C. BRENT BARGERON

HIGH VACUUM SCANNING ELECTRON MICROSCOPY AS A TOOL IN SURFACE ANALYSIS

Scanning electron microscopy is discussed as a tool for surface analysis. The fundamental physical principles of this type of microscopy are presented in a framework that relates the scanning electron microscope (SEM) to other surface investigation techniques. The use of the SEM in corrosion research and other APL projects illustrates its capabilities.

The Milton S. Eisenhower Research Center's Scanning Electron Microscopy Laboratory facilitates the determination of several features of the topography, structure, composition, and electrical behavior of surfaces as well as surface-related phenomena. Its major instruments are an ETEC Corporation high-vacuum SEM and an associated system (a Kevex detector and a Tracor Northern NS-880 analyzer) for the energy-dispersive analysis of X rays that are emitted from the surface as the result of electron impact. The high-vacuum capability (pressures less than 10^{-8} torr, or 10^{-11} atm) is rather unusual. It makes possible the study of surfaces while they are essentially free of contamination from external impurities.

The primary purpose of the SEM itself is to image surfaces. The microscope achieves magnifications up to hundreds of times those of optical microscopes (i.e., up to 240,000×). In its normal imaging mode, the resolution is about 7 nm (70 Å). Another advantage of the SEM is its inherent great depth of field, which is also hundreds of times that of an optical microscope.

To aid in obtaining topographical information, a sample is mounted on a stage with five degrees of freedom (three translational, one tilt, and one rotational). This allows a view of all sides of a specimen except the one facing the stage itself. The tilt and rotational degrees of freedom are useful in obtaining stereoscopic pairs of a surface (cf. Fig. 1). Such a stereo pair removes the ambiguity that is involved in interpreting topographical features in a single SEM photograph. It is obtained by taking two photographs of the same area at two tilt or rotational angles differing by 6 to 10°.

The primary function of the X-ray spectrum analysis system is to determine the elemental composition of surfaces. The X rays emitted by all but the first eight atomic elements (hydrogen, helium, lithium, beryllium, boron, carbon, nitrogen, and oxygen) are detected and identified automatically by means of built-in computer software. When the instrument is used for elemental analysis, its spatial resolution is only about 1 μm (1000 nm) because X rays can escape from a larger region surrounding the impact area of the scanning electron beam than is the case for electrons (this will be explained in more detail later). This resolution is satisfactory for many purposes and, in particular, for the easy identification of minute quantities of surface impurities.

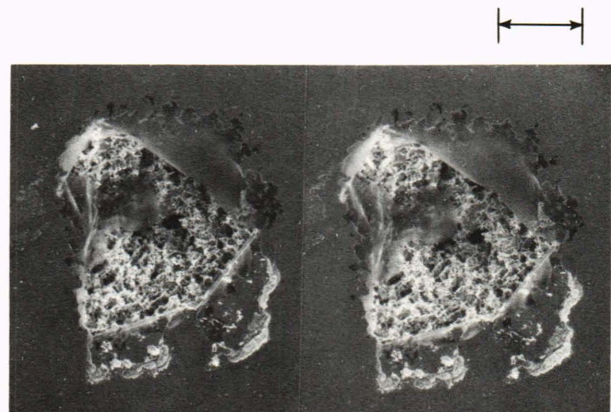


Fig. 1—Stereoscopic micrograph pair of a pit that formed in the surface of high purity aluminum. An 80 nm oxide film was grown (prior to the corrosion tests), pieces of which are draped over the edge and down into the pit, and are also folded back upon themselves (lower side of pit). The piece of oxide draped from the left side of the pit has a rounded portion resting on the bottom of the pit. Viewing in three dimensions removes the interpretational ambiguity associated with a single two-dimensional photograph. Instruments are available to make quantitative measurements from such a stereo pair. The pit can be viewed in stereo by placing an opaque sheet of material perpendicular to the page along the line dividing the two micrographs and allowing the eyes to merge the two images. With some luck the sheet is not necessary. However, a stereoscopic viewer is best if available.

In addition to its use in Research Center investigations, the SEM laboratory is available to other divisions of APL. Two examples of such use are shown in Figs. 2 and 3.

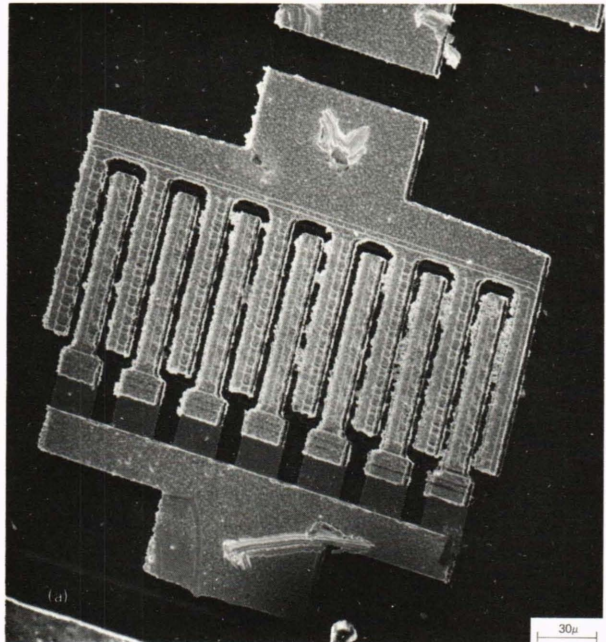
Figure 2 illustrates an unusual type of failure in a hybrid circuit that was submitted for analysis by the Microelectronics Group via the Satellite Reli-

Fig. 2—An unusual failure of a hybrid circuit. The spherical piece of metal (aluminum, as shown by X-ray analysis) was spewed out of the crater that interrupts the metal track. An electrical failure was caused by the open track. The high spatial resolution and mioroanalysis capabilities of the SEM made this failure analysis possible.

ability Group. The micrograph shows that a piece of metal (aluminum, as shown by X-ray analysis) was spewed out of the conducting track, leaving a crater in the conduction path.

Figure 3a is a micrograph of a power transistor submitted for analysis by the Satellite Reliability Group. A similar transistor on the same chip had failed during tests in a satellite transmitter. The photograph shows extraneous material between what should have been cleanly defined tracking. Figure 3b is a similar micrograph of the same transistor. However, the image was made using gold's X-ray line (M line) and hence is a spatial map of gold in the surface. Further X-ray analysis and photographs determined that the extraneous material between the gold tracks was tantalum that was used in manufacturing the transistor and that presumably later migrated between the tracks, eventually shorting the transistor.

Other imaging modes are also available in the SEM, as will be discussed later. For example, a 48-pin electrical feedthrough permits imaging techniques involving induced currents, specimen currents, and applied voltages.



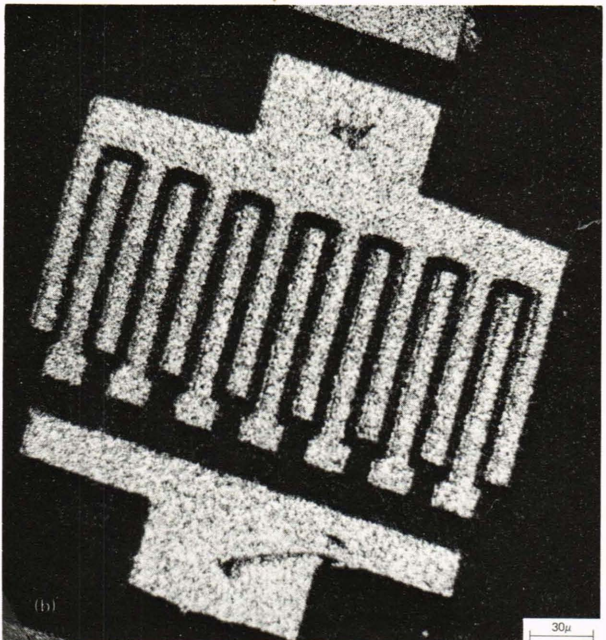


Fig. 3a—View of the interlocking tracks of a power transistor from a satellite transmitter prior to launch. Note that the space between tracks is somewhat cluttered with extraneous material. X-ray analysis identified the extraneous material as tantalum.

Fig. 3b—Dot map of gold on the power transistor in Fig. 3a, produced by placing a narrow window on gold's M line in the X-ray spectrum. Whenever an X ray is detected within the energy limits of the window, a pulse is sent to the SEM screen. The pulse is synchronized with the scanning electron beam and appears as a dot.

PHYSICS OF SURFACE ANALYSIS

Because the physical and chemical properties of surfaces and interfaces play critical roles in the performance of materials and because of technological advances, many techniques have been developed for surface analysis during the last two decades.[1,2] In order to provide some background on the relationship of other methods to those used by the SEM, let us review some of the physics involved. In general, each surface analysis technique can be categorized by the excitation source, the resultant signal, and the obtainable information.

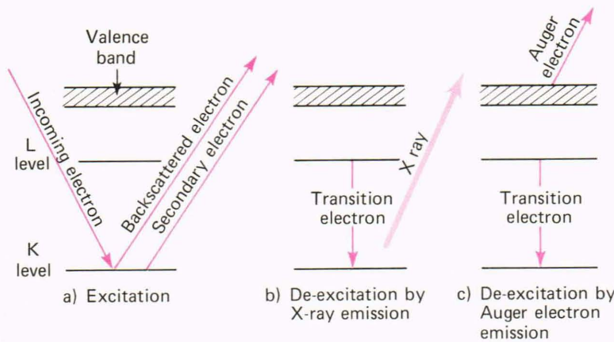


Fig. 4—A schematic energy level diagram describing (a) atomic excitation by an incoming electron, (b) de-excitation by X-ray emission, and (c) de-excitation by Auger electron emission. As shown in the three diagrams, there are four resultant signals: a backscattered electron, a secondary electron, an X ray, and an Auger (tertiary) electron. All of these signals are used prominently in surface analysis.

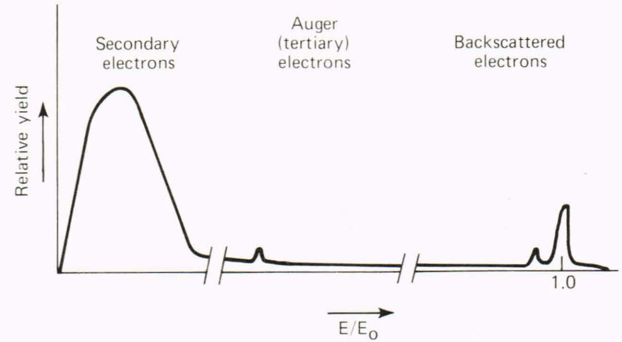


Fig. 5—A schematic energy distribution of emitted electrons. Some of the uses of these various kinds of electrons are described in the text and Table 1.

Common excitation sources are electron beams, ion beams, electromagnetic radiation (X rays, ultraviolet light, etc.), and electric fields whose resultant signals are electrons, ions, and emitted radiation. As an illustrative example, consider Fig. 4. In Fig. 4a, an electron (the excitation source) is scattered from a core electron in an atom in a surface. In the process the incoming (or primary) electron is backscattered, the core electron escapes from the atom (and is referred to as a secondary electron), and the atom itself is left in an excited state. The excited atom can decay by emitting an X ray, as shown in Fig. 4b; this is a one-electron process. In making the transition from the L level to the K level, an electron loses a precise amount of energy that appears as the X ray.

Alternatively, the atom can decay via a two-electron process in which an L-level electron makes a transition to the K level and a second atomic electron (say, one from the valence band) is ejected with a specific amount of energy. The ejected electron is called an Auger electron (in honor of the man who first described the process). This de-excitation process is shown in Fig. 4c. X-ray and Auger electron emission are competing processes, with the latter being favored by the lighter elements. In this simple example the excitation source is an electron. There are four resultant signals, each of which is used prominently in surface analysis. Because there are usually several excitation sources, other resultant signals, and various signal processing possibilities to obtain the available information, there is a proliferation of surface methods.

In order to illustrate a few of the possibilities offered by signal processing for obtaining specific types of information, consider the energy distribution of emitted electrons shown in Fig. 5. The large low-energy peak represents secondary electrons. Most of these electrons have energies between 0 and 30 eV, with an average value between 3 and 10 eV. In the SEM, secondary electrons are especially useful for topographical imaging because they are relatively abundant and easy to collect. The yield of secondary electrons depends on material parameters such as work functions. Thus images obtained by using secondary electrons also reveal contrast between different types of material in the surface.

The second most abundant type of electrons are the backscattered electrons shown in Fig. 5 with a well-defined peak at $E/E_0 = 1$, where E_0 is the primary beam energy. The tails of this peak frequently reveal secondary peaks as shown. Backscattered electrons can be used for topographical imaging; however, because they are generally less abundant and more difficult to collect than secondary electrons, the secondary electrons are usually preferred for this use. The yield of backscattered electrons increases with the atomic number of the atoms in a surface. Thus materials contrast will be revealed in images using these electrons. The secondary peaks in the backscattered electron distribution contain information about the surface states of the material being bombarded. Most SEM's are not equipped with dispersive electron energy detectors. However, the information is valuable and electron energy loss spectroscopy has evolved as a result.

Another use of backscattered electrons is to study surface structure. If a beam energy of 20 to 300 eV is used and if the angular distribution of backscattered electrons can be detected, then (under favorable circumstances) an electron diffraction pattern can be obtained from the surface. Thus, the surface crystal structure can be identified and quantitated. This research field is also a separate discipline and is known as low energy electron diffraction (LEED). Another similar discipline, reflective high energy electron diffraction (RHEED), is used to study structure; however, in this case beam energies are in the 30 to 100 keV range.

In the energy region between the backscattered and secondary electrons in Fig. 5 there are relatively smaller peaks in the electron energy distribution. These are Auger (tertiary) electrons, which are invaluable for determining surface elemental composition and even the chemical state of atoms in the surface. They are generally not abundant enough to obtain a good topographical image;

however, they are very useful in obtaining elemental maps of the surface. The information obtainable from Auger electrons is very important. As with electron energy loss spectroscopy, an electron energy dispersive spectrometer is required. Therefore, Auger spectrometers are usually separate instruments rather than attachments to a SEM. The Research Center has a separate laboratory for Auger electron spectroscopy (AES). This Auger instrument also has a secondary configuration in which LEED can be performed.

The preceding discussion of the energy distribution of emitted electrons is intended to provide insight into the kinds of information that may be obtained by various detection and signal-processing techniques. It is, of course, not all-inclusive, even in dealing with the uses of emitted electrons. If one uses X rays as the excitation source (as opposed to an electron beam), the distribution of emitted electrons is appreciably different. Thus, the techniques used for surface analysis also take on a different character. Table 1 lists a few general surface-analysis techniques relating excitation sources, resultant signals, and obtainable information.

An important feature of the various detectable signals that should be understood is that they

Table 1

SOME SURFACE ANALYSIS TECHNIQUES

Technique	*Excitation Source*	*Resultant Signal*	*Information*
Imaging			
Scanning electron microscopy (SEM)	Electrons (2 – 30 keV, $10^{-9} - 10^{-11}$ A)	Secondary, backscattered, and absorbed electrons, electromagnetic radiation	Topography, spatial distribution of elements
Scanning Auger microscopy (SAM)	Electrons (1 – 3 keV, 1 – 50 $\times 10^{-6}$ A)	Auger electrons	Spatial distribution of elements
Composition			
Auger electron spectroscopy (AES)	Electrons (1 – 3keV, 1 – 50 $\times 10^{-6}$ A)	Auger electrons	Elemental analysis of top 3 nm including oxidation state of elements
X-ray photoelectron spectroscopy (XPS) (also known as ESCA, electron spectroscopy for chemical analysis)	X rays (e.g., Al K_α, 1486 eV)	Photoemitted electrons from core levels	Elemental analysis of top 3 nm with information on chemical bonding
Secondary ion mass spectrometry (SIMS)	Ions (usually inert gas ions) (1 – 10 keV, 1×10^{-9} A)	Mass-selected (sputtered) ions	Elemental analysis of top layers via mass/charge analysis of fragments
Ion scattering spectroscopy (ISS)	Inert gas ions (100 – 1000 eV, 1×10^{-9} A)	Elastically scattered ions	Elemental analysis of top atomic layer only
Energy dispersive analysis of X rays (EDAX)	Electrons (10 – 50 keV)	Characteristic X rays	Elemental analysis of top 1 to 5 μm; 1 μm lateral resolution possible
Structure			
Low energy electron diffraction (LEED)	Electrons (~20 – 300 eV, 1×10^{-6} A)	Angular distribution of elastically scattered electrons	Structure of ordered regions of the surface
Reflection high energy electron diffraction (RHEED)	Electrons (~30 – 100 keV)	Angular distribution of elastically scattered electrons	Structure of surface islands or precipitates
Electronic Structure			
Field emission microscopy (FEM)	High electric field	Angular distribution of field-emitted electrons	Work function variation of different crystal surface orientations
Ultraviolet photoelectron spectroscopy (UPS)	UV light (~20 eV)	Photoemitted electrons	Occupation of molecular orbital states in adsorbates
X-ray photoelectron spectroscopy (XPS) (see above also)	X rays	Photoemitted electrons from valence levels	Density of states of filled valence states

emanate from various depths below the solid surface. To illustrate this point, consider Fig. 6. A small-diameter electron beam is incident on a surface. Typically, the electrons in such a beam are of 2 to 30 keV energy in a SEM. Thus, an electron has a finite range in a material and generally undergoes multiple scattering processes before it loses that energy or is emitted as a backscattered electron. The result is that the finely focused beam spreads out and creates signals within a teardrop-shaped volume as shown. The dimensions of this volume are material-dependent.

For example, for a beam of 20 keV electrons striking an aluminum surface, the teardrop will extend roughly to a depth of 5 μm and have a maximum diameter of about 1 μm, even though the focused beam may only be 0.01 μm in diameter at the actual surface. This has significant implications concerning the information contained by various signals. For example, X rays created within the volume indicated by the dotted line can escape without significant loss of energy from all depths, whereas Auger electrons generally cannot escape from the solid with their characteristic energy from depths greater than about 0.003 μm. This means that the information obtained from an analysis of Auger electrons will be characteristic of the first few atomic layers, whereas information from X-ray analysis will be characteristic of thousands of atomic layers.

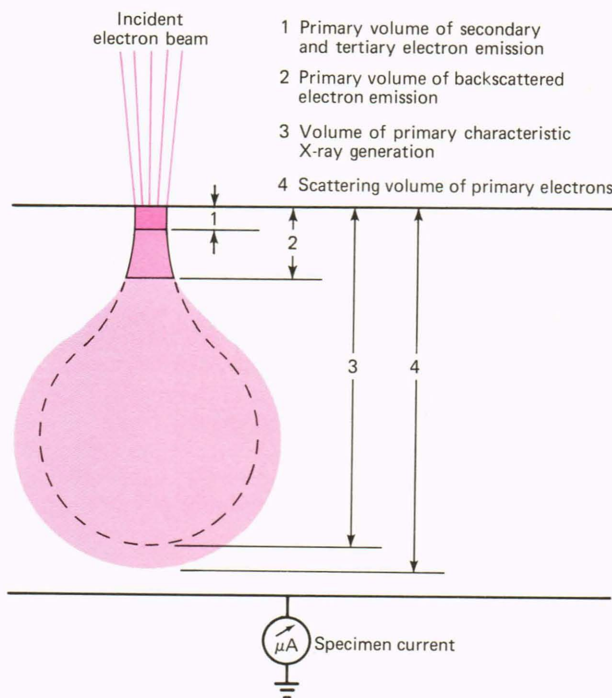


Fig. 6—A schematic representation of the teardrop-shaped scattering volume of an incoming electron beam as it impinges on a solid surface. The dimensions of this volume are material-dependent. The volume of primary characteristic X-ray generation is almost the same size. The primary volume of secondary and tertiary electron emission is much more confined to the actual surface. Characteristic Auger (tertiary) electrons are emitted from the top 0.003 μm. The primary volume of backscattered electrons extends deeper into the solid and also has an increased lateral dimension. Thus imaging with backscattered electrons does not yield as high resolution as with secondary electrons. The difference between the incoming current and emitted current is called the specimen current; it is also useful for imaging.

The spatial distribution of emitted secondary electrons is such that most of them come from the first few atomic layers within a lateral area defined by the beam diameter. Thus, image resolution using secondary electrons is determined by the beam diameter. Higher energy backscattered electrons can escape from greater depths, so that they possess information from greater depths than secondary and Auger electrons.

OPERATION OF THE SEM

Figure 7 is a simplified diagram of a SEM. Electrons are emitted from a filament and accelerated by an electric field to an energy of 2 to 30 keV. These electrons then pass down an electron optical column through a series of apertures and magnetic lenses that focus the beam on a specimen in a target chamber. The target chamber and column is evacuated in our SEM by means of an ion pump. Just before the final aperture, the electron beam passes through a set of scanning coils that scan the beam in a raster across the specimen. Simultaneously, the signal that controls the scanning coils is applied to the sweep of a cathode ray tube (CRT). As the electron beam impacts the sample, the signals previously discussed are emitted. They are detected and converted to voltages that modulate the intensity of the CRT. In this system, the magnification is controlled by the ratio of the size of the raster on the CRT to that of the specimen surface being scanned. Hence, the magnification is increased by reducing the size of the raster on the specimen surface.

As was previously noted, many useful signals are available to modulate the CRT. The Research Center SEM can detect secondary electrons, backscattered electrons, transmitted electrons, specimen current, and X rays. Important modifications using these five signals are also available. Two imaging modifications that are important in semiconductor and integrated circuit work are known as voltage contrast and electron beam induced current (EBIC).

The voltage contrast method uses secondary electrons whose emission from the metallization on an integrated circuit is altered by voltages placed on various circuit terminals, thus altering the normal image contrast. This mode of imaging is especially useful for quality control or failure analysis of integrated circuits.

The EBIC mode is based on the fact that an electron beam impacting on a semiconductor creates many electron-hole pairs. If a voltage is applied across a p-n junction in a semiconductor, the electrons and holes can be collected before recombining. Using this induced current for imaging will re-

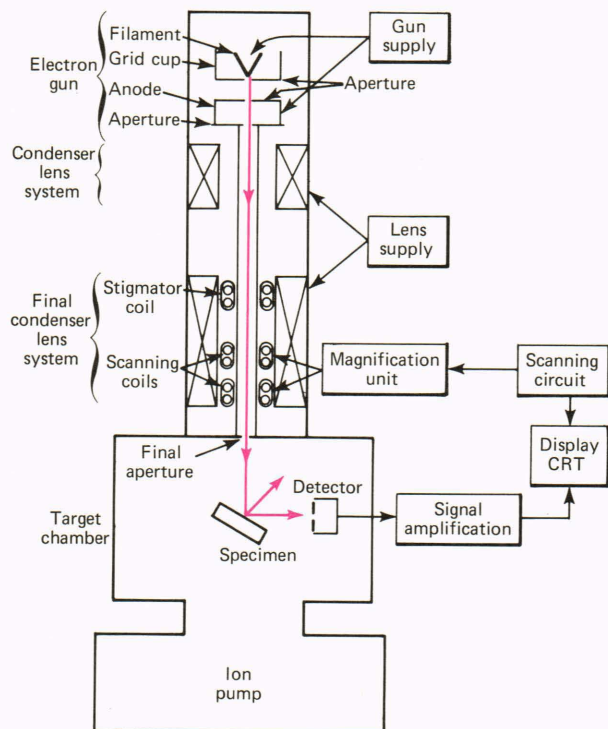


Fig. 7—Schematic diagram of a SEM.

sult in great contrast near the p-n junction. Quantitative methods that measure important parameters (such as excess carrier lifetime, diffusion lengths of carriers, and surface recombination rates) are based on the induced current phenomenon.

In addition to being used for dot maps of elements in a surface, detected X rays can be used for spectroscopy. Both qualitative and quantitative analyses can be performed. The requirements for quantitative work are, of course, much more stringent. Many more details regarding SEM techniques can be found in various books on the subject.[3,4]

CORROSION RESEARCH

In order to illustrate further capabilities of the SEM, a few selected photographs and X-ray spectra will be presented from our research on the localized corrosion of aluminum.[5,6] Aluminum is a chemically active structural metal. In dry air a thin (2 nm) protective layer of oxide forms on its surface, a layer that in many cases prevents further uniform corrosion. When the oxide begins to break down, it does so locally. Thus, the corrosion frequently takes the form of a pit, as shown in the stereo pair of Fig. 1.

Several methods of providing greater protection from corrosion have been developed. One of these is a process called anodization. In this process, the aluminum is made the positive electrode in an electrolytic solution so that a thicker film of oxide is grown on the aluminum. The nature of the anodized film is quite dependent on the specific electrolyte. In our anodization process, 3% ammonium tartrate has generally been used. The resultant film is a nonporous, more protective oxide. The thickness of such oxide coatings is directly proportional to the final voltage across the anodization cell.

Our interest in localized corrosion processes has dealt mainly with initiation processes in aqueous chloride solutions. Thus, events leading up to the local failure of the oxide have been studied. Our observations on anodized aluminum have established an intermediate step in the breakdown process. This step is the formation of a blister in the oxide before it ruptures observably. The blister initiation and growth is caused by a gas-producing chemical reaction at the oxide-metal interface. Figure 8 shows such a blister. The points S_1, S_2, S_3, and S_4 in Fig. 8 are a sampling of spots at which X-ray analysis was performed. The resulting X-ray spectra are shown in Fig. 9. The result of the analysis is that chloride is localized in a band around the blister. Figure 10 is a similar blister, but this time with the stage tilted to 80°. This illustrates the utili-

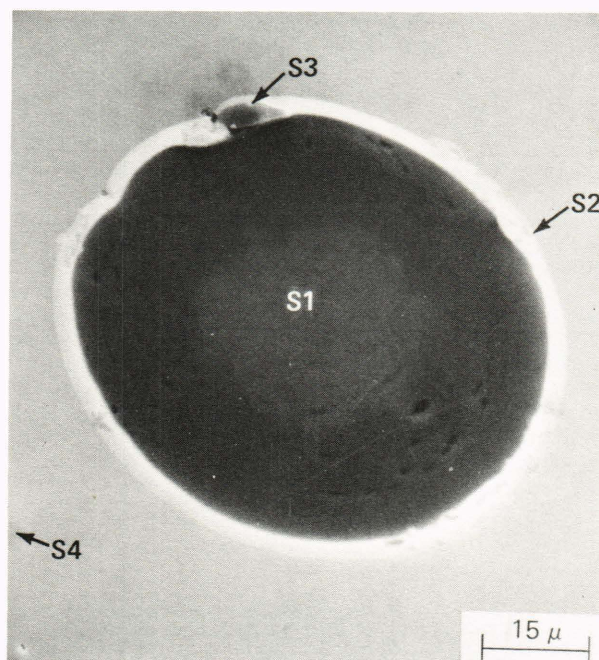


Fig. 8—Micrograph of a blister in the oxide coating of high purity aluminum. The blister was formed during a corrosion test in aqueous chloride solution.[6] The lettered spots (S_1, S_2, S_3, and S_4) were microanalyzed; i.e., the electron beam was positioned at the indicated spots and the resulting X rays were analyzed. Spots S_2 and S_3 showed the presence of aluminum and chloride; spots S_1 and S_4 showed aluminum only. The X rays from elements of atomic number of eight or less are not energetic enough to pass through the thin beryllium window in front of the X-ray detector; therefore, the X-ray lines of hydrogen and oxygen would not appear in the spectrum. The electron beam energy was 20 keV, and the tilt angle of the SEM stage was 45°. The local composition as given by SEM microanalysis cannot be determined by conventional microanalysis techniques. Although AES, SIMS, and ESCA can determine local composition, the resolution is not as high and the quantitation is not straightforward. This results in larger uncertainties.

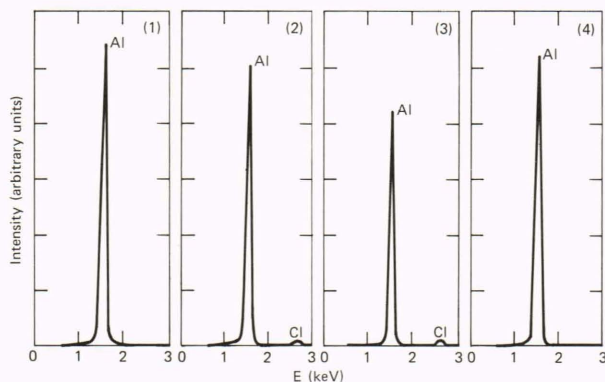


Fig. 9—Energy-dispersive X-ray spectra corresponding to the spots labelled S_1 through S_4, respectively, in Fig. 8. The results show that chloride is confined to a band around the blister perimeter. This band is visible in Fig. 8.

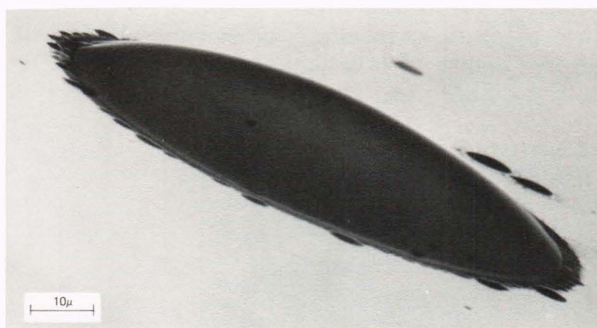


Fig. 10—Micrograph of a second blister. The tilt angle of the SEM stage is about 80°; therefore, one has a side view of the blister. Before the corrosion test, an oxide film about 80 nm thick is grown on the aluminum surface. The corrosion reactions take place at the oxide-metal interface. Because of surface tension, the gas produced during the reactions cannot escape through the oxide into the solution; it stresses the oxide, deforming it as shown here. Calculations show that gas pressures greater than 6 atm were generated.[6] This photograph illustrates the depth of field of the SEM (depth of field is quite limited in an optical microscope).

ty of the tilt motion and the depth of field. Even though the aluminum specimen was dried out for SEM observation, the oxide is observed in a stretched (blistered) shape; the high gas pressures during the blistering stressed the oxide beyond its elastic limit so that it remained deformed.

It is interesting to note that this thin aluminum oxide film has behaved very much like a thin sheet of plastic. After a blister breaks and the aluminum underneath corrodes for a period of time, the result is a pit similar to the one seen in Fig. 1. The piece of oxide draped from the left edge down into the pit has a rounded portion that rests on the bottom of the pit. This rounded portion was the periphery of the blister, which in this case was ruptured by the high gas pressure during the process.

REFERENCES

[1] *Methods of Surface Analysis,* A. W. Czanderna, (ed.), Elsevier Scientific Publishing Co., New York (1975).

[2] *Characterization of Solid Surfaces,* P. F. Kane and G. B. Larrabee (eds.), Plenum Press, New York (1974).

[3] *Quantitative Scanning Electron Microscopy,* D. B. Holt, M. D. Muir, P. R. Grant, and I.M. Boswarva (eds.), Academic Press, New York (1974).

[4] P. R. Thornton, *Scanning Electron Microscopy,* Chapman and Hall Ltd., London (1968).

[5] C. B. Bargeron and R. B. Givens, "Localized Corrosion of Aluminum: Blister Formation as a Precursor of Pitting," *J. Electrochem. Soc.* **124**, pp. 1845–1848 (1977).

[6] C. B. Bargeron and R. B. Givens, "Precursive Blistering in the Localized Corrosion of Aluminum" (submitted for publication).

C. BRENT BARGERON is a member of the Electronic Physics Group of the Milton S. Eisenhower Research Center. Born in Provo, Utah, in 1943, he studied physics at Brigham Young University, did graduate work in physics at the University of Illinois (Ph.D., 1971) where he held an NSF Graduate Fellowship during 1967-71. His thesis was done in the laboratory of Prof. H. G. Drickamer, a well-known researcher in super-high-pressure physics and chemistry.

Since joining APL in 1971, Dr. Bargeron has been involved in problems in solid state physics, light scattering, chemical lasers, fluid flow in casts of arteries, cornea damage from infrared radiation, spectrometry of several types, and the application of the scanning electron microscope to the solution of surface corrosion problems.

His hobbies include athletics as well as piano and organ music; he has been a church organist and choir accompanist for several years.