced protein folding reactions. Additionally, a new optical set-up based on a Mach-Zehnder interferometer will be discussed which allows, for the first time, to measure the real and the imaginary part of the complex refractive index of liquids in a single experiment.

Concerning gas sensing measurement approaches beyond classical absorption spectroscopy will be presented on the example of quantifying small molecules (CS2, SO2, CO) at trace gas concentrations. This will include dispersion spectroscopy, photoacoustic spectroscopy as well as photothermal interferometry.

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MAPPING THE LOCAL PARTICLE PLASMON SENSITIVITY WITH A SCANNING PROBE

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G. Schaffernak, J.R. Krenn and A. Hohenau

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Due to the confinement of localized surface plasmon resonances, molecular sensors with nanoscale sensing volumes can be realized. To detect low analyte concentrations, it is important to maximize the plasmonic response per probe molecule, therefore, the spatial distribution of the sensitivity is important. By scanning a plasmonic particle with a sharp dielectric tip and simultaneously monitoring the plasmon spectra we are able to measure the full spectral changes of a plasmonic resonance induced by a local dielectric perturbation. The spectra are fitted by Lorentzian functions to extract changes of the localized surface plasmon resonance wavelength, scattering intensity and spectral width. The data are plotted over the relative positions of dielectric tip and plasmonic nanoparticle. We find that the plasmon resonance shift is closely related to the near field intensity, in accordance with theoretical predictions. The position dependent increase and decrease of the total scattering cross-section of the combined system can be explained by considering the interference of the dipolar fields of the nanoparticle and the tip. Finally, a change in plasmon linewidth is related to a change in plasmon damping caused by the tip. The possibility to perform local refractive index sensitivity measurements is useful for the development of future plasmonic bio-sensors.

OPTIMISATION OF THE SERS SIGNAL FROM GOLD NANOCYLINDERS ON ITO SUBFILM SUBSTRATE PLASMONIC AND SURFACE ENHANCED RAMAN SCATTERING STUDIES OF GOLD NANOCYLINDERS ON ITO SUBFILM SUBSTRATE

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Gold nanostructures deposited on ITO thin film exhibit some specific optical properties with the observation of localised surface plasmon (LSP) as well as Bragg modes where the propagating and localized modes are resonantly coupled to the array periodicity [1].

To have a better understanding of such SERS substrate, LSP resonance and of the SERS studies have been performed on gold nanocylinders arrays on thin ITO subfilm substrates. The plasmonic nanostructures are composed of 50nm height nanocylinder of diameters from 50 to 250 nm with a periodicity from 350 to 500 nm. These nanodisks are deposited by electron beam nanolithography on a sublayer of ITO on a glass substrate. The position of the LSPR peaks can be easily tuned on a large range of the visible spectrum by using these different configurations of sizes and periods of the nanodisks. We noticed a shift of the Wood's anomaly due to the coupling between the nanocylinders and the arrays itself and leads to a behavior study of the different propagation modes of the plasmonic nanostructures.

We also investigated the SERS response of BPE molecules under a normal excitation wavelength of 633 nm, 660 nm and 785 nm and studied their maximum intensities according to the plasmonic resonance peak. We propose to determine the influence of the geometrical parameters of the substrate on the LSP resonance and on the SERS to be able to optimise both properties and to provide the best susbtrate. Finally, this results obtained on ITO subfilm subtrate allowed us to find the optimum structure to enhance the Raman footprint for low concentration of BPE and used to compare with gold nanostructures deposited on gold thin film.

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THE AUTHORS ACKNOWLEDGE THE INTERNATIONAL ANR PROJECT NANOBIOSENSOR (ANR-15-CE29-0026) FOR FINANCIAL SUPPORT.

OPTIMISATION OF THE SERS SIGNAL FROM GOLD NANOCYLINDERS ON GOLD SUBFILM SUBSTRATEPLASMONIC AND SURFACE ENHANCED RAMAN SCATTERING STUDIES OF GOLD NANOCYLINDERS ON GOLD SUBFILM SUBSTRATE

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Gold nanostructures deposited on gold thin film exhibit some specific optical properties with the observation of localised surface plasmon (LSP) as well as Bragg modes where the propagating and localized modes are resonantly coupled to the array periodicity [1]. It has already been demonstrated that the surface enhanced Raman scattering (SERS) is higher in this configuration compared to the one recorded for gold nanostructures on dielectric substrates (glass or ITO) [2,3].

To have a better understanding of such SERS substrate, LSP resonance and of the SERS studies have been performed on gold nanocylinders arrays on thin gold subfilm substrates. The plasmonic nanostructures are composed of 50nm height nanocylinder of diameters from 50 to 250 nm with a periodicity from 350 to 500 nm. These nanodisks are deposited by electron beam nanolithography on a 20 to 50 nm thick sublayer of gold evaporated on a glass substrate. The position of the LSPR peaks can be easily tuned on a large range of the visible spectrum by using these different configurations of sizes and periods of the nanodisks. We noticed a shift of the Wood's anomaly due to the coupling between the nanocylinders and the arrays itself and leads to a behavior study of the different propagation modes of the plasmonic nanostructures. We also investigated the SERS response of BPE molecules under a normal excitation wavelength of 633 nm, 660 nm and 785nm and studied their maximum intensities according to the plasmonic resonance peak. We propose to determine the influence of the geometrical parameters of the substrate on the LSP resonance and on the SERS to be able to optimise both properties and to provide the best susbtrate. Finally, a comparaison with results obtained on ITO subfilm subtrate allowed us to find the optimum structure to enhance the Raman footprint for low concentration of BPE.

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THE AUTHORS ACKNOWLEDGE THE INTERNATIONAL ANR PROJECT NANOBIOSENSOR (ANR-15-CE29-0026) FOR FINANCIAL SUPPORT.

NEAR-FIELD MICROSCOPY AND SPECTROSCOPY AT THE NANOSCALE

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New nanoscale materials are of growing interest for plasmonic and photonic applications due to their unique characteristics and their broad application range. Their properties are highly sensitive to the composition, the shape, and the local environment, but can also strongly vary on the nanometer length scale, a fact that can severely limit the macroscopic performance and usability in new devices. Thus, analysis tools are needed, which are capable of measuring the optical and electronic properties on the 10-nanometer length scale.

This poster presents the latest scientific achievements in the field of near-field microscopy using our neaSNOM scattering-type scanning near-field optical microscope. The neaSNOM combines the resolving power of near-field microscopy with the analytical aspects of FTIR spectroscopy to perform imaging and spectroscopy with unprecedented spatial resolution. This technique has already proven itself vital for modern nanoscopy and has been used in applications such as chemical identification [1], free-carrier profiling [2], or the direct mapping of propagating plasmons [3,4] and polaritons [5]. The neaSNOM microscope can be used to directly trace the nanoscale optical properties of e.g. single layer materials within the entire visible, near-infrared, mid-infrared, up to THz spectral range. Key information like the local conductivity, intrinsic electron-doping, absorption or the complex-valued refractive index can now routinely be extracted from these measurements.

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NEAR FIELD ENHANCEMENT LOCALIZATION ON PLASMONIC GRATINGS

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Surface Enhanced Raman Scattering (SERS) is a versatile technique based on the exploitation of the near field enhancement produced at the vicinity of metallic nanostructures through their spe-cific optical properties (plasmon excitation, lightning rod effect...). SERS got a growing interest, especially due to the huge enhancement of the Raman signal of molecules that has paved the way of the single molecule observation and with the apparition of new lithography techniques that enables fabrication of reproducible SERS substrates. With such substrates, it is thus possible to control and tune precisely the optical properties of metallic nanostructures as well as their near field enhancement efficiency. SERS method is intensively applied in the detection field in order to observe chemical or biological species at very low concentrations. In this framework, it is of first importance to be able to achieve a better understanding of the near field enhancement and to op-timise it to reach limit of detection as low as possible. One of the main parameters that limits such optimisation is the non homogeneous distribution of the field around the nanostructure and the localization of the highest field enhancement. Several simulations methods, such as Finite element method (FEM), discrete dipole approximation (DDA) or finite-difference time-domain (FDTD), can be used to predict those properties and thus help to further optimize them. Those methods are very accurate when it comes to simulate any properties of the plasmonic structure as extinction, scattering or average electromagnetic field enhancement at the surface of the structures. They can also provide some maps of the near field distribution. However this generated near field distribu-tion is less understood and hardly measurable since few experimental methods exist to measure it actually.

SERS was used to determine the effective near-field enhancement and its localisation. With elec-tron beam lithography, specific samples of gold nanodisks capped or not with silica layers were produced. These latter ones allow us to block the accessibility of the molecules to the nanostruc-ture surface and as a consequence to the enhanced field. We are thus able to compare the SERS signal produced by the nanodisks with or without silica layers and to provide information on the

DIRECTIONAL SURFACE ENHANCED RAMAN SCATTERING ON GOLD NANO-GRATINGS

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Directional extinction spectrum and SERS intensity were investigated for 1D and 2D gold nanostructure arrays deposited on flat gold layer (fig. 1b): three different nanolines gratings with different periods (300, 400 and 500 nm), deposited on a 30 nm gold film and two arrays of nanodisks with diameter of 220 nm and with a period of 400 nm. The angle of incident light was varied by tilting the substrates. Extinction spectrum of both arrays showed other intense resonance bands apart from the localized surface plasmon band of the nanostructures. These bands are red-shifted with increasing incident angle and systematic extinction analysis of different grating periods revealed that the observed bands are due to an excitation of propagating surface plasmon on flat gold surface, which fulfills Bragg condition of the arrays (Bragg mode). Direc-tional SERS measurements were performed at three different wavelengths (633, 660 and 785 nm). They demonstrated the SERS intensity increased up to an order of magnitude, when Bragg mode Plasmon is excited. Hybridized numerical calculations of Finite Element Method and Fourier Modal Method also justified the presence of Bragg mode Plasmon and illus-trated that the enhanced electric field is particularly localized around the nanostructures regardless of their size.

DESIGN OF GOLD NANOPARTICLE-BASED COLORIMETRIC BIOSENSORS FOR STAPHYLOCOCCAL

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Staphylococcal enterotoxin A (SEA) is the most common toxin in staphylococcus-related food poisoning. The development of an accurate, convenient, and rapid assay for SEA is therefore highly desirable for addressing food quality and safety concerns.

Gold nanoparticles (GNPs) have been extensively employed as colorimetric biosensing platforms due to their localized surface plasmon resonance (LSPR). This band is sensitive to local changes and to the dispersion state of the nanoparticles: aggregation leads to a bathochromic shift of the LSPR band.

With this in mind, two types of GNPs bioconjugates were designed using covalent immobilization of anti-SEA antibody and SEA to GNPs. Two different assay strategies have been developed. The detection was monitored by the LSPR peak shift in the UV–Vis extinction spectrum resulting from the change of local refractive index induced by the immunological reaction between the SEA (free (a)/ immobilized (b)) and antibody-GNPs. Various concentrations of toxin were assessed.

In both cases, there was a direct correlation between Plasmon shift and SEA concentration. For strategy (a), the saturation was reached without aggregation even after several hours. However, with SEA conjugated to GNPs, NP aggregation and precipitation occurred. Furthermore, an increase in particle size from 14 nm (initial GNPs) to higher size after conjugation and recognition was observed by dynamic light scattering (DLS).

These results are reasonable since for (a), the interparticle distance is substantially greater than the particle diameter, but as in (b) the interparticle distance decreases to less than the particle diameter, the GNPs aggregate.

The colorimetric immunosensor described herein provides an attractive alternative for the detection of SEA and other toxins in the ng/mL range by standard laboratory equipment and even by the naked eye.

USING ELECTROSTATIC FORCE MICROSCOPY TO MAP BIOPHYSICAL AND BIOCHEMICAL PROCESSES AT HIGH RESOLUTION

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Many, highly important, fundamental biological processes, such as enzymatic reactions, posttranslational protein modifications, or DNA hybridisation, manifest themselves in form of an alteration of the electrostatic charge of the molecules involved. Such charges are usually determined by bulk measurements, e.g., dynamic light scattering or titration. Probe-type methods derived from Atomic Force Microscopy (AFM) could be employed to map surface charges of biomolecular structures with a much higher degree of resolution and sensitivity.

Here, we provide an overview of the application of Kelvin-probe Force Microscopy (KFM), a well-known electrostatic force microscopy method in the semiconductor field, to biological materials and highlight some of the issues and aspects to be considered, such as the relation between in-air and in-water measurements, the influence of tip-sample geometry and other factors.

We report on the influence of sample preparation on the KFM-signal and show first results of protein modification of collagen fibrils due to reaction with aldehydes. The latter can help us to understand better what happens in excessive protein glycation, a side-effect of diabetes, and, thus, could inform the development of better treatments of such a widespread medical condition.

MULTI-FREQUENCY KELVIN PROBE FORCE MICROSCOPY METHOD FOR CHARGE MAPPING WITHOUT DC-BIAS

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Kelvin Probe Force Microscopy (KPFM) [1] is well known for providing high spatial resolution maps of local surface charges. In the classical implementation of KPFM a sinusoidal voltage at frequency ω in combination with a DC-bias is applied to a conductive AFM-cantilever. This DC-bias is restricting some applications, which is addressed in this contribution. In classical KPFM a feedback controller continuously adjusts the DC-bias such that the ω-component of the resulting cantilever oscillation is zero. Due to this nullifying working principle the required DC-bias equals the surface potential in a quantitative way. However, applying a DC-bias is not applicable to every sample since some semiconductors, sensors or catalysts show a DC-bias dependence, and biomolecules often have to be studied in water (in vitro), where a DC voltage causes unwanted electrochemical reactions. To overcome these limitations, Open-Loop KPFM [2] has been introduced, which omits the DC-bias and its feedback controller and evaluates the cantilever oscillations resulting from the electric forces acting on the cantilever at multiple frequencies. Open-loop methods, however, require calibration and compensation factors, which are affected by random signal and environmental variations during a measurement. In this work a novel approach for KPFM at multiple frequencies is presented, which keeps all the benefits of a closed-loop nullifying method but does not need a DC-bias. By applying a second sinusoidal voltage between tip and sample with appropriate amplitude modulation in combination with a feedback controller the charge distribution can be measured without DC-bias. The working principle of this novel method is derived analytically and is proven with control experiments on different samples.

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Bio-UV-SPR: Exploring the UV Range for Water-Bound Analytes

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Surface plasmon resonance (SPR) has become an established technology for biomolecular interaction analysis and detection of chemical and biological species [1]. The majority of SPR biosensors utilize a sensor surface with a gold film or gold nanoparticles in order to probe captured target analytes from aqueous samples at wavelengths in the red or near infrared part of spectrum. In recent years, the usage of surface plasmons resonantly excited on aluminum has been explored in order to enable probing at lower wavelengths in blue and UV part of spectrum [2,3]. The optical detection at such wavelengths holds potential for increasing the SPR sensitivity through exploiting inherent absorption of detected species (e.g. protein absorption at about 200 and 280 nm) and offer means of the implementation of plasmon enhanced fluorescence [4-6], which can be used for direct detection of native DNA, proteins as well as e.g. various odorant binders [7,8].

The paper reports on the development of an aluminum grating-coupled SPR sensor. According to the knowledge of the authors, such type of detection with wavelength interrogation of SPR was utilized for the first time for in situ SPR observation of molecular binding events in aqueous environment at wavelength > 250 nm. It is worth of noting that such measurements are not possible for the more commonly used Kretschmann geometry relying on a silica prism which exhibits a too low refractive index [9].

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ACTIVE CONTROL OF ELECTRONIC/OPTICAL INTERFACE PROPERTIES IN HYBRID ORGANIC-INORGANIC SURFACE

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Research into organic electronic and optoelectronic materials and devices has received sustained interest over the past 40 years, owing to their low cost, light weight, flexibility, and ease of fabrication, and, despite their comparably low performance, several commercial products based on organic materials are now emerging. However, in order to reap the benefits of organic materials to the fullest, device architectures that exploit their advantages, rather than tolerate their shortcomings as inorganic analogues, are necessary in order to yield competitive devices, as well as to develop novel functions.

Since 2010, we have been exploring a novel photodetector architecture in which an insulating layer (I) is introduced between the photoactive semiconducting layer and one of the metal electrodes in a conventional Metal/Semiconductor/Metal (MSM) device [1]. While this additional layer in the so-called MISM device essentially blocks the DC current component, and is, therefore, not immediately applicable to solar cells, the resulting signal is in the form of an intense transient photocurrent peak of opposite polarity for light ON and OFF signals, which is suitable for modulated light signal detection. To date, such photodetectors, with bandwidths up to 1MHz operating at communication relevant wavelengths, could be fabricated, even for low mobility semiconductors [2], and with more optimized molecular design, higher speeds can be anticipated.

Furthermore, the use of ionic liquids (IL) as the insulating layer has significantly increased the responsivity of these IL-MISM devices to 272 mA/W, comparable to commercially available silicon photodiodes, with high stability and high reproducibility. The soft processing conditions and broad freedom of choice of each component allows for sensitive photodetection even for biological systems, here demonstrated for a photoactive protein film [3].

In this contribution, we explore the scope and limits of such devices, and propose future strategies for their continued improvement. Furthermore, we highlight the novel functionalities specific to this architecture, such as the operation under strong background *illumination, and the simultaneous detection of several modulated light sources [4].*

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PLASMONIC PARTICLES IN A GRATING – TRACING THE ORIGIN OF COLLECTIVE LATTICE RESONANCES

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Surface plasmon resonances of metal nanonparticles are a widely discussed topic with applications in, for example, sensors, lighting or photovoltaics. Plasmonic resonances depend on the shape and material used, as well as the environment the nanoparticles are placed in. When arranged in a lattice, these particles can interact with each other and therefore alter their neighbours resonance. These resonances due to mutual interaction are called collective lattice resonances (CLR) and show different appearances depending on their environment (symmetric or asymmetric, with or without waveguide). In case of an asymmetric environment the resonance peaks appear asymmetric, while in a symmetric environment and on a waveguide sharp peaks and dips are present.

There have been some studies on this subject, but none of them lead to a comprehensive understanding of the underlying physics yet. Here, we aim at a full characterization of CLRs by looking at the spectral behaviour of different grating constants, particle sizes and environments with

aluminum and silver as plasmonic materials. As a well known plasmonic material, silver has nevertheless the disadvantage of high damping in the blue wavelength range due to interband transitions. We thus include aluminium in our study, featuring low loss in the blue wavelenght range and revealing up to five lattice-induced coupling signatures in just one spectrum.

With a better knowledge of CLRs we enable a better understanding of the mechanisms of plasmonic gratings in applications like solar cells or LEDs.

THE ADVANTAGES OF ALUMINUM PLASMONICS ON THE PERFORMANCE OF ORGANIC LIGHT EMITTING DIODES

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While emitters based on thermally activated delayed emission (TADF) allow for a realization of OLEDs with an internal quantum yield close to unity, the issue of efficient light extraction and hence a high external quantum yield still represents a major obstacle on the path to highly efficient OLEDs. As a cost-efficient approach to overcome this bottleneck, in this contribution we discuss the integration of aluminum nanodisc arrays into solution-processed oLEDs. Tuning the sizes of the discs and the lattice constants allows a perfect overlap of the surface lattice resonances (SLRs) of the arrays with the respective emitters in the given dielectric media. Emission quenching of the emitters is avoided by a direct integration of the nanodiscs into the hole transport layers (HTL) of the OLEDs. A comprehensive discussion on the impact of the nanodisc arrays on the performance of phosphorescent OLEDs is given based on simulation, photoluminescence as well as electroluminescence studies.

DEVELOPMENT PROCESS OF GRID ELECTRODES FOR USE IN PRINTED (OPTO)ELECTRONICS

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Optoelectronic devices such as organic light emitting diodes (OLEDs) are mostly based on indium tin oxide (ITO) as the transparent electrode. ITO, however, is inherently limited due to its brittleness, expense and its low-throughput method of production. The relatively high conductivity (sheet resistance in the order of 5 Ω/□) is suitable for small area devices, but in larger scale, where higher conductivity is essential, it becomes a limiting factor. It is therefore desirable to use other approaches to replace ITO in order to address these concerns.

One of these is the printing of metal nanoparticle inks, such as Ag and Cu. Using inkjet printing, for example, allows direct-write material deposition, which requires no masks or lithographic pre-patterning of substrates, and which delivers high enough resolution for the printing of fine electrode structures. Inkjet-printing can also be upscaled and transferred to a roll-to-roll process for printed electronics.

However, there are a number of challenges when inkjet-printing metal nanoparticles – the typical feature height of printed structures of several 100 nm tend to exhibit a rough surface, which can lead to shorts in the device. Furthermore, the sintering temperature of the nanoparticle inks needs to be low (< 130 °C) in order to allow deposition and curing on transparent flexible substrates such as PET.

We therefore present the process development of a solution-processed electrode based on inkjet-printed Ag grids, by firstly reducing the printed line height < 100 nm by using UV-O3 surface treatment, and, secondly, embedding the inkjet-printed metal grids.[4] The completed ITO-free OLEDs show high efficiencies of up to 9.4 cd/A. Furthermore, we demonstrate a truly low-temperature sintering route for a Cu nanoparticle ink by using a reducing atmosphere of formic acid. The obtained layers exhibit a resistivity of down to 11 μΩ cm, being equal to 16% of bulk Cu conductivity, while also showing no noticeable increase in resistivity after five days under ambient conditions. The results highlight overall parameters for solution processing and implementing novel metal materials and architectures in printed electrodes.

ACTIVE CONTROL OF ELECTRONIC/OPTICAL INTERFACE PROPERTIES IN HYBRID ORGANIC-INORGANIC SURFACE

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Inorganic/organic hybrid devices combine the most important proprieties of their constituent, e.g. high-carrier conductivity and high-transparency of inorganic materials with tuneable properties of organic molecules such as specific light absorbance, intrinsic dipoles and isomeric configurations. In recent years, ZnO has gain interest as inorganic materials for fabrication of hybrid devices in which can be use as transparent conductive film (TCO) due to its wide band gap (i.e. transparency to visible light), electron acceptor nature with the additional benefit of been inexpensive, abundant and nontoxic.1

Solid knowledge has been obtained on controlling the energy level alignment in hybrid inorganic-organic systems using organophosphonate self-assembled monolayers (SAMs) as interlayer between the inorganic and organic materials. For instance, using SAMs with intrinsic dipole, the work function of ZnO can be tuned over a range of 1.5 eV, depending on the orientation and magnitude of the dipole moment of the molecule used to form the SAM2.

Among the different classes of organic molecules to modify TCO's properties, photochromic molecules have attracted increasing interest for the development of low-cost, easy-processing multifunctional devices, including photo-controlled thin-film transistors 3 and optical memories 4. Due to the photochromism, these molecules can switch reversibly between two independent isomeric states stimulated by light irradiation with different wavelengths.5 Switching between the two states fundamentally changes the electronic structure of these molecules, e.g. the optical gap and the molecular dipole moments. As a consequence, the molecular electron affinity and the ionization energy alter during photoisomerization.

In this contribution, we report on the successful fabrication of a SAM of photochromic diarylethene molecule with a phosphonic anchoring group on (Zn-terminated) ZnO. Via ultraviolet photoemission spectroscopy and kelvin probe we demonstrate the ability to optically modify and tune the ZnO carrier injection barriers.

INVESTIGATION OF RESONANT ENERGY TRANSFER BETWEEN AN INCAN/GAN SINGLE QUANTUM WELL AND A POLY(P-PHENYLEN-VINYLEN) POLYMER OVER LAYER

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Nowadays, gallium nitride (GaN) pumped phosphor based white light emitting diodes (LEDs) have surpassed compact fluorescent lamps in terms of luminous efficacy. Despite the improvement of these LEDs over the last years some challenges still remain. Among these are light out coupling from the quantum wells, efficiency droop at high current densities or long radiative decay of the yellow phosphor [1]. It was shown that some of these challenges can be tackled by structuring the LED into nanopillars [2] as well as utilizing Förster-type non-radiative resonant energy transfer to an organic acceptor [3] instead of radiative pumping of a phosphor.

In this study we investigate non-radiative energy transfer from a single InGaN/GaN quantum well to a thin CN-ether-PPV polymer over layer by means of time-resolved and CW photoluminescence (PL) spectroscopy. Förster-type energy transfer in the hybrid inorganic-organic system is indicated by PL excitation measurements as well as a shortening of the quantum well PL decay time. In order to quantify the contribution of non-radiative energy transfer compared to radiative pumping, the measurements were performed at varying temperature and excitation intensity. By exploiting the faster PL decay time of the polymer compared to conventionally used phosphors, the switching speed in such a hybrid inorganic-organic device can be enhanced.

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HYBRID CHARGE-TRANSFER EXCITONS AT METAL OXIDE/ORGANIC INTERFACES

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Metal oxides are attracting significant interest as candidates for hybrid photovoltaic devices. By combining inorganic with organic semiconductors, hybrid devices offer the potential to exceed the optoelectronic and photonic performance that can be achieved by the individual materials.

We built hybrid solar cells from transparent metal oxides and conjugated polymers. In particular, we studied the type-II interfaces of ZnO, ZnMgO and SnO2 with the poly(3-hexylthiophene) (P3HT). Our studies provide evidence for the formation of hybrid charge transfer excitons (HCTE) across the hybrid interfaces. Infrared electroluminescence corresponds to the offset between the conduction band of the metal oxide and the HOMO of the polymer. Band gap engineering by varying the Mg content in ZnMgO allows tuning of the HCTE energy to conduct a systematic study of charge generation and recombination.

The impact of the HCTE on photovoltaic parameters like the open circuit voltage and short circuit current is demonstrated.

LOWEST COST MULTILAYER ORGANIC LIGHT-EMITTING DIODES WITH A COPPER THIOCYANATE HOLE-TRANSPORT LAYER

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Flexible, individually adjustable semiconductor elements such as OLEDs have the potential in the future to complement or replace components made from silicon. Especially the possibility to use simple processing methods from solutions like spincoating or inkjet printing increases the attractiveness of such technologies. However, suitable materials are required which are not only easy to process, but also incur the lowest possible costs. In order to meet these requirements, it is necessary to replace cost-intensive materials like PDOT: PSS with cheaper alternatives.

For the layers studied here, the top contact and the hole transport layer (HTL), a high transparency, a good conductivity and in particular for the HTL, a large bandgap is desirable.

In this work, a copper thiocyanate (CuSCN) HTL processed from solution as well as a top contact patch made from doped zinc oxide (X:ZnO) are presented. Both materials allow us also to process stable on air.

TUNING LIGHT TRAPPING IN ORGANIC PHOTOVOLTAICS

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The power conversion efficiency of solar cells (PCE) is significantly influenced by the short current density (JSC) and the so called fill factor (FF). In order to obtain devices with a high PCE a high short circuit current and a high fill factor are required. One of the approaches to achieve these goals is to harvest additional light modes by engineering the geometry of particular layers in the solar cell such as the electrode and the active layer.

In this study, the effect of corrugated layers on the device performance was investigated. For this purpose, bulk heterojunction solar cells based on P3HT:PCBM as photoactive material were fabricated. Our results demonstrate that the introduction of the corrugation into the photoactive layer utilizing a hot embossing technique result in improved external quantum efficiencies (EQE) of the organic solar cell for specific wavelengths and polarization angles of incident light. As compared to pristine devices, the corrugated ones show enhancements of up to 200% in the EQE spectra at narrow wavelength ranges for a photoactive layer thickness of 100nm. Increasing the photoactive layer thickness to 250 nm lead to the emergence of additional light modes trapped inside the photoactive layer that improve the spectral current densities in wider wavelength ranges. These findings pave the way for further applications and a better understanding of light-management in organic photovoltaics.

DARK PLASMON MODES REVEALED BY ELECTRON ENERGY-LOSS SPECTROSCOPY AND CATHODOLUMINESCENCE

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Plasmonic nanostructures enable the concentration of light to the deep subwavelength regime and, thus, are the topic of intense fundamental and application oriented research. Electron energy-loss spectroscopy (EELS) in a transmission electron microscope (TEM) became a powerful technique as it enables to map the full modal spectrum of plasmon eigenmodes with unprecedented high spatial resolution [1,2]. Beside EELS, Cathodoluminescence (CL) has also recently been used to gain information about the optical response taking advantage of the same high spatial resolution in a TEM [3]. While it is stated that EELS is linked to the full photonic local density of states (LDOS), the CL signal is related to the radiative LDOS [4].

In this work we present a combined EELS/CL study of plasmon eigenmodes on silver nanodisks, using fast electrons in a TEM. In particular we compare the differences of the EELS and CL response using experimental and simulated data. Precise variation of the disk size is achieved by means of electron beam lithography.

There exist so called dark modes, which are „invisible“ to photons but „visible“ to electrons, and therefore can be measured with EELS but not with light [5]. Here we discuss how dark these dark modes are comparing EELS and CL. In particular, radial breathing modes were predicted to be dark modes [5], although we will show how comparison between EELS and CL can mitigate this statement. Additionally, limitations for the theoretical predictions will be discussed, when the particle size is increased and therefore retardation effects become more important.

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This research has received funding from the European Union within the 7th Framework Program [FP7/2007-2013] under Grant Agreement no. 312483 (ESTEEM2). We acknowledge support by the Austrian Science Fund FWF under project P21800-N20, the SFB F49 NextLite, and NAWI Graz.

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