Surface Analysis Forum Newsletter No. 19 Autumn 1995

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Reference Materials for Surface Analysis

Questionnaire on the type of reference materials currently in use in Surface Science labs.

Surface Science Services Questionnaire 1995

Questionnaire to determine the facilities available within the surface science community.

The results will appear on the web.

British Standards Institute, Secretariat CII/60 - Surface Chemical Analysis

Report of Progress of CII/60 and ISO/TC 201.

Meeting Announcement and Call for Papers

Surface Modification by Design (or Accident?)

Aston University

Wednesday 10th January 1995

The deliberate introduction of ion beam, electron or X-ray damage to sample surfaces is used extensively for lithographic processes in the manufacture of semiconductors. The same surface modification effects are usually a nuisance in surface analysis and all effort is made to avoid them where possible. The theme of this meeting is intended to bring together those who have studied sample degradation processes because of their utility and those who would like to know the origin and extent of these effects and how to avoid them.

The committee would be delighted to receive contributed papers from members or others that have studied sample damage by incident beams. Data regarding the measurement of sample degadation of materials during surface analysis would also form a valuable contribution to this meeting.

Please forward a title and brief abstract before Friday 29th September 1995 to:-

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Meeting Report

In Support of Manufacturing

Cranfield University

5th July 1995

The Group was welcomed by Sue Impey on behalf of the Surface Analysis Group in the Support to Industry and Management Section at Cranfield.

The morning session was opened by Dave Sykes (University of Loughborough) who discussed the reasoning behind the choice of technique. At Loughborough the initial selection of technique may be based on general "suitability" and will include considerations such as area to be analysed, sample conductivity, stability and whether quantitative or qualitative elemental, chemical and/or trace analysis is required. Inevitably, pragmatic considerations such as instrument availability, sample throughput required and, of course, cost also play a significant role. Overall, the analysis should be fit for purpose and should "meet the customers expectations at a price they can afford". Dave suggested that the analyst should disregard the possible consequences of the results, eg. job losses, litigation or bankruptcy, although these are bound to be in the back of their mind.

As examples, Dave cited a company making Plaster of Paris cottages which had problems with painting due to the use of excess silicone mould release agent. In this case SSIMS is used if the requirement is show that silicones are there but XPS would be used if the problem was "How much was there?".

A second routine dynamic SIMS problem was calibrating the acceptable level of trace metals from three furnaces in a semiconductor manufacturing plant. Once the levels rise above the critical value the whole batch of material must be discarded because the processed devices will be useless. Although this result places a severe cost on the plant, the cost of rejecting the batch of completed devices is far greater.

Dave cited a case study where only a tiny fragment from a valuable Greek sculpture was available. In this case the sample size virtually decided that the LIMA technique should be used. At the other extreme, a building with hundreds of 2m x 1 m glass panels showed dark discolouration which was an indication of corrosion of the coating on the glass. The consequences of this analysis were dire for the installer who had not stored the glass properly.

Graham Smith (Shell Research) described how fundamental analysis of oil seal degradation can lead to suggestions for better tests.

An engine oil is a sophisticated blend of additives which has to pass a long list of engine manufacturers specified tests. The crankshaft oil seal is a fluoroelastomer and must not degrade in hot engine oil and leak so it is subjected to a 7-day compatibility test where it is heated in fresh oil at 150C under tension and then a full tensile test is performed on the seal. A loss of less than 20% of the initial tensile strength is acceptable but more than this and the oil fails the test.

These fluoroelastomers are well suited to XPS analysis, particularly using a monochromator, because a large chemical shift occurs for each fluorine substitution onto the hydrocarbon backbone. SEM images of the seals after testing show a crazy paving effect and EDX analysis clearly indicates loss of fluorine from the surface. XRD indicates that the fluorine component has broken down and reacted with calcium hydroxide in the filler to produce calcium fluoride. Cutting a 10 degree taper section and analysing using small spot XPS shows that it is one part of the copolymer blend that degrades preferentially in this manner and this has provided some additional flexibility for developers to formulate new materials. For example, the presence of amines catalyses the cross-linking of CHF groups and allows HF to be formed which can react with the filler.

Use of CF2 groups instead would cause less reactive F2 to be formed.

Graham pointed out that although the test is carried out using a specific fluoroelastomer, this is no longer the favoured formulation used to make oil seals. Also, the test is run using fresh oil which is more likely to fail the test and is unrealistic in a motoring context. The work described here has increased understanding of the degradation process and enabled a more relevant test procedure to be proposed.

Dick Chappell (Pilkingtons) described the AES/XPS analysis carried out in support of glass production at Pilkingtons. XPS is used for general surface analysis and depth profiling AES for analysis and characterisation of coatings on glass.

The bottom surface of float glass contains predominantly Si, O, Na, Ca, Mg and some Sn from the molten tin upon which the glass is floated to form sheets. The top surface has a lower level of Sn (from vapour deposition) and some sulphate and chloride. Tin concentration profiles vary considerably due to glass thickness and bath conditions. XPS produces thermal damage after extended exposure and AES gives electromigration problems and peak shifting that can be so severe as to subject the channeltrons to unexpectedly high count rates - causing reduced lifetimes. An additional problem is the accurate positioning of both electron and ion beams due to local charge build up and deflection of the beams. With high sputtering requirements it is also possible to contaminate the electron optics with insulating material that requires mechanical removal.

During weathering Na, Ca and Mg are preferentially leached, in that order, but under static conditions the concentrations of the leached elements build up and Mg is often back precipitated.

There are many patented coatings for glass to achieve desired heat transmission or reflection. Most of these are carried out on an enormous scale on whole sheets of glass on conveyor belt systems. Some recently developed systems use sputtering or CVD coatings technology on the float bath to coat as the glass sheet is manufactured. Dick described a number of these coatings in which a metallic layer is incorporated as the active layer but this has to be protected by overcoating with a stabilising oxide such as SnO2. One particular system has an aluminium on silver layer structure. During heat treatment, as used for toughening, the aluminium diffuses through the silver layer clearing it of impurities as it goes. Some coatings are surprisingly sophisticated - K glasses have an F-doped SnO2 layer with an SiCO undercoat to produce an interface which reduces reflection.

With such coatings technology it is no surprise to find that many problems occur because the coating is susceptible to "corrosion" under adverse conditions. Many problems arise because the glass has not been treated with sufficient care and according to instructions during storage and installation.

Sue Impey (Cranfield University) described work carried out within the surface analytical facility in support of the research and development programmes in the School of Industrial and Management Science at Cranfield

The first example was a study of the Cr6+ content of the fumes from MIG welding. Reference Cr203 and CrO3 were studied along with samples of the fumes collected on filter papers. Initial results indicated no Cr6+ but it was found that Cr5+ degraded in air to Cr3+ although it was stable in vacuum. This meant developing rapid sample collection

strategies and anaerobic sample transfer.

A second example was given of a Ti:Fe alloy rocket fuel container corrosion due to the presence of N204 oxidiser. An important aspect of this work was definition of the oxide thickness. XPS was used with argon ion depth depth profiling but the alloy is so reactive that it is impossible to remove the oxide completely at the interface. The approach adopted was to ensure that sufficient oxygen was available to keep the surface oxide in equilibrium but to monitor the onset of carbide formation as an indicator of the position of the interface. This occurs because there is no carbon in the oxide itself but once the titanium substrate is exposed it reacts with CO in the vacuum to give a measurable carbide-like feature.

A third example was taken from examination of NiZn plated high strength steel fasteners. The normal cadmium plated devices are susceptible to hydrogen embrittlement and the NiZn alternative can also be affected depending on plating time and pH. An XPS depth profiling study of very thin plated films showed that under the right conditions the Ni layer forms an interfacial barrier to hydrogen between the Zn and steel. In this study the shallow crater edge was imaged by SEM/EDX to confirm the existence of the Ni layer at the interface.

Finally, Sue described some work on graded coatings consisting of mixed BC and WC deposited on steel using a Ni alloy buffer layer. BC has been found to be the most erosion resistant ceramic and is finding increasing applications in high-tech coatings research. XPS is particularly advantageous for studying the chemistry of BC.

Len Hazell (CSMA Ltd) gave his personal view of the surface science support requirements of UK Industry and how well this is serviced by the various surface analytical facilities within the UK. The recession has enforced many recent changes in UK Industry's view of "outsourcing" their analytical requirements and any business now has a number of options to solve its surface problems. The UK Surface Analysis Forum Surface Science Services Survey shows that the UK is unique in its provision of a roughly even split of contract surface analytical facilities involving Universities, Industry and Government or ex-Government agencies. CSMA Ltd is the only independent commercial laboratory offering both electron and ion spectroscopy service in the UK.

Len listed some of the factors which influence manufacturing industry to sub-contract work into the UK service providers network. Clearly, cost, speed of response, quality, expertise and availability ofspecialised facilities are key parameters. However, there are also various European or UK Government subsidy schemes designed to foster closer ties between Industry and the Academic community for longer term projects.

There is a major difference between the UK surface analysis provision and the "rest of the world". Elsewhere, it is illegal for Universities to become involved in day-to-day problem solving in competition to industry and/or independent analytical laboratories. By contrast, in the UK, Government policy has virtually necessitated that Universities compete. Len's view is that this undermines the true value of the industrial laboratory and the independent analysts and does not help the UK surface science base in the long term. He also believes that the Universities do not want to be put under such pressure and would rather be doing what they do best, ie. teaching, fundamental underpinning of the techniques, instrument development and long term applied scientific research. These are areas which he feels have been neglected recently in the UK. For example, with few exceptions, all instrument development is being carried out by the major instrument manufacturers (who are no longer UK owned) and practical technical underpinning is limited to standardisation work

at NPL and BSI initiatives (funded largely by UK User groups).

In summary, Len indicated that problems within manufacturing industry will not go away and the cost culture will introduce more last minute requests for support which demand faster response. We are continually seeing problems at a smaller scale and this trend will continue. While the accountants are still in charge of UK industry there will be more "outsourcing" in the immediate future with some sole provider arrangements and increasing access to networks of analytical services. However, this will only form a stable surface analysis infrastructure in the UK if the government encourages a clearer definition of roles and ensures adequate funding for development.

The afternoon session was dedicated to workshops.

Charge Neutralisation in XPS/AES.

Leaders Len Hazell/Graham Beamson

Raporteur Len Hazell

The workshop began with a discussion of where charge neutralisation is essential in XPS and AES and what the potential benefits are. For XPS, the higher energy resolution from monochromators is available with increased sensitivity, lower sample damage and smaller spot sizes but the neutralisation has to cope with uniform and differential charging. In AES, charge neutralisation is often necessary to obtain a spectrum of any kind.

Charging problems arises on insulating materials due to an imbalance of charge "in" compared to charge "out" of the surface. The precise nature and level of charging depends on the incident beam energy, flux distribution, surface inhomogeneity and roughness effects. These create local electrostatic fields which distort the electron optics behaviour of the analyser and affect the voltage referencing and sensitivity, making quantification unreliable.

Graham Beamson described some methods of charge neutralisation that he had utilised on the Scienta instrument. Simply using a conventional twin anode as well as a monochromator can help but the low electron flux available, the sample damage and the increase in background make this approach unsatisfactory. Early types of electron flood gun had low emission current at the low beam energies used and were particularly poor if the sample angle was changed, as for example in a take-off-angle experiment. The latest flood gun is fairly sophisticated and specially designed for the Scienta. It uses a pulsed filament heating/extraction cycle to give a very monochromatic line profile beam onto the sample. It is a powerful source so it incorporates a dog-leg to avoid infra red radiation from the hot filament damaging the sample. It works well at all sample angles.

Discussion indicated that it was probably not necessary to go to such lengths to obtain satisfactory charge neutralisation on other instruments and some clear ideas were obtained on the approach to take. It appears to be most important to align the sample normal to the flood gun in order to avoid the charge build up deflecting the low energy electrons, typically less than 10eV. the flood gun energy should be adjusted to the lowest possible value but such that any additional voltage shifts the spectrum to a lower binding energy by the same amount.

Other methods such as using a grid suspended above the sample surface, bombarding a nearby gold foil with ~ 100eV electrons to generate a flood of lower energy secondaries,

applying very thin in-situ metallic coatings, use of wet samples and using argon ion bombardment to induce surface conductivity in polymers through surface damage were explored. Bob Bulpett (Brunel) had successfully eliminated differential charging on one oxide sample by applying an extremely thin gold coating from a SEM plasma coating unit. The gold peaks were not intense and did not affect the analysis but confusion due to differential charging was removed.

Surface Analysis on the Production Line.

Leader Steve Harris (British Aerospace)
Raporteur Sukanta Biswas (Cascade Scientific)

The group consisted of companies with in house surface analysis instrumentation, equipment manufacturers and service laboratories. Several questions associated with QA were discussed. Surface analysis itself is quality assured from some labs but not others. Certainly the feeling was that the customers required quality assurance in analysis and there was a demand for QA work in surface analysis, particularly using the mature techniques of AES, XPS and SIMS. ISO9000 is thought of as a good idea and the QA aspect in general was considered important in promoting surface analysis.

The topic of "round robins" was discussed and thought to be a good idea if the experiments are designed properly. Wrong choices of materials and experiments often wastes time and money.

Current limitations in the use of surface analytical techniques in the QA environment covered topics such as, the requirements for better databases, totally automated analysis, reduced cost instruments. All were seen to be important to encourage wider use of surface analysis in manufacturing.

The question of whether instruments will ever be widely installed directly on the production line to check if a product passes or fails was thought to depend on what information needs to be provided. Whether pictures, numbers, depth profiles or some other result is presented was probably a very individual thing, varying from client to client. Also, the question arises as to how we present ourselves to the customer. Are we surface scientists, surface analysts or technicians? Ultimately, we need to change the customers, and their managements, views of the utility of surface analysis in order to keep surface science alive in QA applications.

Depth profiling in AES/XPS

Leader Bob Wild (IAC, Bristol)

Raporteur Albert Carley (University College of Wales, Cardiff)

The workshop concentrated on sputter depth profiling. The two main problems encountered were changes in the chemical state of the surface, such as reduction of metal oxides by ion bombardment, and preferential sputtering which leads to a build up of one of the overlayer components at the substrate overlayer interface. It was felt that the processes involved were not well enough understood to allow reconstruction of the true

profile from the measured one. It is important that the bottom of the eroded crater is as smooth as possible. This is best achieved by rotating the sample during sputtering which also leads to a better defined interface. However, few instruments have this capability.

Measuring the crater depth after profiling allows the sputter rate to be calibrated. Techniques such as SEM and AFM (provided the scanned area is large enough) may be useful for this.

After a brief discussion on some experimental details, such as choice of source parameters and beam and sample geometry, Bob gave his views on the potential problems involved in computer controlled depth profiling. The main difficulty lies in allowing the computer to calculate signal intensities using an adequate algorithm applied within a chosen energy window. Using integrated peak intensities rather than peak heights accommodates changes in peak shape (chemical state) across the interface.

The final discussion concerned the need for reference materials in depth profiling. Few exist, although several are proposed and there is a need for a cheap, widely available material. Pilkingtons tin oxide coated K-glass was suggested as a possible secondary standard and Dick Chappell at Pilkingtons kindly offered to supply some pieces upon request

The UK Surface Analysis Forum AGM

Treasurers Report

The group made a small profit during 1994/95 which was inflated due to inclusion of the payment from the 1993 Nottingham meeting in the 1994/95 accounts. The group has awarded an unusually large number of Prizes during the year in an effort to catch up after a delay caused through loss of literature search facilities in past years. The Group has also made an agreed payment to support the BSI sub-committees and its aim continues to be to break even each year, maintaining a sufficient cash balance for contingencies. In this regard we shall continue to keep the meeting costs as low as possible.

Secretaries Report

The Group had run the usual two meetings during the year and both had been well organised and attended. The Aberystwyth meeting had been a departure from normal, in that it was spread over two days in order to ease travelling. The balance of membership had shifted slightly during the year, increasing the numbers from the academic sphere at the expense of those from industry. The committee continued to maintain involvement with BSI standards committees, it had also collated a surface science services survey into a document that is available to members.

Constitutional Amendment

It was agreed that Clause 7.1 be ammended to state that the committee shall consist of three executive officers and at least three other officers.

Elections

Jim Castle (University of Surrey), after many years of service on the committee, had decided to step down due to pressure of other commitments. He was thanked by the Chairman for his invaluable contribution and has been given an open invitation to attend committee metings when availability permits.

Steve Harris and Martin Seah were re-elected to the non-executive posts on the committee. Graham Smith (Shell Research) was elected to the vacant post and Kathy England was elected to the post of New Members representative on the committee, a post she had carried out in an unofficial capacity for two years. All had been proposed and seconded in accordance with the constitution.

The Chairman thanked the officers for their work on the committee during the year and closed the AGM.

Reference Materials for Surface Analysis

Given the ever increasing need for accurate quantitative information in the field of surface analysis, where do we get or reference materials from in order to do the work? Below is a small questionnaire concerning the type of standards used, their source and the techniques they can be used with. The results of the questionnaire will be published in the Newsletter later in the year. Please send this questionnaire back to me along with the Surface Sciences Services Questionnaire which is below.

Reference Materials Questionnaire

Material Supplier:
List of Materials Available:
Applicable to the Following Techniques:

Other Information:

Surface Science Questionnaire

A database is being compiled of the Surface Science facilities available at the home laboratories of UK Surface Analysis Forum members. The intention is to publish the results as part of these WWW pages.

Service or Group Name:-
Instruments/Techniques available
Other facilities (fracture Stages etc.)
Group Specialisms
Additional Information (such as non-surface science analytical facilities offered)
Return replies to:-
Dr S. J. Harris Sowerby Research Centre, B.Ae, FPC267, PO Box 5 Filton Bristol

Tel. 0117-9363624 Fax. 0117-9363733

E-mail Steve.Harris@src.bae.co.uk

British Standards Institute

Secretariat CII/60 - Surface Chemical Analysis

Report of Progress of CII/60 and ISO/TC 201

This is a convenient time to report the progress that has been made with the CII/60 committee and within the international committee ISO/TC 201 since we are about to hold the third meeting of the main committee in Japan from September 21 to 23rd. I also feel that you should get a regular report in the newsletter to give you some indication of the value you are getting for funding the work of the UK committee and the two UK based subcommittees (SC3 Data Handling and Treatment (Albert Carley) and SC7, XPS, (Bob Wild)).

All the subcommittees have now been constituted with chairmen, secretaries, convenors and experts. During the past year work has begun in earnest to produce standards in all areas. In some areas, where documentation akeady existed that could be readily modified to become a standard, progress has been fast but in others, where no such documentation exists, the progress is much slower. The two UK subcommittees are examples of each situation. In SC3, Data Treatment and Handling, Albert Carley has managed to bring the new work item on the data transfer format to the stage where it will be voted on in Japan to reach the final stages by becoming a committee draft (CD). This is particularly pleasing for those of us in the UK Surface Analysis Forum who first encountered this some years ago via Bill Dench and Martin Seah. In SC7, XPS, we are working towards a standard to describe how an instrument's performance should be specified. This is still in the very early stages but John Watts has identified the manufacturers and they have kindly let him have their methods of instrument specification. From these we hope to put together a document that will be discussed in Japan and chart the way forward but it is unlikely that this will become an ISO standard for some time yet. Other members have been working in related areas; Martin Seah is attempting to identify terminology that can be contentious by having more than one meaning and to then clarify one use of each term while Bob Bradley and Steve Harris are working towards a standard way for reporting data.

Next year the ISO/TC 201 main committee will meet in the UK, from July 11th to 13th, just prior to QSA 9 which is to be held at the University of Surrey. It is proposed that the ISO meeting should be held in a single hotel near to Guildford and John Watts and Mike Wells are looking at possible hotels. This event is unlikely to be held in the UK for at least another six years and we feel is an opportunity to demonstrate our commitment to standards in surface analysis. We also think it is important that we give our intemational delegates a good impression of the UK by making it a pleasant stay for the delegates.

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