

Corrosion in Electronic Devices

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The corrosion failure of electronic devices has long been a major reliability concern. This failure mode is an ongoing concern because of miniaturization of IC and the expanded use of polymers in packaging. This failure is mainly due to the open or short circuiting as a result of metal ion migration corrosion or galvanic corrosion between the metallized conducting lines under conditions of humidity and electrochemically significant bias in circuit.

This paper discusses the effects of contaminants on corrosion, and materials for packaging and the ion migration characteristics of metals used for electronic components. And electrochemical investigations of galvanic corrosion and dendritic growth by the ion migration are also reviewed.

1. Introduction

Corrosion is one of main failure mechanisms feared through the computer and semiconductor industry. The trend of miniaturization in the electronics increases the density of microelectronic integrated circuit on circuit boards of fixed size. The typical 265 Kb DRAM has a line spacing of 5 micron, which is reduced to approximately 0.9 micron for the 1 Mb DRAM. Thinner metals and films, and narrow electrical pathways and connection in the denser circuit package cannot allow even small amounts of corrosion, of

the order of nanograms or less. Electronic component failure rates corresponding to a few tens of failure in 10^9 operating hours (FIT's) are often necessary and these levels of reliability are achievable only if failures from corrosion are essentially eliminated.

Corrosion is an electrochemical process, induced or assisted by ionic contamination in the presence of adsorbed moisture. Such ionic contaminants are derived from (i) the materials, (ii) manufacturing condition, or (iii) operating environments. Moisture can be generated from (i) humid environment, (ii) internal chemical re-

action (e.g., breakdown of organics, residual salts from various process, devitrifiable sealing glass, etc.), (iii) insufficient baking process or (iv) lack of hermeticity. And corrosion and its rate are also depend on conductor materials, conductor spacing, electrical bias, temperature, humidity, and gaseous pollutants.

2. Corrosion mechanism

2.1 Materials for packaing ⁽¹⁾⁽²⁾⁽³⁾⁽⁴⁾ and corrosion

Ceramics and polymers, as well as metal has been used for packaging materials. Ceramics including inorganic glasses is good high-performance enclosures and multi-layer substrates for electronic packaging because they can be thermally conductive (generally heat generated at the IC chip surface is dissipated through the lead frame and packaging material) and electrically insulating due to their dielectric constant values, but most importantly, they resist moisture penetration several orders of magnitude better than

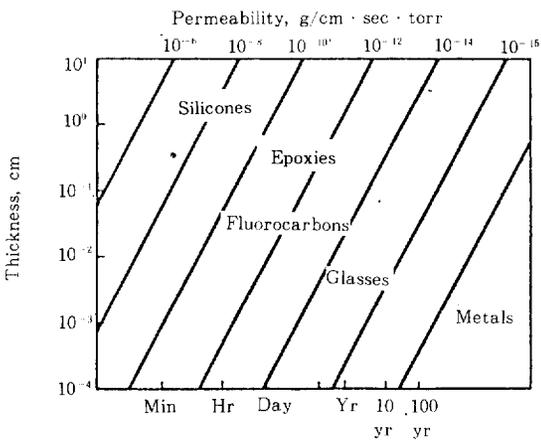


Fig. 1 The time for moisture to permeate various packaging materials(interior levels reaching 50 % of exterior humidity)

organic materials such as epoxy encapsulant.

Fig. 1 shows the time for moisture to permeate various packaging materials. And ceramics can be hermetically sealed to metal with glass or metal. The process control in fabrication such as sintering to achieve dimensional goals with adequate strength is critical. Ceramics used for package are aluminum oxide, beryllium oxide, silicon carbide and aluminum nitride. Polymers, the competing packaging materials, are mechanically resilient and can be molded to the required shape. Because they are substantially cheaper and easier to work with than ceramics, epoxy formulations are widely used to encapsulate high-volume production IC chips in spite of modest chemical resistance, low thermal resistance, and tendency to absorb water. Metals are used as elements of electrical connection and leads attaching the package to the printed circuit board.

In most cases, exposed metal connections are coated with other metals. If microgaps are formed between the metal leads and the epoxy encapsulant⁽⁵⁾ in packaging as shown in a Fig. 2, the metal-polymer interface provides a direct route to the chip surface for moisture-driven corrodents such as chloride ions and then contami-

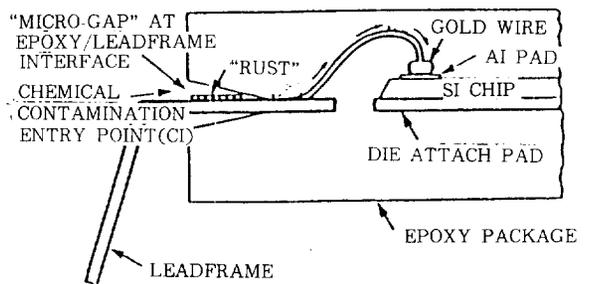


Fig. 2 Schematic illustration of the interfacial contamination entry point and migration path in molded plastic packages.

nant ions migrate from lead along the bond wire that connects the lead to the chip. And the corrosion takes place in the presence of moisture at the gold wire and aluminum pad interface by forming a galvanic cell in which gold act as a cathode to the aluminum. The corrosion is accelerated in the presence of Cl^- ion.

The areas of critical importance with respect to corrosion in plastic packaging are the thin layer of plastic covering the chip (area 1) and the interface (area 2) between the plastic and the metal leadframe as shown in a Fig. 3. Consequently, the thermal expansion coefficient and relative adherence at this interface is very important to maximize adherence. These corrosion failure factors related with packaging of IC are shown in a Table 1.

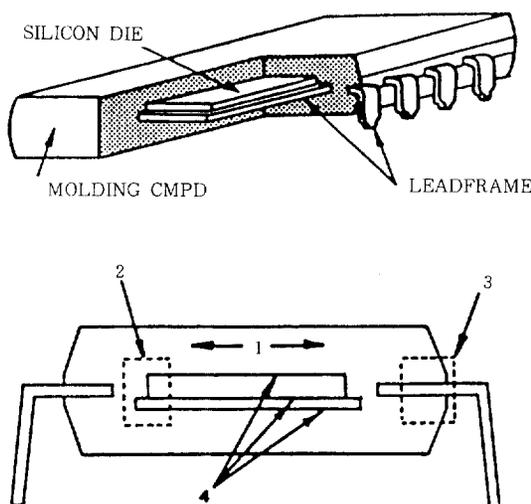


Fig. 3 Schematic representation of four critical areas among the structural elements of a molded plastic package

Table 1, Causes of corrosion related failure in IC⁽⁶⁾.

1. Water permeable molding compound.
2. Low molecular weight organic in packaging.
3. Faulty or damaged seals.
4. Thermal expansion difference in bond wire and molding.
5. Moisture ingress at bond wire or lead frame.
6. Moisture entrapment during packaging/sealing.

2.2 Metal ion migration and galvanic corrosion

Electrolytic metal ion migration⁽⁷⁾⁽⁸⁾⁽⁹⁾ is defined as a process by which a metal, in contact with insulating materials under humidity and electrical potential bias conditions, is removed ionically from its initial anodic location and is redeposited at some other cathodic location as illustrated in a Fig. 4. This migration corrosion consists of voids, which form at places from which conductor atoms are depleted, and hillocks or whiskers which form where atoms accumulate as shown in a Fig. 5. The location of anode between the same metal conductors will be decided by electrical bias condition. And if the conductor lines are dissimilar metals, galvanic corrosion can occur without electrical bias.

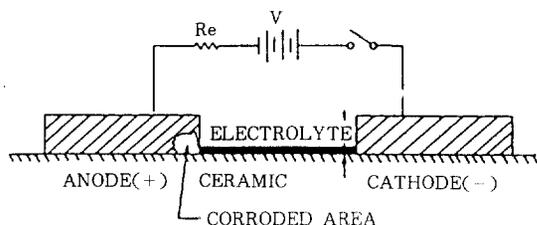


Fig. 4 Cross section of corrosion process*

Corrosion occurs at the anode (positive electrode) under a DC potential gradient (voltage bias). Electrolyte forms on ceramic substrate between electrodes due to water adsorption from humid atmosphere. Conductivity of electrolyte increases with dissolved ions.



Fig. 5 SEM photographs of hillocks due to electromigration extruding through glass overlay (upper), and void (dark region) and hillocks occurred along stripe (lower)

The migration process is one of corrosion mechanisms⁽¹⁰⁾, and induced or assisted by water-soluble ionic contamination substances shown in Table 2 and 3. The adsorbed moisture diffused from the gas phase to the substrate is main source of electrolyte. The result⁽¹¹⁾ of water adsorption measurement on clean alu-

Table 2. Concentrations (micrograms/cm³) of pollutants within electronic equipment location⁽¹²⁾⁽¹³⁾

Pollutant	Mean	Range
Sulfide dioxide	5.4	ND* - 39.6
Nitrogen oxide	24	3.0 - 56
Chlorine gases	0.51	0.08 - 2.2
Reduced sulfur	0.80	ND - 4.2
Ammonia	40	11 - 159
Particles	10	2.8 - 33

ND* ; not detected

Table 3. Some of the atmospheric pollutants⁽¹⁴⁾

Pollutants	Remarks
1. Hydrogen sulfide	Corrodes Cu, Ag and other metals in the presence of water vapor.
2. Sulfur oxide	Corrode metals in the presence of water vapor, and sulfur dioxide deteriorates polymer.
3. Chlorine	Corrodes Cu and other metals in the presence of water vapor, and also has synergistic effect of increasing corrosion rate of hydrogen sulfide on Cu.
4. Nitrogen oxide	Deteriorate polymer, and oxide and particulate nitrates corrode stressed metals in the presence of water vapor.
5. Ammonia	Decreases insulation resistance and increases loss factor of some insulation, and corrodes Al and stressed brass.

mina substrate shows that about one monolayer of water is adsorbed at 35% relative humidity (RH), and for above 70% RH, more than five monolayers of water was adsorbed. Similarly, the surface conductivity due to normal ionic dissociation of water increases with increasing water adsorption. And with small conductor line

spacing, fields in excess of 10,000 V/cm may be present across surfaces and in dielectrics, bring about distributions of electrical potential.

This migration process is fundamentally an ion and mass transport process (similar to electroplating) requiring an electrolyte, electrical bias and time, and often results in lowered resistance, dielectric failure, open-circuiting or short-circuiting. These types of failures are due to the electrochemical growth of dendrites between the metalized conducting lines and the apparent loss of conducting materials. Two types of metal migration path, surface and bulk, were observed during accelerated tests. Alumina and other nonporous substrates exhibit only surface migration, but porous substrates (e.g., fiberglass reinforced epoxy) exhibit both surface and bulk migration.

2.3 Measurement of ion migration

The methods of metal migration investigation can be classified as water (solvent) drop test and temperature-humidity-bias tests. The water drop test involves placing a drop of deionized water across the gap between adjacent conductors and applying a bias. Temperature-humidity-bias (THB) test involves placing dry adjacent conductors in a humidity environment at a given temperature and applying a bias.

On the experiment to investigate the migration of several metals, two metal plates were placed opposite on a moist filter paper which was placed on a glass slide and constant voltage were applied as shown in a Fig. 6. And the migration phenomenon was observed under the microscope while the current was recorded against time as shown in a Fig. 7. Their results showed the sus-

ceptability to metal migration is as follows⁽¹⁵⁾,

Ag > Mo > Pb > Solder > Cu > Zn > Bronze

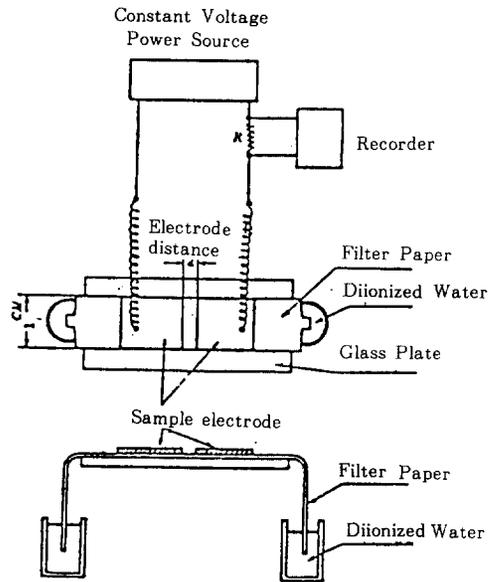


Fig. 6 Schematic drawing of experimental apparatus for metal migration

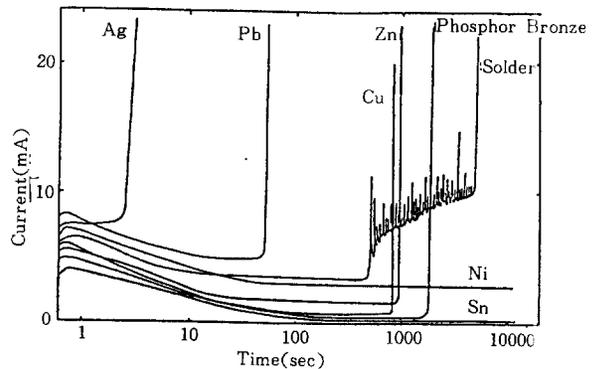


Fig. 7 Current-time curve for various metal electrodes at 100V, $D=0.1\text{cm}$

Silver is the most notable metal to exhibit ion migration because of its low first ionization potential and the heat of vaporization as shown in a Table 4⁽¹⁶⁾. DerMarderosian⁽¹⁷⁾ performed experiment to determine which metals would migrate with just distilled water and an applied bias across the metal electrodes and which metals would migrate upon addition of a chloride contaminant. The results are shown in a Table 5. And metal ion migration and its rate are affected by the variables listed in a Table 6.

Table 4. Physical properties of thick-film metals related to migration resistance

Element	Ag	Au	Cu	Pd	Pt	Ni
First Ionization Potential (V)	7.58	9.23	7.73	8.34	9.0	7.65
Vaporization Heat (KJ/mol)	250	334	300	357	510	370

Table 5. Conditions of metal migration*1

Cc Conditions	Migration Metals
1. Metals which migrate without contaminant.	Bi, Cd, Cu, Pb, Sn, Ag, Zn.
2. Metals which require sodium and potassium chloride contaminant*2.	Au, In, Pd, Pt.
3. Metals which may need other conditions to migrate.	Al, Sb, Cr, Fe, Ni, V, Ti, Rh, Tl

*1. Substrate: aluminium oxide based ceramics, Electrode Spacing: 1 mm, and Applied bias: 1 - 45V (DC).

*2. 0.1 - 0.001M NaCl, KCl.

Table 6. Variables affecting electrolytic metal migration⁽⁷⁾

1. Conductor composition.
2. Conductor pretreatment and surface condition.
3. Substrate composition.
4. Conductor configuration.
5. Electrical bias.
6. Conductor spacing.
7. Humidity.
8. Electrolytes/electrical conductivity.
9. Gaseous pollutants.
10. Ambient air velocity.
11. Temperature.

2.4 Dendrite growth by the ion migration

A common mode of failure⁽¹⁸⁾ encountered in the microelectronic world is the formation of metallic dendrites and subsequent electrical degradation (shorting) due to the formation of leakage paths across insulator surfaces. This phenomenon, identified as migrating-metal-resistive-shorts (MMRS) can occur with almost any metal, including gold, silver, tin, lead and copper.

Fig. 8 shows dendritic gold deposits⁽¹⁹⁾, migratory-gold-resistive-shorts (MGRS), which formed a dendritic bridge between metal stripes. The substrate is silicon with a thermally grown oxide. On top of the thermal oxide are two neighboring multilayer TiW-Au-TiW stripes overlaid with a layer of electron beam evaporated quartz. This quartz layer does not provide a complete coverage, thus exposing the edges of the metallization stripes to ambient environment. The dendritic deposits appear to progress from the negatively-biased stripe (cathode) toward the

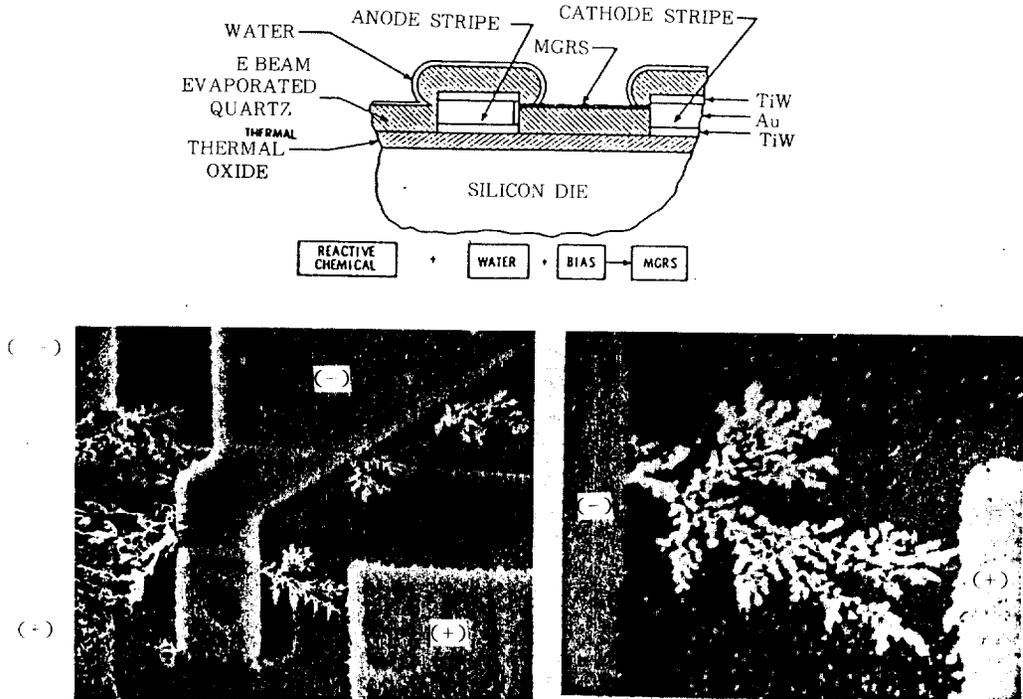


Fig. 8 Migratory-gold-resistive-shorts (MGRS) in TiW-Au-TiW metallization system and SEM photographs of MGRS

positive stripe through opening and discontinuities in quartz layer. And there exists a threshold value to occur MGRS failure. No MGRS with water vapor below 1.5% at 25°C is indicative of a water threshold value for MGRS. And Paul⁽²⁰⁾ showed the insulation failure between biased adjacent ternary Ag-Au-Pd alloy conductor (spacing; 2.95 mils, bias; 50V) due to silver dendrite migrating through borosilicate glass overlays which was formed by firing process. It is referred to as dry migratic because it occurs in the absence of humidity.

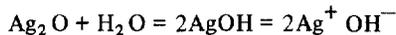
3. Ion migration of metal.

3.1 Silver ion migration

Several investigators⁽¹⁷⁾⁽²¹⁾ have proposed mechanisms based upon observations of silver migration in a continuous water film under an applied voltage bias. The water is ionized to H^+ and OH^- . The hydroxyl ion migrate to the anode and dissolves the silver as silver hydroxide. The silver hydroxide is soluble in water and is ionized to Ag^+ and OH^- . The Ag^+ ions are precipitated as white silver chloride in the presence of chlorides.

Kohman⁽²¹⁾ proposed a different mechanism. Silver ions dissolve at the anode in the water film due to the electrical bias. Hydrogen is discharged at the cathode. Hydroxyl ions move toward the anode but encounter the silver ions moving from anode. As the concentration of silver and hydroxide reach the solubility product ($K_{AgOH} =$

1.5×10^{-8} at 20°C), the unstable silver hydroxide is formed and this unstable product decomposes to dark silver oxide, Ag_2O around the anode. Thus, the concentration of silver ions leaving the zone of Ag_2O precipitation is regulated by the following equilibrium;



After their formation, the silver ions migrate to the cathode and dendrites form at cathode. And there exist a limiting potential gradient between two electrodes below which silver dendrites will not form. A narrow stripe of gold between the silver electrode is proposed as effective silver migration barrier, and two layer coating, undercoating resin layer and overcoating layer as moisture adsorption barrier, was also proposed to prevent silver migration.

3.2 Gold ion migration

Gold is used for many high reliability application because of its high corrosion resistance properties. And there are two mechanisms⁽²²⁾ that can result in the electrolytic migration corrosion failure of thin film and integrated circuits having gold metallization. In the presence of a contaminating salt containing complexing anion such as a chloride, failure of gold metallized circuits by a short circuit can be occurred by gold dendritic growth. Gold dissolves in the presence of chlorides according to the following reaction⁽²³⁾.

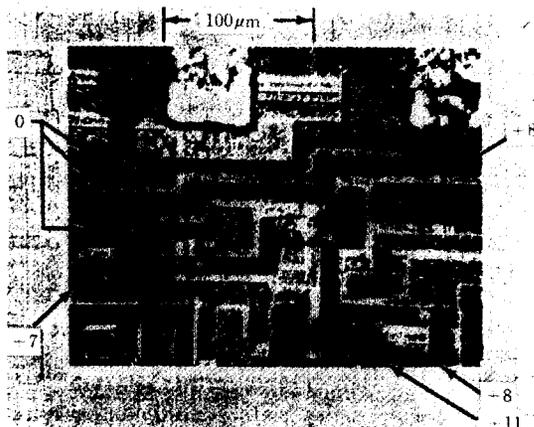
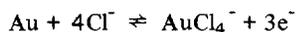


Fig. 9 Example of a corrosion failure due to the anodic formation of $\text{Au}(\text{OH})_3$. Applied voltage is shown next to conductor path.

The dendritic growth of gold requires four condition; reaction chemicals, a water film, bias and operating time⁽¹⁹⁾. In absence of complexing anion, the anodic oxidation of gold produces mainly $\text{Au}(\text{OH})_3$ as shown in a Fig. 9, if a sufficient moisture is present and if either the voltage between the conductor stripes is sufficiently high or the spacing between them is sufficiently small. Failure of a device may result either from increased conductor resistance as the gold anode is converted into the hydroxide or from leakage between conductor caused by the spreading of the corrosion product across the device surface.

Mazenk⁽²³⁾ reported that approximately 16% of the beam lead sealed integrated circuit tested in accordance with specification MIL-STD-883 were failed because of gold migration. Rinsing in water is recommended to alleviate gold migration problems due to residual fluxes, processing salts and fingerprints, and encapsulation by the RTV silicon rubber is proved to effective

in preventing failure due to gold migration. And there exist a humidity threshold⁽²⁵⁾ for gold migration for contaminants such as 44, 52 and 65% at 23°C for KI, NaCl and KCl respectively.

3.3 Copper ion migration

The majority of copper migration investigations have dealt with copper conductors on flexible printed circuit board substrates⁽²⁶⁾⁽²⁷⁾. The prevalent failure mode of copper printed circuits during THB tests is copper migration between conductors on the same side of the substrate (surface migration). And it is reported⁽²⁸⁾ that dendrites will grow through the UV - cured coating resins used in the electronics industry.

3.4 Aluminum ion migration

Aluminum metal is the material most widely used for the metallization of silicon devices. Corrosion of aluminum metal can occur at cathodic and anodic sites⁽²⁹⁾. Aluminum corrosion rates are mainly dependent upon the phosphorus concentration at the oxide/metallization interface⁽³⁰⁾⁽³¹⁾. Cathodic corrosion in semiconductor circuits can occur with chemical-vapor-deposit (CVD) SiO₂ passivation, but it is much more rapid at high humidity and high phosphorus content which is added to alleviate crack problem in SiO₂ glass. The medium time to failure (MTF) of the patterned Al lines on undensified CVD PSG with [P₂O₅] variation shows a following relation;

$$\log(\text{MTF}) = a - b(\text{P}_2\text{O}_5)$$

where $a = 2.30$, $b = 0.30$ at 100°C, 85% RH

with 50V applied voltage between conductor lines.

The anodic corrosion of aluminum was reported with chloride ion containing electrolytes and involves a four step process⁽³²⁾ as follows;

- (1). Adsorption of an aggressive anion (Cl⁻) on to the protective anodic aluminum oxide film.
- (2). Chemical reaction of Cl⁻ with Al⁺⁺⁺ in the oxide lattice

$$\text{Al}^{+++} + 2(\text{OH})^- + \text{Cl}^- \Rightarrow \text{Al}(\text{OH})_2\text{Cl}$$
- (3). Thinning of the oxide by electrochemical dissolution.
- (4). Direct attack of exposed Al by Cl⁻ ions

$$\text{Al}^{+++} + 4\text{Cl}^- \Rightarrow \text{AlCl}_4^-$$

$$\text{AlCl}_4^- + 2\text{H}_2\text{O} \Rightarrow \text{Al}(\text{OH})_2\text{Cl} + 2\text{H}^+ + 3\text{Cl}^-$$

Chloride is contained in several of the fluids used in processing, principally the solder fluxes used in finishing leads and in solder attachment to printed circuit board.

4. Prevention of corrosion

Proper attention and strict control of the following factors⁽²⁵⁾⁽³³⁾ will ensure electronics impervious to corrosion as a failure mode;

- (1). moisture control (keep moisture away from the chip surface).
- (2) dry internal package environment.
- (3) careful choice and engineering of packaging materials.
- (4) low moisture permeation encapsulants for molded packages.
- (5) low leak rates for hermetic packages.
- (6) high-integrity die passivation films.
- (7) rigorous package and substrate cleaning techniques.

- (8) the end use of device should be considered (will the operating environment enhance or preclude migration?).

5. Conclusion

This paper has dealt with galvanic corrosion and chemical processes of ion migration that can result in corrosion of electronic devices. And this failure mode is an electrochemical process which is related with the presence of (1) moisture, (2) ionic contaminants, (3) electrical bias, and problem of (4) design of devices or (5) selection of materials. Clearly, this failure mode has close relation with reliability of electronic devices and an understanding of these mechanisms which is based on a materials and electronic engineering is essential to any strategy for controlling the corrosion failure.

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