

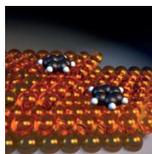
Interdisciplinary Surface Science Conference (ISSC-21)

10–13 April 2017

Royal Northern College of Music, Manchester, UK

<http://issc-21.iopconfs.org>

Organised by the IOP Thin Films and Surfaces Group



Monday 10 April

Session 1

(invited) **Surfaces and interfaces in the light of synchrotron radiation**

J Zegenhagen

Diamond Light Source, UK

Synchrotron radiation (SR) has contributed strongly to our understanding of surfaces and interfaces with the help of diffraction, scattering and spectroscopic techniques and their combination. The penetration power of photons, in particular X-rays, and the high brilliance of SR allows exact and thorough quantitative analysis not only of idealized surfaces in UHV but of real surfaces/interfaces. I will present a few selected illustrative examples. Significant further advance, especially exploiting coherence and the time domain, is expected with the upcoming extremely brilliant SR sources and X-ray free electron lasers.

An atom beam microscope for surface imaging

M Bergin, D Ward, J Ellis, A Jardine and W Allison

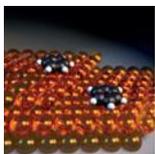
University of Cambridge, UK

Traditional microscopies can often damage delicate samples due to the high energy of the probe beams employed. Scanning Helium Atom Microscopy (SHeM)[1,2] is a new real space imaging technique that uses low energy (<100meV) neutral beams with a small de Broglie wavelength (<1Å) that produce no surface damage. The Cambridge application of the technique offers unique surface sensitivity combined with a large depth of field, allowing us to investigate samples that are difficult to image using charged beams.

The instrument uses established methods to generate a supersonic helium beam[3], collimate it, then raster a sample under the beam. By measuring the flux of scattered atoms into a detector at each point on the sample, a micrograph of the surface of the sample can be constructed. Images of a variety of insulating and conducting surfaces are presented, and the intensity and contrast within are discussed.

The partial pressures of helium produced are necessarily small, such that a high sensitivity helium detector is required for efficient acquisition[4]. The detector we have developed is a magnetic sector mass spectrometer with a large ionisation region to increase the probability of generating helium ions. A conversion dynode and electron multiplier are used to multiply the signal to obtain a high sensitivity to helium. The resulting increase in sensitivity (2% detection efficiency of incoming atoms) facilitates an improvement in resolution and acquisition time compared to previously published images.

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- [2] Barr, M., A. Fahy, A. Jardine, J. Ellis, D. Ward, D. A. MacLaren, W. Allison, and P. C. Dastoor. "A Design for a Pinhole Scanning Helium Microscope." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms, 20th International Workshop on Inelastic Ion-Surface Collisions (IISC-20)*, 340 (December 1, 2014): 76–80. doi:10.1016/j.nimb.2014.06.028
- [3] Pauly, Hans. *Atom, Molecule, and Cluster Beams I: Basic Theory, Production and Detection of Thermal Energy Beams*. Springer Science & Business Media, 2012
- [4] Alderwick, A. R., A. P. Jardine, H. Hedgeland, D. A. MacLaren, W. Allison, and J. Ellis. "Simulation and Analysis of Solenoidal Ion Sources." *Review of Scientific Instruments* 79, no. 12 (December 1, 2008): 123301. doi:10.1063/1.3030858



Interdisciplinary Surface Science Conference (ISSC-21)

Towards intelligent autonomous SPM

P Moriarty¹, M Møller¹, S Jarvis², L Guérinet³, P Sharp¹, R Woolley¹, S Freeney⁴, J Catton¹ and P Rahe⁵

¹University of Nottingham, UK, ²University of Lancaster, UK, ³Institut National des Sciences Appliquées de Toulouse, France, ⁴University Utrecht, Netherlands, ⁵University of Osnabrueck, Germany

A major bottleneck in improving the throughput and efficiency of scanning probe microscopy is the component that is at the very core of the technique: the probe itself. Many hours of a probe microscopist's time can be wasted on generating, or recovering, a tip that provides atomic or (sub)molecular resolution, or, as is increasingly the case, the correct type of atomic resolution. We will discuss progress in developing automated strategies to "tune" the tip apex to provide a particular type of atomic resolution image. An essential prerequisite for the intelligent tip engineering strategies we are developing is the realisation of robust image classification schemes. We have used the Si(100) surface and its hydrogen-passivated counterpart as platforms for the development of image recognition schemes that can be coupled to atomic manipulation strategies. [1]

[1] Morten Møller, Samuel P Jarvis, Laurent Guérinet, Peter Sharp, Richard Woolley, Philipp Rahe and Philip Moriarty, Nanotechnology (accepted)

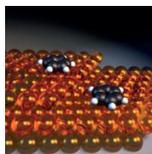
Surface diffusion of van der Waals bonded systems with entropic effects

H Hedgeland¹, M Sacchi², D J Ward³, P Singh⁴, A J McIntosh³, A P Jardine³, G Alexandrowicz⁵, S J Jenkins³, W Allison³ and J Ellis³

¹The Open University, UK, ²University of Surrey, UK, ³University of Cambridge, UK, ⁴The Perse School, UK, ⁵Technion - Israel University of Technology, Israel

Diffusion and transport on surfaces remain of interest as they underlie heterogeneous catalysis and self-assembly processes. The rate of diffusion of a molecule will depend on how easily it is excited across an energetic barrier, and hence is determined by both the magnitude of the barrier and the ongoing exchange of energy between the molecule and the thermal bath of the surface. Helium spin-echo spectroscopy allows us to follow the motion of a low coverage of benzene molecules adsorbed on Cu(001). As a benchmark van der Waals adsorbate, benzene is of interest from both the computational and experimental perspective: our combined experimental and density function data allow us to examine the diffusion rate in detail [1]. We find the rate of diffusion for the hexagonal benzene molecules is significantly higher than can be achieved using a conventional, point-particle model, motivating us to consider the molecular coordinates as well. The anomalously high diffusion rate can be described in terms of an entropic contribution enhancing the population of molecules in the transition state. Our finding is relevant for the wider class of molecular systems and illustrates the importance of the pre-exponential factor as well as the activation barrier in studies of surface kinetics.

[1] J. Phys. Chem. Lett., 2016, 7 (23), pp 4819–4824



Session 2

(invited) **Metal-organic coordination via non-specific interaction: Assembly and thermally activated re-shaping of magic number $(C_{60})_mAu_n$ clusters**

Q Guo

University of Birmingham, UK

Two-dimensional metal organic frameworks (MOFs) can be fabricated on solid surfaces in the conventional manner by utilizing specific chemical bonding between metal atoms and organic ligands. For a particular combination of metal and organic molecule, it is largely predictable what would be the stable structure of the resulting MOF. However, there are many examples where specific bonding between an organic molecule and a metal atom does not exist. In such cases, making regular ordered structures becomes a real challenge. Here I discuss the strategies for the realization of metal organic complexes that are stabilized by globally optimized interactions involving many atoms and molecules. I will demonstrate the formation of magic number $(C_{60})_mAu_n$ clusters. The smallest cluster consists of 7 C_{60} molecules and 19 Au atoms, I will also show how to re-shape the clusters by STM-triggered thermal re-organization.

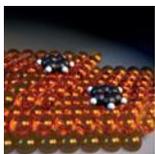
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Strong metal-support interaction and catalytic edge-effects for controlling electrical transport in nanocontacts to nanowires

A Lord, J Evans and S Wilks

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Semiconductor nanowires grown by techniques catalyzed with metal nanoparticles present a bottom-up solution for new technological devices. Here, we discuss a strong metal-support interaction (SMSI) that encapsulates the Au growth particle adding material to the edge-region of the interface between the catalyst and the ZnO nanowire. The electron microscopy analysis shows the process occurs at room temperature over a long time period and in ambient benign conditions. It is shown by directly correlating atomic-resolution electron microscopy to electrical transport measurements of individual nanowires that the nature of the SMSI-diffused ZnO material at the interface edge creates a channel that affects the quantum-mechanical tunneling electron transport. The results are confirmed by using the enhanced catalytic activity of the Au-ZnO interface edge to etch away the ZnO at the edge-region undercutting the metal nanoparticle. The microscopy analysis and transport measurements show the etch process removes the material from the edge-region and eliminates the quantum-mechanical tunneling path. This work correlates catalytic edge-effects with electrical transport edge-effects found in metal-semiconductor electrical contacts.



Interdisciplinary Surface Science Conference (ISSC-21)

Light-induced translation of motorized molecules on a surface

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A key component of molecular nanotechnology are molecular machines that can perform controlled work. The motion of such machines should be triggered remotely in order to address a large number of molecules at the same time, with light being an attractive stimulus as a single source. Here, we report the photo-induced translation of molecular machines across a surface by characterizing single molecules before and after illumination. Illumination of molecules containing a motor unit results in an enhancement in the diffusion of the molecules. The effect vanishes if an incompatible photon energy is used or if the motor unit is removed from the molecule, revealing that the enhanced motion is due to the presence of the wavelength-sensitive motor in each molecule.

Photoemission studies of band bending and passivation in PbS colloidal quantum dot films for next generation solar cells

P Clark¹, C-R Ke¹, R Ahumada Lazo¹, A Williamson¹, M Leontiadou¹, A Walton¹, A Thomas¹, D Neo², M Law², A Watt³, I Pis⁴, S Nappini⁵, F Bondino⁵, E Magnano⁸ and W Flavell¹

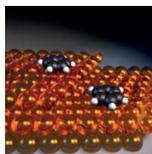
¹University of Manchester, UK, ²University of California, USA, ³University of Oxford, UK, ⁴Elettra-Sincrotrone Trieste S.C.p.A., Italy, ⁵Laboratorio TASC, Italy

Solar cells that incorporate films of PbS colloidal quantum dots (CQDs) have recently reached efficiencies of 10.6 % [1]. Improvements in efficiency and air stability have been made by altering the surface composition of the CQDs, for example exchanging lead atoms for cadmium, and exchanging organic ligands for halides [2]. Organic linker molecules have also been used to decrease the space between the CQDs to improve charge transport. The modification of CQD surfaces also allows control over the doping level and type of the film. Using doped CQD films allows for the engineering of band alignment [3].

To investigate different surface passivation methods we used standard laboratory XPS and UV-vis-NIR absorption to study PbS colloidal quantum dot films (approximately 50 nm thick) treated with a variety of solid state ligand exchanges as prepared in reference [2]. Using synchrotron radiation excited X-ray Photoelectron Spectroscopy XPS we have also examined the chemical composition of the quantum dots as a function of sampling depth, by changing the photon energy to measure core level XPS at different kinetic energies. We discuss the effectiveness of different passivation treatments, and relate this to the surface composition changes when two surface treatments are combined. We find that the halide and cadmium form a sub-monolayer shell on the PbS surface with the halide binding the lead rather than cadmium.

Additionally, we have tested for band bending at the surface of CQD films, in studies aimed at understanding the electronic structure of depleted heterojunction CQD solar cells. For this we used synchrotron-radiation-excited XPS to study the surface photovoltage (SPV) shift in the core levels and valence band of photoexcited PbS CQD films. Unlike bulk semiconductors, there is no obvious mechanism for the creation of surface defect states to cause band bending at the surface. Nevertheless, we are able to observe a significant SPV shift, of the order of up to 70 meV in doped films. Results from films subjected to different ligand treatments and thicknesses are discussed.

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- [3] C.-H. M. Chuang, P. R. Brown, V. Bulović, and M. G. Bawendi, *Nat. Mater.* 13, 796 (2014)



Tuesday 11 April

Session 3

(Woodruff Prize Lecture) **Self-assembly of monolayers of aromatic carboxylic acid molecules on silver and copper modified gold surfaces at the liquid-solid interface**

H Aitchison

University of St Andrews, UK

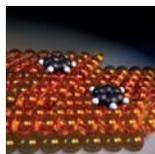
Exploiting coordination bonding of aromatic carboxylic acids at metal surfaces, this work explores new directions in the design of self-assembled monolayers (SAMs). Frequently utilised as components of 3D metal-organic frameworks (MOFs) and in 2D supramolecular networks, where the plane of the aromatic rings lies parallel to the surface, aromatic carboxylic acids are versatile and well-studied organic linkers. In contrast, studies of SAMs of densely packed aromatic carboxylic acids in non-flat adsorption geometries are more uncommon.

Here, a library of aromatic carboxylic acid molecules were adsorbed on both Cu and Ag modified surfaces at the liquid-solid interface. These systems were studied using a multi-technique approach comprising of a complementary combination of scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) spectroscopy.

The process of layer formation and the final structures of the SAMs are found to be strikingly dependent on the combination of molecule and substrate, which is discussed in terms of the intermolecular and molecule-substrate interactions, bonding geometries and symmetry of the organic molecules. This is illustrated by the dramatic difference between molecular adsorption on Ag and Cu for biphenyl-3,4',5-tricarboxylic acid. In the case of self-assembly on Cu, the molecule-substrate interactions play a decisive role in the resulting SAM structure, whereas on Ag, the intermolecular interactions dominate over the weaker molecule-substrate binding.

To further understand how intermolecular interactions influence the final arrangement of molecules, a homologous series of para-oligophenylene mono- and dicarboxylic acids adsorbed on Ag were studied. In all cases, highly crystalline SAMs are formed with the molecules adopting an upright orientation anchored to the surface by a carboxylate. Distinct differences in the arrangement of the dicarboxylic acid molecules compared to the monocarboxylic acid molecules demonstrate the pronounced influence of the second COOH group on the SAM structure. Unlike other classes of SAMs, these systems are determined by intermolecular interactions, with molecule-substrate interactions playing a secondary role. Coordinatively bonded carboxylic acids on silver should therefore provide considerable flexibility in the design of SAM structures.

This exploration of the balance of interactions that lead to the formation of these SAM structures lays the foundation for a systematic design of the structures and properties of aromatic carboxylic acid based monolayers. Examples range from highly anisotropic monolayers which open an exciting prospect for nanoscale molecular manipulation to SAMs where metal-organic coordination is decisively dependent on the steric configuration.



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Co-adsorption of alanine and water on Ni{110}

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¹University of Reading, UK, ²University of Surrey, UK, ³Elettra Sincrotrone, Italy, ⁴University of Reading/Diamond Light Source, UK

Enantioselective catalysis is of key importance, since it can provide products with valuable biological activity. Alanine acts as a chiral modifier in the enantioselective hydrogenation of β -ketoesters over Ni catalysts [1].

The present study explores the chemical state and thermal stability of alanine and water on clean Ni{110} using Temperature Programmed Desorption (TPD), X-Ray Photoelectron Spectroscopy (XPS), Temperature Programmed XPS (TP-XPS) and Near Edge X-Ray Adsorption Fine Structure Spectroscopy (NEXAFS). In addition, the co-adsorption of alanine and water on Ni{110} was also investigated. XPS results of alanine on clean Ni{110} at different coverages provide evidence that the amino acid exists in the chemisorbed layer mainly in its anionic form, forming three surface bonds: two via the carboxylate group and one through the amino group. In the multilayer, alanine is in its zwitterionic form. TP-XPS and TPD results show that the multilayer desorbs around 300 K while the chemisorbed alanine dissociates around 400-420 K. The temperature is well above the temperature of the catalytic reactions and is the highest observed on any nickel surface [2].

The presence of multilayer water changes the chemical state of alanine, enhancing the formation of zwitterionic alanine. Low coverages of water influence the decomposition path of the amino acid, without changing its chemical state. In both cases water does not alter the decomposition temperature of alanine.

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- [2] REJ Nicklin, A Cornish, A Shavorskiy, S Baldanza, K Schulte, Z Liu, RA Bennett, and G Held. Surface Chemistry of Alanine on Ni f111g. *The Journal of Physical Chemistry C*, 119(47):26566-26574, 2015

Molecules within molecules: a NIXSW study of H₂O@C₆₀

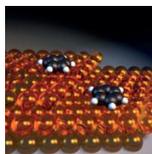
S Jarvis¹, S Taylor², S Mamone², J Leaf², A Saywell², P Rahe², A Sweetman², P Moriarty² and R Jones²

¹Lancaster University, UK, ²University of Nottingham, UK

The encapsulation of molecules within a C₆₀ cage provides a unique environment to study their properties unperturbed by strong intermolecular interactions. Through the process of so-called molecular surgery [1, 2], a limited number of large molecules can now be encapsulated within a C₆₀ cage. In the case of fullerene-encapsulated H₂O, it has been possible to identify spin isomerisation [3] and modifications in the dielectric properties due to *ortho-para* conversion of the H₂O [4]. Despite these recent observations the precise location of the H₂O molecule within the fullerene cage, and moreover, the effect it has on the electronic properties of the fullerene molecular orbitals, remains largely unknown.

Here we describe a combined high-resolution scanning probe microscopy (SPM) and normal incidence x-ray standing wave (NIXSW) study (performed at the Diamond light source) of H₂O@C₆₀ deposited onto single crystal Cu(111) and Ag(111) samples. We show that through the use of NIXSW measurements taken using different crystal planes of the supporting Ag(111) crystal, a triangulation can be made to determine the exact position of the H₂O within the C₆₀ cage. Interestingly, we find that scanning tunnelling microscopy (STM) and non-contact atomic force microscopy (NC-AFM) show very little difference between filled and empty cages, suggesting that electronic coupling between the two molecules is minimal.

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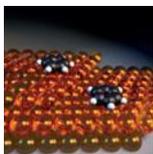
Enhanced π back-donation driven by lateral adsorbate interactions in weakly chemisorbed systems

J A Garrido Torres¹, K L. Finley¹, H A Früchtl¹, P B Webb² and R Schaub¹

¹University of St Andrews, UK, ²Sasol UK Ltd, UK

Finding relationships between structure and activity of heterogeneous catalysts is essential to the 'smart' design of next generation processes. Ever since the revolutionary concept of active sites was introduced by Taylor almost a century ago [1], defining the structure of active sites is far from trivial and remains one of the greatest challenges in catalysis [2-4]. One approach is to study changes in the electronic character of a probe molecule upon adsorption. Carbon monoxide is the archetypal probe of surface structure owing principally to its prevalence in catalysis and the sensitivity of its vibrational frequency to local environment [5]. The nature of CO adsorption on transition metals is well understood but the behaviour on weakly interacting surfaces cannot be explained easily by the same bonding models. Upon adsorption, the IR bands of this molecule typically blue shifts with increasing coverage on mostly all transition metals [6]. However, a red shift is observed when CO is adsorbed on coinage metals [7]. A number of alternative models [7,8] have been proposed to explain this observation, differing largely in how the balancing act between σ and π bonding is considered. Hence no consensus has been reached. To explore further the intermolecular interactions of CO on noble metals we have investigated the adsorption of CO on Cu(110). Atom-resolved microscopic imaging coupled to orbital theory calculations allow monitoring the local environment of the molecules and their intermolecular interactions. Our studies reveal that lateral adsorbate interactions, which are constrained by the catalyst surface, control the bonding between adsorbate and substrate. Anisotropic CO-CO coupling is seen to arise from a localised charge accumulation in the intermolecular regions, leading to an increased charge back-donation. We propose an alternative bonding mechanism, which is regulated by these lateral interactions, to account for the unusual chemisorption behaviour of CO on coinage metals. An increasing CO coverage leads to a concomitant increase in the population of anti-bonding states of CO, in contrast to CO adsorption on more reactive metals, and this manifests as a weakening of the CO bond. Our results shed new light on the chemisorption behaviour of CO on noble metals and provide detailed insights into the long-standing debate concerning frequency shifts of adsorbates on weakly interacting metals.

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- [2] G. Ertl, *et al.* *Science* 273, 19688 (1996)
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- [5] J. Winterlin, *et al.*, *Science* 278, 1931 (1997)
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Session 4

(invited) **Interfaces: Modeling and computational strategies**

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In this talk, our work on complex interface systems will be reviewed. The first part is devoted to the TiO₂/polyethylene glycol and TiO₂/water interfaces, whereas the second part to the metal/graphene ones.

Titanium dioxide is a well-known key material in many technological applications. Furthermore, during the last few years it is gaining increasing attention as nanocarrier material for biomedical applications [1]. In this context, the scientific community is very keen in understanding and controlling the interaction between TiO₂ surfaces and the human body environment.

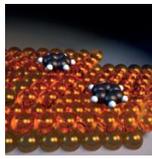
By means of ab initio density functional theory (DFT), we have investigated the interface between the most exposed anatase TiO₂ (101) surface with polyethylene glycol (PEG), which is an FDA approved, cheap and easy-to-use polymer, often employed in medicine to protect external bodies from the immune system. We considered different coverage densities and possible covering configurations assessing the risk of desorption of the PEG in presence of water, the most abundant molecule in the cytoplasm.

Although DFT is a powerful tool to study surface/molecule interfaces, it may become too computationally costly when aiming at the investigation of large polymeric molecular systems. We have performed a benchmark study of the performance of density functional tight-binding (DFTB) [2] with reference to DFT calculations for the description of the prototype anatase TiO₂ (101)/water interface. We demonstrate that, with our modified set of DFTB parameters, the static and dynamic behavior of this interface is accurately reproduced.

Graphene is another material of central interest for its potential applications. However, the poor reactivity of non-defective graphene has, so far, impeded its use in catalysis. On the other hand, defective graphene exhibits a good reactivity with small molecules or nanoclusters [3].

Here the focus is on an emerging field in catalysis, dealing with reactions taking place in the confined region between graphene and a metal support, i.e. catalysis under the graphenic cover [4]. Our DFT study is devoted to the investigation of water reactivity at the interface between pristine and defective graphene with Cu(111) and Pt(111).

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Metallization of SrTiO₃ surface by hydrogen and alkali metal deposition

M D'angelo¹, M Silly², R Yukawa³, K Akikubo³, O Kenichi⁴, D Schmaus⁵, G Marcaud⁵, S Yamamoto³ and I Matsuda³

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Transition-metal oxide and especially perovskite-type oxides have been extensively studied in the past decades for their large range of intrinsic properties such as superconductivity, magnetoresistance or ferroelectricity. Among these oxides, SrTiO₃ (STO) appears as a key material for the new emerging field of all-oxide electronics especially since the discovery of two-dimensional gas (2DEG) at the LaAlO₃ / SrTiO₃ interface [1] or at the STO (001) surface cleaved under vacuum [2].

Here, we present an angle-resolved photoemission study of hydrogen and cesium adsorption on the STO(001) surface [3,4]. In both cases, we evidence an adsorbate induced insulator <-> metal transition at the oxide surface. Further investigation of the polarization dependence of the photoemission intensity gives some deeper insight into the nature of the states responsible for the metallization of the surface and into the mechanisms leading to the formation of the 2DEG [6]. For hydrogen deposited surface, electron doping from the adsorbates to the substrate results in the progressive downward bending of the bands. For a sufficient charge transfer, the minimum of the conduction band would eventually cross the Fermi level, resulting in the surface metallization. In that case, the observed peak at the Fermi level has t_{2g} symmetry in agreement with the nature of the bottom of the SrTiO₃ conduction band which is mainly from Ti3d t_{2g} states. This t_{2g} symmetry is observed also for the 2DEG of the LaAlO₃/STO system and for the surface cleaved under UHV. Interestingly, for Cs deposition our results show that the metallic band has e_g symmetry. This e_g-derived state is likely to be a bonding state composed of the Cs s-orbital and the Ti d-orbital, as predicted in previous theoretical calculation [5].

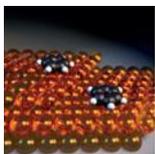
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Benchmarking DFT+U calculations: geometric adsorption site of copper and silver adatoms on magnetite

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Normal incidence X-ray standing wave (NIXSW) measurements of the adsorption geometry of copper (Cu₁) and silver (Ag₁) adatoms on the (001) termination of magnetite were utilized to benchmark DFT+U calculations. The NIXSW confirmed the theoretical prediction, and scanning tunneling microscopy interpretation, that the adatoms sit in a tetrahedral-Fe bulk continuation site. The predicted dramatic difference in height, between Cu₁ and Ag₁, was qualitatively observed. Specifically Cu₁ was found to adsorb $0.43 \pm 0.03 \text{ \AA}$, and Ag₁ $0.96 \pm 0.03 \text{ \AA}$, above the oxygen and octahedral iron plane. A quantitative comparison of the experimental data and the theoretical calculations provides insight into the accuracy of DFT+U calculations for the Fe_{3O₄}(001) surface, and allows benchmarking of the Hubbard-like term, U_{eff}.



Interdisciplinary Surface Science Conference (ISSC-21)

Ultrathin films of TiO_x and NbO_x on Au(111)

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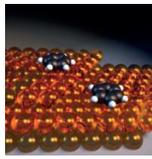
There is a great deal of interest in the surfaces of metal oxides because of their broad range of applications in catalysis, microelectronics, and gas sensing. However, oxides that are created as ultrathin films have electronic, optical, magnetic and chemical properties that may be quite different from their bulk crystal counterparts [1]. This is because of the strong interaction between the oxide film and the substrate that it is grown on. Many ultrathin metal oxide films that are only a few atomic layers thick should be considered as 2D hybrid structures - part bulk, part interface, and part surface. This talk covers ultrathin oxides in general and then concentrates in detail on the work we have carried out on TiO_x and NbO_x ultrathin films on Au(111) substrates.

Ultra-thin films of TiO_x and NbO_x were grown on Au(111) by evaporating low coverages of Ti and/or Nb in UHV onto the Au substrates and subsequently annealing the samples in an environment containing oxygen [2]. For certain processing conditions a 2×2 Ti_2O_3 honeycomb structure is created on the surface. We have studied this structure with STM, LEED, AES, XPS, ARPES and DFT. We can also create a 2×2 Nb_2O_3 honeycomb structure.

Because the Ti_2O_3 honeycomb structure is a 2×2 overlayer there is the possibility that neighbouring domains are offset with respect to each other. This gives rise to domain boundaries where the usual hexagonal rings are no longer stable. The boundary structures have been studied by STM, which shows that [11-2] and [1-10] oriented boundaries are most common. The structures consist of combinations of rings of 8, 7, 5 and 4 Ti atoms for the different boundaries. DFT has been used to calculate the boundary energies. There is a good fit between the most frequently observed boundary structures seen in STM and the lowest energy structures as determined by DFT.

The honeycomb structure provides a unique environment for the adsorption of ad-species, and in this instance we evaporated Ba atoms on the structure. STM imaging shows that the Ba atoms adsorb individually in the hollow sites of the HC network [3]. Depending on the Ba coverage (x) which ranges from 0 to $2/3$, two ordered phases can be identified at $x = 1/3$ and $x = 2/3$. A disordered labyrinth-like phase is observed for values of x between $1/3$ and $2/3$. Theoretical modelling shows that the structural character of these films is driven by the charge transfer that occurs between the electropositive Ba atoms and the electronegative $\text{Ti}_2\text{O}_3/\text{Au}$ support. This results in a number of calculated effects including an increase in the film rumpling and a reduction of the film work function with increasing x . The evolution of the structure of the thin films as a function of Ba coverage can be described using a lattice gas model with first-, second- and third-nearest-neighbour Ba-Ba repulsive interactions, and modeled using Monte Carlo techniques. The range of the dipolar interactions is a key factor in understanding the behaviour of Ba ordering.

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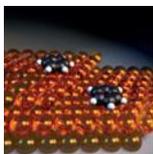
Depth profile of surface oxidation on FeCo thin film by depth resolved X-ray absorption spectroscopy

M Sakamaki and K Amemiya

High Energy Accelerator Research Organization, Japan

We have developed depth-resolved x-ray absorption spectroscopy (XAS) and x-ray circular magnetic dichroism (XMCD) techniques with a sub nm depth resolution so far. In these techniques, we use angle resolved electron detector, and probing depth is controlled by emission angle of the Auger electrons. By analyzing the set of data with different probing depths, we can directly observe the electronic and magnetic in-depth distribution of thin films. However, it is difficult to measure in the electric or magnetic field because these techniques are based on the electron yield detection. Therefore we developed them into fluorescence yield depth-resolved XAS/XMCD system, which enables observation of wider range in-depth distribution up to several tens of nm. Furthermore, operando observation under the electric or magnetic field is available. Using this technique, we investigate oxidation state around the surface of FeCo thin films.

FeCo alloy is a typical material used for magnetic head components such as the free and pinned magnetic layers. Device structure is usually fabricated by ion milling and fine lithography. As each layer is getting thinner and narrower, surface and edge damage caused by ion milling has to be controlled. So we compare the as-deposited and ion milled surfaces and observe the in-depth distribution of magnetic and chemical states of FeCo thin films by using this technique.



Session 5

(invited) **Programmed assembly of molecular frameworks**

C Wöll

Karlsruhe Institute of Technology (KIT), Germany

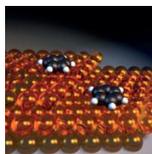
The demand for advanced materials with novel combinations of different functionalities requires the development of new types of solids. In this context supramolecular chemistry holds unique prospects. Self-assembly of one or different types of functional units can be employed to fabricate crystalline arrangements, yielding complex but at the same time structurally well defined, highly ordered “Designer Solids”, which exhibit functionalities going well beyond that provided by the individual building blocks.

In this presentation, it will become evident that a recently introduced class of supramolecular materials, metal-organic frameworks, or MOFs, carry an enormous potential with regard to the fabrication of solids with unusual physical properties [1]. MOFs are stable materials, with decomposition temperatures well above 200°C (in some cases > 500°C). With selected examples, we will demonstrate the interesting, and often surprising (e.g. negative thermal expansion coefficient), mechanical, electronic, magnetic and optical properties of these molecular, crystalline materials.

This fairly recent class of porous solids, introduced in the 1990s, is very large in number, already more than 20.000 different structures have been reported. In order to exploit the properties of these materials for applications in solid state physics, we have developed a liquid phase epitaxy (LPE) process, which allows growing MOFs on modified substrates using a layer-by-layer procedure [1]. The availability of cm-sized, highly oriented MOF thin films with thickness in the mm-regime allows to determine the basic physical properties (mechanical [2], optical [3], electronic [4], magnetic [5]) of these porous, molecular solids using standard methods. A unique feature of the LPE-process is the ability to use heteroepitaxy [6] to add further functionality to these materials by creating multilayer systems [7].

The porous nature of these crystalline solids opens up the prospect of adding additional functionality by placing molecules [8] or nanoobjects inside the voids within the MOFs, e.g. metal clusters or dye molecules [9]. We will demonstrate the potential of this approach by loading the three-dimensional porous scaffolds, or “designer solids”, with metal-containing molecules such as ferrocene and then determining the change in conductivity using electrochemistry [10].

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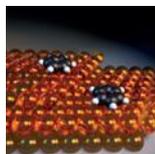
Two-dimensional covalent-organic frameworks (2D-COF) via schiff-base condensation reactions between porphyrins

C Nowicka-Dyła, M Blunt, N Goodeal, Y Hu and H Bronstein

University College London, UK

We present an investigation of the growth and properties of 2D covalent-organic frameworks (2D-COFs) supported on solid surfaces. By careful selection of molecular building blocks and the environmental conditions during growth; the structure, composition and electronic properties of these novel 2D materials can be controlled. An important step forward in the growth of 2D-COFs is the formation of highly ordered, defect free structures. The molecular precursors used in this work are 5,10,15,20-tetrakis-(4-aminophenyl) porphyrin (TAPP) or 5,10,15,20-tetrakis-(4-aminophenyl) porphyrin-Zinc(II) (Zn-TAPP) which are linked together via a Schiff-base condensation reaction with benzene-1,4-dicarboxaldehyde (BDA). The 2D-COF growth process is performed on a supporting graphite substrate. In order to produce highly crystalline 2D structures a thermodynamically controlled growth process is employed where water acts as a regulating agent to control the equilibrium position of the Schiff-base condensation. Scanning tunnelling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) are used to study the structural and chemical composition of the resulting 2D-COF layers. In demonstrating the versatility of these porphyrin precursors and the thermodynamically controlled growth process, we aim to produce more complex, defect-free structures with increased crystallinity and domain size. In addition to structural and chemical analysis, the use of transient absorption spectroscopy (TAS) allows us to study the optoelectronic properties of 2D-COFs. These studies include investigating the behaviour of transient photo-generated species present in these novel conjugated materials on nanosecond time scales. The growth of the highly ordered and conjugated 2D-COFs presented here offers a versatile route to the formation of complex nanostructured organic thin films. These materials have potential for applications in organic photovoltaics and molecular electronics. Gaining a deeper understanding of how we can control the structure of 2D-COFs and, in turn, how that structure influences their photo-physical properties, is a vital step toward such applications.

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Interdisciplinary Surface Science Conference (ISSC-21)

Exploring adsorption within porous catalyst supports with NMR relaxometry and DFT

N Robinson, C Robertson, L Gladden, S Jenkins and C D'Agostino

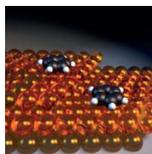
University of Cambridge, UK

A detailed understanding of surface-adsorbate interactions is of paramount importance for the rational design of active materials in heterogeneous catalysis. Liquid-phase catalytic reactions are vital for a variety of green chemical processes, such as the production of fuels and chemicals from biomass. During such reactions, the high molecular density within the liquid-phase leads to the total saturation of surface adsorption sites, where competitive adsorption interactions between reagent, product and solvent molecules determine the relative molecular populations within the adsorbed surface layer. The ability to predict adsorption energetics based on molecular functionality and surface structure is therefore essential for the optimisation of selective catalytic processes in the liquid-phase.

Nuclear magnetic resonance (NMR) relaxometry has recently emerged as a non-invasive and chemically selective method for the comparison of adsorption dynamics within liquid-saturated mesoporous catalyst materials.[1,2] In particular, relaxation measurements have been shown to correlate directly with the experimental heats of adsorption of water in catalyst pellets, as observed with temperature programmed desorption.[3] The method uses NMR spectroscopy to measure and compare the nuclear spin relaxation time constants (T_1 and T_2) of nuclei within the imbibed liquid phase; the ratio of which is now well established as a measure of the relative surface affinities of adsorbed species, averaged over the pore structure under study.

In the present work we explore how such mesoscopic measurements are related to specific adsorption interactions occurring at the molecular level. To this end, we have combined 2D NMR relaxation measurements with density functional theory (DFT)-based calculations. As a prototypical example of liquids exhibiting molecular functionality relevant to green chemical processes, we examine the adsorption of primary alcohols at the surface of amorphous silica. Our results indicate for the first time that the T_1/T_2 ratio of short-chain alcohols may be directly correlated with the results of DFT adsorption energy calculations, when performed on single adsorbate molecules interacting with an idealised silica surface. Furthermore, we observed through our DFT calculations that the adsorption energetics of hydroxylated adsorbates at silica surfaces are determined by a combination surface-adsorbate hydrogen bonding interactions with polar surface groups, and the presence of adsorbate-adsorbate dispersion interactions between extended carbon chains. Overall, these results highlight NMR relaxometry as a powerful method for determining adsorption energetics within porous solids, and provide insight into the ability of this technique to aid in our understanding of catalytically relevant liquid/surface interactions at the molecular level.

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Morphology and growth mechanisms of self-assembled films on insulating substrates: Role of molecular flexibility and entropy

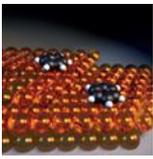
J Gaberle¹, D Z Gao¹, M B Watkins^{1,2}, A L Shluger¹ and C Loppacher³

¹University College London, UK, ²University of Lincoln, UK, ³Aix-Marseille Université CNRS, France

We present the results of computational modelling of adsorption and diffusion of large organic molecules on terraces and step edges on the KCl (001) surface, focussing on the effects that molecular flexibility has on their dynamic behaviour. Two functionalised organic molecules: a rigid 1,3,5-tri- (4-cyano-4,4biphenyl)- benzene (TCB) and flexible 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB), were studied on the KCl (001) surface using density functional theory (DFT) and classical molecular dynamics (MD) simulations. MP2 calculations within CP2K code were used to benchmark the performance of van der Waals corrected DFT-D3 calculations of adsorption energies and geometries and a classical force field was parameterised for the interaction of each of the molecules with KCl(001) using a genetic algorithm.^[1] These force fields allowed us to perform long time-scale simulations to study the motion of molecules on the surface.

In order to better understand adsorption of TCB and CDB molecules at elevated temperatures, potential of mean force calculations and thermodynamic integration methods were employed. It was found that the entropy change on adsorption constitutes almost half of the adsorption free energy.^[2] Diffusion coefficients for molecular diffusion on terraces were calculated using molecular dynamics and the activation energies evaluated as 0.52 eV for TCB and 0.36 eV for CDB. Furthermore, adhesion to step edges was investigated along with the associated changes in entropy. While the flexible CDB molecule can readily adapt to step edges, the rigid TCB molecule is unable to and exhibits a significant entropy loss upon step adhesion. We show that a simple rigid rotor model can accurately estimate entropy loss upon step adhesion for TCB but fails for CDB. Furthermore the formation of TCB dimers was investigated and free energy profiles of their formation give insight into their stability at 300K. They were found constitute the main building block for self-assembled films of TCB on a KCl (001) substrate. These results highlight how molecular flexibility directly influences surface dynamics, which can lead to different self-assembly growth modes.

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Session 6

(invited) **Surface science and electrochemistry combined to understand corrosion mechanisms of metals and alloys at the nanoscale**

P Marcus

CNRS-Chimie ParisTech, France

After a short general introduction on the surface science approach of corrosion, and a brief review of the techniques used for high resolution characterization of surface structure, chemical composition, and corrosion processes, various aspects related to the role of the surface structure and composition of metals and alloys in corrosion processes will be presented.

The following key issues will be emphasized:

- The metal-water interface: early stages of interaction studied *in situ* by Electrochemical Scanning Tunneling Microscopy on metals (Cu, Ni, Ag)
- The reactivity of grain boundaries: localized dissolution at GBs
- The structure of oxide passive films on metals (Cu, Ni, Cr) and stainless steel
- The local electronic properties of passive films (investigated by Scanning Tunnelling Spectroscopy)
- Localised corrosion: its origin at the nanoscale
- The role of step edges at the exposed surface of oxide grains on the dissolution of the passive film
- Atomistic modeling of corrosion using DFT

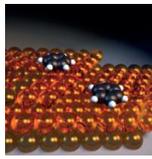
A surface science approach to oilfield corrosion

M Acres¹, H Hussain², C Muryn¹ and R Lindsay¹

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Dissolved CO₂/H₂S are primary reagents for internal (sweet/sour) corrosion of oilfield equipment fabricated from carbon steel. The resulting aqueous phase species stimulates corrosion primarily through supplying reactants for the cathodic process; iron dissolution occurs at anodic sites. Solid corrosion products may also appear as a consequence of CO₂/H₂S induced corrosion. If adherent to the carbon steel substrate, such solids can significantly reduce the rate of corrosion and so are integral to material sustainability.

Given the importance of sweet/sour corrosion scales, there is significant on-going effort to understand them. Substantial progress has been made, in particular as regards established scales. Lacking, however, are nanoscale details about the nucleation and growth of these scales, including the surface structure/chemistry prior to scale initiation. On this basis, we have adopted a surface science type approach in attempt to address these topics. Using ultra high vacuum scanning tunnelling microscopy, in tandem with a near ambient pressure dosing cell (NAP-cell), and (NAP-) X-ray photoelectron spectroscopy, we have examined the adsorption of H₂S/CO₂ (along with H₂O and O₂) onto Fe(110) across a range of pressures and substrates temperatures. STM images demonstrate that even under the extremely low exposures (from an engineering perspective) employed in this work, significant modification of the substrate surface structure does occur, and is dependent on adsorbate identity. Intriguingly, however, for H₂O/CO₂/O₂ adsorption, XPS data indicate that the surface chemistry is apparently essentially invariant, i.e. all surfaces are simply decorated with chemisorbed O's. Data for H₂S also suggest that in the low exposure regime simple chemisorption of S occurs. In sharp contrast, much higher exposures of H₂S result in a range of previously unknown surface phases, including the formation of hexagonal nano-pillars, demonstrating the complexity of the growth process.



Material growth and erosion in extreme environments

A Bell and P Mulheran

University of Strathclyde, UK

We aim to develop a molecular dynamics (MD) model capable of simulating the surface chemistry and material erosion of materials in extreme environments, such as might be encountered by a space re-entry vehicle descending through the atmosphere. We have been using standard MD methodologies to impact a crystal surface with energetic atoms, initially focusing on metal growth modelled with Sutton-Chen potentials. In our simulations, we generate the sputter yield and the sticking probability for the atomic impacts. We have also developed an algorithm that allows us to identify surface atoms to monitor the average surface height and surface roughness, helping us to optimise the system parameters such as size and thermal treatment of the surface region. The angle of incidence for the impacting atoms dramatically affects the kinetics, causing growth at low angles and erosion at high, independent of azimuthal angle. The simulation also reveals interesting surface kinetic effects for the growth of ad-islands, vacancy islands, and the mobility of these species as a function of size. This information is vital for the development of efficient kinetic Monte Carlo simulations that can correctly capture the complex growth physics. In future work we plan to develop our methodology to simulate metals and their oxides bombarded by energetic oxygen ions.

Understanding corrosion mechanism of steel by sulphate-reducing bacteria using XPS depth profiling

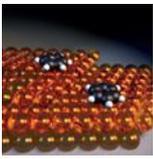
S Ray

University of Brighton, UK

Accelerated low water corrosion (ALWC) has been recently identified as a phenomenon involving the rapid, microbially mediated, corrosion of steel piles in the marine environment at or close to the low water mark. It is also unquestionably accepted that the sulphate reduction is a widespread process in bed sediment. Microbiological analyses indicate that there is close correspondence between sediment bacterial colonies and ALWC associated bacteria colonies, but not with bacteria from the harbour water column. This supports a model of sulphate-reducing bacteria (SRB) colonisation of steel from microbial colonies below the sediment surface when sediment is disturbed and water turbidity increases. Mineralogical analyses of corrosion products suggest diagnostic differences between ALWC and other corrosion types, and also indicate the presence of intermediate oxidation state sulphur compounds within ALWC blisters. These are consistent with the identification of a range of sulphur oxidising bacteria in ALWC samples.

X-ray photoelectron spectroscopy (XPS) combined with Ar⁺ ion etching is a powerful concept to the complex and diverse structures of the top-surface corrosion layers in depth profiles, important for obtaining information underneath surfaces or at layer interfaces. Understanding the variation of sulphate reduction depending on the depth of the interface layer could potentially reveal the chemical process associated with this mechanism of corrosion.

By means of mineralogical and chemical characterisation and micro-biology analyses, along with detailed XPS depth profiles, we have proposed a mechanism of the process and provided insights on how SLB accelerated corrosion rates.



Interdisciplinary Surface Science Conference (ISSC-21)

Disentangling the role of phonons versus electron-hole pairs in dynamic friction on metal surfaces

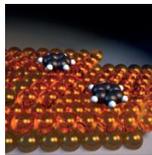
D Ward¹, S Rittmeyer², P Gütlein², A Jardine¹, J Ellis¹, W Allison¹ and K Reuter²

¹University of Cambridge, UK, ²Technische Universität München, Germany

Energy dissipation during surface dynamical processes is of paramount technological importance while providing an intriguing fundamental richness. With the development of spin echo helium spectroscopy^[1] it is possible to routinely investigate surface diffusion on the pico to nanosecond timescales which is providing a growing catalogue of data which may be used to probe new areas of fundamental physics.

In the current work helium spin echo experiments combined with ab initio based Langevin molecular dynamics simulations are used to quantify the adsorbate-substrate coupling during the thermal diffusion of Na atoms on Cu(111). Experimental work and models are presented as time-correlation functions, known as the intermediate scattering function, which is demonstrated to be the natural domain in which to perform the work. An analysis of Langevin trajectories within the local density friction approximation allows the contribution from electron-hole pair excitations to be quantified separately from the total energy dissipation^[2]. Despite the minimal electronic friction coefficient of Na and the relatively small mass mismatch to Cu promoting efficient phononic dissipation, about (20±5)% of the total energy loss is attributable to electronic friction. The results suggest a significant role of electronic nonadiabaticity in the rapid thermalization generally relied upon in adiabatic diffusion theories.

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Wednesday 12 April

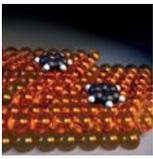
Session 7

(invited) **Surface and Interface Science for the 21st century: wet, warm and dense**

M Salmeron

Lawrence Berkeley National Laboratory and University of California Berkeley, USA

Over the past century the science of surfaces has undergone an enormous progress. The atomic and electronic structure, reactivity, and dynamics of many material surfaces have been uncovered. Several Nobel prizes have marked the great accomplishments of our predecessors, from I. Langmuir in 1932 to G. Ertl in 2007. This progress has been fostered and propelled by the continuous development of powerful techniques that have provided atomic and molecular level details of surfaces, adsorption and desorption phenomena, vibration and electronic spectra, electron diffraction and real space imaging by the Scanning Tunneling Microscope. The nature of many techniques has constrained Surface Science to ultra-high vacuum environments, and often under cryogenic temperature to achieve measurable coverage of weakly bound adsorbates. And yet practical surfaces are surrounded by gases and liquids at ambient conditions of pressure and temperature. Under these conditions the surfaces are covered with dense layers of adsorbed molecules in equilibrium with the gas phase, while the relevant ambient temperature unlocks many kinetic processes that are frozen at low temperatures. One consequence of this is that under realistic conditions the structure of surfaces can be very different from the pristine structure obtained after preparation in high vacuum with traditional Surface Science techniques. I will review the physics and chemistry of surfaces with dense layers of adsorbates and show new phenomena that derive from this, including the effect of reactant gases such as O₂, H₂O, CO and CO₂ on the structure of Pt and Cu surfaces. Prospects for similar studies of the solid-liquid interface, a new frontier in the field, and their impact in environmental science, electrochemistry and energy storage will be discussed.



Interdisciplinary Surface Science Conference (ISSC-21)

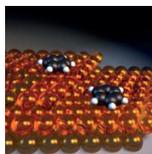
Near-ambient-pressure x-ray photoelectron spectroscopy study of ultra-stable aerosol-assisted-chemical-vapour-deposition-processed Cs_2SnI_6 double perovskite

C-R Ke, D Lewis, A Thomas, A Walton, P O'Brien and W Flavell

University of Manchester, UK

Halide perovskite materials have emerged as highly promising photovoltaic absorbers typically due to excellent absorptivity and diffusion length, which allows power conversion efficiency (PCE) to reach satisfactory values by only using a small amount of raw materials. However, poor stability has limited their development for commercialisation, which has resulted in enormous worldwide research effort in the reduction of degradation as well as the enhancement of PCE. An inorganic lead-free double-perovskite material, Cs_2SnI_6 , has recently attracted immense attention owing to its high stability and low energy bandgap.

In this work, an ultra-stable Cs_2SnI_6 material is successfully fabricated *via* low-temperature aerosol-assisted chemical vapour deposition (AACVD) with a direct energy bandgap of 1.26 eV and a highly pure phase composition. After aging under ambient atmosphere for up to 100 days, we find that the crystal structure shows a negligible change and its bandgap retains a very low value. This result suggests that AACVD-processed Cs_2SnI_6 thin films can be strong candidates for use in future perovskite photovoltaic devices. Near-ambient-pressure X-ray photoelectron spectroscopy (NAPXPS) is used to investigate the interaction of the films with water, by monitoring the CsI to Cs_2SnI_6 ratios in the spectra of the Cs 3d and I 3d core levels. The result clearly shows the ratios do not change following exposure to H_2O vapour and no other components appear in these spectra or in the Sn 3d spectra during the exposure. This suggests that the surface state of the film is unchanged by exposure to H_2O vapour with a pressure of up to 9 mbar, approximately equivalent to a relative humidity of 30%. In summary, our work presents not only a highly promising photovoltaic material fabricated by AACVD but it also illustrates the importance of NAPXPS for surface studies of perovskite-related materials under various environmental conditions, in order to understand the interaction between the surfaces of the perovskites and atmospheric molecules.



Development of a high intensity electrospray source for UHV deposition of large molecules for STM studies

D Warr, L Perdigao, J Blohm, H Pinfeld, M Barrow, A Colburn and G Costantini

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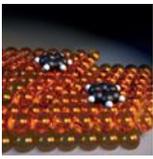
Surface engineering through the adsorption of molecular units is emerging as one of the most powerful technologies for the fabrication of advanced nanostructured materials [1]. With the tremendous range of functions available in biological molecules and the almost unconstrained capabilities of modern synthetic chemistry, the real limiting factor in molecular surface engineering is the restricted ability to prepare reproducible high quality organic thin films.

Electrospray ionisation beam deposition (ESI-BD) is quickly becoming a versatile technique for depositing large thermally labile molecules for study on surfaces in vacuum [2]. The technique has been used to demonstrate deposition and study of a wide range of molecules from fragile molecular magnets [3] to porphyrin nanorings [4].

In this work we present a new design for a high efficiency, high transmission ESI-BD source coupled to a scanning tunnelling microscope (STM) offering the ability to study these complex systems with the ultimate spatial resolution of STM. The design principles upon which the system has been based are to produce a high intensity ion beam, to keep a compact size, to minimise the amount of user optimisation needed for the source, to allow deposition at 10^{-10} mbar (ultrahigh vacuum, UHV), and to be highly versatile and easily expandable.

These goals have been reached through the use of a new ion funnel design with extremely high transmission and hexapole ion guides which have been designed and optimised for high transmission and little need for user optimisation. Careful design of vacuum chamber conductance limits has allowed the number of differentially pumped sections to be minimised, delivering a high intensity ion beam to the substrate surface in UHV.

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Interdisciplinary Surface Science Conference (ISSC-21)

Persistent photoconductivity in non-polar ZnO as a function of surface OH coverage probed by laser-pump synchrotron radiation-probe XPS and NAP-XPS

A Williamson¹, P Clark¹, R Ahumada Lazo¹, A Walton¹, C Muryn¹, A Thomas¹, M Silly², F Sirotti² and W Flavell¹

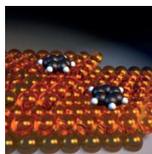
¹University of Manchester, UK, ²Synchrotron SOLEIL, France

ZnO is a transparent conducting oxide (TCO) with varied potential optoelectronic applications including next generation solar cells [1] but a more complete understanding of how oxygen vacancies, hydrogen impurities and surface OH adsorbates affect the overall conductivity of the material is required to fully optimise these systems [2].

Here, we employ laser-pump, synchrotron radiation-probe x-ray photoelectron spectroscopy (XPS) to probe the charge dynamics within a few nm of the surface in a chemically resolved way [3]. Determining these dynamics requires measurement of a surface photovoltage (SPV) in the ZnO crystal, which is known to vary depending on the conductivity of the crystal [4,5]. Photoexcited carrier lifetimes of the order of 10-100 ms are measured, limited by the persistent photoconductivity (PPC) of the ZnO surface. This is shown to vary as the surface OH coverage on the crystal is dynamically increased by conducting the experiment in an oxygen atmosphere, with the lifetime increasing by approximately 50%. An increase in the carrier lifetime is consistent with an increase in the carrier concentration at the surface of the crystal arising from hydrogen in the OH surface species donating electrons into the surface layer.

We have conducted complementary measurements using near-ambient pressure (NAP) XPS on non-polar ZnO in oxygen and water vapour environments at 5 mbar to monitor the effects of surface adsorption on O 1s and Zn 3d core level spectra. Here we observe an increase in size of the OH and molecular H₂O O 1s species consistent with the results obtained from the time-resolved experiment.

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Session 8

(invited) **Breaking and making the ice**

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There are few molecules, if any, more important than water. Yet remarkably little is known about how it interacts with solid surfaces, particularly at the all important atomic-level. This is true despite widespread general interest and compelling environmental and economic incentives. For example, water-solid interactions play a crucial role in the activity of fuel cells, the chemistry of the atmosphere, global warming, corrosion, catalysis, the operation of membranes, and so on. In this talk I will discuss some of our recent work in which we have been using classical and quantum molecular dynamics approaches as well as advanced electronic structure methods to better understand the structural and dynamical properties of water-solid interfaces. This will include work focused on understanding the formation of ice [1-3], confined water in nanocapillaries [4], and water diffusion and friction [5-7].

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Atomic-scale diffusion and friction on a topological insulator surface: H₂O on Bi₂Te₃(111)

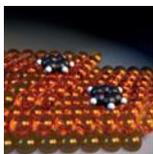
A Tamtögl¹, N Avidor², I Calvo-Almazán², P Townsend², D J Ward², M Bianchi³, P Hofmann³, J Ellis², W Allison², M Sacchi⁴ and W E Ernst¹

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Water is ubiquitous in everyday life, yet the simplest mechanisms controlling its molecular motion at a surface have to be revealed by experiment[1-3]. We have studied the diffusion of H₂O on the Bi₂Te₃(111) surface using helium-3 spin-echo spectroscopy[4], a reciprocal-space technique that places tracer and collective diffusion on the same footing. While it is known that water does not react with Bi₂Te₃[5], information about the diffusion of adsorbates on topological insulator surfaces is scarce. Notably, surface diffusion measurements are capable of providing new bench-mark data for energy landscapes on topological insulator surfaces with their peculiar electronic surface effects.

The diffusion of H₂O on in-situ cleaved single crystals of Bi₂Te₃(111) was studied by applying a water overpressure in the temperature range of 135 – 160 K. The molecular dynamics extracted from spin-echo measurements shows thermally activated diffusion with a jump mechanism and an activation energy of 36 meV. The dependence upon the momentum transfer is characteristic for jumps on a hexagonal lattice in accordance with the preferred adsorption site from density functional theory calculations. Furthermore, the measurements indicate that interactions between the individual water molecules play a significant role in the diffusion mechanism of water.

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Vicinal ZnO(10-14): surface structure and stability upon H₂O exposure

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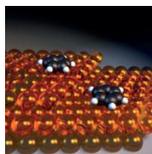
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Zinc oxide (ZnO) based catalysts are commonly used, often together with Cu nanoparticles, in important chemical reactions such as methanol synthesis ($\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$), low temperature water-gas shift ($\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$), and methanol steam reforming ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + 3\text{H}_2$) [1]. ZnO plays not only the role as nanoparticle support; instead it is much more actively involved in many reactions, with detailed reaction mechanisms under current discussion [2]. Determination of the stable ZnO surface structure and studies of how it interacts with the gases is essential for understanding these catalytic processes.

Of the commonly studied low index surfaces of ZnO, (0001), (000-1) and (10-10), the two former are polar, resulting in an instability of these surfaces. The stabilization of the Zn-terminated (0001) surface in UHV occurs through reconstruction, where the exact structure depends on the annealing temperature. The most commonly observed reconstruction consist of O-terminated triangular islands and pits [3,4], while the most stable has been suggested to have large areas faceted into the vicinal ZnO(10-14) surface. The proposed model for this surface, based on STM observations, consist of Zn-terminated (0001) terraces and O-terminated steps, resulting in a charge neutral, high step-density, vicinal surface [5]. The interaction between steps on vicinal surfaces plays a crucial role for the equilibrium structure, and very little is still known about the equilibrium structure of vicinal oxide surfaces. Here first studies performed on vicinal ZnO(10-14) single crystals will be presented. Using techniques such as low energy electron diffraction, surface x-ray diffraction (SXR), x-ray photoelectron spectroscopy (XPS) and scanning probe microscopy we have characterized the bare ZnO(10-14) surface. We have confirmed that the vicinal surface is stable in UHV and based on SXR measurements we will discuss its atomic structure.

Further, the stability of such a vicinal surface under gas exposures is of uttermost importance in catalytic applications. The interaction of water, which plays a key role in several of the reactions mentioned above, with vicinal ZnO surfaces has been theoretically shown to depend on the step density [6]. While experimental studies of the flat ZnO(0001) surface have shown that H₂ [3] and H₂O [7] exposures can cause restructuring of the surface, the effect of water exposure on vicinal ZnO is hitherto unexplored. Using SXR and XPS we have obtained both structural and chemical information of the water exposed ZnO(10-14) surface.

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A molecularly resolved study of palladium coordination to a self-assembled monolayer (SAM)

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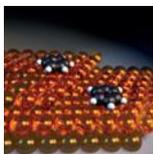
Metal-organic coordination in SAMs is of interest in areas as different as surface based metal organic frameworks and spintronics but its exploitation will depend on the level of control of coordination chemistry at interfaces. As part of our efforts to unravel the factors controlling metal-organic coordination at the liquid/solid interface, palladium complexation to monolayers functionalized with the tridentate ligand di-pyrazolyl pyridine (DPP) was studied.

SAMs of 4-(2,6-di(pyrazol-1-yl)pyridine-4-yl)benzoic acid (DPPBA) only and coadsorbed with 1-adamantanecarboxylic acid (AdCOOH) were investigated on a Au/mica substrate modified by an underpotential deposited Ag bilayer. The layers were characterised spectroscopically by X-ray photoelectron spectroscopy (XPS) and near edge X-ray absorption fine structure (NEFAXS) spectroscopy, and microscopically by ambient scanning tunnelling microscopy (STM).

Both molecules bind to the substrate through a bidentate coordination bonding of the carboxylic acid moiety. Pure DPPBA SAMs exhibit a distinct row structure where the DPP moieties are orientated upright and densely packed with an intrarow and interrow separation of about 4 Å and 10 Å, respectively. Depending on the DPPBA/AdCOOH ratio the structure in mixed layers varies from short rows to a random distribution of DPPBA.

Exposure of the SAMs to a solution of [Pd(MeCN)₄](BF₄)₂ in acetonitrile gives rise to distinct changes in the SAMs which are pronouncedly dependent on the structural details of the layers. For the mixed SAMs characteristic height changes indicative of Pd coordination are seen in the STM images. These are not observed for the pure DPPBA SAM where molecules are densely packed. The STM results are corroborated by XPS where the presence of ionic Pd is only seen for the mixed layer.

The experiments demonstrate that steric requirements are a crucial aspect in the ability of the DPP moiety to coordinate metals. Also, more generally, imaging complexation in SAMs at the single molecule level is an important step towards a better understanding of metal-organic coordination at the liquid-solid interface.



Interdisciplinary Surface Science Conference (ISSC-21)

Session 9

(invited) *In situ* x-ray scattering studies of the atomic structure/charge distribution at the electrochemical interface

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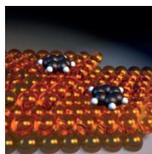
Electrochemical interfaces play a crucial role in many systems used for clean energy production, conversion and storage as well as for material processing. The structure of the electrode and electrolyte, as well as stability effects and charge transfer mechanism are the underlying properties and processes which can crucially affect reactivity and performance of electrochemical applications.

In-situ surface x-ray diffraction has enabled an atomic/molecular-level understanding of the interface under reactive conditions, including its potential and time dependence, to be developed. While information about the atomic structure of the electrode surface in electrochemical *in-situ* cells has been widely investigated, insight into the charge distribution and the structure of the electrolyte at the interface is still lacking. Advances in these directions offer possibilities in elucidating atomic scale models of the electrochemical interface and thus will help to establish structure-stability-reactivity relationships.

A fundamental understanding of the nature of the charge transfer, especially the influence of the applied potential and the screening by the electrolyte, is a major goal in electrochemistry. However, *in-situ* studies of the chemical bonding are rather difficult due to the presence of the electrolyte, as standard characterisation techniques which are mostly UHV based cannot be applied. Thus combining x-ray spectroscopy and x-ray diffraction to gain site specific information about the charge distribution at buried interfaces is a promising tool.

Electrochemical processes are governed by the properties of ions in solution and at the interface. Obtaining information about structural reordering in the electrolyte, e.g. as a function of potential or electrolyte composition, is crucial for system which do not consist of aqueous, oxygen-free electrolytes. Again probing the structure of the electrolyte is difficult as scanning probe techniques cannot be employed and as ordering effects are not as pronounced as in solid materials thus the signal often governed by the signal of the adjacent electrode.

Examples of how the use of surface x-ray scattering techniques can help to characterise electrochemical interfaces *in-situ* in order to link, structure, reactivity and stability will be presented.



Model Cu/Au catalytic surfaces for coupled dehydrogenation/hydrogenation reactions

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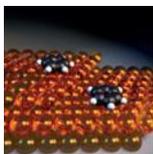
Alumina supported Au can operate as a catalyst for furfural hydrogenation to furfuryl alcohol with a very high selectivity [1], however the high activation barrier for H₂ dissociative adsorption limits the rate of hydrogenation. A way to supply reactive (atomic) hydrogen to the system is to generate such species *in situ* via a parallel dehydrogenation reaction [2]. Hydrogen-free hydrogenation of nitrobenzene coupled with 2-butanol dehydrogenation over supported Cu has been successfully demonstrated [3]. These studies suggest the possibility of using supported bimetallic Cu/Au systems as catalysts for coupled dehydrogenation/hydrogenation reactions.

Herein, we investigate a prototype 2-butanol/furfural system with the focus being on the characterisation of the adsorption behaviour of each molecular species as a function of the surface morphology and composition of the Cu/Au system.

Scanning tunnelling microscopy (STM) studies show that 2D Cu particles nucleate at specific places within the Au(111) herringbone reconstruction elbows [4]. In the high coverage regime, ordered Cu-Au surface alloys are characterised by regular successions of distinct Cu and Au rows.

The adsorption of 2-butanol and furfural has been investigated with temperature programmed desorption (TPD), scanning tunnelling microscopy (STM) and high resolution electron energy loss spectroscopy (HREELS) on Cu(111), Au(111) and on Cu/Au(111) surfaces, at different Cu loadings. We discuss how the reactivity of the adsorbed species depends on the surface morphology and composition.

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Interdisciplinary Surface Science Conference (ISSC-21)

STM and AFM investigation of bi-isonicotinic acid assemblies on Au(111) using CO terminated tips

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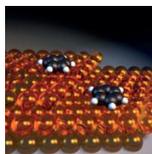
¹University of Nottingham, UK, ²University of Osnabrück, Germany

The possibility of using dye complexes adsorbed on a semiconductor surface to split water molecules is a fascinating area which holds particular promise for novel applications [1][2]. Common complexes used in water splitting also function as a catalyst in the reaction, and so the physical chemistry underpinning the splitting process is dynamically intricate. The complexes themselves, and their component ligands, have been the focus of a great deal of study with regard to the charge transfer and structural properties. One of these ligands is the bi-isonicotinic acid molecule [3]. This exists in both a cis and trans configuration although, to date, its precise bonding structure when adsorbed has not been elucidated. We carried out a series of scanning probe measurements, combining both STM and ultrahigh resolution dynamic force microscopy (with a CO-terminated tip apex) to determine, with single chemical bond resolution, the combined structural and electronic properties of bi-isonicotinic acid molecules on the Au(111) surface.

Bi-isonicotinic acid forms large, well-ordered 2D assemblies on Au(111) which, due to their structural integrity and robustness, are particularly amenable to imaging using dynamic force microscopy with the type of small tip-sample separations required for imaging of the type pioneered by Gross et al. [4]

STM and AFM experiments were conducted at 4K with a CO-terminated tip. It was observed that the molecules existed primarily in a trans phase and aligned in a way that suggested hydrogen bonding within the entire assembly. Of particular interest was the observation of carboxylic-to-carboxylic alignment, alongside the substantially more common carboxylic acid-to-nitrogen based molecular alignment. AFM simulations were also conducted based on the analytic potential model introduced by Hapala et al [5]. They yielded remarkable agreement with the experimental observations and thus provided important insights into the imaging mechanism.

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Physics with single molecules

W Schwarzacher¹, R Brooke¹, A Vezzoli², S Higgins² and R Nichols²

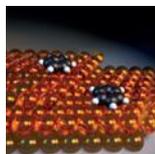
¹University of Bristol, UK, ²University of Liverpool, UK

Single molecule devices are of interest for what they reveal about fundamental aspects of electron transport and the interactions of molecules with surfaces. They represent the ultimate level of miniaturization in molecular electronics and are also of potential interest in sensor applications. We use a scanning tunnelling microscope to make and characterize junctions bridged by a single molecule at room temperature. By taking advantage of electrochemistry, we can not only keep the junctions free of oxide and other unwanted contaminants, but also gate them so that they form single molecule transistors. Most work in this field uses passive gold electrodes, but a whole range of interesting effects become accessible when the electrodes are semiconducting or magnetic.

We have created a single-molecule transistor consisting of a 4,4'-bipyridine molecule with Ni electrodes, the latter aligned magnetically via an applied field [1]. The interest in this device lies in the exceptional sensitivity to the gating field (greater than for a similar device with Au electrodes) and in the fact that calculations suggest that the current through the device is highly spin-polarized. When the central molecule is replaced with 4,4'-vinylenedipyridine, unexpected new behavior is introduced. Firstly, the measured conductance becomes extremely sensitive to the electrolyte pH as well as the gating potential, so that we have created a unique class of single-molecule 3-terminal sensor, and secondly, we observe unexpected fluctuations in the conductance during a single junction-stretching experiment.

The replacement of one of the metal electrodes by a compound semiconductor presents further opportunities. We have shown recently that single-molecule transport effects can be seen in rectifying GaAs-molecule-metal junctions, and that the choice of molecule also strongly affects the rectification ratio.

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Session 10

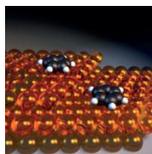
(invited) **Surface and interface chemistry in next generation solar cells**

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University of Manchester, UK

There is an urgent requirement to make better use of the 120,000 TW of power provided by the Sun, by using it to generate power, or by using its energy directly to make useful chemical feedstocks. Around the world, there is an explosion of research activity in new systems for harvesting solar energy, including solar cells based organometal halide perovskites, and colloidal quantum dots (CQDs). Issues of key importance are the interfacial energy level line-up of the cell components, and the influence of the surface properties of these materials on charge separation in the devices. Indeed, the deployment of both CQDs and perovskites in solar cells is currently limited by their high reactivity and rate of surface oxidation. Thus a key problem for surface scientists is to develop an understanding of the interface chemistry of solar heterojunctions in order to develop passivation strategies. I show how a combination of techniques including synchrotron and laser spectroscopies together with electron microscopy and near-ambient pressure X-ray photoelectron spectroscopy may be used to investigate the surface chemical composition as a function of depth [1,2], surface ageing [1,3-6] and passivation [1], and the energy level-line-up and charge dynamics in novel solar cell heterojunctions [7-9].

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Organic photovoltaics and electro spray deposition: in-situ growth of thin-films probed with soft x-ray spectroscopy

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Organic photovoltaic (OPV) devices [1] have the potential to provide low cost solar cells that can be made onto flexible substrates using abundant materials. At the heart of these devices is an interface between regions of electron acceptor and donor molecules. An exciton, created by a photon interacting with the donor molecule, diffuses to this interface where the electron and hole separate and diffuse to the electrodes of the device allowing electrical work to be done. Understanding these devices is fundamentally a surface science problem - gaining an insight into the bonding, morphology and charge transfer between the interfaces involved is important to fully understanding the operation of the devices thus aiding their future development and optimisation. Soft x-ray synchrotron techniques such as X-ray photoemission spectroscopy, X-ray absorption spectroscopy and resonant photoemission spectroscopy are now routinely used to probe the bonding and charge transfer between molecules and surfaces. Applying these analytical techniques to the OPV molecular systems however require the in-situ growth of thin films in UHV environments. In this case, using the traditional method of sublimation/evaporation is not possible as the molecules are too large and fragile.

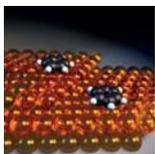
Electrospray deposition [2] is an emerging technique in the surface science community that provides a solution to this problem. By applying a large voltage (~2kV) to a dilute solution flowing through a narrow capillary tube, electro spray ionisation [3] causes the liquid to form a jet that explodes into a stream of small droplets that can be fired into a differentially pumped vacuum system. Due to a combination of the electrical charge on the drops and solvent evaporation, the drops repeatedly break-up into ever-smaller drops until all that remains is a beam of molecular ions that can be soft landed onto a surface. This method for growing thin films in vacuum has previously been applied to a range of molecules - including dye molecules, polymers, proteins, molecular magnets and nanoparticles - that cannot be deposited in UHV using any other technique.

The molecules studied here are the electron acceptor PCBM (Phenyl-C61-butyric acid methyl ester) - a functionalised fullerene - and P3HT (Poly(3-hexylthiophene)) - a conductive polymer and electron donor. These molecules and blends of the two were deposited in vacuum using electro spray. We present experiments exploring the core level shifts of the molecules and the charge transfer between them and the Au(111) surface using x-ray absorption and photoemission spectroscopy. We go on to make comparison to the competing technology of organic dye sensitised solar cells (DSSCs). Traditionally DSSCs have used organometallic dyes (commonly ruthenium based) but recently purely organic alternatives have been developed. We present photoemission data of one such molecule ("SQ2" by Soleronix) again deposited by electro spray. Finally, we discuss the suitability of electro spray to produce real molecular devices.

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Surface chemistry of biomimetic $\text{In}_{2.77}\text{S}_4$ and its effects in photocatalytic hydrogen production

R Ahumada-Lazo¹, P C J Clark¹, H Radtke¹, M A Leontiadou¹, W R Flavell¹, K Handrup², O A Carrasco-Jaim³, C Gomez-Solis³ and L M Torrez-Martinez³

¹University of Manchester, UK, ²Maxlab, Sweden, ³Universidad Autónoma de Nuevo León, Mexico

Indium sulfide is a typical III–VI group chalcogenide which has a number of phases. The most stable structural form is the $\beta\text{-In}_2\text{S}_3$ phase (typically sulfur-deficient $\text{In}_{2.77}\text{S}_4$) with a cubic or tetragonal structure. This compound has been thoroughly investigated as a nontoxic substitute for CdS in $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based solar cells and a visible-light photocatalyst due to its stable chemical composition, high photoconductivity and suitable band gap (2.0 – 2.2 eV) [1]. As a way to further improve solar energy harvest and conversion, *Mimosa pudica* leaves (remarkably sensitive to sun light) were selected as a template for the controlled synthesis of biomimetic $\text{In}_{2.77}\text{S}_4$ using a hydrothermal process. Optimally-prepared biomimetic $\text{In}_{2.77}\text{S}_4$ showed an increment by a factor of three in the hydrogen production rate *via* photocatalytic water splitting compared with the control sample prepared without template [2].

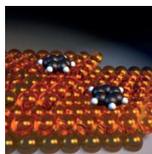
In this work the surface characterization of the control and biomimetic materials is carried out by X-ray photoelectron spectroscopy (XPS) using synchrotron radiation in order to compare their chemical compositions and understand the effects of surface species on the photocatalytic activity. Overall significant changes in surface chemistry between the control and templated samples were found. A very large amount of residual C- and O-containing organic matter is present at the surface of the templated material. Additionally, iron oxide (Fe_2O_3), and a number of products of the oxidation of $\text{In}_{2.77}\text{S}_4$ such as surface sulfur attached to oxygen ($-\text{SO}_2$), $\text{In}_2(\text{SO}_3)_3$ and $\text{In}_2(\text{SO}_4)_3$, were detected in the biomimetic material, but absent in the control sample. The conduction band of Fe_2O_3 (2.0 – 2.2 eV) is located under the reduction potential of water and therefore is not active for hydrogen production on its own. However, its valence band is well-positioned for water oxidation and its involvement in the oxygen evolution half-reaction has been reported. In addition, the partially-oxidized sulfur species ($-\text{SO}_2$ and SO_3^{2-}) are easily oxidizable and can act as sacrificial electron donors promoting the hydrogen evolution reaction by proton reduction at the conduction band of indium sulfide [3].

Besides chemical differences in the surface, the addition of the template also caused physical changes. A decrease in the sizes of the microcrystallites and of ‘marigold-like’ microspheres made up from them (characteristic of $\beta\text{-In}_{2.77}\text{S}_4$ superstructures) with a corresponding increase in surface area was observed. In addition, a decrease in the average pore diameter, but an increase in their density was observed in templated samples. We show that the optimum photocatalytic activity in H_2 production is achieved through a balance between increased surface area and contamination of the surface with organic material. Transient photocurrent spectroscopy shows evidence of charge separation and long-lived surface holes in the case of the templated material. This is discussed in the context of the surface composition and the enhanced catalytic activity.

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RIXS and ultra-fast molecule-surface charge transfer dynamics

J O'Shea¹, K Handrup² and R Temperton¹

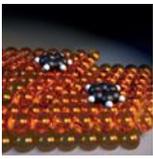
¹University of Nottingham, UK, ²Lund University, Sweden

In devices such as dye-sensitised solar cells, the dynamics of charge transfer at the electron injection interface – from the molecule into the semiconductor substrate – play a key role and are typically very fast. The charge transfer dynamics of the molecule biisonicotinic acid adsorbed on a titanium dioxide surface was found to occur on the low femtosecond timescale – using a core-hole clock implementation of resonant photoemission (RPES) [1]. This process relies on the competing channels of core-hole decay and ultra-fast charge transfer to the surface. An electron emitted by a core-hole decay process in which the originally excited core-electron is a direct participant is easily distinguishable from the electronic debris by its kinetic energy and evinces electron localisation in the excited molecular orbital on the timescale of the core-hole lifetime. It has long been proposed that the photons emitted during radiative core-hole decay should be equally informative, allowing femtosecond charge transfer to be probed in more realistic environments due to the large escape depth of the photons in what would be resonant inelastic x-ray scattering (RIXS) compared to the electrons of resonant photoemission (RPES).

In the event that the originally excited core-electron is a direct participant in the decay process, radiative decay will give rise to what is essentially an elastically scattered soft x-ray photon, perhaps modified by any ultra-fast processes within the core-excited molecule. Our early RIXS core-hole clock results of biisonicotinic acid adsorbed on a rutile TiO₂(110) surface were consistent with this simple idea that the abundance of elastically scattered photons would be diminished in the presence of the charge transfer out of specific molecular orbitals known to occur in this system on the order of a few femtoseconds [2]. Moreover, the other photons emitted in the experiment – the inelastic scattering – provide valuable insight character of the occupied molecular orbitals and their relationship to each other. This is most evident when the RIXS is mapped over all the highest occupied molecular orbitals as a function of core-excitation into all the lowest unoccupied molecular orbitals.

Our recent experiments performed at the SOLEIL synchrotron have focussed on obtaining two-dimensional RIXS maps of biisonicotinic acid monolayers and multilayers on the TiO₂(110) surface and of the crystalline molecule. The high energy resolution reveals a complex vibrational structure around the LUMO resonances close to the elastic peak and how this is modified by coupling of the molecule to the oxide surface and the resulting ultra-fast charge transfer of electrons from those orbitals that overlap energetically with the conduction band edge. RIXS maps have also been measured for the simpler molecule isonicotinic acid and the more complex dye molecule N3 – of which biisonicotinic acid is the binding ligand – resulting in an understanding of how a core-hole clock implementation of RIXS can be applied to probe ultra-fast charge transfer dynamics in real dye-sensitised solar cell interfaces.

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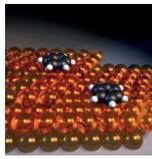
Interdisciplinary Surface Science Conference (ISSC-21)

C_8H_8 at Cu(111) - structure and dynamics

N Avidor¹, J A Lau¹, I Calvo-Almazan¹, P S M Townsend¹, D J Ward¹, J Ellis¹, W Allison¹ and B J Hinch²

¹University of Cambridge, UK, ²Rutgers University, USA

Recent developments in scattering experiments have allowed motion on a molecular scale to be explored in the pico- to nano- second timescales, using ^3He Spin Echo spectroscopy. We have applied this method to study the mobility of 1,3,5,7-cyclooctatetraene (COT, C_8H_8) on Cu(111). We have measured the dynamics both at low coverage (isolated motion) and medium coverage, at temperatures between 200K-450K. The diffusive translational motion of COT proceeds by jump diffusion over a bravais-lattice with a short residence time of 2 picosecond and a low energy barrier of ~ 30 meV. In addition, we see evidence for another fast diffusion mechanism, and an inter-molecular interactions between the adsorbates. We have also studied the structure of COT as function of temperature, using Helium diffraction experiments. At 205K we measure a diffraction pattern of $7\sqrt{3} \times 7\sqrt{3} R30^\circ$ with various missing peaks. We assign the diffraction pattern to a hexagonal hi-order commensurate ad-layer, where the COT takes a flat benzene-like conformation. We have observed commensurate-incommensurate transition which will also briefly discussed.



Thursday 13 April

Session 11

(invited) **Surprises at the surfaces of 3D topological insulators**

M Golden

University of Amsterdam, Netherlands

The prediction and observation of the quantum spin Hall effect in 2D topological insulators was one of the hallmark physics discoveries of the last decade. Three dimensional topological insulators have also come of age, and possess 2D, topologically protected surface states which are highly accessible to angle resolved photoemission (ARPES). In this talk, I'll give an overview of recent research in Amsterdam on these new flagship quantum matter systems.

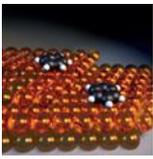
After presenting the current status as regard the growth and investigation of single crystals of bulk-insulating 3D TI's, I will show how the combination of band bending and photon-induced effects can be used as a micrometric patterning tool of the topological surface electronic structure of the system. I'll also discuss our most recent work on Dirac semimetals, showing how a potential 2D Dirac semimetal could be disguised in the bulk of a 3D crystal.

Fabrication and characterisation of buried dopant nanostructures in silicon

N Curson¹, A Kölker¹, T Stock¹, S Schofield¹, T Lim¹, H Solanki¹, G Aeppli², G Gramse³, E Brinciotti⁴ and F Kienberger⁴

¹London Centre for Nanotechnology, UCL, UK, ³ETH and Paul Scherrer Institut, Switzerland, ⁴Johannes Kepler University, Austria, ⁵Keysight Technologies, Austria

For decades, the development of novel semiconductor devices have benefitted from knowledge gained from scanning tunnelling microscopy (STM) and other surface science techniques. However, in recent years STM has become a lithography tool in its own right, principally through its ability to pattern a single atomic layer of hydrogen on silicon (the hydrogen resist), in ultra-high vacuum. The patterned resist is subsequently exposed to a precursor gas (phosphine), allowing local doping of the silicon in the patterned regions of the resist. Encapsulation of the patterned layer with a few monolayers of silicon completes the device. Here we present the fabrication of nanostructures in dimensions ranging from 3 to 0, and describe what we have learnt about the properties of such devices. In particular we discuss the characterisation of these devices using the technique of scanning microwave microscopy (SMM). The SMM measurements, which are completely non-destructive and sensitive to as few as 4200 P atoms 15 nm below a silicon surface, yield electrical and geometric properties in agreement with those obtained from electrical transport and secondary ion mass spectroscopy (SIMS) for un-patterned phosphorus delta-layers containing $\sim 10E+13$ P atoms. The lateral imaging resolution was 55 ± 4 nm; however, finite element modeling (FEM) simulations indicate that the resolution increases when structures are located closer below the surface. Additionally it can be substantially improved using further optimized tips and microwave gradient detection. Our results suggest that SMM is the ideal diagnostic for use in the development of fabrication processes for surface code quantum computers.



Interdisciplinary Surface Science Conference (ISSC-21)

Spin polarisation and domain formation at the Si(110) "16 x 2" surface

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¹University of Manchester, UK, ²CNR, Italy, ³Cockcroft Institute, UK

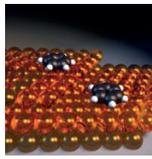
Silicon nanowires are of particular interest to the spintronics community as spin transport in them measurements have shown longer spin lifetimes and diffusion lengths relative to bulk materials [1, 2]. Spin and chirality are interrelated as electron scattering experiments have shown that randomly oriented chiral molecules cause the incoming electron beam to become spin-polarised [3].

Thus the Si(110) "16x2" reconstruction is interesting from the point of view of spintronics and semiconductor nanowires. Firstly, it is a low-index surface with a reconstruction that is 2D chiral and that can be made to exist as a single enantiomer over areas of millimetres squared [4]. Secondly, the reconstruction consists of channels and has been used as a template to form nanowires [5]. Therefore, the interaction of heavy element nanowires such as gold may have interesting spin properties due to the fact that the underlying substrate is chiral.

Experimental LEED and STM studies as well as models of the "16x2" reconstruction are presented, indicating that the enantiomer that forms is a result of the direction of the monoatomic vicinal steps present at high temperature (above 770 C). This is in contrast to previous proposals [4] that suggested electromigration drives the formation of large scale enantiomerically pure domains. We show that the direction of the monoatomic steps is influenced by the direction of off-polish from the (110) surface because it results in either the (15 17 1) or (17 15 1) surfaces. This allows for selection of the enantiomer and channel directions before the Si(110) wafer is placed into vacuum.

Spin-resolved photoemission conducted at the Elettra APE-LE beamline is presented, which shows that as-formed Si(110) "16x2" reconstruction does not produce spin-polarised electrons above a statistical error of 2%. However, preliminary work at the beamline showed an out-of-plane polarisation of -6% for the gold nanowires on Si(110) "16x2" reconstruction.

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Session 12

(invited) **Moiré minibands in graphene-hBN heterostructures**

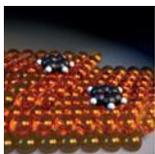
V I Fal'ko

University of Manchester, UK

Encapsulation in hBN enables one to achieve a micron-length collision-less propagation of electrons in graphene, whereas technology of making low-resistance edge-contacts with normal and superconducting opens ways to manufacture ballistic electronic devices: electronic lenses and focusing beam splitters [1], as well as superconducting proximity effect transistors and interferometers [2]. Moreover, electrostatic gating of hBN-G-hBN structures permits to open a large and spatially modulated band gap in bilayer graphene [3], hence offering new routes towards creating quantum wires, dots, and their various circuits.

When graphene lattice is aligned with the hBN lattice, a long-wavelength periodic moiré pattern forms due to a weak incommensurability of the two lattice structures, leading to a long-range superlattice affecting properties of electrons in graphene. We shall discuss the effects produced by such moiré superlattice on electrons at low and strong magnetic field. At weak fields, electron states form minibands with peculiar properties [4-6], and also lead to the low-energy umklapp scattering of electron from acoustic phonons. At high magnetic fields, electron spectrum transforms into a fractal sequence of Brown-Zak magnetic minibands, known under the nickname of Hofstadter butterfly [5-8]. Experimentally available magnetic fields are enough to provide flux φ through the moiré superlattice cell comparable to the magnetic flux quantum φ_0 and to observe the manifestation of magnetic minibands in magneto-transport and magneto-capacitance measurements [5,6]. As a result, a single device can offer a multiplicity of two-dimensional electron systems, realised at rational flux values $\varphi = \varphi_0, \varphi_0/2, 2\varphi_0/3$, etc., each with its own intricate topological properties, including quantum Hall effect physics related to the effective Landau levels emerging from these magnetic minibands at the nearby range of magnetic fields [6].

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Interdisciplinary Surface Science Conference (ISSC-21)

Optical and electron emission from the low index surfaces of diamond and boron nitride

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The surface properties of superhard, wide-gap materials such as diamond and boron nitride can influence their many applications from gems and abrasives to electronic, photonic and quantum devices. For example, the electronic properties can be significantly different for differently prepared surfaces, as strikingly demonstrated for the low index faces of diamond where the electron affinity can be changed from negative to positive by changing the surface termination. High quality synthetic material can be produced and their surfaces can be prepared by chemical, plasma and thermal processing. Phase changes to the planar allotropes (graphene/graphite and hexagonal BN) can also be induced in diamond and cubic boron nitride during processing and use. Engineering surfaces for various applications thus requires a knowledge of how the surface structure and composition changes during processing and how these changes influence properties such as electrical conductivity, spin and light emission. Vacuum annealing and in-situ plasma exposure have been applied to produce low-index faces terminated with oxygen and hydrogen in an experimental system where the processing is carried out alongside and also during characterization by electron diffraction, electron spectroscopy and optical spectroscopy. As an example, real time monitoring of the high temperature annealing of variously-terminated surfaces by photoelectron spectroscopy and Raman spectroscopy has revealed each stage from room temperature to the adsorbate-free, reconstructed surface at high temperature. The onset temperature for oxygen and hydrogen desorption has been determined for each surface and distinct temperature regimes have been discovered with different desorption rates, surface conductivity, band bending and surface states.

Combined STM and DFM study of molecules on insulating CaF₁ and CaF₂ thin films

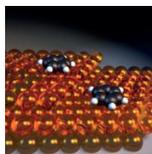
P Rahe¹ and P J Moriarty²

¹Universität Osnabrück, Germany, ²University of Nottingham, UK

Thin insulating films on surfaces of conducting or semiconducting materials play a key role in the study of single atoms and molecules. In particular, the reduced interaction with an underlying conductor, which usually causes strong modifications of the adsorbate electronic structure, allows atomic or molecular properties to be studied in an electronically decoupled environment [1], and can enable functionality based on charge state modification [2] as used, for example, in molecular switches [3]. Although the NaCl-on-metal system has been investigated extensively in this context, to date a similar thin layer system for single molecule decoupling from semiconductor substrates has not been exploited.

Here, we introduce an important analogue to the NaCl-on-metal prototype: CaF₂ films grown on the Si(111) surface [4,5]. The morphology of the CaF₁/Si(111) interface layer, in addition to that of CaF₂ multilayers grown on CaF₁/Si(111), has been investigated in a combined high-resolution scanning tunnelling microscopy (STM) and dynamic force microscopy (DFM) study at low temperatures, where we focus on microscopic details – such as the film orientation and defects – important in the context of molecular adsorption. Subsequently, the interaction between a planar molecule and the insulator-on-semiconductor substrate was investigated by mapping the molecular structures that result after the deposition of PTCDA molecules. Besides clear differences in the orbital structure of PTCDA adsorbed on Si(111) and on insulating layers, we find that the adsorption on the CaF₁ interface layer leads to different molecular arrangements than are present on the CaF₂ multilayer areas.

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Graphene-based nanomaterials: Synthesis, chemical / physical properties, and applications

J X Zhao, X Wu and M Wu

University of North Dakota, USA

A few graphene-based nanomaterials have been developed in our research group. In this presentation, the methods of making these nanomaterials will be covered. For example, a facile bottom-up method for the synthesis of graphene quantum dots (GQDs) will be discussed using a one-step pyrolysis of a natural amino acid, L-glutamic acid, with the assistance of a simple heating mantle device. The developed graphene-based nanomaterials have demonstrated advanced chemical and physical properties. This presentation will mainly introduce their optical properties. For instance, GQDs showed strong blue, green and red luminescence under the irradiation of ultra-violet, blue and green light, respectively. In addition, the GQDs emitted near-infrared (NIR) fluorescence in the range of 800-850 nm with the excitation-dependent manner. This NIR fluorescence has a large Stokes shift of 455 nm, providing significant advantage for sensitive determination and imaging of biological targets. The fluorescence properties of the GQDs, such as quantum yields, fluorescence life time, and photostability, were measured and the fluorescence quantum yield was as high as 54.5 %. The morphology and composites of various graphene-based nanomaterials were characterized using TEM, SEM, EDS, and FT-IR. The feasibility of using these nanomaterials was investigated in biological field.

Imaging and force based atomic manipulation of Sn chains on Si(100) by NC-AFM

A Sweetman, I Lekkas and P Moriarty

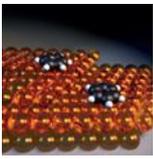
University of Nottingham, UK

The self-assembly of atomic chains on the Si(100) surface has been investigated for multiple species, including group III and group IV metals. These chains grow in a direction perpendicular to underlying Si dimer rows and are composed of metal dimers oriented parallel to Si substrate dimers. The atomic scale imaging of these chains and their structural composition has been previously studied extensively via STM and NC-AFM [1-2]

In this work we discuss the imaging and manipulation of Sn chains on the Si(100) surface at low temperature via the use of non-contact atomic force microscopy (NC-AFM) in the qPlus configuration. In particular, we show how the atomic scale buckling configuration of the Sn dimers may be controllably modified by mechanochemical means due to the close approach of the tip at 5K [3], using a similar mechanism to that described previously for the intrinsic silicon dimers of the Si(100) substrate [4].

Surprisingly, we find that manipulation of the Sn ad-dimers has no observable influence on the buckling of the underlying Si substrate, despite their covalent coupling, and also discuss spontaneous motion of the dimers observed at intermediate temperatures (78K) and the relationship of this motion to previously estimated energy barriers for Sn dimer flip-flop motion.

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Interdisciplinary Surface Science Conference (ISSC-21)

Posters

P.01 Uncovering the mechanisms of island formation from the gap and capture zone distributions in one dimension

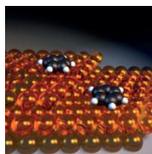
H Krcelic, P Mulheran, M Grinfeld

University of Strathclyde, UK

Understanding of the mechanisms of island nucleation and growth during thin film deposition from the observed statistical properties of the island patterns is an important problem. To be able to predict and control the evolution of nanostructures, we need a systematic way to deduce the laws for nucleation, such as the critical island size, whether the islands are mobile, etc. One established approach is to perform kinetic Monte Carlo (kMC) simulations with pre-defined rules, and compare the resulting island patterns to select the set of rules that give the best fit for the data. However, this is not entirely satisfactory. In this work we explore another possibility, that is to solve the inverse problem using numerical techniques designed for this task.

We focus on one-dimensional substrates that mimic the behaviour of monomers diffusing along a step edge. We generate trial data from kMC simulations, in which monomers are randomly deposited onto a one-dimensional substrate where they diffuse and undergo reversible attachment to islands or to other monomers to nucleate point islands.

Mathematically, the nucleation process can be translated to the fragmentation of a line into inter - island gaps. We model this using Distributional Fixed Point Equations which lead to integral equations for gap and capture zone distributions. These equations belong to the broad class of Fredholm integral equations of the first kind, and they incorporate information about the critical island size and the nucleation mechanism (monomer diffusion or impingement driven nucleation). The inverse of these equations is ill-posed and requires regularisation techniques. The obtained solutions reflect well the different critical island sizes and fit fairly well within the bounds imposed by diffusion-limited or impingement-limited nucleation. However, they are susceptible to a high level of uncertainty due to the ill-posed nature of the inverse problem and the noise present in the kMC data, so further refinement of the regularisation is under way.



P.02 Structure of the anatase TiO₂ (101) and H₂O(l) interface

I Nadeem^{1,4}, X Torrelles², H Hussain³, A Wilson⁴, G Cabailh⁵, O Bikondo⁶, J Zegenhagen⁴ and G Thornton¹

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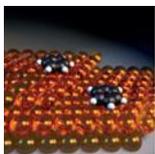
Light harvesting, metal oxide semi-conductors have been widely utilised as photovoltaic materials for H₂ fuel generation. Naturally, oxide based materials are favoured due to their stability against oxidation. Titanium dioxide (TiO₂) is a widely utilised photovoltaic material for generating H₂ fuel. It is a low cost, highly photo-stable and non-toxic material that displays high catalytic efficiency. Three polymorphs of TiO₂ exist in nature - rutile, anatase and brookite - with research extending from applied studies of engineering materials to fundamental work on model surfaces. Anatase and rutile are amongst the most studied TiO₂ polymorphs for photovoltaic H₂ fuel generation where the former is considered more photo-active. Anatase TiO₂ (101), the lowest energy face of anatase, has been the subject of numerous studies pertaining to its interface with H₂O_(g), however, experimental research into the interface of the surface with H₂O_(l) has thus far been lacking. The interface of anatase TiO₂ (101) and H₂O_(l) is of great importance to understand the behaviour of this surface under more technologically pertinent conditions. We present a surface x-ray diffraction (SXR) insight into the surface structure of anatase TiO₂ (101) in contact with H₂O_(l). An anatase TiO₂ (101) crystal has been prepared in UHV and characterised (in UHV) with scanning tunnelling microscopy (STM), low energy electron diffraction (LEED), x-ray photoelectron spectroscopy (XPS) and SXR. Subsequently, in an N₂ environment, SXR measurements are taken whilst the surface is in contact with a droplet of ultra-pure H₂O (resistivity: 18.2 MΩ cm). Our results indicate that the surface maintains mixed associatively adsorbed H₂O and dissociatively adsorbed terminal OH (OH_t) and bridging OH (OH_{br}) groups. Additionally, a hydration layer exists above the mixed H₂O/OH surface over-layer.

P.03 Scanning tunneling microscopy investigation on the bridging hydroxyl bound excess electrons of rutile TiO₂(110)

M Allan, C Ming Yim, C Lun Pang and G Thornton

University College London, UK

Here we present a scanning tunneling microscopy (STM) study on the temperature dependence of the distribution of the bridging hydroxyl (OH_b) associating excess electrons on rutile TiO₂(110). By imaging simultaneously individual OH_bs on TiO₂(110) in both empty- and filled- state at low temperature ranging between 7 and 78 K, we observed the distribution of the excess electrons surrounding a single OH_b to retain a symmetric, four-lobe structure at 7 K as that observed at 78 K. This indicates that unlike the oxygen vacancy (Ob-vac) bound excess electrons whose hopping between Ti sites surrounding an Ob-vac is quenched at low temperature (7 K) [C. Yim et. al, Phys. Rev. Lett. 117, 116402], the OH_b associating excess electrons can still hop between Ti sites surrounding the OH_b species at 7 K, hence suggestive of OH_bs being weaker as charge traps than Ob-vacs. In addition, by sequentially removing the capping H of the OH_b species with tip pulses and monitoring the corresponding change(s) in the filled-state STM, we found that every capping H removal is accompanied by disappearance of some STM contrast surrounding the removed H, hence confirming the direct correlation between OH_b and their excess electrons.



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P.04 Density functional theory study of benzene adsorption on Fe surfaces

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Aromatic adsorption on metal surfaces plays a key role in many fields including heterogeneous catalysis, electrochemical devices, photovoltaics, corrosion protection and chemical sensing. As the simplest aromatic molecule, benzene has been widely studied on a variety of metal surfaces both computationally and experimentally. [1-3] However, one metal surface which has received very little attention in this context is iron. Experimental UHV adsorption studies carried out on iron surfaces are complicated by the metal's reactivity and strong tendency to passivate, which result in significant difficulty obtaining a high purity metal surface. Still, iron is deserving of study as it is the major component of steel and catalyses important industrial reactions such as the Fischer-Tropsch and Haber processes. A computational study of the surface chemistry of benzene on iron will provide novel insight on this system as well as a level of detail which would not be afforded using experimental techniques.

We have carried out a density functional theory (DFT) study of benzene adsorption on the three most stable surface facets of bcc iron, including flat ({110}), kinked ({100}) and stepped ({211}) surfaces. All identified stable adsorption sites are presented and the most energetically favourable sites are compared across the three surfaces. To support the energetic and geometric results of our study, charge density differences, residual spin densities, density of states (DOS) and work function changes have also been calculated and analysed. Finally, we have studied the effect of van der Waals corrected DFT on binding site energetics and geometries using the Tkatchenko-Scheffler (TS) correction. [4] Such corrections have been shown to provide results in better agreement with experiment for aromatic adsorption on certain metal surfaces. [1]

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[3] Netzer, F. P. Langmuir 1991, 7(11), 2544-2547

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P.05 Nucleation and Growth of magic number $(C_{70})_m(Au)_n$ complexes on Au (111) surface at low temperature

Y Wang and M Fard

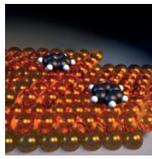
University of Birmingham, UK

Magic number $(C_{60})_m(Au)_n$ Complexes have been intensively investigated in our lab [1]. These complexes are found to have a single atomic layer gold island which is wrapped by a self-selected number of C_{60} molecules. The smallest structure, $(C_{60})_7(Au)_{19}$, has a preferred orientation on the sample surface and is stable up to 400K. C_{70} molecules and gold atoms are also expected to form the similar structures. Magic number clusters with other molecules are expected to form on Au(111). Here we extend our work by the examining the form of $(C_{70})_m(Au)_n$ clusters.

C_{70} molecules and gold atoms were in-situ deposited onto the Au(111) surface, simultaneously or sequentially at a sample temperature of 110K. Omicron VT STM are used to scan the Au(111) surface from low temperature to room temperature in order to learn how and where C_{70} -Au clusters are formed and how they ripen with temperature.

We find that C_{70} molecules and gold atoms can form magic number complexes at the elbow sites. By changing the ratio and the substrate temperature, we try to find how different types of magic number $(C_{70})_m(Au)_n$ clusters.

[1] Y. Xie, L. Tang, Q. Guo, PRL 111,1, (2013)



P.06 Multi-scale material growth in extreme environments

A Bell and P Mulheran

University of Strathclyde, UK

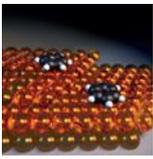
We aim to develop a kinetic Monte Carlo (kMC) model of surface evolution in extreme environments when a crystalline material is bombarded by high energy atoms causing sputtering, growth and surface roughening. We exploit results of Molecular Dynamics (MD) simulations to develop the kMC, which has the potential to capture the important growth physics while being orders of magnitude faster, allowing us to simulate on time and length scales that would be unfeasible for MD due to the computational cost. Here we use a lattice-based model with deposition, sputtering and surface diffusion rules inspired by the MD simulations. While we can successfully capture many features of the surface evolution, challenges remain to fully replicate the movement of ad-clusters and vacancy islands. Nevertheless the tool allows us to consider finite size effects and the scale-up to long time and length scales. Ultimately, we wish to explore the feasibility of coupling the KMC to computational fluid dynamics (CFD) methodologies such as direct simulation Monte Carlo (DSMC) applicable to rarefied gas environments.

P.07 Surface modification of diamond grits with silane coupling agent to improve adhesion between diamond abrasive and resin bond

C Cui¹, J Lu¹, Y Yu¹, Y Wang² and X Xu¹

¹Huaqiao University, China, ²Yanshan University, China

Diamond has been widely applied in cutting and grinding tools. Nearly all uses of diamond require embedding the crystals into or onto a medium. Since diamond is covalent crystal, there is no chemical affinity between diamond and the matrix. Besides the respective properties of diamond abrasive and resin bond, it is the adhesion between diamond grits and the bond that determine the tool's efficiency and lifetime. Coating diamond grits with suitable materials is an effective way to improve the adhesion between diamond abrasive and the matrix. The silane coupling agent molecules have multifunctional groups with a general chemical formula of R_nSiX_{4-n} , which could tie an inorganic substrate through an -O-Si- group and an organic matrix through a resin-compatible functional group R. Due to this bi-functionality, SCA is commonly utilized to increase the bonding strength by providing the chemical bridge to connect the inorganic material and the resin. In this paper, a new and simple method has been developed to coat diamond grits with organic film from silane coupling agent vinyltriethoxysilane (VTES). The surface analysis was performed by Fourier transform infrared (FTIR) spectra. Scan electron microscope (SEM) was also utilized to observe the morphology of the organic film. The results indicate that a relatively rough coating with vinyl functional groups has been deposited on the diamond grit surface. According to the bending strength of resin bond diamond blade containing coated and uncoated grits, the theoretic calculation shows that the interface bonding strength between diamond and the polyimide resin bond has increased significantly for the coating obtained from aqueous and alcoholic VTES solution.



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P.08 Research on removing the residual stress of the sapphire lapping wafer by corrosion

Z Hu, L Xiao, H Guo, Y Yu and X Xu

Huaqiao University, China

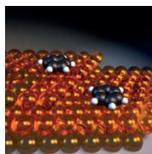
Sapphire is the main material of LED substrate, as LED substrate, sapphire wafer needs to be machined by the main process of wire cutting, double-sided lapping, single-sided copper lapping, single-sided CMP. After double-sided lapping, the sapphire substrate surface will produce certain residual stress, and the residual stresses in both sides surface layers are balanced. If not eliminate the surface residual stress of the wafer, in the subsequent single-sided copper lapping and CMP, the residual stresses will become difference between the two sides of the wafer, which leads to the large deformation of the wafer. Therefore, it is necessary to eliminate the residual stress of the wafer before single-sided copper lapping. At present, the residual stress of wafer is mainly eliminated by annealing in industry, while during annealing of sapphire substrate, which have many disadvantages such as high cost, high energy consumption, harsh conditions (need to protect the atmosphere), light transmission. Based on these, the paper puts forward a method to remove the surface residual stresses of sapphire by corrosion. Using the concentrated acid (the ratio of sulfuric acid and concentrated phosphoric acid is 3:1) at high temperature (280°C) to corrode sapphire lapping wafer. The wafers after corroding different time were polished by CMP on single side until the damage layer removed all. Then measuring the Bow and Warp of the wafer, the variable quantities of bow and warp could indirectly reflect the size of the residual stress. When the sapphire substrate material removal thickness by corrosion was less than 10 microns, the smaller the corrosion material removal layer thickness was, the larger the bow and warp of wafer after single-sided CMP were, however the bow and warp would become small ($\leq 5\mu\text{m}$) after annealing. When the sapphire substrate material removal layer thickness by corrosion was more than $15\mu\text{m}$, the bow and warp of sapphire substrate had almost no change after single-sided CMP, the values of bow and warp had no differences between after single-sided CMP and after annealing, which reflected that the residual stress has been removed all by corrosion. Along with the corrosion, wafer surface damage layer gradually removed, wafer surface residual stress also gradually decreases, and finally the complete removal of wafer residual stress can be realized.

P.09 Research on the Trajectory Simulation and its Uniformity of Slice in Planetary Double-Sided Grinding Process

Y Yu, L Wang, Z Hu, C Fang and X Xu

Huaqiao University, China

Double-sided planetary grinding is known as the popular precision technology for slices. The relative movement between slices and abrasive grains in the grinding process is very complex, which play an important role in wafer surface quality especially uniformity. In order to improve the wafer surface uniformity, it is necessary to establish a mathematical model based on the analysis of the relative motion between slice and abrasive grains for machine parameter optimization. This paper discussed the relative movement between wafer and abrasive grains in the double-sided planetary grinding process and establishes a mathematical model based on the Peter Wolter AC700 grinding machine. Using the calculation method and with the help of Matlab Software, the trajectories left on the wafer by abrasive grains are simulated. The slice surface was divided into many equal areas, and trajectory dots in each area were counted up, then its standard deviation was calculated to directly represent the surface uniformity. In addition verification experiments were performed on sapphire slices. The uniformity of slice surface under different speed ratio was indirectly represented by calculating standard deviation of Ra that obtained from different areas of slice surface. Finally the experimental results and simulation results have a good consistency under different speed ratio, which validated the reliability of the simulation results.



P.10 In-situ observation of water-induced reordering in ultrathin ionic liquid films

Z Henderson¹, A Walton², A Thomas² and K Syres¹

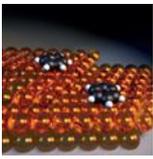
¹University of Central Lancashire, UK, ²University of Manchester, UK

Ionic liquids (ILs) are salts that are liquid at, or around, room temperature; and are composed of ions that are held together by a strong Coulomb potential. ILs have very low vapour pressures, allowing them to be studied using ultra-high vacuum techniques. They are currently being investigated for a vast range of applications, including lubricants, corrosion protection, as an electrolyte in batteries and photovoltaic devices, and CO₂ capture and storage [1]. ILs also have potential applications in catalysis, and are an integral part of a homogeneous catalysis system known as Supported Ionic Liquid Phase (SILP) catalysis. This method requires only a very thin film of IL (with the desired homogeneous catalyst dissolved in the film) on the surface of a high-area, porous support material [2].

The ordering and structure of ILs is determined by the structure of the constituent ions, and for imidazolium-based ILs it has been seen that the cations arrange to form a layer of alkyl chains facing out towards the vacuum, creating a charged underlayer that contains the anion and imidazolium ring of the cation [3]. It is this ordering at the surface that is believed to govern the gas adsorption and uptake by ILs. Water is often present as a contaminant in ILs, and has shown to affect their physical properties [4].

In this work, the interaction of water with the IL 1-butyl-3-methylimidazolium tetrafluoroborate ([C₄C₁Im][BF₄]) has been studied using near-ambient pressure X-ray photoelectron spectroscopy (NAPXPS). An ultrathin film of IL was deposited on rutile TiO₂ (110) at room temperature and exposed to water at 7 mbar at 283 K, corresponding to a relative humidity of ~70%. The ultrathin film was estimated to have a thickness of (10.8±0.9)Å, consisting of approximately three IL layers. Results indicate that water is trapped on the IL film, triggering a reordering of the ions at the surface. As water is pumped out of the near-ambient pressure cell, the IL begins to revert to its original surface structure.

- [1] M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nature Materials*, 8, 621-629 (2009)
- [2] C. P. Mehnert, R. A. Cook, N. C. Dispenziere, M. Afeworki, *J. Am. Chem. Soc.*, 124, 12932-12933 (2002)
- [3] V. Lockett, R. Sedev, C. Bassell, J. Ralston, *Phys. Chem. Chem. Phys.*, 10, 1330-1335 (2008)
- [4] S. Rivera-Rubero, S. Baldelli, *J. Am. Chem. Soc.*, 126, 11788-11789 (2004)



P.11 A scanning probe implementation of a Maxwell's Demon

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Maxwell's description of a gedankenexperiment involving a demon that could autonomously identify individual molecules, target them based on their speed, and sift them accordingly (by opening a nanoscopic door between two chambers) is one of the most quoted passages in physics [1]. The apparent violation of the second law of thermodynamics, and the subsequent solution of the paradox based on the relationship between information and entropy, has been the subject of almost continuous debate and discussion among scientists since Maxwell's demon first was spawned [2].

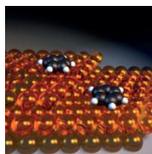
We have developed a strategy to implement a version of Maxwell's demon based on scanning probe microscope-based tracking of the positions of individual molecules. We will report the details of the protocol itself and also describe the results of a series of Monte Carlo simulations designed to determine the most appropriate region of the parameter space (spanning number density, temperature, binding energy, and diffusion barrier height) for experimental realisation of the demon.

We foresee that an atom-tracking unit, of the type generally used to eliminate thermal drift in SPM experiments [3] will be used to monitor the gap between two 2D "chambers" fabricated via a combination of automated dangling bond patterning and controlled manipulation of C₆₀ molecules. Fullerene molecules bound at dangling bonds will be chemisorbed and immobile, forming the walls of the chamber, while a dilute 2D gas of molecules will be contained within.

The Monte Carlo simulation we have developed to model this system comprises a C₆₀-terminated probe and a surface potential which describes the energy landscape both for diffusion on the passivated H:Si(100) surface and for intermolecular interactions. The simulation has been used to estimate the temperature range required in order to ensure the best balance between the surface hopping rate and the bandwidth (of order a few kHz) of the atom tracking detection system. A number of chamber geometries were also explored in order to optimise the molecular diffusion between chambers.

Our results demonstrate the viability of the protocol and indicate that a temperature of 210 K is optimal for operation of the scanning probe demon.

- [1] Maxwell's Demon: Entropy, Information, Computing, H. Leff and A. Rex (Princeton Press (1990))
- [2] Juan M. R. Parrondo, Jordan M. Horowitz, and Takahiro Sagawa, Nature Physics 11,131 (2015)
- [3] Philipp Rahe, Jens Schütte, Werner Schniederberend, Michael Reichling, Masayuki Abe, Yoshiaki Sugimoto, and Angelika Kühnle, Rev. Sci. Instr. 82 063704 (2011)



P.12 Synthesis of Nanodiamond-SnO₂ core-shell nanocomposite and its application for nitrite electrooxidation

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Tin oxide is well known for its wide band gap, low resistivity and high optical transmittance, which make it an attractive material for a variety of applications, such as in photocatalysts, n-type semiconductor, gas sensors, dye-based solar cells and transparent conducting electrodes. Decorating SnO₂ nanoparticles on nanocarbon substrate can prevent the nanoparticles from aggregation and increase the specific surface area, leading to the significant increase of the catalytic activity of SnO₂.

In order to satisfy these applications, some preparation techniques of SnO₂ nano-coating have been developed, including sol-gel, chemical bath deposition, and gaseous detonation. However, most of these methods explore the preparation of crystalline SnO₂ in harsh environment of high temperature, which might undermine the structure of nanocarbon materials. Otherwise, sp²-bonded carbon is susceptible to corrosion and microstructural degradation during anodic polarization, leading to a loss of activity or even an electrode failure. While, sp³-bonded nanodiamond possessing unparalleled stability is a more promising candidate for electrode material because of its wide potential window together with low background current.

Nanodiamond-supported crystalline SnO₂ nanoparticles (SnO₂/ND) were successfully synthesized from ND-dispersed SnCl₄ • 5H₂O aqueous solution via the isothermal hydrolyzing method at 60 °C. The XRD and TEM results showed that SnO₂ layer was composed of rutile nanocrystals rather than amorphous clusters and the different hydrolyzing parameters did not change the phase structure, but the concentration and the reaction time affected the morphology of SnO₂ coating. The nitrite electrooxidation experiments indicated that the SnO₂ which was prepared with low concentration and short reaction time had ellipsoid shape and small particle size, leading to better electrocatalytic activity. And the UV irradiation could reduce the resistance of the electrode, accelerate the electron transfer capacity and increase the catalytic activity of nitrite oxidation.

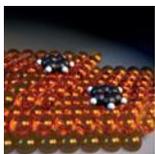
P.13 Probing for the Superatom Molecular Orbitals and Switching Properties of Li@C₆₀ on Au(111)

H Chandler¹, A Nanoh¹, M Stefanou², E Bohl², E Campbell² and R Schaub¹

¹University of St Andrews, UK, ²University of Edinburgh, UK

One reason that fullerenes are interesting is the presence of the Superatom Molecular Orbitals (SAMOs) which have been studied both theoretically and experimentally [1,2]. By using femtosecond photoelectron spectroscopy in the gas phase, and scanning tunnelling microscopy and density functional theory on a Au(111) surface we have determined the effect on the SAMOs resulting from the doping of buckminsterfullerene with a lithium atom (Li@C₆₀). We seek to determine the properties that may be useful in molecular electronics, ie. molecular switching.

- [1] Feng, M., Zhao, J. & Petek, H. Atomlike, Hollow-Core-Bound Molecular Orbitals of C₆₀. Science 320, 359-362 (2008)
- [2] Johansson, J. O., Bohl, E. & Campbell, E. E. B. Super-atom molecular orbital excited states of fullerenes. Philos. Trans. R. Soc. A 374, 20150322 (2016)



Interdisciplinary Surface Science Conference (ISSC-21)

P.14 Experimental and theoretical investigation of the linear fit approach of NEXAFS signals with calibrant spectra applied to anodically-grown amorphous Al₂O₃ films

D Scopece¹, A Beni¹, C Cancellieri¹, D Rentsch¹, C N Borca², T Huthwelker², M Iannuzzi³, P Schmutz¹, L P H Jeurgens¹ and D Passerone¹

¹Empa, Switzerland, ²PSI, Switzerland, ³University of Zurich, Switzerland

Thin amorphous layers of anodized aluminum oxide are extensively applied in corrosion protection and functionalization of Al surfaces.

Their structure, stability and adhesion are highly dependent on the growth conditions, thus creating a wide variety of microstructures and a complex structure-property relationship.

In order to optimize the production a detailed understanding of the structure is needed.

A widely adopted non-destructive technique to understand the local structure of the materials is the Near Edge X-Ray Absorption Fine Structure (NEXAFS or XANES). With this technique, quantitative information on the composition of a multiphase system can be gained by a linear combination fit of the NEXAFS spectra of crystalline phases (calibrants), a procedure known to work in crystalline samples, provided that the chosen phases are representative for the system.

In this work we report on NEXAFS spectra of thin Al oxide layers obtained at the local PSI beamline and highlight the successes and limitations of the linear fit approach applied to such signals.

Adopting as calibrants the ones suggested by the Al coordination revealed by NMR, a joint theoretical (DFT) and experimental approach is followed.

The information gained from ab initio simulations supports the experiment with novel insight, for example on the atomistic origin of the observed electronic transitions and the role of the foreign atoms in the chosen calibrants.

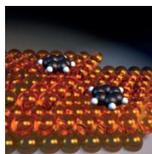
P.15 Adsorption of Cancer Treatment Molecules on Diamond Surfaces

S Astley¹, D Hu¹, J Wells², S Cool², J Williams³ and A Evans²

¹Aberystwyth University, UK, ²Norwegian University of Science and Technology, Norway, ³Chester University, UK

Fluorouracil (5-FU) is a widely used drug in the treatment of conditions such as leukaemia and bowel cancer. It is usually delivered through catheters that are often coated with anti-bacterial films such as silver. The interaction between the molecule and the catheter surface is not normally considered, but we have recently shown by x-ray photoelectron spectroscopy (XPS) that a silver surface can catalyse the dissociation of the 5-FU molecule to release HF, while a graphene surface is inert.

In order to compare diamond as coating material, the adsorption of 5-FU on the oxygen and hydrogen terminated diamond(001) surfaces has been studied using XPS, NEXAFS, Raman, and density functional theory (DFT). XPS showed the 5-FU films deposited at room temperature desorbed with time as the intensity reduction of the core levels was more pronounced on the H-terminated surface than the O-terminated surface, indicating a stronger adhesion of the film on the latter. DFT calculations show an agreement with the XPS data, and surface enhanced Raman spectroscopy (SERS) has shown this interaction is maintained with 5-FU nanoparticles.



P.16 Transfer & characterisation of catalytically-grown graphene on the (111) diamond surface

B Reed and A Evans

Aberystwyth University, UK

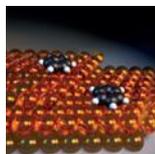
As an alternative to exfoliated and CVD-grown graphene, high quality epitaxial graphene can be fabricated on carbon-containing crystalline substrates using the base material as the source of carbon. Diamond offers the potential of improved material due to the closer lattice matching, as well as an ideal dielectric substrate for device fabrication. However, the high temperatures and low pressures required to controllably graphitise the diamond surface have proved more challenging compared to other carbon sources, such as SiC. By depositing a thin catalytic layer of iron onto the diamond surface, the graphitisation temperature is significantly reduced allowing controllable production of single and multilayer graphene. The stages of the growth process have been monitored using real-time electron emission spectroscopy (REES); from the catalytic breakdown of sp^3 -bonded carbon, transfer of interstitial carbon through the catalyst to the surface, and the emergence of sp^2 -bonded carbon on the iron surface forming into layers of graphene. Graphene grown in this manner was also transferred to Si/SiO₂ substrates using a wet-etch technique in conjunction with a polydimethylsiloxane (PDMS) support. The transferred graphene was subsequently analysed ex-situ using Raman spectroscopy, atomic force microscopy (AFM), and electronic force microscopy (EFM) to confirm its quality. In vacuo, the graphene-Si/SiO₂ sample was further characterised by use of x-ray and ultraviolet photoelectron spectroscopy (XPS/UPS). The effect of iron oxide is also considered after exposure to atmosphere following the growth of a patchy graphene layer.

P.17 Controlling the conductivity and energetics at ZnO(0001) surfaces and interfaces

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Transparent conducting and semiconducting oxides are widely used in photonic devices where their interfaces with light absorbing layers are often the limiting factors in performance. ZnO is an attractive material due to its earth abundant constituent elements, its wide band gap, high work function, UV absorption and controllable conductivity. The (0001) Zn- and O-terminated surfaces are known to have different electronic properties that are dependent on the surface structure and composition. In this study, ZnO single crystal surfaces have been prepared by in-vacuo plasma and heat treatment and these processes have been monitored by electron diffraction and electron spectroscopy. Using a combination of UV and X-ray irradiation, the energy band profiles of both surfaces have been determined, including the conditions for downward band-bending at the surface of n-type materials that leads to a highly conductive 2D hole accumulation layer. Changes in composition and band-bending during surface processing have been determined by monitoring the intensity, line-shape and binding energy of core and band-edge photoelectron spectra in real-time. Surfaces with 2D accumulation layers were then used as substrates for the growth of thin organic semiconductor films (phthalocyanine, fullerene) to fabricate heterostructures as found in photonic devices. Thin film growth was monitored in real-time to provide the thin film growth mode, interface bonding and energy band profiles. For inorganic-organic interfaces formed on the Zn-terminated surface, uniform organic films have been achieved that modify the work function but preserve the surface accumulation layer within an energy band profile with significant interface dipoles and large valence band offsets.



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P.18 Self-assembly and on-surface reactions of binol molecules on copper surfaces

J Lawrence¹, L Đorđević², S Orsborne³, D Stassen⁴, D Bonifazi⁵, G Costantini³

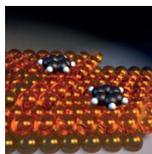
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The formation of covalent bonds during on-surface chemical reactions can be utilised to form strong, stable nanostructures with potential applications in nano-engineering science and technology. Many different types of structures can be formed, such as porous layers¹, linear polymers and nanoribbons². Various chemical functional groups have been utilised in efforts to create new nanostructures³.

In this study, scanning tunnelling microscopy (STM) has been used to examine the deposition of binol (1,1'-Bi-2-naphthol) molecules on a Cu(111) surface. Binol has been shown to undergo a ring closing reaction between its hydroxyl and C-H groups in solution with a copper(I) catalyst⁴, and it is believed that this may also be possible on a model surface under ultra-high vacuum.

When deposited at less than a monolayer coverage on a room temperature Cu(111) surface, the binol molecules were found to form regular clusters. Different phases of molecular self-assembly were found to occur at close to full monolayer coverage, potentially relating to the required density of packing. Upon annealing the molecules to 470K, they were observed to form nanostructures that consisted of chains and clusters, albeit of varying order. The distances between the sub-units are consistent with covalent linkages, most probably from an intermolecular C-H dehydrogenation.

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- [2] Cai, J. et al. Atomically precise bottom-up fabrication of graphene nanoribbons. *Nature* 466, 470–3 (2010)
- [3] Gourdon, A. On-surface covalent coupling in ultrahigh vacuum. *Angew. Chemie - Int. Ed.* 47, 6950–6953 (2008)
- [4] Stassen, D., Demitri, N. & Bonifazi, D. Extended O-Doped Polycyclic Aromatic Hydrocarbons. *Angew. Chemie - Int. Ed.* 55, 5947–5951 (2016)



P.19 The Zinc Phthalocyanine/ $\text{Al}_9\text{Co}_2(001)$ interface

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Organic electronics are an intensely researched field of nanotechnology, with attention placed upon replacing expensive or inefficient in-organic materials in devices such as transistors or photovoltaics with superior organic alternatives. ZnPc is a member of a family of metal phthalocyanines (MPcs, carbon based macrocyclic compounds, with metallic centres) that are primarily used in industry as dyes or pigments [1]. However, MPcs are semiconductors whose properties are dependent on their crystalline structure [1] - as such, tuneable ordered molecular growth is a desirable goal for functionality.

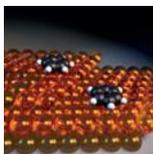
Complex metallic alloys (CMAs) are a fascinating area of research due to their outstanding physical properties (brittle nature, high hardness, catalytic activity etc. [2]), which indicate promising potential applications. In turn, their surfaces are of interest due to the often-differing behaviour when compared to bulk properties, structure, and their 'simple' cousins. Often, their chemistry, symmetry or distribution of surface atoms provide interesting substrates for molecular overlayer growth. The cluster-based Al_9Co_2 CMA can be thought of as an intermediary in complexity between the simple B2-AlCo and decagonal Al-Ni-Co quasicrystal; its (001) plane produces an Al terminated surface which is electronically modulated by sub-surface Co atoms [2]. This modulation provides an intriguing adsorption environment, in contrast to 'pure' aluminium surfaces.

Scanning Tunnelling Microscopy (STM) and preliminary Density Functional Theory (DFT) calculations have been used to investigate both the effect of this surface complexity on ZnPc adsorption behaviour and to determine any long range molecular ordering or polymerisation. STM results indicate 3 distinct adsorption sites - categorised either by STM contrast (bright and dark) or topology (rotation). These sites are critically dependent on the surface and sub-surface atomic structure, which is confirmed by DFT energetic calculations. Close-packing of ZnPc is observed at points of critical coverage, indicating the start of crystalline nucleation. In addition, molecular diffusion is observed - showing individual ZnPc molecules switching between the 3 adsorption sites.

These findings illustrate the (possibly advantageous) modulated electronic structure of the $\text{Al}_9\text{Co}_2(001)$ surface, whilst also providing an insight into molecular kinetics at complex intermetallic surfaces.

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[2] S. A. Villaseca et al., *J. Phys. Chem. C*, 115 (30), pp 14922-14932 (2011)



Interdisciplinary Surface Science Conference (ISSC-21)

P.20 In-situ studies of functional materials by Near-Ambient Pressure X-Ray Photoelectron Spectroscopy

A Walton

University of Manchester, UK

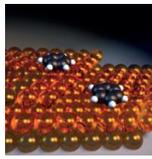
Near-Ambient Pressure X-Ray Photoelectron Spectroscopy (NAP-XPS) is a revolutionary new approach to electron spectroscopy, which removes the necessity of an ultrahigh vacuum sample environment, and allows for the analysis of samples in the near-ambient pressure regime (1-100 mbar) pressure. This takes XPS beyond a post-mortem technique and enables the study of gas/solid surface chemistry in-situ. The equilibrium vapour pressure of water is 23 mbar at room temperature, so at near-ambient pressures it is also possible to study surfaces where liquid water is present - potentially allowing for the study of liquid-water interfaces and electrochemical reactions in-situ.

The University of Manchester's NAP-XPS system finds a diverse range of applications across a variety of research themes. These include:

- Extending “traditional” surface science measurements across the pressure gap into the near-ambient regime.
- The study of gas-phase catalysis, both on model systems (single crystals and ultrathin oxide films) and real catalysts
- The study of functional organic-inorganic materials in operando, such as Metal-Organic Frameworks (MOFs) as selective gas absorbers or hybrid organic-inorganic perovskite materials as solar cells.

We also have an active development program, the focus of which is finding new ways to access the liquid-solid interface using XPS and perform electrochemical measurements in-situ.

My poster will present some case studies highlighting examples from each of the research themes. I will also present recent progress in our instrument development program and our plans for the future.



P.21 Change of electron crystal conductivity under incomplete compensation of the holding potential. Modeling

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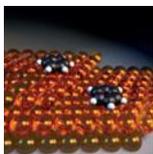
The surface electrons over liquid helium (Wigner crystal) is a spatially ordered state of a two-dimensional system of classical particles with the Coulomb interaction. Ordering occurs when the ratio between the potential and kinetic energies (plasma parameter Γ) of the particles exceeds a certain value ($\Gamma > 130$). The order-disorder transition in this system is a Berezinski-Kosterlitz-Thouless-type phase transition. The phase transition can be observed while investigating the transport characteristics of the electron layer (complex conductivity) which are different in the ordered and disordered states.

When the crystal is exposed to an external electric field directed along the surface of the liquid (guiding field), the layer conductivity varies nonmonotonically with the increasing field. In the limit of high guiding fields both the components of the crystal conductivity are close to the conductivity of a disordered electron layer.

It is found [1] that the conductivity of a Wigner crystal changes drastically as the holding potential decreases. The sharp changes in the conductivity may be accounted for by the disturbance of the crystalline order when the holding field decreases and a solid disordered phase is formed.

The experimental study the sharp change of electron crystal conductivity under incomplete compensation of the holding potential, have been found before [1] is continued. To understand the behavior found, the molecular dynamics study is performed. It is shown that a possible reason for the observed response is not a result of the layer conductivity change, but is due to features of the capacitance measurements of the two-dimensional electron system transport characteristics.

[1] K. A. Nasyedkin, V. E. Syvokon, A. S. Neoneta, Pisma v ZhETF 2010, 91, 652-655



P.22 Reconstruction of molecular wave functions with iterative phase retrieval algorithms

P Kliuiev, T Latychevskaia, J Osterwalder, M Hengsberger and L Castiglioni

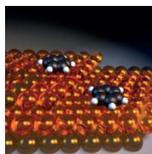
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Spatio-temporal visualization of electron dynamics in molecular adlayers is necessary for further advancement in efficiency of organic light-emitting diodes, photovoltaic cells and photocatalytic devices. Angle-resolved photoelectron spectroscopy (ARPES) of well-ordered layers of organic large planar molecules provides means for unequivocal reconstruction of initial state molecular wave functions [1,2]. Within the plane wave approximation for the photoelectron final state, the ARPES intensity distribution is proportional to the squared modulus of the Fourier transform of the initial state wave function and the latter can be therefore retrieved via inverse Fourier transform of the square root of the ARPES data, provided the phase of the photoelectron wave distribution in the detector plane is known. The phase distribution may be gained from the parity of the wave function [1], dichroism measurements [3] or iteratively, employing knowledge about the shape of the wave function [2].

We suggest solving the phase problem in reconstruction of wave functions from ARPES data in a more robust manner by employing its analogy to the phase problem in coherent diffraction imaging (CDI) [4]. Given that the far field optical or photoelectron intensity distribution fulfills the oversampling condition, both the amplitude and the phase of the object distribution can be reconstructed from the modulus of its Fourier transform without any information about shape and symmetry properties of the object by applying state-of-the-art phase retrieval algorithms used in CDI [5,6]. We perform an optical analogue experiment on micrometer-sized structures [7] and reconstruct both their amplitude and phase distributions from the far field diffraction patterns. By applying the same algorithm to a set of ARPES data, we reconstruct both the amplitude and the phase of the lowest unoccupied molecular orbital (LUMO) of a sub-monolayer of pentacene molecules [7].

Up to today, orbital tomography has been applied only to polycyclic aromatic hydrocarbons and organic dye molecules [1-3,7]. Currently, we are working on its extension to molecular systems relevant to catalysis by analysing photoemission electron microscope data recorded from pyrphyrin (Pyr) and cobalt-pyrphyrin (Co-Pyr) molecules on Ag(110). Pyr molecule is used as a carrier for catalytically active atoms of transition metals and its metalated form Co-Pyr is a promising water reduction catalyst in photocatalytic water splitting [8]. Ability to reconstruct molecular orbitals in these systems is important for validation of theoretical models [9] and extension of orbital tomography to a broader class of molecular systems.

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- [2] D. Lueftner et al. "Imaging the wave functions of adsorbed molecules", *PNAS* 111, 605 (2014)
- [3] M. Wiessner et al. "Complete determination of molecular orbitals by measurement of phase symmetry and electron density", *Nature Communications* 5, 4156 (2014)
- [4] J. Miao et al. "Extending the methodology of X-ray crystallography to allow imaging of micrometersized non-crystalline specimens", *Nature* 400, 342 (1999)
- [5] J. R. Fienup "Reconstruction of an object from the modulus of its Fourier transform", *Optics Express* 3, 27 (1978)
- [6] S. Marchesini et al. "X-ray image reconstruction from a diffraction pattern alone", *Phys. Rev. B* 68, 140101 (2003)
- [7] P. Kliuiev et al. "Application of iterative phase-retrieval algorithms to ARPES orbital tomography", *New Journal of Physics* 18, 093041 (2016)
- [8] E. Joliat et al. "Cobalt complexes of tetradentate, bipyridine- based macrocycles: their structures, properties and photocatalytic proton reduction", *Dalton Trans.* 45, 1737 (2016)
- [9] Y. Gurdal et al. "Non-innocent adsorption of Co-pyrphyrin on rutile (110)", *PCCP*. 17, 22846 (2015)



P.23 Photodesorption of NO from Au(100) using 3D-velocity map imaging

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Velocity map imaging (VMI) techniques have been successfully applied to many gas-phase photodissociation and crossed-beam experiments over the last 20 years. Here, we have combined the velocity map imaging technique with the time-of-flight technique to investigate the photo-stimulated desorption of NO pre-adsorbed on an Au(100) single crystal. The 3-dimensional velocity distribution of NO desorbing from Au(100) can be determined through the acquisition of TOF data that yields the velocity component along the surface normal and velocity map imaging which yields the velocity component in the plane parallel to the surface, respectively. NO molecules are photo-desorbed from a Au(100) surface using a 355 nm, 266 nm desorption laser. A REMPI probe laser was focussed using a cylindrical lens to create a laser 'sheet' a few mm in front of the Au crystal to detect a large range of angular distributions.

The overall speed distribution for the 355 nm is rather narrow and faster than a thermal Maxwell-Boltzmann distribution at the surface temperature would be.

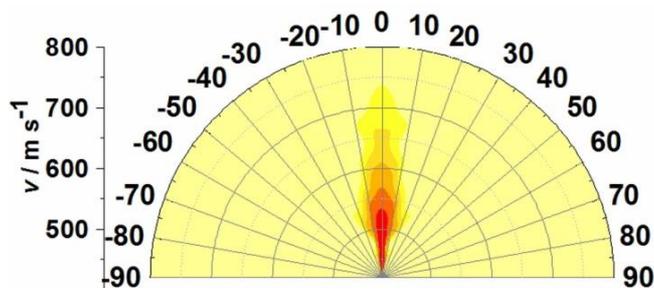
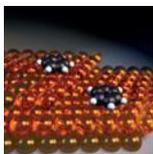


Figure 1: Angle-resolved speed distribution of NO desorbing from Au(100).



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P.24 Chemomechanical manipulation of Pb atoms on the Si(100) surface using dynamic force microscopy

F Louly Quinan Junqueira¹, I Lekkas¹, C Tschirhart², A Sweetman¹ and P Moriarty¹

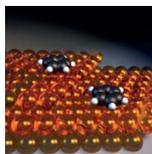
¹University of Nottingham, UK, ²University of California Santa Barbara, USA

In a fascinating series of experiments, Morita, Sugawara, Custance and co-workers have demonstrated that it is possible to manipulate single Sn, Pb and Ge atoms on the Si(111) surface using novel mechanochemistry protocols involving atom exchange between the apex of the tip of a dynamic force microscope and the underlying surface [1-3].

We have expanded these investigations of the manipulation of Group XIV atoms on silicon to the Si(100) surface with the ultimate objective of exploiting the mechanisms identified by Sugawara et al. [3] for 3D atomic manipulation protocols.

A combination of STM and AFM was used to characterize the Si(100) surface in which a low coverage Pb was deposited at low temperatures. It is known that Pb forms chains on the Si(100) surface along its rows [4, 5]. We have reproduced the manipulation process of single metal adatoms, described by Ternes et al. [6] for a metal surface, on a semiconductor substrate. A series of controlled lateral manipulation events has been used to modify single atom-wide Pb chains on Si(100) via direct chemical force. Systematic force-distance spectroscopy has been used to quantify the force thresholds needed to induce lateral manipulation of single Pb atoms.

- [1] Ruben Perez Oscar Custance and Seizo Morita. *Nature Nanotechnology*, 4:803- 810, 2009
- [2] Shinji Hirayama Noriaki Oyabu Oscar Custance Yoshiaki Sugimoto, Masayuki Abe and Seizo Morita. *Nature Materials*, 4:156-159, 2005
- [3] Y. Kinoshita R. Turansky Y. Naitoh Y.J. Li Y. Sugawara I. Åa tich J. Bamidele, S.H. Lee and L. Kantorovich. *Nature communications*, 4776, 2014
- [4] Hanyi Sheng Zhen Chao Dong; Daisuke Fujita, Taro Yakabe and Hitoshi Nejoh. *Journal of Vacuum Science and Technology B: Microelectronics and Nanometer Structures*, 18(1):2371, 2000
- [5] J.-Y. Veuillen L. Jure; L. Magaud, P. Mallet. *Surface Science*, 482-485(1):1343- 1349, 2001
- [6] Markus Ternes; Christopher P. Lutz¹; Cyrus F. Hirjibehedin¹; Franz J. Giessibl and Andreas J. Heinrich¹. *Science*, 319:1066-1069, 2008



P.25 An investigation into the nucleation and subsequent growth of small Ag clusters on the surface of anatase TiO₂(101): A combined XPS and STM study

M Wagstaffe

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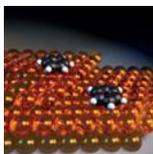
Metal clusters supported on ordered metal oxide surfaces are of great interest due to their application in a wide variety of fields, including photovoltaics and transition metal catalysis. The structural, chemical and electronic properties at the interface between the metal clusters and the oxide surface have been shown to have a strong influence on the catalytic and photocatalytic activity and so an understanding of this interaction is essential. By using a combination of synchrotron photoelectron spectroscopy and scanning tunnelling microscopy, the initial nucleation and subsequent growth of Ag clusters on anatase TiO₂(101) has been investigated. Adsorption of Ag on the surface of anatase(101) led to a small reduction in titania suggesting an interfacial charge transfer occurs between the two. In addition to this, a downward shift with increasing cluster size is observed for both the FWHM and binding energy of the Ag 3d peak. This has been attributed to a combination of initial and final state effects resulting from the variation in cluster size, as corroborated by the STM data, which also suggests that Ag clusters show a slight preference to forming on step edges.

P.26 Manufacturing application study of CdZnTe wafers using automated x-ray metrology

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Digital X-ray diffraction imaging (XRDI) and high resolution X-ray diffraction (HRXRD) are used to analyze defects in a non-destructive way on commercially made (111) CdZnTe substrates. The X-ray tools automatically aligned, measured and analysed the samples. The XRDI images show clear differences between the CdZnTe substrates which correspond to high and low yield. HRXRD rocking curve data correlates with the presence of the defects seen in XRDI images. These results suggest that X-ray metrology is an essential tool for the production monitoring of CdZnTe substrates in an automated environment.



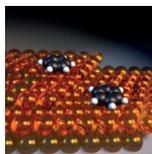
Interdisciplinary Surface Science Conference (ISSC-21)

P.27 Growth of copper doped $\text{Ca}(\text{OH})_2$ nano structures on conducting fabric for the remediation of toxic residues of dye

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¹University of Exeter, UK, ²University of Agriculture, Pakistan, ³National Institute of Biotechnology and Genetic Engineering, Pakistan, ⁴National Textile University, Pakistan

Nano scaled $\text{Ca}(\text{OH})_2$ is a photocatalyst with wide band gap, high pore volume, excessive surface area, easy hydroxylation and efficient adsorbability. Doping with copper ion render it capable of excellent solar light harvesting and develop crystal defects, enhancing the photocatalytic activity. Carbon fabric has a graphene sheet based conducting structure which synergistically aids the photocatalytic process. Nano structures of copper doped $\text{Ca}(\text{OH})_2$ have been grown on carbon fabric using low temperature hydrothermal route after getting it functionalized and seeded. The characterization of treated fabric has been done by EDX, SEM, AFM, TEM and XRD analysis. Different band gaps of doped $\text{Ca}(\text{OH})_2$ nano structures containing a range of concentration of Cu^{+2} ion led to the variation in their photocatalytic activity, determined by the rate of degradation of reactive black 5 dye as a model compound, in aqueous medium. The variable reaction parameters such as pH of the solution, concentration of dye solution and H_2O_2 , illumination time to simulated sunlight (D65) have been optimized by applying response surface methodology (RSM). The extent of degradation of dye has been evaluated by HPLC, FTIR and UV/vis spectroscopy. It was found that copper doped CaO can exhibit remarkable photocatalytic activity than undoped nano $\text{Ca}(\text{OH})_2$ for the removal of toxic dye residues present in waste water. Evaluation of water quality parameters BOD, COD and TOC before and after photocatalytic treatment revealed that treated water is reusable for irrigation and industrial operations.



P.28 Mining byproducts as a sustainable source of high tech materials

C Murray and D Fernandez

Trinity College Dublin, Ireland

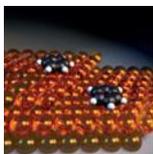
The European Institute of Innovation and Technology (EIT) Raw Materials project examines the sustainable production and recovery of valuable materials within the context of ever increasing societal demand. Currently, the raw materials market is presented with a series of challenges that emerge from a rapidly increasing population, a high globalized awareness and much better life-quality standards. These factors trigger a higher and rapidly growing demand of raw materials. Beyond the base metals, industrial minerals and alloy compounds, there is a growing need for advanced materials, which exhibit specific properties in relation to their aspect ratio and surface properties. Such is the case of transition metal dichalcogenides (TMD), 2D-materials and other nanoparticles. The surface properties of these materials confer on them the title of “high-performance” materials, with applications ranging from the semiconductor industry to translational nanomedicine. TMDs for example have attracted particular interest in the semiconducting industry as a possible alternative to silicon in some applications, due to their superior on/off ratios¹. Magnetite nano-particles are interesting in nano-medicine applications due to their magnetic behaviour and benign interaction in biological systems. Other potential end users technologies include the solar cells, batteries and water splitting to name just a few. Such is the importance of raw materials, the European Union has developed a list of critical materials that are of key industrial relevance². This list is constantly been re-evaluated.

It is interesting to note that many of these materials exist already in natural form, with a range of dimensions. They are actually present and unused within current mining production lines around the globe and normally end up as waste material. The technological demand for small-sized materials poses the question as to whether or not these naturally sourced materials deserve closer attention. It may be possible to identify inexpensive and potentially high-performance materials in the massive production lines of mines. In this poster we examine the potential of mining by-products as a source of materials such as TMD and magnetites. The physical and chemical properties of a series of ore samples recovered from mid- and end-of-line metal extraction processing are examined. The relative ratios of the various remaining minerals available in these samples was measured using x-ray fluorescence and diffraction. The morphology of the materials was examined using SEM/EDX, TEM and Raman spectroscopy. We compare these data to that of a set of high-quality, pure samples available in the market that have been synthetically produced.

Based on these results, some use cases for these materials are presented. The economic viability of their extraction will not be addressed specifically as this is the subject of a separate project in the EIT Raw Materials project.

[1] Wang et al, Nature Nanotechnology, Vol. 7, pp 699-712

[2] European Commission – Report on Critical Raw Materials for the EU, May 2014, p.34



Interdisciplinary Surface Science Conference (ISSC-21)

P.29 Controlling the wettability of nano/micro-textured ZnO thin films to enhance the proliferation rate for cell culture and tissue engineering

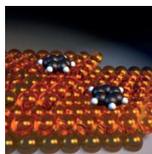
K Bhavsar¹, D Ross¹, M H Nandakrishnan² and R Prabhu¹

¹Robert Gordon University, Aberdeen, UK, ²CIIRC, Jyothy Institute of Technology, India

The proliferation of cells is an important process for applications in many biology and medical areas, especially in cell culture and tissue engineering. The behavior of proliferation and migration of cells and tissue on materials depends on the surface characteristics of the materials such as topography, wettability and chemical properties. Other important influencing factors are the properties of the cell itself, their density, properties of medium and environmental conditions. Although there are many factors, high proliferation rates were reported under moderate hydrophilic surface conditions for different cell types.

Investigations of various organic/inorganic structures and materials as cellular substrates are gaining research interest. Cells are extremely sensitive to nano/micro-textured natural/artificial surface topographies and chemistries, which may permanently change their fate. During the last decade, semiconducting metal oxide materials such as ZnO and TiO₂ are being widely investigated for a wide range of applications in biology, medicine and environmental science due to their special structural, electrical and optical properties. Furthermore, their properties such as multi-functionality, biocompatibility and special wetting properties (super-wetting/anti-wetting) have attracted considerable interest as cellular substrates. Usually synthesized nano/micro-textured thin film surfaces of these materials tends to show hydrophobic nature. In order to change their wettability, most of the methods reported are ex-situ. These methods involve high energy light sources of X-ray, UV or laser and ultrahigh vacuum or high-temperature environments. Other chemical based methods involve modifying the surface with low/high energy chemicals which are undesirable and not suitable for cell culture and tissue engineering applications as it changes the surface properties and damages the cells.

Herein, we demonstrate a simple, economical and safe methodology to control the wettability of developed nano/micro-textured ZnO surfaces on glass substrates. The developed method use light irradiation using different LEDs to control the wettability of the developed ZnO surfaces. Desired wettability can be achieved by controlling the parameters such as illumination time, intensity and emission wavelength. Experimental results show that different hydrophilicity value can be achieved, just by changing the irradiation wavelength for the same exposure time and vice versa. This enables to achieve enhanced proliferation rate for cell and tissue culture. The nano/micro-textured surfaces of ZnO have been developed using hydrothermal synthesis method. Synthesized ZnO thin film was hydrophobic in nature. Surface topography was characterized using scanning electron microscope and the wetting angle was measured using a contact angle measurement system. Developed method can be readily applied to other similar metal oxides based materials such as TiO₂ and their various topographic surfaces for cell culture and tissue engineering applications. The developed wettability controlling method has many potential applications in the field of microfluidics, automobiles, biotechnology, environment and agriculture.



P.30 Sensitivity analysis of graphene coated SPR sensor for glucose concentration monitoring

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The Surface plasmon resonance (SPR) is a well-known, rapid and sensitive technique used for probing the biomolecular interactions in real time. Potential of this technique is due to its very high sensitivity towards the change in refractive index of sensing medium, which occurs through adsorption or binding of biomolecules and their concentration. Typical conventional SPR biosensors include a thin metal film coated on a prism isolating the sensing medium from the prism. Several new approaches have been suggested to improve the sensitivity of SPR sensors over the last two decades. Most of them are based on creating nanoparticles, nanowires, nanorings, nanoholes and nanoslits on the metal surface to enhance the localized E-field and therefore, it is quite challenging to have control over their optical properties.

Graphene, a single layer of carbon atoms arranged in a honeycomb structure, is emerging as the most popular material of the decade which is under intense research. Graphene has a very high surface to volume ratio and strong binding/adsorption affinity towards biomolecules due to its carbon ring structure from π - π stacking interactions. Recently, there have been few reports on using graphene on a metal film to improve the sensitivity.

Herein, we report computational investigations to analyse the sensitivity of graphene coated SPR sensor for glucose concentration monitoring. The reflectivity of p-polarized incident light has been calculated using the N-layer model for the most common Kretschmann configuration. Investigations include effect of graphene layers, effect of wavelength and sensor design parameters to measure the glucose concentrations (0 - 100 g/l) in water. Optimum parameters will be utilized to develop a highly sensitive glucose sensor for real-time monitoring applications.

P.31 XPS study of Zn₃N₂ thin film grown by RF magnetron sputtering

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Zinc nitride is a semiconducting material with interesting properties for example, high transparency, high electron conductivity, and its potential use in optoelectronics, sensors, and renewable energy. We have grown zinc nitride thin films on fused silica at 300 °C growth temperature by RF magnetron sputtering. Highly pure zinc target was sputtered in the presence of nitrogen and argon gas. Films were grown at different N₂/Ar flow rate ratios of 0.20, 0.40, 0.60, 0.80, and 1.0. After the growth the surface morphology of the samples were examined using atomic force microscopy. We found that the samples have grain-like surface morphology with an average surface roughness of 4-5 nm and an average grain size of 13-16 nm. zinc nitride samples grown at lower N₂/Ar ratio are polycrystalline and contain secondary phases of ZnO. These ZnO phases did not exist for the sample grown at higher N₂/Ar ratio. Highly aligned films were achieved at N₂/Ar ratio of 0.60. Hall effect measurements reveal that films are n-type semiconductors, and the highest carrier concentration and Hall mobility was achieved for the films grown at N₂/Ar ratio of 0.60. X-ray photoelectron spectroscopy was performed for the chemical analysis of the film and it confirmed the formation of Zn-N bonds. The depth profile XPS analysis of the films reveal that the intensity of N1s peak reduces whereas O1s peak intensity increases deeper in the film. This indicates more nitrogen vacancies are formed at the start of the film, and the atmospheric oxygen compensates those vacancies. Higher nitrogen vacancies at the start of the film can be attributed to the stress caused by the film-substrate lattice mismatch.

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