

UKSAF Winter Meeting 2007

Advanced Data Processing Techniques for Surface Analysis *a joint UKSAF / MNT Measurement Club Workshop*

Tuesday 9 January 2007

Host: University of Newcastle upon Tyne

Venue: The Centre for Life, Newcastle upon Tyne

Quantitative XPS of Surface Nano-Structures by Analysis of the Peak Shape

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Measured XPS-peak intensities and peak shapes depend strongly on the nano-scale atom depth distribution because the mean path between inelastic scattering is only ~ 1 nm. Quantification based on analysis of the peak shape gives therefore substantially more quantitative information than the peak intensity alone. The problem was basically solved ~ 15 years ago by developing algorithms for the detailed analysis of the energy distribution of emitted electrons [1]. The amount of information contained in the inelastic background is substantial and therefore even quite crude models give much quantitative information on the surface nano-structure. The validity of these algorithms have been tested extensively through series of experiments some of which are summarized in [2,3]. In general it is possible to determine the depth distribution of atoms with sub nano-meter resolution and amount of atoms in the outermost ~ 5 - 10 nm with $\sim 10\%$ accuracy. Practical application of these algorithms has increased after ready to use software packages were made available [4] and they are now being used in laboratories worldwide. The technique is non-destructive and it is therefore also possible to determine the gradual changes in composition on the nano-scale caused by e.g. chemical reactions or thermal annealing.

In the talk, several examples will be given of the practical application of these algorithms going through all analysis steps starting with the raw data and ending with the nano-structure result.

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- [2] S. Tougaard Surf. Interf. Anal. 26, 249 (1998)
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Monte Carlo Methods - Uncertainties in Peak Fits

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Monte Carlo simulation provides a valuable tool for understanding the uncertainties associated with data reduction for XPS/AES spectra.

The essence of the Monte Carlo procedures available in CasaXPS is to take a data set, remove the noise from the data, then repeatedly add noise to the synthesized data to generate a set of simulated experimental results and apply the set of analytical (peak fitting) operations to that artificial data. The results represent a distribution for each of the parameters from which an error matrix and tabulated parameter distributions can be extracted. Monte Carlo error analysis highlights when a quantification parameter is poorly determined by the combination of model and optimization procedure. It also enables the influence of constraints within a model to be evaluated. Adding information about chemical shifts, relative peaks widths and/or peak areas can alter the manner in which noise adjusts the parameters from their initial value. Monte Carlo derived scatter plots can often help to understand how rigid models based upon chemical knowledge can reduce the range of outcomes for a given set of parameters, and the visual feedback offered by CasaXPS Monte Carlo simulations provides an insight for analysts who feel less comfortable with a mathematical description of the same concepts.

Adjustments to peak parameters of this nature are inherent in any optimization procedure and the choice between the possible combinations of peak intensities is made based upon a chi-square or root-mean square metric [1]. The problem that Monte Carlo simulation addresses is identification of the point at which these goodness-of-fit metrics fail to produce results that can be believed, and then provide some means of illustrating the degree of uncertainty. The simulation procedure can also take account of the background as well as the peaks [2], and so determine a global error matrix for the calculation rather than one that focuses on the stability of the peak parameters alone. Examples showing the influence of these different factors were outlined.

The presentation focused on three examples of the use of Monte Carlo simulation plots: the NPL "synthetic PVC" peak fit, to show the effects of constraints, a high resolution PET C 1s spectrum, to show the stability of the "alpha substituent" peak and the complexity of the shake-up, and the C 1s of a real dental cement, to show that correlations are not always obvious [1].

Monte Carlo simulations do not provide magic solutions for peak fits, but can confirm the stability of a model and indicate which parameters need adjustment. This type of insight can help in understanding what (chemical) constraints do to a fitting procedure as well as provide a rule-of-thumb estimate for error bars.

[1] "The Casa Cookbook Part 1: Recipes for XPS data processing" N. Fairley and A. Carrick, ISBN 0-9549533-0-4, p. 353, and also Chapters 11 and 8.

[2] K. Harrison and L.B. Hazell, Surf. Interface Anal. 18 , 368 (1992)

A Guide to the Practical Use of Chemometrics – with Applications for Static SIMS

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Chemometrics was developed in the 1950s with its roots founded in the study of behavioural science in the 1930s. It is now widely used in analytical chemistry to provide identification and quantification for a range of spectroscopies and forms part of the burgeoning field of cheminformatics. Early users of TOF-SIMS were quick to utilize the benefits of this approach and today, with increased power and throughput of modern instruments, it has become a common method for data processing. However, for many scientists, there have been much ambiguities, confusion in terminology and jargon, low confidence in the results, and a general need for an improved understanding of basic and practical aspects. This situation needs resolution, since the procedures are well established mathematically and can be very helpful indeed for many practical analytical situations.

This workshop will provide a basic tutorial in the use of chemometrics, in particular multivariate analysis, and its application to the interpretation of static SIMS spectra and images. There will be a focus on factor analysis techniques including Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR), along with Partial Least Squares Regression (PLS). These will be placed in context with the wider field of cheminformatics. The workshop will aim to demystify the concepts and terminology, provide guidance on data preprocessing and present a route-map to select the most appropriate methods. Example applications to SIMS spectra and images will be given.

Data Processing for Angle-Resolved XPS Studies

Kevin Robinson

Thermo Fisher Scientific

This workshop session will demonstrate how parallel angle resolved XPS data may be acquired processed and analysed to provide qualitative and quantitative information. The practical demonstration will work through sets of angle resolved data and show the steps required to obtain SiO_xN_y film thickness and nitrogen dose measurements. The use of maximum entropy methods to reconstruct profiles from the data will be demonstrated and the assumptions and constraints discussed. To show the application of the methods to other materials, data from a self-assembled monolayer (SAM) material will containing a PEO-thiol will also be analysed to determine the orientation of the SAM..

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Nanoindentation & Microscopy:

Gaining Insights into the Small-Scale Mechanical Properties of Materials

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At scales of the order of a few microns and below, many of the mechanical properties of solids are scale-sensitive. Further, many state-of-the-art technological systems employ very small, but critical, materials assemblages and components at these same scales. Thus there is an urgent need to understand, be able to measure, and to predict, the mechanical properties of solids at high spatial resolutions. Nanoindentation - or *instrumented indentation techniques (IIT)* - is one such proven group of methods and has been one of the speaker's research focuses for nearly 20 years, especially in the domains of ceramic materials and of thin-film coated systems.

With regard to coatings, the Newcastle group has been continuing to determine the ways in which the *mechanical properties of coated systems*, including those with very thin (<100nm) coatings and multilayers, can best be characterised to reveal the scale-sensitive manner in which the coating 'adds value' to the substrate. This thrust is essentially to increase our fundamental understandings of materials behaviour to better inform current technology.

Our approach has been to critically assess the differing types of sample information available from simple load-displacement ($P-d$) curves, $P-d^2$ analyses and $P-S^2$ data (where S = contact stiffness), with parallel deformation-mode and microstructural insights coming from the use of transmission electron microscopy (TEM), high resolution scanning electron microscopy (HRSEM) and scanning probe microscopy (SPM). The differing scale-sensitive effective hardnesses and elastic moduli of such systems imply that there is a critical contact scale at which a *maximised elastic response* is experienced - a critical effect which still needs to be properly exploited for both friction and damage control.

Such techniques can also be used to explore unusual materials responses to contact stresses, such as pressure-induced phased transformation in silicon, where instrumented indentation can be used as a means of creating the necessary high pressures. While this has been a fertile ground for study over two decades, reflecting a long-term fundamental interest in the balance of deformation modes in solids (that is whether they deform plastically to preserve their crystal structures (e.g. by block shear, dislocation slip or deformation twinning) and/or undergo structural collapse/re-organisation/re-constructive transformations), it is still an area awaiting technological application of our understanding of these unusual effects.

This lecture will emphasise the critical linkages required between microstructural and mechanical characterisations and will highlight areas where high resolution microchemical investigations are still required before a complete property-structure understanding can be achieved.

Investigating the Surface Chemistry of Chiral Heterogeneous Catalysis

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The enantioselective hydrogenation of beta-ketoesters (e.g. methylacetoacetate, MAA) is one of very few examples of heterogeneous asymmetric catalysis. The key step in achieving enantioselectivity is the adsorption, from solution, of chiral molecules such as alpha-hydroxy acids (e.g. (R,R)-tartaric acid) or alpha-amino acids (e.g. (S)-glutamic acid). In order to achieve a detailed understanding of the modification process, we have carried out a systematic investigation of the adsorption of (R,R)-tartaric acid and (S)-glutamic acid on Ni{111}; 2-D Ni clusters on Au{111}-v3x22 and Au/Ni bimetallic surfaces using UHV-STM and RAIRS. In addition, using in situ PM-RAIRS, we demonstrate how modification temperature and solution pH influence the adsorption process. Finally, we report how the nature of the chirally modified Ni surface affects the subsequent adsorption (via vapor deposition in UHV or from solution) of the pro-chiral reagent, MAA. The implications for understanding the mechanism of the enantioselective heterogeneous reaction are discussed.

Time-of-Flight SIMS for the Molecular Characterization of Organic Surfaces

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Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) in static conditions is a powerful technique for the molecular surface characterization of organic materials. Indeed, this technique presents a high sensitivity with a high mass resolution and allows surface molecular imaging at a sub- μm scale. Moreover, when considering molecular secondary ions, an uppermost surface selectivity can be achieved [1].

However, there is still a need to increase the sensitivity, mainly for molecular imaging in order to improve the signal to noise ratio per pixel. For that purpose, two possible ways are to be investigated: to increase molecular emission (due to the sputtering process) or/and to increase ionization probability.

The aim of the presentation is, based on our recent results, to illustrate the molecular sensitivity of the technique and to present methods to increase the sensitivity.

After recalling the ToF-SIMS principle and the experimental set-up [2], the molecular sensitivity will be shown in a study of protein adsorption on polymer substrates [3]. Moreover, the possibility to obtain information about the conformation of adsorbed proteins will be discussed [4].

Two methods to the increase sensitivity will be presented for different kinds of organic samples, either by using cluster ion beam (C_{60}^+) instead of atom beams (Ga^+) [5,6] and/or by noble metal nanocluster deposition at the surface [7,8,9].

Finally, the present limitations of ToF-SIMS analyses will be pointed out in the case of micro/nano-structured surfaces produced by self-assembling in immiscible binary polymer systems [10,11]. The requirement of a multi-technique approach to get a complete understanding of the investigated system will be underlined.

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Characterization of Morphology and Electronic Properties of Surface Nano-Structures by Photo- and Reflection Electron Spectroscopy

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Interaction of 100 – 2000 eV kinetic energy electrons with matter is ideal to study phenomena on the nano-scale. This is so because their distance between inelastic scattering events is on the order of just 1 nm. Interpretation of the inelastic scattering processes that occur as the electron moves in the material can therefore be applied to extract information on the electronic properties of surface nano-structures. The energy lost by the moving electron depends on the distance traveled and variations are seen as the distance changes by only a fraction of one nm. The XPS and AES energy spectra vary therefore characteristically with the depth distribution of electron emitting atoms. This is the basis for the by now well known and widely used method to determine atomic depth distributions with nano-meter resolution by analysis of the peak shape.

Inelastic electron scattering is conveniently described by the dielectric function which describes the interaction in time and space between the electric fields of the moving electron and the valence electrons in the surface nano-structure. For practical applications in routine analysis, the concept of a universal inelastic scattering cross section is essential. To extract the electronic properties of the solid, the details of the loss structure must however be studied. This requires more comprehensive scattering models that take into account both the presence of the surface and the interaction with the static core hole in AES and XPS. Such models were developed by Yubero, Tougaard et al a few years ago and they have been successfully applied to study electronic properties by interpretation of XPS, AES and REELS experiments.

Complex algorithms, even if accurate, are not particularly helpful for practical analysis work unless they are implemented in the form of user friendly software and easy to follow procedures. In recent years, several such software packages were made generally available.

Some Novel Nanomaterial Processings

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We wish to present various experimental techniques for chemical analysis of nanostructured materials, and illustrate their use on two recent examples.

Undecyl-capped Si nanocrystals could play important role as biological markers. We have studied their optical and electronic properties by X-ray optical luminescence and X-ray emission, in order to determine the origin of the luminescence in this nanostructured material. In addition we have found that the SiNCs can evaporate intact at relatively low temperatures in ultra high vacuum. We have used this effect to deposit SiNCs on variety of substrates placed in the vapour. Photoemission spectroscopy showed that the undecyl-capped Si nanocrystals evaporate with no gross chemical changes, but atomic force microscopy, scanning tunnelling spectroscopy and confocal/ Raman luminescence indicate that the smaller particles are preferentially evaporated [1]. Aberration corrected scanning transmission electron spectroscopy confirmed the crystalline nature of the silicon cores in the evaporated material as well as the local chemical structure of individual SiNCs. The ability to evaporate and deposit nanocrystals in ultrahigh vacuum may be useful for the controlled preparation of new nanoscale quantum-confined structures.

The effect of atomic hydrogen treatment upon the surface of partially graphitized nanodiamonds has been studied by photoemission spectroscopy. The C1s core level peak and valence band spectra of a partially graphitized nanodiamond sample were compared with those following hydrogen treatment and following subsequent annealing. The data confirms that the graphitic layers which initially cover the nanodiamond particles can be removed through exposure to atomic hydrogen [2].

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- [2] M. Yeganeh, P.R. Coxon, A.C. Brieveva, V.R. Dhanak, L. Šiller and Yu.V. Butenko, submitted

Self-Assembled Monolayers on Silicon Surfaces

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Self-assembled monolayers can be formed at hydrogen-terminated silicon surfaces by reaction of unsaturated organic molecules. A wide range of chemical functionality can be incorporated in silicon surfaces and nanoparticles by this chemistry. The reaction can be driven thermally or photochemically and the monolayers cover the surface in a conformal manner so that the step-terrace structure of Si(111)-H is retained. These monolayers are anchored by a chemically inert Si-C bond and the reaction is essentially irreversible in contrast to the formation of gold-thiolate SAMs. The mechanism of the reaction is an unusual surface-confined radical chain process whose kinetics are described in terms of self-avoiding walks and have been studied using isotopic labelling experiments.