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## UKSAF Summer Meeting 2008

### ***Solutions to Real World Problems: Challenges & Opportunities***

**10.00 a.m. – 5.15 p.m. Wednesday 2 July 2008**

**Host: The University of Ulster**

**Venue: The Assembly Hall, Jordanstown Campus, Northern Ireland**

9:30 -10:00

***Registration – Coffee/Tea***

10:00 -10:15

***Welcome & Introduction***

*Dr. Dave Sykes, UKSAF Chairman*

**Surface Engineering Strategies for the Control of Cellular Responses to Biomaterials**

10:15 -11:00

*Prof. Brian Meenan, Nanotechnology & Integrated Bioengineering Centre (NIBEC)*

*University of Ulster*

**Thin Films & Surfaces – Critical to the Disc Drive Industry**

11:00 -11:35

*Dr. Rob Hardeman, Seagate Technology (Ireland)*

*Springtown Industrial Estate, Londonderry*

***Final of the Young Surface Analyst (YSA) Competition - Oral Presentations***

*Joanna Lee - National Physical Laboratory*

*Paolo Marino - University of Surrey*

11:35 -12:25

*David Reid - Shell Global Solutions UK*

*Michael Taylor - University of Nottingham*

*Ignacio Villar-Garcia - University of Nottingham*

*Mischa Zelzer - University of Nottingham*

12:25 -12:40

***UKSAF Annual General Meeting***

12:40 -14:00

**Lunch and YSA Poster Viewing (including judging)**

**Characterising the Active Surface of Gold Based Water Gas Shift Catalysts**

14:00 -14:35

*Dr. Alex Goguet, School of Chemistry & Chemical Engineering  
Queen's University, Belfast*

**Surface Analysis Opportunities at the Diamond Light Source**

14:35 -15:10

*Dr. Chris Nicklin, Diamond Light Source  
Harwell Science & Innovation Campus, Didcot, Oxfordshire*

**Applications of TOF-SIMS and LEIS to Real World Samples**

15:10 -15:45

*Dr. Derk Rading  
ION-TOF GmbH, Munster, Germany*

15:45 -16:00

**YSA Competition Results & Award of the Riviere Prize**

16:00 - 16:15

**Coffee/Tea**

**Computer-Assisted Interpretation of TOF-SIMS Data: Fun With Raw Files**

16:15 -17:15

*Dr. Steven Pachuta, Corporate Research Analytical Laboratory  
3M, St. Paul, Minnesota, USA*

17:15

**Close of Meeting**

18:30

**Transport to Belfast Castle**

19:00

**Joint UKSAF – NPL Meeting Dinner**

## **Surface Engineering Strategies for the Control of Cellular Responses to Biomaterials**

*B.J. Meenan, Nanotechnology & Integrated Bioengineering Centre (NIBEC)*

*University of Ulster*

The nature of the response that occurs at the interface between a biological system (cell, tissue, and/or organ) and a medical implant surface is critical to the attendant clinical outcome in terms of post-operative device survival and thereby patient benefit. As such, control of these interactions is central to the development of biomaterials that have properties to allow for their direct application in tissue engineering and regenerative medicine where tissue repair and regeneration are a central requirement. It is widely accepted that cells can be influenced by relatively subtle differences in surface chemistry and topography and that certain combinations of these properties can direct their response in a way that can ultimately affect the rate and quality of new tissue formation. However, whereas several strategies have been developed for the provision of such effects, the surface engineering techniques required to provide them are often very difficult to translate to the actual devices.

In this presentation, several of the surface engineering strategies that can be employed to provide the relevant micro-, meso- and nano-scale features on both hard and soft biomaterials are considered. In particular, the need to develop cost-effective methods to create smart surfaces is highlighted. In all cases, the important role that effective surface analysis plays in confirming and quantifying the required chemical and topographical functionality is addressed. The requirement for such analysis to be carried out on "real world" specimens is a major challenge in this respect. Exemplar studies are used to illustrate how the appropriate surface conditioning, provided via targeted surface engineering approaches, can guide the progression of cell phenotype in vitro and how this might allow for translation to more effective implant performance in vivo.

### **Thin Films & Surfaces – Critical to the Disc Drive Industry**

*R. Hardeman, Seagate Technology (Ireland)*

*Springtown Industrial Estate, Londonderry*

The disc drive lies at the heart of data storage, not only for the personal computer, but also for everything from the enterprise servers that power the Internet, personal video recorders to satnavs, mp3 players and other portable devices.

As a precision electro-mechanical device it has few equals, with demands of extreme reliability and low-power operation alongside a constant challenge to deliver more data density at lower cost.

This talk will illustrate some of the complexity that lies behind this ubiquitous device with examples of the types of layers, interfaces and surfaces that must be created and controlled, in particular demonstrating the use of a variety of analytical techniques to support the manufacturing process for the drive and some of its components.

Examples will include;

- End point detection for control of plasma processes using SIMS
- Characterisation of multi-layer metal and dielectric stacks by FIB, TEM and atom-probe
- Tribological coating analysis using XPS and ToF SIMS

The talk will also touch on some of the methods based on synchrotron radiation that have been employed in developing the unique materials set necessary for the future demands of the disc drive industry.

## Characterising the Active Surface of Gold Based Water Gas Shift Catalysts

C. Hardacre,<sup>1\*</sup> J. Breen,<sup>1</sup> R. Burch,<sup>1</sup> Y. Chen,<sup>1</sup> A. Goguet,<sup>1</sup> F. Meunier,<sup>1</sup>  
P. Hu,<sup>1</sup> R.W. Joyner,<sup>1</sup> B.S. Mun,<sup>2</sup> R. Pilamsombat,<sup>1</sup> D. Thompsett,<sup>3</sup> D. Tibiletti<sup>1</sup>

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Recent results on Au supported on CeO<sub>2</sub><sup>(1,2,3,4)</sup> have displayed promising results for the WGS reaction, however, there is a difficulty in preparing highly active gold catalysts which do not deactivate<sup>(5)</sup>. For these systems the deactivation has been associated with the formation of carbonates<sup>(6)</sup> or formates<sup>(7)</sup>, and the loss of oxide surface area<sup>(8)</sup>. However, there has been no consensus, to date. The present paper reports on the use of *in situ* EXAFS, DRIFTS, high pressure XPS coupled with DFT calculations to elucidate the deactivation mechanism of highly active Au/CeZrO<sub>4</sub> catalysts for low temperature WGS and a method of stabilising the activity.

Excellent low temperature WGS activity was found for the 2% Au/CeZrO<sub>4</sub> catalysts with the equilibrium conversion reached at ~200 °C. However, on increasing the WGS reaction temperature above 250 °C, significant deactivation was observed with the temperature for 50% conversion rising from 140 °C to 220 °C. A similar decrease in activity was also observed if the temperature was maintained at 200 °C with the catalyst showing a gradual deactivation over a period of 30 h. The rate of deactivation was determined by the water content and under high humidity (>10% water) rapid loss of activity was found. EXAFS of the fresh catalyst showed that the local structure around the gold is dominated by the presence of oxygen co-ordination at ~ 2 Å which is consistent with bond distances found in a gold oxide. Additional features at 3-4 Å were also found and were fitted to cerium co-ordination in the second shell. Under the WGS reaction conditions, the *in-situ* EXAFS showed that the gold transforms into Au<sup>0</sup> state forming metallic clusters of ~ 50 atoms. Importantly, despite the change in activity of the catalyst on thermal cycling no agglomeration of the metal particles was observed and the 1<sup>st</sup> shell co-ordination remained at ~ 6. High pressure XPS on the 2% Au/CeZrO<sub>4</sub> catalyst under reaction conditions at 150 °C and 300 °C also showed the presence of Au<sup>0</sup> in good agreement with the XANES. However, at higher temperature a decrease in intensity of the gold 4f XPS peaks was observed. *In-situ* DRIFTS studies also indicated that the Au<sup>0</sup> is where the CO adsorbs. Under WGS conditions a single band at 2096 cm<sup>-1</sup> was found assigned to a CO-Au<sup>0</sup> species. This feature is found to reduce in intensity with increasing reaction time. Both thermal and hydrothermal deactivation mechanisms are thought to be the result of the Au particle dewetting and the loss of metal-support interaction. This is in excellent agreement with DFT results which indicate that the presence of surface hydroxyl groups destabilise gold clusters and that, even in the absence of hydroxyls, the gold cluster-support interaction is less favourable than gold-gold interactions. Although the thermal deactivation is not affected, on stream deactivation may be reduced by pretreating the catalyst in the full WGS mix and then switching to a CO<sub>2</sub> free feed.

(1) Q. Fu, H. Salzborg, M. Flytzani-Stephanopoulos, Science 301 (2003) 935.

(2) G. Jacobs, E. Chenu, P.M. Patterson, L. Williams, D. Sparks, G. Thomas, B.H. Davis, Appl. Catal. A 258 (2004) 203.

(3) A. Amieiro Foncesca, J. Fisher, D. Thompsett, unpublished results.

(4) D Tibiletti, A Amieiro-Fonseca, R Burch, Y Chen, JM Fisher, A Goguet, C Hardacre, P Hu, D Thompsett, J. Phys. Chem. B 109 (2005) 22553.

(5) C.H. Kim, L.T. Thompson, J. Catal. 230 (2005) 66.

(6) M. Schubert, A. Venugopal, J.J. Kahlich, V. Plzak, R.J. Behm, J. Catal. 222 (2004) 32.

(7) A. Luengnaruemitchai, S. Osuwan, E. Gulari, Catal. Commun. 4 (2003) 215.

(8) Q. Fu, W. Deng, H. Salzborg, M. Flytzani-Stephanopoulos, Appl. Catal. B56 (2005) 57.

## **Surface Analysis Opportunities at the Diamond Light Source**

*C. Nicklin, Diamond Light Source*

*Harwell Science & Innovation Campus, Didcot, Oxfordshire*

Diamond has a selection of facilities that will be used for different types of surface analysis, ranging from structural studies to detailed measurements of the electronic and magnetic structure. I will give a general introduction to the range of beamlines currently available within the 'Surface and Interface Village' at Diamond Light Source and future stations.

More detail will be given specifically about the surface and interface diffraction beamline at Diamond which will become operational in Summer 2009. Currently this beamline is under-construction and when commissioned will provide a range of different experimental geometries that will allow either surface diffraction, or grazing incidence small angle x-ray scattering measurements to be carried out on samples held in different environments. These are powerful techniques that allow structures on a surface to be monitored with high resolution and for a range of different length scales. Diffraction measurements of well ordered reconstructions can yield the positions of all atoms within a unit cell to a resolution of better than 0.05 Angstroms, while GISAXS measurements provide information about the shape of nanostructures on a surface. The use of high energy x-rays for these measurements means that they are not confined to an ultrahigh vacuum environment but can be carried out in real-environments such as high gas pressures or in solid-liquid studies. Numerous examples will be discussed.

## **Applications of TOF-SIMS and LEIS to Real World Samples**

*D. Rading, T. Grehl and E. Niehuis*

*ION-TOF GmbH, Heisenbergstr. 15, D-48149 Munster, Germany*

Low Energy Ion Scattering (LEIS) and Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) enable the analysis of the chemical surface composition of vacuum sustainable samples. Applying LEIS, the surface of a sample is bombarded by noble gas ions (He<sup>+</sup>, Ne<sup>+</sup>, ...) of low energy (1-8 keV). Elastic collisions with individual surface atoms cause backscattering of the projectiles. By analysing the energy of these scattered ions the identity (mass) of the atomic collision partner can be calculated. Therefore, LEIS enables the quantitative determination of the elemental composition of the sample's outermost monolayer.

In ToF-SIMS the sample is also bombarded with atomic or polyatomic ions. In contrast to LEIS the energy (10-25 keV) and the mass (e.g. Bi<sup>3+</sup>: 627 u) of these projectiles is relatively high. Among others, the impact of these projectiles leads to the emission (sputtering) of atomic as well as molecular ions via collision cascades. The mass of these secondary ions is measured by their time of flight to the detector. Due to the physics of the sputter process the secondary ions originate from the first 1-3 monolayers. Therefore, ToF-SIMS provides detailed elemental and molecular information from the first 1-3 surface monolayers.

Both techniques provide useful information on the surface composition of solids. However, the information differs for LEIS and ToF-SIMS with respect to information depth, quantification, sensitivity, mass resolution, etc and complement one another very well. In this contribution we will discuss the possibilities and limitations in surface analysis of these two techniques by means of several real world examples.

## **Computer-Assisted Interpretation of TOF-SIMS Data: Fun With Raw Files**

*Dr. Steven Pachuta, Corporate Research Analytical Laboratory*

*3M, St. Paul, Minnesota, USA*

The relentless demand for corporate growth places ever increasing demands on industrial surface analysis laboratories, with speed and quality being paramount. Balancing these requirements is a struggle, since the two are generally inversely correlated. Add to this the increasing complexity of surface analysis instruments, with the large quantities of data they produce, and the surface analyst can be easily overwhelmed.

The availability of so-called raw instrument files, in which a complete mass spectrum is available for every pixel in an analyzed area, enables a number of computer-based strategies for speeding up and simplifying TOF-SIMS data processing and interpretation, while increasing quality. Application of these strategies to industrial surface analysis problems will be demonstrated.

The discussion will include principal component analysis (PCA), multivariate curve resolution (MCR), automated image generation, automated region-of-interest spectra generation, topographic correction, mass resolution improvement, quantitation, and “decision-making” assistance.

### Biography: Dr Steven J. Pachuta

Steve Pachuta is a Senior Research Specialist in 3M's Corporate Research Analytical Laboratory in St. Paul, Minnesota and is Group Leader of the surface analysis section, as well as Business Lead for 3M's corporate analytical database.

Steve was born in New Jersey and raised in Indiana, California, and Georgia. He received his B.S. in chemistry from the University of Georgia in 1981, and his Ph.D. in analytical chemistry from Purdue University in 1986. His thesis work under Professor Graham Cooks was in the areas of tandem mass spectrometry and secondary ion mass spectrometry.

Steve served on the local arrangements committee for the 1995 AVS National Symposium in Minneapolis, and he has been Secretary and President of the ASMS Minnesota Mass Spectrometry Discussion Group and is currently Secretary of the AVS Applied Surface Science Division. Within 3M he has served as a Technical Forum senator and for several years was coordinator of the Industrial Advisor Program, a mentoring program which matches 3M scientists with local undergraduates. He has authored or coauthored thirty peer-reviewed papers and holds three patents.

Steve's research interests are centered on industrial applications of surface analysis—in particular secondary ion mass spectrometry—with emphasis on polymer analysis, imaging, quantitation, data systems, chemometrics, and automated data interpretation.

His general interests are nineteenth and early twentieth century literature, running, digital photography and recording, and music.