

# **ABSTRACTS OF INVITED LECTURES**

**in alphabetical order of the lecturer's name**

## **ELECTRONIC ENERGY LEVEL ALIGNMENT AT DYE SENSITIZED OXIDE SURFACES**

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Dye sensitized solar cells (DSSCs) offer a promising alternative to conventional photovoltaics. In these devices, a wide band-gap oxide semiconductor is activated by the adsorption of organic dye molecules with an energy gap between the highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) that is in useful portion of the solar spectrum. Effective charge transfer of photoexcited electrons from the molecule to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of several dye-related molecules and determine their alignment with the band edges of single crystal and nanostructured TiO<sub>2</sub> and ZnO substrates. We have compared the position of the HOMO and LUMO levels of the N3 ruthenium-based dyes with those of isonicotinic acid. Our results are consistent with the electronic transfer scheme where N3 excitation occurs from the HOMO localized on the central ruthenium ion, to the LUMO delocalized on the dye linker to the surface. These experimental results will be compared and contrasted to theoretical predictions from the literature.

Another class of dye molecules with the potential of great flexibility in structural and electronic configuration is the metalloporphyrins. As these molecules play an essential role in photosynthetic mechanisms, they are natural candidates for electron transfer mediator in DSSCs. Among the possible metalloporphyrins, the zinc tetraphenylporphyrins (ZnTPP) derivatives have been found to have similar electron injection and charge recombination properties as the important standard ruthenium dye N3 for DSSCs, as well as reasonable performances using TiO<sub>2</sub> or ZnO as substrates. We are investigating the electronic structure, energy level alignment, and their changes with altered surface bonding geometries, using a selective functionalization with carboxylic anchoring groups of the meso-phenyl, of functionalized ZnTPP on single crystal TiO<sub>2</sub> and ZnO surfaces. Recent results will be discussed.

## ULTRA-THIN LAYERS OF GROUP IVB METALS ON W(100): MORPHOLOGY, STRUCTURE AND INTERMIXING PHENOMENA

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Titanium, zirconium and hafnium are sister metals in the Group IVB elements of the periodic table which chemical and physical properties are similar. All are characterized by high melting points and high degrees of reactivity, forming extremely stable oxides, nitrides, borides and silicates. Beside classical applications in aeronautics and nuclear power industry, they have growing applications in the other industrial branches like production of pharmaceuticals and ultrahigh purity chemicals for the electronics industry. The best-known, valuable property of these metals is their general inertness to a wide variety of corrosive agents, resulting from a tight and stable oxide film formation that protects the metal from chemical exposures over wide temperature ranges, and makes them extremely attractive, environmentally friendly constructional materials in anticorrosive applications. Oxides of these metals are of fundamental importance in applications such as heterogeneous catalysis, metal-ceramic interfaces, gas sensors and solid-state electronic devices. Research on nanostructures and structures of reduced number of dimensions based on these metals and their compounds has been on the increase for several years.

The (100) surface of tungsten has been the subject of numerous experimental and theoretical studies [1]. Ultra-thin films of the insulating, wide-band-gap oxides of Ti and Zr grown on W(100) provide systems which are particularly suited for study of their surface properties, since in the form of the ultra-thin films they are conductive enough to allow the application of advanced surface sensitive electron spectroscopy measurement techniques and scanning tunneling microscopy [2]. It has been well known from a long time that W(100) surface covered with ultra-thin film of ZrO has remarkably low work function at high operating temperatures close to 1800 K [3]. Similar reduction of work function has been observed also for Hf/W(100) adsorption system [4].

The aim of this report is to review briefly selected details concerning morphology and electron as well as atom structure of the ultra-thin layers of group IVB metals on W(100), and to discuss intermixing phenomena taking place at the surface and at the substrate-adsorbate interface with the emphasis on ordered surface alloy formation.

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## **STM/STS CHARACTERIZATION OF DEFECTS, MOLECULES AND NANOSTRUCTURES ON MONOCRYSTALLINE SURFACES**

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Small clusters and molecules on silicon and metal substrates are commonly used in nanoelectronic technology [1]. Periodic structure of the substrate or defects may serve as pinning points for growing clusters or nanostructures. Scanning tunneling microscopy (STM) is one of the most suitable technique to analyze the atomic or molecular structure of substrates and created nanostructures. Their electronic and chemical properties may be characterized by tunneling spectroscopy (STS) methods even with subnanometer spatial resolution [2].

At first, results of STM/S characterization of semiconducting substrates (as Si(111) and Si(100)) and metallic substrates (as Pt, Cu, Mo) will be presented. The second part will be devoted to examples of metallic clusters creation as growth of  $(Ag)_n$  clusters on Si(111)7×7 surface, creation of metal silicides nanostructures on both silicon and metallic substrates. Finally, results on adsorption of individual azobenzene derivative molecules on Cu(111) surface and electron induced switching from *trans* to *cis* configuration will be reported.

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## **SURFACE PASSIVATION AND HIGH- $\kappa$ DIELECTRICS INTEGRATION OF GERMANIUM-BASED FIELD EFFECT TRANSISTORS: FIRST-PRINCIPLES CALCULATIONS AND IN SITU CHARACTERIZATIONS**

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Surface passivation and high- $\kappa$  dielectrics integration are two critical issues for fabricating high performance Ge-based CMOS devices. We have carried out first-principles calculations and experimental characterizations to study these two issues. High quality GeO<sub>2</sub> dielectrics were grown on Ge (001) substrates and the band offsets were determined. The calculated PDOS show that oxygen and Ge vacancies formed at different oxidation stages may be the reason for the large discrepancies in reported VBO values. It was also found that the nitrogen incorporation in GeO<sub>2</sub> lowers its VBO, while enhances its thermal stability slightly. First-principles calculations were carried out to study electronic, optical, and intrinsic defect properties of bulk Ge<sub>3</sub>N<sub>4</sub>. The calculated band gap and dielectric constant of  $\beta$ -Ge<sub>3</sub>N<sub>4</sub> satisfy the requirements of gate dielectrics. However, nitrogen vacancies likely become charge trapping centers. Growing  $\beta$ -Ge<sub>3</sub>N<sub>4</sub> in nitrogen rich ambient would reduce nitrogen vacancies, while depositing a thin layer of Si on Ge surface before nitridation process could be another effective way to reduce nitrogen vacancies in  $\beta$ -Ge<sub>3</sub>N<sub>4</sub> thin films. We propose a new interface structures for  $\beta$ -Ge<sub>3</sub>N<sub>4</sub> (0001)/Ge (111) which does not have dangling bonds and is much more energetically favorable. The calculated VBO and CBO of this stable interface are 1.23 and 2.10 eV, respectively. Experimentally, crystalline Ge<sub>3</sub>N<sub>4</sub> was grown on Ge (111) substrate at 400±C, and the band offsets determined by XPS are consistent with the theoretical predictions. We also investigated SrZrO<sub>3</sub> as a possible high- $\kappa$  on Ge (001) substrate. The VBO and CBO at this interface were measured to be 3.26 eV and 1.77 eV, respectively. Theoretically, various interface structures of cubic SrZrO<sub>3</sub> (001)/Ge (001) were studied. The calculated band offsets are larger 1.0 eV.

**A CASE STUDY OF A METAL/ORGANIC INTERFACE AT THE MOLECULAR LEVEL:  
A TIP/C<sub>60</sub> CONTACT**

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A complete theoretical study of the approach of two Au(111)-based tips to a C<sub>60</sub> molecule is presented. Energy, forces, conductance, deformation and Density of States are calculated using a TB-DFT code. From this calculation we are able to obtain: (a) the height barrier for the Au/C<sub>60</sub> interface; (b) the effective intrasite Coulomb interaction for electrons in the molecule (corresponding to the quantum well of the molecule between two metals); and (c) the effective C<sub>60</sub> energy gap, which is found to be a function of the tip-molecule distance and the metal screening. Also, several parameters of the IDIS-model for metal-organic interfaces as applied to the tip/C<sub>60</sub>/tip case are calculated and compared with a C<sub>60</sub>/Au(111) (2√3×2√3)R30° monolayer. Finally, the case of a single C<sub>60</sub> molecule upon a Au(111) surface is analyzed using this approach and compared with other experimental and theoretical work.

## **ELECTRON EMISSION FROM OLD AND NEW MATERIALS: FEMTOSECOND LASERS MEET NOVEL FIELD EMITTERS**

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Sharp metal tips are ideally suited for electron field emission, as due to the sharpness a modest voltage suffices to generate large electric fields at the tip apex and thus enables tunneling of electrons. Field emission as well field ion microscopy were invented more than half a century ago and have recently found renewed interest with the advent of new emitters such as single atom-tips and carbon nanotubes. In parallel, laser sources have become available with pulse durations that reach down to typical timescales of solid state systems, i.e. the femtosecond range. We will present our progress on transferring the extremely high degree of control current phase stable laser oscillators offer into the electron domain. To do so we focus sub-3 cycle laser oscillator pulses onto field emission tips and investigate the emission behavior. We have evidence that we have reached a regime in which the electron tunnel current follows the laser electric field as opposed to the laser pulse envelope. Thus electron pulses with emission duration of less than a single optical period ( $\sim 2.5$  fsec) are generated. With single-atom tips, which we can produce in our laboratory, we aim at building special electron sources with sub-poissonian emission behavior and unprecedented brightness. We will present recent experimental progress.

## **CHARACTERIZATION AND MODIFICATION NANOSTRUCTURES AT ATOMIC SCALE USING SPM**

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Nano-science aims to study and modify properties of objects like complex circuits, macromolecules or biological cells at nanometer scale. The increasing importance of quantum phenomena at this scale is a significant attractive feature. An analysis, control and modification of molecules, surfaces or nanostructures are great challenges of last years. Nanoprobe techniques such as the Scanning Tunneling Microscope (STM) and the Atomic Force Microscope (AFM) provide not only a variety of experimental information at the atomic scale, but they are also widely used as the assembly mechanism for creating potential nanotechnology devices using both contact and non-contact modes of operation. One of the most promising scanning probe techniques to explore Nano-scale is so called Non-Contact AFM (NC AFM) with a fast growing application in surface science and nanotechnology. In this talk, brief introduction and roadmap of NC AFM technique will be provided. Recent development and outstanding achievements of the technique will be presented, such as chemical identification [1] of individual atoms, atomic manipulation [2] and complex atomic patterning [3] on semiconductor surfaces. Recent progress tends to combine both the tunneling current and forces signals developing a new generation of SPM techniques. Here a detail understanding of the relation between the current and force is required [4].

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## **GRAPHENE: SHAPING DIRAC FERMIONS FOR APPLICATION**

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After first transport characterizations, graphene has become a material of immense interest for science and technology [1]. Most notably, graphene based electronics has a potential to replace silicon based electronics [2]. However, there are many challenges in front of us before graphene will be used in devices, e.g. large scale graphene production. Epitaxial growth of graphene on a metal is a viable route which can give answers to some of the challenges. I will present results of our most recent studies of graphene monolayer on Ir(111), a representative of the class of transition metals that interact weakly with graphene. Through the surface science approach for the material which is typically investigated with the whole arsenal of wide range of solid state methods, we have investigated the influence of the mismatch of graphene and iridium lattices to graphene electronic structure. Angle resolved photoelectron spectroscopy reveals intact Dirac cone, slight p-doping and opening of minigaps in the band structure of graphene due to a superperiodic potential [3]. Epitaxial graphene was also used as a starting point for further electronic structure manipulation. Electronic doping of graphene by alkalis (Na, Cs, K) at varying concentrations shifted the position of the Dirac point up to 1.4 eV below the Fermi energy. Moreover, upon the intercalation of alkalis the effects of the superperiodicity vanished and the minigaps disappeared. For large doping, graphene Fermi surface becomes pronouncedly trigonal and an anisotropic effect of the  $\pi$ -band dispersion renormalization was clearly observed. We interpret this as a signature of an enhanced electronphonon coupling in doped graphene [4], which may be a key for high critical temperature in intercalated graphite.

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## CATALYTIC SURFACE REACTIONS ON THE ATOMIC SCALE

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Recent developments in the field of surface chemistry and catalysis employing field emission microscopy along with local chemical probing will be reviewed. Examples will be given for the dynamic adsorption/thermal desorption and for the reactive co-adsorption of gases on selected areas of nanosized metal tips using the atom-probe principle. Comparison with local probe techniques will be made where possible.

In a first example, plane-specific kinetic data for the thermal equilibration of adsorbed layers are presented for the NO/Pt system. It is demonstrated that steps act as trap sites for NO molecules on the surface of the Pt nanotip. This is concluded from measurements of the mean residence times of NO molecules before their thermal desorption at properly chosen temperatures. The binding energy of the step-trapped NO molecules is determined from the temperature dependence of their mean residence times. The respective values are of 139 kJ/mol for stepped (111) and 150 kJ/mol for stepped (001). The data are in good agreement with those provided by molecular beam techniques in studies with oriented single crystal surfaces.

In a second example, the combined application of video-FIM/atom-probe is demonstrated to image the catalytic water production from H<sub>2</sub> and O<sub>2</sub> on a Rh tip and to determine the chemical surface composition while imaging. In this case, water molecule ionisation provides direct information on the distribution of the catalytically active sites. Spatio-temporal image patterns are observed and can be correlated to variations of the catalytic activity. Oscillatory behaviour is produced for certain conditions of temperatures and partial pressures. To explain the occurrence of this strongly non-linear behaviour a feedback mechanism has been developed which is based on both, experimental evidence and theoretical modelling. Accordingly, surface oxygen is subject to a reversible subsurface diffusion followed by nucleation and (reversible) RhO<sub>2</sub> precipitation. It is shown that the presence of electric fields facilitates subsurface diffusion which usually occurs only at much higher pressures in the absence of these fields.

## TRANSPORT PROPERTIES OF QUANTUM WIRES BY FIRST-PRINCIPLES CALCULATIONS

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Molecular devices are potential candidates for the next step towards nanoelectronic technology. A great deal of experimental work has been carried out to demonstrate an element of such an electronic device using either a single- or a finite-number of small organic molecules. The main challenge in molecular devices is to establish that nanoscale materials are capable of performing all of the basic functions of conventional electronic components such as wires, diodes and transistors. Our group has covered a wide range of nanoscale wires, which have potential application in molecular electronics using first-principles calculations and nonequilibrium Green's function formalism [1]. Our target materials are nanoscale wires between metal electrodes, self-assembled nanowires on silicon surface [2], porphyrin [3], metallocene, fused-ring thiophene wires, and so on.

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## EXPLORING MOLECULAR ASSEMBLY AT SURFACES

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The adsorption and self-assembly of organic molecules at surfaces has recently been investigated extensively, both because of the fundamental interest and for prospective applications in nanoelectronics [1,2]. Molecule-molecule and molecule-substrate interactions can be tuned by appropriate choice of substrate material and symmetry. Upon molecular adsorption, surfaces typically do not behave as static templates, but often rearrange to accommodate different molecular species [3,4]. We review recent experiments using Scanning Tunnelling Microscopy, providing new insight into fundamental properties such as molecular diffusion [5,6] and self-assembly via surface templating [7-9] and H-bonding driven by co-adsorption [10-12]. Our approach is to modify surfaces providing suitable surface cues, that may guide the assembly of adsorbates and more complicated building blocks like living cells on biomaterials [13-15]. We jokingly call this approach 'Playing Tetris at the Nanoscale' [16]. Recent advances in using the substrate as catalyst for surface confined polymerization reactions will also be discussed [17,18].

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## **A STEPPING STONE TO MINIATURISATION: ACETYL-BASED MOLECULES ON THE Si(001) SURFACE**

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There is currently great interest in the chemical modification of semiconductor surfaces by chemisorbing organic molecules onto these surfaces to create a new class of systems that utilize individual molecules as their principal components. Such systems promise major technological advances in areas such as quantum computing, quantum optics and molecular electronics. To be viable, however, such semiconductor-adsorbate systems must not only reproduce the requisite properties, but must also form well-characterised structures that remain robust under the appropriate working conditions.

In this paper we present a comprehensive study of the interaction of three acetyl-based molecules, acetaldehyde [ $\text{CH}_3\text{CHO}$ ], acetone [ $(\text{CH}_3)_2\text{CO}$ ] and acetophenone [ $\text{C}_6\text{H}_5\text{COCH}_3$ ], with the technologically important Si(001) surface. We show that combining temperature-dependent scanning tunnelling microscopy and first-principles density functional calculations leads to a complete description of the interaction of these molecules with Si(001), including the resultant equilibrium structures and the underlying reaction processes. Detailed comparison will also be made between the theoretical predictions and the experimental data. Of particular interest, will be the demonstration that all of these structures follow a general reaction pattern, and form strong Si-O and Si-C bonds which makes them particularly stable. This offers the exciting possibility of changing the residue R in these acetyl-based R-COCH<sub>3</sub> molecules to achieve additional functionality, while ensuring that the molecules form stable and well-defined structures.

## **SPONTANEOUS NANOSTRUCTURE FORMATION AT SURFACES**

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Surfaces are natural templates for the formation of periodic nanostructure arrays. Besides acting as a mere support for the individual nanoscale entities the structure of the supporting surface may or may not influence the lateral arrangements of the elements of the array as a whole. The decisive parameters are the adsorbate-substrate- and the adsorbate-adsorbate-interaction as well as the magnitude of activation barriers. In this lecture examples for nanostructure formation will cover the spontaneous growth of periodic arrays of monodispers metal clusters, the formation of ordered organic layers at metal/electrolyte interfaces, and the self-organization of epicuticular wax sculptures from plant leaves.

## **OXIDE SURFACE RECONSTRUCTION UNDER THERMODYNAMIC EQUILIBRIUM AND NON-EQUILIBRIUM CONDITIONS**

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The method of ab initio atomistic thermodynamics provides a powerful theoretical framework with which to describe and understand the processes of surface reconstruction. The method has long history of success, in particular in elucidating the surface oxidation/reduction processes of materials in contact with an oxygen-containing environment. In this talk, I will illustrate the application of this method to two catalytically active surface science systems, and will highlight some of the present day challenges (and opportunities). Cu/ZnO(0001) is a potent catalyst system for water-gas-shift and methanol synthesis reactions. Thermodynamic analysis allows us to resolve some of the stable Cu-containing surface phases that are potentially active in the catalytic cycle. Rutile TiO<sub>2</sub> is a prototypical photocatalyst and is widely referred to as a “model surface science system” for the relative ease and extent that it has been studied. However, the theoretical modelling of this surface is far from straightforward. I will describe how a successful thermodynamic treatment of this system requires that the persistent non-equilibrium conditions of this material are taken into account.

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## THE STRUCTURE OF METAL/ALKYLTHIOLATE SELF-ASSEMBLED MONOLAYER INTERFACES

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Alkylthiolate ( $\text{CH}_3(\text{CH}_2)_{n-1}\text{S}$ -) monolayers on noble metal surfaces, and particularly on Au(111), are the archetypal self-assembled monolayer (SAM) systems, and can be formed by surface reaction with alkanethiols (by deprotonation) or alkyldisulphides (by S-S bond scission), from either the gas phase, or from solution. Despite increasing exploitation of these SAMs, there has, until recently, been very little understanding of the structure of the metal/thiolate interface. Typically bonding has been assumed to occur on an unreconstructed metal surface, the S headgroup atom occupying the highest coordination site. A number of total-energy calculations, mostly based on density functional theory – DFT) have been conducted, most of which have supported this view.

There is now clear evidence that on Cu(111) and Ag(111), overlayers of methylthiolate ( $n=1$ ) and other thiolates with short alkane chains ( $n\sim 4-8$ ) induce major reconstructions of the surface; on Cu(111) a lower-density pseudo-square (Cu(100)-like) surface layer is formed, on Ag(111) a lower-density hexagonal overlayer is formed creating a local Ag-S structure similar to that in F-cubic  $\text{Ag}_2\text{S}(111)$ . Even the much-studied Au(111) surface is now also believed to be reconstructed at the Au/thiolate interface, though the exact structure remains in doubt; however, all the newly-favoured models all involve Au-atom-thiolate surface moieties. The conflicting evidence from X-ray and electron diffraction, X-ray standing waves, photoelectron diffraction, near-edge X-ray absorption and photoelectron core level shifts, as well as DFT calculations, will be presented in order to identify what we do, and do not, understand about this important system.