Nano and Photonics
Mauterndorf 2019

20th – 22nd March 2019

Mauterndorf, Salzburg
Austria

www.nanoandphotonics.at

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

Conference Content

Scope of Nano and Photonics

The purpose of this conference 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 a 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. Therefore, the Nano and Photonics seminar continues with the long-standing tradition of the Mauterndorf LASERSEMINARS.

Nanotechnology as a crossover technology enables application-based product and system innovations in different industries and has obtained 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 spanned acros a wide range of topics from light emitting devices based on inorganic and organic semiconductors, through theoretical aspects of photonics to photonic structures and structuring techniques.

Information and Registration

Mauterndorf

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

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, etc.).

Accomodation

There are several hotels, and bed and breakfast 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, 20. 3. 2019 – Afternoon

13:30 – 14:00	**Registration**
14:00 – 14:30	**Opening by F. Aussenegg, E. List-Kratochvil and greetings by Mayor of Mauterndorf Herbert Eßl**
14:30 – 15:00	**B. Hecht** (Universität Würzburg, Würzburg/GER) *“Strong Plasmon-Matter Coupling, Nano-Spin Optics, Electro Plasmonics: A Review of Recent Developments”*
15:00 – 15:30	**A. Pogany** (Bundesministerium für Verkehr, Innovation und Technologie, Wien/AUT) *“Austrian Research Policy in Nanotechnology and Photonics”*
15:30 – 16:00	**Coffee**
16:00 – 16:30	**O. Hofmann** (Technische Universität Graz, Graz/AUT) *“Polymorphism in the Nanoworld: A Computational Perspective”*
16:30 – 17:00	**R. Heer** (AIT Austrian Institute of Technology, Wien/AUT) *“Printing Electrochemical and Photonic Nano- and Biosensors for Analyzing Liquid Biopsy”*
17:00 – 17:30	**M. J. Bojdys** (Humboldt-Universität zu Berlin, Berlin/GER) *“Where Exactly Lies the “Goldilocks Zone” for the Ideal Polymer Semiconductor?”*
17:30 – 18:00	**P. Dombi** (Wigner Research Centre for Physics, Budapest/HUN) *“Plasmon-Plasmon Coupling Probed with Sub-nm Sensitivity”*

Program and Time Line

Thursday, 21. 3. 2019 – Morning

09:00 – 09:30 **J. Krenn** (Karl-Franzens-Universität Graz, Graz/AUT)
"Probing Radiative and Dark Plasmons with Electrons "

09:30 – 10:00 **J. Dostalek** (AIT Austrian Institute of Technology, Wien/AUT)
"Plasmonic Amplification of Optical Spectroscopy Signals for Ultrasensitive Biosensing"

10:00 – 10:30 **W. Fritzsche** (Leibniz Institute of Photonic Technology, Jena/GER)
"Sensing and Manipulating Molecules Using Plasmonic Nanoparticles"

10:30 – 11:00 **Coffee**

11:00 – 11:30 **T. A. Klar** (Johannes Kepler University Linz, Linz/AUT)
"From Plasmonic Horizons and Plasmon Voltammetry"

11:30 – 12:00 **A. Schwaighofer** (Technische Universität Wien, Wien/AUT)
"Beyond FT-IR Spectroscopy: Latest Advancements in Laser-Based Mid-IR Spectroscopy for Analysis of Proteins"

Thursday, 21. 3. 2019 – Afternoon

15:30 – 17:30 **Poster presentations and poster session**

17:30 – 18:00 **G. Schitter** (Technische Universität Wien, Wien/AUT)
"Extending Nano-Mechanical and Electrical Measurement Modes in AFM"

18:00 – 18:30 **P. Mesquida** (King's College London, London/UK)
"Sugar Exposure Alters the Surface Charge of Collagen Fibrils on the Nanometre Scale"

Program and Time Line

Friday, 22. 3. 2019 – Morning

09:00 – 09:30	**T. Dimopoulos** (AIT Austrian Institute of Technology, Wien/AUT) *“Vacuum- and Solution-Processed Transparent Electrodes for Flexible Solar Cells”*
09:30 – 10:00	**F. Hermerschmidt** (Humboldt-Universität zu Berlin, Berlin/GER) *“Printed Organic Electronics – From Printed Copper to Perovskite Light Emitting Devices ”*
10:00 – 10:30	**F. Mathies** (Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin/GER) *“Utilizing Inkjet Printing for Organic/Inorganic Metal HalidePerovskite Optoelectronic Devices”*
10:30 – 11:00	**Coffee**
11:00 – 11:30	**D. Nees** (Joanneum Research Forschungsgesellschaft mbH, Weiz/AUT) *“Roll-to-Roll UV Nanoimprint Lithography for Large Area Manufacturing of Bionic Surfaces”*
11:30 – 12:00	**S. Kawata** (Osaka University and RIKEN, Osaka/ JPN) *“Plasmonics for Molecular Nano-Raman Imaging Beyond the Limits”*
12:00 – 12:30	**Z. Sekkat** (University Mohammed V, Rabat/MAR) *“Light-Fueled Molecular Machines Move Matter”*
12:30 – 12:45	**Closing remarks by W. Knoll**

Oral Presentation Abstracts

STRONG PLASMON-MATTER COUPLING, NANO-SPIN OPTICS, ELECTRO PLASMONICS. A REVIEW OF RECENT DEVELOPMENTS

B. Hecht

Universität Würzburg, Würzburg/GER

We are fabricating highly reproducible, detailed and precise plasmonic nanostructures from large but ultrathin monocrystalline gold platelets. I will review some recent experiments in which the enhanced structure quality plays a crucial role. In strong plasmon-matter coupling we exploit the ultrasmall mode volume of a plasmonic resonator fabricated at the apex of a scanning probe to achieve strong coupling to single quantum dots at ambient condition [1]. In nano-spin optics we study a plasmonic nano device based on two-wire transmission lines that is able to sort photons according to their spin. Its working principle bears some similarities to an electronic spin transistor [2]. In electro plasmonics we demonstrate pretty efficient light generation in a planar plasmonic antenna by utilizing inelastic electron tunneling over the antenna gap. It is now possible to direct the light emission by means of a Yagi-Uda design [3].

[1] H. Groß et al., Science Adv. (2018) 4.
[2] E. Krauss et al., arxiv:1812.03721 (2018).
[3] M. Ochs et al., in preparation (2019) 12.

AUSTRIAN RESEARCH POLICY IN NANOTECHNOLOGY AND PHOTONICS

A. Pogány

Federal Ministry for Transport Innovation and Technology, 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.

POLYMORPHISM IN THE NANOWORLD: A COMPUTATIONAL PERSPECTIVE

O. T. Hofmann

Technische Universität Graz, Graz/AUT

The electronic and photonic properties of a material are strongly governed by the atomistic structure it assumes in the solid state. This is a particular issue for nanotechnology applications, where the interactions within the active (organic) material and those at the interface to the substrate compete, leading to rich and diverse polymorphism. Since the different crystal structures are often very close in energy, the structure obtained in practice often depends strongly on the preparation condition.

Fist principle calculations can provide valuable insight into the properties of the material. However, since there are often millions of different possible polymorphs, these calculations are inherently dependent on foreknowledge of the atomistic structure of the thin film. At the same time, an experimental determination of the structure of thin films is difficult at best. Imaging technologies, such as STM, do not penetrate the top layer, inherently missing the atomistic structure beneath. At the same time, thin films often contain too little material to apply diffraction techniques.

In this contribution, we will show how machine-learning techniques can be exploited to determine possible interface and thin film structures. By enforcing a few simple, physically motivated rules, we can limit the search space and obtain a good overview over the properties not only of the best structure, but also many other energetically low-lying polymorphs and defect structures. Furthermore, this technique directly provides insight into the interactions within the molecules and at the interface, allowing us to tailor the potential energy landscape and, hopefully, design molecules with a propensity to crystallize in desired structures. Here, we demonstrate our ansatz for a number of systems, including acences and acencequinones on coinage metal surfaces.

PHOTONIC NANO- AND BIOSENSORS FOR ANALYZING LIQUID BIOPSY

R. Heer

AIT Austrian Institute of Technology, Wien/AUT

The usability of functional inks for the surface modification of microfluidic electrochemical and photonic biosensors is demonstrated. In detail, the modification of electrodes for electrochemical sensors and the sensing arms of Mach-Zehnder interferometer sensors with receptor molecules is shown. The surface modification for both sensing concepts is demonstrated by the measurement of Thrombin, BNP and CRP in liquid samples.

A novel inkjet printing based biofunctionalization concept of screen printed electrodes for the realization of electrochemical biosensors is presented. Gold graphene nanocomposites are tailored for selectively capturing biomolecules in liquids and serve as target specific inks. Aptamers and antibodies carrying redox labels act as both, transducers and amplifiers. The hybrid nanomaterials are attached onto surfaces of semi-finished graphite working electrodes by a novel bioinkjet printing technique.

To demonstrate the usability of inkjet printing processes for the functionalization of photonic sensors, an integrated four-channel silicon nitride (Si_3N_4) waveguide based Mach-Zehnder interferometric sensing platform, operating at a wave-length of 850 nm (TM-mode), is used.

The quantitative measurement of Thrombin, BNP and CRP in liquids is shown to demonstrate the proof of concept of this versatile, time saving and cost efficient functionalization method.

Finally, a novel lens less microscopy technology for imaging cellular features is introduced.

WHERE EXACTLY LIES THE "GOLDILOCKS ZONE" FOR THE IDEAL POLYMER SEMICONDUCTOR?

Y. Kochergin, J. Huang, R. Kulkarni, and M. J. Bojdys

Humboldt-Universität zu Berlin, Berlin/GER

Chemically resistant covalent bonds and a "functional" surface area are flaunted as the main advantages of the next generation of covalent organic frameworks, of conjugated microporous polymers and of polymers of intrinsic microporosity, but there are few case studies that make genuine use of both these properties simultaneously.

There is an on-going debate in the materials science, and catalysis communities about "What makes an ideal heterogeneous photocatalysts for water splitting?" [1], and it is a question of paramount importance for a truly sustainable hydrogen economy. There is anecdotal evidence that the photocatalyst's bandgap has to be around 2.3 eV or that defects play an important role as the sites of charge-separation and hydrogen reduction.

Likewise, a truly "rational design principle" – i.e. the answer to "Is crystallinity at all important for a good photocatalyst?" – has not emerged, yet, simply because COFs and CMPs are built on fundamentally different design principles and from non-interchangeable building blocks.

Here, we will discuss the importance of overall π-conjugation and electron transport [2], donor-acceptor interactions [3], and the internal structure [4] for polymer semiconductors in applications as sensors, heterogeneous photocatalysts and energy storage devices.

[1] M. J. Bojdys et al., Nat. Rev. Mater. (2017) 2.
[2] M. J. Bojdys et al., Adv. Mater. (2017) 29.
[3] M. J. Bojdys et al., Angew. Chem. Int. Ed. (2018) 57.
[4] M. J. Bojdys et al., ChemSusChem (2019) 12.

PLASMON-PLASMON COUPLING PROBED WITH SUB-NM SENSITIVITY

P. Dombi

Wigner Research Centre for Physics, Budapest/HUN

Full spatiotemporal reconstruction of plasmonic fields is a major goal in plasmonics in order to investigate the buildup and decay of collective electron phenomena. As a first step in this direction, one has to determine field enhancement on the natural scale of plasmonic near-fields, i. e. few nanometers. Photoelectrons were shown to be sensitive tools for ultrahigh-sensitivity near-field probing [1-3].

We have shown that using this technique, plasmonic field enhancement can be experimentally measured with unprecedented surface sensitivity with the help of photoemitted and rescattering electrons [1].

It was demonstrated that the cutoff region of these photoelectron spectra is made up of electrons emitted from plasmonic hot spots of the nanoparticles [1]. We successfully used this method to investigate the coupling between localized and propagating plasmon modes, reaching ~ 7 Ǻ surface sensitivity [2]. Our experiments establish photoelectron probing as a sensitive tool in plasmonics with a potential to tailor plasmonic nanostructures for various applications.

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[1] P. Rácz, et al., Nano Lett. 17 (2017) 1181.
[2] J. Budai, et al., Nanoscale 10 (2018) 16261.
[3] E. Marsell, et al., Nano Lett. 15 (2015) 6601.

PROBING RADIATIVE AND DARK PLASMONS WITH ELECTRONS

F.-P. Schmidt[1], A. Hohenau[1], H. Ditlbacher[1], A. Losquin[2],
M. Kociak[2], F. Hofer[3], and J. R. Krenn[1]

[1] Karl-Franzens-Universität Graz, Graz/AUT
[2] CNRS UMR, Paris/FR
[3] Technische Universität Graz, Graz/AUT

The high spatial and spectral resolution of electron energy loss spectroscopy (EELS) and cathotoluminescence (CL) combined with electron microscopy has recently enriched our experimental reach towards a more detailed view on nanooptical systems. Here, we investigate on one hand radial breathing modes in plasmonic silver nanodiscs that due to a vanishing dipole moment couple only weakly to light. While increasing the disk size lifts the dark mode character due to retardation, the combination of EELS and CL signals enables a detailed analysis of the involved radiative and non-radiative processes [1]. On the other hand, we use EELS to identify the coupling of plasmon modes within a single nanoparticle, giving rise to bonding and antibonding edge modes. This and related effects can be approached in even more detail by the recent addition of 3D imaging capabilities to the EELS toolbox [3].

[1] F.-P. Schmidt, et al., ACS Photonics, 5 (2018) 861.
[2] F.-P. Schmidt, et al., Nano Lett. 16 (2016) 5152.
[3] G. Haberfehlner, et al., Nano Lett. 17 (2017) 6773.

IMAGING LOCALIZED SURFACE PLASMONS WITH ELECTRON- AND DIELECTRIC PROBES

N. G. Quilis[1], D. Kotlarek[1], S. Fossati[1], S. Hageneder[1],
C. Petri[2], U. Jonas[2], and J. Dostalek[1]

[1] Karl-Franzens-Universität Graz, Graz/AUT
[2] University of Siegen, Siegen/GER

The paper reports on the development of actively tunable plasmonic nanostructures and their implementation for optical affinity biosensors relying on plasmonically enhanced fluorescence spectroscopy [1]. They rely on responsive polymer architectures [2] that enable rapid modulation of resonant excitation of surface plasmons [3] and at the same time serve as affinity binding matrix [4]. Thermo-responsive UV-cross-linkable polymers were employed for the preparation of various hydrogel nanostructures [5-7] by the use of UV-laser interference lithography and nano-imprint lithography and polymer backbone was post-modified by ligand molecules specific to target analyte. Similar techniques can be used for the preparation of metallic nanostructures [8] and thus can be readily combined with thermo-responsive polymer architectures.

There will be discussed structures supporting collective localized surface plasmons on periodic arrays of gold nanoparticles and hybrid architectures comprising metallic films with arrays of nanopores. Implementation of such structures for the interaction analysis of molecules with weak affinity aptamer [9,10] and peptide ligands [11] as well as implementation to highly sensitive detection of trace amounts of biomarkers in bodily fluids will be presented.

[1] D. Kotlarek, et al., in preparation (2019).
[2] C. Petri, et al., in preparation (2019).
[3] M. Toma, et al., Journal of Physical Chemistry C, 117 (2013) 22.
[4] A. Aulasevich, et al., Macromolecular Rapid Comm. 30 (2009) 872.
[5] F. Pirani, et al., Macromolecular Chemistry and Physics 218 (2017) 6.
[6] N. Quilis, et al., in preparation (2019).
[7] N. Sharma, et al., Optics Express 24 (2016) 3.
[8] N.G. Quilis, et al., in preparation (2019).
[9] K. Sergelen, et al., ACS Sensors 2 (2017) 7.
[10] K. Sergelen, et al., Analyst 142 (2017) 2995.
[11] D. Bernhagen, et al., ACS Comb. Sci. in preparation (2019).

SENSING AND MANIPULATING MOLECULES USING PLASMONIC NANOPARTICLES

W. Fritzsche

Leibniz Institute of Photonic Technology, Jena/GER

Metal nanostructures are able to interact highly specifically with visible light due to localized surface plasmon resonance (LSPR), a phenomenon based on the interaction of light with the conduction electrons. This effect depends – beside material, size and shape – also on the surrounding refractive index, which is the base for (bio)sensing applications. Hereby highly specific-binding receptor molecules are attached to the nanoparticle sensor surface, and allow only the target molecule to bind and thereby to change the local refractive index, resulting in a shift of the LSPR band, which is then used as sensor signal. We will demonstrate multiplexed DNA sensing using spotted (previously chemically synthesized) nanoparticle sensor arrays.

Beside this rather passive use of LSPR, a connected effect – the release of excited „hot“ electrons – can be used for more active applications like plasmonic catalysis or biomolecule manipulation, which will be demonstrated in the second part of the presentation.

FROM PLASMONIC HORIZONS AND PLASMON VOLTAMMETRY

T. A. Klar

Johannes Kepler University,Linz/AUT

The localized plasmon resonance of noble metals or other plasmonic materials such as highly doped semiconductors depends on the square root of the density of conduction electrons. The latter can either be tuned by directly via biasing the plasmonic material or by redox-reactions taking place at the surface of the plasmonic material. Beyond this rather trivial circumstance, we found that chemical reactions or physisorption of adatoms lead to spectral shifts beyond those given by the surface capacity and the applied potential. Further, physisorption or chemical surface reactions lead to spectral broadening which is not explainable by the sheer change of the electron density [1].

Within the potential boundaries of water splitting, localized plasmon voltammetry shows excellent agreement with simultaneously recorded cyclic voltammogramms up to the onset of oxygen evolution. Importantly, localized plasmon voltammetry still appears to provide meaningful signals even beyond that point. Further, with localized plasmon voltammetry, the pH dependent reduction potentials of electrochemically grown gold oxides were determined and show a linear characteristic over the investigated pH range according to Nernst's equation [2].

A further topic to be discussed will be gold intrinsic fluorescence which stems from electron-hole recombination inside gold nanoparticles [3]. Such fluorescing events are the most nanoscopic light bulbs to excite localized plasmons, basically localized on one unit cell. We argue that such nanoscopic light bulbs are a useful tool to investigate the plasmonic horizon.4 This is formed by the short lifetime of a plasmon (on the order of 6 fs) and the finite speed with which the information that a plasmon is created can be transported. This actually leads to the fact that a localized creation of a plasmon cannot reach throughout a plasmonic nanosponge larger than 120 nm in diameter within the lifetime of the plasmon.

[1] S. K. Dondapati, et al., Nano Lett. 12 (2012) 1247.

[2] B. Steinhauser, et at., J. Phys. Chem. C 8 (2018) 122.

[3] D. Sivun, et al., Nano Lett. 16 (2016) 7203.

[4] C. Vidal, et al., Nano Lett. 2 (2018) 18.

BEYOND FT-IR SPECTROSCOPY: LATEST ADVANCEMENTS IN LASER-BASED MID-IR SPECTROSCOPY FOR ANALYSIS OF PROTEINS

A. Schwaighofer[1], M. Montemurro[1,2], S. Freitag[1], and B. Lendl[1]

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One of the advantages of mid-infrared (IR) spectroscopy in biomedical research lies in its capability to provide direct information on the secondary structure of proteins in their natural, often aqueous, environment. A drawback of IR investigations of proteins in aqueous solution is the strong absorbance of the HOH-bending band that overlaps with the amide I band, confining the path length to values below 10 µm for transmission measurements in conventional Fourier-transform infrared (FTIR) spectrometers.

External-cavity quantum cascade lasers (EC-QCLs) are new broadband light sources for the mid-IR region that provide polarized and coherent light with spectral power densities several orders of magnitude higher than thermal emitters. Employing these new light sources, we developed a broadband IR transmission setup for analysis of the protein amide I and amide II bands at large optical paths, accompanied with considerable improvement of the signal-to-noise ratio and robustness compared to established FTIR measurements. Spectral features characteristic for different protein secondary structures could be identified at concentrations as low as 1 mg mL−1 in aqueous solutions. Furthermore, this setup was successfully employed to monitor dynamic changes of protein and polypeptide conformation induced by chemical denaturation and thermal perturbation. Most recently, we applied EC-QCL mid-IR transmission spectroscopy for quantification of individual proteins in commercial bovine milk without sample pre-processing by partial least squares regression models.

EXTENDING NANO-MECHANICAL AND ELECTRICAL MEASUREMENT MODES IN AFM: A SYSTEM INTEGRATION APPROACH

G. Schitter[1], M. Poik[1], D. Kohl[1], and P. Mesquida[1,2]

[1] Technische Universität Wien, Wien/AUT
[2] King's College London, London/UK

Atomic force microscopes (AFM) are very versatile instruments for characterizing surfaces at nanometer resolution, also beyond the conventional measurement of topography, by various measurement modes, including nano-mechanical and electrical measurements.

For the direct measurement of mechanical material properties, such as Young's modulus and adhesion, of the sample surface with high spatial resolution, the general disadvantage of AFM being a tactile measurement method is utilized as an advantage for recording a set of force-distance curves at every pixel. While state-of-the-art measurement modes and conventional implementations have successfully demonstrated feasibility for nano-mechanical measurements, they are limited in measurement speed by the dynamic behavior of the force sensor and AFM positioning system. This contribution discusses a system integration approach by utilizing mechatronic system design and modern control methods to ameliorate this limitation by two orders of magnitudes, enabling force mapping at rates of 10.000 force curves per second and beyond.

Another measurement mode in AFM for measuring surface charges at high-spatial resolution is known as Kelvin-Probe force microscopy (KPFM). However, the application of KPFM is limited in some cases by the need to applying a DC-offset to the AFM-cantilever for the charge measurement. To address this challenge, a new measurement mode is discussed that replaces the conventional KPFM signal by a set of sinusoidal signals applied to the AFM-tip for measuring the surface charges. As in conventional KPFM, the new mode keeps the closed-loop feedback to take advantage of a compensation-based measurement principle. In a second step this new measurement mode is extended to radio-frequency signals up to several GHz, which will enable the characterization of electronic components and circuits directly on the wafer or device level during operation.

Extending the frequency range of nano-mechanical and electrical measurement modes in AFM will not only pave the way to new applications, but will in the future also enable spectroscopic measurements with these systems in material and life-science applications, as well as in industrial development, analysis and in-process measurement.

SUGAR EXPOSURE ALTERS THE SURFACE CHARGE OF COLLAGEN FIBRILS ON THE NANOMETER SCALE

P Mesquida[1,2] , D. Kohl[1], and G. Schitter[1]

[1] Technische Universität Wien, Wien/AUT
[2] King's College London, London/UK

It has long been speculated whether sugar is not just harmful in an obvious way, namely through excessive consumption leading to obesity, but could also have more subtle, long-term effects on human tissue. The idea was raised that sugars react with “healthy” proteins in the body, specifically extracellular matrix proteins in various tissues, and thereby could cause an alteration of their mechanical and electrostatic properties. Such processes are known as glycation and could have devastating long-term effects on a range of very fundamental, biological functions such as cell adhesion, blood vessel elasticity, etc.

We investigated such a hypothesised alteration of the mechanical and surface chemical properties of collagen fibrils, the main structural constituents of connective tissue. It was found that glycation leads to stiffening of fibrils and a reduction of their surface charge on the nanometer scale. To this end, we had to use advanced techniques such as Atomic Force Microscopy-based nanoindentation and Kelvin-probe Force Microscopy, coupled with our own electronics in order to achieve the necessary sensitivity.

The observed reduction of surface charge could interfere with the attachment of cell adhesion proteins on collagen fibrils and, ultimately, cell adhesion itself, which could disturb numerous processes and overall function of tissue.

VACUUM- AND SOLUTION-PROCESSED TRANSPARENT ELECTRODES FOR FLEXIBLE SOLAR CELLS

T. Dimopoulos

AIT Austrian Institute of Technology, Wien/AUT

Transparent electrodes (TEs) represent an extensive market, expanding from optoelectronics to lighting, and further to photovoltaics and functional window coatings. Transparent conducting oxides (TCOs) are the predominant class of TE materials. TCOs are highly-doped, wide-bandgap semiconductors. One of the most implemented TCOs is indium-tin-oxide (ITO), offering high transparency and low resistance. On the down side, indium is a rare and expensive element and high quality, sputtered ITO requires high processing temperature, which is not compatible with sensitive plastic substrates. Also, for certain applications and products, solution-based processes offer lower capital expenditure and maintenance costs than vacuum processing, which has a strong impact for large-scale production.

In this presentation we will describe 2 different TE technologies. The first is one is based on sputtered, ultra-thin metal films (Ag, Cu, or Au), with a thickness of 5-15 nm, combined with dielectric layers (such as doped ZnO, TiO2 and others) to form dielectric/metal/dielectric multilayers, which: (i) can be vacuum-processed at ambient temperature on rigid or flexible substrates, (ii) are stable against mechanical stress, (iii) have a larger figure-of-merit (transparency over resistance) than state-of-the-art ITO electrodes on flexible substrates. We will focus on the optical design of these electrodes to maximize their transmittance, as well as on their implementation in solar cells of the hybrid perovskite type. Further, we will elaborate on a solution-processed TE technology especially developed for rough solar cell absorber surfaces, where conformal coverage of the surface, as well as high processing speed are critical features. This TE is based on a combination of ZnO nanoparticles, a chemical-bath-deposited, doped-ZnO layer and finally a highly conducting Ag-nanowire network. We demonstrate that photovoltaic cells and modules, of the so-called “monograin layer” architecture, implementing this type of TE deliver equal photovoltaic performance as reference devices employing sputter-processed layers.

[1] M. Bauch, et al., Mater. Des. 104 (2016) 37.

[2] D. Ebner, et al., Optics Express 25 (2017) A240.

[3] S. Edinger, et al., J. Mater. Sci. 52 (2017) 9410.

PRINTED ORGANIC ELECTRONICS: FROM PRINTED COPPER TO PEROVSKITE LIGHT-EMITTING DEVICES

F. Hermerschmidt[1], and E. J. W. List-Kratochvil[1,2]

[1] Humboldt-Universität zu Berlin, Berlin/GER
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By using solution-based materials, the field of printed organic electronics has not only made new devices accessible, but also moved the process of manufacture toward a high-throughput industrial scale. One of the major advantages of these types of electronic devices is that they can be manufactured using a solution-based processing route, i.e. from inks that contain the active material dissolved in a suitable solvent system. These solutions can then be deposited using standard lab-based techniques such as spin coating, but also using sophisticated, technology-relevant processing systems such as inkjet-printing.

Organic field effect transistors, organic photovoltaics and high-performance organic light emitting diodes have been fabricated with the use of inkjet printing [1,2]. Its versatility is underlined by the fact it is an additive, upscalable, direct write technique that requires no masks or lithographic pre-patterning of substrates. However, for full compatibility with flexible, low cost substrates, the processing conditions of the deposited structures need to be continuously investigated.

This contribution highlights our work on utilizing inkjet-printing to deposit copper nanoparticles. A reductive sintering approach is presented as an alternative to commonly used laser or flash lamp curing techniques [3]. In order to form conducting structures within a range of electronic applications, specifically optoelectronic devices and printed circuits, the continuous process development and implementation methods are discussed to improve the conductive and interfacial properties [4].

The findings presented address the importance of continuing work in improving the effectiveness of printed conductive structures together with optimized carrier transport layers and high efficiency active material systems, e.g. perovskites, in their use in organic and hybrid (opto)electronic devices, in order to target efficient and fully solution-processed and flexible electronics.

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UTILIZING INKJET PRINTING FOR ORGANIC/INORGANIC METAL HALIDE PEROVSKITE OPTOELECTRONIC DEVICES

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In recent years, organic metal halide perovskites (OMHP) have been one of the most exciting research topics for scientists of a wide variety of backgrounds. Mainly driven by photovoltaics, the exceptional optical and electrical properties of OMHPs on a laboratory scale lead to an efficiency of over 23%. In addition, perovskites are beginning to have an impact on lighting and sensor applications. It is not only the broad spectrum of possible applications, but also the ease fabrication from solutions that promises OMHP to achieve a strong market presence as a low-cost semiconductor material.

We develop a deeper understanding of the formation of perovskite layers, starting with the solution chemistry of the ink to the later crystallization using various coating and printing techniques. Inkjet printing offers the possibility of large-area, high-throughput digital printing. By controlling the ink formulation, e.g. surface tension, viscosity, boiling point and solubility, as well as the post-processing parameters, we are able to change the crystallization dynamics and thus control the film roughness and thickness of the printed perovskite layers [1, 2]. Preliminary work on multication perovskite solar cells in combination with a vacuum annealing post-treatment step leads to efficiencies of 15% for an n-i-p solar cell on a sub-cm² cell surface [3]. We now focus on the in-situ characterization of perovskite film formation kinetics as a function of the composition and process conditions of the precursor to demonstrate the role of solution chemistry and intermediate states in determining sample morphology and quality. The findings presented in this study pave the way for large-area, low-cost, high-throughput optoelectronic devices with inkjet printing on perovskites.

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ROLL-TO-ROLL UV NANOIMPRINT LITHOGRAPHY FOR LARGE AREA MANUFACTURING OF BIONIC SURFACES

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Roll-to-roll UV nanoimprint lithography (R2R-UV-NIL) gains increasing industrial interest for large area nano- and micro-structuring of flexible substrates because it combines nanometer resolution with many square meter per minute productivity [1].

Beside the classical application fields of nanoimprint lithography like micro-electronics and micro-optics currently biomimetic micro- and nano-structured surfaces get increasing attention for e.g. viscous drag reduction (shark skin effect), water and dirt repellence (lotus effect) and anti-reflection (moth-eye effect) coatings.

In this study we report the set-up of a custom made R2R-UV-NIL pilot machine which is able to convert 10 inch wide polymer web with velocities up to 50 m/min. For imprint as well as polymer working stamp material UV-curing resins based on urethane acrylates and thiol-ene chemistry were designed to meet the requirements of R2R-UV-NIL processes being strong adhesion to polymer substrates, fast curing speed and high imprint fidelity.

The mechanical properties, surface chemistry and refractive index of these UV imprint resins can be tuned over wide ranges by choice and ratio of urethane acrylate oligomers and acrylate or thiol monomers – and surface active dopants. We have achieved Young's moduli be-tween 5 MPa and 5 GPa, refractive indices nD25 between 1.4 and 1.7 and surface energies between 15 mN/m and 65 mN/m [2].

Furthermore, new strategies have been developed to achieve excellent abrasion resistance and utmost weathering stability of the nanoimprinted biomimetic polymer surfaces in harsh outdoor applications.

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PLASMONICS FOR MOLECULAR NANO-RAMAN IMAGING BEYOND THE LIMITS

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Surface plasmons propagate along the boundary between metal surface and dielectric material with velocity smaller and wavelength shorter than those of light propagating in free space. The velocity can be even zero (no propagation but oscillating) on the metal surface [1]. Optical microscopy using surface plasmons was the first reported by Knoll in 1998 [2]. Localized mode of surface plasmon polaritons was also used for microscopy with a metallic nano-probe for nano-resolution imaging [3]. The intensity of nano-light spot localized in the vicinity of probe tip is enhanced due to the resonance of localized mode of surface plasmons [4]. Super resolution and field enhancement of plasmonic microscopy are both beneficial to the Raman analysis of bio-molecules, nano-materials, and nano-devices. In this presentation, I will introduce the principle of tip-enhanced Raman scattering (TERS) microscopy and review its recent progress [5]. Spatial resolution of TERS microscopy is limited by the size of probe tip [6], while it can be exceeding beyond the limit by pressuring a sample with a tip to introduce the localized structural deformation of molecules [7]. Three-dimensional molecular distribution in a living cell can be also obtained with use of a gold nano-particle [8]. Spatial resolution of this microscope is ~ 65nm and temporal resolution ~50ms. In the presentation, movies of particle motion and a molecular map in a cell will be shown with many other results. For imaging the distribution of nucleotides and proteins, deep UV light has been used for exciting resonant Raman scattering in Lanthanide ion solution where photo-degradation is suppressed [9]. Plasmonic materials in deep UV will be also discussed [10].

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LIGHT-FUELED MOLECULAR MACHINES MOVE MATTER

Z. Sekkat

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Moroccan Foundation for Advanced Science and Innovation and Research, Rabat/MAR
Osaka University, Osaka/JP

In this talk, I will give an overview of the theory of matter motion induced by photoisomerization. I show that besides photoisomerization, a gradient of light intensity is necessary to generate motion; e.g. generate a photoisomerization force to move matter. The photoisomerization force requires a photochemical process, in contrast to the optical gradient force, introduced by Ashkin, which requires a contrast of refractive index to move particles. Molecular machines become mobile when they are photo-selected in a gradient of light intensity. The motion occurs in the direction of the vector of the intensity gradient, and its efficiency depends on the respective orientations of the vectors of light polarization and intensity gradient. Directional motion is imparted into materials containing smart photoisomerizable molecules. The theory describes well experimental observations, and its application to different types of gradients and light polarization excitations is considered. In concept, matter motion is due to competing forces, including viscous and photoisomerization forces, and possible radiation pressure and elastic forces, as well as a random force due to thermal fluctuations. In solid films of azo-polymers, the photoisomerization force overcomes other forces due to softening and decrease of viscosity of the material by photoisomerization. The photoisomerization force scales with the density of the photoreactive molecules, and it is orders of magnitude larger than radiation pressure. Important perspectives for the transport of matter by light are foreseen [1,2].

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Poster Abstracts

List of Posters

S. Fossati.............................. Plasmonic Nanohole Arrays with Thermo-Responsive Hydrogel Cushion – Towards Flow-Through Biosensor

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M. Heyl ....Crystal-Limited Exfoliation of Centimeter-Scale MoS$_2$ Monolayers

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N. Mutz...Transition Metal Dichalcogenides (TMDC) Monolayers and Heterosturctures for Hybrid Optoelectronic Devices

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PLASMONIC NANOHOLE ARRAYS WITH THERMO-RESPONSIVE HYDROGEL CUSHION – TOWARDS FLOW-THROUGH BIOSENSOR

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The combination of plasmonic sensing systems with microfluidics has proven to be an important tool in biosensing with small sample volumes or analyte concentration [1]. In typical applications the sample solution is flowed over a surface functionalized with specific receptors. For low concentration of analytes, the diffusion driven mass transport limits the capture of target molecules on the surface. To overcome mass transport limitations, microfluidic flow-through systems with plasmonic nanostructures have been developed in which fluid flow is channeled through pores to sensitive detection area [2,3]. Such approaches however mostly rely on expensive, low throughput methods including electron beam lithography, focused ion beam or photolithography. These designs are static in nature and susceptible to hydrodynamic deformation due to applied pressure [4].

To address these challenges, we report on metallic nanohole arrays supported by a thermo-responsive hydrogel cushion with embedded gold nanoparticles. The resulting system of coupled propagating surface plasmons and localized plasmon resonances of the nanoparticles provides a rich spectrum of modes probing different areas of the structure, including a plasmonic hotspot at the pore. Furthermore, actuation of the optical properties by small temperature changes is enabled by the thermo-responsive nature of the employed hydrogel. Numerical simulations are employed to study and optimize the optical properties for sensing application. The nanostructures are then fabricated by cost effective nanoimprint lithography and are subsequently transferred to a porous membrane by template stripping. In this structure capillary forces drive the transport of the sample to the hydrogel matrix. Therefore binding events occur preferably in close proximity to the plasmonic pore. The nanostructures are characterized by microscopy, optical wavelength spectroscopy and the optical response is compared to simulation results. Finally, the performance of the system is demonstrated with a model immunoassay.

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INVESTIGATION OF RESISTIVE SWITCHING IN ORGANIC/INORGANIC MEMORY DEVICES

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Resistive switching devices are considered as promising candidates for future non-volatile memory/storage technology, due to low cost of fabrication and compatibility with flexible support substrates. When an appropriate bias voltage is applied to the device's two metallic electrodes, separated by a thin organic/inorganic film, an electrochemical reaction causes the formation/rupture of a localized conductive pathway (filament) within the material. After a period of preconditioning, this allows reversible switching of the device's electric properties between two distinct resistive states (high resistance state and low resistance state).

As part of this work, we doped a polymeric insulator (poly methyl methacrylate, PMMA) with an ion transport material (poly ethylene glycol, PEG) to investigate the effect on resistive switching behavior. By combining both polymers into a blend structure, reliability as well as ion transport improved significantly, reflected in the electric current-voltage as well as current-time characteristics. Purely organic basic devices do however often lack in switching stability, thus encouraging exploration of alternative materials. While primarily known for their optoelectronic application, organic-inorganic hybrid perovskite materials also exhibit promising properties in their use as memory devices. However, the switching mechanisms are not yet fully understood. Characterization of switching behavior in methylammonium lead iodide (perovskite) based devices was therefore another focus of this work. While no preconditioning of the device was necessary, remarkably low switching voltages (<1 V) and high on/off ratios where noted. By applying appropriate voltage biases, unipolar switching was observed, motivating further investigation.

QUANTUM DOT PHOTOCONDUCTIVITY IN PLASMONIC GAPS

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Recent advances in the room-temperature synthetization and deposition techniques have made, on the one hand, colloidal semiconducting quantum dots (QDs) important low-cost materials for optoelectronic devices such as photodetectors or solar cells [1, 2]. On the other hand, top-down fabrication with electron beam lithography allows nowadays to design well defined structures at the nanoscale. We exploit this to fabricate metal nanostructures (MNS) that display plasmonic effects such as the local optical field enhancement. Applied to, e.g., photodetectors this could result in increased speed, lower noise detection and reduced power consumption [3].

The subject matter of this poster is the investigation of QD photoconductivity in plasmonic MNS and whether a plasmonic enhancement of photocurrent is possible. The MNS are so-called bowties, which consist of two opposed triangles with a gap in-between. In this gap the incoming light intensity gets enhanced up to a thousand times. Ligand-exchanged QD films of either the semiconducting materials CdSe or PbS are spinned on the plasmonic gaps. With the help of a scanning stage and a focused laser beam, we create maps of the local photocurrent and of the local optical transmission. On selected points of the sample, viz. the bowties, we analyze the dependence of the photocurrent on the voltage bias, the laser power and -polarization, as well as photocurrent response to temporal changes in laser intensity. The measured data indicate that it could be possible to prove a plasmonic enhanced photocurrent with an improved measurement setup and sample design.

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Improving Detection Limits using Plasmon-Enhanced Fluorescence Biochips Suitable for Scaled-Up Production

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Fluorescence-based techniques are among the most widely spread optical methods for detection of (bio-) molecules in various fields. There is a persistent need to detect and quantify lowest amounts of analytes using highly sensitive fluorescence immunoassays broadly adaptable to clinical and biological laboratories and point-of-care testing, especially when it concerns the early diagnosis of cancer and infectious diseases [1,2]

For the purpose of improving the sensitivity and limit of detection of fluorescence based assays, metallic nanostructures which allow coupling of fluorophore labels of an assay with the confined electromagnetic field of resonantly excited surface plasmons are utilized. The highly enhanced field intensity interacting at the adsorption and emission wavelength with the fluorophores allows increasing their brightness making it possible to detect target molecules at minute amounts [3]. However, these structures are typically prepared by costly techniques such as electron beam lithography, which are not suitable for a large scale production. We report on disposable plasmonic structures made by UV-nanoimprint lithography and roll-to-roll processes which provide enhanced fluorescence intensity emitted from fluorophore labels by a factor up to 300. These structures are used on a device with array detection format and integrated microfluidics with a limit of detection in the fM range, which additionally allows for the measurement of affinity binding kinetics.

The developed array chips are characterized in terms of morphology and assay performance, especially in comparison with laboratory-scale produced samples.

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ACHIEVING HIGHLY CONDUCTIVE INKJET-PRINTED COPPER FILMS WITH LOW-TEMPERATURE REDUCTIVE SINTERING

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Inkjet-printed electrodes have been utilized in a wide variety of (opto) electronic devices [1, 2]. Inkjet-printing is an additive, direct write technique that requires no masks or lithographic pre-patterning of substrates, with droplets only deposited where required on the substrate, therefore minimizing material loss. Moreover, inkjet-printing can be transferred to a roll-to-roll process, able to access high productivity but also small feature sizes. This paves the way to fully solution-processed devices, with all layers including the electrodes being deposited from an ink.

Many approaches to printable conductive metal electrodes have focused on silver, due to its high oxidation resistance and good electrical conduction even in its oxidized states. The required sintering step to form uniform films of merged nanoparticles is therefore less demanding, i.e. simple thermal processes can be applied. However, the high cost of silver and its susceptibility to electromigration demand a shift of focus towards alternatives, for example copper. However, due to its susceptibility to oxidation, the usual post-deposition treatment methods include expensive and instrumentally elaborate flash lamp and laser sintering approaches.

This contribution introduces a truly low temperature (130 °C), easy to scale process using formic acid to sinter structures that have been inkjet-printed using an industrial scale copper nanoparticle ink. Electrical conductivity of up to 16% bulk Cu is reached after sintering at 130 °C and more than 25% bulk Cu conductivity is achieved above 150 °C. Four-point measurements and photoemission spectroscopy detail the formation of a conducting Cu film, while adhesion and bending tests confirm the stability of the printed structures.

The developed sintering process is compatible with flexible plastic substrates that are often themselves not particularly temperature stable and underline the suitability of the inkjet process for upscalable and large area Cu electrode production in electronic devices [3].

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CRYSTAL-LIMITED EXFOLIATION OF CENTIMETER-SCALE MoS_2 MONOLAYERS

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Following in graphene's wake, transition metal dichalcogenides (TMDCs) received tremendous attention as a promising class of two-dimensional semiconductors. To date, the isolation of high quality large-area TMDC monolayers still poses a key challenge on the path to advanced applications of two-dimensional TMDC materials. A well-designed isolation method ought to master the balance between purity, defect density and yield, while being robust and accessible. Mechanical exfoliation is the perfect candidate, mainly impeded by low yield.

In this work, a chemically enhanced mechanical exfoliation method was explored. Gold provides the necessary selective „stickiness“ for these chalcogenide-terminated sheets, rendering it an ideal surface for the isolation of TMDCs. The affinity between sulphur and gold enables isolation of single-layers since the interaction of the exfoliation substrate with the interfacing MoS_2 layer is stronger than the interlayer interaction in the layered crystal. The resulting method provides MoS_2 monolayers with lateral dimensions up to several millimetres in a robust and accessible fashion, limited primarily by the dimensions of the parent-crystal. These readily available single-layers enabled the facile implementation in optoelectronic devices.

FROM STED NANOSCOPY VIA STED NANOLITHOGRAPHY TO STED PHOTOCHEMISTRY

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Stimulated emission depletion (STED) microscopy proved to break the diffraction limit of resolution. Besides, it was proposed already in the early experimental reports that the STED-confined excitation volume should be applicable to spatially control chemical reactions on the nanometer scale [1]. Recently, this prediction has been experimentally realized in the field of optical nanolithography [2,3]. Using negative tone resists based on acrylates or methacrylates, three dimensional structures with sizes of around 55 nm in all three spatial directions can be written with visible light of 500 to 800 nm wavelength [4]. This clearly breaks the diffraction limit and not only allows for writing three dimensional structures but also to use low quantum energies, less harmful to organic matter than those of deep UV-light or electron- or ion beams. Applications include the design of three dimensional nano-environments for biomedical and physiological research. Multicomponent structures comprising some parts which are protein repellant and other parts (“nanoanchors”) which catch proteins or antibodies will be discussed [5,7]. Yet, negative tone lithography is only a very special case of photochemistry. An outlook will be given how to extrapolate diffraction unlimited structuring to nano-localized photochemistry, the far-goal being optically triggered covalent binding to the nanoscopic spot.

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EMPLOYING LIGHT TO "REMOTE" CONTROL THE OPTICAL PROPERTIES OF AN ORGANIC LIGHT EMITTING DIODES

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The performance of opto-electronic organic devices can be significantly improved by tuning the energy barriers within the device's interlayers. In particular on bottom electrodes self-assembling monolayers (SAMs) are commonly employed to enhance charge carriers injection/blocking into the materials. Beside aspiring for enhanced device performance, one could aim for adding a multifunctional nature to devices, for instance the ability to regulate/control the devices' output via different input stimuli.

This paper reports on the functionalization of a transparent electrode such as indium tin oxide (ITO) with SAM realized with a molecular switch (diarylethene). As a proof-of-principle an organic light emitting diode was realized implementing a monolayer of the molecular switch chemically bound on a ITO electrode. The illumination of the two terminal device with defined external wavelengths enables reversible control on the device luminescence. This is due to the ability of the molecular switch to change between two distinct isomers, each with a different electronic configuration. The optically-induced changes in the electrostatic landscape at the ITO electrode allows for the control of the extraction of carriers hence modulates the device output. Functionalization of electrodes with programmable SAMs could be exploited for fabricating smart multifunctional devices and the realization of opto-electronic circuits.

TRANSITION METAL DICHALCOGENIDES (TMDC) MONOLAYERS AND HETEROSTURCTURES FOR HYBRID OPTOELECTRONIC DEVICES

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Transition metal dichalcogenides (TMDC) hold promise as building blocks for flexible ultrathin optoelectronic devices. Their application and study requires the growth of continuous monolayers, heterostructures and alloys in a controlled fashion. To this end, a facile pulsed thermal deposition method was developed which allows the growth of two-dimensional systems under ultrahigh vacuum conditions. We demonstrate the versatility of this method by fabricating alloys of $Mo_{1-x}W_xS_2$ over the entire composition range x, as well as heterostructures comprising semiconducting MoS_2 and metallic TaS_2. Tuning of the band gap by intermixing Mo and W is shown in absorption and photoluminescence spectroscopy of $Mo_{1-x}W_xS_2$ monolayers. High-resolution transmission electron microscopy reveals atomically sharp interfaces in MoS_2/TaS_2 vertical stacks, rendering the presented method suitable for the fabrication of complex alloys and heterostructures.

ACTIVE SURFACE-PLASMON-POLARITON MODULATION BY MEANS OF PHOTOCHROMIC MOLECULES FOR FUNCTIONALIZED HYBRID INTERFACES

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In the last five decades, the development of electronic (logical) devices exploded predicted by Moore's law. With increasing demands after higher efficiency combined with faster acquisition time, the common electronic circuits start to face physical limits in terms of space and energy consumption. To overcome these issues plasmonic got into the focus of the current research as one possible solution. Surface plasmon polariton (SPP) as well as the localized surface plasmon are electron waves in close proximity to metal surfaces able to confine and to guide photons on nanoscale metal surfaces (subwavelength structures). Particularly in recent years, much effort was made towards active plasmonic and plasmonic waveguides to enable plasmonic circuit or network, which exhibits the vast data transfer capacity of the fiber optic in the nanoscale.

Therefore, in this study we examine the photochromic molecule, e.g. diarylethene, as means to modulate SPPs in optical hybrid inorganic organic devices by performing attenuated total reflection spectroscopy in Kretschmann configuration. As proof of concept, we demonstrate the capability of the photochromic molecules as multi-bit optical memory as well as neuromorphic functionalities for possible deployment in plasmonic circuits.

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