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Using Electron Spectroscopy for Chemical Analysis (ESCA) in Failure Analysis: Some Recent Developments

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USING ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA) IN FAILURE ANALYSIS: SOME RECENT DEVELOPMENTS

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Abstract

Electron spectroscopy for chemical analysis (ESCA) is receiving increased attention as a surface-sensitive failure analysis technique because of several recent developments. These are: first – substantially improved spatial resolution, allowing a much broader range of problems to be studied; second – new ways to apply analytical results to practical problems, resulting from better technical understanding of ESCA and better data reduction techniques; and third – the development of sample handling systems which can handle large, outgassing samples, making ESCA a relatively non-destructive technique.

In this paper we consider ESCA's niche as a surface analysis tool, and discuss the impact of the new features mentioned above on the types of analytical problems we have routinely encountered in failure analysis and problem solving for industry. It should be noted that this technique is also known as X-ray photoelectron spectroscopy (XPS). The terms ESCA and XPS describe the same technique.

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Introduction

Failure analysis is a very demanding application for most analytical techniques. The samples to be studied are usually complex and heterogeneous, consisting of metallic and dielectric elements in close proximity with relevant features often buried or otherwise inaccessible to routine testing methods. Morphological studies are not always definitive in assigning the cause of a failure, and compositional techniques are resorted to in order to aid or confirm a diagnosis.

Surface techniques, particularly Auger electron spectrometry (AES) or sometimes secondary ion mass spectrometry (SIMS) have been very successfully used in this capacity. While sensitive to only the first 3 to 10 layers of atoms on a surface, these techniques often provide definitive information for several reasons. In the first place, most defects, errors, or contaminants affecting a fabricated part are introduced through a surface during some process step. Secondarily, an increasing number of modern technologies rely in a very pivotal way upon the surface properties of materials (semiconductor devices, optical elements, polymeric materials, and catalysts are examples).

In the past, ESCA has not been used extensively for failure analysis, although it has been a productive analytical tool for years. When we examine the reason for this, it is clear that one of the features critical to those applications – spatial resolution – has been missing. In order to study heterogeneous samples effectively, an analytical technique must focus on small features (AES does this with a focussed electron beam and SIMS with a focussed ion beam), but ESCA, because of the difficulty of focussing X-rays, did not.

Given a solution to the spatial resolution problem, ESCA does offer a number of unique advantages that complement, extend, or surpass the other techniques. These include: (a) the ability to more easily analyze insulating samples as well as conducting ones, (b) extremely low sample damage, (c) high tolerance to poorer vacuum, and (d) the presence of chemical information for many surface atoms. However, these features have not been widely exploited in failure analysis because of the problem of spatial resolution.

New Developments in ESCA

A number of innovations have appeared in the last few years which dramatically change the

situation just described, and make ESCA an increasingly useful analysis tool (2). These are described in more detail in the following paragraphs.

High Spatial Resolution

Much of the success Auger electron spectroscopy has had in failure analysis is due to its excellent spatial resolution. The microcircuit field and the study of metallurgical problems are strong examples of this. There are, though, a broad range of practical applications for which Auger electron spectroscopy is unsuited, either because the sample (or feature being studied) is non-conductive, or because it suffers considerable damage from the electron beam, as in the case of organic materials.

Several manufacturers have recently introduced ESCA spectrometers with small analysis areas, as small as 150 microns in diameter in our case. While not in the same league with AES, this represents an analysis area 1000 times smaller than was available several years ago. There is a broad range of new applications which this capability can uniquely address. Some of these are illustrated graphically in Figure 1. While several different technical approaches have been used to obtain this increased resolution, the approach reported on here involves focussing a small, bright X-ray source onto the sample with a spherically bent quartz diffractor. The resulting well defined image on the sample defines the analysis region.

Improved Data Analysis/Interpretation

ESCA has been used for fifteen years as an industrial problem solving tool, during which time, a number of very effective procedures and data handling techniques have been developed. Foremost among these, in the authors' opinion, is the ability to quantitate spectra routinely to obtain the relative atomic abundance of the constituents on a surface. Since ESCA can detect all the elements in the periodic table except hydrogen, it is thus possible in most cases to give a complete description of surface composition; i.e., to tell what is not present to defined detection limits as well as the relative concentration of constituents found to be present.

Quantitation is a relatively straight-forward procedure (5) when the sample is homogeneous and the calculations can be automated in a computerized data system. The photoemission process is well enough understood so that theoretical line intensities can be used, and because matrix effects are small, no sample-dependent corrections need be made. Peak areas (A_i) of relevant ESCA lines are measured and the relative number of atoms of element i present (N_i), are computed from the relationship:

$$N_i = A_i \, / \, (\sigma_i \, \chi(E) \, T(E))$$

where σ_i is the line strength for element i, $\chi(E)$ is the electron escape probability (a function of the electron energy involved) and $T(E)$ is the spectrometer efficiency at that energy.

For the work presented here, these values are normalized so that

$$\sum_i N_i = 100\%.$$

This simple quantitation scheme makes the assumption that the surface layer is homogeneous,

but it provides useful insight even when the assumption is violated. Figure 2 shows the accuracy and repeatability obtainable on a pure polymer with this technique.

It is also, of course, better to use standards or reference materials for quantitation whenever possible (1).

Another significant improvement in ESCA data collection is the ability to do rapid depth profiles as in traditional Auger spectroscopy. The impediment to doing this previously was that since ESCA analyzed large sample areas, a large area had to be ion etched, which is necessarily slow and non-uniform; also data collection rates were slow. With the small analysis area available today and the high data rates obtainable with improved electron optics and parallel detection, rapid profiling with ESCA is now possible. This is illustrated in one of the examples presented below.

Large Sample Capability

In failure analysis applications, it is usually necessary to examine one or more regions of a larger assembly. Often, with traditional surface analysis techniques, this requires the assembly to be broken in order to analyze it. While this limitation can in principle be eliminated by a larger sample introduction system, large heterogeneous samples may have components that outgas badly, degrading the vacuum quality to an extent that analysis is impossible. Fortunately, ESCA does not require vacuum levels better than 10^{-7} torr, and cryopumps are now available with adequate pumping capabilities for the outgassing sometimes associated with large, real world samples.

Examples of Using a Modern ESCA for Failure Analysis

The following three examples were performed on one of our Surface Science Instruments' X-Probe ^{TM} Spectrometers. These instruments permit samples of up to 17 cm diameter to be analyzed, have an X-ray probe beam selectable in size from 150 microns to 1 mm, and expose the sample to a maximum of about 1 microwatt/mm^2 of energy (10^3 less than an Auger electron beam).

Electrical Leakage of a High Quality IC Package

Figure 3 shows a picture of a glass frit sealed DIP device which was experiencing electrical leakage between adjacent pins.

SEM/EDX analysis of the package revealed no contaminants in the glass frit; Auger analysis could not be used because of severe charging. A survey scan taken of the indicated region with the small spot ESCA is shown in Figure 4. This spectrum shows the expected spectrum of the soft lead glass, containing Si, O, Pb, Zr, Ti, and S; and some surface carbon as well. A further analysis - a high resolution scan of the Pb region - showed something very distinctive, however. This scan appears in Figure 5, showing that two distinct chemical species of Pb are present: metal and oxide, presumably as Pb_2O_3, and as a metal. The latter, being highly conductive, should not be present in the frit.

An investigation of the fabrication process of the IC revealed that the IC was heated in hydrogen after sealing, thereby reducing some of the Pb to its elemental form. Elimination of this step solved
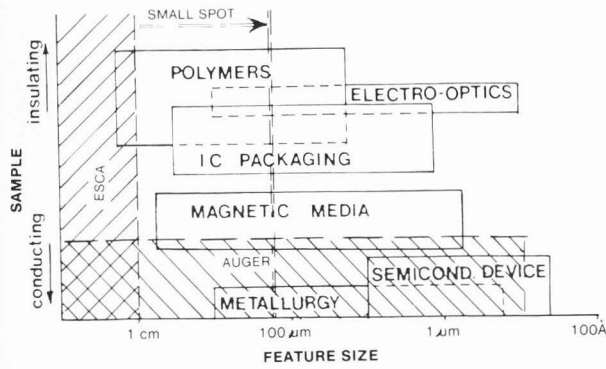
Figure 1 – Some important application areas for ESCA, Auger spectroscopy, and ESCA with improved spatial resolution.
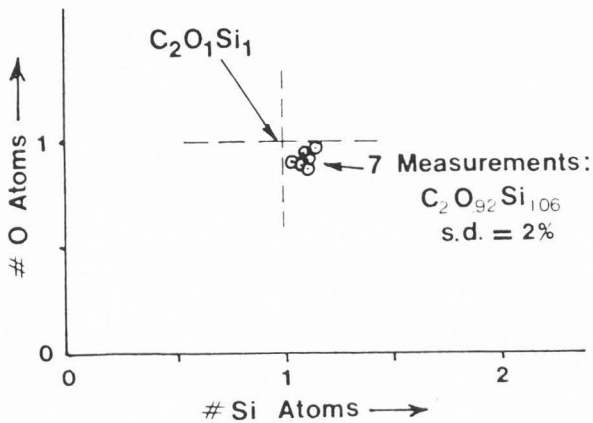

Figure 2 – An example of the accuracy and repeatability of quantitative ESCA results. Seven measurements of different sheets of dimethyl silicone yielded a stoichiometry very nearly the theoretical one, with a standard deviation of $\pm$ 2%.

Figure 4 – An ESCA survey analysis of the glass frit shown in Figure 3. The components found are typical of Pb glass frit. Peaks with dots next to them are other Pb lines.
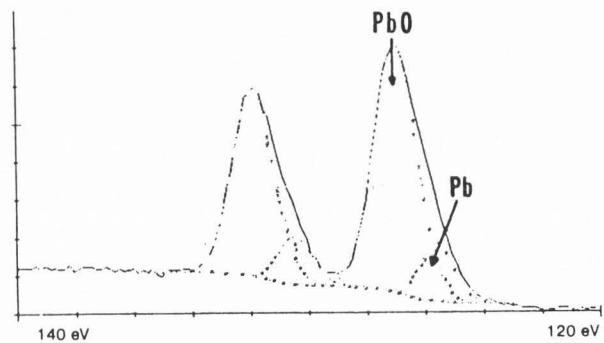
Figure 5 – A high resolution scan of the Pb region of the spectrum shown in Figure 4. Note the presence of two Pb species: the oxide and a small amount of metal. The leakage was caused by this metallic Pb formed by a reduction of the glass.

Figure 6 – An ESCA depth profile of a multilayer electrical device. The profiling rate was 50 A/min. The quantitation procedures described in the text were used to determine the relative atomic abundance.
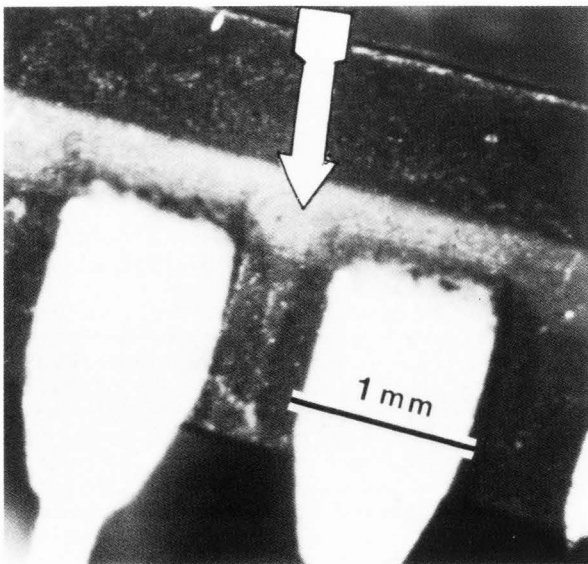

◄Figure 3 – Electrical leakage occurred between these pins of a glass-frit-sealed DIP package. The small spot ESCA analysis was performed at the location of the arrow.
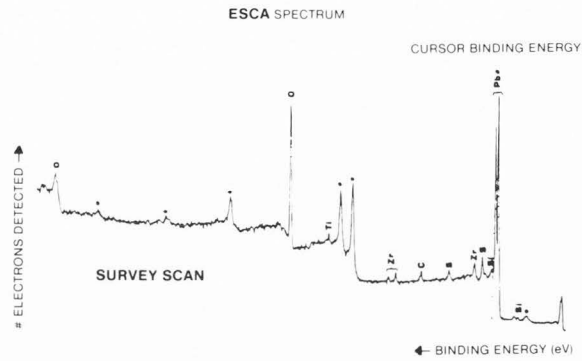
the leakage problem.

Analysis of a Thin-Film Device

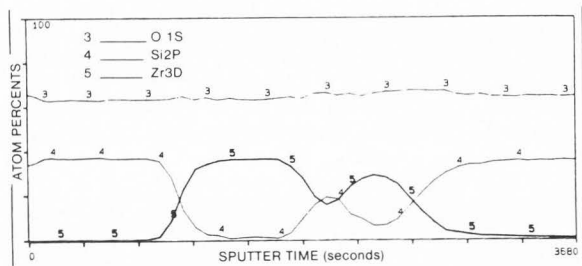Devices made of multiple dielectric layers are being used increasingly in applications associated with many technologies. The bandpass wavelength, efficiency, and longevity of such devices are critically affected by sub-monolayer contaminants in or between the dielectric layers. A depth profile of such a device is very difficult with Auger spectroscopy because of its low conductivity, but is straightforward with ESCA.

Figure 6 shows an ESCA depth profile of the device showing the alternating layers of SiO_2 and ZrO_2 as expected.

This profile represents a new capability for ESCA. It was taken by etching the sample with an argon ion beam for approximately one minute, doing a rapid analysis for each element present, then repeating the etch. The area analyzed was about 300 microns in diameter, and the analysis time per element was only about 10 seconds because of the high sensitivity collection optics. Figure 7 shows a 10 second accumulation of an oxygen spectrum, illustrating the good signal-to-noise ratio obtainable in that time. The profile was compiled by automatically measuring the area under such peaks for the major elements present, quantitating the results in a manner described previously, and plotting the results as a function of time.

Other information is also available from the profile data, as Figure 8 illustrates. There, the oxygen peak is presented as a function of time during the profile. The peak is seen to shift from one layer to another, giving information about the different chemical and electrical environments of the atoms in the different layers. Such information can help substantially in determining the chemical compounds present.

In the case of the device discussed here, no inner layer contamination was found, but a significant amount of carbon ($\sim$ 30 Atom %) was present on the first surface.

Winchester-Type Disc Failure

Surface analysis has helped to solve many contamination and reliability problems on magnetic media (6). This section summarizes a number of such problems.

The general types of problems encountered on discs, heads, and drives, are listed below.

Discs: - spots and streaks
        - head crash and track marks
        - inclusions and corrosion

Heads: - solder and polishing residue
        - organic contamination and stains
        - stiction

Drives: - greases
        - stains
        - corrosion

Our analysis often finds the same contamination source underlying each of the above problems. A brief summary of our findings appears below.

Discs - Although the fluorocarbon lubrication thickness determination with ESCA using angle-resolved measurements is well known among disc manufacturers (4), the ability of this measurement to detect organic contamination is not.

Since the lubricant thickness measurement for films on the order of 1 to 100 Angstroms thick involves measuring carbon signals from both lubricant and resin, any organic contamination will cause a change in the observed peak ratios associated with resin carbon bonding. Careful analysis of these changes can help in assigning the type and thickness of organic contamination.

Most spots and streaks found on disc surfaces are associated with organic oils and greases. They tend to be mixtures of hydrocarbon and silicone oils, long chain fatty acid esters and/or surfactants. Very often these features are on the order of 0.1 mm and require small spot ESCA for spatially resolved analysis. In some instances, light or dark brown tracks on discs are associated with abrupt but narrow changes in lubrication thickness. Often, these tracks are seen as part of head wear or a crash. In these cases, the tracks can be erosion of the resin itself, or residue from the contamination. Sometimes these tracks are the only concentration of contamination on the disc, and can provide enough information to pinpoint the source of the problem. Greases, especially bearing and silicone, are viscous enough to cause stiction problems. When the head cannot lift from the disc during start-up, the low speed/high contact friction can cause significant damage during the first hundred revolutions. This spreads the initial head/disc contaminant into a streak.

Inclusions in discs tend to be on the order of 0.01 mm or less in diameter and require the Auger and SEM techniques for analysis. These inclusions actually have no vertical height, since burnishing has removed most of the large obstructions. Analysis has shown these inclusions to consist of FeO particles, polishing materials, and sometimes chunks of high molecular weight polymers and pieces of head debris. On plated media, inclusions are sometimes trapped underneath the top layer, and thus are not amenable to surface analysis. However, surface pitting and small corrosion features have been investigated using Auger and SEM, especially on surfaces exposed to inorganic corrosives.

Heads - Perhaps the most overlooked surface in promoting disc contamination is the disc head. Since the head is in intimate contact with the disc surface, it has a "gettering" effect when flown over contaminated surfaces. In addition, analysis of organic contamination on the head, compared to the disc, has no interference from the carbon signals of the resin. This is of special importance when the head has broken away from the flexure and is physically stuck to the disc as shown in Figure 9. After prying the head off the disc, much of the contaminant may be on the head.

Analysis of new heads and those flown over a disc for several hours can be helpful in characterizing low levels of disc contamination which concentrates on the leading edge of the air bearing surface.

Common contaminants on new and flown heads include Sn and Pb, possibly from solder flux residue, cleaning solvents and greases, especially silicones.

Figure 10 shows the carbon spectrum of a damaged disc area and a normal area for comparison.

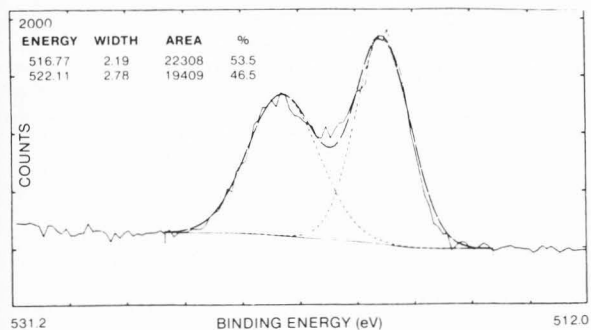| ENERGY	WIDTH	AREA	%
516.77	2.19	22308	53.5
522.11	2.78	19409	46.5

Figure 7 - A typical 10-second measurement used to produce the high spectral resolution depth profile shown in Figure 8. This spectrum shows that two different oxygen species are present. Also shown are computer generated peaks and baseline used in interpreting the data. The areas of the peak were used for the quantitation.

Conclusions

ESCA, because of recent technical improvements, is becoming an important surface-sensitive failure analysis tool. The three examples shown are indicative, but by no means all inclusive, of the kinds of problems which can be addressed. Figure 11 is a summary of some of the attributes of ESCA to put ESCA in some perspective with other surface capabilities of Auger Spectroscopy and SIMS. (For a comparison to other techniques, see reference 3).

If, however, sensitivities on the order of 0.01 to 0.1 monolayers are adequate, and extreme spatial resolution is not required, ESCA is often the method of choice. Its ability to provide good, quantitative results from a very broad range of samples, is being used increasingly for solving failure analysis problems.
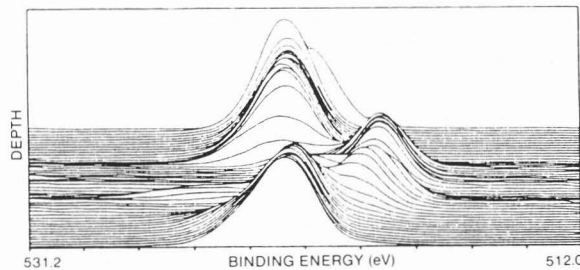

Figure 8 - A perspective view of all the oxygen spectra used in the profile. This plot provides a qualitative view of variations in chemistry or surface electrical parameters as a function of depth.
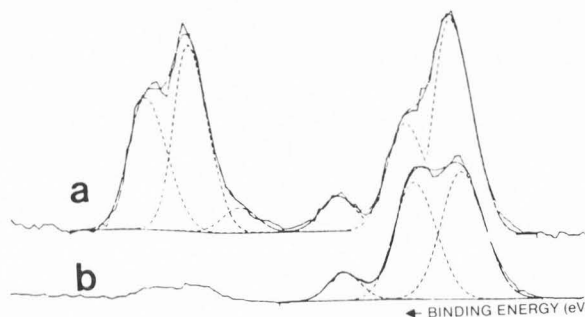

Figure 10 - Typical high resolution scans of the carbon region of (a) a normal disc, and (b) at a failure location. The peaks at the left are the carbon atoms associated with a thin fluorocarbon lubricant; those at the right are hydrocarbons associated with the ferrite bonding matrix and a contaminant, probably a surfactant.
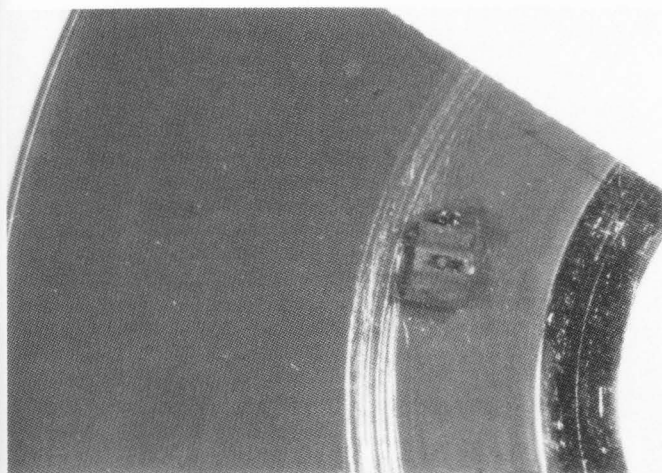

Figure 9 - An extreme 5 1/4" diameter Winchester disc failure. The head has become bonded to the recording medium. Note the badly damaged regions near the head.

Figure 11 - Major Characteristics of ESCA
1. Elemental Analysis
   a. all elements except H
   b. good specificity
2. Sensitivity
   a. bulk = 0.1 atomic %
   b. surface = 0.01 atomic layers
3. Speed = 3 min/survey analysis; as short as 10 seconds for high resolution spectrum. Depth profiles $\sim$ 50A/min.
4. Materials - all: insulators, conductors, organics, powders, etc. (cooling required for volatile materials)
5. Sample damage: very little
6. Area analyzed: = 150 microns diameter to several mm^2
7. Quantitative accuracy
   a. precision 2-5%
   b. relative abundance 20%
8. Mean analysis depth $\sim$ 40A
9. Special features: chemical information

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References

(1) Bakale D, Bryson III CE. (1982) "You Can Solve Material Problems by Surface Analysis". Industrial Research & Development, August, 86-89.

(2) Kelly MA. (1984) "More Powerful ESCA Makes Solving Surface Problems a Lot Easier". Industrial Research & Development, January, 80-83.

(3) Linder R, Bryson III CE, Bakale D. (1985) "Surface Analysis for the Semiconductor Industry". Microelectronic Manufacturing and Testing, February, 1, 9-13.

(4) Linder R, Mee P. (1982) "ESCA Determination of Fluorocarbon Lubricant Film Thickness on Magnetic Disc Media". Presented at the 3rd Joint Intermag-Magnetics and Magnetic Materials Conference, Montreal, Canada, July, (a copy can be obtained from R. Linder at SSL, 1206 Charleston Road, Mountain View, CA 94043, (415) 962-8767).

(5) Seah MP, (1983) "Quantification of AES and XPS", in Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, edited by D. Briggs and M.P. Seah, John Wiley & Sons, NY, 181-216.

(6) Teasley L, Cormia R. (1985) "ESCA Can Identify Your Contamination Problems". Industrial Research & Development, October, 123-124.

For additional information on many of these topics, see papers in reference 5; each has an extensive bibliography.

Discussion with Reviewers

T. Massopust: Could you comment on the usefulness of angle-resolved ESCA analysis for profiling very thin films?
Authors: We have found that angle resolved ESCA data is excellent for defining the order of stratification - what, on the average, is over what. However, our experience has been that surface roughness and layer interpenetration questions severely limit quantitative applications.

S. Ingrey: It is stated that Auger spectroscopy uses 10^3 times more power than ESCA, i.e. microwatt/mm^2. How was this comparison made?
Authors: The calculations were based on source power in incident beam for typical conditions.

S. Ingrey: With reference to your comment on "thickness determination of fluorocarbons using ESCA", could you comment on how thicknesses are obtained using this technique?
Authors: The direct non-destructive measurement of film thicknesses on the order of 100A or less can be accomplished with high precision and accuracy using electron spectroscopy for chemical analysis (ESCA). The method relates thickness to the relative angular dependence of signals from the overlayer to signals from the substrate.

The measurement of carbon and iron oxide concentrations on the disc surface before and after removal of the lubricant by ion etching provides a calibration. Once calibrated for a given lube/resin system, measurement of hydrocarbons and fluorocarbon concentrations yield the lube thickness. The measurement takes about 10 seconds per location.

Routine ESCA measurements of lubricant thickness and uniformity provide QC and a direct measure of process variations. The ESCA method of film measurement is very precise and can be used to improve the process with confidence that measurements will be reproducible and comparative.

A detailed treatment of these types of measurements is given in text reference 4.

J. Reimer: What sub-monolayer contaminants have you encountered when analyzing dielectric layers in semiconductors by ESCA?
J. Reimer: Does the depth profile in Figure 6 relate to a failure? What are the contaminants detected, and what would a "clean" profile look like?
Authors: All information that we can provide has been included in the paper. We regret that due to proprietary nature of the work, we cannot provide any additional information.

J. Reimer: In Table 1, you are suggesting that ESCA causes "very little" damage to a sample. Please comment on what damage ESCA can cause to a specific sample of a thin-film, and how this may alter the analysis report.
Authors: Damage from ESCA is extremely minor compared to electron beam techniques. The only damage we've been able to document has been small (but detectable) on polymer samples like PTFE, where certain bonds may break after extensive (hours) exposure to X-rays.

J. Reimer: When you analyze a client's semiconductor device thin-film for chemical composition and possible interface contamination, do you compare your results to a known comparison sample or a standard material sample? Please comment on how you handle this problem.
Authors: It is, of course, preferable to use similar samples or standards which have been independently characterized, if possible. For routine analysis without such comparisons available, a mixture of empirical and theoretical relative sensitivities are used. Thin film standards are particularly difficult to obtain.

Reviewer II: The authors state that ESCA offers a higher tolerance to poorer vacuum than AES and SIMS. This is not correct. With respect to detection, AES and ESCA/XPS have identical vacuum requirements stemming from limits on emitted electron-background gas collisions which modify measured electron energy distributions (spectra). With respect to sources of excitation, a typical X-ray source operating at 5 to 15 keV has less tolerance for poor vacuum than a filament electron source used in AES due to possible sputtering of the X-ray target by the residual gas.
Authors: We refer to the fact that a higher carbonaceous background results in electron beam polymerization at the surface during AES analysis.