An Overview of Surface Analysis Techniques and It's Practical Application in Electroplating Industries

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Modern surface analysis techniques including Auger Electron Spectroscopy (AES), Electron Spectroscopy for Chemical Analysis (ESCA, also known as XPS), Secondary Ion Mass Spectrometry (SIMS), Scanning Auger Microscopy (SAM), Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM) will be reviewed and discussed in terms of its strength and weakness. The potential of the surface analysis for investigating failure modes and new products development will be demonstrated using various case studies. Also a comparison of the aforementioned techniques to traditional failure mode analysis methods such as Scanning Electron Microscopy (SEM), SEM with energy dispersive spectrometer (EDS) or wavelength dispersive spectrometer (WDS) and Electron Probe X-ray Microanalysis (EPMA) will be made.

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Introduction

Modern surface analysis techniques have been widely used in many industries including electronic (semiconductor, PWB, Connector etc.) catalysis and automotive. High surface sensitivity and the ability to detect submonolayer species on the surface has been useful for understanding various surface phenomenon such as adhesion (peeling), wettability, solderability, contact resistance, corrosion, friction, wear resistance and many others.

High surface sensitivity of modern surface analysis techniques originates from the fact that either electrons or atoms (ions) are used as the probe. Due



to the strong interaction of electrons and atoms (ions) with the matter, the penetration depth into the substrate is restricted to a few monolayers. This is illustrated in Fig.1, where the mean free path of an electron is plotted versus the kinetic energy of the electron [1]. The mean free path of an electron with energy between 50 and 1000 eV is only 2 to 7 monolayers.

In electroplating, the surface is plated with a thin metal film ranging from 0.01 to several microns. The purpose of this plated film is either to achieve certain functionality such as wear resistance, solderability, wire bondability, corrosion resistance or certain appearance such as glossiness, whiteness and brightness. The chemical composition, microstructure and adhesion to the substrate of the plated thin film ultimately determine its performance. Surface analysis, which can be used to determine the chemical composition and structure of these films, provides unique diagnostic tools to study these phenomena In this paper, various surface analysis techniques including AES/SAM, XPS (ESCA), SIMS and STM/AFM will be and compared to the techniques such as SEM/EDS. The strength and weakness of individual techniques will be discussed and illustrated using various case studies.

1. Overview of the surface analysis techniques

1.1 Auger and Scanning Auger Microscopy (SAM)

Auger phenomena, discovered first by the French Physicist Auger in 1925 [2], is illustrated in Fig.2. The inner (core) level hole, generated by high



energetic primary beam such as electrons, is not stable and can be re-occupied by an outer layer electron. When an electron jumps from the outer layer to the inner layer, energy is released. This released energy can be used to eject a second electron, which is called Auger electron. The kinetic energy of the Auger electron is very characteristic for individual elements and can be used for elemental analysis.

If Auger electrons are emitted from a solid sample, the kinetic energy of the Auger electron (E_{Auger}) is given by:

$$E_{Auger} = E_o - E_1 - (E_2 + e\phi)$$

where φ is the work function of the sample, E_o is the energy of the core level hole, E_1 is the energy of the electron jumping into the core level hole, and E_2 is the energy of the electron to be ejected.

The chemical environment of an element will the Auger process resulting in a chemical shift of the Auger electron. This chemical shift is used for chemical analysis such as identification of the oxidation state. However, due to the complexity of Auger process (three energy levels involved) and consequently broad Auger peak, AES is rarely used for chemical analysis.

Since electron beams can be easily focused and scanned over the surface, Auger microscope with spatial resolution down to 50 nm is commercially available. The elemental distribution over the surface and elemental composition of submicron features can be easily obtained.

1.2 Electron spectroscopy for chemical analysis (ESCA/XPS)

In XPS, a monochromatic X-ray with energy hu is used to eject electron from the core level and the kinetic energy of the ejected electron is measured



using an electron analyzer. The binding energy (E_B) of the electron can be then calculated using following equation:

$$E_B = h\upsilon - E_K$$

Since the binding energy depends also strongly on the chemical environment, it can be used to determine the chemical state (oxidation state) in addition to elemental identification. The intensity of the photoelectron can be used to determine the elemental concentration in particular chemical state.

The Auger parameter, defined as:

A.P. = $E_{\text{kinetic}}(\text{Auger}) + E_{\text{binding}}(\text{photoemission})$

has been often used for the chemical state analysis. The advantage of using Auger parameter instead of the binding energy alone is that the Auger parameter is independent of energy referencing. The problem associated with the sample charge and instruments drift is minimized. Therefore, small shifts in Auger parameter can be measured with high accuracy and used for the chemical state identification.

Due to the difficulty of focusing x-ray beam, the lateral resolution of XPS is usually poor, especially compared to AES. However, the so-called scanning XPS has been also developed and instruments with micron spatial resolution are commercially available.

1.3 Secondary Ion Mass Spectrometry (SIMS)

When an energetic ion beam strikes a surface, elemental and molecular ions will be generated and ejected from the surface. These secondary ions will be analyzed using a mass



spectrometer. Elemental (including isotope ratios) as well as molecular information in the top surface layer can be obtained. The sensitivity of SIMS is generally higher than XPS and Auger. However, the quantification is rather difficult due to the strong matrix effect and strongly varying ionization cross section. The quantification is only possible when proper standards are available.

1.4 Scanning Tunneling Microscopy (STM) and Atomic Force Microscopy (AFM)

When two objects are brought in close approximate (less than 1 nm), electrons will tunnel between the two objects. The tunneling current depends on the voltage applied between the two objects and exponentially on the distance between the two objects [3]. The strong distance dependence of the tunneling current provides a way to measure the distance between two objects with sub-angstrom accuracy. In STM, a sharp metal tip is used to scan over a surface (see Fig. 5). The x, y, and z motion is provided by a scanner made of piezo ceramic with sub-angstrom accuracy. Surface topography (more accurately contours of constant electron density) can be mapped with atomic resolution.



Since the invention of STM by G. Binning and H. Rohrere in 1982, several variations have been appeared [3]. In the atomic force microscope, nanoscale force between two objects such as van der Waals, magnetic, chemical, and electrostatic forces are measured instead of tunneling current. A sharp tip is mounted on a cantilever and scanned across a sample surface, and the force is measured by monitoring the deflections of the cantilever (see Fig.6). Information regarding surface topography, magnetic domain, electric field gradient distribution, difference in local surface potential and surface adhesion, relative elasticity/stiffness of surface features, and friction force can be imaged with atomic and nanometer resolution.



3.1 Solderability and reflowability of tin and tin-lead electrodeposits

Tin and tin/lead coatings have been used extensively in the electronics industry as interconnection materials and as final surface finishes [4, 5]. One of the requirements for the coatings is to have "long term" solderability and be reflowed without dewetting. The following factors, as



schematically represented in Fig. 7, affect solderability and reflowability of electroplated Sn and SnPb electrodeposits: organic inclusion, surface oxides and intermetallic compounds.

Organic inclusions are particularly significant since most electroplating processes utilize "organic addition agents" to impart brightness to the deposits. It is known that organic inclusions can have a detrimental affect on solderability and reflowability. Table 1 attempts to quantify this relationship.

Table 1			
	CARBON	THERMAL	
FINISH	CONTENT, %	BAKE TEST	
Satin bright		Pass: no dewetting,	
tin	0.004	No discoloration	
Satin bright		Pass: no dewetting,	
90/10 tin/lead	0.01	No discoloration	
Bright 90/10		Pass: no dewetting,	
tin/lead, A	0.02	No discoloration	
Bright 90/10		Fail: dewetting,	
tin/lead, B	0.07	No discoloration	
Bright 90/10		Fail: dewetting,	
tin/lead, C	0.1	Slight discoloration	
Bright tin		Fail: dewetting,	
	0.2	Severe discoloration	

3.1.1 Solderability

3. Case Studies

Sn plated battery contacts show solderability failure when soldered to boards. Auger and SAM were used to identify the possible cause.

Fig.8 shows typical secondary electron



Fig.8 Typical SE images of the surface

images of the surface. To determine the origin of various features observed, Auger Spectra were taken at various points of the surface. This result is



Fig.9 Auger spectra at various points

summarized in Fig.9. Sn, C, O, and S were found on the surface. The atomic concentration is provided in Tab.2. The stain (point 1) is apparently due to Scontaining organic.

Tab.2 Atomic Concentration (%)*				
	С	Sn	0	S
Point 1	67.3	13.3	14.8	4.5
Point 2	77.2	13.5	9.3	
Point 3	100			

* H can not be detected in AES.

The thickness of tin oxides at points 1 and 2 was also determined using Auger sputter profile, which is provided in Fig.10. At both points, carbon disappears after one cycle of sputter (2 nm removed). At point 2, oxygen disappears also after the second sputter cycle (4 nm removed). This corresponds to a

tin oxide thickness of 2-4 nm, typical for a native oxide formed on Sn surface at normal condition. At



Fig.10 Auger depth profile

point 1, however, the tin oxide was measured to be as thick as 20 nm. Apparently, the stain promotes tin oxide formation. Summarized, stains with Scontaining organic are found on the surface, which can be attributed to the poor rinsing after Sn plating. Sputter profile shows much thicker tin oxide formation under the stain as regular area, which results in the solderability failure.

3.1.2 Dewetting

Connector samples, plated with SnPb(90/10), were found to exhibit solderability problems in the form of dewetting. Auger electron spectroscopy and Auger depth profile are used to determine the possible cause. Fig.11 shows typical SEM Micrographs for a de-wetted sample and one exhibiting good solder coverage.



Fig.11 SEM images of a surface with excellent Solderability (left) and a dewetted surface

Auger depth profiling of two dewetted areas and one good area was performed to ascertain the elemental composition of the SnPb layers and the SnPb/Cu interface. In all two dewetted areas, Cu was observed at or near the surface indicating that the dewetting occurs at the interface between the SnPb and Cu layers. As can be seen in Figure 12, large amounts of carbon are present at the SnPb/Cu interface in the dewetted areas. These results seem to indicate that the carbon accumulation at the SnPb/Cu



Fig.12 Auger depth profile

interface is the origin of the dewetting problem.

Furthermore, the amount of carbon found in this particular SnPb film is on the order of 0.7% in all dewetted samples. Carbon is generally included in the SnPb layer during the electrodeposition process. Large amounts generally can contribute to dewetting of the SnPb during reflow or subsequent soldering operations.

3.2 Bondability and wirebonding of nickel/palladium

plated leadframes

Palladium surface finishes have been increasingly applied to semiconductor leadframes, Fig. 13 [6,7]. The superior functionality and lower total cost of palladium pre-plated leadframes (Pd PPFs), due to process simplification and positive environmental impact of replacing tin-lead solder have provided the impetus for this technological change.



with silver/solder or nickel/palladium, after die attachment, wirebonding and encapsulation and before trimming and forming.

The technology utilizes high speed nickel and palladium plating, (Pd/Ni) of the entire leadframe surface to replace the standard selective silver plating for die attach and wirebonding, and solder plating of the external leads for solderability. The latter usually applied after package assembly.

The Pd thickness is ~0.1 μ m and can be Au flashed (GFPdNi) to enhance solderability and wetting speed. It is expected that the Pd PPFs will meet the following criteria:

<u>Solderability</u> Coverage/Dip & Look = >95% Wetting Speed = < 1 sec. <u>Wirebonding</u>: Pull Force = $7g \pm 10\%$ 3.2.1 The effect of base metal impurities on the solderability and wirebonding

An electronic device manufacturer requested Au-flashed Pd/Ni on Cu leadframes with "reduced" Pd and Au thickness as a cost reduction. The plated leadframe must exhibit excellent solderability and wirebonding. The following analysis were undertaken to ascertain the feasibility of the customers request:

- Solderability Tests: Dip-and-Look and Wetting Balance
- Wirebonding and Pull Tests
- Auger Electron Spectroscopy (AES) Surface Analysis

Leadframe samples with standard and reduced thickness of GFPd/Ni were prepared as follows:

- Standard Thickness 0.006 μm Au/ 0.10 μm Pd/1.0 μm Ni/ 150 μm Cu substrate
- Reduced Thickness 0.003 μm Au/ 0.05 μm Pd/ 0.5 μm Ni/ 150 μm Cu substrate



Solderability results shown in Fig. 14 demonstrate the

superior performance of the standard samples which exhibit wetting speeds of <1 second, and significantly higher wetting force of 0.84 mN/mm. The reduced thickness samples, on the other hand, show a wetting speed of >10 seconds and a negative wetting force of -0.15 mN/mm at 2.50 seconds time interval.

Wirebonding results are exhibited in Table 3 and Fig. 15, and demonstrate that the standard samples outperform the reduced thickness samples which do not meet any of the specified requirements.

Pull Force (g)	Reduced	Standard	Requirement
Mean	5.26	7.35	≥7.00
Std. Dev.	1.82	0.67	≤10% of Mean
Minimum	1.15	5.37	≥5.00
Table 2 Au Winshanding Degulta			

Table 3 Au Wirebonding Results

Fig. 15 demonstrates that the wirebonding failure was at the wire/leadframe interface; whereas in the standard sample, the break occurred above the ball bond, which is acceptable. The results indicate that the reduced thickness of GFPd is unacceptable compared to the required criteria.



Fig. 16 Auger Electron Spectra

Surface analysis performed via Auger Electron Spectroscopy (Fig. 16) demonstrates higher concentration of Ni, Cu and O on the surface of the leadframe with the reduced thickness of Au and Pd. promotes limited thickness significant The interdiffusion and formation of base metal oxides which are deleterious for solderability and wirebonding. In conclusion, a sufficient thickness of Pd and Ni finishes as specified in the "standard" is required to minimize surface oxidation and ensure solderability and wirebonding performance.

3.2.2 Die attachment using conductive adhesive

Samples, which show adhesion problem towards the conductive adhesive, are submitted for Surface Analysis. Previous Auger measurement by a independent surface analysis lab shows no difference between the "good" and "bad" samples.

Fig.17 show SEM images of the three



samples as received. White spots are observed in the images on all three surfaces and are due to the adsorbed carbon-containing species according to Auger spectra. Consistent with previous Auger measurement, virtually identical Auger spectra were obtained for the three surfaces. A single carbon peak at 284.6 eV is also observed in XPS, typical for the adventitious carbon, which interferes with the XPS analysis of the samples. To remove the organic particulate, which most likely is adsorbed onto the surface during handling of the sample, the samples were ultrasonically cleaned in methanol for 15 min. As the Fig.18 shows, most organic particulate is



removed from the surface after the cleaning. Very similar morphology is also observed for the three surfaces. XPS is used to determine the elemental composition and valence states of adsorbed species on the surface. The atomic concentration is provided in Tab.4. No significant difference in the elemental concentration is seen between the three samples, consistent with the Auger results. However, the chemical states of adsorbed sulfur are somewhere different for the "good" sample compared to the other two samples, as the Fig.19 demonstrates. In addition to S²⁻ found on the two "bad" samples, S⁴⁺ containing species was also found on the "good" sample. Apparently, species containing S in 4+ oxidation state



acts as adhesion promoter between the Pd surface and this particular conductive adhesive.

Tab.4 Atomic Concentration of all detected elements*

	С	Pd	S
"good" sample	64%	18%	18%
"bad" sample 1	58%	24%	18%
"bad" sample 2	60%	23%	17%
"bad" sample 2	60%	23%	17%

• H can not be detected in XPS.

3.2 Gloss and Surface Roughness

Sn and Sn alloys are widely used as protective and solderable coating in various industries. The appearance of the Sn and Sn alloy coating is one of the important characteristics in these applications and has been often classified as matte, satin bright and full bright. This qualitative appearance classification is obviously subject to interpretation and can often lead to misunderstanding in the appearance description of the Sn and Sn alloy films. Previously [8], we have demonstrated, that the surface appearance of Sn can be quantitatively described by the gloss reflectance factor and is mostly determined by the surface roughness. Fig.20 provides AFM topographic images of the bright, satin bright and matte Sn. Consistent with previous SEM and TEM results, the bright Sn shows a fine grain structure with grain size in the range of 50 to 100 nm. The satin bright and matte surfaces, on the other hand, have a much larger grain size of several microns. It is also apparent in Fig.20, that the surface roughness increases going from bright to satin bright and further to matte. The arithmetic average roughness, calculated from AFM images over 100x100 μ m, is summarized in Tab. 5. The gloss reflectance factor measured at 60° light incident angle is also included.



	Bright	Satin bright	Matte
Roughness	19 nm	113 nm	176 nm
Gloss	719	89	12

As the Tab.5 demonstrates, there is a clear correlation between the surface roughness and gloss: the smoother the surface, the glossy the surface. Consistent with previous conclusion, the gloss of a surface is mostly determined by the surface roughness.

4. Conclusion

Modern surface analysis techniques have been reviewed and it's potential in the failure mode analysis and new products development in the electroplating industries are demonstrated in various case studies. With the continuing miniaturization in the electronic industries and reduction of the thickness of the plated films in general, the application of surface analysis in the electroplating industries will become even more important and necessary in the future.

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