

# STRUCTURE FORMATION AND ALIGNMENT OF POLYMER SEMICONDUCTORS IN THIN FILMS

**Mukundan Thelakkat<sup>a</sup>, Christian Müller<sup>a</sup>, Christopher R. McNeill<sup>b</sup> and Eliot Gann<sup>b</sup>**

<sup>a</sup>Applied Functional Polymers, Macromolecular Chemistry I, University of Bayreuth, 95440 Bayreuth, Germany

<sup>b</sup>Department of Materials Science and Engineering, Monash University, Wellington Road, Clayton, Victoria, 3149, Australia

In thin films of semiconductor polymers, the polymer chains typically exhibit distinct orientation with respect to the substrate. The planar pi-face of the backbone can orient either in edge-on or face-on manner. Especially, an edge-on alignment is favorable for transport in thin film transistors, whereas face-on alignment is considered to improve vertical transport as desired in solar cells. However, molecular orientation is among the very few parameters that usually cannot be controlled when tailoring new semiconducting polymers. Here we show that both the mode of orientation as well as the degree of alignment can be well controlled by exploiting diffusive non-covalent interactions along the backbone using polydiketopyrrolopyrroles (PDPPs) as a case study.

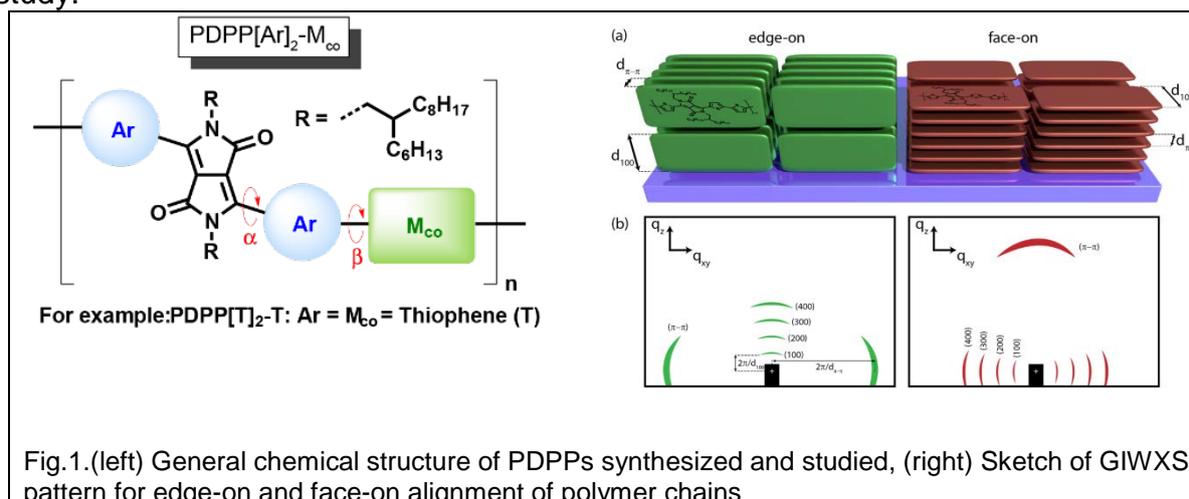


Fig.1.(left) General chemical structure of PDPPs synthesized and studied, (right) Sketch of GIWAXS pattern for edge-on and face-on alignment of polymer chains

By strategically varying the chemical structure in a systematic way, we attribute for the first time, the precise control of orientation based on diffusive non-covalent interactions. Our results demonstrate how orientation in thin films of semiconducting polymers can be controlled and optimized by rational design. This study enables high-performance organic semiconductors with the additional benefit of tailored orientation that fits the desired application.

**Keywords:** Charge transport; Polydiketopyrrolopyrroles, molecular orientation, GIWAXS, conjugated polymers

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# ELECTRONIC STATES TUNING FOR CdSe/ZnS QUANTUM DOTS UPON SELF-ASSEMBLY WITH ONLY ONE FUNCTIONAL DYE MOLECULE

**E. Zenkevich<sup>a</sup>, A. Stupak<sup>b</sup>, C. Göhler<sup>c</sup>, C. Krasselt<sup>c</sup>, and C. von Borczyskowski<sup>c</sup>**

<sup>a</sup>National Technical University of Belarus, Minsk 220013, Belarus

<sup>b</sup>B.I. Stepanov Institute of Physics, 220072 Minsk, Belarus

<sup>c</sup>Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany

It is known that capping organic shell (including surfactants and ligands) have considerable impact on the semiconductor quantum dot (QD) surface structure and optical properties of QDs (hot carrier relaxation, quantum efficiency and photoluminescence, PL energy). Recent progress in quantum chemical calculations of structures and electronic properties of QDs has set new milestones in the understanding of QD surfaces and the capping ligand role. However, detailed and specific experimental studies on the influence of only one (or at least a few) ligand or surface attached dye molecules on surface states are difficult to conceive.

Here, we present spectral and time resolved PL data (from temperature dependent ensemble experiments) for CdSe/ZnS QD-porphyrin nanoassemblies (at molar ratio 1:1) in solvent giving rigid glassy matrix at low temperature. We have succeeded to detect the sensitivity of QD PL parameters to the chemical nature of the respective porphyrin molecules and the impact of the competing ligand layer. In addition, the results of such an elaborated investigation on an ensemble of QD-porphyrin nanoassemblies have been compared with those obtained by a newly designed and complementary (time and spectrally resolved) spectroscopy on single QDs [1]. We concluded that electronic states of different nature with varying PL energies and decay dynamic are subsequently explored on slow time scales typical for blinking phenomena which are buried but nevertheless present in ensemble experiments. Upon temperature variation the ordering of at least 2 energetically deconvoluted PL states is abruptly changed at the “phase transition”. The temperature dependence of the PL observables reveals both the influence of electron-phonon coupling between 77 K and 290 K and a “phase transition” of the capping TOPO shell at  $T_{\text{crit}} \approx 220$  K. According to time resolved experiments we found at least 3 basically different types of emissive states. The specific selectivity of QD PL properties to the surface-attached only one dye molecule provides new and not yet reported experimental insights into QD surface properties. Modifications of PL properties of nanoassemblies are assigned to dye induced ligand removal accompanied by spectral blue shifts and formation of surface trap states in the band gap, and the temperature controls the energetic ordering of electronic states. The basic conclusion is that a dye molecule removes ligands from (specific) surface sites thus acting as a new “ligand” creating a modified set of new surface responsible for “Non-FRET” PL quenching upon QD-dye nanoassembly formation but not leading to FRET or charge transfer events. Such dye molecule may be considered as single molecular surface probe.

*Keywords:* Semiconductor quantum dots, Porphyrins, Perilene-bisimids, Ligand dynamics, Photoluminescence, Surface traps, Temperature surface “phase” transition, Blinking.

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# NON-STOICHIOMETRIC Cu-In-S@ZnS NANOPARTICLES PRODUCED IN AQUEOUS SOLUTIONS BY A “GREEN” METHOD AS LIGHT HARVESTERS FOR LIQUID-JUNCTION PHOTOELECTROCHEMICAL SOLAR CELLS

**O. Stroyuk<sup>a</sup>, A. Raevskaya<sup>a</sup>, O. Rosovik<sup>a</sup>, A. Kozytskiy<sup>a</sup>, V. Dzhagan<sup>b,c</sup>, D. Zahn<sup>b</sup>**

<sup>a</sup> L.V. Pysarzhevsky Institute of Physical Chemistry of Nat. Acad. Sci. of Ukraine, prosp. Nauky 31, Kyiv 03028, Ukraine

<sup>b</sup>Semiconductor Physics, Technische Universität Chemnitz, Reichenhainer Str. 70, 09107 Chemnitz, Germany

<sup>c</sup>V.E. Lashkaryov Institute of Semiconductor Physics of Nat. Acad. Sci. of Ukraine, prosp. Nauky 41, 03028, Kyiv, Ukraine

A direct “green” aqueous synthesis of mercaptoacetate-stabilized copper indium sulfide (CIS) nanoparticles (NPs) and core-shell CIS@ZnS NPs is reported. The NPs can be easily deposited onto the surface of nanocrystalline FTO/TiO<sub>2</sub> films yielding the visible-light-sensitive photoanodes for the liquid-junction solar cells.

Systematic variation of the NP composition, that is the content of copper, indium and sulfur, as well as the amount of ZnS deposited as a protective shell on the surface of CIS NPs showed that the highest photoelectrochemical activity was demonstrated by a TiO<sub>2</sub>/CIS@ZnS photoanode with a molar Cu:In:S ratio of 1:5:10 and a ZnS shell produced as a molar Zn:Cu ratio of 1:1.

The photoelectrochemical activity of TiO<sub>2</sub>/CIS@ZnS heterostructures and the photoluminescence (PL) intensity of original colloidal CIS@ZnS NPs were found to change in a similar manner at the variations of copper and indium content allowing to use PL as an indicative parameter when designing CIS-based absorbers for the solar cells. The Raman spectra of CIS NPs revealed a set of features typical for stoichiometric and copper-poorer chalcopyrite phases that is preserved after the ZnS shell formation and deposition of the CIS@ZnS NPs onto the titania surface. The X-ray photoelectron spectroscopy confirmed the copper and indium present as Cu(I) and In(III) and successful formation of a ZnS shell in the case of CIS@ZnS NPs.

The optimized TiO<sub>2</sub>/CIS@ZnS photoanodes with Cu:In:S and Zn:Cu ratios of 1:5:10 and 1:1 were tested in two-electrode solar cells with aqueous polysulfide electrolyte and TiO<sub>2</sub>/Cu<sub>2</sub>S heterostructures produced by an original photo-assisted method as counter-electrodes. The cells revealed good stability providing steady photoelectrochemical parameters during more than 2-h continuous illumination and at least a week period of intermittent illumination as well as the excellent reproducibility of the light conversion efficiency that varied in the studied sequence of six identical solar cells not higher than by 1%. Under illumination by a xenon lamp with an intensity of 30 mW/cm<sup>2</sup> lamp the optimized cells showed the average light conversion efficiency of 8.2% with the average open-circuit voltage close to 0.6 V and the average fill factor of 0.42. Similar solar cells based on CIS NPs that were not covered with a ZnS shell demonstrated a far inferior activity with the light conversion efficiency around 5.8% indicating a crucial role of the passivation of surface defects of CIS NPs for achieving efficient charge collection from the TiO<sub>2</sub>/CIS photoanodes.

The work is supported by the Volkswagen Foundation (project “New functionalities of semiconductor nanocrystals by controllable coupling to molecules”).

# PLASMONIC ENHANCEMENT OF RAMAN SCATTERING AND IR ABSORPTION BY QUANTUM DOTS DEPOSITED ON METAL NANOSTRUCTURES

A.G. Milekhin<sup>a, b</sup>, L.L. Sveshnikova<sup>a</sup>, T. A. Duda<sup>a</sup>, E. E. Rodyakina<sup>a, b</sup>, I.A. Milekhin<sup>a, b</sup>, S.L. Veber<sup>cc</sup>, S.A. Kuznetsov<sup>b</sup>, V.M. Dzhagan<sup>d</sup>, A.V. Latyshev<sup>a, b</sup>, and D.R.T. Zahn<sup>d</sup>

<sup>a</sup>A.V. Rzhzanov Institute of Semiconductor Physics, Lavrentjeva, 13, 630090, Novosibirsk, Russia

<sup>b</sup>Novosibirsk State University, Pirogov str. 2, 630090, Novosibirsk, Russia

<sup>c</sup>International Tomography Center SB RAS, 630090, Novosibirsk, Russia

<sup>d</sup>Semiconductor Physics, D-09107 Chemnitz, Technische Universität Chemnitz, Germany

Metal nanostructures can lead to localised surface plasmon resonances (LSPR) with energies located in the spectral range from ultra-violet to far-infrared depending on their morphology. They can be effectively used for surface-enhanced Raman scattering (SERS) and infrared absorption (SEIRA) by semiconductor quantum dots (QDs).

Here we present the results of an investigation of SERS and SEIRA by semiconductor QDs homogeneously deposited on arrays of Au nanoclusters, dimers, and nanoantennas. The structural parameters of semiconducting and metal nanostructures were confirmed by scanning electron microscopy (SEM). The LSPR energy in the arrays of Au nanoantennas and nanoclusters as a function of their size was determined by means of IR and optical spectroscopies.

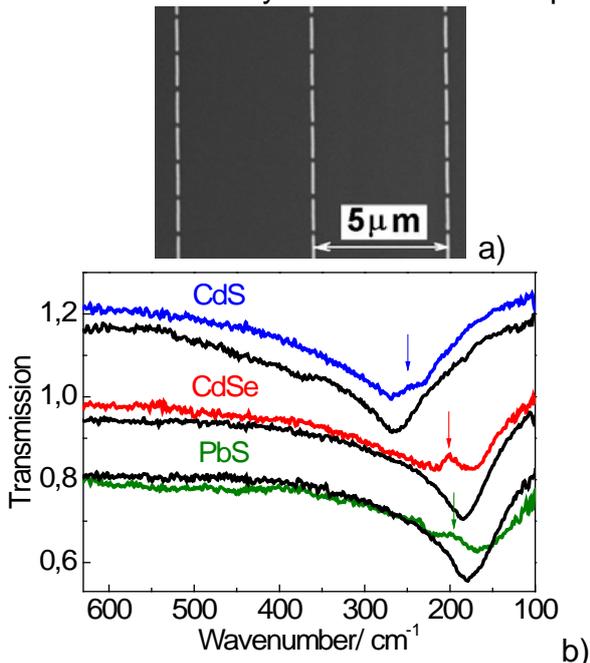


Fig.1 a)- SEM image of a Au nanoantenna array. b)- SEIRA spectra of 1 monolayer of CdS, CdSe, and PbS QDs. The IR spectra of the arrays without QDs are given for comparison.

CdSe QDs deposited on Au nanocluster arrays reveal SERS effect by confined longitudinal optical (LO) phonons in QDs. The SERS enhancement factor (EF) depends resonantly on the metal nanocluster size and thus on the LSPR energy. EF shows a polarization anisotropy for CdSe QDs on Au dimers. A confinement-induced shift of the LO phonon mode was observed for CdSe QDs deposited on the structures with single Au dimers. This shift depends on the CdSe QD size and indicates quasi-single QD Raman spectra being obtained.

3D electrodynamic simulations were used to calculate structural parameters of nanoantennas providing the maximal SEIRA enhancement at the energy of optical phonons in QDs. SEIRA by surface optical modes in monolayers of CdS, CdSe, and PbS

QDs on nanoantenna arrays was observed (indicated by arrows in Fig.1b).

This work was supported by Russian Science Foundation (project 14-12-01037).

**Keywords:** enhancement; Raman scattering; IR absorption; phonons

# Magnetic Nanostructures Designed For Hard Disk Drive Applications

Olav Hellwig

San Jose Research Center, HGST, a Western Digital Company, San Jose, CA, USA  
Institute of Physics, Chemnitz University of Technology, 09107 Chemnitz, Germany  
Institute for Ion-Beam-Physics and Material Science,  
Helmholtz-Zentrum Dresden-Rossendorf, 01328 Dresden, Germany

Continued progress in hard disk drive areal density for conventional perpendicular magnetic recording (PMR) based on granular media has become increasingly difficult [1]. Although adoption of energy assisted magnetic recording (EAMR), specifically Heat Assisted Magnetic Recording (HAMR) [2] is widely viewed as a promising solution for thermal stability issues, challenges in grain size scaling and managing media noise may limit the rate of progress for EAMR based on granular media. Bit patterned recording (BPR) stands as an attractive alternative to granular media, offering a path to thermally stable recording at high density and significantly reduced media noise by replacing the segregated random grains of PMR media with lithographically defined single domain islands [3,4]. Figure 1 compares and summarizes basic characteristics of currently used conventional PMR based on granular media and BPR based on pre-defined bits.

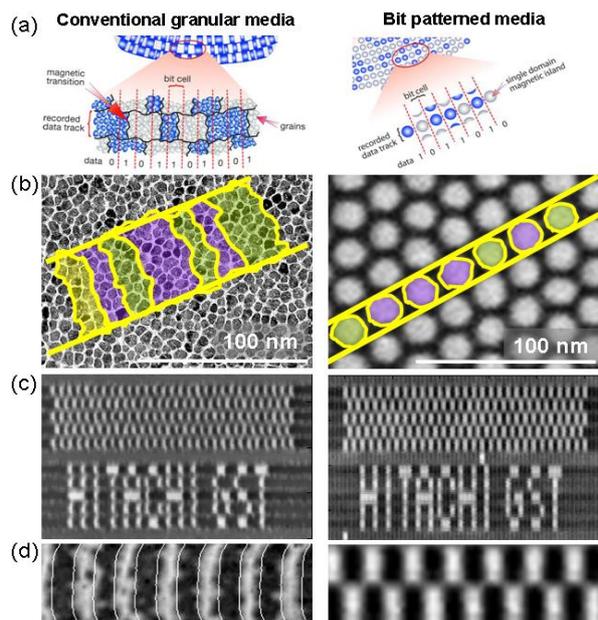


Fig. 1. Comparison of granular PMR (*left*) and BPR (*right*) media systems. (a) Bit scheme for both recording systems. (b) Bit definition within the lateral recording media microstructure. (c) Comparison of static read/write testing on both media systems. (d) High resolution images with alternating up-down bit structure for both recording systems. Bit dimensions in (c) and (d) are 145 nm cross track and 45 nm down track ( $\sim 100$  Gb/in<sup>2</sup>).

In my talk I will discuss various choices for BPR magnetic materials, such as Co/Pd and Co/Pt multilayers as well as CoCrPt and FePt L1<sub>0</sub> alloys. I will highlight advantages and disadvantages of the different magnetic material systems with respect to potential applications in BPR and outline the specific challenges when comparing conventional PMR, BPR and currently emerging HAMR systems.

*Keywords:* magnetic recording, hard disk drive, perpendicular magnetic recording, bit patterned recording, heat assisted magnetic recording

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# LONG LIFETIME OF EXCHANGE-DOMINATED SPIN WAVES IN ULTRA-THIN COBALT FILMS

H. Ibach<sup>a,b</sup>, C. M. Schneider<sup>a,b</sup>, A. T. Costa<sup>c</sup>

<sup>a</sup>Peter Grünberg Institut (PGI-6), Forschungszentrum Jülich, 52425 Jülich, Germany

<sup>b</sup>Jülich Aachen Research Alliance, Germany

<sup>c</sup>Instituto de Física, Universidade Federal Fluminense, 24210-346 Niterói, R. J., Brazil

The miniaturization of magnon-based devices into the nanometer range requires the utilization of exchange-dominated spin waves with wave-length in the nm-range. Only those spin waves possess sufficiently large group velocities for a fast transport of the spin information. High group velocities are realized in particular by spin waves in ultra-thin cobalt-films. These spin waves were studied extensively in the last years using inelastic scattering of low-energy electrons [1,2]. However, because of limitations in the energy resolution the experimental data base was confined to wave vectors between about  $3\text{nm}^{-1}$  and the boundary of the surface Brillouin zone. In that range, the lifetime of spin waves is extremely short ( $<100\text{fs}$ ) [3]. Correspondingly, the mean free path of a spin wave packet (defined as the product of group velocity and lifetime) is only of the order of 1nm. For that reason the acoustic spin wave modes of 3d-metals were not considered as possible candidates for spin wave based devices.

Recent improvements in the technology of electron energy loss spectrometers now enable the studies of spin waves of wave-vectors down to  $1.5\text{nm}^{-1}$  with an energy resolution down to 2meV [4,5]. In this presentation we report on high resolution data of those spin waves in ultra-thin fcc cobalt layers deposited on Cu(100) surfaces. The results are compared to a theory of spin excitations which takes into account the itinerant character of the electrons. For eight atom layer (8ML) films with a small density of surface steps and wave vectors  $q < 2\text{nm}^{-1}$  we find lifetimes of several picoseconds, in agreement with our theory. However, those long lifetimes are observed only for well-annealed films with a small density of surface steps.

Ongoing studies on films with regular step arrays obtained by deposition on Cu(1123) and Cu(1113) substrates show that the step-induced damping is particularly severe when steps cross the path of spin waves.

*Keywords:* Spin waves; Cobalt films, Electron spectroscopy

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# MAGNETIC MOMENTS AND HYSTERESIS OF AN ENDOHEDRAL SINGLE-MOLECULE MAGNET ON A METAL

**B.Buechner<sup>a</sup>, R. Westerstrom<sup>b</sup>, K. Junghans<sup>c</sup> and Y. Zhang<sup>d</sup>**

<sup>a</sup> Institute for Solid State Research, IFW Dresden, Germany

<sup>b</sup> Physik-Institut, Universität Zürich, Switzerland

<sup>c</sup> Institute for Solid State Research, IFW Dresden, Germany

<sup>d</sup> Institute for Solid State Research, IFW Dresden, Germany

Endohedral fullerenes containing clusters of lanthanides are a new interesting class of molecular magnets. The magnetism of these systems depends on the number of lanthanides, their spatial arrangement and their magnetic quantum number. The magnetic hysteresis which is characteristic for single-molecule magnets, is also observed when the fullerenes are deposited on metal substrates. In my talk I will present studies on Dy-nitride cluster fullerenes. It will be shown that the interaction between the endohedral unit in the single-molecule magnet Dy<sub>2</sub>ScN@C-80 and a rhodium (111) substrate leads to alignment of the Dy 4f orbitals. The resulting orientation of the Dy<sub>2</sub>ScN plane parallel to the surface is inferred from comparison of the angular anisotropy of x-ray absorption spectra and multiplet calculations in the corresponding ligand field. Element specific magnetization curves from different coverages exhibit hysteresis at a sample temperature of 4 K. From the measured hysteresis curves, we estimate the zero field remanence lifetime during x-ray exposure of a submonolayer to be about 30 seconds.

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**A microscopic view of atomic and molecular contacts:  
Magnetoresistance, switching, forces**

**Richard Berndt**

Institut für Experimentelle und Angewandte Physik, Christian-Albrechts-Universität  
zu Kiel, Germany

The electron transport through single atoms and molecules is investigated with low-temperature scanning probe microscopy. In the experiments, which aim at maximizing the control over the junction properties, the conductance and the acting force are probed. The talk will address the magnetoresistance of single adsorbed metal atoms and molecular switches including spin state switching.

*Keywords:* contact, single molecule, single atom, magnetoresistance, atomic force microscopy, spin crossover, Kondo effect

# COLLECTIVE ELECTRONIC EXCITATIONS IN THIN FILMS

V. M. Silkin<sup>a,b,c</sup>, X. Zubizarreta<sup>d</sup> and E. V. Chulkov<sup>a,b</sup>

<sup>a</sup>Donostia International Physics Center, San Sebastian, Spain,

<sup>b</sup>Departamento de Física de Materiales, Facultad de Ciencias Químicas, Universidad del País Vasco/Euskal Herriko Unibertsitatea, San Sebastian, Spain

<sup>c</sup>IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

<sup>d</sup>Institut de Mineralogie, de Physique des Matériaux et de Cosmochimie (IMPMC) Université Pierre et Marie Curie (UPMC), Paris, France

Collective electronic excitations at metal surfaces are well known to play a key role in numerous phenomena, ranging from physics and material science to biology and medicine. From the fifties it is known [1] that at the planar vacuum/metal boundary a mode, called surface plasmon, emerges with frequency  $\omega_{sp} = \omega_p / \sqrt{2}$ , where  $\omega_p$  is the bulk plasmon frequency. This relation between the bulk and surface plasmon frequencies is a manifestation of the fact that in a long-wavelength limit both quantities are entirely determined by the bulk dielectric function properties. In particular, the surface plasmon properties at small momentum transfers can be studied on base of a surface response function  $g$  [2] related to bulk dielectric function  $\epsilon$  as  $g = (\epsilon - 1)/(\epsilon + 1)$ . In thin films, due to the presence of two surfaces, the interaction of corresponding surface plasmons produces its hybridization [1]. As a result, the dispersion of two symmetric and antisymmetric surface modes of a film with thickness  $L$  is expressed as  $\omega_{sp}^{\pm} = \omega_{sp} \sqrt{1 \pm e^{Lq}}$ , where  $q$  is an in-plane momentum.

In real metallic systems the dielectric function is often very different from the predictions of the free-electron-gas mode. In particular, recently it was demonstrated that indeed in many materials, like normal [3], charge-density-wave [4,5] and superconducting [6-10] metals and intercalated graphite [11], additionally to the conventional bulk plasmon, there exists a number of other bulk collective modes characterized by significantly lower frequencies. In this contribution we analyze which impact the presence of such low-energy modes in the bulk may produce on collective electronic excitations in thin films.

Keywords: Thin films; Surface plasmon; Dielectric function

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# MAGNETISM AND HALL EFFECTS IN THIN FILMS OF TOPOLOGICAL INSULATORS

**E.V. Chulkov<sup>a,b,c,d</sup>, V.N. Meh'shov<sup>a,e</sup>, S.V. Ereemeev<sup>a,c,d,f</sup>, M.M. Otrokov<sup>a</sup>, V.V. Tugushev<sup>a</sup>, and A. Ernst<sup>a</sup>**

<sup>a</sup>Donostia International Physics Center (DIPC), 20018 Donostia - San Sebastián, Spain

<sup>b</sup>Departamento de Física de Materiales, UPV/EHU, Apdo. 1072, 20080 and CFM - MPC, Centro Mixto CSIC - UPV/EHU, 20018 Donostia - San Sebastián, Spain

<sup>c</sup>Saint Petersburg State University, Saint Petersburg 198504, Russian Federation

<sup>d</sup>Tomsk State University, pr. Lenina 36, 634050, Tomsk, Russian Federation

<sup>e</sup>National Research Centre Kurchatov Institute, Kurchatov Sqr. 1, 123182, Moscow, Russian Federation

<sup>f</sup>Institute of Strength Physics and Materials Science, RAS SB, Tomsk 634021, Russian Federation

<sup>g</sup>Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, D-06120 Halle, Germany

<sup>h</sup>Department, Address, Institution, Country

Topological insulators (TIs) are narrow-gap semiconductors characterized by Dirac-like surface state and protected by time-reversal symmetry. Magnetic field (external or internal) breaks this symmetry and causes splitting of the topological surface state at the Dirac point thus making the surface insulating.

Internal magnetic field in TIs can be create in various ways, in particular, by introducing vacancies or carbon atoms [1], doping with 3d-transition metal atoms [2], displaying magnetic semiconductors or organic overlayers as well as bulk materials on the surface of three- or two-dimensional TIs [3-5].

Here we present and discuss recent results of the study of magnetic impurities as well as magnetic proximity effects on electronic and spin structure of TIs and splitting of the topological surface state. We propose a method for engineering of heterostructures that result systematically in big splitting of the Dirac cone. We also analyze magnetic effects in two-dimensional topological insulators and heterostructures and discuss recent results for quantum spin and anomalous Hall effects [6,7].

*Keywords:* Topological insulators; Dirac surface states; ferromagnetism; Hall effects

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# PHOTONS, ELECTRONS, AND PHONONS AT THE NANOSCALE WITH TIP-ENHANCED RAMAN SPECTROSCOPY AND PHOTOTHERMAL IMAGING

**Raul D. Rodriguez<sup>a</sup>, Adarsh Reddy<sup>a</sup>, Rayhan Rasel<sup>a</sup>, Zoheb Khan<sup>a</sup>, Teresa I. Madeira<sup>b</sup>, Harsha Shah<sup>a</sup>, Eugene Bortchagovsky<sup>c</sup>, and Dietrich R.T. Zahn<sup>a</sup>**

<sup>a</sup>Semiconductor Physics, Technische Universität Chemnitz, D-09107 Chemnitz, Germany.

<sup>b</sup>BioISI – Biosystems & Integrative Sciences Institute, Faculdade de Ciências da Universidade de Lisboa, Campo Grande, C8, 1749-016 Lisboa, Portugal

<sup>c</sup>Institute of Semiconductor Physics of NASU, pr.Nauki 41, Kiev 03028, Ukraine

The diffraction limit of light was regarded as a fundamental unbreakable barrier that prevented the visualization of objects with size smaller than half the light wavelength, until super resolution optical methods and near-field optics allowed overcoming that constraint [1,2]. We report on a new approach based on tracking the photo-thermal expansion (nano-vis) in combination with tip-enhanced Raman spectroscopy (TERS). A commercial TERS system based on atomic force microscopy is coupled to a mechanical switch for intermittent

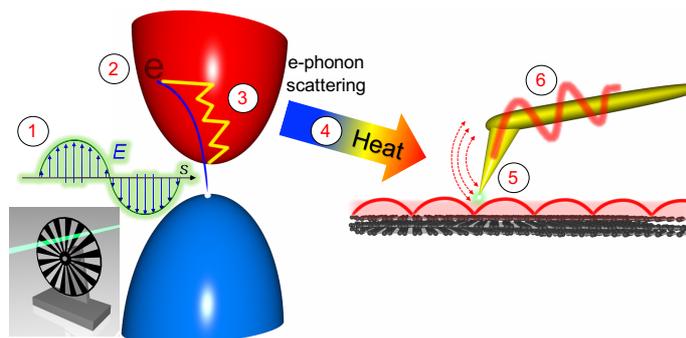


Figure 1: (a) Physical schematics behind nano-vis: (1) a chopper allows the intermittent passage of photons with energy high enough to excite an electron from the valence band to a high energy level (2) in the conduction band, non-radiative relaxation (3) mediated by e-phonon scattering induces (4) heat increase that results in the thermal expansion of the sample (5) and the cantilever deflection (6).

visible light excitation. This simple configuration allows detecting small changes in the nano-object volume. Contrary to nano-IR that is based on the detection of molecular and lattice vibrations [3], the principle behind nano-vis involves tracking the heat generated from electronic transitions and scattering during the relaxation in the sample material that occurs due to optical absorption in the visible spectral range. The sensitivity and spatial resolution are further improved by the combined effect of electric field enhancement obtained by excitation of localized surface plasmons, and the synchronization of mechanical resonance of the tip-cantilever system with the intermittent light excitation. Our concept is demonstrated by the TERS and nano-vis analysis of a two-dimensional material (GaSe) on graphite and by an array of multi-walled carbon nanotubes lithographically designed in a silicon oxide matrix. In addition to TERS, an unprecedented spatial resolution for optical absorption below 10 nm is reported.

*Keywords:* nano-optics, photo-thermal imaging, tip-enhanced Raman spectroscopy, TERS, plasmonics, atomic force microscopy, optical absorption

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# PHONON EFFECTS IN PLASMONIC SPECTRA

J. Vogt<sup>a</sup>, C. Huck<sup>a</sup>, F. Neubrech<sup>b</sup>, and A. Pucci<sup>a</sup>

<sup>a</sup>Kirchhoff Institute for Physics, Im Neuenheimer Feld 227, 69120 Heidelberg,  
Heidelberg University, Germany

<sup>b</sup>4th Physics Institute, Pfaffenwaldring 57, 70569 Stuttgart, University of Stuttgart,  
Germany

Plasmonic resonances of metallic nanowires in the infrared are well known to be beneficial for vibrational sensing of molecules. They are also very sensitive to phononic excitations, which in case of strong coupling to phonon-polaritons leads to qualitatively different spectral behaviour. What has been considered only seldom is the influence of the metal phonons on the plasmonic resonance. In the infrared, the measurement of plasmonic resonances allows to obtain valuable quantitative information on the conductivity of the wires.[1] For example, our study of the temperature dependent plasmonic resonance spectrum of nanowires with a high crystalline quality revealed a phononic damping of the electronic excitation that with temperature increases, the stronger the thinner the wires.

*Keywords:* Infrared plasmonics; electronic damping; phonons; nanostructures

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# Field enhancement at silicon-oxide interface layers generated by Au island films

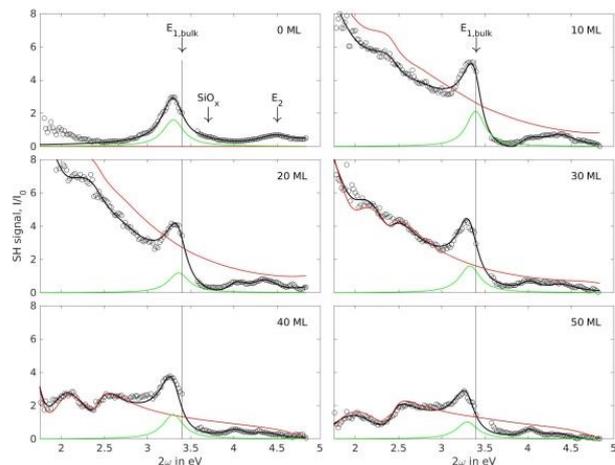
Hans Ulrik Ulriksen and Kjeld Pedersen

Department of Physics and Nanotechnology, Skjernvej 4A, 9220 Aalborg, Aalborg University, Denmark

A promising applications of nanoplasmonics is the design of metallic structures that enhanced light absorption in thin film solar cells [1] where the active layer has poor light absorption. In this work field enhancements from Au ellipsoids with diameters from 30 to 250 nm deposited on a Si substrate with a thin 1 nm thick surface oxide have been investigated by second harmonic generation spectroscopy. *The basic idea of this work is to follow the relatively sharp SHG resonance from Si near the  $E_1$  critical point in order to deduce the field enhancement inside a thin Si interface layer.*

The measured linear optical properties are well described by the island film model [2] and are used in the investigation of the SHG signal.

At energies below the  $E_1$  critical point energy a strong SHG signal originating from plasmon resonances in the Au particles is observed. By following the evolution of the characteristic Si SHG-resonance it is found that the Au particles affect the Si SHG signal in two ways: 1) charge transfer from the substrate to the metal modifies the band bending in Si and gives rise to E-field induced SHG (EFISH) and 2) local enhancement of the field at the Si-oxide interface. For small particles the EFISH part dominates while for larger particles the field enhancement at the Si-oxide interface dominates the SH signal and a field enhancement factor in Si of 4 is found experimentally. This is about a factor of 5 less than the corresponding factor calculated by the local field factors when the separation between Au islands and the Si interface region is neglected. It is suggested that the fast decay of the local field away from the metal islands reduces the observed field enhancement.



**Keywords:** Plasmonics; Field enhancements; Nonlinear optics

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Improved *ab initio* calculation of surface second-harmonic generation from  
Si(111)(1×1):H

S. M. Anderson,<sup>a</sup> N. Tancogne-Dejean,<sup>b,c,d</sup> B. S. Mendoza,<sup>a</sup> and V. Véniard.<sup>c,d</sup>

<sup>a</sup> Institut für Festkörperforschung, Leibniz Universität Hannover, Appellstraße 11A, D-30559 Hannover, Germany

<sup>b</sup> European Theoretical Spectroscopy Facility, EUSF, Palaiseau, France

We report an improved *ab initio* calculation of the surface second-harmonic generation (SHG) from the Si(111)1×1 surface. The surface is modeled using a slab geometry and the SHG is calculated using the density functional theory (DFT) and the many-body perturbation theory (MBPT). The results show that the SHG is dominated by the surface atoms and the bulk contribution is negligible. The calculated SHG intensity is in good agreement with the experimental data.

Keywords: Surface second-harmonic generation, *ab initio* calculation, Si(111)1×1 surface.

Abstract: We report an improved *ab initio* calculation of the surface second-harmonic generation (SHG) from the Si(111)1×1 surface. The surface is modeled using a slab geometry and the SHG is calculated using the density functional theory (DFT) and the many-body perturbation theory (MBPT). The results show that the SHG is dominated by the surface atoms and the bulk contribution is negligible. The calculated SHG intensity is in good agreement with the experimental data.

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# INTERACTION OF SURFACE AND LOCALIZED PLASMONS PROBED BY ELLIPSOMETRY

**E. Bortchagovsky<sup>a</sup>, K. Hingerl<sup>b</sup> and T. Mishakova<sup>c</sup>**

<sup>a</sup>Institute of Semiconductor Physics of NASU, pr.Nauki 41, Kyiv 03028, Ukraine

<sup>b</sup>ZONA, Johannes Kepler Universität Linz, Altenberger Str. 69, 4040 Linz, Österreich

<sup>a</sup>Institute of High Technologies, Taras Shevchenko National University of Kyiv, ave. Glushkov 4G, Kyiv 03022, Ukraine

Interaction of two resonances results in their hybridization and splitting what produces the energy gap between two hybridized dispersion curves instead of their intersection. We investigated the interaction of surface plasmon with localized resonances of nanoparticles deposited on the surface.

Ellipsometry in the Krechman geometry was performed for such structures. Ellipsometry was chosen as the relevant method for the registration of surface plasmon [1] and interparticle interactions [3]. Some results are shown in Figs.1-2.

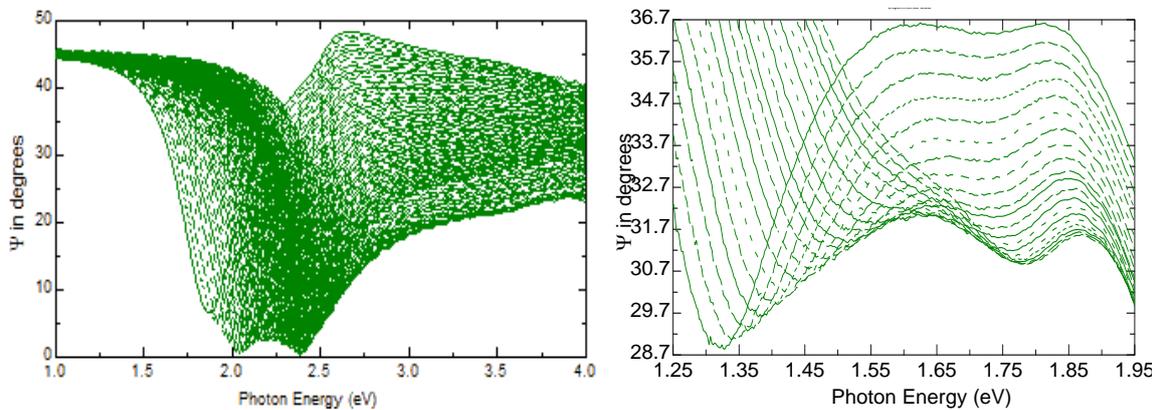


Fig.1. Spectral behaviour of ellipsometric angle  $\Psi$  for the system with deposited nanoparticles measured at internal reflection with the excitation of surface plasmon at different angles of incidence.

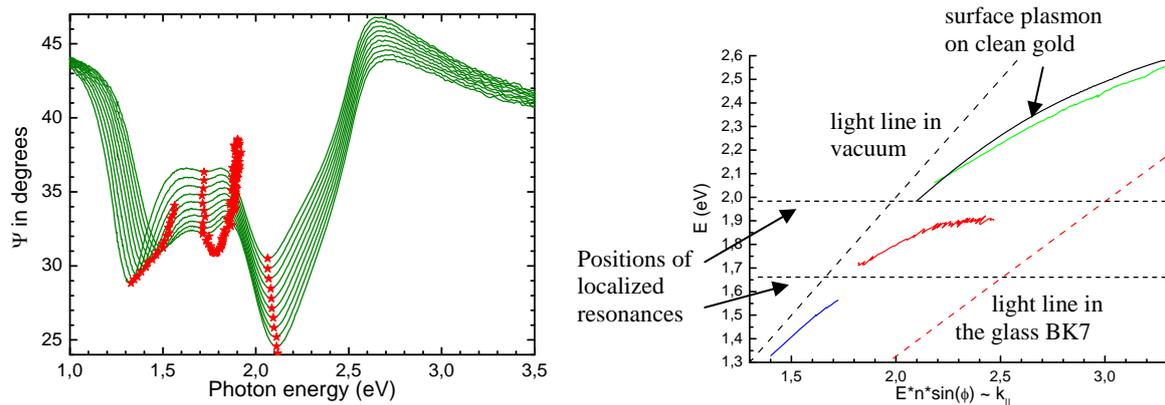


Fig.2. Position of minima of the spectra of  $\Psi$  and resulted dispersion curves.

**Keywords:** ellipsometry, surface plasmon, localized plasmon, splitting

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# APPLICATIONS OF IMAGING ELLIPSOMETRY AND BREWSTER ANGLE MICROSCOPY IN BIO-FUNCTIONALIZATION AND SENSING – AN OVERVIEW

Peter H. Thiesen<sup>a</sup>

<sup>a</sup>) Accurion GmbH, Stresemannst. 30, 37079, Göttingen, Germany

A homogenous functionalization of equivalent surfaces and an accurate patterning of arrays is the desired case in bio functionalization and sensing, but the experimental reality is often different. Uncoated areas are frequently contaminated with remnants from coating of different treated sample areas (Fig. 1) or with additives of the coating process. The doughnut effect and similar issues can occur in case of drying. In some cases particles are formed by aggregation or by competitive reactions to the grafting as is frequently the case for silanization with trifunctional silanes. From the point of view of biomolecular interactions, model membranes like supported bilayers are of increasing interest. In case of mixed lipid layers, phase transition can take place forming rich and pure domains. In this case an overall averaging method is misleading. Perhaps the initialization of biofouling can be considered as a localized bio functionalization.

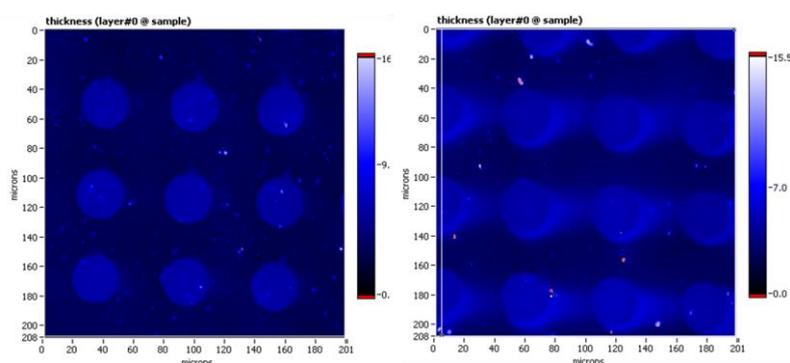


Fig. 1. Protein array on Si-wafer after washing, measured at 658 nm (laser)

The mentioned scientific questions require very sensitive, label free detection methods with a microscopic lateral resolution. The contributed paper will give an overview how Imaging Ellipsometer, Brewster Angle Microscopy and imaging Surface Plasmon Resonance Enhanced Ellipsometry (i-SPREE) can contribute in solving these questions.

*Keywords:* Imaging ellipsometry, Brewster angle microscopy, i-SPREE, LB-films, supported bilayers, biomolecular interaction