#### **REFERENCES AND NOTES**

- S. A. Goudsmit and G. E. Uhlenbeck, Naturwissenschaften 13, 1953 (1925); Nature (London) 117, 264 (1926).
   J. Kessler, Polarized Electrons (Springer-Verlag, Berlin, 1976).
   D. T. Pierce et al., Rev. Sci. Instrum. 51, 478 (1980).

- D. T. Pierce and F. Meier, Phys. Rev. B 13, 5484 (1976)

- D. I. Pierce and F. Meier, Phys. Rev. B 13, 5484 (1976).
   J. Kirschner, Polarized Electrons at Surfaces (Springer-Verlag, Berlin, 1985).
   J. Unguris, D. T. Pierce, R. J. Celotta, Rev. Sci. Instrum. 57, 1314 (1986).
   J. Kirschner, Phys. Rev. B 30, 415 (1984).
   D. T. Pierce, R. J. Celotta, J. Unguris, H. C. Siegmann, ibid. 26, 2566 (1982).
   R. Feder and H. Pleyer, Surf. Sci. 117, 285 (1982).
   G. Rado, Bull. Am. Phys. Soc. II 2, 127 (1957).
   D. L. Mills and A. A. Maradudin, J. Phys. Chem. Solids 28, 1855 (1967).
   K. Binder and P. C. Hohenberg, Phys. Rev. B 6, 3461 (1972).
   S. F. Alvarado, M. Campagna, F. Cicacci, H. Hopster, J. Appl. Phys. 53, 7920 (1982).

- (1982)
- 14. D. Weller, S. F. Alvarado, W. Gudat, K. Schroder, M. Campagna, Phys. Rev. Lett.
- 15.
- 17.
- D. Weller, S. F. Alvarado, W. Gudat, K. Schroder, M. Campagna, *Phys. Rev. Lett.* 54, 1555 (1985).
  K. Binder and D. P. Landau, *ibid.* 52, 318 (1984).
  H. W. Diehl and A. Nüsser, in preparation.
  E. Kisker, K. Schroder, M. Campagna, W. Gudat, *Phys. Rev. Lett.* 52, 2285 (1984); *Phys. Rev. B* 31, 329 (1985).
  E. M. Haines, R. Clauberg, R. Feder, *Phys. Rev. Lett.* 54, 932 (1985).
  J. Unguris, A. Seiler, R. J. Celotta, D. T. Pierce, P. D. Johnson, N. V. Smith, *ibid.* 49, 1047 (1982). 19

- 20. C. S. Feigerle, A. Seiler, J. L. Pena, R. J. Celotta, D. T. Pierce, ibid. 56, 2207 (1986)
- M. Landolt, in *Polarized Electrons in Surface Physics*, R. Feder, Ed. (World Scientific, Singapore, 1985), pp. 385–421.
   M. Taborelli, R. Allenspach, G. Boffa, M. Landolt, *Phys. Rev. Lett.* 56, 2869
- (1986).

- J. Unguris, D. T. Pierce, A. Galejs, R. J. Celotta, *ibid.* 49, 72 (1982).
   E. Kisker, W. Gudat, K. Schroder, *Solid State Commun.* 44, 623 (1982).
   H. Hopster *et al.*, *Phys. Rev. Lett.* 50, 70 (1983).
   M. Landolt, R. Allenspach, D. Mauri, *J. Appl. Phys.* 57, 3626 (1985).
   J. Unguris, G. G. Hembree, R. J. Celotta, D. T. Pierce, *J. Magn. Magnetic Mater.* 54, 57 (1986).
- Sta-57, 1629 (1986).
   R. J. Celotta and D. T. Pierce, in *Microbeam Analysis*, K. F. J. Heinrich, Ed. (San 28.
- K. Koike and K. Hayakawa, J. Appl. Phys. 57, 4244 (1985).
  K. Koike, H. Matsuyama, H. Todokoro, K. Hayakawa, Jpn. J. Appl. Phys. 24, 29
- 30. L542 (1985); *ibid.*, p. 1833.
   R. Feder, Ed., *Polarized Electrons in Surface Physics* (World Scientific, Singapore,
- 1985)
- 32. M. Onellion, M. W. Hart, F. B. Dunning, G. K. Walters, Phys. Rev. Lett. 52, 380
- (1984). H. C. Siegmann, F. Meier, M. Erbudak, M. Landolt, Adv. Electron. Electron Phys. 62, 1 (1984). 33.
- C. L. Fu and A. J. Freeman, *Phys. Rev. B* 33, 1755 (1986). We are pleased to acknowledge our collaborators in the SEMPA measurements, J. 35. Unguris and G. Hembree, for their contributions to the previously unpublished work shown in Fig. 5. Supported in part by the Office of Naval Research.

# **Corrosion of Electronic Materials and Devices**

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Electronic materials and devices corrode in the same ways as automobiles, bridges, and pipelines, but their typically small dimensions make them orders of magnitude more susceptible to corrosion failure. As elsewhere, the corrosion involves interactions with the environment. Under control, these interactions can be put to use, as in the formation of protective and functional oxide films for superconducting devices. Otherwise, they cause damage, as in the electrolytic dissolution of conductors, even gold, in the presence of humidity and ionic contamination from atmospheric particles and gases. Preventing corrosion entails identifying the damaging interactions and excluding species that allow them to occur.

LMOST EVERY USE OF MATERIALS INVOLVES THE POSSIBILIty of corrosion. This arises from the thermodynamic instabilities inherent in the interactions between the materials and their use environments. The importance of corrosion to technology is reflected in a long history of work in corrosion science and engineering that incorporates knowledge from many scientific disciplines. Corrosion may occur uniformly or locally and at a continuous or discontinuous rate. It eventually results in material failure, and the time scale for this failure determines either the useful life of

the structure of which the material is a part or the time cycle required for maintenance and repair. Corrosion and catastrophic corrosion failures are minimized by the selection of appropriate combinations of corrosion-resistant materials, such as protective coatings, and by the application of corrosion-preventing technologies, such as inhibitor systems.

The current advanced state of the electronics industry is based largely on the use of materials selected for their electronic, magnetic, or optical properties and not for their corrosion resistance. Continued advances depend on the use of new materials with improved and novel properties and on new combinations of materials in novel structures. The devices and other components utilizing these materials are typically incorporated in large numbers in electronic systems and must perform with a high degree of reliability if the systems are to function. Component failure rates corresponding to a few tens of failures in 10<sup>9</sup> operating hours (FIT's) are often necessary, even with redundant system designs. These levels of reliability are achievable only if failures from corrosion are essentially eliminated.

The corrosion phenomena encountered in electronic materials and devices are the same as those found in automobiles, bridges, pipelines, and other familiar objects in the everyday world. Like steel, both elemental and compound semiconductors, ranging from silicon to gallium arsenide to mercury cadmium telluride, are subject to atmospheric corrosion, as are most of the metals and alloys used in electronic devices and systems. As in plumbing and construction, combinations of dissimilar materials, such as aluminum alloys and gold or copper, may suffer from galvanic corrosion through the formation of local electrochemical cells. Finally, as in almost all

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electrically powered systems, the potentials normally applied in electronic circuitry are sufficient to cause the electrolytic corrosion of conductors.

Although the corrosion phenomena are the same, the structural elements involved in electronic devices are often very small, with widths, separations, and thicknesses measured in micrometers or fractions of a micrometer. Thus, even small amounts of corrosion, of the order of nanograms or less, can cause problems and complete device failure. Particularly when corrosion is localized, the structural elements themselves can be altered by the corrosion, and the electrical properties of adjacent regions can be changed by the generation of corrosion products. With small conductor separations, fields in excess of 10,000 V/cm may be present across surfaces and in dielectrics, bringing about ionic motion and distributions of potential and ionic charge different from those usually studied in electrolytes. Finally, diffusional transport can be effective in changing the composition and properties of materials over distances that are comparable to their thicknesses.

The corrosion behavior of any material or structure is determined by the nature of its local environment. Important factors include humidity, temperature, and electrical potential, as well as species present by design, species deriving from contamination in materials and in manufacture, and species derived from the surroundings. Given the susceptibility of most electronic materials to corrosive attack and the functional sensitivity of most electronic structures to corrosion, some degree of isolation of the structure from the environment by the use of protective or passivating films and by packaging is required. The general principles of this approach are well established and have been applied successfully for many years. But as new electronic structures are developed and as existing structures are modified to provide improvements in cost and performance, a more detailed knowledge and understanding of the environment and of the specific environmental interactions that cause corrosion are needed.

The following discussion covers some of the recent work in these areas. In many of these efforts, analytical techniques developed in recent years, such as Auger electron spectroscopy, photoelectron spectroscopy, and ion chromatography, have played an important role, particularly in the analyses of surfaces. Enhancements in analytical sensitivity and in the ability to analyze small areas promise further advances in the understanding and prevention of corrosion in electronic materials and devices.

## The Environment

The environment to which electronic materials and devices are exposed derives from two sources: the materials themselves and the outside world. For devices that are sealed in hermetic cavities, only the first source is important. Here the environment comprises the fill gas used at sealing, including contaminants, and substances outgassed from packaging or enclosed materials. These substances may be controlled by materials selection, this selection generally focusing on function and compatibility within a particular structure. The substances contributed by external sources are subject to some control through air filtration. Until recently, however, the exposure of equipment to many of these substances has not been well defined, even though these are usually the species against which protective packaging is directed. For devices in the more commonly practiced level of packaging-restrictive packages, encapsulants, and protective coatings-the degree of restriction determines the extent to which components from internal and external sources are available to degrade performance. The packaging materials themselves are exposed to an environment whose source is primarily external, although substances from internal sources are also present. The same is true for such components as printed wiring boards, connectors, through-air optical transmission devices, bare chips mounted directly on substrates, relays and other discrete devices, backplane wiring systems, and hardware for equipment frames.

Through design, packaging, and environmental control, many corrosive interactions can be minimized or eliminated, provided these interactions and the elements of the environment involved are recognized and understood. Among the elements that are well recognized and protected against are water vapor and atmospheric oxygen; thus it is generally other species, often in combination with these, that provide the opportunity for corrosion processes to occur.

Substances from internal sources. Most substances derived from internal sources that become involved in performance-degrading interactions are low molecular weight organic compounds. Because of their mobility and volatility, they can diffuse to and from surfaces through other organic materials and become widely distributed in electronic equipment areas through the vapor phase. Traeger (1) has reviewed substances outgassed from organic materials that are used in microelectronics, and Weschler and Shields (2) have identified a number of components in packaging and insulation materials that are present in both the vapor and condensed phases at electronic equipment locations. Among these are various phthalate esters, other plasticizers (including organic phosphates), and dimethylsiloxanes, none of which is expected to interact directly in corrosion processes. However, their oxidation and hydrolysis products, particularly the low molecular weight organic acids, can solubilize passivating oxide films and, in combination with adsorbed moisture, can form electrolytes on surfaces and at interfaces.

The distribution of these low molecular weight organic compounds is largely determined by their vapor pressures. Those having vapor pressures greater than about  $10^{-4}$  torr are likely to be eliminated from the local environment by evaporation, whereas those having vapor pressures less than about  $10^{-8}$  torr will be limited in their distribution by the extent to which they can diffuse through materials or migrate across surfaces. In the intermediate range, volatilization and recondensation lead to a wider distribution that reaches an equilibrium state on surfaces in hermetically sealed packages. Even in open environments, some partitioning between the vapor and condensed phases is expected as long as the source is not depleted. Under conditions that usually exist in electronic equipment areas, the surface coverage, *m*, expressed in units of monolayers is given by an analog of the Brunauer, Emmet, and Teller equation (3),

$$m=\frac{cp}{p_{\rm o}+cp}$$

in which p, the gas pressure, is much less than  $p_0$ , the saturation pressure, and the constant c is much greater than 1. Here, m is likely to be substantially less than 1 but is not necessarily the fractional surface coverage because there may be stacking of adsorbed molecules.

Evidence for volatilization and recondensation of low molecular weight organic compounds is seen (i) in noncorrosion-related processes that cause performance degradation, notably in contact activation, where the erosion of arcing relay contacts is markedly accelerated by the formation of carbon deposits (4), and (ii) in the formation of frictional polymer, where vibrational motion of metallic interfaces, particularly those involving palladium, results in a partially oxidized, low hydrogen content organic insulator (5, 6).

Substances from external sources. Most substances from external sources that can become involved in corrosion processes derive from the atmosphere or from humans. Gill and co-workers (7) have compiled a list of organic compounds found in the atmosphere with

Table 1. Concentrations (in micrograms per cubic meter) of pollutants within electronic equipment locations. ND, not detected. Data from (9) and the authors.

Pollutant	Arithmetic mean	Range
Sulfur dioxide	5.4	ND-39.6
Nitrogen oxides	24	3.0-56
Chlorine gases	0.51	0.08-2.2
Reduced sulfur	0.80	ND-4.2
Ammonia	40	11–159
Particulates*	10	2.8-33

\*Less than approximately 15 µm aerodynamic diameter.

vapor pressures in the range  $10^{-8}$  and  $10^{-4}$  torr whose behavior is expected to resemble that of compounds of similar vapor pressure from internal sources. Several common inorganic compounds also have vapor pressures in this range, notably NH<sub>4</sub>Cl and NH<sub>4</sub>NO<sub>3</sub> ( $\sim 2 \times 10^{-5}$  torr).

Most corrosion studies involving airborne substances have been done on metals in outdoor environments. Dating back to the early work of Vernon (8), sulfur dioxide, its acidic oxidation products, and moisture are well established as the principal causes of outdoor corrosion of many metals. Vernon clearly demonstrated the relevance of a critical relative humidity, above which the corrosion rate is rapid because of substantial acquisition of moisture by the metal surface but below which the corrosion rate is low. For most metals, the critical relative humidity is in the range of 70 to 80%.

In indoor environments, metallic corrosion studies are considerably more limited. Rice and colleagues (9) examined the corrosion rates of copper, silver, nickel, cobalt, and iron at eight indoor locations in the United States and found the rates to be dramatically less than those outdoors for all the metals except silver. This reduction was clearly due in part to the lower indoor concentrations of corrosive gases (sulfur dioxide, nitrogen oxides, and chlorine-containing species). Further, the relative humidity (RH) rarely exceeded Vernon's critical range. Typical indoor airborne concentrations are given in Table 1.

Although measures of airborne concentrations are informative, they tell little about conditions on surfaces where corrosion is taking place. These are determined by the rates of arrival and sticking probabilities of the atmospheric species at a surface and by the amount of adsorbed water on the surface. It is the combination of adsorbed moisture and accumulated atmospheric species that provides the local environment for corrosion to occur.

At large electronic equipment locations, the RH in equipment areas is usually maintained in the range of 30 to 60%; consumer electronics, of course, are exposed to a broader range. The power dissipated in most equipment, however, elevates the internal temperature sufficiently that exposure to greater than 70% RH during operation is unusual, except for humid outdoor exposures. Within this range, several monolayers of water are present on clean metal surfaces (10); however, as even slightly hygroscopic atmospheric species accumulate, the adsorption of moisture increases.

Accumulation of gaseous atmospheric components at a surface is determined largely by the components' reactivity with or solubility in the existing surface structure. For reduced sulfur compounds and silver surfaces, the accumulation rates correspond to sticking probabilities near unity, but for most gaseous species and most surfaces of interest the sticking probabilities are likely to be small. Particles, on the other hand, are expected to have sticking probabilities close to unity for the range of air flow conditions likely to be encountered indoors.

Surface accumulation rates of water-soluble ionic substances have

been measured at 36 telephone company locations across the United States (11). Table 2 shows the ranges and means of the accumulation rates of a number of ions. Comparison of the accumulation rates of sulfate with tropospheric concentrations of sulfur dioxide gas and of sulfate in particulates at these locations indicates that most of the sulfate accumulation derives from particulate deposition rather than from reaction with sulfur dioxide. Except for chlorides and sulfides, it appears that the accumulation of inorganic ionic substances on indoor surfaces is due almost entirely to particulate deposition. In the case of chloride, comparison of accumulation rates on zinc and aluminum surfaces indicates the presence of at least one reactive chlorine-containing gas, most likely hydrogen chloride, that reacts specifically with zinc.

In two studies (12, 13), the relations between outdoor and indoor airborne concentrations of ionic substances in particulates from separate fine (0.1 to 2.5  $\mu$ m diameter) and coarse (2.5 to 15  $\mu$ m diameter) fractions were investigated at three telephone switching equipment locations, as were the relations between indoor concentrations and horizontal and vertical surface accumulation rates. The indoor/outdoor ratios for species with no internal sources, such as humans, depended on the type of air filtration (14), as expected, with standard filters giving ratios of 0.3 and 0.05 for fine and coarse particles and high efficiency filters giving ratios of 0.07 and 0.02. The indoor concentrations and the accumulation rates gave deposition velocities of 0.004 cm/sec for ions in fine particles and 0.6 cm/ sec for ions in coarse particles, consistent with the view that surface concentrations of relevant ionic species are principally determined by particulate accumulation. This applies also to manufacture, where materials and devices have not yet been provided with sufficient protection against the environment, although special attention is now being paid to air filtration and the times of exposure have been decreased. Highly localized contamination during manufacturing can also result from human activity.

Chloride is often considered the most corrosive species because of its ability to disrupt normally protective oxides and to facilitate electrolytic attack through the formation of soluble complexes. With adsorbed moisture, however, all ionic species can support the ionic current that must be present in electrolytic corrosion. Thus ionic contamination is usually the most important factor in the corrosion of electronic materials and devices when moisture is present.

### **Environmental Interactions**

Electronic materials themselves are affected primarily by air oxidation, whereas devices are most sensitive to moisture and ionic contaminants.

Oxidation processes and protective films. Except for gold and platinum, all metals and semiconductors are thermodynamically active and can oxidize in air at room temperature. When oxidation is neither self-limiting nor inhibited, as in the case of metallic corrosion, it is destructive. When it results in the formation of insulating, protective, or passive oxides, as for example on stainless steel or aluminum (15) and on silicon (16), it may be useful.

The controlled formation of thin oxide films is critical for numerous electronic technologies. For example, silicon can be passivated with SiO<sub>2</sub>, and silicon metal-oxide-semiconductor technology utilizes SiO<sub>2</sub> films as gate oxide dielectrics (17). This science and technology is well understood. On the other hand, the passivation of III-V compound semiconductors (for example, GaAs and InP) is significantly more complex, and problems in applying suitably protective films have been an impediment to the development of III-V-based semiconductor technology and devices. Research on the passivation III-V materials has been approached from two directions. In the first (18), the semiconductor surface is oxidized in an attempt to form a passivating film. Problems arise, however, because of the many phases that can be formed among the group III and group V elements and oxygen and because of their dependence on temperature and oxygen pressure. Both the thermodynamics of the system and the kinetics of the possible reactions must be considered. In the second effort, dielectrics, such as SiO<sub>2</sub>, Si<sub>3</sub>N<sub>4</sub>, or Al<sub>2</sub>O<sub>3</sub>, are deposited onto the III-V material. However, it is frequently difficult, if not impossible, to avoid the presence of the thin (~20 Å) native oxide at the interface. Further, methods for its removal may create electrically active defects. Although many devices are currently being manufactured with either deposited dielectric films or the native oxide, improvements in the passivation film are needed for efficient, large-scale manufacturing of reliable devices.

The corrosion protection afforded by oxides and other deposited dielectrics depends on the continuity of the films, their ability to act as barriers to the species in the local environment, and their own resistance to corrosion. Materials currently used to protect microelectronic devices, such as  $SiO_2$  and  $Si_3N_4$ , are not subject to attack by species normally found in the use environment. New applications, however, bring new requirements, such as optical transparency or close matching to the thermal expansion coefficient of the substrate. These may well be difficult to meet with materials as inert as  $SiO_2$ .

For many electronic materials and devices, low-temperature oxidation may be detrimental. In low-force, low-voltage electrical contacts and connectors, oxide or tarnish films as thin as 100 Å may have sufficient resistance to give an effective open circuit (19). Further, in some applications, even small changes in contact resistance can introduce unacceptable noise into a circuit. To avoid tarnish films, the contact area is normally coated with a thin layer of a noble metal, such as gold, or an alloy of this metal. Unless the system is carefully selected for the service conditions to be encountered, however, either the alloying metal may diffuse out to the surface or the substrate metal may diffuse through the noble metal at pores, grain boundaries, or other defects. In either case, the base or less noble metal will be oxidized at the surface, producing a high contact resistance.

Josephson tunnel devices, on the other hand, require a dielectric film no more than 10 to 20 Å in thickness to provide the necessary junction. For practical applications, this film, usually an oxide, must be highly reproducible in composition and thickness. The simplest preparative approach is air oxidation, and van Dover and co-workers (20) found that such a treatment of magnetron-sputtered, superconducting NbN thin films gives high-quality, reproducible junctions. Studies in which Auger electron spectroscopy was used in conjunction with argon ion sputtering (21) showed that the native and junction oxides on this superconductor consist of a one- to twomonolayer thick film of a niobium oxynitride formed by the reaction

$$NbN + \frac{x}{2}O_2 \rightarrow NbNO_x$$

in which x increases with temperature. The oxynitride film is stable at temperatures up to 200°C. Above 200°C, this desirable passive film breaks down as the mechanism of oxidation changes radically, resulting in the formation of Nb<sub>2</sub>O<sub>5</sub> at a constant rate. The reaction products were identified by observing changes in the position and shape of the Auger electron spectral peaks and comparing them to peaks from appropriate standards.

Oxidation processes that produce films of readily controlled thicknesses with a fixed stoichiometry are not common, particularly with compounds and alloys. More typically, electronic materials develop thin protective oxides at room temperature, but at elevated temperatures these oxides grow in thickness and change in composi-

Table 2. Accumulation rates (in micrograms per cubic centimeter per year) of ionic substances on indoor surfaces. Data from (13).

Substance	Arithmetic mean	Range
Chloride	0.18	0.06-0.55
Sulfate	0.29	0.05 - 0.77
Nitrate	0.13	0.03-0.25
Sodium	0.06	0.03-0.11
Ammonium	0.04	0-0.14
Potassium	0.05	0.02-0.10
Calcium	0.18	0.04-0.39
Magnesium	0.02	0.005-0.05

tion and properties. In addition, polycrystalline materials often undergo preferred oxidation and corrosion at grain boundaries.

Amorphous thin films based on iron or cobalt and a rare earth metal, such as terbium or gadolinium, have magnetic and magnetooptic properties that make them potential candidates for future generations of storage media in high-density mass memories. Their critical magnetic properties, however, are strongly degraded by oxidation or corrosion. These alloys are reasonably stable at room temperature because of the formation of very thin (<100 Å) passivating oxide films on their surfaces. However, in storing data, the films are heated locally to temperatures as high as 200°C with a pulsed laser, providing an opportunity for further oxidation. The effect of oxidation on the magnetic properties of amorphous Fe0.74Tb0.26 thin films has been studied by van Dover and coworkers (22), and the kinetics and mechanism of oxidation of these films at 200°C have been examined by Auger electron spectroscopy combined with ion etching to determine the composition and thickness of the various reaction product layers (23). It was found that, on initial exposure to air at room temperature, the alloy is passivated by a duplex film consisting of an outer 10- to 20-Å layer of an iron spinel and an inner 60-Å layer of  $Tb_2O_3$ . When the alloy is heated in air at 200°C, these oxide films initially do not change in composition or thickness. Instead, an internally oxidized zone (24) grows inward from the oxide-alloy interface. This zone consists of an intimate mixture of Fe<sub>0.93</sub>Tb<sub>0.07</sub> alloy and a lower oxide of terbium, as determined from the shape, position, and intensity of the Auger electron spectral peaks. As the zone grows, stresses build as a result of the introduction of oxygen into the alloy matrix. Eventually the stresses are relieved, yielding defects that permit more rapid diffusion of all the species present. At this point, the outer two oxide layers, which were formed on initial exposure of the alloy to air, begin to grow again.

Complex behavior of this sort should be expected in many of the thin film alloy systems that are likely to be developed. Understanding this behavior depends on continued development of analytical techniques capable of providing quantitative information about composition as a function of depth in the film.

Interactions involving water and contaminants. As noted earlier, electrochemical effects due to the presence of moisture and other contaminants can be critical in the reliability of electronic materials and devices. Moisture in the atmosphere can affect the rate of oxidation of a material, the composition and structure of its oxidation product, and the electrical properties of the product (16). Low-force, low-voltage electrical contacts and connectors are often protected from corrosion by thin coatings of a noble metal, such as gold. If the coating is porous and the substrate metal corrodes, however, the corrosion product may creep out of the pores and across the gold surface, giving rise to high contact resistance. For gold on copper in a sulfiding environment, the rate of creep of the mixed copper oxide–sulfide tarnish product is greatly increased by

the presence of water vapor in the atmosphere and may extend more than 1 mm in 220 hours in air saturated with flowers of sulfur at 75% RH and 50°C (25). A nickel barrier layer between the copper and gold inhibits their interdiffusion and generally eliminates pores extending down to the copper on contact surfaces, but creep from exposed copper at contact edges can still occur in poor storage environments where sulfur vapor—for example, from cardboard containers—and high humidity are present. These reactions consist of local cell action involving migration of metal cations in the tarnish product and simultaneous migration of electrons through the metal phase to the reaction front (26). The creep rates are determined by ionic mobilities in the tarnish films, which in turn depend on the composition of the films and hence on the environment in which they formed.

Electrolytic corrosion of devices most frequently involves moisture and ionic contaminants. Most thin film and integrated circuit (IC) devices are encapsulated in plastics, usually an epoxy molding compound, which are permeable to water vapor. Ionic contaminants are also present at some level from manufacturing contamination before packaging and from ionic impurities in the plastic. In combination with water, these form an electrolyte that provides an ionic connection between adjacent conductor paths at different applied potentials. Given conductor separations approaching 1 µm and adjacent conductors differing in applied voltage by 1 V or more, the electrolytic conductance and the potential available at the anodes (the positively biased conductors) can easily be sufficient to cause conductor oxidation and corrosion. Open circuits can be produced in typical device conductors, generally aluminum but also gold, by the removal of only about 10<sup>9</sup> metal atoms, which requires the passage of less than  $10^{-9}$  C.

On dielectric surfaces and at interfaces, conductivity and corrosion rate increase with increasing humidity, that is, with increasing thickness of the water-electrolyte film. However, the moisture film thickness depends also on the temperature of the surface, decreasing with increasing temperature (27-29). Consequently, powered devices generally experience less water adsorption and hence lower corrosion rates than expected from the relative humidity of their surroundings.

Yan and colleagues (29) studied water adsorption and surface conductivity on clean  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> substrates as a function of RH. About one monolayer of water is adsorbed at 35% RH. For RH's greater than 70%, more than five monolayers are adsorbed, and the amount increases dramatically with increasing water vapor pressure. Similarly, the surface conductivity due to the normal ionic dissociation of water increases with increasing water adsorption.

High levels of chloride contamination and humidity can result in the total corrosion of positively biased aluminum bonding pads in device structures (30), where the protective layer of either phosphorus-doped SiO<sub>2</sub> or off-stoichiometric silicon nitride is deliberately removed to permit attachment of bonding wires. At these locations, the metal is in direct contact with moisture that has reached the chip, and the normal passivating aluminum oxide is dissolved in the presence of chloride, forming tetrachloroaluminate ions. Continued positive bias (with respect to nearby bond pads) normally results in an open circuit by complete anodization and dissolution of the bond pad, again with the formation of soluble  $AlCl_4^-$ . A similar process can occur at positively biased chip metallization sites if a defect, such as a pinhole or crack, exists in the passivation layer protecting the metal.

Recent reductions in the contaminant content of plastic encapsulants from several hundred parts per million (ppm) ionizable chloride to less than 5 ppm have resulted in improvements in device reliability by factors of 10 to 100 (*31*). However, ionic contamination, particularly chloride, in molding compounds and the possibili-



Fig. 1. Simplified cross section of a portion of an IC showing an n-type inversion layer induced in a p-type substrate by surface ions. The positively charged ions bias the silicon nitride passivation layer surface to the potential of the aluminum bond pad. The inversion layer thus formed electrically connects the two n-type diffusion regions, causing a circuit malfunction.

ty of ionic contamination during manufacturing or use clearly increase the risk of device failure from electrolytic corrosion when moisture is present, as it commonly is.

Cathodic corrosion of aluminum may also occur. At exposed cathodic metal, the *p*H increases locally as water and oxygen are reduced, generating hydroxyl ions. The increased local alkalinity promotes the corrosion of the aluminum through the formation of the  $Al(OH)_4^-$  complex (32, 33).

Many IC manufacturers employ phosphorus-doped  $SiO_2$  below the aluminum metal for contouring purposes, and some use phosphorus-doped  $SiO_2$  as a protective film for the metal. If phosphorus doping is excessive, moisture can leach the phosphorus from the oxide, reacting to form phosphoric acid, which not only provides an ionically conducting electrolyte but also causes chemical attack.

A small fraction of IC's use gold metallization. For gold conductors, two different corrosion mechanisms have been observed, depending on the presence or absence of a complexing agent, such as chloride, in addition to moisture (34). In the presence of chloride, the gold anode is oxidized to the tetrachloroaurate ion, which then migrates to the cathode where gold is redeposited, usually in the form of dendrites. These grow in the direction of the anode and eventually produce a short circuit. Similarly, copper migration in the presence of chloride or other complexing agents may result in short circuits on circuit boards and in IC's that use copper or copper alloy leads as a part of their packaging. In the absence of the ionic contaminant, gold oxidizes to form Au(OH)3, resulting either in an open circuit if all the gold is oxidized or in a short circuit if the voluminous corrosion product makes contact with the cathode. The kinetics and mechanism of electrolytic gold oxidation have been studied in aqueous solution as a function of chloride concentration, pH, and electrode potential (35, 36). Results from these studies are completely consistent with device experience (34). Open and short circuits have been observed in hermetic packages as a result of the inclusion of moisture at sealing or from ingress of moisture at faulty or damaged seals.

Another failure mechanism (37) involves surface moisture and ionic contaminants but does not result in chemical changes to the IC materials. Rather, ions of opposite charge in the moisture film are separated by the electric field parallel to the surface between conductors at different potentials, producing surface concentrations of net charge. By this means, a net surface charge layer propagates across the device insulator surface, extending the electric potential of a metal structure beyond the metal. These surface potentials can induce parasitic high conductance regions in the underlying silicon, thereby increasing leakage current. On high-voltage IC's, the surface potential adds to the silicon potential at the silicon surface, resulting in reduced breakdown voltage. Such failure mechanisms are often reversible and may be difficult to diagnose because no material changes need be involved. The surface density of net ionic charge for device failure is only about 10<sup>11</sup> per square centimeter to 10<sup>12</sup> per square centimeter. The detection limit for conventional analytical techniques is typically 10<sup>13</sup> atoms per square centimeter.

An example of this type of surface ion failure is illustrated in Fig. 1, which shows a cross section of a region of an IC. Two independent *n*-type diffused circuit elements, which might be resistors in an IC network, are shown in a p-type substrate. The ntype diffusions are normally electrically isolated from each other because each is reverse biased with respect to the substrate. Positive ions migrating from the positively biased bond pad have biased the insulator surface to a positive potential almost equal to that of the bond pad. The positive surface potential induces an inversion layer of negative charge (electrons) at the surface of the *p*-type region. This inversion layer electrically connects the two *n*-diffusion regions, possibly causing a circuit malfunction. Similar failure mechanisms are possible on a wide variety of IC's, and therefore special precautions must be taken in device design to ensure that unwanted surface charge inversion layers cannot be formed between circuit elements.

#### **Future Concerns**

For printed wiring boards, connectors, and other, more standard electronic components, the continuing search for less expensive materials and manufacturing methods brings with it the necessity of looking for new failure modes that must be identified and overcome. The incorporation of fiber optics into systems for data transmission and manipulation is likely to introduce new corrosion issues to be studied and understood.

In state-of-the-art electronic equipment, conductor spacings and dimensions range from a few millimeters for printed wiring board and connector elements to 0.5 µm for DRAM (dynamic random access memory) chips. Historical trends and recent research results project feature sizes as small as 0.1 µm in a few years.

For devices with submicrometer features, not only will reliable corrosion-free materials combinations that can withstand unprecedented electric fields (for ordinary electronics) be required, but providing a nearly contamination-free manufacturing environment will be a substantial challenge. Clearly, devices with 0.1-µm features must be manufactured in environments free of particles larger than 0.05 µm. Only a few Class 1 manufacturing environments, in which the air contains only one particle larger than 0.3 µm per cubic foot, are claimed to exist in the world today. Further, most airborne particles less than 0.1 µm in diameter are the highly corrosive earlystage oxidation products of SO2 and NOx. Fundamental understanding of the manufacturing environment seems to be a certain prerequisite for successful development of devices in the future.

Similarly, the identification of localized contamination on surfaces with submicrometer features presents extraordinary challenges in the development of surface analytical techniques to achieve adequate sensitivity and spatial resolution. Even so, these techniques will only facilitate the understanding of corrosion problems. The best solutions to these problems are contamination-proof designs.

#### REFERENCES

- R. K. Traeger, Proc. Electron. Compon. Conf. 27, 408 (1977).
   C. J. Weschler and H. C. Shields, Proceedings of the Annual Air Pollution Control

- C. J. Westner and TL. C. Sinches, Proceedings of the Annual No Fountan Control Association Meeting, in press.
   S. Brunauer, P. H. Emmet, E. Teller, J. Am. Chem. Soc. 60, 309 (1938).
   L. H. Germer and J. L. Smith, Bell Syst. Tech. J. 5, 769 (1957).
   H. W. Hermance and T. F. Egan, *ibid.*, p. 739.
   B. T. Reagor and L. Scibles, in Proceedings of the Holm Seminar on Electrical Contacts (Illinei Institute of Technology: Officero, 1980), p. 95
- Cillinois Institute of Technology, Chicago, 1980), p. 95.
   P. S. Gill, T. E. Graedel, C. J. Weschler, *Rev. Geophys. Space Phys.* 21, 903 (1983).
   W. H. J. Vernon, *Trans. Faraday Soc.* 31, 1668 (1935).
- D. W. Rice, R. J. Cappell, W. Kinsolving, J. J. Laskowski, J. Electrochem. Soc. 127,
- D. W. Rice, P. B. P. Phipps, R. Tremoureux, *ibid.*, p. 534.
   J. D. Sinclair and L. A. Psota-Kelty, in *Proceedings of the International Congress on Metallic Corrosion* (National Research Council of Canada, Ottawa, 1984), vol. 2, p. 2022. 296.
- , C. J. Weschler, Atmos. Environ. 19, 315 (1985)
- 13 , in Joint Proceedings of the Corrosion Effects of Acid Deposition and Corrosion of Electronic Materials Symposia, F. Mansfeld and J. D. Sinclair, Eds. (The Electro-
- Chemical Society, Pennington, NJ, 1986), p. 328.
   E. J. Bauer, B. T. Reagor, C. A. Russell, Am. Soc. Heat. Refrig. Air-Cond. Eng. J. 13, 53 (1973). 14
- R. P. Frankenthal and J. Kruger, Eds., *Passivity of Metals* (The Electrochemical Society, Pennington, NJ, 1978).
   F. P. Fehlner, *Low-Temperature Oxidation: The Role of Vitreous Oxides* (Wiley, New Context)
- York, 1986), chaps. 8 and 9.
- F. F. H. Nicollian and J. R. Brews, MOS (Metal-Oxide-Semiconductor) Physics and Technology (Wiley, New York, 1982), p. 40.
   G. P. Schwartz, Thin Solid Films 103, 3 (1983).

- R. Holm, Electric Contacts: Theory and Applications (Springer-Verlag, New York, ed. 4, 1967), chap. 30.
   R. B. van Dover, D. D. Bacon, W. R. Sinclair, Appl. Phys. Lett. 41, 764 (1982).
   R. P. Frankenthal, D. J. Siconolfi, W. R. Sinclair, D. D. Bacon, J. Electrochem. Soc. 130, 2056 (1983).
- R. B. van Dover, E. M. Gyorgy, R. P. Frankenthal, M. Hong, D. J. Siconolfi, J. Appl. Phys. 59, 1291 (1986).
   R. P. Frankenthal, D. J. Siconolfi, R. B. van Dover, S. Nakahara, J. Electrochem.
- Soc., in press
- 24 25.
- Sole., in press.
  R. A. Rapp, Corrosion 21, 382 (1965).
  V. Tierney, J. Electrochem. Soc. 128, 1321 (1981).
  C. Ilschner-Gensch and C. Wagner, *ibid.* 105, 198 (1958).
  H. Koelmans, Annu. Proc. Reliab. Phys. 12, 168 (1974).
  R. B. Comizzoli et al., *ibid.* 18, 282 (1980). 26. 27
- 28
- R. B. Comizzoli et al., ibid. 18, 282 (1980).
   B. D. Yan, S. L. Meilink, G. W. Warren, P. Wynblatt, Proc. Electron. Compon. Conf. 36, 95 (1986).
   S. C. Kolcsar, Annu. Proc. Reliab. Phys. 12, 155 (1974).
   M. T. Goosey, unpublished results.
   W. M. Paulson and R. W. Kirk, Annu. Proc. Reliab. Phys. 12, 172 (1974).
   R. B. Comizzoli, RCA Rev. 37, 483 (1976).
   R. P. Frankenthal and W. H. Becker, J. Electrochem. Soc. 126, 1718 (1979).
   R. P. Frankenthal and D. E. Thompson, ibid. 123, 799 (1976).
   B. S. Duncan and R. P. Frankenthal, ibid. 126, 95 (1979).

- 37. M. M. Atalla, A. R. Bray, R. Lindner, Proc. IEE 106, 1130 (1959).