



Surface Analysis Forum Newsletter No. 20

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Meeting Announcement and Call for Papers

"Joint" Studies in Surface Analysis

British Aerospace, Bristol

Wednesday 3rd July 1996

The purpose of this meeting is twofold. Firstly, it is intended to cover the use of surface analysis to understand and improve the manufacture of "joints". Secondly, it presents an opportunity to describe and discuss the merits of "joint" studies, i.e. those involving collaboration between industrial, academic and/or service groups. These two topics can be linked together because the success of the first very often involves the second. It is all the more appropriate because one of the foundations of the UK ESCA User Group is to encourage the pooling of expertise in order to solve problems in surface analysis.

The committee would be delighted to receive contributed papers from members or others that have been involved in studies of mechanical or chemical bonding or have operated collaborative projects that have generated scientific understanding that would otherwise not be possible on a similar timescale. Experiences relating to the management of "joint" projects involving surface analysis, not necessarily confined to adhesion, would also provide a valuable contribution to this meeting.

If you would like to submit a paper please email a title and brief abstract **before Friday 29th March 1996** to S.Morton@uksaf.org

Or if you would just like to attend email me for details.

Meeting Report

Surface Modification by Design (or Accident?)

Aston University

Wednesday 10th January 1996

The Group was welcomed by Prof. Mike Cardwell, the Head of the Department.

John Sullivan (University of Aston) opened the morning session with a talk describing work done in his group on low energy, up to ~5keV, ion beam damage in semi-conductors and insulators. The collision can either result in reflection of the incident ion, giving rise to the possibility of analysis by ISS, or in penetration of the ion which causes sputtering or internal damage. For low energy incident ions, the sputtered atoms are emitted from within 1 - 2 atom layers of the surface whereas the implanted ion can go as deep as 10's nm . The damage produced in the form of dislocations can, however, extend for several microns into the solid.

At low beam current densities the disruptive effects of any single incident ion are complete before the next ion impact. This means that Sigmund's linear cascade theory should be applicable to the process and this model works for pure elements. However, for alloys or compounds the impact energy is shared differently between the atoms in the solid. Therefore, preferential sputtering is inevitable and the theory cannot be used in a useful predictive manner. The relative elemental sputtering yields of atoms in an alloy are not a good predictor of the likely amount of preferential sputtering produced in the alloy.

John has initiated a program to investigate the parameters that affect surface composition changes of metal oxides under ion bombardment in order to investigate a more appropriate theory due to Malherbe et Al. The amount of reduction suffered by the oxides is found to be independent of incident ion energy but is related to the beam current density used. Charge is also a significant factor since ions cause about twice the reduction produced by a similar dose of atoms. These factors lead to the conclusion that preferential sputtering is a combination of cascade sputtering and Gibbsian equilibrium segregation. In this case a term related to the relative elemental surface energies (surface tension modified by surface stress/strain effects) is found to be a better predictor of preferential sputtering composition. The mechanism of Gibbsian segregation requires self diffusion. However, at room temperature this is too slow to accomplish equilibrium so it is clear that ion bombardment increases the vacancy and dislocation population in the near surface region and thereby facilitates greatly enhanced surface diffusion. Since the mechanism proceeds to thermodynamic equilibrium, only those compounds that are thermodynamically stable are produced during sputtering, for example Al_2O_3 is never produced during reduction of Al_2O_3 to Al .



Graham Beamson (RUSTI, Daresbury) discussed the mechanism and measurement of damage in polymers such as PTFE and PET under X-ray irradiation. Spreading thin polymer films onto high secondary electron emitting substrates greatly increases the degradation rate so it is concluded that the damage process is mediated by photo- and Auger secondary electrons rather than the incident X-ray photons directly. Bremsstrahlung exacerbates degradation by generating both higher energy electrons and more low energy secondaries. Thermal radiation from the X-ray source is not a serious problem, nor are the very low energy, $<10\text{eV}$, flood gun electrons used for charge neutralisation with monochromatic sources.

The breaking of a C-H bond in a polymer produces a radical chain reaction which can only be terminated by mutual annihilation of two free radicals in forming a C-C bond. This leads to cross-linking in the polymer and the formation of higher molecular weight material. Alternatively, the breaking of C-C bonds can lead to production of molecules of lower molecular weight which may be sufficiently small to be volatile in vacuum, causing a pressure rise in the spectrometer. For example, PTFE emits CF_4 and C_2F_6 fragments under X-ray irradiation.

Since these are chemical reactions, the rate of degradation can be slowed by cooling. Alternatively, the degradation rate can be increased when there are additional elements in the polymer which are comparatively strong X-ray absorbers, e.g. fluorine. This leads to increased electron generation in the near surface region, particularly if the element has an absorption edge just below the X-ray energy. However, this propensity for increased degradation has to be balanced against the stabilising effect of the element in quenching free-radical reactions. For example, a highly fluorinated polymer should degrade faster than a less fluorinated variety due to the absorption effect. This is not always the case experimentally because there is less opportunity for radical reactions to take place. It is

found, however, that -CF₃ end groups are formed from broken C-C bonds and the average molecular chain length is reduced.

Polymers containing aromatic ring structures are most stable, as might be expected. Desorption of incorporated elements such as halogens depends on how long a side chain the element is attached to. If it is an end group, one bond has to be broken to release the halogen. If it is on a short chain, say C₄, then breaking any one of the bonds in the chain will probably result in loss of the halogen, albeit with some very short molecular chain attached.



Ian Gilmore (NPL, Teddington) described a novel modification to quadrupole SIMS which enabled a detailed study of the process of degradation of polymers under ion bombardment. The value of XPS is limited in this application because information on chain length and cross-linking cannot be extracted from the C1s or valence band peaks. The modification involves placing an additional neutralisation plate in front of the quadrupole. This is bombarded by a 1keV electron beam to produce secondary electrons which compensate for charging of the sample. The essential feature is that a bias oscillating at 6.5kHz is applied to this plate and the sample so that the energy of the emitted ions is swept. This has the effect of making the quadrupole insensitive to the different energy distributions of the emitted ion and molecular fragments. As a consequence, accurately reproducible spectra are obtained from any polymer and the variation as a function of ion dose can be monitored quantitatively.

Ian showed curves of the fragment intensity variations with time of bombardment, i.e. ion dose. Some fragments were unusually sensitive to degradation - undergoing a 10% change in intensity after an ion dose equivalent to 1 incident ion per 3000 surface atoms. The damage in PET was found to occur at ~3 times faster than PTFE even though this is opposite to the case in XPS.

In order to understand the formation of the fragments detected and their temporal variation, Ian has devised a model based on the probability of multiple bond breaking. As an example, to generate a C₃ fragment from a polymer side chain may only require one bond to be broken and sufficient momentum transfer in order to eject it from the surface. In contrast, to produce this fragment from the backbone of a polymer requires two bonds to be broken simultaneously from next nearest neighbour atoms without the bond between them being broken. Sufficient momentum has also to be transferred to the fragment at the same time. The probability of these cases can be calculated and the effect of fragments produced by one impact being ejected subsequently by another could also be taken into account. When this was done, the fits to the fragment intensity variation curves was found to be excellent. The most easily produced fragments decay fastest and fragments requiring prior damage grow in intensity from time zero through a maximum.

It was also found that there were limits to the size of fragments that could be produced by this mechanism and this limit was related to the range over which a single impacting ion can transfer its energy.



Roger Webb (University of Surrey) showed video recordings of Molecular Dynamics Simulations of ion impacts on single crystals. The technique involves solving Newton's Law of motion for a many body system. With past generation computers, simple pair-wise potentials were used and systems of up to a few hundred atoms could be solved in a few tens of hours. The latest machines use many body potentials applied to ten of millions of

atoms such that the deformation of a small chunk of material impacting on a solid can be simulated.

By far the greatest majority of ions simply follow channels into the solid, undergoing low impact events which produce no sputtered species and cause hardly any disruption to the lattice. Occasionally, if the ion impacts close to a surface atom, some sputtering occurs and considerable disruption of the solid results. Very rarely, a high impact event occurs where the ion hits very close to an atom in the solid. This can result in a large number (30-40) of sputtered atoms for one incident ion and produces vast amounts of lattice disruption. Events which produce sputtered atoms are very rare but they dominate our interest because it is sputtering that we are most interested in during, for example, depth profiling.

The impact of a single ion on graphite was shown. As the ion penetrated the crystal an acoustic wave was produced which radiated out from the impact site. However, the weak bonding between the planes of graphite allowed the incident ion to scatter in the gap between the planes and come to rest leaving a bump on the outer surface. These bumps have been detected using STM but were not explained until this simulation showed what was happening.

As a finale, Roger showed the impact of a large copper cluster onto a surface which caused tremendous disruption. He also showed a carbon "Buckyball" impact which was seen to bounce off a graphite lattice but stick to a silicon crystal.



Chris McConville (University of Warwick) described how low energy electron loss spectroscopy, HREELS, could be used to characterise damage in III-V semiconductors by studying the variation in plasmon energy as a function of depth. In these materials the plasmon energy is related to the compound present or the effective dopant concentration in the locality where it is generated.

From the commercial viewpoint it is important to produce clean, ordered substrates upon which to grow specialised semi-conductor materials for device manufacture. For {110} surfaces, cleaving in vacuum is sufficient. Clean {100} surfaces can be grown by MBE techniques but some materials require ion bombardment cleaning and thermal anneal cycles at close to their melting point to produce the desired surfaces. In these cases, the dopant concentration is synonymous with lattice damage.

In HREELS the electron interacts with the solid through long range dipole fields and, even though the electron penetration is very low, it is possible to detect the consequences of plasmon generation in the material through peaks with extremely small energy loss, $\sim 100\text{meV}$. In addition, the depth at which the plasmon is produced is dependent upon the incident electron energy so the sampling depth can be varied over $\sim 200\text{nm}$ for an electron energy up to 200eV .

Chris showed the small but clearly significant differences in the optical phonon and conduction band electron energy losses on $\text{InSb}\{100\}$ resulting from oxidation. He had also "depth profiled" the oxidation level by sweeping the incident electron beam energy.

Two experiments are possible to investigate the effects of damage. Initially, the electron interaction depth can be fixed and the annealing temperature increased after ion bombardment. Alternatively, the electron energy can be ramped. Using both approaches gives information about the rate and mode of recrystallisation and changes in the carrier concentrations as a function of depth. Chris showed that, on InSb , ion beam damage

always produces n-type material close to the surface and, since the first region to anneal is the surface, a brief anneal can lead to a p-n-p type structure extending over 100nm depth.



The afternoon session was devoted to workshops and an introduction to the UK Surface Analysis Forum World Wide Web page on the Internet. Anyone with access to the Internet will find the site at

<http://www.surrey.ac.uk/MSE/ESCA/ESCA/home.html>
(the capital letters must be entered as shown).

This site has been set up on the initiative of Dr Simon Morton (Webed. Fame at last ;-)
(E_mail address S.Morton@uksaf.org) who responded to a suggestion at one of the recent workshops that a web site be set up as an information resource in surface science under the auspices of the UK Surface Analysis Forum. Simon explained how the site was organised and demonstrated the features already available. After only a very short time Simon has produced an extremely professional, informative and technically useful facility which all members are urged to inspect in their own time. Meeting reports and future meeting information and registration forms will be available on the page to download directly.



Workshop Reports

Non-destructive depth Profiling?

Leader and Rapporteur Dave Sykes (ISST, Loughborough)

"Non-destructive depth profiling" was the title for the workshop, "a discussion of how to get reliable depth information by XPS and ion profiling" said the programme. I was really looking forward to this workshop which I imagined would go along the lines.....

Leader: Non-destructive depth profiling

Audience: You can't do that!

Leader: Oh yes you can!

Audience: Oh no you can't!

Then the leader would explain to a rapturous audience how it could be done.... that was until I was asked to lead the workshop!

We got off to a good start by agreeing that we really needed to re-define the title of the workshop, we were of one mind in thinking that non-destructive ion profiling was a contradiction in terms. We had heard, in the morning sessions, how ion beams damaged surfaces, both chemically and physically and that even exposing the sample to the X-ray excitation necessary for XPS analysis caused sample damage in some systems.

Against that background our topic was a non-starter. We discussed whether non-perturbing depth analysis was possible and, having considered angle resolved XPS, variations in photon energy and ion scattering (RBS, MEIS), we came to the conclusion that in some cases it may be possible.

Could we get reliable information by XPS and ion profiling?

Again we were not certain about this but felt that sometimes we could get useful information. In general, there was a feeling that depth profiling in XPS was a last resort, something one would not choose to do, but, if the customer insisted and was prepared to pay, then..... and sometimes there was a useful result at the end. A pragmatic view, from a user with a range of techniques available, was that given a sample from which depth information was needed, choose SIMS first, Auger second but XPS only as a last resort, a view I have some sympathy with.

Another faction of the audience, however, chose XPS every time. The question of depth resolution and depth range over which one might profile in XPS was raised and it seemed that our requirements were based on an acceptance of what instruments were capable of delivering rather than demanding more of them. For example, the depth one might sputter to was limited by the time taken to etch a crater large enough for XPS analysis rather than the need to profile a given distance; the depth resolution that was acceptable was defined by crater geometry rather than the fundamental limit of atomic mixing.

So, at the end of the day, can we get reliable depth information by XPS and ion profiling? No one was sufficiently confident to say "YES, YOU CAN!", equally no one was shouting "OH NO, YOU CAN'T!". It was more a case of not being able to show that the information was not reliable.



Damage Limitation in XPS/AES

Leader Len Hazell (CSMA Ltd)

Rapporteur Kathy England (University of Manchester)

The workshop started with a brief discussion of current ideas on the cause of damage under X-ray and electron bombardment. This was an extension of the results presented in the talks in the morning session and included a description of Auger induced ion emission by electrostatic field effects in ionic solids. All damage mechanisms were discussed, including mechanical and direct vacuum desorption.

The worst case situations were where high irradiation dose was required because long acquisition times were necessary, e.g. looking for low levels of elements in small areas and/or take-off-angle studies, particularly on very sensitive materials such as thin polymer films on metals.

Methods of acquiring spectra with the minimum possible X-ray dose were discussed. Use of largest possible area at the poorest acceptable resolution with the minimum settings of instrument "settle times" were recommended. Reducing the sample temperature was useful provided adsorption from the vacuum was not a problem. Acquiring and keeping each individual sweep and only adding together those that showed acceptable damage had been tried. Datasystems do not allow this routinely but it is a way of inspecting the data before quantification.

Use of monochromators was universally accepted as the most advantageous way of damage limitation provided the flood gun energy is as low as possible and definitely <10eV.

On large area samples that are "known" or expected to be uniform over the surface it is

possible to use small spot X- ray sources and move the sample between acquisition of each spectral region or sweep. This "fresh sampling" strategy would give the minimum possible amount of degradation but there was some scepticism as to whether the quantified data would be acceptable. It was felt that the initial assumption of surface uniformity may have to be previously justified, although conventional large area sources effectively average any spatial variation out in a similar way.

There was similar scepticism as to whether post acquisition correction could be carried out in any scientifically valid way after the rate of degradation had been established on a similar material. It was pointed out that the rate would have to be determined on the same material and establishing what this was required damage free analysis in the first instance.

Finally, data processing methods such as deconvolution were discussed which would enable poorer data quality to be tolerated.

In summary, it was agreed that samples should always be checked for the likelihood of rapid degradation and a strategy such as "fresh sampling" adopted to minimise this in the first place. As always, the minimum amount of data manipulation is advisable and it was generally accepted that comparison of good and bad samples was the safest way to proceed in commercial analysis.



The Proposed Instrument Specification Standard.

Leader & Rapporteur: Bob Wild (IAC, Bristol)

This workshop was organised to help with the production of two proposed standards for Instrument Performance Description in AES and XPS. The scene was set by describing the progress during the last year. All the major instrument manufacturers had been approached with a request that they provide a description of their current methods of specifying instruments. Specifications had been received from all the manufacturers and the information used to produce tables showing where there was and where there was not a common approach. These tables had been used during discussions at the last ISO meeting to determine where a specification could be accepted. Following that meeting two draft work items have been produced for both AES and XPS. These were considered by those present at the workshop.

Items discussed included the anode power to be used for maximum counts. It was felt that a power should be used at which the anode would be guaranteed for a given period, but how was this to be specified. Performance drift was also discussed with some wanting data over short periods of say ten minutes while others were more concerned with long periods of, say, 12 hours. A number of useful comments were made during the workshop and the draft work items will be modified prior to sending out to member countries.



Report of ISO/TC 201 Meeting in Pacifico Yokohama, Japan


21-23 September 1995

The 4th full meeting of the ISO/TC 201 Committee, together with subcommittee meetings

of SC1, SC2, SC3, SC4, SC5 and SC7, took place in the Pacifico Yokohama Congress Centre, Yokohama, Japan from Thursday September 21st to Saturday 23rd 1995. This is a brief report of the proceedings of those meetings.

Dr Powell took the Chair and set the scene for the meeting by re-stating some of the more important rules and explaining some important changes. In particular he drew attention to the requirement for realistic timescales within a three year band to be set for each work item to be brought to a conclusion


The seven members of the UK delegation were Mike Wells, Dave Sykes, Albert Carley, Bob Bulpett, Alan Carrick, Steve Harris and Bob Wild. VAMAS was represented by Martin Seah



SC1 - Terminology (Chairperson M Seah)

During the year a letter was sent to all members of the WG proposing to review ASTM 673 document. A copy with some changes was then circulated. Following comments and

discussions some terms were deleted and approximately 80 new definitions added to get the ball rolling. It was proposed that a NWI be prepared and submitted by ANSI. To do this WG1 would be terminated since the review had now been completed and a new WG created to define the terms



SC2 - General Procedures (Chairperson C Anderson)

Charles Anderson had taken over the chair of this committee from Guy Davis who had resigned.

WGI - Specimen Handling (Convenor C Anderson)


Two draft guides have been prepared with similar titles; Specimen preparation, mounting, and analysis for AES, XPS and SIMS. The larger document is intended for the provider of a surface analysis while the shorter document is intended for the purchaser of the service.

WG2 - Reference Materials (Convenor W Gries)

Werner Gries reported that the search was continuing for suitable reference materials. In particular for an ion implanted reference standard for SIMS. At Golden two new work items were proposed; NW1 concerned the criteria and parameters for certification of ion-implanted reference materials for analysis of semiconducting wafers, NW2 was concerned with ion- implanted dosimetry calibration. NW1 has been sent to the secretary of SC2 to be submitted to ISO. NW2 will only be submitted after NW1 is well under way.

WG3 - Reporting Data (Act. Convenor S Harris)

Steve Harris described the information required when reporting spectra. All data should be traceable with the minimum amount of data on each spectrum. It was felt that each spectrum should include 1) Laboratory, 2) Sample name/description, 3) File No., 4) Date, 5) Peak Label (where appropriate), 6) Axis labels, 7) Specific Comments.



SC3 -Data Treatment and Management (Chairman D Sykes)

Albert Carley reported on the years progress. In particular the progress in getting the NWI from WGI Data Transfer format) to the stage of voting to become a committee draft and that NW 1 from WG2 (Data models) failed on ballot.

WGI - Data Transfer and Storage (Convenor M Seah)

The US delegation led by K Bomben argued long and hard against this method of data transfer format becoming a standard. However they appeared to be in a minority of one and a number of formal votes supporting the NWI were received at the meeting.

WG2 - Surface Science DataModels (Convenor D Watson)

This WG has put forward a NWI with the following title and scope; Title - A data dictionary for the description of XPS and AES data records.

WG3 - Algorithms for Data Treatment (Convenor P Coxon)

Pressure of work has forced the resignation of Peter Coxon and Mark Dowsett. However Mark Dowsett has produced a discussion document on peak fitting. Martin Seah said that many of the algorithms could be defined under SCl. It was proposed that WG3 should be terminated but that it should be reconstituted as a study group.



SC4 - Depth Profiling (,Chairman S Hofmann)

WGI - Definitions and Procedures (Convenor S Hofmann)

The group considered methods to independently measure crater depth and more work was considered necessary here. ASTM have a group working on this. There was some discussion on the most suitable methods. agreed to write documents on each technique.

WG2 - Reference Materials (Convenor K Kajiwara),

where was considerable discussion and criticism of both the title and scope of the document. There was concern as to whether instrument performance was being measured in which case only one layer was required or a property of the material specific to multilayers. In Japan it was required to check the depth resolution in sputtering in the semi-conductor industry



SC5 - AES (Act. Chairman C Anderson) and SC7 - XPS (Act. Chairman R Wild)

These two committees have much in common with two joint working groups. They therefore each dispensed with the bureaucracy before adjourning to consider the WG business.

SC5/WGI - Quantification (Convenor C Anderson)

There was a proposal for an International Standard to specify procedures by which Auger electron and X-ray photoelectron spectral intensities may be measured. Then T Sekine presented the need for AES energy calibration followed by Martin Seah with a proposed NWI with a form 4 and a draft of a standard for XPS energy calibration. It was agreed that

a working group be formed to develop these two NWIs with Martin Seah as convenor. It was agreed that the WG should be located in SC7 since this would ease the administration.

SC7/WG1 - Instrument Specification (Act. Convenor R Wild)

Bob Wild reported that the manufacturers had been approached requesting methods specifying instrument performance. The delegates were then asked for guidance on areas where it might be possible to obtain agreement and move forward with a NWI. Many areas were amenable to specification but others were highly contentious. In particular problems with specifying power, specimen influence .etc. were acknowledged to be difficult. It was however agreed that two NWIs should be produced based on the comments in Yokohama one for AES and one for XPS. Mike Wells gave a presentation of the UKs plans for the 1996 meeting. The dates will be July 11-13 just ahead of QSA-9 and the meeting will take place in the Stakis Hotel in Arundel.

New VAMAS Project - XPS of Insulators

Charge Neutralisation
Charge Stabilisation
Charge Referencing

A new VAMAS project is to start to look at methods for charge neutralisation, stabilisation and referencing. This is an initiative from Germany (Unger at BAM) in conjunction with Sweden (Gelius of Uppsala). They will put effort into colloids/Au particles/and similar methods. To balance this we need people to

(i) provide the push in other areas - foil wrapping, mesh screens, electron flooding, etc.

(ii) to analyse test samples to other's protocols as far as possible.

Anyone interested, even if you can only do a small amount of work in the future, should contact

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