



OSI-14

The 14th International Conference on Optics of Surfaces and Interfaces

19-23th February 2024
Mauterndorf, Austria



TECHNISCHE UNIVERSITÄT
CHEMNITZ



Preface

The International Conference on Optics of Surfaces and Interfaces (OSI) is a well-established biennial meeting that gathers researchers from all over the world from diverse fields of surface/interface optics, including nano-systems and metamaterials.

Optical spectroscopy provides non-invasive, in-situ, operando, real time (and sometimes femtosecond time-resolved) probing of surfaces and buried interfaces over macroscopic areas, features that complement atomic-scale probes such as scanning-tunneling microscopy, and has a particular focus on both experiment and solid state theory.

Since its inception back in 1995, the International Conference on Optics of Surfaces and Interfaces (OSI) has included cutting-edge experimental and theoretical work in ellipsometry, reflectance-anisotropy spectroscopy, magneto-optics, Raman scattering and non-linear optics (second-harmonic and sum-frequency generation). More recent OSI conferences have also featured work on optical methods that resolve sub-wavelength structures, plasmonics, organic and biological interfaces, nanostructures, graphene-like surfaces including transition metal dichalcogenides, meta-surfaces and single nano-objects. An emerging field of metamaterials applied to subwavelength optical devices is now present in the OSI plethora of topics.

The OSI biennial conference started in Rome in 1995. Subsequent conferences were held in Ålesund (Norway), Sainte-Maxime (France), Bad Honnef (Germany), León (México), Aalborg (Denmark), Grand Targée (USA), Ischia (Italy), Akumal (México), Chemnitz (Germany), Austin (USA), in Dublin (Ireland) and in León, México (in 2019). The conference has alternated between Europe and the Americas reflecting its international profile. After 2019 it was originally planned to organize OSI-14 in Raleigh, North Carolina, USA in 2021. However, the biannual series of conferences had to be interrupted due to COVID-19 restrictions.

Now, however, the OSI series is re-started again, and we are pleased to welcome you in Mauterndorf, Austria.

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N. Esser (TU Berlin and ISAS Berlin)
D.R.T. Zahn (TU Chemnitz)

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Program Overview

Monday, 19.02.2024

10:00	Start Registration
13:45-14:15	Welcome reception
14:15-14:30	Opening
14:30-15:30	Friedhelm Bechstedt (I) <i>Ab-initio approaches toward a quantitative description of the dielectric function: bulk, surfaces, nanostructures</i>
15:30-16:00	Luis Mochan <i>Efficient homogenization of multi-component metamaterials: chiral effects</i>
16:00-16:30	Coffee Break
16:30-17:00	Bernardo Mendoza <i>Ab Initio Theory of Third Harmonic Generation</i>
17:00-17:45	Raul Esquivel Sirvent (I) <i>Super-Planckian emission and the Optical Properties of Surfaces</i>

(I) – invited presentation

Program Overview

Tuesday, 20.02.2024

- 08:30-09:15 Manuela Schiek (I)
*The Marvel of Charge-Transfer
Excitons in Chiral Squaraine Thin Films*
- 09:15-09:45 Robert Schwarzl
*Higher excited states in anilinosquaraines resolved
via transient absorption microscopy*
- 09:45-10:15 Kjeld Pedersen
*Optical characterization of oblique angle deposited
piezoelectric nitride nanowires*
-
- 10:15-10:45 Coffee Break
-
- 10:45-11:15 Mateusz Rebarz
*ELI ERIC: new capabilities for applications in
molecular, bio-medical and material science*
- 11:15-11:45 Ferdinand Bammer
*Ellipsometric Measurements on Oil-layers on
Technical Surfaces*
- 11:45-12:15 Shirly Espinoza
*Insights into the ultra-fast optical
behavior of ellagic acid thin films*
-
- 18:00-20:00 Poster Session

Program Overview

Wednesday, 21.02.2024

08:30-09:15 Naresh Kumar (I)
Monitoring On-Surface Catalytic Processes at the Nanoscale using Tip-Enhanced Raman Spectroscopy

09:15-09:45 Norbert Esser
Raman scattering at surface phonons

09:45-10:30 Davide Sangalli (I)
Room Temperature Superfluorescence in Lead Halide Perovskites and its Implications for Quantum Materials

10:10-10:25 Coffee Break

11:00-11:45 Volodymyr Dzhagan (I)
Optical spectroscopy of colloidal quantum dots

17:00-17:30 Claudia B. Lopez Posadas
Posadas Molecular orientation of DHTAP on Cu(110) and the nano-structured Cu-CuO stripe phase

17:30-18:00 Claudio Goletti
Reflectance anisotropy spectroscopy of GaAsBi alloys: from strain-engineered to growth-faulted sample

18:00-18:30 Coffee Break

18:30-19:15 Roberto Rosati (I)
Interface engineering of charge-transfer excitons in 2D lateral heterostructures

19:15-19:45 Dietrich Zahn
Optical spectroscopy of twisted bilayers of two dimensional transition metal dichalcogenide semiconductors

Program Overview

Thursday, 22.02.2024

- 08:30-09:15 Matthias M. May (I)
Electrochemical Reflection Anisotropy Spectroscopy on III-V Photoelectrodes and Al Batteries
- 09:15-09:45 Luis Rosillo Orozco
Spectroscopic Ellipsometry as a method to study band-bending in solid liquid interfaces
- 09:45-10:15 Christoph Cobet
The Formation of Copper-Oxides in Electrochemical Environments
-
- 10:15 10:45 Coffee Break
-
- 10:45-11:15 Alexey Minenkov
Understanding the Evolution of Electrochemically Treated ITO layers with operando Ellipsometry enhanced by Electron Microscopy and Spectroscopy
- 11:15-12:00 Alberto Calloni (I)
Combining optical and microscopic investigations to disclose the intercalation mechanisms at the graphite/electrolyte interface
-
- 18:00-22:00 Dinner

ATMOC SATELLITE MEETING

Friday, 23.02.2024



- 08:30-09:00 Nando Hegemann
Solving inverse problems in scatterometry through diffusion modelling
- 09:00-09:15 Maren Casfor
Forwardmodel for Scatterometry measurements to estimate Optical Constants using Bayesian Inversion
- 09:15-09:45 Oliver Henze
Bayesian inversion and error modelling to determine optical constants for ultra-thin layer systems
-
- 09:45-10:15 Coffee Break
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- 10:15-10:45 Julian Plaickner
Synchrotron-based VUV ellipsometry on passivated Si samples for optical thin film metrology
- 10:45-11:15 Mattia Mulazzi
Determination and cross-validation of the optical constants of Silicon and native SiO₂ in the VUV energy range by ellipsometry and reflectometry
- 11:15-11:45 Manuela Schiek
Imaging Ellipsometry of Sub-Wavelength Gold Nanostructures including Cross-Polarization Effects
-
- 11:45 Farewell Drink

Abstracts – Oral Presentations

Ellipsometric Measurements on Oil-layers on Technical Surfaces

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We examine the usefulness of IR-ellipsometry for the measurement of the thickness of oil layers on metals, or more generally, of dielectric layers on metallic substrates. IR-ellipsometry may offer in inline applications like rolling or deep-drawing more robustness than the currently used methods, based on IR-spectroscopy or fluorescence, which are too dependent on the type of substrate and/or the type of oil.

This work concentrates on the determination and evaluation of the ellipsometric angle ψ , which is the tangent of the amplitude-ratio of the p- and the s-reflection from the surface of interest. This ratio can be measured easily via a polarizing beam splitter, enabling the easy realization of a fast IR-imaging-ellipsometer, similar to the VIS/NIR-imaging-ellipsometer described in [1]. This basic work however evaluates first the ψ -behaviour on typical technical surfaces and technical oils in the IR, including the problem of dealing with surface roughness.

As a typical result, Figure 1 shows data and the fitted theory for wavelength $\lambda = 10.6\mu\text{m}$ and for angle of incidence $\text{AOI} = 85^\circ$ for dressed galvanized steel (Zd) with an oil layer in the thickness-range 0-6 μm . Three different oils are compared, namely two hotmelts E1 and 39SX (which are solid at room temperature and need to be preheated to be applied to metal) and the liquid oil 39S.

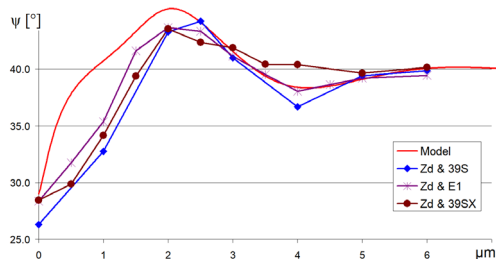


Figure 1. ψ -measurement vs. theory – three different oils on steel Zd. $\text{AOI} = 85^\circ$, $\lambda = 10.6\mu\text{m}$

The graphs show clearly that a unique thickness measurement in the range 0-2 μm is possible, with little influence from the type of oil. Similar results were found for other steel types and for Al-alloys.

Despite the long wavelength roughness still has an important influence on the measurement [2]. To achieve a good fit of the mathematical model with the measurement the absorption of the oil layer must be increased to an effective value, for which a direct dependence on the roughness was found.

- [1] F. Huemer, M. Jamalieh, F. Bammer, D. Hönig, *Technisches Messen*, **83** (10), 549-556 (2015)
- [2] K. Hingerl, *J. Appl. Phys.*, 129, 113101 (2021)

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Ab-initio approaches toward a quantitative description of the dielectric function: bulk, surfaces, nanostructures

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In the last decades, based on first principles, theoretical and computational schemes have been developed to allow not only for the description and understanding but also the prediction of optical properties of matter, e.g. novel materials as well as novel atomic geometries such as nanostructures in zero, one or two dimensions. The progress made also by the OSI community and the basic methods applied will be reported in this talk.

In general, a three-step procedure (see Fig. 1) is applied to describe the optical spectra by the dielectric function in a wide frequency range and for different light polarization [1]. (i) As an important ingredient of a parameter-free treatment the atomic geometry of the investigated bulk crystal, two-dimensional material layer/surface/interface, one-dimensional wire arrangement or zero-dimensional nanocrystal is calculated by minimizing the total energy by means of the density functional theory (DFT) with a certain exchange-correlation functional. (ii) To overcome the gap underestimates of the accompanying Kohn-Sham electronic structure, in a second step the formation of quasiparticles in the interacting electronic system after photonic excitation is considered. (iii) In the third step the mainly screened attraction of the excited quasidelectrons and quasiholes, the real or virtual formation of excitons, is taken into account.

Several examples for application of the combined approaches are presented to illustrate the predictive power and accuracy of the methods. Among them are several optical spectra, e.g. absorption spectra as displayed in Fig. 1.

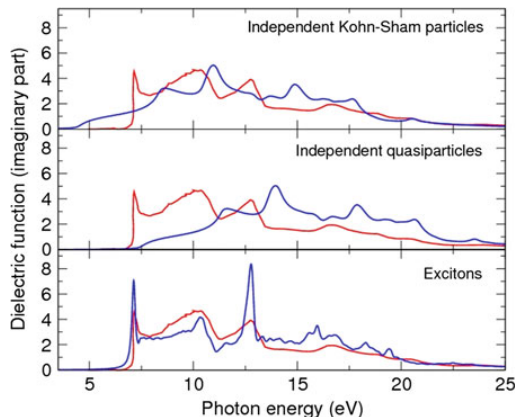


Figure 1. Dielectric function of rs-MgO (blue line) calculated in three different approximations on many-body effects [2] and compared with a measured spectrum (red line) [3].

- [1] F. Bechstedt, *Many-Body Approach to Electronic Excitations*, Springer, Berlin (2015)
- [2] A. Schleife et al., *Phys. Rev. B* **80**, 035112 (2009)
- [3] M.L. Bortz et al., *Phys. Scr.* **41**, 537 (1990)

Combining optical and microscopic investigations to disclose the intercalation mechanisms at the graphite/electrolyte interface

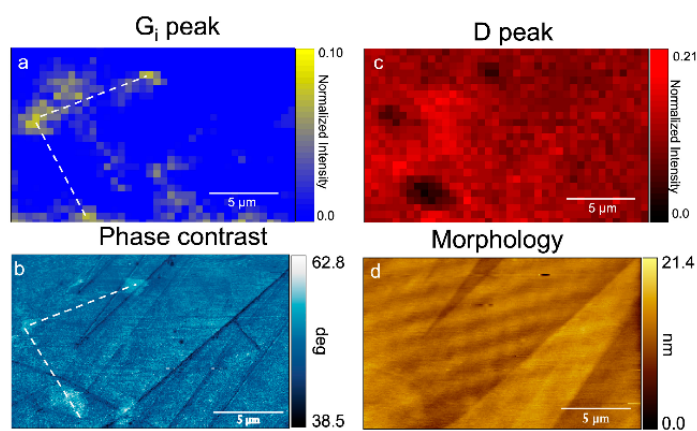
Alberto Calloni, Rossella Yivlialin, Marco Menegazzo, Claudia Filoni, Franco Ciccacci, Lamberto Duò and Gianlorenzo Bussetti

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The possibility of performing spectroscopic and morphological investigations on the same sample, at comparable length scales and in a controlled environment is a key factor enabling for a better comprehension of complex microstructures and physical phenomena evolving at the mesoscale. Here, an original setup is presented combining Raman spectroscopy and atomic force microscopy (AFM), applied to the in-situ characterization of the solid-liquid interface inside an electrochemical reactor.[1]

This system is used to study, in real time, the modifications occurring at the graphite surface during the process of electrochemically induced ion exchange with the electrolyte, called ion intercalation. As a consequence of ion intercalation, a considerable swelling of the graphite surface is detected by AFM, with the formation of defected regions and bulges likely related to the incorporation of gaseous species within the graphite stratified structure.[2,3] The process induces a significant detriment of the graphite basal plane with the formation of clusters of residual compounds. The chemical analysis, as obtained by TofSIMS,[4] reveals indeed a plethora of compounds. However, AFM and TofSIMS cannot be compared in detail. Conversely, an in-situ Raman spectroscopy analysis is used to overcome this limitation and better describe the intercalation process with the goal of establishing a one-to-one correspondence between the observed structures and their chemical and electronic nature.

In this respect, we observed that some specific Raman features, generally related to an intercalated crystal (G_i) or to defects (D peak) are instead due to the adsorption of chemical compounds in areas close to steps. This investigation shines a light on the potentialities offered by the combined system and, in particular, on the intercalation mechanism which is crucial in the preparation of electrodes in modern ion-batteries.



Combined Raman/AFM analysis of the graphite surface. Top: intensity map of Raman G_i and D peaks; bottom: AFM scan. From [1]

References:

- [1] Bussetti *et al.* *Materials* 2023, 16, 2239
- [2] Yivlialin *et al.* *J. Phys. Chem C* 2016, 120, 6088
- [3] Jagadeesh *et al.* *J. Phys Chem C* 2018, 123, 1790
- [4] De Rosa *et al.* *Nano Research* 2022, 15, 1120

Forwardmodel for Scatterometry measurements to estimate Optical Constants using Bayesian Inversion

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Scatterometry measurement is an important tool for profile reconstructions of nanostructures. We expect the measurement to be sensitive to the optical constants, hence it is of special interest to determine these values precisely.

The here discussed nanostructure is a silicon line grating with a pitch of 160nm and a very thin oxide layer on top. Both thickness and material composition of the oxide layer are not known exactly. A simulation of the measurement varying the optical constants and geometric parameters, like the layer thickness, gives us the needed data for a reconstruction using Bayesian Inversion and a Markov Chain Monte Carlo method (MCMC). The scatterometry measurement is simulated with JCMSuite [1] by solving Maxwell's equations with a finite element approach. In this talk we are mainly interested in the impact of the optical constants on the measurement. Hence, we want to discuss a sensitivity analysis and the reconstruction of the material densities of grating and oxide layer among other geometric parameters.

[1] JCMSuite: <https://jcmwave.com/jcmsuite>

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The Formation of Copper-Oxides in Electrochemical Environments

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A metal electrode in an electrochemical environment is a standard scenario in science, in technological applications and often used even in school demonstration experiments. The ideal idea of a “clean” metal surface with the expected metal atoms in contact with the electrolyte is most of the time questionable also for very stable noble metals like platinum. On the other hand the dynamics of all kinds of reaction as in electrocatalytic reactions depend a lot on surface terminations. It turned out that even the preparation of a clean copper surface is not correct in many cases. We have analyzed the type of the first sub-monolayer oxide at the copper surface and the conditions at which it occurs by means of a polarization optical approach and XPS. The in-situ compatibility and the very high sensitivity against any kind of surface modification on the atomic level allows here a quantitative analysis concerning the specific condition (pH, oxide concentration, and potential) where the surface oxidation starts. The surface chemistry is studied with XPS in ex-situ experiments with special precautions regarding sample transfer.

Optical spectroscopy of colloidal quantum dots

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The progress achieved in synthesis of colloidal semiconductor nanocrystals (NCs) or quantum dots (QDs) over decades has shown an impressive control over their structure, morphology, as well as electronic and optical properties [1]. The invention of this elegant and powerful way of creating new materials and properties was consequently awarded the Nobel Prize in 2023. Optical properties are among most promising and admirable, while optical spectroscopies have been all the way a powerful characterization tool that allowed achieving the necessary structural perfection and electronic level structure. Here, we shortly recall the classical QDs based on II-VI semiconductors, which benchmarked the size-tunable light absorption and emission spectra, as well as (photo)catalytic properties. In more detail, we consider the class of heavy metal-free multinary QDs, such as AgInS_2 and $\text{Cu}_2\text{ZnSnS}_4$, and their off-stoichiometry analogs, which have emerged recently as a less toxic alternative to CdSe, PbS, or HgTe, but apparently will have their own application niche [2]. Along with optical absorption and photoluminescence spectroscopy, which are the main optical methods for QD characterization, we discuss the capabilities of Raman scattering in providing specific structural data, as well as spectrally and spatially localized electronic features (resonances) related with the peculiarities of the lattice structure or chemical composition [3,4]. Unveiling the internal structure of core-shell or other types of heterogeneous NCs (CdSe/CdS, $\text{CuInS}_2/\text{ZnS}$, etc.) and bringing them into accord with model expectations is even more challenging than for their homogeneous counterparts. But particularly in this case resonant Raman spectroscopy is very valuable as a source of information about nanointerfaces, strain, and composition variation on the nanoscale. Due to their large surface-to-volume ratio, QDs behave very actively in composites with polymers or other nanomaterials, e.g. 2D semiconductors, resulting not in new non-additive properties. We will illustrate such hybrid nanostructures with several examples, referring to different applications.

Finally, an outlook for the probable emerging applications of QDs and research directions, in particular for solving the challenges faced by optical spectroscopies will be outlined.

- [1] F. Pelayo García de Arquer, D.V. Talapin, V.I. Klimov, et al., *Semiconductor quantum dots: Technological progress and future challenges* Science 373, 640 (2021)
- [2] O. Stroyuk, A. Raevskaya, N. Gaponik, *Solar light harvesting with multinary metal chalcogenide nanocrystals*. Chem. Soc. Rev., 47, 5354 (2018)
- [3] V. Dzhanan, Yu.M. Azhniuk, A.G. Milekhin, D.R.T Zahn, *Vibrational spectroscopy of compound semiconductor nanocrystals*. J. Phys. D: Appl. Phys. 51 (2018) 503001.
- [4] V Dzhanan, AP Litvinchuk, MY Valakh, DRT Zahn. *Phonon Raman spectroscopy of nanocrystalline multinary chalcogenides as a probe of complex lattice structures*. J. Phys.: Cond. Matter 35, 103001

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Insights into the ultra-fast optical behavior of ellagic acid thin films

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Ellagic acid (EA) is a plant-based polyphenol, which has been recently explored for the creation of functional materials [1-3]. In this work, we present the analysis of the transient changes of the optical properties of thin films of EA induced by a pump pulse. By femtosecond pump-probe spectroscopic ellipsometry technique [4-5] we followed photo-induced changes in the dielectric constant of two samples of EA prepared according to Bittrich et al.[6]: 75 nm EA film deposited via thermal evaporation on a substrate of an opaque 80 nm thick gold layer on quartz glass, and a 30 nm EA film deposited on Silicon [(100), native SiOx]

The transient Ψ and Δ spectra, taken at different time delays between the 3.1 eV pump and the probe pulses, were modelled through a uniaxial optical dispersion using an effective medium approximation. Transient effects, caused by the incidence of the pump pulse on the different substrates, were recorded by measuring pump-probe ellipsometry spectra on the substrates alone, and were used for the modelling. Effects on the near-UV range previously assigned to aromatic π - π^* transitions [6] were observed.

Support by the project Advanced research using high intensity laser produced photons and particles (CZ.02.1.01/0.0/0.0/16-019/0000789) from the European Regional Development Fund is gratefully acknowledged.

- [1] E. Bittrich, J. Domke, M. Levichkova, et al. *ACS Appl. Energy Mater*, 4, 12, 14273–14286 (2021)
- [2] T.K. Sahu, A. Gupta, V. Agarwal, et al. *ACS Appl. Eng. Mater*, 1, 12, 3194–3204 (2023)
- [3] Y. Feng, P.Li, J. Wei. *Coordination Chemistry Reviews*, 468, 214649 (2022)
- [4] S. Espinoza, S. Richter, M. Rebarz, et al., *Appl. Phys. Lett.* 115, 052105 (2019)
- [5] S. Richter, M. Rebarz, O. Herrfurth, et al, *Rev. Sci. Instrum.* 92, 033104 (2021)
- [6] E. Bittrich, J. Domke, D. Jehnichen, et al., *J. Phys. Chem. C*, 124, 30, 16381–16390 (2020)

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Raman scattering at surface phonons

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Despite of the small scattering cross section for inelastic light scattering, vibrational Raman spectroscopy has become a standard analytical tool to study organic and inorganic materials, molecules, layer structures or nanostructures. Electric field enhancement (TERS, SERS) can be employed to increase the sensitivity of Raman spectroscopy by several orders, which is mandatory for the analysis of nanoscopic structures, like molecules or inorganic nanostructures.

Another route to increase Raman cross sections is the Resonant Raman scattering. Even without field enhancement like in SERS or TERS, Surface Resonant Raman Scattering is sensitive enough to record surface phonons, e.g. vibrational modes confined within the uppermost few atomic layers of a solid. This is accomplished by resonance enhancement involving surface electronic transitions. Since surface and bulk electronic band structures of solids differ, a surface specific resonance enhancement is possible by choosing an appropriate energy of the exciting photons (laser line) [1].

I will give a short introduction into the mechanism of the surface resonant Raman scattering. By combining experimental Raman spectra with ab-initio calculations of vibrational and electronic surface structures or full surface Raman spectra a very structure specific surface analysis method can be employed.

I will discuss few examples, e.g. Si(111) surfaces with In and Au submonolayer termination forming 1D atomic wires [1], and Cu(110) surface (clean and O terminated) [2]. In collaboration with theory groups performing DFT-based calculations of surface structure, vibrational modes and full Raman spectra, spectral lines can be assigned to surface phonon modes, atomic structures clarified and the basic mechanisms of Surface Raman Scattering understood.

[1] E. Speiser, N. Esser, B. Halbig, J. Geurts, W.G. Schmidt, S. Sanna, *Vibrational Raman Spectroscopy on Adsorbate Induced Low Dimensional Surface Structures*, Surface Science Reports **75** (2020) 100480.

[2] M. Denk, E. Speiser, J. Plaickner, S. Chandola, S. Sanna, P. Zeppenfeld, N. Esser, *Surface Resonant Raman Scattering from Cu(110)* Phys. Rev. Lett. **128**, 21 (2022) 216101.

Reflectance anisotropy spectroscopy of GaAsBi alloys: from strain-engineered to growth-faulted samples.

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The growth of high-quality samples of gallium arsenic bismide alloys (GaAs_{1-x}Bi_x) - a family of ternary alloys with extremely high potential applications in the optical fiber communication network as well as for THz applications - is a challenging issue. Devices with more and more demanding performances call for a high level of Bi incorporation in the alloy, as the red-shift of the bandgap (88meV/% Bi) and the related noteworthy properties depend directly upon that value. Unfortunately, the quality of grown GaAs_{1-x}Bi_x crystals rapidly decays with the amount of Bi, imposing new and sometimes unconventional growth strategies to gain a higher incorporation of Bi in GaAs: low temperature of the substrate, variable flux of Bi, 1:1 As to Ga flux ratio for favoring the Bi incorporation, and lately the tensile or compressive state of the sample imposed by the substrate. The necessity to precisely control these parameters makes molecular beam epitaxy (MBE) the preferred technique for the growth of GaAsBi [1], although metal organic vapor phase epitaxy (MOVPE) is sometimes used [2].

We present an experimental study by reflectance anisotropy spectroscopy (RAS) of GaAsBi(001) samples grown in MBE with the increasing concentration of Bi, up to the higher value of about 7%, and different strain conditions (either compressive strain or tensile strain) [1,3-4]. A characteristic anisotropy signal below 2.5 eV is connected to the presence of Bi and, in particular, to the local strain produced in the sub-surface region by the voluminous Bi atoms. Its amplitude directly relates to the Bi quantity, and its sign gives information about the local clustering/ordering of Bi atoms in the sub-surface region of the grown sample. This interpretation of RAS spectra offers the opportunity to utilize this technique to follow in real time the optical/electronic properties during the growth of GaAsBi in MBE and MOVPE. Extending the application of RAS to "faulted" GaAsBi samples, i.e. samples that after growth result not satisfactory for research because of problems or errors risen during the complex deposition process (wrong growth temperature, excess or deficiency of Bi flux, formation of dislocations, etc.), we demonstrate that also in these cases RAS offers a useful characterization, singling out the occurrence of faults eventuality, and thus validating its potential applicability to an all-optical real time monitoring of the deposition process [5].

- [1] E. Tisbi, E. Placidi, R. Magri, et al. Phys. Rev. Applied **14**, 014028 (2020).
- [2] O. Maßmeyer, T. Hepp, R. Günkel, et al., App. Surf. Sci. **533**, 147401 (2020).
- [3] C. Goletti, L. Fazi, E. Tisbi, et al., Appl. Phys. Lett. **120**, 031902 (2022).
- [4] B. Bonanni, L. Fazi, E. Tisbi, et al., phys. st.sol. b, **259**, 2200237 (2022).
- [5] C. Goletti, B. Bonanni, L. Fazi, et al., phys. st.sol. b, submitted (2023).

Room Temperature Superfluorescence in Lead Halide Perovskites and its Implications for Quantum Materials

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Raleigh, North Carolina C USA

The increasing demand for advancements in computing, communication, and cryptography underscores the critical need for the discovery of novel "quantum materials." Despite the known properties required for most applications, clear guidelines for synthesizing and processing these materials remain elusive. Particularly intriguing are materials demonstrating macroscopic quantum effects, although achieving these at room temperature presents a significant challenge due to the short lifetime of quantum coherent states.

A fundamental question arises: Are thermal processes an insurmountable obstacle to designing materials with extended quantum coherence? Our recent discovery involving room temperature superfluorescence in hybrid perovskites suggests a promising avenue.[1,2] Superfluorescence, an optical quantum effect, emerges from the macroscopic coherence of electronic dipoles. Here, an initially incoherent ensemble of dipoles spontaneously synchronizes, forming a giant dipole that emits a burst of photons (Fig.1). Our exploration of the kinetics of a dipole ensemble transitioning from an incoherent to a coherent state provides compelling evidence for an intrinsic vibration isolation mechanism. This mechanism shields the quantum system from ambient thermal noise, facilitating superfluorescence. In this presentation, we will delve into the room temperature superfluorescence observed in lead-halide perovskites and discuss the Quantum Analog of Vibration Isolation (QAVI) model. QAVI model holds potential for guiding the design and development of high-temperature quantum materials across diverse quantum applications.

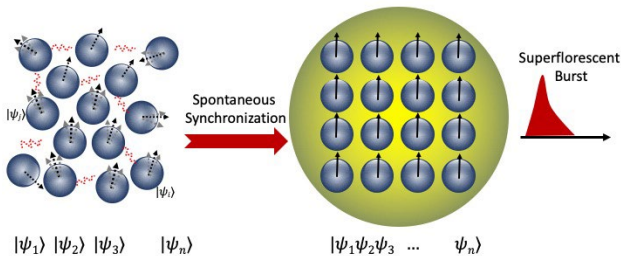


Figure 1. Superfluorescence formation: An incoherently prepared system of excited dipoles spontaneously develops macroscopic coherence from vacuum fluctuations and produces a delayed pulse of coherent light

- [1] Melike Biliroglu, Gamze Findik, Juliana Mendes, Dovletgeldi Seyitliyev, Lei Lei, Qi Dong, Yash Mehta, Vasily V Temnov, Franky So, Kenan Gundogdu, *Nature Photonics*, **16** (4), 324 (2022)
- [2] Gamze Findik, Melike Biliroglu, Dovletgeldi Seyitliyev, Juliana Mendes, Andrew Barrette, Hossein Ardekani, Lei Lei, Qi Dong, Franky So, Kenan Gundogdu, *Nature Photonics*, **15** (9), 676 (2021)

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Solving inverse problems in scatterometry through diffusion modelling

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Diffusion models are a particular type of generative models which combine the theories of stochastic differential equations with artificial neural networks. In this talk we investigate the application of such diffusion models to sample from a Bayesian posterior distribution, which arises in the context of parameter reconstruction in scatterometry. In particular we compare the results of our diffusion approaches to standard Markov chain Monte-Carlo sampling schemes the shape reconstruction of a silicon line grating.

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Bayesian inversion and error modelling to determine optical constants for ultra-thin layer systems

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Obtaining accurate measurements of optical constants in the EUV regime of around 13.5 nm is still a challenging task vital for e.g. the manufacturing of optical components.

In this talk, we discuss the use of Markov Chain Monte Carlo methods (MCMC) to obtain estimates and associated uncertainties for the optical constants of thin material layers in the EUV regime, using EUV-reflectometry measurements for varying material thicknesses as data source for a Bayesian approach. A transfer matrix approach [1] is employed to obtain a computationally efficient forward model for the MCMC.

Special focus is placed on investigating the influence of the chosen prior distributions on the estimates as well as the explicit inclusion of measure error estimates derived from measurement data into the error model.

- [1] Ciesielski, R., Saadeh, Q., Philipsen, et al., Determination of optical constants of thin films in the EUV, *Appl. Opt.* **61**, 2060-2078 (2022)

*Corresponding author: email: oliver.henze@ptb.de

Monitoring On-Surface Catalytic Processes at the Nanoscale using Tip-Enhanced Raman Spectroscopy

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Over the past two decades, Tip-Enhanced Raman Spectroscopy (TERS) has emerged as a powerful tool for nanoscale surface chemical analysis [1]. By combining the high spatial resolution of scanning probe microscopy with the chemical sensitivity and specificity of surface-enhanced Raman spectroscopy, TERS allows visualization of surface chemical transformations beyond the diffraction limit of visible light [2].

In this presentation, I will first provide an overview of the fundamental principles of TERS, with a particular focus on the strengths and limitations of AFM- and STM-based TERS techniques. In the second part of my talk, I will demonstrate the practical applications of TERS in the field of heterogeneous catalysis by sharing findings from two different studies conducted in our laboratory. The first study showcases how hyperspectral TERS imaging in combination with molecular-resolution STM imaging and DFT modeling can provide molecular-level insights into the reactive arrangements involved in on-surface photocatalytic coupling reactions [3]. In the second study, I will discuss how TERS can elucidate mechanistic understanding of oxygen activation on bulk Au(111) surfaces [4].

Overall, this presentation will highlight the potential of TERS in the nanoscale investigation of surface catalytic processes. Through high sensitivity and nanoscale hyperspectral imaging, TERS can offer valuable insights to advance our mechanistic understanding of surface chemistry.

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- [2] N. Kumar, S. Mignuzzi, W. Su, D. Roy, *European Physical Journal Techniques and Instrumentation*, 2(1), 9 (2015)
- [3] Z.-F. Cai, J. P. Merino, W. Fang, N. Kumar, J. O. Richardson, S. D. Feyter, R. Zenobi, *Journal of the American Chemical Society*, 144, 538-546 (2022)
- [4] Z.-F. Cai, N. Kumar, *Angewandte Chemie International Edition* (2024)

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Molecular orientation of DHTAP on Cu(110) and the nanostructured Cu-CuO stripe phase

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The structure and orientation of 5,14-dihydro-5,7,12,14-tetraazapentacene (DHTAP) layers deposited on Cu(110), Cu(110)-(2x1)O and the Cu(110)/Cu(110)-(2x1)O stripe phase was studied using Reflectance Difference Spectroscopy (RDS) and Scanning Tunneling Microscopy (STM). The evolution of the RDS signal allows to identify the sequential formation of up to three monolayers as well as a phase transition upon completion of the first one.

On Cu(110), DHTAP molecules in the first monolayer are always lying flat with their long molecular axis aligned parallel to the [-110]-direction of the Cu(110) surface [1]. However, for subsequent layers the orientation critically depends on the deposition temperature T. At T=240K the DHTAP molecules are mostly aligned parallel to the ones in the first layer, whereas at room temperature (RT) and above their preferential orientation is orthogonal to the molecules in the first layer. On Cu(110)-(2x1)O, DHTAP molecules in the first monolayer are aligned parallel to the [001]-direction. In contrast with the monolayer on Cu(110), the molecular orientation does not change for subsequent layers at RT.

The main optical transitions and the orientation of the transition dipole moments of the DHTAP layers were extracted from the RDS spectra.

On the Cu-CuO stripe phase, DHTAP molecules preferentially adsorb on the Cu(110) stripes, where they are always lying flat with their long molecular axis aligned parallel to the [-110]-direction. In contrast, on the subsequently covered Cu(110)-(2x1)O stripes, the DHTAP molecules are aligned with their long molecular axis parallel to the [001]-direction. The evolution of the RDS signal allows to monitor the sequential adsorption and orientation of DHTAP during monolayer formation and the subsequent multilayer growth for different oxygen pre-coverages and, hence, different Cu and CuO stripe widths. Interestingly, beyond the first monolayer, the DHTAP molecules adopt a preferential orientation which critically depends on the initial oxygen coverage, revealing the influence of the Cu-CuO stripe width and the possibility to tune the overall optical anisotropy of these films.

[1] Antony Thomas et al. J. Phys. Chem. C 2018, 122, 20, 10828–10834

Electrochemical Reflection Anisotropy Spectroscopy on III-V Photoelectrodes and Al Batteries

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(Photo)Electrochemistry faces the challenge that reactions at the electrode-electrolyte interface are typically not accessible in real-time with atomic resolution as surface science methods struggle to convey through the liquid electrolyte. Yet this information on electronic and real-space structure is crucial for understanding and designing for instance water-splitting photoelectrodes or batteries. In this talk, I will present the potential, but also the challenges of electrochemical reflection anisotropy spectroscopy, which is a promising emerging technique in this field.

While reflection anisotropy spectroscopy (RAS) has proven to be a highly interface-sensitive tool for in situ growth control in gas-phase ambient, we are exploring the potential of this method for understanding and controlling electrochemical processes. Our initial work focused on wafer-based InP(100) in contact with aqueous electrolytes. Here, we could show that an electrochemical parameter space with respect to potential and electrolyte (concentration) exists, where ordered interfaces can be reversibly prepared as a function of the applied potential without apparent corrosion [1]. For an atomistic understanding of the related spectra, correlation with other experimental techniques is challenging due to the short lifetime of the surfaces when the applied potential is broken. To establish structure-spectra relationships, we therefore use computational RAS in combination with molecular dynamics, which accounts for the high structural variability of the solid-liquid interface in the time-domain [2]. More recently, we applied our electrochemical RAS approach to epitaxially grown multi-junction photoelectrodes for solar water splitting, monitoring the interface conditioning process in situ. While the insights gained here helped to achieve high solar-to-hydrogen efficiencies, the complexity of the structure at this point limits us to a fingerprint-like understanding [3]. An even more challenging case are next-generation battery electrodes, as the non-aqueous electrolytes are more complex than aqueous ones and are optically more active, which reduces signal intensities significantly. Here, initial results show that analysis of noisy transient signals in the frequency domain help to identify growth regimes of Al-metal deposition and stripping with applied potentials [4].

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Ab Initio Theory of Third Harmonic Generation

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We derive a theoretical expression to calculate the third harmonic generation from semiconductors that take into account the finite wave vector q of each of the three incoming electrical fields E that drive the non-linear response. Then, we evaluate the response tensor $\chi^{abcd}(q_1, \omega_1; q_2, \omega_2; q_3, \omega_3)$ for different choices of the incoming frequencies ω_1 , ω_2 and ω_3 and incoming wave vectors q_1 , q_2 and q_3 for cubic and hexagonal semiconductors, like Si and Te. In particular, we explore four wave mixing in a self-diffraction configuration for silicon, where photons of frequency ω_1 from pulse P_1 are diffracted by a transient grating generated by two coherent non-collinear beams one of which is $\omega_1 - P_1$ and the other is $\omega_1 - P_2$.

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Understanding the Evolution of Electrochemically Treated ITO layers with *operando* Ellipsometry enhanced by Electron Microscopy and Spectroscopy

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Cutting-edge opto-electronic and photovoltaic devices as well as advanced bio-electronic and photo-electro-catalytic applications are barely feasible without transparent conductive materials such as ITO. Despite considerable interest, its electrochemical degradation process is far from a brimming comprehension. In this regard, *in situ/operando* approaches are a mighty tool for real-time tracking of material evolution in operational conditions. We apply *operando* ellipsometry, which combines cyclic voltammetry (CV) and spectroscopic ellipsometry (SE), to monitor ITO layers' optical and electrical properties under wet electrochemical conditions. It was revealed that the optical properties start altering before the electrical ones stepwise and irreversibly during chemical reduction within a negative bias interval. For instance, even after 15 CV cycles ranging from -1.5 V to +0.8 V, there is still an intact underlying ITO layer that maintains conductivity and allows the CV cycle to continue (Figure 1), while the reductive loss of oxygen has already degraded ITO transparency in the visible spectral range from pristine 80% to less than 20%. Apart from commercial ITO on glass substrates, for deeper morphological and chemical insights, we also investigated ITO films on silicon wafers with insulating silicon dioxide layers as more suitable specimens for *post operando* scanning and transmission electron microscopy (SEM, TEM) as well as X-ray photoelectron spectroscopy (XPS) and energy dispersive X-ray spectroscopy (EDX). During electrochemical treatment, indium-based inclusions agglomerate in the initially homogeneous ITO layer, first increasing its roughness and eventually disrupting the integrity. Due to this, the evaluation of ellipsometric data is stretched to its limits. At the same time, tracing the change of optical and electrical sample parameters via the suggested *operando* approach was proven to be reliable during multiple electrochemical CV cycles (Figure 1).

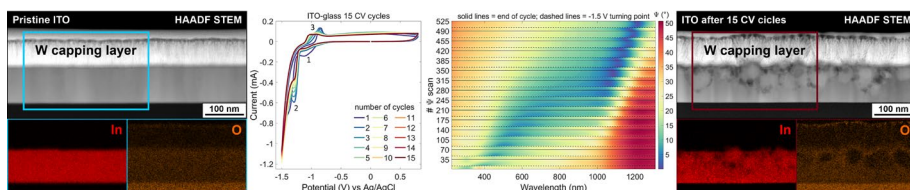


Figure 1. STEM EDX characterization of the pristine and treated ITO layer together with a recap of 15 CV cycles in pH-neutral Krebs-Ringer electrolyte and corresponding ellipsometric Ψ spectra (35 per CV cycle).

- [1] Alexey Minenkov, Sophia Hollweger, Jiri Duchoslav, Otgonbayar Erdene-Ochir, Matthias Weise, Elena Ermilova, Andreas Hertwig, and Manuela Schiek, Monitoring Electrochemical Failure of Indium Tin Oxide Electrodes via *operando* Ellipsometry complemented by Electron Microscopy and Spectroscopy, ACS Applied Materials & Interfaces, (Under Review).

Efficient homogenization of multicomponent metamaterials: chiral effects

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We extend an efficient homogenization procedure based on a Haydock representation of the microscopic wave operator for the calculation of the macroscopic dielectric response of a periodic composite to the case of an arbitrary number of components of arbitrary composition. To that end we introduce a non-Hermitian metric and a spinor-like representation that allows expressing the wave operator as a symmetric matrix that may be readily converted to a tridiagonal form. As a test, we apply our numerical procedure to the calculation of the optical properties of a Bouligand structure, made of a large number of anisotropic layers stacked on top of each other and progressively rotated. This system constitutes a photonic crystal with circularly polarized electromagnetic normal modes, naturally occurring in the cuticle of several arthropods, and which has a gap for one helicity, which corresponds to the observation of circularly polarized strong metallic like reflections. Our numerical procedure is validated through its good agreement with the analytical solution for this simple chiral system.

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Determination and cross-validation of the optical constants of Silicon and native SiO₂ in the VUV energy range by ellipsometry and reflectometry

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In the present contribution, we address the problem of determining the optical constants of pure bulk Si and SiO₂ naturally grown on Si, two fundamentally important materials for the semiconductor industry. Therefore, a precise determination of the optical constants of Silicon is very important for the determination design of new mirror structures and of the refraction index and absorption coefficient of the overlayers.

While reference data for Si exist, they are dated, they are limited to the visible region and provide no uncertainty related to the measurement and the analysis. Surface oxidation and surface roughness are critical parameters which influence the determination of Si optical data. It is therefore important to separate surface and bulk optical properties to avoid intermixing them in the data analysis.

We measured angle-dependent reflectivity and ellipsometry spectra in the VUV spectral range using photon energies from 2.5 eV to 10 eV on Si(111) wafers with native oxide and after etch-back of the oxide layer using 40% NH₄F solution leading to flat and H-terminated Si(111) surfaces as revealed by infrared spectroscopic ellipsometry. Photoemission spectra showed no formation of SiO₂, even after exposure to air for about 10 minutes, while physisorbed oxygen was detected. We obtained the dielectric function by the best-fitting of the reflectometry data, the former comparing well with experimental data from samples treated in the same conditions. The experimentally determined dielectric function could be used to calculate ellipsometric spectra and compare them to independently measured experimental data.

Since the two datasets for Silicon are in agreement with each other within a relative difference of a few percent, it was possible to use the n and k of Si to independently derive the self-consistent optical constants for SiO₂.

We observe that for the case of Silicon, differences to data from Palik's handbook [1] are clearly present, which can be as large as 20% at some photon energies. For the case of SiO₂, the real part of the complex refractive index is in qualitative agreement with the literature [2], while the absorption coefficient is significantly higher and presents prominent peaks at some specific energies, a finding that can be attributed to the presence of surface defects, like oxygen vacancies in the SiO₂ lattice.

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Optical characterization of oblique angle deposited piezoelectric nitride nanowires

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Nitrides like AlN and GaN are interesting as piezoelectric films in actuators, sensors, and energy generators. Grown as nanowires they are ideal for design of compact devices, offering the possibility to optimize mechanical coupling to the surroundings. In this work, AlN films grown on Si substrates with a 250-nm TiN film using reactive sputter deposition at normal and glancing angle deposition (GLAD) are compared. GLAD leads to growth of nanopillars with structures that can be adjusted through deposition conditions. Their optical properties are investigated using linear reflection and second harmonic generation (SHG) spectroscopy.

Figure 1a compares reflectivity spectra from a 430-nm thick nanostructured AlN film grown at normal incidence to a GLAD film on a substrate with Ag seed particles. Reflectivity from the TiN film shows that the light will not reach the TiN/Si interface. The reflectivity from the normal incidence grown film shows interference oscillations with a period that is well described using refractive index data from literature. The low reflectivity towards the IR part of the spectrum is caused by plasmon resonances in the Ag seed particles. The GLAD film shows interference oscillations with a lower contrast due to the roughness of the film.

The PZ effect and SHG are described by third-rank response tensors with the same selection rules. AlN has three independent nonlinear coefficients χ_{xxx} , χ_{zzx} and χ_{zzz} where z is along the c-axis. Either the pump or the SH field must have a component along the c-axis for SHG to occur. Films deposited at normal incidence grow with the c-axis perpendicular to the surface and do not provide SHG when probed with light at normal incidence. Conversely, if the c-axis forms an angle with the surface normal, SHG depend strongly on the azimuthal rotation of the sample around the surface normal as shown in Figure 1b. The signal disappears when the light is polarized perpendicular to the AlN columns and is highest when the projection of the columns on the surface is along the polarization direction. This shows that the AlN nanostructures formed by GLAD grow with the c-axis inclined relative to the surface normal with little deviation of direction among pillars.

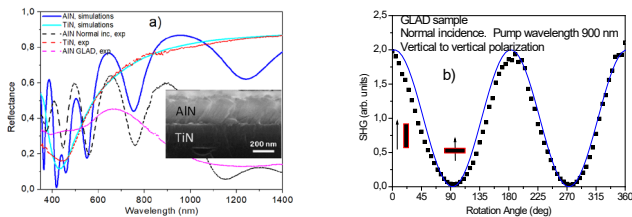


Figure 1. a) Linear reflection from AlN samples along with simulations. Insert shows SEM cross section of GLAD sample. b) Rotational SHG from GLAD sample at normal incidence.

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Synchrotron-based VUV ellipsometry on passivated Si samples for optical thin film metrology

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Optical reference materials in the vacuum ultraviolet (VUV) spectral range (between 3 and 20 eV) were studied. In this range, a lack of reliable data on optical properties exist due to the extreme surface sensitivity and the requirements of a high brightness light source. The synchrotron-based VUV ellipsometer[1] at the Metrology Light Source (MLS) and numerical modeling in a hybrid metrology approach has been used for a reference-free determination of the optical properties. The developed methods were tested on substrates with well-defined surface structures, i.e. on chemically-passivated vicinal silicon substrates with variable step density.

We will present results of ellipsometry test measurements on H-passivated Si surfaces and ALD-prepared Al₂O₃ samples in the VUV spectral range. Well-defined error budgets will be provided. X-ray photoelectron spectroscopy (XPS) and IR ellipsometry measurements serve as quality cross checks for the prepared surfaces. In the spectral range between 2 and 6 eV, results were compared to reference measurements made with a SENTECH ellipsometer SER 850.

The financial support by the European Union through EFRE 1.8/13 and ProFIT OptiRefS (Nr. 10185437) is acknowledged.

[1] M. D. Neumann et al., Rev. Sci. Instrum. 85, 055117 (2014)

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ELI ERIC: new capabilities for applications in molecular, bio-medical and material science

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Extreme Light Infrastructure (ELI) is a European Project forming a pan-European Laser facility to provide the most intense femtosecond lasers in the world for fundamental and applied research [1]. The Extreme Light Infrastructure European Research Infrastructure Consortium (ELI ERIC) was established on 30 April 2021 to jointly manage operations of ELI Beamlines in the Czech Republic and ELI-ALPS in Hungary. A third facility, ELI-NP in Romania, is supposed to join in the coming years. ELI ERIC founding Members are the Czech Republic (Host), Hungary (Co-host), Italy, and Lithuania, with founding Observers Germany and Bulgaria. The scientific activities of all ELI facilities are based on the utilization of ultrashort pulse lasers with a unique combination of pulse profile, repetition rate, and intensity.

One of the important missions of ELI is to develop a new generation of laser-driven sources for ultrashort pulses covering the ultrabroad electromagnetic radiation range (from THz to γ -ray) based on plasma effects in gases, solids as well as relativistic electron acceleration. All sources have the potential to be used in combination with beams split off from their corresponding drive lasers for pump-probe experiments. In contrast to the situation at accelerator base light sources, like synchrotrons and FELs, the fact that the pump pulse can be split off from the same laser pulse that generates the probe pulse provides an intrinsic synchronization and enables monitoring of ultrafast processes from fs to ms.

Here we introduce the experimental research capabilities offered by ELI ERIC to researchers working in molecular, bio-medical and material science. In particular, we highlight unique infrastructure available at ELI Beamlines facility which is focused on developing the complementary capabilities in optical, VUV and X-ray science in one location, with advanced sample preparation abilities [2]. The complex ultrafast phenomena in solids, liquids or gas phase can be studied utilizing pulsed lasers and laser-driven X-ray sources such as a High Harmonics Generation (HHG) source and a Plasma X-ray Source (PXS) [3]. The experimental stations include: Atomic, Molecular and Optical (AMO) Science and Coherent Diffractive Imaging (CDI) [4]; Soft X-ray Science; Hard X-ray science (diffraction, spectroscopy and pulse radiolysis); Ultrafast UV-VIS-IR spectroscopy (Ellipsometry [5], Transient Absorption and Stimulated Raman Spectroscopy).

ELI is thought of as a user facility open to all scientists. Details of how to submit a proposal to carry on experiments using ELI ERIC infrastructure will be also provided.

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[2] <https://www.eli-beams.eu>

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[4] E. Klimesova et al., *EPJ ST*, 230, 4183 (2021)

[5] S. Richter et al., *Rev. Sci. Instrum.* 92, 033104 (2021)

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Interface engineering of charge-transfer excitons in 2D lateral heterostructures

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While van der Waals heterostructures obtained by vertical stacking of different 2D materials have been largely explored, much less is known about lateral heterostructures, where two different monolayers are grown in the same plane. While they can host peculiar transport both across [1,2] and along [3] the junction, the possibility of bound charge transfer (CT) excitons [4] at their interface has still been debated. In this joint theory-experiment study [5], we demonstrate the appearance of the CT-exciton peak of hBN-encapsulated lateral MoSe₂-WSe₂ heterostructures. Our fully microscopic theory reveals the many-particle processes behind the formation of CT excitons and how they can be tuned via interface- and dielectric engineering. For interface widths smaller than the exciton Bohr radius we theoretically predict and experimentally confirm the appearance of a new CT-exciton peak in low-temperature PL spectra [5]. We show that CT excitons typically exhibit small binding energies of few tens meV and large dipole moments. The resulting efficient exciton dissociation and fast dipole-driven exciton propagation makes thus lateral heterostructures promising materials for optoelectronics devices.

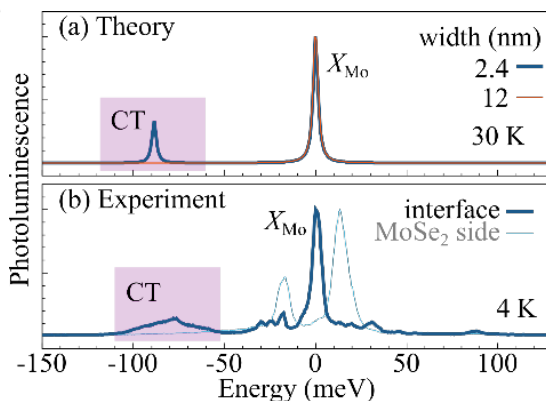


Figure 1. Predicted (a) and experimental (b) photoluminescence spectrum (PL) after excitation at the interface of a hBN-encapsulated lateral MoSe₂-WSe₂ heterostructures, showing a low-energy feature attributed to CT excitons (box). Larger junction widths (thin in (a)) or excitation on the MoSe₂ side (thin in (b)) do not give rise to CT excitons.

[1] D. Beret, I. Paradisanos, H. Lamsaadi, et al., npj 2D Mater. Appl. **6**, 84 (2022)

[2] H. Lamsaadi, D. Beret, I. Paradisanos, et al., Nat. Commun. **14**, 5881 (2023).

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The Marvel of Charge-Transfer Excitons in Chiral Squaraine Thin Films

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Quadrupolar anilino squaraine dyes exhibit distinct excitonic signatures in their visible to near-infrared absorption spectra due to strong intermolecular interactions. These excitons originate from the spatial arrangement of the molecular backbones, which is steered by non-chromophoric terminal functionalization patterns. They can be of predominantly Frenkel-excitonic nature [1] or are hybridized with intermolecular charge transfer [2] and may feature especially in aggregated thin films an extraordinary strong excitonic circular dichroism [3].

The reason for this extraordinary strong excitonic CD remains unclear, which is mostly evident for ProSQ-C16 thin films, see Figure 1. Theoretical modeling with modified essential state models based on “true” magneto-electric CD finds two possible scenarios for dispersed colloidal ProSQ aggregates carrying variable terminal functionalization: two concomitant aggregate species or a single aggregate type involving intermolecular charge transfer [4]. Ongoing transient absorption spectroscopic investigations on ProSQ-C16 thin films give unambiguous insights into the excitonic nature of ProSQ-C16 aggregates [5].

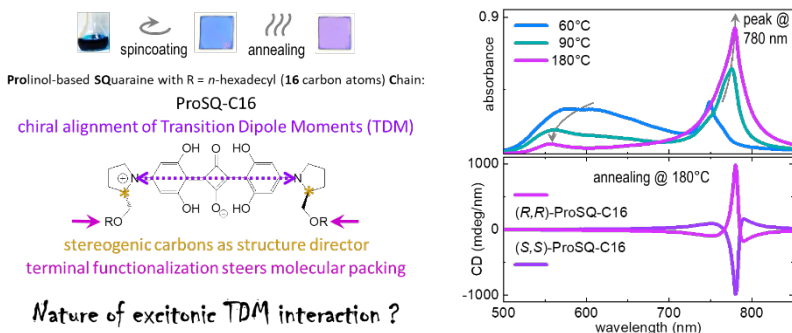


Figure 1. The preparation of aggregated chiral ProSQ-C16 thin films is outlined and resulting absorbance and excitonic circular dichroism (CD) spectra exhibiting a giant CD peak around 780 nm of opposite sign for opposite handedness are shown according to Reference [3].

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Higher Excited States in Anilino Squaraines Resolved via Transient Absorption Microscopy

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Squaraines are a versatile class of chromophores and organic semiconductors. Their absorption in the visible to near-IR spectral region enables the development of biomarkers, optical sensors and photovoltaic devices. Moreover, in the crystalline phase, a pronounced structure--function relationship allows tuning of optical properties by changing the morphology. The optical properties of squaraines were thus thoroughly investigated in the frequency domain with steady-state spectroscopy. Due to short excited-state lifetimes in the picosecond range, however, higher excited states have evaded observation so far.

In this talk, I present first measurements of higher excited states obtained with transient absorption microscopy, a technique that provides femtosecond temporal and micrometer spatial resolution [1]. Transient spectra of collective excitations in anilino squaraines in the orthorhombic morphology are compared to molecular excitations in dilute, solid solutions. Experiments are supported by simulations within the semi-empirical essential states model for donor-acceptor-donor chromophores. These results form the basis for a polarization- and time-resolved analysis for higher excitations and will provide insight into population dynamics between Davydov-split states in molecular aggregates, a phenomenon that is unique to interacting molecules in oblique arrangements.

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Optical spectroscopy of twisted bilayers of two-dimensional transition metal dichalcogenide semiconductors

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Twisted 2D bilayer materials are created by artificial stacking of two monolayer crystal networks of 2D materials with a desired twisting angle θ . The material forms a moiré superlattice due to the periodicity of both top and bottom layer crystal structure. The optical properties are modified by lattice reconstruction and phonon renormalization, which makes optical spectroscopy an ideal characterization tool to study novel physics phenomena. Here, a Raman investigation of the interlayer coupling between two layers of transition metal dichalcogenides [1] and of a full period of a twisted bilayer (tB) WSe₂ moiré superlattice (*i.e.* $0^\circ \leq \theta \leq 60^\circ$) [2]. The intensity of the B_{2g} mode is found to be sensitive to the interlayer coupling while the intensity ratio of two Raman peaks, namely B_{2g} and E_{2g}/A_{1g} correlates with the evolution of the moiré period. Using a series of temperature-dependent Raman and photoluminescence measurements as well as *ab initio* calculations, the intensity ratio is explained as a signature of lattice dynamics in tB WSe₂ moiré superlattices. By further exploring different material combinations of twisted hetero-bilayers, the results are extended for various kinds of Mo- and W-based transition metal dichalcogenides.

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Abstracts – Poster Presentations

Structural fingerprints in the reflectance anisotropy of AlInP(001) surfaces

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The surface optical anisotropy of AlInP(001) surfaces is studied from both experiment and theory. The comparison of the data measured on epitaxially grown $\text{Al}_{0.52}\text{In}_{0.48}\text{P}(001)$ epilayers lattice-matched to GaAs with spectra calculated for energetically favored AlInP(001) surface structures suggests that the surface is covered with a monolayer of buckled phosphorus dimers, where half of the phosphorus atoms are hydrogen-saturated. While the optical anisotropies for photon energies below about 3 eV provide clear fingerprints for the structure of the outermost surface atomic layer, the spectral features at higher energies provide insight into the near surface bulk ordering of AlInP. In particular optical anisotropies at the AlInP critical point energies are found to be related to the CuPt ordering in the material.

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Peculiar optical properties of planar lattices of nanoparticles

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Planar ordered lattices of plasmonic nanoparticles on substrates supporting propagation of surface plasmons attract strong attention due to the tunable interacting electromagnetic excitations. However, standard approaches to describe optical properties of such structures cannot be considered adequate.

Long time ago, it was shown that even a layer of randomly distributed nanoparticles besides of the difference in planar and transverse properties has an effective planar anisotropy [1]. On the base of calculated lattice sums we demonstrated that at inclined illumination of planar lattices this anisotropy depends on the angle of incidence [2]. Such a behavior creates difficulties for the description of planar lattices of nanoparticle by a standard effective dielectric tensor.

Moreover, symmetry considerations reveal that no cross-polarization exists when the lattice is illuminated with the plane of incidence along of any axes of symmetry of the lattice as confirmed in our experiments. For square lattices there are four such directions – along two rows of squares and along two diagonals contrary to standard birefringent materials. It means that the effective axes of the birefringence are given not by the “crystallography” of the lattice but by the plane of incidence.

All these effects are the result of spatial dispersion exhibited in the optical properties of planar lattices. Such effects are practically not visible in normal crystals as the atomic separation is much less than the light wavelength but become visible in artificial lattices with periods comparable with the light wavelengths.

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The use of birefringence in conventional TEM sample preparation

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Birefringent materials exhibit thickness-dependent interference colours in transmission between two polarisers. This phenomenon was published the end of the 19th century by Auguste Michel-Lévy along with a colour chart for different birefringence values (**Figure 1 (a)**). Polarised light passing through birefringent crystals, splits into two components based on their refractive indices n_o and n_e , resulting in an optical path difference called retardation. Recombining both components with an analyser leads to annihilation of certain wavelengths of the white light through destructive interference, revealing observable interference colours.

Our study applies this phenomenon to optimise mechanical thinning in conventional sample preparation for transmission electron microscopy (TEM) [1]. We discuss our findings on dimpled and wedge-polished 4H-SiC/Al₂O₃ two-materials specimens (**Figure 1 (b) and (c)** respectively). For materials with small birefringence, where interference colours vanish at larger thicknesses, we propose a complementary colour chart for a parallel polariser orientation, supplementing the Michel-Lévy chart for crossed polarisers. The thickness of the thinnest sample region can be estimated by eye, where its colour is directly linked to the corresponding thickness in a colour chart, or by simple geometrical models and a more complex RGB analysis of the occurring colours. In both cases the achieved accuracy of thickness monitoring, validated by scanning electron microscopy (SEM), considerably exceeds the measurement capabilities given by built-in mechanical gauges of the thinning instruments. The proposed method streamlines mechanical thinning to low thicknesses, subsequently reducing the required ion-milling time to achieve electron transparency for TEM. Its convenience extends to all other materials, if birefringent materials are thinned along them as a thickness reference.

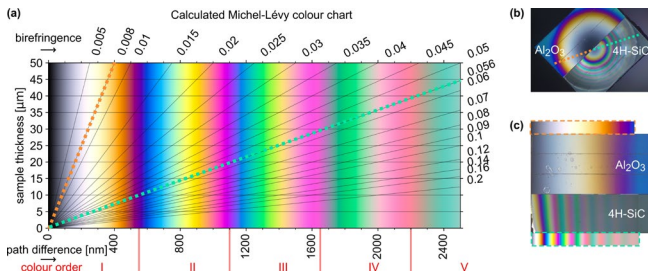


Figure 1. (a) Section of the Michel-Lévy chart containing the orange dotted 0.008-birefringence line of Al₂O₃ and the cyan dotted 0.056-birefringence line of 4H-SiC.; Top-view polarization microscopy image of (b) the dimpled Al₂O₃/4H-SiC sample and (c) the wedge-polished Al₂O₃/4H-SiC sample, with attached respective sections of the Michel-Lévy chart in orange and cyan dashed line frames.

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Operando optical tracking of oxidation state changes of NiFe electrocatalysts by Reflectance Anisotropy Spectroscopy

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The oxygen evolution reaction (OER) is a key reaction involved in water splitting and has attracted increasing attention for hydrogen generation for clean energy uses. Nickel/iron (NiFe)-based compounds have been known as active OER catalysts for decades, and there has been increasing interest in developing NiFe-based materials for higher activity and stability. Reflection Anisotropy Spectroscopy (RAS) in the visible spectral range is a polarisation sensitive optical spectroscopy technique used to study morphological and electronic structure changes of surfaces and thin films in-situ. It achieves high sensitivities in the detection of ultrathin layer structures down to the sub-nanometer scale and can follow the optical changes of the surface during catalytic reactions. By combining in-situ RAS and cyclic voltammetry (CV), the different optical properties of the hydroxide and oxy-hydroxide phases associated with changes in the redox states during OER activity can be optically tracked.

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Spectroscopic Ellipsometry of Microcrystalline Organic Semiconducting Films on SiO₂ Surfaces

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Organic semiconductors have found their way into modern (opto-)electronic applications, and can provide viable alternatives for, or supplementations to existing inorganic technologies. Some of their most useful traits are the high material efficiency, the tuneability of their opto-electronic properties, morphology, and processability by chemical as well as physical means, such as thermal annealing. Polymeric semiconductors, however, suffer from a few disadvantages, prominently, for example, batch-to-batch variations in connection with high dispersity. Recently developed monodisperse, discrete oligomers based on naphthalene diimide (NDI) and bithiophene (T2) show similar properties as their polymeric counterpart P(NDI-T2) while avoiding these typical downsides [1]. The polymer P(NDI-T2) is well known to exhibit different polymorphous forms corresponding to their molecular alignment, which leads to uniaxial optical anisotropy that changes upon thermally induced crystallization.[2].

We carried out variable-angle spectroscopic ellipsometry studies on thin films of the discrete oligomers NDI-(T2-NDI)₂ and T2-(NDI-T2)₂ deposited on thermally oxidized silicon surfaces and compare their properties in the as-cast case and after thermally induced crystallization. The ellipsometric spectra are analyzed utilizing uniaxially anisotropic modelling to illuminate the dielectric response of molecules aligned parallel or perpendicular to the substrate surface. To enhance the optical response of organic thin films and thus improve the accuracy of the modelling, interference enhancement is employed by the incorporation of thick dielectric SiO₂ interlayers [3]. The thus achieved models are then applied to microscopically resolved imaging ellipsometry maps to identify the lateral distribution of the crystalline alignment.

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Verification of a model for the spectroscopic ellipsometry analysis of plasma-activated Si wafers for direct wafer bonding

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The impact of plasma treatment on Si wafers with a native oxide was systematically investigated using spectroscopic ellipsometry. A general applicable three-layer optical model for ellipsometry data fitting was developed and employed on samples treated with N₂, O₂ and N₂/O₂ mixture plasma. [1] Oxide-growth, amorphization of crystalline Si and the formation of a transition layer between the SiO₂ and the amorphous Si were detected. The resulted thicknesses of the determined layer structure were confirmed by complementary methods which allow precise layer-thicknesses detection, namely angle-resolved X-ray photoelectron spectroscopy and transmission electron microscopy. The depth-resolved chemical composition and the direct thickness measurements of the produced amorphous structure revealed pronounced elemental gradients and the absence of sharp interfaces. Nitrogen gas used in the plasma process was found to be implanted mainly at the interface of the SiO₂/transition-layer in form of Si₃N₄. However, it was verified that it is feasible to employ one general SE model consisting of SiO₂/transition-layer/amorphous Si on crystalline Si for all plasma species due to comparably low Si₃N₄ concentrations and similar to SiO₂ in refractive index *n* and absorption *k*. It can be concluded that the present approach of SE model development and verification is well suited for plasma-activated direct wafer bonding processes.

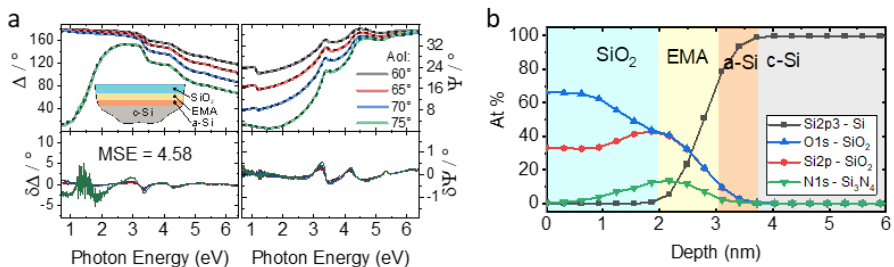


Figure 1. (a) Comparison of ellipsometry experimental and modelled data for a N₂ plasma activated Si wafer. Applied ellipsometry model indicated as schematic layer structure. (b) Layer thicknesses by ellipsometry and complementary angle-resolved X-ray photoelectron spectroscopy depth profile data.

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Phonon Polaritons Launched by Natural Boron Nitride Wrinkles Probed with Nano-FTIR Spectroscopy

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Phonon polaritons (PhPs), which result from strong coupling of light with phonons, in layered 2D materials provide the promising opportunity to manipulate and guide light at the nanometer scale. While there are several publications about such PhPs launched by edges of flakes [1,2], only few deal with wrinkle-launched PhPs [3].

Here, we transferred an exfoliated hexagonal Boron Nitride (hBN) flake with a thickness of approximately 16 nm onto a gold substrate. The substrate was prepared by evaporating approximately 100 nm of gold onto a piece of polished silicon wafer. We characterized the flake by micro-Raman (514.7 nm excitation) and nano-FTIR spectroscopy using a LabRam Raman spectrometer and a neaSNOM nano-FTIR spectrometer, respectively. The Raman spectra show no difference between points on the flat surface and points on the wrinkles of the flake. Nano-FTIR spectra, while comparable to conventional IR spectra on the flat surface, show a strong change in the form of a second absorption peak appearing near the wrinkle. This second absorption peak shifts to higher wavenumber and becomes more intense as the probed spot gets closer to the wrinkle. This is consistent with the behavior of PhPs when approaching the scattering point that is launching them. We can thus conclude that the wrinkles effectively launch PhPs.

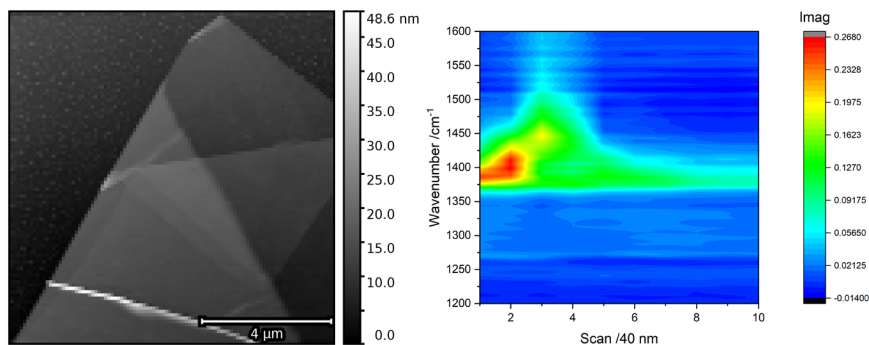


Figure 1. Left: AFM topography image of the hBN flake. A wrinkle can be seen at the bottom. Right: Change of nano-FTIR absorption ($\text{Im}(\sigma)$) when scanning across a hBN wrinkle. The shape arises from the asymmetry of the wrinkle.

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Optical properties of quaternary Cu-Ni-Sn-S nanocrystals in colloidal solutions and thin films

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Semiconducting Cu₂ZnSnS₄ (CZTS) is well-known as a light-absorbing material for photovoltaic applications [1-4]. However, the efficiency of CZTS solar cells is limited due to defects and cation disorder [2]. Substitution of Zn in the Cu₂ZnSnS₄ crystal structure by other metals such as Mg, Ba, Fe, Co, and Ni can reduce the number of defects and tune its electronic and optoelectronic properties [3]. However, studies of cation-substituted quaternary chalcogenide nanocrystals (NCs) are scarce compared to CZTS NCs. Here, we report the optical properties of novel cation-substituted Cu-Ni-Sn-S (CNTS) NCs prepared by a "green" synthesis method in aqueous solutions.

The CNTS colloidal NCs were obtained via an exchange reaction between aqueous solutions of Ni, Cu, and Sn thioglycolates and sodium sulfide at normal pressure and air conditions. Similar CZTS NCs were obtained by us earlier [1], while for CNTS NCs such a synthesis is reported for the first time. The structure and composition of CNTS NCs were characterized by X-ray diffraction (XRD), Raman spectroscopy, and X-ray photoemission spectroscopy (XPS). The NC size is estimated from the XRD peak broadening as 2-3 nm. The resonant and non-resonant Raman spectra indicate a cation-disordered kesterite structure of CNTS NCs similar to that of CZTS NCs [1]. XPS revealed a Sn deficiency and Ni excess indicating a non-stoichiometric composition of CNTS NCs.

Thin films of colloiddally prepared CNTS NCs were deposited on glass substrates by spin coating. The optical properties of the thin films were studied using transmittance, reflectance, and spectroscopic ellipsometry (SE). The film thicknesses were determined in the range of 20-50 nm. The absorption coefficient revealed a continuous featureless absorption extending from the visible to the UV range, similar to the absorption of these NCs measured in colloidal solutions. Such a behavior is likely to be caused by defects or an intrinsic nonstoichiometric composition of the NCs. The absorption coefficient of $\approx 10^4$ cm⁻¹ at 700 nm reveals that this material is promising for absorbing layers in photovoltaic applications.

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Catalytic performance by in situ UV-vis spectroscopy of ZnO, TiO₂, CeO₂ on multiwalled carbon nanotubes

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There is a great interest in the study of catalysts dedicated to the remotion of organic contaminants contributing to a healthy environment. In this work, three catalysts were synthesized with MWCNTs decorated with ZnO, TiO₂ and CeO₂, and Ag nanoparticles by microwave irradiation. The morphology of the obtained catalysts Ag@ZnO/MWCNTs, Ag@CeO₂/MWCNTs, and Ag@TiO₂/MWCNTs was characterized by HRTEM, Raman and UV-Vis spectroscopies. The process commonly used for the degradation of organic contaminants is carried out by the reduction of 4-nitrophenol (4 NP) to 4-aminophenol (4 AP) in the presence of NaBH₄ as a reducing agent. When the catalyst is added, the electrons are transferred from BH₄⁻ to nitrophenol contaminant via the surface of nanoparticles and hence the nitrophenol is reduced into aminophenol. Applying in situ UV-vis spectroscopy, the evolution of the degradation of organic compound in the presence of the catalyst was tracked. The characteristic absorbance peak of the 4-NP gradually decreased which indicates it is reduced, and the characteristic peak of the 4 AP is increased. The complete disappearance of the absorption peak of the reactant after some time marked the end of the reaction. The progress of the reaction for first-order kinetics is described with the apparent rate constant $k_{app} = \ln(C_t/C_0)$, where C_t is the concentration of nitrophenol at any time t and C_0 is the initial concentration at zero time. By Raman spectroscopy, the catalysts were characterized to obtain information related to the functionalization which was confirmed by HRTEM. Founding a relation between the degree of functionalization of the MWCNTs with the oxides and Ag nanoparticles, and the catalytic performance. The values obtained of the apparent rate constant k_{app} are superior to similar materials reported in the literature. In addition, the catalyst exhibits remarkable catalytic stability for the reduction of 4-NP.

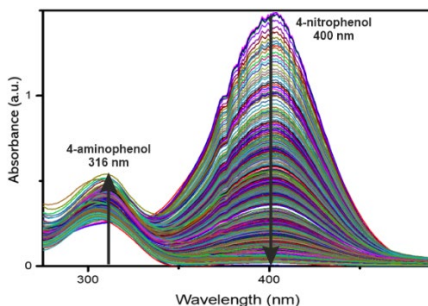


Figure 1. UV-vis spectra in situ during the reduction of 4 NP (400 nm) to 4 AP (300 nm).

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Optimization of silver surface quality for use in high performance mirrors

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The optical properties of the materials, especially in thin film form, are heavily dependent on the fabrication technology. Nevertheless, once measured, they get into tabulated handbooks, which are frequently used for the design of the optical devices and instruments and interpretation of experimental data. One such highly respected source is the multi-volume "Handbook of optical constants of solids" by E.D. Palik [1]. Optical fabrication technologies, however, are constantly evolving and such optical materials database needs frequent revising. The one of the goals of the EU EMPIR ATMOC project is such comprehensive revision of the materials database in a wide spectral range.

One of important materials for optics is silver, which is used for mirror fabrication, for instance [2]. We show, on the example of silver, how the deposition parameters affect optical properties of sputtered silver, measured by spectroscopic ellipsometry. In many cases direct inversion of ellipsometric data is allowed, provided there are no overlayers or roughness present on the surface of material and the thickness of the film is sufficiently large to treat it as semi-infinite media.

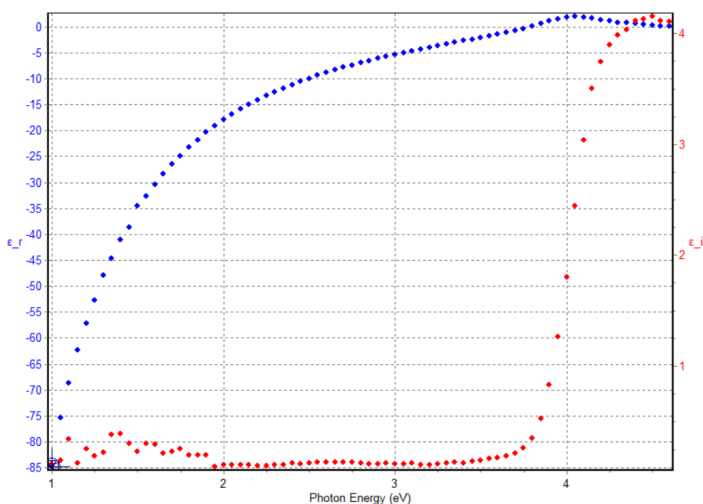


Figure 1. Dielectric function of silver obtained by the direct inversion of ellipsometric measurements.

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Mueller polarimetry for diagnostic imaging of biological surfaces at macro- and microscale

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It has been proven that polarized light is extremely sensitive to the microstructure of biological tissue. While early pathological changes in tissues may not be visible with a naked eye, the contrast between healthy tissue and pathological zones can be increased significantly in polarized light images [1]. It can be explained by the alterations of fine fabric of healthy tissue even at the early stage of disease development. Wide-field imaging Mueller matrix polarimetry operating in a visible wavelength range has already demonstrated its potential for a fast imaging of biological tissue surfaces for non-invasive diagnosis and following treatment. After the appropriate decomposition of measured Mueller matrix images the polarimetric maps of tissue depolarization, retardance and diattenuation may help clinicians to detect the diseased zones and delineate their exact borders for subsequent excision, if necessary. The results of our studies of biological tissues of brain (Fig.1) [2] and stomach [3] using wide-field imaging Mueller matrix polarimetry at both macro- and microscale and appropriate data post-processing algorithms will be presented and discussed.

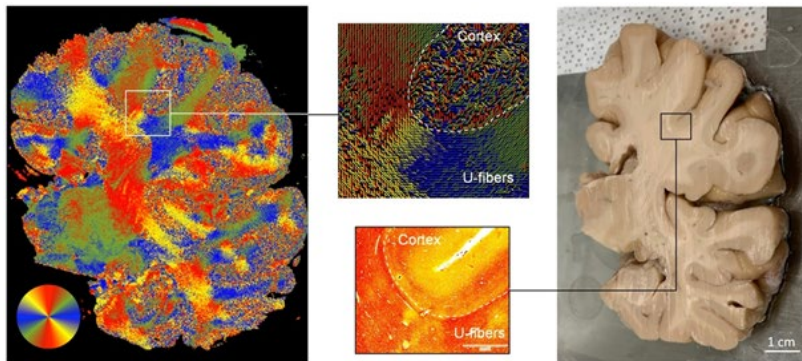


Figure 1. Polarimetric map of the azimuth of the optical axis (left panel) of thick section of formalin fixed human brain (right panel). Orientation of the optical axis in the zone of U-fiber (top central panel) demonstrate compelling correlation with the direction of brain fibers in the image of silver-stained thin histological section of the same zone (bottom central panel).

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- [2] P. Schucht *et al.* "Visualization of White Matter Fiber Tracts of Brain Tissue Sections with Wide-field Imaging Mueller Polarimetry", *IEEE Trans. Med. Imaging*, 39(12) 4376-4382 (2020)
- [3] M. Kim *et al.* "Optical diagnosis of gastric tissue biopsies with Mueller microscopy and statistical analysis", *J. Europ. Opt. Soc. Rapid Publ.*, 18(2), 10 (2022)

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In situ monitoring of surface termination of $\text{Ti}_3\text{C}_2\text{T}_x$ MXene with Raman spectroscopy

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In the last years, a family of 2D materials called MXenes has attracted attention due to an interesting combination of physical properties, such as versatile surface chemistry, metallic conductivity, mechanical flexibility and high hydrophilicity. The most studied MXene so far, $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes, are synthesized by etching a Ti_3AlC_2 MAX phase and exhibit a typical mixed surface termination of $\text{T}_x = \text{OH}$, O , and/or F . A better knowledge of the surface chemistry of MXenes is critical for the implementation in technological applications (e.g. energy storage, sensors, biomedicine). A promising investigation approach is annealing-induced desorption of surface terminations, because it might leave parts of the MXene surface unterminated, making the surface very active for further functionalizations.

In this work, we discuss Raman spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes taken under chemically inert conditions in ultra-high vacuum, for the first time. In particular, we compare the spectra at room temperature before and after annealing with regard to effects on structural disorder and surface termination[1]. Significant changes in the Raman spectra are correlated with the desorption of 80% of the F surface termination at approximately 650 °C. This was confirmed by mass spectra and X-ray photoemission spectra. Above 650°C a structural decomposition of the MXene in UHV sets in, accompanied with a change in electronic properties. Most of the observed spectral features show a significant broadening already before annealing. We attribute this to the intrinsic disordered nature of the MXenes due to a mixed surface termination and a broad background associated to electronic Raman scattering. With this study we identified the vibrational signatures associated with F-termination and provided new insights into the interpretation of the vibrational spectra of $\text{Ti}_3\text{C}_2\text{T}_x$ MXenes.

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Filling the gaps, status of the OCDB project for accurate optical constants in the soft X-ray, EUV and VUV spectral range

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The optical constants n & k are a fundamental basis for the development of many optical systems. Especially in the EUV and VUV spectral range, there are still many gaps in the existing data sources and valid investigations of the uncertainties are almost non-existent. Therefore, PTB is establishing a new database (ocdb.ptb.de) in close cooperation with several European partners with the aim to close these data gaps over a large spectral range (soft X-ray to VUV). The electron storage rings BESSYII and the Metrology Light Source are ideal sources for this kind of metrological materials science and allow the creation of a suitable reference measurement infrastructure.

As part of the ATMOC project, PTB is validating reflectometry (as well as ellipsometry) measurements for n & k determinations of thin film systems from the soft X-ray spectral range of 1 keV to the VUV range around 220 nm. This includes measurements on 2-3 beamlines at two different synchrotrons. On the experimental side this is also one of the biggest challenges to get consistent results over all spectral ranges. On the theoretical side, which is required to determine the optical constants from the reflectivity measurements, the large spectral range also creates a further challenge. On the one hand, numerically due to the required data density, but also physically due to strong changes in optical contrasts or different sensitivities, e.g. in the description of surface roughness. In order to work effectively with a standardized theoretical model in the future and to speed up evaluations, parameter sensitivities must be included in the analyses. Furthermore, the forward models need to be massively accelerated numerically to allow uncertainty analysis based on statistical methods. We present first results and discuss possible next steps.

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A MODIFIED REFLECTANCE ANISOTROPY SPECTROSCOPY SPECTROMETER FOR ELLIPTICITY MEASUREMENTS

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Reflectance anisotropy spectroscopy (RAS) has been largely used to investigate clean surfaces of metals and semiconductors in ultra-high vacuum (UHV), low-dimensionality solid state systems and finally organic layers. In all these experiments, RAS has been limited to the study of the anisotropy of the linear dichroism of matter. The same technique can be used to investigate the ellipticity in transmittance by a proper modification in the experimental apparatus, opening intriguing perspectives in the experimental study of chirality [1]. In a typical RAS system, the photoelastic modulator (PEM) is properly driven by an oscillating circuit at the resonance frequency of the piezoelectric crystal to introduce a phase shift equal to $\pm\pi$ between light beams propagating along ordinary and extraordinary axes, thus modulating the linear polarization of light between two orthogonal independent states. By a proper modification of the applied voltage to introduce a phase shift equal to $\pm\pi/2$, the PEM produces outgoing light alternatively right and left circularly polarized, with a resulting signal that opens interesting possibilities to investigate the chirality of organic and biological layers. Although commercial spectrometers already exist to measure the ellipticity of substances, the “open structure” of this new spectrometer and its higher flexibility in design makes it possible to couple it with UHV systems or other experimental configurations. Here, we give some insights about the use of this RAS spectrometer in transmission to measure ellipticity features of porphyrins in solution and in solid films, comparing the spectra obtained with the ones produced by a commercial spectrometer apparatus (JASCO).

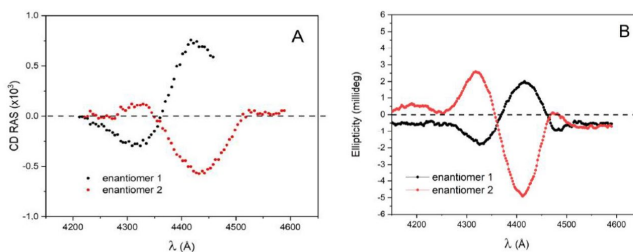


Figure 1. Panel A: CD-RAS experimental spectra for enantiomer 1 (red curve) and enantiomer 2 (black curve). The two enantiomers have been obtained from a 50 μl droplet of a ZnOEP solution in dichloromethane deposited onto a glass substrate and measured in transmission mode. The resulting film has an average thickness estimated in the range 10-15 nm from Atomic Force Microscope images. Panel B: ellipticity spectra measured on the same samples by a commercial spectrometer for Circular Dichroism for enantiomer 1 (red curve) and enantiomer 2 (black curve).

[1] Tomei, I., Bonanni, B., Sgarlata, A., Fanfoni, M., Martini, R., Di Filippo, I., Magna G., Stefanelli M., Monti D., Paolesse R., Goletti, C. (2023). Chiral Porphyrin Assemblies Investigated by a Modified Reflectance Anisotropy Spectroscopy Spectrometer. *Molecules*, 28(8), 3471.

Laser Induced Damage and Contamination in Optical Coatings Study by Imaging Ellipsometry

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During exposure to laser irradiation, optical coatings undergo various transformations, leading to potential harm and damage. The immediate and post-experiment identification of severe damage poses challenges, particularly in assessing alterations in coloration and contamination growth resulting from laser exposure solely through the analysis of reflected or scattered light intensity. Imaging ellipsometry, however, offers a unique perspective by revealing changes in polarized light reflection at irradiated sites.

Our investigation delved into a comprehensive assessment of diverse mirror designs to determine the impact of electric field distribution and material properties on laser-induced contamination phenomena. High-energy, high-repetition-rate laser systems face significant challenges from laser-induced damage and contamination (LID and LIC), necessitating early detection during operation and the application of more sensitive measurement techniques. While conventional methods primarily focus on changes in light intensity for resistivity assessment during optical coating irradiation, our study highlights the potential insights gained by incorporating phase changes into complex measurements.

The focus of our research centered on the analysis of sputtered and evaporated high reflectivity mirrors (HRs). S-on-1 measurements were utilized to identify distinct LID modes such as discoloration and catastrophic damage. Imaging ellipsometry played a crucial role in examining subtle alterations at irradiated sites, including those with discoloration and catastrophic damage. Additionally, we subjected HRs, deposited using e-beam technology, to intensive ultrafast laser pulses for extended durations. Mirror designs varied, exploring the impact of material and electric field distribution on LIC accumulation.

Two specific designs were built on quarter wavelength optical thickness (QWOT) layers: the first featuring a high refractive index film (hafnia in our case), while the second utilized a double QWOT of a low refractive index film (silica in our case) as its final layer. Electric fields for the latter two coatings were manipulated by adjusting the thickness of the final silica layer. All samples exhibited LIC below the damage threshold, with notable differences observed through confocal microscopy for each coating. To quantitatively compare different coating designs during the LIC process, imaging ellipsometry was employed on the same samples.

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Nanoassemblies based on Ag-In-S/ZnS quantum dots and porphyrins: formation principles, interface events and energy relaxation processes

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Over the last three decades, the synthetic pathways to prepare semiconductor-based nanoassemblies have vastly expanded and developed. These developments allowed the formation of various hybrid nanosystems composed of different material combinations. The specific material combination can dictate the physical, chemical, and optical properties and interface effects for the resultant hybrid nanosystems.

Recently [1, 2] we described the first results of comparative study (steady-state absorption/ photoluminescence, time-resolved experiments, Raman spectroscopy, dynamic light scattering) describing Coulomb electrostatic interactions of positively charged 5,10,15,20-(tetra-N-methyl-4-pyridyl)porphyrin molecules with negatively charged glutathione stabilized core/shell semiconductor quantum dots (QD) AgInS/ZnS leading to the formation of stable QD-porphyrin nanoassemblies in water (pH 7.5) at ambient temperature.

Using elaborated size-consistent quantum chemical atomistic 3D model for AIS/ZnS/GSH QD (based on method MM+), we propose a detailed physico-chemical description for the interaction of the porphyrin macrocycle with the glutathione capped QD. It includes electrostatic interactions of the positively charged porphyrin free base molecule with negatively charged capping ligand (glutathione), followed by a very fast metalation of porphyrin free base (formation of the axial aqua Zn-complex, (H₂O)ZnP⁴⁺). It was shown that, spectral properties of attached Zn-porphyrin reflect the interaction of central Zn ion of the porphyrin macrocycle with a strong ligand on QD surface. It follows from the elaborated 3D model that in AIS/ZnS/GSH QD – porphyrin nanoassemblies, the tetracation ZnP⁴⁺ lies on the SH-facet surface, forming an axial coordination bond (≡S)-ZnP⁴⁺ between zinc ion in ZnP⁴⁺ and surface sulphur atom (manifesting a strong extra-ligation effect), accompanied by multiple ≡SH-π interactions, thus resulting in the final “guest” geometry via chemisorption (docking) of (L)ZnP⁴⁺ molecule on the SH facet.

Then, on the basis of the quantitative comparison of the results for the strong “quasi-static” quenching of QD PL and the fluorescence sensitization of attached (L)ZnP⁴⁺ molecule, it was evaluated that the dynamics and pathways of excitation energy relaxation processes in AIS/ZnS/GSH QD – porphyrin nanoassemblies are caused by two main competitive non-radiative processes, namely Förster resonance energy transfer AIS/ZnS/GSH QD → Zn-porphyrin (in ps time scale), and the electron tunnelling beyond the AIS/ZnS core under conditions of quantum confinement.

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