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INDUSTRIAL PROBLEM SOLVING WITH MICROBEAM ANALYSIS

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Abstract

The objective of this paper is to provide an overview of the microbeam analytical techniques and to help select the appropriate one to solve complex problems often arising in today's high-tech industries. Case histories are given to show how renowned analytical service laboratories and microbeam experts formulated their strategies to approach a real life problem, what type of conclusions were deduced from the data and, finally, how the problem was solved.

Introduction

The microbeam instruments are an important group of the new analytical tools which revolutionized analytical chemistry and materials characterization during the last few decades. Their major advantage is that they allow insight into the surface and internal structure of materials at the micron and submicron scale. The application of microbeam instruments reveals a close correlation between the microstructure and the macroscopic properties (e.g. mechanical strength, corrosion resistance, conductivity, adhesion, catalytic activity, etc.) of solid state materials, thus if we wish to understand and possibly control the properties of materials, we must characterize their microstructure. In many cases the distribution of the components is of central importance and major efforts are made to develop and apply techniques for distribution analysis.

Discussion

Instrumentation.

The methods of microbeam analysis include in situ microanalysis, surface analysis, interface analysis and depth profiling. The instruments most widely used in industry can be divided into photon, electron and ion probes (Table 1). A glossary of the acronyms is provided.

Note that selected area electron diffraction (SAED) is a built in capability of the TEM, no attachment needs to be applied. Energy dispersive X-ray analysis (EDX), wavelength dispersive X-ray analysis (WDX), electron energy loss spectroscopy (EELS) and extended electron energy loss fine structure (EXELFS) all require an attachment. When the TEM or the scanning transmission electron microscope (STEM) is interfaced with these attachments, the instrument is called an analytical electron microscope (AEM) because one instrument is virtually a complete analytical laboratory. Both EELS and EXELFS are still in the developmental stage, thus problem-solving with these techniques becomes a research project. The scanning electron microscope (SEM) also provides special techniques, essential for materials

KEY WORDS: Problem solving, industrial, Case histories, Trouble shooting, Microbeam analysis, Polymers, Microelectronics, Fibers, Corrosion, Food, Industry.

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Glossary of acronyms

AEM	Analytical Electron Microscope
ATR	Attenuated Total Reflectance
AES	Auger Electron Spectroscopy
BEI	Backscattered Electron Imaging
CB	Collector Base
CL	Cathodluminescence
EB	Emitter Base
EBIC	Electron Beam Induced Current
EELS	Electron Energy Loss Spectroscopy
EDX	Energy Dispersive X-ray Analysis
ESCA	Electron Spectroscopy for Chemical Analysis (also: XPS)
ESD	Electrostatic Discharge
EXELFS	Extended Electron Energy Loss Fine Structure
FR	Flame Retardance
IMA	= IMMA
IMMA	Ion Microprobe Mass Analysis
IR	Infrared
ISS	Ion Scattering Spectrometry
LAMMA	Laser Microbeam Mass Analysis
MED	Micro Electron Diffraction
LRM	Laser Raman Microprobe
MOLE	Molecular Optical Laser Examiner
OM	Optical Microscope
ppm	parts per million
ppb	parts per billion
RBS	Rutherford Backscattering Spectrometry
ROI	Region of Interest
SAED	Selected Area Electron Diffraction
SAM	Scanning Auger Microprobe
SEI	Secondary Electron Imaging
SEM	Scanning Electron Microscope
SIMS	Secondary Ion Mass Spectroscopy
STEM	Scanning Transmission Electron Microscopy
TOF	Time of Flight
TEM	Transmission Electron Microscopy
VC	Voltage Contrast
WDX	Wavelength Dispersive X-ray Spectrometry
XPS	X-ray Photoelectron Spectroscopy (also: ESCA)

 characterization as well as product control and failure analysis in the electronics industry. These are the electron beam induced current (EBIC), voltage contrast (VC) and cathodluminescence (CL) modes.

The principles and the operation of the above instruments and techniques are discussed in numerous textbooks and publications (see Bibliography). Each technique has its advantages and limitations, and its specific areas of applications. The information obtained with the individual instruments is often complementary, but at times overlaps. Since both the price (2-8 x 10⁵ US dollars) and the operating cost of these instruments are high, it is of major importance that the users consider which instrument or combination of instruments are to be used for a most efficient, cost-effective analysis.

Table 1

Microbeam instruments.Photon probes

Visible Light Instruments:

Optical Microscope (OM)
 Laser Scan Microscope (LSM)
 Laser Raman Microprobe (LRM)
 Laser Microprobe Mass Analyzer (LAMMA)

X-Ray Instruments:

Electron Spectroscopy for Chemical Analysis (ESCA)

X-Ray Microprobe

Infrared Instruments:

Infrared Microscope
 Infrared Microspectrophotometer

Electron probes

Transmission Electron Microscope (TEM)
 Scanning Electron Microscope (SEM)
 Scanning Transmission Electron Microscope (STEM)
 Electron Energy Loss Spectrometer (EELS)
 Scanning Auger Microprobe (SAM)

Ion probes

Secondary Ion Mass Spectrometer (SIMS)
 Ion Microprobe Mass Analyzer (IMA)
 Ion Scattering Spectrometer (ISS)
 Rutherford Backscattering Spectroscopy (RBS)

Strategy; fitting the technique to the problem. Selection of the most suitable technique.

Microbeam analysts are challenged daily by the sophisticated problems which arise in our high-technology manufacturing processes. They provide vital information needed by scientists and engineers to develop new products and to maintain the quality of existing products. They are primarily problem solvers who must have an in-depth knowledge of the microbeam techniques and a good working knowledge of a wide range of non-microbeam methods.

The analysts have to work in close cooperation with the sample submitters, with the plant engineers and with quality assurance personnel to thoroughly understand the history of the sample, the process and the manufacturing operation. It is essential to carefully define the problem. This enables the analyst to optimize the analytical procedure and find the most promising and most cost-effective solution.

A quick initial check in a stereomicroscope, in the polarizing microscope or in the SEM/EDX is highly advisable. These low cost techniques often show that the problem can be solved without further analysis. Should application of the high priced, more sophisticated instruments prove necessary, these initial checks permit the selection of "regions of interest", (ROI), i.e. regions of the sample which are suspect and need further analysis.

It is also important that the analyst be supplied with one or more reference samples. These

are samples in which no problem has occurred (Bakale and Bryson, 1982) and which sample submitters are inclined not to submit. Reference samples can sometimes be "before" and "after". (For example both samples have the problem, but one has been solvent washed). The analyst should insist on a set of "good" and "bad" samples because submitters tend to investigate non-critical factors when they attempt to solve problems solely from findings on the "faulty" material or part. It has been amply documented that cooperative studies are invaluable in failure analysis and in problem solving. Once the problem has been defined and preliminary "quick checks" have been performed, more thorough investigation can be planned. Often the necessary techniques emerge during analysis. The analyst must be flexible in such cases and tailor the plan of attack.

At the outset of the work the analyst should clarify with the sample submitter, to what extent the analysis should be carried. Table 2 displays an example of a typical interview (Bakale and Bryson, 1983) when a problem was encountered in the production of microcircuits.

The problem arose when the photoresist would not adhere to the surface of some silicon wafers after oven heating. SEM/EDX (with Be window) failed to show any difference between "good" and "bad" samples. It was deduced, therefore, that EDX was unsuccessful due to one or more of the following possibilities:

- The contaminants may consist of elements with atomic numbers below 10 (windowless detector was not available to the analyst).
- The concentration of the contaminant is below the detection limit of EDX.
- The contaminant is present as an extremely thin surface layer.

Electron spectroscopy for chemical analysis (ESCA) was selected to elucidate the problem. This proved to be a good choice, since ESCA analyzes ~10 nm thick surface layers, the minimum detection limit is 0.1% and it yields information about the molecular composition.

Other techniques which could have been chosen are SIMS and LRM. They both yield molecular information. However, SIMS is a much more expensive technique and the spectra are prone to interference. LRM is less suitable than ESCA for analyzing thin surface layers. Thus the strategy of Bakale and Bryson (1983) was well planned.

ESCA did reveal a surface silicone layer in addition to elemental silicon and silicon dioxide. These latter two were revealed by the ESCA spectrum of the control (which has not been treated in the oven). Based on ESCA results, the problem was traced to the gasket of the oven. Gaskets are often made of long-chain silicones impregnated with short-chained silicones to retard hardening. The slowly evaporating low-molecular weight additive contaminated the atmosphere in the oven and condensed on the surface of the wafers causing the adhesion problem.

Apart from failure analysis the microbeam analyst has the task of guiding research and

Table 2

Typical questions in formulating strategy.*

Statement of the problem?

Photoresist would not stick to the surface of some silicon wafers.

Elements of interest?

Unknown.

Feature size?

0.5 cm to 4 in.

Sample size?

4 in.

Number of samples available?

Many.

Matrix composition?

Silicon dioxide on silicon.

Mobility?

Unknown.

Sample history? Handling? Age?

Silicon wafers (thermal oxide on epi) were packaged and shipped in a Teflon boat. An oven was used to drive off moisture, a pretreatment for photoresist application. The problem was unique to the wafers treated in one oven. Nonstiction appeared to worsen over time. SEM/EDX analysis gave no indication of contamination.

Expected contaminant depth?

Unknown.

Analysis time available?

As needed to solve.

Budget? Importance?

Open. Critical to production.

Is chemical information needed?

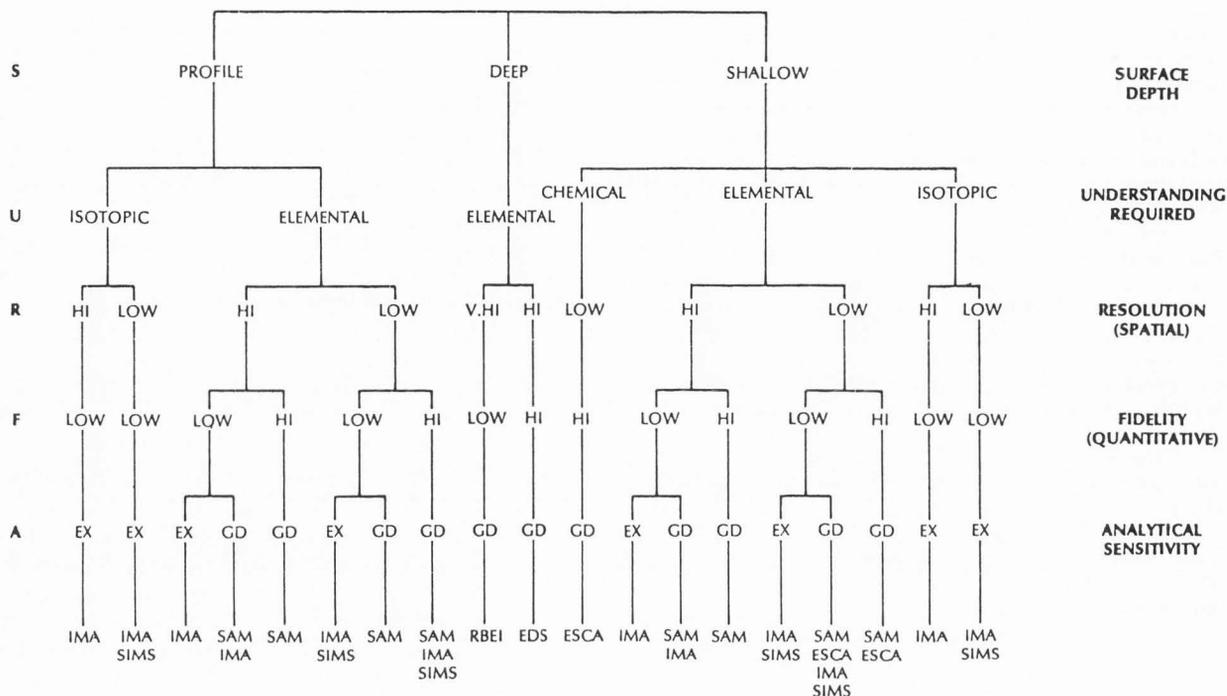
It is likely to be important in understanding the cause.

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development efforts in a variety of fields. Close interaction with the submitter is also essential here to formulate strategy. Ultimately each analyst must optimize his/her approach according to the particular need dictated by the problem on hand. Though each problem or characterization study requires a different approach, a brief summary of the most widely used microbeam techniques, two Tables (3 and 4) and selected examples of strategy are given to help the microbeam analyst select the most effective

Table 3.

CAPSULE REFERENCE FOR SURFACE ANALYSIS *



* Courtesy of PhotoMetrics, Inc.

instrument or instrument combination. When contemplating the optimal analytical approach, the advantages and limitations of each instrument available to the analyst should be considered.

Selection guide in a nutshell. (Kiss, 1987).

- OM Surface and internal morphology, crystallographic information, identification of particulates. Maximum magnification ~1000X. Special techniques: phase contrast-, interference contrast- and infrared microscopy, micro infrared spectroscopy, dispersion staining, microanalytical and fusion techniques.
- SEM Surface and internal morphology with <10 nm resolution, Special techniques to characterize semiconductor and magnetic devices.
- EDX Qualitative and quantitative simultaneous elemental analysis and elemental maps with ~0.5-5 μm spatial and depth resolution. With a Be window detector Na through U, with a thin window detector C through U can be analyzed. Detection limit ~0.1%
- WDX As above but no simultaneous elemental analy-

sis can be performed. Advantage: no peak overlaps. Detectable elements C through U, detection limit ~0.02%.

TEM-
SAED Surface (using replicas) and internal ultra-structure. Spatial resolution 0.2 - 0.5 nm. Ultrathin specimens needed. Phase determination (often with stained specimens) capability. Crystallographic information from ~400 nm^2 area.

AEM-
SAED (Analytical electron microscope - selected area electron diffraction). As TEM, but elemental and crystallographic information can be obtained from ~10-50 nm^2 areas. Useful for identification of phases in metals, ceramics, refractories; active metals and promoters in catalysts; inorganic additives in polymers and coatings, etc.

AES-
SAM (Auger electron spectroscopy - scanning Auger microprobe). Elemental surface analysis (Li through U), high-resolution (~50 nm) from the top ~1-2nm layer. Some valence state information. Depth profiling. Applied for the determination of contaminating surface films causing color, haze, poor wetting, contact resistance, etc.

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ESCA As above but spatial resolution $\sim 150 \mu\text{m}$; (XPS) analysis from the top $< 10 \text{ nm}$ layer, depth profiling. Non-destructive depth information for layers which are thinner than the escape depth of photo- and Auger electrons. Reveals valence state of elements, molecular composition can be deduced from peak shifts.

SIMS Dynamic: ultrahigh sensitivity in qualitative elemental (H through U) and molecular compound analysis, $\sim 0.2 \mu\text{m}$ spatial resolution, isotope analysis, elemental- or molecular fragment maps, depth profiling. Spectra interpretation and quantitation difficult. Used to determine dopants in semiconductors, very low level impurities in coatings and reactive materials, hydrogen embrittlement of metals, hydride formation, isotope concentrations, etc.

Static: (including SIMS-TOF [time of flight]). Molecular information without quantification.

LRM Molecular information on $0.1\text{-}1 \mu\text{m}$ layers or particles. Spatial resolution $\sim 1 \mu\text{m}$. Molecular maps. Useful in studying organic coatings, inclusions, crystallographic changes, etc.

ISS Monolayer or less contaminant can be analyzed in the ppm (parts per million) range. Elemental information.

RBS Quantitative analysis of major and minor constituents within the first $0.5\text{-}2 \mu\text{m}$ of a material surface. Depth resolution $2.5\text{-}20 \text{ nm}$. Detectable elements: He through U. Detection limit: $0.001\text{-}10 \text{ atom}\%$. Most extensively used in the characterization of thin films and ion implantation damage regrowth of electronic materials (Bakale et al., 1985).

LAMMA High speed analysis of both organic and inorganic species of microregions. Spatial resolution $\sim 2\text{-}20 \text{ nm}$. All elements and their isotopes are detected with ppm detection limit. High molecular weight, non-volatile or thermally unstable organic compounds can be analyzed. Molecular information obtained without charging problems.

Several techniques yield partially overlapping information, but each offer some unique features. Answering the following questions may clarify strategy.

- How much specimen is available? Is it sufficient for parallel tests or sequential analysis if needed, starting with non-destructive methods?
- Atomic or molecular information is required? In the latter case is chemical bonding information adequate?
- Qualitative or quantitative analysis required?
- Bulk or trace analysis is needed? In the latter case what detection sensitivity is acceptable?
- What spatial and depth resolution is acceptable?
- Is elemental/molecular mapping and imaging required?
- Films (ultrathin, thin or thick), cross

sections, interfaces or bulk samples are to be characterized?

- Is depth profiling needed?
- Is sample charging a problem, is the specimen an insulator, semiconductor or conductor?
- What is the best technique for this problem? Can a combination of several techniques provide a more definitive answer?
- What is the cost limit?

In the selection process, the following shortcomings of the various techniques must be also considered:

- SAM Electrostatic charging may interfere with the analysis.
- BEI (Backscattered electron imaging). The elements cannot be identified (except on some samples with calibration).
- EDX Elements with very low atomic number and monomolecular surface layers cannot be analyzed.
- ESCA Determination of depth profiles and spatial resolution limited.
- SIMS Peak interferences, wide variation in basic sensitivity by elements and severe matrix effects limit the accuracy of quantitative analysis.
- IMA Frequent peak interferences; quantitative analyses with limited accuracy.
- LRM Fluorescence and thermal effects limit application.
- RBS Poor lateral resolution. Emerging technique.
- LAMMA Destructive analysis, quantitation difficult Emerging technique.

Apart from all the mentioned viewpoints, the cost of the instrument, as well as of the study has to be carefully weighed. The relative costs are the following:

Technique	Cost
SEM	\$
BEI	\$
EDX	\$
TEM	\$\$
SAM	\$\$
LRM	\$\$
RBS	\$\$
ESCA	\$\$
AEM	\$\$\$
SIMS	\$\$\$
IMMA	\$\$\$
LAMMA	\$\$\$

SEM, EDX and BEI are the least expensive microbeam analytical techniques. We can expect that rapid growth in popularity combined with gradual erosion of their cost will make even the most expensive techniques more and more accessible to the industrial analyst.

Table 4.

ACRONYM	SEM	BEI	EDX	WDX	AEM	EELS
TECHNIQUE	Scanning electron microscopy	Backscattered electron imaging	Energy dispersive X-Ray spectroscopy	Wavelength dispersive	Analytical electron microscopy	Electron energy loss spectroscopy
INCIDENT (EXCITING) RADIATION	electron 1-50 keV	electron 5-50 keV	electron 2-50 keV	electron 0.5-50 keV	electron 100-200 keV	electron 100-750 keV
PARTICLE EMITTED	secondary electrons	backscattered primary electrons	characteristic X-ray photons		transmitted electrons, characteristic X-rays	inelastically scattered electrons
DEPTH INFORMATION	no	1 μm		0.5-5 μm depends on matrix	0.01-0.1 μm	0.01-0.1 μm
SPATIAL RESOLUTION	10 nm	100 nm		0.5-5 μm depends on matrix	0.2-0.5 nm	<0.04 μm
DETECTION LIMIT	n.a.	0.5%	0.1%	~0.02%	0.1 %	<0.1 %
DETECTABLE ELEMENTS	none	difference only	Na-U (C-U)*	Li - U	Li - U	Li - U
DEPTH PROFILING	no	no	no	in cross sections	no	no
CHEMICAL INFORMATION	no	no	no	no	some	some
QUANTITATIVE ANALYSIS	no	no	yes, relative error ~2%	<1%	yes	yes
IMAGING	yes	yes	no	no	yes	no
MAPPING	no	yes	yes	yes	yes	yes
LINE TRACES	yes	yes	yes	yes	yes	yes
MOLECULES DETECTED	no	no	no	no	no	no
CRYSTALLOGR. INFORMATION	yes	no	no	no	yes	no
MATERIALS	any	solid	matter		any solid	any solid
APPLICATIONS AND INFORMATION OBTAINED	surface and internal morphology	detection and mapping of elements	elemental analysis of bulk or near surface regions		thin film, elemental analysis, structure of materials, lattice imaging	ultrathin film, elemental analysis

* thin window or windowless detector

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Comparative summary. →

ACRONYM	ESCA	AES/SAM	RBS	ISS	SIMS	LRM
TECHNIQUE	Electron spectroscopy for chemical analysis	Auger el. spectroscopy scanning Auger micro-probe	Rutherford backscatter. spectroscopy	Ion scattering spectroscopy	Secondary ion mass spectrometry	Laser Raman microprobe
INCIDENT (EXCITING) RADIATION	X-ray or UV photons	electron 0.1-5 keV	He ⁺ 2-6 MeV	ions at 0.2-2 keV	ions	mono-chromatic light
PARTICLE EMITTED	photo-electron	Auger electron	backscattered He ⁺ , He ⁺⁺	scattered ions	secondary ions	scattered light
DEPTH INFORMATION	~0.5-2 nm	~1-20 nm	~1 μm	top exposed layer	3 nm	~0.1 μm
SPATIAL RESOLUTION	150 μm - 1mm	50 nm - 1μm	1 mm	1-100 μm	< 2 μm	~1 μm
DETECTION LIMIT	0.1 %	0.1 %	0.01 - 1 %	100 ppm-0.1% (bulk)	0.01-0.0001%	~1%
DETECTABLE ELEMENTS	Li - U	Li - U	He - U	Li -U	H - U	functional groups
DEPTH PROFILING	yes	yes	yes, non-destr.	semi-quantitative	yes to 2 μm	no
CHEMICAL INFORMATION	yes	some bonding	no	no	some bonding	yes
QUANTITATIVE ANALYSIS	yes, to ~2% rel.err.	yes, to ~10% rel.err.	yes	yes	yes, to ~25% rel. error**	yes
IMAGING	no	yes	no	no	yes	yes
MAPPING	some	yes	no	no	yes	yes
LINE TRACES	no	yes	no	no	yes	yes
MOLECULES DETECTED	yes	no	no	no	yes	Raman active molecules
CRYSTALLOGR. INFORMATION	no	no	yes	no	no	yes
MATERIALS	any solid, frozen liquids	any solid matter	any solid matter	any solid matter	any solid matter	any solid, liquid, gas inclusions
APPLICATIONS AND INFORMATION OBTAINED	elemental composition, chemical binding	absorbate analysis, elemental analysis of surface	elemental composition, location of adsorbed species	elemental composition, location of adsorbed species	elemental and molecular composition	compound identification on surfaces

** due to peak interferences and chemical matrix effects

Case histories.Polymer science.

A streaking problem on printed polyethylene film. (Cormia, 1984). Polyethylene film was surface treated (oxidized) in a corona discharge system to transform the nonpolar surface into one, wettable with ink solvents and thus printable. The film exhibited unprintable regions in the form of narrow streaks of 0.1 mm wide and several centimeters long at random portions of the film. The location of the failed regions indicated that the film was contaminated as it traveled on the rollers of the system.

Based on weak aluminum and magnesium signals on the small-spot ESCA spectra taken from the contaminated regions it was suspected that excess heating of aluminum caused spitting of this metal onto the rolling film. Magnesium is commonly present in aluminum alloys and it is known to aggregate to the surface when the alloy is heated.

The presence of both aluminum and magnesium on the streaked areas supported the above hypothesis. Examination of the corona discharge electrode indeed showed extensive pitting of its surface. Testing the power supplies revealed electronic problems which could supply the excess current to the bar and result in overheating and spitting of bar material onto the film during rolling, leading to the formation of the streaks. When the electrical defects in the treatment system supply were corrected, no further streaking or printing problems have occurred.

Small spot ESCA was the technique of choice because the contaminant was expected to be an extremely thin surface deposit of some organic material. EDX was not even attempted, since the film was expected to be too thin to give useful EDX signals. Regular ESCA could not be used because the sample area was limited to 0.1 mm in one direction. AES has also small area analysis capability but it is difficult to use on plastic films due to extensive charging.

IRM identification of "fisheye" in high impact polystyrene. (Andersen, 1983). A 200 μm thick high impact polystyrene - polybutadiene copolymer contained "fisheyes". The contaminated region was cross-sectioned by a razor blade revealing a transparent 40 μm inclusion. The Raman spectra of the matrix and contaminant were practically identical. The only difference was that the small peak at 1650 cm^{-1} , indicative that cis polybutadiene was present in the spectrum of the matrix (Figure 1a) but not in that of the contaminant (Figure 1b). The latter was therefore identified as virtually pure polystyrene. Based on this information corrective action was taken to avoid the formation of homopolymers.

Inclusion in polymer. (Andersen, 1984). Inclusions in a polyethylene film caused product failure. They were easily distinguishable in the polarizing microscope under polarized light (Figure 2). The region containing the inclusions was cut out of the film and examined with EDX. The latter revealed a low level of sulfur in the

investigated region. Analysis of another inclusion with the laser Raman microprobe identified the contaminant as undispersed, sulfur containing antioxidant (Figure 3). Improvement in dispersion technique eliminated the problem.

This example is indicative of the limitation of EDX. It correctly identified the presence of sulfur in the contaminant but gave no information regarding the actual composition.

Vinyl sheeting with poor adherence. (McCrone, private communication) A silicone-caused failure was documented for gypsum wallboards covered with vinyl sheeting. The latter is printed or embossed and then glued to the gypsum board.

A problem arose - the vinyl sheeting failed to adhere to the wallboard. There was no apparent reason for it since the process and materials were the same ones used successfully for years. Fresh lots of adhesive, vinyl sheeting and other materials were tried to no avail.

First optical microscopy was used to show that the adhesive was adhering to the gypsum board but separating from the vinyl side. Then all raw materials and process chemicals were examined with ESCA. The chemicals and the wallboard revealed nothing unusual, but ESCA demonstrated that the first 2 - 3 nanometers of the vinyl surface contained 9% silicone. Since it was found to be free of silicone when it entered the plant, contamination was occurring somewhere in the manufacturing process.

Using ESCA, a step-by-step investigation revealed that the rubber rollers of a machine that printed the design on the vinyl sheet had a high concentration of silicon on the surface. It was then established that the roller manufacturer had switched to silicone rubber without advising the vinyl printer; silicone transfer from the rubber to the vinyl caused the problem.

In this case optical microscopy directed the investigation to the vinyl component and ESCA showed that the trouble - causing contaminant was on the very surface of the vinyl sheeting. The ability of ESCA to identify silicone was crucial in this investigation. An elemental analysis would have shown the presence of silicon and oxygen, but this information may have been insufficient, leaving the investigator in doubt about the molecular structure of the contaminant.

Pigment-dispersion problems in plastics. (Berenson, 1972). Poor pigment dispersion in plastics results in speckling, streaking, or irregularly textured or opacified surfaces. Figures 4a and 4b display examples of "bad" and "good" pigment dispersion in a plastic matrix.

A problem was encountered for example with an extruded low density polyethylene pigmented with about 1 phr (parts per hundred) TiO_2 . The product exhibited white specks. The severely irregular surface of the material is evident from the low magnification SEM photograph displayed in Figure 5. The cross section was investigated with the SEM, and it was found that the problem is directly related to the presence of agglomerated TiO_2 pigment particles (see Figures 6 through 8). EDX

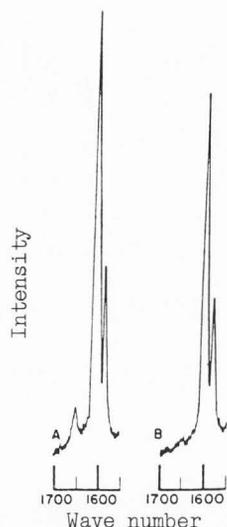
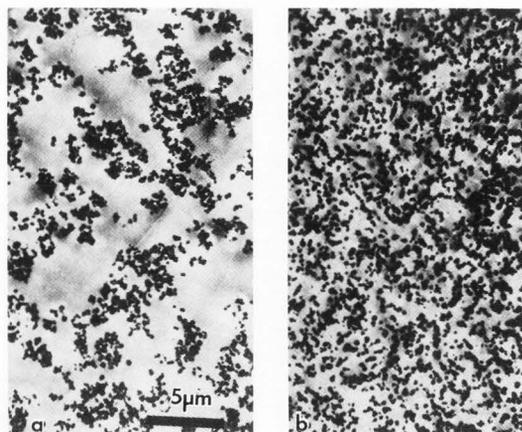


Figure 1. Raman spectrum of high-impact polystyrene (A) and inclusion in high-impact polystyrene (B). Leitz 100x(0.90 N.A.) objective. (Reprinted with permission from *Advances in Chemistry* series #203, pp.383-395. Copyright 1983, American Chemical Society.)



a. "Bad" dispersion b. "Good" dispersion

Figure 4. Dispersion of pigment in plastic matrix. (Courtesy of the Society of Plastics Engineers)

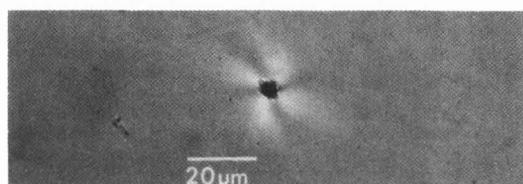


Figure 2. Inclusion in polymer film surrounded by strain birefringence. (Copyright © 1984 by San Francisco Press, Inc. Reproduced by permission.)

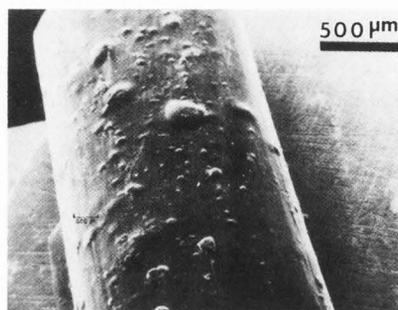


Figure 5. SEM micrograph of the surface of low-density polyethylene strand displaying severe surface irregularity. (Courtesy of the Society of Plastics Engineers)

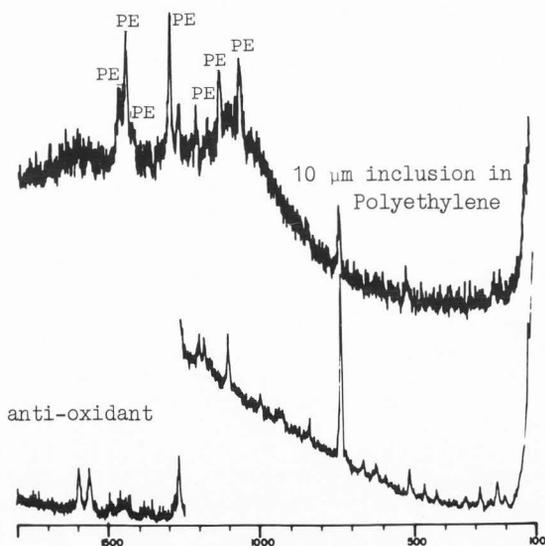


Figure 3. Raman spectra of inclusion in polymer film compared with that of anti-oxidant additive. (Copyright © 1984 by San Francisco Press, Inc. Reproduced by permission.)

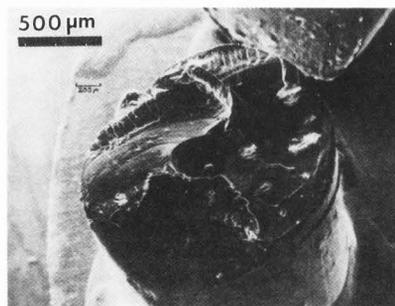


Figure 6. Extruded low density polyethylene (LDPE) cross section at low magnification. (Courtesy of the Society of Plastics Engineers)

demonstrated that the agglomerated globules indeed contain Ti. Inspection of the machinery showed faultless operation, thus the fault clearly lay with the pigment. The problem was solved by substituting the TiO₂ with a grade of better dispersion.

A similar dispersion problem occurred in rayon fiber delustered with TiO₂. It was found that the tensile strength of the fibers delustered

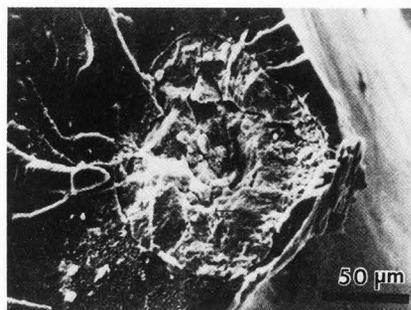


Figure 7. Extruded LDPE cross section at higher magnification. (Courtesy of the Society of Plastics Engineers)

with one grade of TiO_2 (grade A) was inferior to those delustered with grade B TiO_2 . In this case SEM revealed very little, but TEM of ultrathin sections of fibers clearly correlated the higher tensile strength with superior dispersion. This problem was resolved by switching to the best dispersing pigment.

Poor bonding in reinforced plastics. A frequent problem in reinforced plastics is poor bonding between the plastic matrix and the reinforcing additive (glass fibers, glass balloons or spheres, carbon particles, carbon fibers, mica, fibrillar calcium sulfate, etc.) There are a number of reasons to use reinforcing additives in plastics. They not only improve the physical characteristics of plastics but in a synergistic way they may impart novel properties to the material. They also decrease the cost of the product, decrease shrinkage, improve water and weather resistance, etc. The properties of the additive-matrix interface play an essential role in achieving reinforcement. The formation of an intimate bond between additive and matrix must be obtained. In practice coupling agents, e.g., silanes and titanates are used to improve bonding. The selection of a poor coupling agent or nonuniform coating by the coupling agent on the surface of the additive particles can cause poor bonding and thus inferior product. Typical "good" and "poor" bonding in glass sphere reinforced polycarbonate is shown in Figure 9. (Dekkers and Heikens, 1984).

Here the additive was treated with a silane bonding agent in the case of the plastic shown in Figure 9a. It is obvious that an intimate bond has formed between the treated glass and the polycarbonate. On the surface of the glass spheres pulled fibers indicate that matrix failure rather than interfacial failure has taken place. Wetting of the reinforcing additive by the polymer is good and bonding by the resin matrix is strong. Figure 9b shows the fracture surface of the same plastic when there is no bond between the matrix and the additive. Here the additive was treated with a silicone. The very smooth surface of the glass sphere and the large gap between sphere and plastic shows no adhesion.

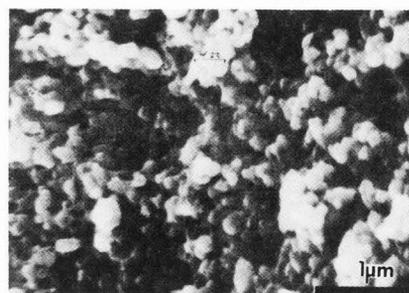


Figure 8. Extruded LDPE cross section at very high magnification. (Courtesy of the Society of Plastics Engineers)

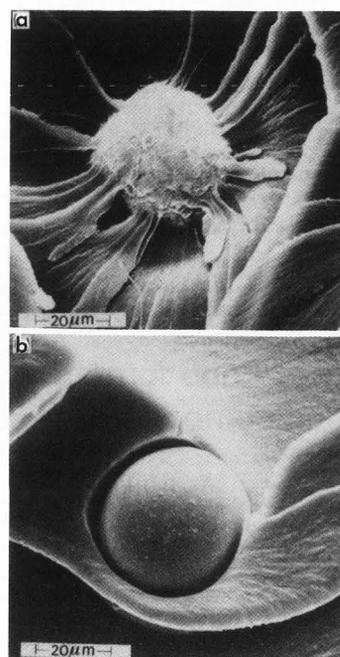


Figure 9. Scanning electron micrographs of fracture surfaces of polycarbonate-glass bead composites. (a) Excellent interfacial adhesion obtained with gamma-aminopropylsilane. (b) Poor interfacial adhesion with silicone oil. (Dekkers and Heikens, 1984. Reprinted by permission of Chapman and Hall, Ltd.)

ESCA analysis of plastics, polymer films and fibers. Polymer films, natural and synthetic fibers, rubber surfaces and products treated with organic coatings such as lubricants and microencapsulating materials are often surface treated to improve wettability, dyeability, printability, adhesion, etc. The composition of the treated surfaces must be monitored during process development as well as during manufacturing for quality assurance. ESCA is the preferred tool for this analysis. Attenuated total reflectance (ATR) infrared spectroscopy, previously used for this purpose, has a sampling depth of several hundred nanometers. Thus it is less than ideal

for the analysis of these extremely thin surface layers by itself. LRM has the same sampling problem. Other modern surface techniques such as SIMS and Auger spectroscopy are plagued by severe charging problems, destroy organic surfaces and often do not provide as much chemical-molecular information as ESCA. Techniques, such as contact angle measurements are sensitive to the uppermost molecular layer but they do not provide chemical information about them. It is understandable, therefore, that ESCA is widely used to characterize such layers.

Process control and quality assurance for surface treated fluoropolymers. (Riggs and Parker, 1975). Fluoropolymers are frequently treated with sodium/ammonia to promote adhesion to their surface and ESCA is the preferred analytical technique to study surface chemistry during this process. Figure 10 shows the chemical information provided by the ESCA spectra. The control Teflon shows the characteristic high-binding-energy carbon 1s peak and a high intensity fluorine peak. After the sodium/ammonium treatment the carbon peak is shifted to the lower-binding-energy characteristic of a hydrocarbon 1s peak. The presence of some oxidized component is also apparent from the high-binding-energy tail of the hydrocarbon 1s peak. The presence of this tail verifies that oxidation also occurs during this treatment. The fluorine peak is practically absent, indicating that the surface reaction extends through a layer >5-10 nm thickness, thus no signal is detected from the fluorocarbon substrate. When the sodium/ammonia treated surface layer is etched with Chlorox, the thickness of the oxidized hydrocarbon layer decreases. The intense fluorine peak reappears and the carbon spectrum displays two peaks. The high-binding-energy peak is due to the C-F bond, while the low-binding-energy peak is characteristic of the C-H bond.

Microelectronics applications.

The fabrication of microelectronic devices consists of many steps. During these steps contamination can be introduced from a number of sources. The use of microbeam techniques is essential to pinpoint the cause of the contamination and thus prevent the fabrication of off-spec products and lengthy halts in the manufacturing process.

Table 5. lists important problem-solving and trouble-shooting activities in semiconductor technology and processing (Bakale et al., 1985). The tools most often applied are: OM, SEM-EDX, EBIC, VC, CL, ESCA-Auger, SIMS and LRM.

Short circuit in transistor. Short circuit occurred between the emitter and the collector in a shallowly diffused planar transistor shown in Figure 11. (Burgess et. al., 1975). In the case of a good device, the EBIC images of the collector base (CB) and the emitter base (EB) are complementary depending on the junction polarization applied during the analysis (Fig. 11a). On the other hand, on the EBIC image of the faulty device (Fig. 11b) both the EB and CB junctions were visible regardless of the junction polarization.

Table 5

General Applications/Problem Solving in Semiconductor Technology and Processing.*

- Detecting impurities.
- Analyzing for contaminant distribution.
- Identifying residues - from rinsing, polishing, etching, plating, cleaning, gas line contamination ...
- Determining the sources of haze, discoloration, spots & streaks - from roughness, oxides, residues, pump oil, thickness variation, particulates, deposits, impurities ...
- Identifying particulates.
- Monitoring solvents and other liquids for potential residue.
- Locating surface segregation problems.
- Investigating plating problems, i.e. poor grain integrity, solderability, delamination.
- Tracing the source of high resistivity.
- Tracing the source of electrical leakage from contaminants.

* (Courtesy of Surface Science Laboratories, Mountain View, CA)

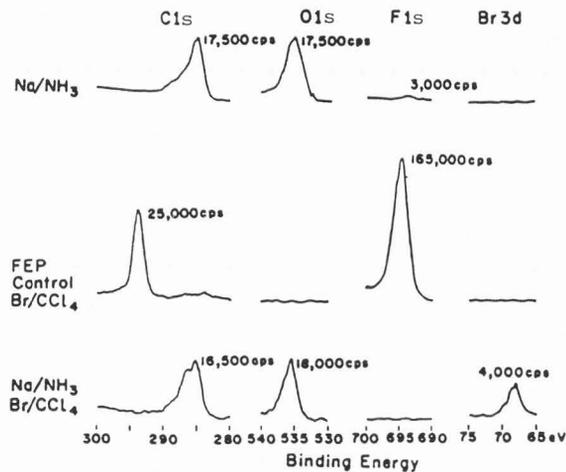


Figure 10. Spectra from Teflon surfaces showing bromination of carbon-carbon double bonds in Na/NH₃ treated sample. (Courtesy of Elsevier Scientific Publishing Co.)

A high magnification secondary electron image of the emitter base (Fig. 11c) showed that the masking technology was correctly carried out and the corresponding EBIC image revealed that the short circuit appeared just at the oxide interface (Fig. 11d). Here the junction was deformed and enhanced diffusion has taken place within a 5 μm region. Chemical etching of similar devices permitted identification of these defects as dislocations localized in the Si epitaxial layer. The conclusion was that up to a base thickness of about 1.5 μm enhanced diffusion within 5 μm of the defects is the origin of the emitter-collector short circuit.

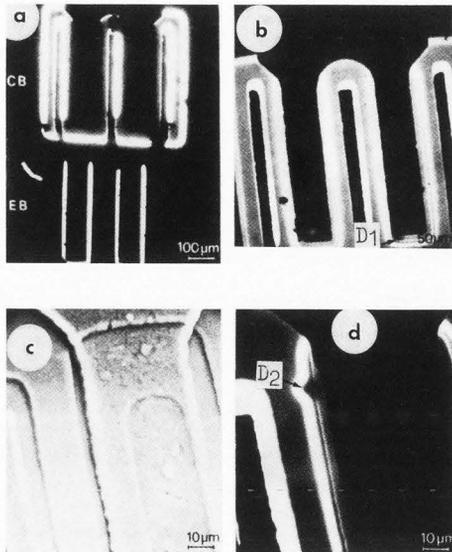


Figure 11. Analysis of collector-emitter short circuits. a. Charge collection image of CB and EB junction for a good device. b. Charge collection image of a faulty device D_1 , electrical defect. c. Secondary electron image. d. Charge collection image with a defect D_2 and enhancement of diffusion induced by D_2 . (Burgess et al., 1975)

Diffusion failure in diodes. Another diffusion related failure occurred in about 25% of the diodes in 10x10 diode arrays which exhibited excess reverse leakage (Beall, 1981). Again, EBIC was applied to identify the cause of the problem. A secondary electron micrograph of a leaky diode showed no indication of the damage. The EBIC micrograph of the same cell, however, identified a diffusion pipe. Once the cause of the leakage was thus pinpointed, the failure was easily corrected.

Diffusion of chromium into gold. (Leybold-Heraeus) A different type of problem, the diffusion of chromium into gold at elevated temperature was reported by the staff of Leybold-Heraeus GmbH. Chromium was used to bond gold to glass. When producing the layer by means of a sputter process heavy heating of the substrate can occur depending on the prevailing process parameters. Investigation of the electrical properties of such layers has shown unexpected phenomena. Profile analysis with ESCA revealed that the chromium entered the gold film by diffusion and was finally fairly evenly distributed throughout the cross section of the film. Figure 12 shows the ESCA profiles for two layers, one without and the other with diffusion.

Tracing the cause of bond failure. (Staff of the Surface Science Laboratories, 1982, 1983). A series of headers, used to package semiconductor devices, was tested to establish the bond-failure mechanism. Figure 13. shows a gold-plated header. Each of the four insulating pins is 0.018" (0.46

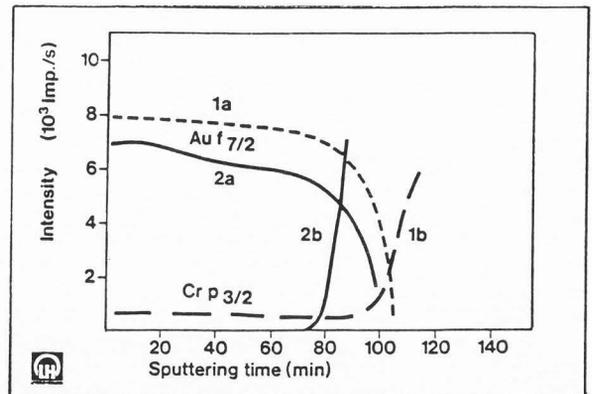


Figure 12. ESCA depth profile of a gold layer sputtered upon chromium as the bonding agent. 1. Diffusion of chromium into the gold layer at elevated temperature. 2. No diffusion takes place at low substrate temperature. (Courtesy of Leybold-Heraeus GmbH)

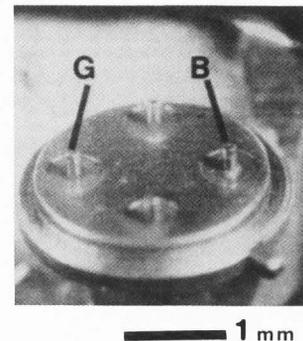


Figure 13. Photo of semiconductor device header taken through the binocular microscope mounted on the SSX-100. The two pins labeled "B" and "G" were analyzed. They are 0.46 mm in diameter. (Surface Science Laboratories, 1982, 1983)

mm) in diameter. The insulating pins are used to connect the device to the header with small wire bonds. Wire bonds often fail due to corrosion and these cases are often referred to service laboratories which specialize in problem solving. The laboratory staff can often determine the exact nature of the contaminant at the spot where the bond failed. Generally a combination of SEM, AES and ESCA is used for this purpose. The most common contaminants are chlorine, fluorine and phosphorus. Chlorine and fluorine are often left by the plasma etching or acid cleaning process. Phosphorus produces phosphoric acid in the presence of moisture, and this powerful acid corrodes the wire and leads to bond failure.

In this particular example small spot ESCA was needed because of the small size of the investigated area. Comparison of the ESCA spectra taken for identical length of time of "good (G)" and "bad (B)" pins (Figure 14) revealed several differences.

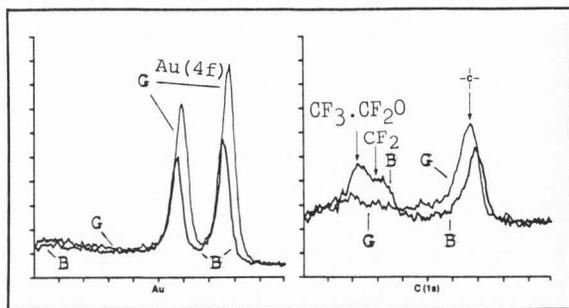


Figure 14. C(1s) and Au(4f) spectra taken of pins "B" and "G" with the SSX-100. (Surface Science Laboratories, 1982, 1983)

1. The carbon spectra indicated the presence of hydrocarbon on both pins, but the spectrum of the "bad" pin showed peaks corresponding to $-CF_3$ and $-CF_2$ groups as well. This indicated the presence of a thin fluorocarbon contaminating layer. About half of the carbon present was associated with the fluorocarbons.

2. The gold peaks were about half as intense for the "bad" pin as for the good one, suggesting that the fluorocarbon overlayer was about 3 nm thick.

Haze and discoloration problems. Analytical laboratories are often confronted with samples which are visibly discolored or hazed. Such samples are usually screened with SEM-EDX to check for particulate matter or surface roughness. Then they are analyzed by a surface technique to determine the major components. If the "good" and "bad" areas have the same morphology and particulates are not detected, ESCA is used. (If only one sample is available, ESCA is applied immediately to avoid possible electron-beam damage). If particulates are found in the discolored area, small spot ESCA or SAM is used to separate the composition of the particle from that of the surface.

Discoloration is often caused by relatively thick (several micrometer) film. In this case EDX analysis can give the composition. These films are often due to contamination (oil from diffusion pumps, various oxides, dust or silicon particulates) or accidental deposits in the plasma chamber.

White film on silver-plated silicon wafer. In one puzzling case a white film appeared consistently on silver-plated silicon wafers almost exactly two weeks after the silver was deposited. Several different ways were tried for storing and treating the wafers, but the mysterious two-week haze persisted. Surface analysis on the wafer revealed a residue of sulfuric acid, left on the wafer from a previous cleaning step, which took two weeks to corrode the silver film and create a haze. This problem was solved by eliminating the sulfuric acid traces.

Problem with gold-plated PC board. (Miller et al., 1984). Hazy plating was experienced on the output of a printed circuit (PC) board - tab gold

plating machine. Only boards originating from one particular outside contractor exhibited this haze which could not be due to fingerprints because these would have been removed during the cleaning cycles along with other light surface contaminants. Plating bath problems were ruled out, since some parts plated perfectly.

SEM analysis showed that the hazy plating was caused by the buildup of gold in irregular islands and in some places by peeling. EDX analysis has shown that chlorine was present in the solder mask that coats all surfaces except the fingers and the contact during tab plating.

Since SEM/EDX showed that the problem is related to the solder mask, the entire solder-mask operation was scrutinized. It was discovered that an oven used to cure the solder mask after its application and prior to tab plating was vaporizing and redepositing solder mask material onto the uncoated fingers and contacts. It was necessary for the vendor to switch to a different solder mask since even routinely cleaning the oven did not solve the problem.

Failures in electronic devices due to deposits.

Thin film deposit contaminants frequently cause failures in the performance of electronic components (Evans and Strathman, 1983). When the layers are only a few nanometers thick, ion probes or Auger-ESCA are the methods of choice. In these cases EDX and MOLE do not suffice, because the contaminant layers are too thin to give a signal.

These films often form during sputtering, a commonly used rapid method for depositing thin films. Many technologies use metals deposited on a wide variety of bases including insulators, such as glass or plastic. Unfortunately, the potential for film contamination by residual vacuum species and the sputtering gas (typically argon) is high; thus preparation of these materials produces minute amounts of contaminants, causing performance failure.

LAMMA determination of contaminant on integrated electronic circuit. (Heinen and Holm, 1984.)

An organic deposit on an integrated circuit was shown by LAMMA to consist of a phenyl-group containing compound. The characteristic peaks of the contaminant also occurred in the control spectrum obtained from the adhesive used to mount the chip. It was deduced therefore, that careless use of the adhesive caused the contamination. The problem was solved by improving the technique of the application of the adhesive. The Raman microprobe and the electron microprobe provided no indication about the nature of this 1 μm thick film, which had an extension of about 100 μm , except that in the latter case the absence of clear signals suggested that the layer might consist of organic materials.

Pitted chromium layer on plastic film. (Evans and Strathman, 1983). The failure of a chromium metal layer on a plastic was investigated. Failure was characterized by localized regions of poor adhesion (bubbles). Auger electron spectroscopy or secondary ion mass spectroscopy of the metal/organic interface is generally used to find

these surface contaminants. These techniques, however, are complicated by charging when the base is an insulator. Beam damage and residual vacuum degradation can cause problems as well. ESCA was not applicable due to the localized nature of the contaminant and to the poor spatial resolution of ESCA. (The most modern small spot, high resolution ESCA might have solved the problem, but at the time of this work it was not yet available).

In this case Rutherford backscattering spectroscopy (RBS) identified the cause of the problem within a 15 minute spectral acquisition. The RBS spectrum revealed a chromium layer on a hydrocarbon substrate with a thin intervening layer which contained a substantial amount of Si and/or Al. These two elements could not be differentiated. Since silicon oil was used in the manually operated vacuum diffusion pump, the poor adhesion was attributed to an accidental backstreaming of oil contaminating the plastic surface.

Whenever failure is due to poorly adhering thin layers, the analyst should keep in mind that silicon oil from the diffusion pump frequently proves to be the culprit.

Until recently RBS was an expensive, emerging technique available only at a few service and university laboratories. The more readily available methods of Auger spectroscopy or SIMS were often applied taking precautions to minimize charging. Lately at least one manufacturer offers a more reasonably priced unit (<\$300,000 US) bringing it within reach of more laboratories (General Ionex Corp. Brochure).

Stains on printed circuit board. (PhotoMetrics Inc., 1981). Stains were observed on the gold contacts of a printed circuit board. Auger micro-analysis was used to establish the thickness and the elemental composition of the surface contaminant and ESCA was used to get specific information about its molecular structure.

The ESCA survey spectrum indicated that the contaminant layer consists mostly of carbon. A detailed look at the carbon (1s) peak with high-resolution ESCA (Figure 15) showed subpeaks representing C-C and C-H chains (c), ether groups (b) and a few ester groups (a). Peak c is normal surface hydrocarbon, but the substantial amount of other groups represented an unusual contamination. The source was found in fumes from a nearby bath and the problem was quickly corrected.

Problem with printed circuit boards. (Bakale and Barth, 1983). Contaminant on a PCB was analyzed by small spot ESCA. Figure 16 shows a small region of the PCB at 15X magnification. The whitish contaminant is present at the "A" location. Using the binocular microscope of the small spot ESCA unit the sample was positioned so that region "A" and region "B" (an uncontaminated area of fiberglass) could be separately analyzed. Figure 17 displays the ESCA spectra obtained from two regions of the board. Region B shows the presence of -CH and -CO groups, the characteristic composition of epoxy resins, expected from the fiberglass PCB. Region A, which shows the whitish

contaminant, gives rise to an ESCA spectrum which reveals the presence of a large amount of fluorocarbon. Identification of the contaminant allowed the engineers to assess the process, find the source of the fluorocarbon deposit and introduce the necessary precautions to prevent its formation.

Leads separating from a circuit upon touching. (Conley, 1973). The interface at which the lead-bond failure has taken place had to be established to prevent the manufacture of faulty products.

The first approach was EDX analysis on both the failed leads and on the region of the circuit from which the lead has detached. X-ray images revealed the presence of a thick chromium layer and no tantalum nitride film on the lead. However, a continuous tantalum nitride film was found in the "circuit board area", over which patches of a thin chromium film was deposited.

The EDX analysis leads to the assumption that the bond failure has taken place at the chromium-titanium nitride interface. Subsequent AES analysis demonstrated, however, that the EDX data lead to an incorrect conclusion. AES has shown the presence of a thin continuous film of carbon on top of the chromium film which was responsible for the failure. The identification of the carbon film permitted the correction of the manufacturing problem.

This example shows that while EDX analysis should be applied first due to its low cost, at times it is unsuitable to solve the problem. It is advisable to follow up with AES or ESCA, both of which are highly sensitive to very thin films of elements of very low atomic number. This is especially true for bonding problems, where the surface layer has a major effect on the quality of bonding.

Problems caused by ionic contaminants. (Evans and Deline, 1985). Ions such as Li^+ , Na^+ and K^+ can incorporate into semiconductor devices and deteriorate their performance. SIMS is used to determine the ionic species and their location, because it gives more information than indirect detection of the contaminants by observing the actual failure of the device under temperature and voltage stress.

Ionic contaminants can be incorporated from the production environment (dust and dirt) or can be introduced during production from contaminated equipment or from the starting materials.

Quantitative SIMS with depth profiling can reveal the nature of the incorporation process. In the case of "crustal abundance" (the abundance of the analytes is close to their abundance in dust and dirt), the contaminant originates most probably from the environment. Alternately, if the elements are in different proportion than would be expected from the environmental contaminant, then it was probably introduced during processing.

Defects in electroluminescent devices. (Burgess et al., 1975). The samples were analyzed in the EBIC and cathodoluminescent modes of an SEM. Figure 18 shows the images of several faulty GaAs infrared devices, with the EBIC image on the left

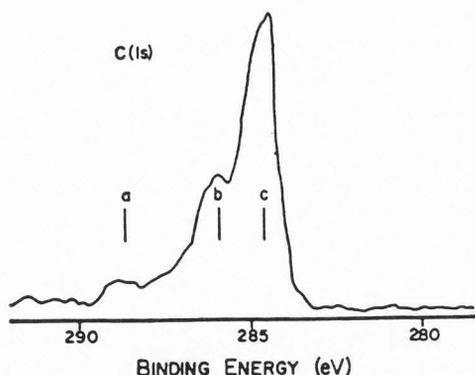


Figure 15. High resolution ESCA spectrum of carbon (1s) peak of stain on gold contact of printed circuit board. (Courtesy of PhotoMetrics, Inc.)

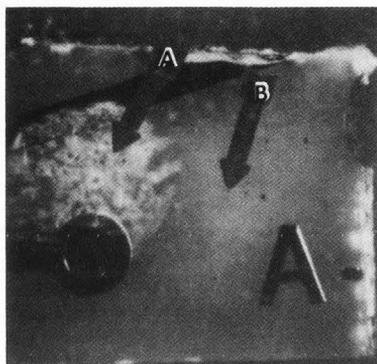


Figure 16. PC board analyzed using ESCA with x-ray probe. Region A (arrow) shows presence of whitish contaminant, while Region B provided normal reference. (Reprinted with permission, *Circuits Manufacturing*, ©, 1983)

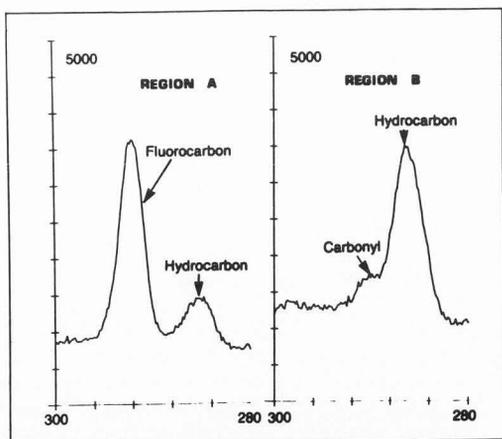


Figure 17. C(1s) spectra for the two regions of PCB shown in Figure 16. Analysis of region B produced normal spectra for epoxy/glass laminate, while Region A shows presence of fluorocarbon contaminant. (Reprinted with permission, *Circuits Manufacturing*, ©, 1983)

and the cathodoluminescence images on the right. According to the authors Figure 18(a) displays strong current variation with well localized defects. The corresponding cathodoluminescent image Figure 18(b) reveals that the defects are not limited to localized diffusion, but the substrate quality is very bad, strongly affecting the luminescence yield. In the second device, apart from the inhomogeneous charge collection in Figure 18(c), it appears that the structural quality of the substrate is good, and, in this case, the distinction between the variable junction thickness and an anomalous precipitation in the diffused zone cannot be made. The high efficiency cathodoluminescence areas in Figure 18(f) are attributed to regions where the diffusion lengths are shortened. (Small zones shown in Figure 18e). Assuming that the luminescence yield is related to the doping level, the variations shown in (e) and (f) are presumably due to an inhomogeneous distribution of the dopant and thus limit the luminescent performance of the device.

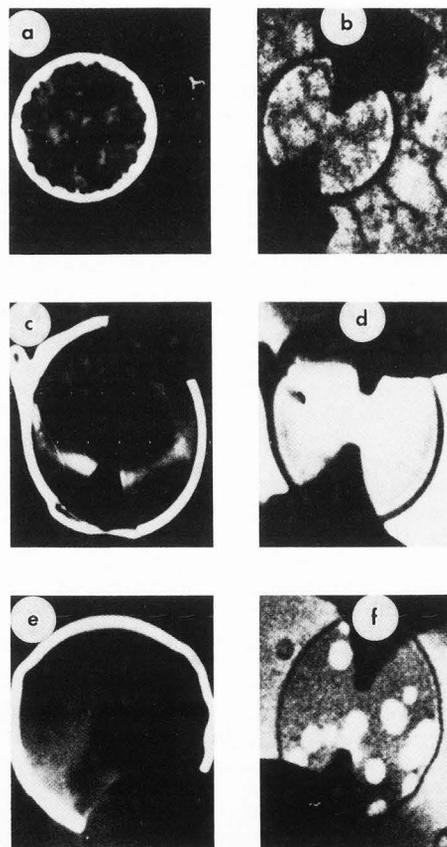


Figure 18. Comparison of charge collection images (a, c, e) and infrared cathodoluminescence images (b, d, f) of GaAs electroluminescent devices. Diameter of diffused zones: 100 μm . (Burgess et al., 1975)

Failed large scale integrated circuits. (Burgess et al., 1975). Defects in large scale integrated circuits were investigated by voltage contrast. VC micrographs of such a device, which failed during DC test taken in the SEM with -1V applied to the external contacts, quickly identified the faulty regions. It showed the outside aluminum line to be an open circuit with respect to some of the boron diffused region.

Corrosion.

Analysis of corrosion mechanism in steam boiler tubes. (Newbury and Yakovitz, 1975). A steel steam boiler's efficiency decreased dramatically due to corrosion deposits on the inner surface of the condenser tubes. The deposit was shown by SEM/EDX to consist of large groups of nodules, rich in copper (Figure 19). This unexpected finding permitted the pinpointing of the source of the problem. A rust inhibitor was circulated in the steel pipes, which in turn was connected to copper pipes. Copper ions carried into the steel tube caused the formation of an Fe-Cu galvanic cell and the copper ions plated onto the inside of the tube. The problem was solved by installing insulating joints between the steel tubes and the copper pipes.

Corrosion problem on nickel sheets. (Photo-Metrics Inc., 1986). The nickel sheets of a manufacturer exhibited discoloration. ESCA spectra (Figure 20) immediately showed that this was an oxidation problem, since the peak of unoxidized nickel would have appeared at lower binding energy than the experimental nickel peak. The oxygen peaks revealed that the oxygen was present as the hydroxide rather than the oxide. This fact can be easily discerned, since there is a chemical shift between the oxide and the hydroxide form of nickel.

Glass and ceramics.

Inclusion in glass. (Andersen, 1984). A bright yellow, strongly birefringent inclusion in glass was requested to be identified. LRM was used first and it gave an intense spectrum which did not match any of the available references. The particles were extracted from the glass and analyzed by SEM/EDX. It gave the composition as: sodium, arsenic and sulfur at the approximate ratio of 1:1:2. Selected area electron diffraction pattern was taken in a TEM. The pattern matched the ASTM reference pattern of NaAsS₂. Subsequently, the Raman microprobe was used to rapidly confirm the presence of this material in additional samples, and an LRM procedure was developed for rapid routine analysis.

Contamination in laser windows. (McCrone, 1983). A leading laser manufacturer found impurities in the glass of laser windows. This contaminant caused a sparkling effect, which not only disturbed the laser beam, but also caused window-expansion. As the absorbed light transformed to heat the windows broke prematurely.

OM showed small, thin flakes of 10-20 μm in diameter and about 1 μm thick. The flakes were removed from the glass after grinding and investigated by EDX. The latter showed that the contaminant was platinum.

This information was not sufficient, since

platinum has been used throughout the manufacturing process of the laser window, therefore SIMS was used to compare trace impurities in the contaminated platinum chip and in all the different types of platinum used in the process. Identification of the presence and relative concentration of each impurity in all the above samples showed that the contaminant originated from the platinum crucible used to hold the molten glass near the end of the process. The sparklers flaked off the sides of the crucibles.

Here OM, EDX and SIMS were used to solve the problem. Optical microscopy isolated the sparklers as discrete particles of distinct size and shape and allowed the separation of the contaminant particles from the glass after grinding. EDX identified the sparklers as platinum and the precise types and amounts of impurities determined by SIMS identified the source of the platinum causing the problem.

Identification of foreign material in optical fibers. (Adar, 1984). Breakage in a batch of AT&T optical fibers was traced to contaminant particles. LRM identified these as ZrO₂. Figure 21 shows an SEM micrograph of a break; a ZrO₂ particle inclusion in the silica fiber is pointed out by an arrow. Identification of both the molecular composition and the crystalline polymorph enabled the engineers to trace back the contamination to the furnace used to draw the optical fibers from the preform. Elemental microanalysis yielded insufficient information in this case because it determined only the chemical composition but could not identify which ZrO₂ material was the contaminating source.

Fibers.

Identification of extraneous material in polymer. (Cody, 1980). Well woven synthetics can be produced only with uniform strands of thread. Nonuniform strands with snarls lead to faulty products. For example Figure 22 shows two strands of polyester fibers about 20 μm in diameter. One of them is unblemished and clear, while the other one is coated with a contaminant layer and an extreme bit of material. Raman spectra taken from the clear strand and from the unidentified contaminant are clearly different.

The 1614 cm^{-1} band which appears on the scan of both is characteristic of the polyester, while the band at 1578 cm^{-1} in scan 22b belongs to the blemish. This information was used to establish and eliminate the source of the contaminants.

Insufficient diffusion of flame retardant pre-polymer into cotton. (Eisenberg et al., 1974, Kiss, 1977). A durable phosphorus-based finish is applied to cotton to impart flame retardance (FR). The finishing process is based on diffusing an oligomeric vinyl phosphonate monomer (Fyrol 76) into the core of the cotton fibers and react it in-situ with methylol acrylamide in the presence of a free radical catalyst (e.g. potassium persulfate). A crosslinked network is thus formed, which provides a durable FR finish.

The FR fabrics generally have a soft, pleasant, desirable "hand" in spite of the high

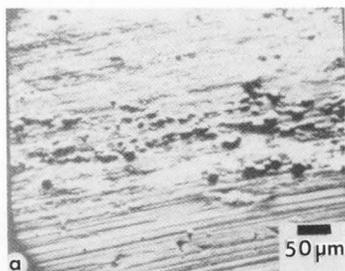


Figure 19. Electron probe analysis of corrosion product in condenser tube. (a) Secondary electron image. (b) Copper X-ray map. (c) Iron X-ray map. (Newbury and Yakowitz, 1975. Copyright, 1975 Plenum Publishing Corporation. Reproduced by permission).

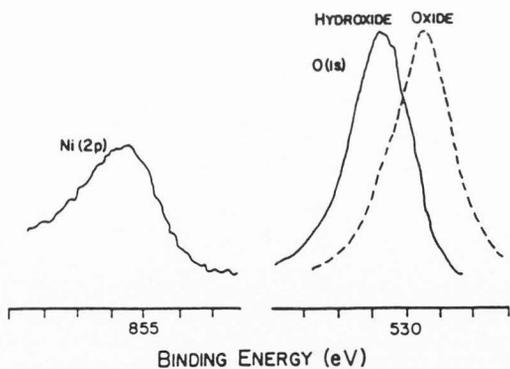


Figure 20. ESCA spectrum of discolored surface of Ni sheet. (Courtesy of PhotoMetrics, Inc.)

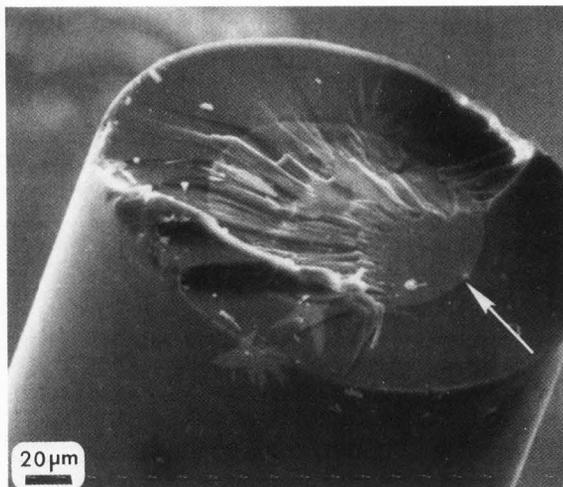


Figure 21. SEM micrograph of ZrO_2 inclusion precipitating break in an optical fiber. (Adar, F, 1984)

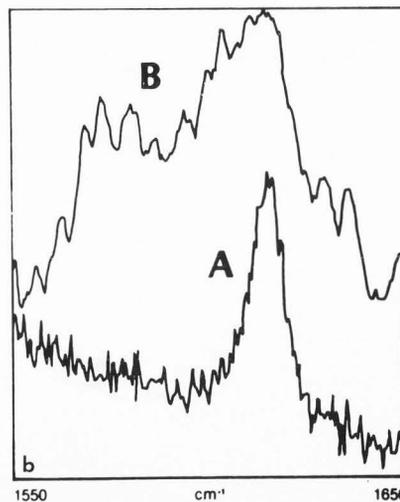
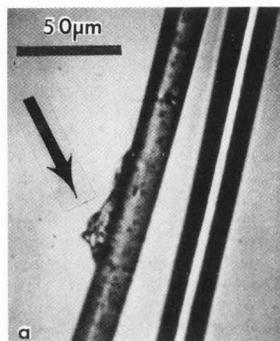


Figure 22. (a) Photomicrograph of contaminated and uncontaminated polyester strands. The strand marred by a trace of extraneous material, picked up somewhere between spinnerette and loom, is pointed out by an arrow. (b) Micro Raman spectra of a fiber (A) and the contaminant (B). (Courtesy of SPEX Industries)

level of FR agent, sometimes amounting to 25-30% of total solids. In view of its high phosphorus content, the EDX technique was selected to establish the distribution of the FR finish within the cross section of the fibrils after the finishing process and after 50 laundering cycles.

A point by point analysis for phosphorus demonstrated that the FR resin is uniformly distributed within the cross section of the fiber, provided that the finishing process is properly performed. In this case the SEM photographs of the surface of the finished fibers are practically identical to those of the unfinished ones (Figure 23). This figure compares representative micrographs of the surfaces of: a. untreated cotton fiber and b. fiber treated with Fyrol 76. The latter originates from a fabric of good "hand". Apparently the two samples are practically identical. The characteristic bark-like surface of the unfinished cotton can be observed both before and after finish and interfibrillar polymer is not discernible. The surface characteristics appear to be unchanged, indicating that if there is any surface coating, it is too thin to be

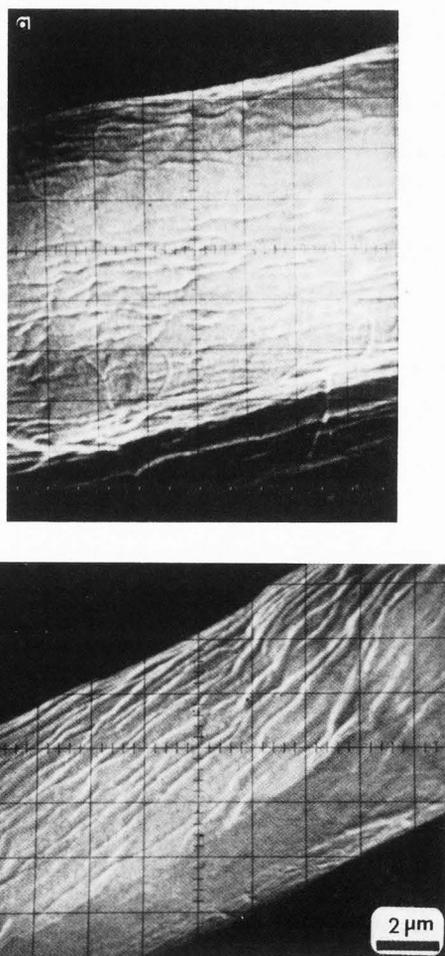
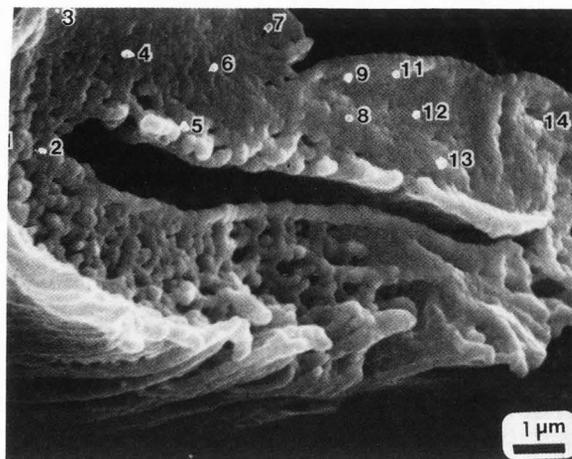


Figure 23. Surface topography of: (a) untreated cotton (control) and (b) flame retarded cotton.

distinguished by high-magnification SEM. Therefore it was deduced that the reagent diffused into the core of the fibers prior to the polymerization, in spite of the relatively high molecular weight (700-1000). The interfibrillar location and uniform distribution of the FR finish was substantiated by X-ray microanalysis for this case (Figure 24) and was shown to persist after 50 laundering cycles.



POINT #	RELATIVE CONCENTRATION AS EXPRESSED IN X-RAY COUNTS
1	2050
2	2005
3	2485
4	2368
5	2396
6	2385
7	2006
8	2110
9	1929
10	1917
11	1952
12	2458
13	2709
14	2356

STATISTICAL EVALUATION:

Average:	2223
Standard Deviation:	225
% Relative Error at	
95% Confidence Level:	+ 22.4

Figure 24. Distribution of Fyrol 76 in the cross section of a typical cotton fibril.

In another case, however, the fabric displayed a hard, undesirable "hand" and the finish had a low wash fastness. It was suspected that Fyrol 76 failed to penetrate into the fiber due to improper manufacturing conditions and the polymer formed inter rather than intrafibrillar. Indeed, SEM photographs of the surface of these fibers showed heavy deposits. The irregular

surface features and polymer film bonding several fibrils together are clearly visible (Figure 25).

The authors found SEM-EDX to be a rapid, efficient and suitable method for quality assurance and failure analysis for the above finishing process.

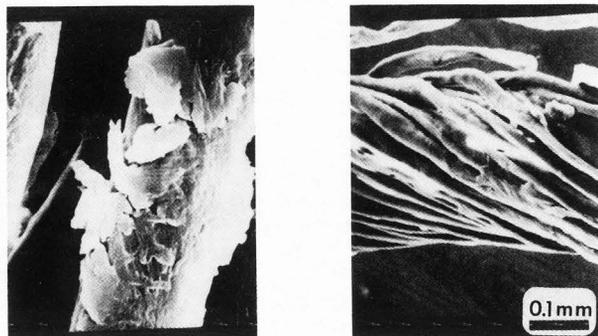


Figure 25. Interfibrillar, heavy FR finish deposit on cotton fibers.

Food products

Microbial spoilage problem in retorted pouch products. (Chung, 1987). A retortable pouch is a preformed bag made with aluminum reinforced polymer films for packaging prepared foods. The various food items are machine filled into the bags, retorted, then the bags are sealed by thermally pressing their open ends. The finished products can be safely stored at room temperature until served. They require no freezing or refrigeration, and give ready - to - eat convenience by simply reheating the entire pouch in boiling water.

Food products packaged in retorted pouches developed spoilage problem during storage even though the most stringent sterilization procedures were applied. The problem was due to unwarranted growth of microorganisms in the pouch caused by faulty filling or sealing operations. The retorted pouch packaged beef stew displayed pouch expansion and swelling after several days of storage, due to microbial gas formation. OM investigation of the cross sections of the sealed pouch ends revealed that the temperature applied in the sealing operation was uneven, resulting in excessive melting and breakdown of the laminated polymer material of the pouches. Minute amounts of food product were also found between the pouch sheets which prevented the complete sealing when thermally pressed.

Figure 26a, a photomicrograph of the cross section of the unsealed pouch shows that it is made of laminated polymer films. Figures 26 b,-c,

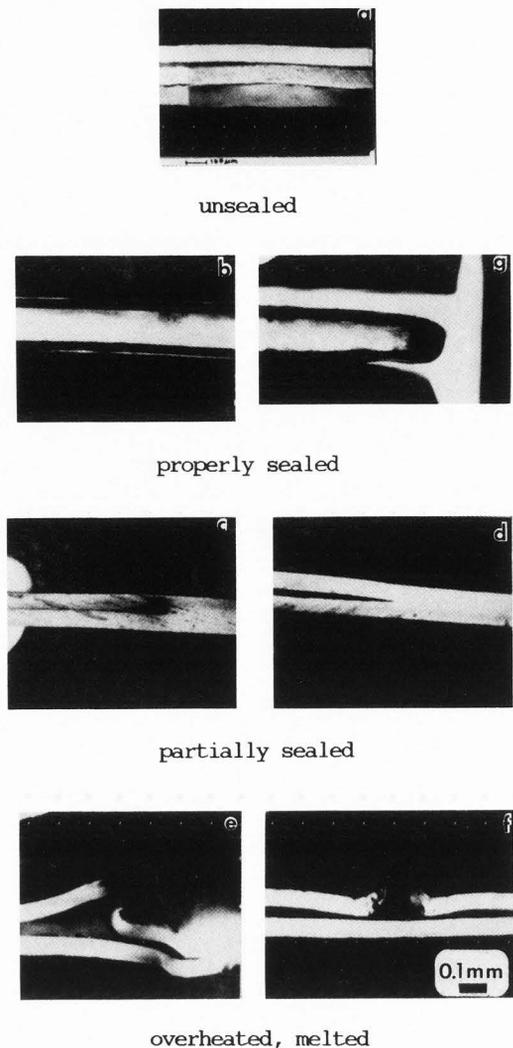


Figure 26. Photomicrographs of the cross section of retort pouches made of polymer film and aluminum foil. (Chung FH, 1987)

and -d compare sections of properly sealed and partially sealed top and bottom ends of pouch materials. Figures 26 e to -f are photomicrographs of sections of defective sealing. Excessively high sealing temperature actually melted the polymer causing non uniform film thickness (Figure 26c). A clean sealing of the pouch ends is shown in Figure 26g for comparison. Figures 27a and -b demonstrate that minute amounts of food fragments lodging between the pouch ends actually prevented the complete sealing of the films. Their presence was determined by dye staining for fat and protein

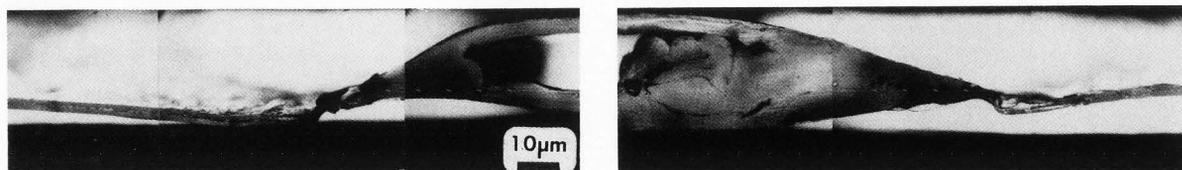


Figure 27. Photomicrographs of sections of poorly sealed retort pouch. (Chung FH, 1987)

using Sudan Black O and Safranin O stains, respectively.

Identification of foreign matter in food. (Stasny, 1981). Sources for the contamination of the human food supply include extraneous particulates associated with raw materials, food handling and packaging processes. Another source of contamination is pest fragments and droppings. The prime concern for all contaminants is whether they represent a hazard (direct or indirect) to human health.

In recent years SEM has supplemented conventional light microscopy as an identification tool. The surface sculpture patterns, setae and setal pits of an insect fragment observed in the SEM can be associated with insect family and possibly even with insect species. Thus, an assessment of the origin of the insect contamination can be made and appropriate processing changes implemented to correct the problem.

Contaminants from the environment or the processing of the food include sand and oil particles, asbestos and glass particles. Sand and oil come primarily from ineffective cleaning of produce. Asbestos may come from additives or filtration media. Glass particles arise from glass containers when chipping, rough handling, etc., occurs during filling or closure. Similarly, paint chips in food can reflect a poorly maintained physical plant and metal fragments might mean improper adjustment of machinery.

Cosmetics.

Lack of substantivity of polymer films on human hair. (Kiss, 1987). Polymer solutions are widely used in the cosmetic industry. One of their major uses is in hair care. Some of the polymer films have a tendency to peel off the hair strands during combing and to form undesirable, dandruff-like particles in the hair. The selection of setting lotions, therefore, requires care and it is of primary importance that the polymer yield a substantive, flexible coating on the hair which maintains its integrity after combing and brushing. SEM micrographs are suitable to establish the surface morphology of the hair strands and to characterize the coating.

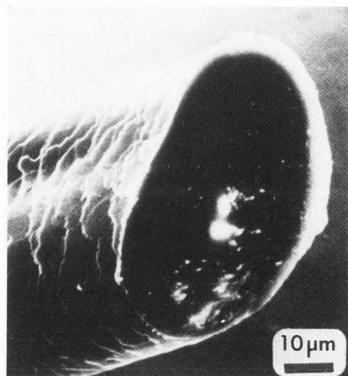


Figure 28. Typical uncoated human hair.

For the comparison of substantivity, small swatches of hair are treated, after washing and rinsing, with the various setting lotions, dried with a hair dryer and combed for identical periods.

Figure 28 shows a typical uncoated human hair at high magnification, with the cuticle cells highly visible. Figures 29 and 30 represent hair strands treated with a solution containing high substantivity and a low substantivity polymer respectively. Figure 29 demonstrates that the uniform, unbroken, smooth polymer coats the cuticles very well to such a degree that they are practically unrecognizable. The coating remained intact during combing, but tests demonstrated that this layer can be removed by washing. Such a coating is highly advantageous for the care and protection of damaged hair, particularly that of overbleached hair. Figure 30 clearly shows that the non-substantive polymer coating breaks off during combing, peels off and forms dandruff-like particles.

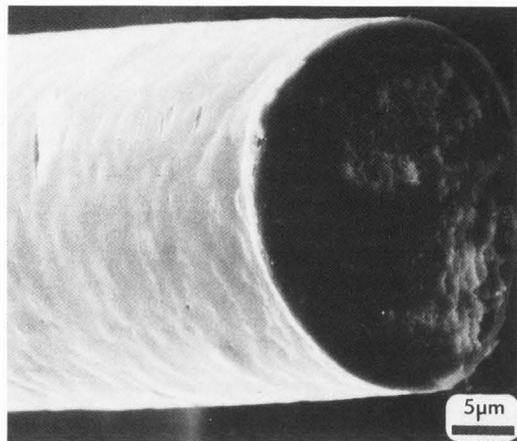


Figure 29. Human hair coated with high-substantivity polymer.

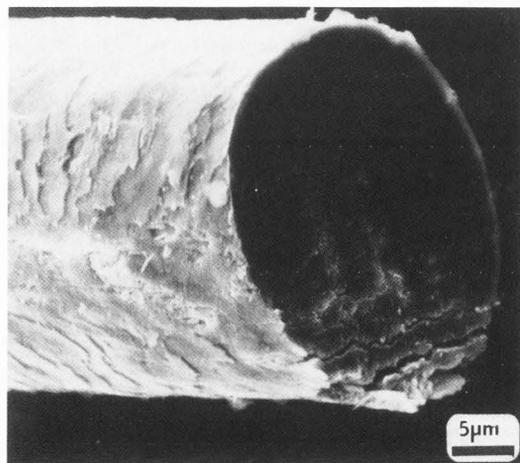


Figure 30. Human hair coated with low-substantivity polymer.

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Editor's Note: All of the reviewer's concerns were appropriately addressed by text changes, hence there is no Discussion with Reviewers.