SSN 1466-8858 Volume 16, Preprint 67 submitted 27 November 2013 Role of Environmental Conditions in the Corrosion Induced Degradation of

Electronic Systems: A Review

V.K.Tapas^{a*} and P.V.Varde^{a,b}

a. Bhabha Atomic Research Centre.b. Homi Bhabha National Institute,Reactor Group Dhruva Complex,Bhabha Atomic Research Centre,Mumbai, India 400085.

* Corresponding author: Tel.: +91 22 25594335 E-mail: <vktapas@barc.gov.in>

ABSTRACT

More than 50% of electronic system failure is due to the environmental conditions such as humidity, ionic or organic contaminants, atmospheric corrodents, temperature, residuals; etc. which can accelerates an electrochemical reactions and causes corrosion of microelectronic components. Corrosive gases and water vapours from humid condition come into contact with the base metal results in buildup of various chemical reaction products. Ionic contamination responsible for electrochemical reaction, forms soluble complexes with metals, it can degrade the protective oxide film that forms on the positively biased metallization and/or lead to change in the local pH. Deterioration of metal components of electronic circuitry due to electrochemical migration and whisker growth need to be controlled in order to reduce the corrosion. With explosive increase in demand and miniturization in microelectronics resulted in smaller components, closer spacing and thinner metallic path, it is expected that the corrosion and deterioration of microelectronic systems may become cause of concern. This paper presents a comprehensive review and summerises the current understanding of chemistry behind possible causes of corrosion of electronic devices and its failure mechanism.

Keywords- Electronic devices, Failure mechanism; Reliability; Whisker Growth; Electrochemical migrations.

Electronic industry has seen growing evolution at brisk pace for the past several decades from thick to thin films and to ever increasing miniaturization. Spectacular scientific and engineering advances in microelectronics has great influence in our day to day living, from all forms of communication to extremely delicate and sophisticated medical applications to super computers for defence and space exploration. With the invention of transistor in 1948 and integrated circuit chips soon thereafter, development in transistor technology continue to follow an exponential progress represented by Moore's law-doubling the number of devices per chip every 18 months phenomenal reduction in size and increased performance in microelectronics are result of continuous developments in electronic materials, processing technologies and unique integration scheme [1]. Miniaturization of circuitry, which leads to products that perform faster and better, has been chiefly responsible for this revolution. Shrinking the electronic devices has yielded lower cost, expanded performance, and higher reliability. Development of a microelectronics begin with a demand from industry which allows far greater compatible device to be built into many more everyday items, such as: computers, from inexpensive personal computers through business computers to powerful supercomputers; communications systems, including switching stations and satellite communications; consumer products, such as electronic watches, video games, and pocket calculators; control systems for industrial applications, automobiles, and home appliances and military systems for national defence. Each type of device requires circuit design, component arrangement, preparation of a substrate, and the depositing of proper materials on the substrate [2,3]. These devices are made from semiconductors like silicon and germanium. Several components are available in microelectronic scale such as transistors, capacitors, inductors, resistors, diodes, insulators and conductors. Microelectronics can be divided to its subfields which in turn are connected to other micro related fields. These subfields are micro electromechanical systems, nanoelectronics, optoelectronics and single electron devices [4,5]. While microelectronics community continues to invent new solutions around the world to keep Moore's law alive and even to go beyond Moore with disruptive technologies, there are ever-increasing awareness, R&D effort that are based upon or derived from silicon technologies. Along with the technology development, the business trends of SSN 1466-8858 Volume 16, Preprint 67 submitted 27 November 2013 microelectronics are represented by cost reduction, shorter-time-to-market and outsourcing [5,6,7]. However, as the demand for increasingly effective electronic systems continues, improvements will continue to be made in state-of-the-art microelectronics to meet the demands. In Large-Scale Integration (LSI) and Very Large-Scale Integration (VLSI) a variety of circuits can be implanted on a wafer resulting reduction in size and weight of the device. LSI and VLSI are the results of improved microelectronic production technology. In Complementary metal oxide semiconductor (CMOS) transistor is the most common transistor used in the industry owing to its ease of integration and low static power dissipation. A smaller size of components being used to manufacture microelectronics typically is too small for humans to efficiently solder onto printed circuit boards. Thousands of components can be placed per hour utilizing a surface mount technology machines to place each component efficiently on the circuit board. These automation makes the entire manufacturing process more efficient which also reduces the overall cost. Intel Corporation researchers have achieved a significant breakthrough by building the world's smallest and fastest CMOS transistor. This breakthrough will allow Intel to build microprocessors containing more than 400 million transistors, running at 10 gigahertz (10 billion cycles per second) and operating at less than one volt. Smaller transistors are faster, and fast transistors are the key building block for fast microprocessors, and several other smart devices. These new transistors, which act like switches controlling the flow of electrons inside a microchip, could complete 400 million calculations in microseconds [8]. Microfluidic chips a new generation device fitted on smart handheld gadgets is an effective equipments can be used by doctors in their clinical laboratories [9]. Many large universities in the world conduct research in microelectronics to make the components smaller than the existing size of the components .Thus, even as existing capabilities are being improved, new areas of microelectronic use are being explored [10]. With the aggressive scaling of advanced integrated circuits (ICs) to deep submicron levels, the signal delay caused by the interconnect became increasingly significant compared to the delay caused by the gate [11,12,]. To suit the needs of those who use the products based on microelectronic devices, intensive research and several efforts have been carried out in microelectronics aimed at making circuits more reliable. The circuit should have a less power requirement and minimum heat is to be generated. These goals are prioritized in different ways depending



Volume 16, Preprint 67 submitted 27 November 2013 on the end use. When selecting the most useful packaging technique, its environmental and electrical performance and the maintainability aspects are to be considered.

2. Microelectronics Reliability

Reliability of a system or component is defined as the ability to perform its required function under given conditions for a specified period of time [13]. The concerns for reliability of electronic components are driven by two major trends in the current electronics industry [14,15,16,]. The first trend is to accommodate a large number of circuits on a single chip. This involves the increase of packaging density of electronic circuits, the decrease of size and weight of associated elements and structures, and the increase of connection numbers in individual systems. The second trend is to implement lead-free soldering techniques in electronics industry, solder joints connect different electronic elements. Failure indicates the device non-operational due to damage caused by a failure mechanism, generally accelerated by external and/or internal stresses [17,18,]. The microelectronic system components reliability is evaluated by a variety of established isothermal and thermal tests based on relevant standards [19,20,21,]. Design rules, operating voltage, and maximum switching speeds are selected to ensure functional operation over the intended lifetime of the product. To determine the ultimate performance for a given set of design constraints, reliability must be modeled for its specific operating condition. Reliability modeling for the purpose of lifetime prediction is, therefore, the ultimate task of a failure evaluation. Over the last several decades, physical behavior of the critical failure mechanisms in microelectronic devices has grown significantly. Confidence in historical reliability models has led to more aggressive design rules that have been successfully applied to the latest Very Large Scale Integration technology. One result of improved reliability modeling has been accelerated performance; that is, performance beyond the expectation of Moore's Law. A consequence of more aggressive design rules has been a reduction in the significance of a single failure mechanism. Hence, in modern devices, there is no single-failure mode that is more likely to occur than any other within a range of specified operating conditions. This is practically guaranteed by the integration of modern simulation tools in the design process. The consequence of more advanced reliability modeling tools is a new awareness that device failures result from a combination

SSN 1466-8858 Volume 16, Preprint 67 submitted 27 November 2013 of several competing failure mechanisms. Until the 1980s, the exponential, or constant failure rate (CFR), model [22] had been the only model used for describing the useful life of electronic components. During the 1980s and early 1990s, with the introduction of integrated circuits (ICs), more and more evidence was gathered suggesting that the CFR model was no longer applicable. In the 1990s, attempts were focused on finding an electronic system reliability assessment methodology, including causes of failures, that could be used in the design and manufacturing of electronic systems. To cover the vast range of electronic devices, the concept called "similar-system" was introduced which refers to a system that uses similar technology and is built for similar application, or performs a similar function [23]. The next step was to find whether the "similar-system" was used for existing field data. The data from a predecessor system could be used to generate the prediction of a new "similar-system" to the extent that the new generation was evolutionary [24]. These reliability device simulators successfully model the most significant physical failure mechanisms in modern electronic devices, such as timedependent dielectric breakdown, negative bias temperature instability, electromigration and hot carrier injection. These mechanisms are modeled throughout the circuit design process so that the system will operate for a minimum expected useful life [25,26, 27, 28, 29]. The possible failure modes and mechanism of every component can be predicted successfully by a system reliability models. Accelerated life tests (ALTs) provide a consistent basis for the prediction of the probability of failure after the given time of service. This information can be extremely helpful in understanding the reliability of the product and its viable design. Therefore accelerated life tests, along with the (accelerated) product development/verification tests and qualification tests should play an important role in understanding and predicting the short- and long-term reliability of microelectronics equipment and devices. Generally for an accelerated test an Arrhenius model has been widely applied at high temperatures to evaluate the product reliability data in a reasonable amount of time. By exposing the devices to elevated temperatures, it is possible to reduce the time to failure of a component, thereby enabling data to be obtained in a shorter time. Such a technique is known as "accelerated testing" and is widely used throughout the semiconductor industry. The rate at which many chemical processes take place is governed by the Arrhenius equation.

$$R = A \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

Where,

 $R = Rate \ of \ the \ process, \ A = a \ proportional \ multiplier, \ E_a = Energy \ of \ activation,$

k = Boltzmann's constant,

T = Absolute temperature in Kelvin.

While the Arrhenius model emphasizes the dependency of reactions on temperature, the Eyring model is commonly used for demonstrating the dependency of reactions on stress factors other than temperature, such as mechanical stress, humidity or voltage.

$$t_f = AT^{\acute{\alpha}} \exp\left\{\frac{\Delta H}{kT} + (B + \frac{C}{T})S_I\right\}$$
 (2)

Where,

 t_f is the life characteristic related to temperature and another stress. A, α , B and C are constants. T is absolute temperature. S_I is a stress factor other than temperature.

A set of parameters for failure mechanisms and major wearout were identified and the algorithms of extracting these parameters for a given technology were developed by accelerated tests on test structures. A circuit simulator, such as SPICE [30, 31], was employed to calculate the electrical parameters of fresh and degraded devices to predict their degradation or failure from these parameters. In the simulation, an Age parameter was calculated for each device with the following formula:

$$Age\left(\tau\right) = \int_{t=0}^{t=\tau} \left(\frac{I_{sub}}{I_{ds}}\right)^m \frac{I_{ds}}{WH} dt \tag{3}$$

Where,

W is a width of the transistor; m and H are technology dependent parameters determined from experiments; I_{sub} is the substrate current; I_{ds} is the drain current; s is the time for stress [32].

This reliability simulation method can help designers to understand the devices degradation within the circuits and make design compromise between performance and reliability in the product design stage.

3. Major Microelectronic Components

3.1 Interconnects

Interconnects may consist of conductive lines, pads, vias, wires and joints that form interconnected networks. Signal transmission along the interconnects has become increasingly important in limiting the speed, the size, the functionalities, and the reliability of modern microelectronic devices. In recent years, more integration and performance demands have required use of the alloys of copper, silver, tin, gold, zinc and nickel to form interconnects at various levels of the device [33,34]. Current density in interconnects can reach values of 1-2x10⁵A/cm² during device operation at 125⁰C. Copper offers low electric resistivity, high thermal and electric conductivity, easy fabricating and joining, and wide range of attainable mechanical properties have made copper as one of main materials for lead frames, foils for flexible circuits, heat sinks, and traces in PWB in electronic packaging [34,35,36]. The performance of the interconnect is strongly dependent on the composition, microstructures, processing and service condition of the interconnect alloys. Now a days industry is using copper due to its higher electrical conductivity and better electromigration properties. However copper corrosion can occur during the copper interconnect manufacturing processes due to its exposure to the chemical or ambient environment, and it can be further enhanced by the exposure to the light due to (photovoltaic effect) its connection to p-n junctions on the wafer. There are two different mechanisms of copper oxidation. In aqueous environments at ambient temperature, a thin layer of Cu₂O forms first on the copper surface by the oxidation and reduction partial reaction. The growth of the Cu₂O takes place on the top of surface through the mass transport of the Cu+ ions and electrons in a direction normal to the surface via vacancies [37,38,39].

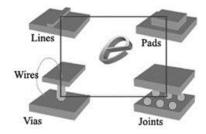


Fig1: (Image courtesy: http://www.synl.ac.cn/org/mic/)

Volume 16, Preprint 67

submitted 27 November 2013

The second stage of oxidation, the formation of the CuO from Cu₂O is usually a slower process. It is governed by the in-diffusion of oxygen into the oxide.

$$4Cu + 2H_2O \rightarrow 2Cu_2O + 4H^+ + 4e^-$$
 (4)

$$O_2 + 2H_2O + 4e^- \rightarrow 4(OH)^- \tag{5}$$

The primary effects of copper oxidation in copper interconnection wires and copper lead frames are,

- 1. Copper oxidation at the interface of Cu-Al bonding area causes the cracks, decreases the interfacial shear strength, and weakens the Cu-Al bonding [40].
- 2. Copper oxidation in the area of the copper lead frames die pad and molding compound causes the delamination of packages [41].
- 3. Copper oxidation induces poor adhesion in the area of copper lead frame and molding compound so that the moisture is able to penetrate through the crevices creating corrosion problem in packages [42].

Corrosion inhibitor, such as Benzotriazole (BTA), can be used to reduce copper corrosion in the manufacturing process. Corrosion of copper, particularly due to photovoltaic effect can be reduced using the dark environment during the manufacturing process. Forming a higher corrosion resistant layer or layers with a displacement plating process at the top surface of the copper interconnects can be helpful to reduce or eliminate the problem. For example, the metal used for the displacement plating layers may be Palladium, Platinum, Rhodium, Ruthenium, Gold, Silver, Lead, Nickel, Cadmium, Tin, or other noble metals and their alloys. The use of displacement plating to selectively coat copper interconnects with higher corrosion resistant metal or metal alloy layers during the manufacturing process of copper interconnects will minimize the occurrence of copper interconnect corrosion[43].

3.2 Connectors

Connector provides a separable connection between two elements of an electronic system without unacceptable signal distortion or power loss. Corrosion of connectors relates primarily to the contact interface and the contact finish. The contact interface consists of parallel resistances of metallic and film covered regions. Corrosion increases contact

area due to penetration of corrosion products into the interface. In case of Edge Connectors, Contacts may be made solely of copper or gold-plated over a nickel-plated copper substrate, and are both susceptible to corrosion. A thin layer of gold plating is provided over the conducting surface of the PCB to ensure that the electrical contact between the board and the connector is maintained with the highest integrity over a long period of time. Noble metal like gold, palladium and alloys of these metals and non noble metal primarily tin or tin/lead provide corrosion protection for the base metal. Noble finishes minimize film formation, while for tin finishes the surface oxides are easily disrupted [44]. Electroplated hard gold is most widely used as a contact finish for connectors. Commonly employed hard gold plating baths contain KAu(CN)₂ as the source of gold, a citrate buffer of pH 3.5 to 4.0 and a small amount of a Co or Ni salt as the hardening agent .Those baths abbrivated as CoHG and NiHG. Palladium and palladium alloys, especially Pd-Ni and Pd-Co, capped with a thin layer of hard gold are also employed as contact finishes [45,46,47,48]. Compared with various properties of hard gold (NiHG), Pd-Ni and Pd-Co deposits, it was shown that both hardness and wear resistance increases in the order NiHG < Pd-Ni < Pd-Co, which clearly indicate the superiority of the palladium alloys compared to NiHG [48]. The small grain size of the hard gold is attributed to the inhibition of crystal growth caused by incorporated impurities or inclusion.

3.3 Solder

Soldering provides electrical, thermal and mechanical continuity in electronics assemblies, it is a well-known metallurgical joining method and material with a melting point below 425° C is used for solder joints [49]. It also serves as a path for dissipation of the heat generated by the semiconductors. Oxidation of solder alloys depending upon the environments in which solders are placed, the extent of oxidation can be controlled by restricting the oxygen content in the environment so that the oxidation can be kept to a minimum. It is essential to use H_2 as reducing gas to prevent further oxidation. Thermodynamic free energy ΔG^0 of oxide formation determines whether an oxide film will form spontaneously for a given set of environmental conditions [50,51]. The solder is thus not only exposed to air, but also moisture and other corrosives such as chlorine and sulphur compounds. In addition, solder alloys are electrically connected with

ISSN 1466-8858 Volume 16, Preprint 67 submitted 27 November 2013 other metallic components in the electronic device, most notably the copper conductors.

Therefore, there is also the potential for galvanically induced corrosion of the solder, which could aggravate any atmospheric corrosion that might be occurring. The most widely used Pb-Sn solder has the eutectic composition. The corrosion behavior of 52In-48Sn soldered on Au substrate in the presence of 15-25 ppb Cl₂ at 85°C and 85% relative humidity was studied by Abtew [52] and the corrosion product was identified as In (OH)₃. Vincent and Richards [53] tested Bi, Zn, Ag, Cu, and Sb with Sn eutectic in an environment containing 200ppm NO₂, 100 ppb H₂S, 20 ppb Cl₂ at 30°C and 70% relative humidity. In case of Sn-9Zn precipitation of ZnCl₂ were observed. If Δemf between the phases present in the solder alloy is large, corrosion is likely to take place because the electrochemical coupling in the presence of moisture is high. Some metals such as Cu, Au, Ag, Ni, and Pd are frequently used in microelectronic with various compositions. Corrosion of solder alloys, in the presence of a suitable electrolyte can occur either due to the potential difference between the major phases in the alloy or galvanic coupling between one or more phases of the alloy and other parts of the devices. In the electronics industry, the lead generated by the disposal of electronic assemblies is considered as hazardous to the environment because of lead's toxicity. In 1986, a review of the use of lead in electrical and electronic applications actually revealed a dramatic decrease [54]. The use of lead for electronic soldering accounts for approximately 40-50% of the total for all soldering uses. It is expected that industries will be required to increase the extent of recycling of lead. But the use of recycled lead for electronics application displays higher ά-particle emission than virgin lead. This can have detrimental effects on the performance of integrated circuits because άparticle emission leads to the occurrence of soft errors. Therefore, developing viable alternative Lead-free solders for electronic assemblies is of paramount importance. There are several Pb-free solders, such as Sn-Au, Sn-In, Sn-Ag, Sn-Bi, that have been in use in the electronics industry for special applications. A Pb-free alloy also needs to be environmentally friendly. Lead, Zinc, Copper, Antimony, Bismuth, Tin, Silver, Indium are the major elemental metals used in solders. A relatively large number of Pb-free solder alloys have thus far been proposed, and are summarized in Table 1, with their elemental compositions. The solder alloys listed below are binary, ternary and some are even quaternary alloys. A total of 69 alloys were identified from the literature. It can be noticed

that a very large number of these solder alloys are based on Sn being the primary or major constituent. The two other elements that are major constituents are In and Bi. Other alloying elements are Zn, Ag, Sb, and Cu.

Table 1: Pb free solder with their elemental compositions.

Alloys	Sn	In	Zn	Ag	Bi	Sb	Cu
42Sn-58Bi	42				58		
77.2Sn-20In-2.8Ag	77.2	20		2.8			
85Sn-10Bi-5Zn	85		5		10		
91Sn-9Zn	91		9				
90Sn-7.5Bi-2Ag-0.5Cu	90			2	7.5		0.5
96.3Sn-3.2Ag-0.5Cu		96.3			3.2		0.5
95Sn-3.5Ag-1.5In	95	1.5		3.5			
96.2Sn-2.5Ag-0.8Cu-0.5Sb	96.2			2.5		0.5	0.8
96.5Sn-3.5Ag	96.5			3.5			
98Sn-2Ag		98			2		
99.3Sn-0.7Cu	99.3						0.7
97Sn-2Cu-0.8Sb-0.1Ag	97			0.1		0.8	2
95Sn-5Sb	95						

4. Chemistry behind Corrosion

Corrosion is defined as the deterioration of a base metal resulting from a reaction with its environment. Corrosion essentially involves an electrochemical process and the basic requirements for electrochemical corrosion include electrically conductive anode, cathode, interconnecting electrolyte (humidity environment) and driving force. The driving force for electrochemical corrosion is the difference of electrochemical potentials between anode and cathode. The driving force can result from coupling of two dissimilar materials, on concentration gradient or externally applied electrical bias [55,56]. Degradation process can occur rapidly or over many years depending on the particular concentration level and

combination present at a site. As the chemical reaction continue, these corrosion product can form insulating layers on circuits which can lead to thermal failure or short circuits, pitting and metal loss can also occur. There are two aspects to analyse any type of corrosion reaction viz. thermodynamic feasibility and its kinetics. Driving force gives the thermodynamic feasibility and kinetics is determined by the variables of the system. The electrochemical corrosion kinetics (rate) depends on various factors such as area ratio of anode to cathode, the polarization resistance of anode and cathode, conductivity of electrolyte solution, solution pH value, temperature, contamination, and driving force. Small anode and big cathode system corrodes much faster than big anode and small cathode. For instance, gold is deposited onto aluminum pad to prevent aluminum from corrosion. If defects of deposit gold layer exist and small area of fresh aluminum is exposed to the corrosive environment, aluminum gets corroded much faster because of small anode of exposed aluminum and big gold deposit layer around. The most common and important electrochemical reaction between the metal and its surrounding environment can be explained by the following reaction. Corrosion of metal occurs as a result of chemical reaction between the metal M and moisture. A simple anodic oxidation/reduction corrosion reaction takes place,

$$M \rightarrow M^{n+} + ne$$
 Oxidation (6)

$$2H_2O + O_2 + 4e^- \rightarrow 4 OH \qquad Reduction \tag{7}$$

$$M^{n+} + n (OH) \rightarrow M (OH) n$$
 Corrosion Product (8)

In general it has been obsreved that the corrosion of aluminium is the most common failure mechanism in microelectronic device. The electrolysis of water which produces hydroxyl and hydrogen ions is given by an anodic reaction specifying the oxidation of water. There are three general reactions [57] by which aluminum may react anodically in the presence of water.

Dissolution of metal takes place at Anode

(a) At low pH value,

$$Al \to Al^{3+} + 3e^{-} \tag{9}$$

$$Al^{3+} + 3H_2O \rightarrow Al\ (OH)_3 + 3H^+$$
 (10)



ISSN 1466-8858 (b) From weak acid to neutral pH range.

$$2Al^{3+} + 3H_2O + 6e^{-} \rightarrow Al_2O_3 + 6H^{+}$$
 (11)

(c) At some high pH (high alkaline solution))

$$Al + 2H_2O + 3e^{-} \rightarrow AlO_2^{-} + 4H^{+}$$

$$\tag{12}$$

Following reactions takes place at cathode:

(a) Evolution of hydrogen from solutions.

$$3H^+ + 3e^- \rightarrow \frac{3}{2}H_2$$
 (acid solution) (13)

$$2H_2O + 2e^- \rightarrow H_2 \uparrow + 2 OH^- (neutral/alkaline)$$
 (14)

Creation of H⁺ ions leads to a more acidic (PH <7) environment near the anode, while the creation of OH⁻ leads to more basic environment (PH>7) near the cathode. The local pH strongly influences the corrosion behaviour of metals, preventing the charge transfer by minimizing current flow between the anode and cathode is therefore an important consideration in prevention of corrosion. The corrosion product of aluminum is usually believed to be Al(OH)₃ in the microelectronic packaging because the moisture environment is usually weak acid or neutral, but it actually depends on the pH value of electrolyte solution and activity of aluminum ions in the solution. It has been observed that the corrosion activity for Al is relatively low and is nearly independent of the applied voltage, the strong native oxide (Al₂O₃) on aluminium serves as a self-passivation layer.

In order for the corrosion to continue at a rapid rate, the ions must be able to diffuse rapidly to and from the regions of oxidation/reduction. However, for dry or ambient corrosion, the activation energy for diffusion is generally higher and the corrosion rate is very dependent on the percentage relative humidity (%RH).

Example of Field failure:

In light water Primary Cooling System of Nuclear Reactors, a generation of liquid waste takes place due to the regeneration activities of various ion exchange columns. These regenerants are chemical in nature consists of corrosive and radio active liquids. Depending up on the quality of liquid waste, these effluents are sent in to respective annular sumps and treated either with acid or with the alkali before its final disposal into the Sea. Annular sumps are equiped with microprocessor level controllers for giving alarm into the control room when the sump is full. Regular inspections of these devices showed a severe corrosion on the surface of the circuit board. Failure of circuit system was found to be significantly higher due to frequent regeneration activities of Ion Exchange Bed with Sulphuric acid. In this board metullargy, the plating left significant amount of exposed copper which then react with sulphur compound causing bridges between the leads of components and system failures. The corrosion product is clearly composed of a copper and sulphur compound which is shown in figure 2.

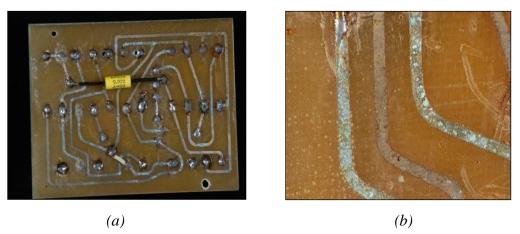
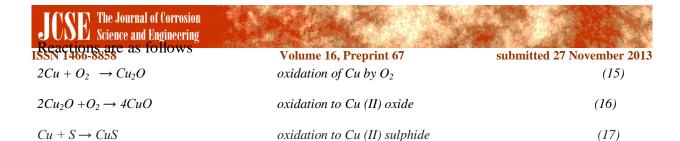


Fig.2: (a) Corrosion found on circuit board after exposure to high elemental sulphur environment. (b) Prominent deposition of green hydrated copper sulphate residues on circuit track.

Air oxidation of Cu form cuprite (Cu_2O) which gradually oxidise further to the black oxide (CuO) and black sulphide (CuS) products. The black layer of CuO and CuS slowly react with sulphur dioxide and carbon dioxide again in presence of moisture in the atmosphere to form green hydrated copper sulphate $Cu_4SO_4(OH)_6$



CuO and CuS slowly reacts with carbon dioxide (CO₂), sulphur trioxide (SO₃) and hydroxide ions (OH⁻) in water from the air to eventually form Cu₂CO₃ (OH)₂ and Cu₄SO₄ (OH)₆.

$$2CuO + CO_2 + H_2O \rightarrow Cu_2CO_3(OH)_2$$
 (18)

$$4CuO + SO_3 + 3H_2O \rightarrow Cu_4SO_4(OH)_6$$
 (19)

The extent of humidity and sulphur related air pollution has significant impact to form green hydrated copper sulphate Cu₄SO₄ (OH) _{6.}

6. Corrosion and Failure Mechanism:

Corrosion of metals is a chemical reaction caused primarily by attack of gaseous contaminants and is accelerated by heat and moisture. Rapid shifts in either temperature or humidity cause small portions of circuits to fall below the dewpoint temperature, thereby facilitating condensation of contaminants. Relative humidity above 50% accelerates corrosion by forming conductive solutions on a small scale on electronic components. Microscopic pools of condensation then absorb contaminant gases to become electrolytes where crystal growth and electroplating occur. Above 80% RH, electronic corrosive damage will occur regardless of the levels of contamination. The most widely used metal for silicon based microelectronic circuit is thinned film aluminium, usually containing 0.5 to 4% Copper and 0.5 to 2 % Silicon. Tungsten is used as a 'plug' to connect silicon area to the first level aluminium. Titanium and titanium nitride are some time used as adhesion /barrier layer above and below the aluminium interconnection layer. Thin film gold in a trimetal combination with a base metal such as titanium as the adhesion layer, platinum or palladium as a barrier metal and gold as the current carrying layer is used for high speed and high drive current circuit. The thin film metallization is typically connected to the package leads, allowing the circuit to be connected to the outside world with gold wire [58]. A variety of other metals are commonly used for inter connection on the circuit boards and hybrid circuits, including silver, copper, tin and lead. As electronic devices become more and more common, they become increasingly exposed to much harsher conditions. In the presence of absorbed moisture, corrosion of one or more of these metal can occur. The most common reason for electronic failure is environmental contaminants and conditions. Contribution of various acidic gases such as hydrogen sulphide, sulphur and nitrogen oxides, chlorine and hydrogen fluoride, caustic gases such as ammonia and oxidising gases such as ozone can cause corrosion of electronic equipments, acidic gases are typically the most harmful, for instance it take only 10 parts per billion (ppb) of chlorine to inflict the same amount of damage as 25,000 ppb of ammonia. Various contaminants include fine and coarse particles of species such as chloride, sulphates, sodium, ammonium, potassium, magnesium and calcium. Presence of these ionic contaminants can accelerate delamination. Once the delamination occurs, moisture can adsorb or condense on to the surface of the microelectronic device. The delamination creates surface leakage paths in an area of the device where two metal interconnection lines reside at two different potentials. The surface leakage current leads to metal oxidation at the anode in the form of M⁺ ions and to reduction of water at the cathode in the form of hydroxyl ions (OH) shown in fig 3. The metal ions can oxidise near anode and form a passive oxide film that protect the underlying metal from future corrosion. However, if the pH is low or halide ionic contaminants are present then this passive oxide can break down, leading to further corrosion. If the oxidation of the metal ion formed at the anode does not occur then the metal ion can migrate towards the cathode and form a soluble salt. These contaminants can also form soluble complexes with metals resulting in dendrite formation and destroy the protective oxide film that forms on the positively biased metallization and/or lead to change in the local pH. Ionic contaminants commonly found on the die surface include chlorine from the encapsulants, phosphorus from the passivation, bromine and antimony trioxide from the flame retardants and sodium and potassium from semiconductor device processing. Therefore ionic contamination can have profound influence on the susceptibility of thin film metallization to corrosion [59,60,61]. The presence of water and electrical bias is sufficient to initiate electrolytic corrosion [62]. Schematic diagram of a variety of the most common corrosion induced reaction that can

lead to device failure is shown in Fig. 3.

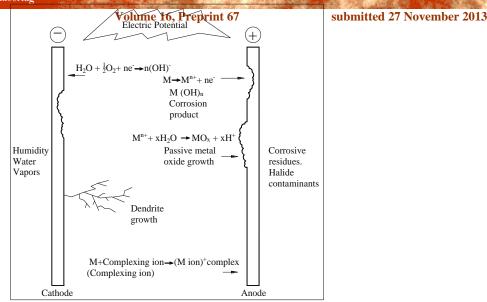


Fig.3: The most common corrosion induced reaction that can lead to device failure.

Similar effects related to the formation of hydrolysed metal ions can also lead to device failure. The negatively biased interconnection line (i.e. the cathode) is also susceptible to corrosion. Failure occurs as a result of an open circuit. Alkaline contaminants lead to higher solution pH. They also tend to migrate to the cathode. Therefore they increase the susceptibility of the metal to cathodic corrosion induced failure [63,64]. It is necessary to minimise corrosive environment such as humidity, condensation, and corrosive residues to eliminate the potential of destructive corrosion by metal migration. Destructive electrochemical migration occurs only under specific conditions. Growth of metal filament is initiated with the presence of an electrolytic solution dissolving metal ions in an electric field. Metal ions are electrodeposited along electrical leakage path forming a metal filament (dendrite) that may bridge the gap (short) between electrodes. The presence of the electrolytic solution across a potential at any environment results in as little as minor electrical leakage or as much as corrosive metal migration depending on the quantity of each of these factors. To understand the failure due to corrosion in polymer encapsulant with relative humidity and temperature, Time to failure t_f, is modeled as the sum of an induction time t_i and a time for the corrosion attack and failure t_c.

Therefore,

$$t_f = t_i + t_c: (20)$$

The time required for a non-hermetic package to reach an external vapor pressure is

$$t_i = \frac{-4L^2}{\pi^2 D} \ln \left(1 - \frac{P_{in}}{P_{out}} \right) \tag{21}$$

Where:

L is the length from edge of the chip to the outside of the package, D is the permeation constant, P_{in} is the inside partial pressure and P_{out} is the outside partial pressure.

The corrosion time is given by

$$t_c = \left(\frac{K_1 K_2 K_3}{K_A}\right) \left(\frac{w^2 hndF\rho}{4MVz}\right) \tag{22}$$

Where,

M is the atomic weight of a metal conductor,

d its density, n the chemical valence, V the voltage applied and ρ/z the sheet resistance of the electrolyte.

 K_1 is a measure of the resistivity to corrosion normalized to that of gold. K_2 is the coating integrity index and accounts for the existence and integrity of the passivation layer covering the diemetallization. K_3 is the duty cycle correction factor related to power cycling.

Thus the corrosion rate is decreased when the die temperature is increased by power dissipation. From above equation (eq.22) the environmental correction factor K_4 , can be used to determine the time to failure for various temperature and humidity conditions. The K_4 term is modeled as

$$K_{4} = \frac{(RH_{R})^{n}}{(RH)^{n}} \frac{exp(E_{a}/K_{T_{R}})}{exp(E_{a}/K_{T})}$$
(23)

Where:

 RH_R and T_R are reference relative humidity (%) and reference temperature (K), respectively and n is a constant.

It has been observed among the environmental issues, a significant problem is the residue as well as the dust particles found on the circuit board. Residues are the contamination on the surface due to the remains of the chemicals used for manufacturing process, a small fractions of these chemicals are enough to accelerate the corrosion process. And the dust

malfunctions by interrupting electrical contact between mating pairs of contact on connector or relays at relatively low humidity such as 50-70 % [65].

Whisker growth is an another phenomenon in electronics degradation, it is a filamentary growth reported to be a form of induced recrystallization related to metallurgical imperfections and occur under the influence of stress. Another type of failure involves the formation of metal bridges between two metal lines at different potentials which is associated with noble metals, such as silver and gold. In the presence of complexing contaminant, such as chloride residues from the package encapsulation polymer, soluble gold complexes form at the anode. These complexes diffuse from the anode to the cathode. At the cathode, gold complex is reduced to the metallic state and precipitate out of solution liberating the complexing ion. The ion will then under the influence of electric field, migrate towards anode. When it reaches anode it can participate once again in complex formation. When gold ion precipitates out at the cathode, there is small but real decrease in line to line spacing and therefore the local electric field which drives the process increases there. Thus the next gold complex that forms will be more likely to migrate to this location along the cathode. As this process continue, a dendrite forms. When the dendrite bridges the gap between the two metal lines, a short circuit is formed leading to a permanent failure or temporary device malfunction [66].

It is also possible for moisture-induced electrochemical degradation of the dielectric to occur if the current flowing through the dielectric is large enough, then the dielectric can corrode, changing its physical size and properties. This could lead to device failure. Silicon-based dielectrics, such as silicon nitride, silicon dioxide and alloys of two, are hydrolysed when exposed to moisture [67]. These hydrolysed reaction products dissolved slowly in condensed water. Thus, if the solubility limit of dissolved silicon based reaction product is not reached before the dielectric is breached, then water can come in contact with the metallization and /or any underlying dielectric thin films such as phosphorus-doped silica. In such a way the susceptibility of the device to corrosion induced failure is increased.

Another possible corrosion induced metal loss is related to decrease in line width. The loss of interconnection cross-sectional area leads to an increased local current density. Since the electromigration resistance (i.e.current induced diffusion) decreases as the current density

Science and Engineering

ISON 1466-8858 is possible that partial corrosion of a metal line will eventually lead to volume 16, Preprint 67 electromigration -induced device failure. The increase leakage could cause the device to fail. Finally local corrosion of small sections of the metallization can initiate arcing that leads to device failure [68,69,70,71]. The damage to the microelectronic components resulting from corrosion attack is irreparable and compromising to the reliability of microelectronic devices.

7. Electrochemical Migration

Electrochemical migration is a typical form of corrosion occurs due to the presence of a potential gradient between two susceptible conductors (Cu, Ag, Sn, Pb, etc.) connected by a thin layer of solution under ambient temperatures (<100°C) at low current densities (<1mA/cm²). ECM involves the dissolution of a metal at the anode (oxidation reaction) and the transportation of the metal ions or conductive metal complexes formed along the moisture path to the cathode (reduction reaction). At the cathode, these metal ions are reduced and deposited as pure metal, which then grows back toward the anode in the form of dendrites [72] Metal compounds with low solubility product give fewer ions for migration, while those with high hydrogen overvoltage will not deposit. The signature metallic dendrites, conductive anodic filament (CAF), and colloidal staining are all manifestations of electrochemical migration have been observed in microelectronic device. Growth of dendrites shown in Fig.4 finally leads to electric short between two points, which cause component failure or malfunction. And electrical failure in the device occurs as a result of either (i) an "open" circuit due to the dissolution of the metal anode resulting in a broken. Conductor or (ii) a "short" circuit arising from the cathode-to-anode bridging of metallic dendrites [73].

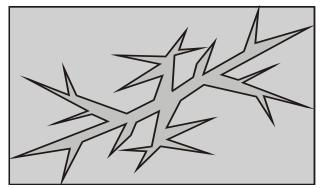


Fig4: Dendrite Growth: As the crystal grows, it tends to develop spikes and its shape changes into a tree like form.

Volume 16, Preprint 67

submitted 27 November 2013

There are different forms of dendrites which have been identified as

- (i) Trunk-type: a single dendrite growing within a fluid bridge from cathode to anode,
- (ii) Lace-/tree type: growth along a film or damp surface between the electrodes, and
- (iii) *Sludge type*: burnt-out dendrites due to high current flow from bridging of electrode gap.

Thus transport of metal ions under the influence of an applied electric field primarily manifested as bridging metallic dendrites, that results in electrical failures of microelectronic devices. Ion transport in an electrochemical cell can take place due to the following mechanisms:

- 1. Diffusion Due to concentration or chemical potential gradient from metal dissolution.
- 2. Migration Action of an electric field force on the metal ion.
- 3. Convection Driven by coulombic forces

The Nernst-Planck equations for ion transport refer to the convective, diffusive, and electromigrative contributions to the flux, represent the flux (J) of an ionic species (i) in a dilute electrolytic solution.

$$J_i = C_i V - D_i (\nabla C_i) - (D_i Z_i F/RT) C_i (\nabla_{\omega}), \tag{24}$$

where, J_i is the flux vector of the ith species (mol cm⁻² s⁻¹); C_i is the concentration (mol cm⁻³); Z_i is the electrical charge (mol equiv mol⁻¹,positive for cations, negative for anions); where $i = 1, 2, 3, \ldots, n$; V is the fluid velocity vector (cm s⁻¹); F is the Faraday constant (9.65×10⁴ C[mol equiv]⁻¹); F is the universal gas constant (8.3143 F mol⁻¹); F is the absolute temperature (F); F0 is the electrical potential (F); F1 is the ionic diffusion coefficient of the ith species (cm² s⁻¹) which is equal to F1, and F1 is the electrical mobility of the ith species (cm² molF1).

The first, second, and third terms in equation (24) refer to the convective, diffusive, and electromigrative contritions to the flux, respectively. Chazalviel [74] introduced a 1D numerical model for ion transport in electrochemical deposition with only diffusion and migration as the transport modes. The model predicted the existence and behavior of a depletion layer next to the cathode. Following this Fluery et al. described a model for electrochemical deposition (ECD) and ionic motion in which the growth speed of the metallic deposit equals the speed of anions withdrawing from the zone invaded by the

metallic filaments. At every moment during growth, both cations and anions drift in the electric field in opposite directions; the cations meet the growing front and add on to it, while the anions pile up near the anode [75] as shown in fig 5. The front of the metallic dendrites is always rushing and remaining just behind the withdrawing anions.. The zone enclosed between the filaments is completely depleted of ions of any kind. Fluery et al. also proposed that the Hecker effect, during the growth of the metallic deposits, is produced by changes in the solution due to positively charged impurities from the anode or encounters with zones of different pH. Initially, the impurities are on the edge of the anode but as the deposit grows, the impurities leave the anode, drifts in the bulk, and move toward the deposit. Initially impurities that reach and hit the growing dendritic front will induce a change in the morphology of the growing filaments. These are H ⁺ and OH ions impurities, in the context of H₂O molecules thereby providing a protonic drift; other impurities may also exists. Thus, maintaining the proper pH and controlling the impurities would enable to manage the dendritic morphology [75] and, consequently, mitigate the threat from ECM as filamentary-type dendrites are more dangerous than dense, compact dendrites. It has been observed that percolative moisture path, supply of migrating ions, and a bias voltage are the basic ingredients responsible for electrochemical migration to occur and device failures.

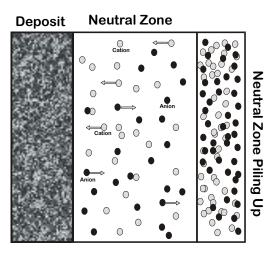


Fig.5: schematic view of cation and anion concentration evolution during growth.

Contributing factors for dendrite growths

i) Humidity

The duration of a percolative moisture path is a key factor in determining the mean time to failure (MTTF) of microelectronic devices. This moisture path can be broken (dried up),

regenerated, or reformed as a different path, depending on the ambient conditions. With 2013 relative humidity (RH) and temperature (T) under the same conditions, the MTTF remains somewhat similar and is independent of the onset of the bias voltage [76].

ii) Effect of Voltage

Since the minimum voltage required for water hydrolysis is 1.2 V, it is conceivable that below 1.2 V, little or no ECM activity may be expected. At higher voltage, however, more ions are made available as the pH drop due to water hydrolysis becomes conducive for metal dissolution [77]. When differently spaced conductor lines are biased together, there is a preferential propensity for dendrite/filament growth in regions of the narrowest spacings. This indicates that the critical electrical variable may be the voltage gradient (electric field) across the spacing. However, quantifying the electric field acting on the migrating ion is non-trivial due, in part, to the time dependency of the variables involved in the equation, i.e., branching and tortuosity of the electrolytic paths in the insulator and a constantly changing path length, ionic concentration, and conductivity [78].

iii) Temperature

The main effect of temperature is to increase conductivity, probably due to an increase in ion mobility with temperature and/or a decrease in the viscosity of surface solution. Higher temperature increases the susceptibility to ECM, especially when coupled with high relative humidity. Thus, an Arrhenius relationship is commonly used to model the temperature dependency of this failure mechanism.

$$MTTF_{ECM} \propto \exp\left(-\frac{E_a}{kT}\right)$$
 (24)

iv) Effect of Ionic Contaminants

The ECM activity is directly proportional to the concentration of the ion impurities. The higher the ionic impurities, the more the metal-ion complexes formed and the faster these metals succumb to dendritic growth and short circuit. In certain corrosion-resistant metals (e.g., Au, Pd, and Pt), the presence of ionic impurities, especially chlorides (Cl[¬]), allows a series of complexation reactions to happen that will liberate the metal or metal–complex cations. Corrosion-resistant metal like gold can also be rendered susceptible to, an impurity-induced, electrochemical migration process. The discovery of gold dendrites inside ceramic packages leads to simulation experiments to induce their growth, it was

found that the gold dendrites would grow only in the presence of all three factors, namely 185N 1466-8858

(i) bias voltage, (ii) hygroscopic nonylphenol (as the moisture trap or vehicle), and (iii) Au(CN)₂ (the complexation agent in the gold plating bath) [77 79 80]. The influence of ionic impurity is rather complex and involves various counteracting effects that change depending on the nature of the conductor and the concentration of the impurity ions.

v) Material and flux residue

Polymeric insulator materials (epoxies, phenolics, or silicones) used to protect microelectronic devices are non-hermetic and highly susceptible to moisture penetration. At any RH, the moisture absorption tendency of the microelectronics package is dependent on the surface condition of the insulator material [81 82]. The main effects of absorbed moisture are moisture-induced plasticization and/or micromechanical degradation. The mechanical and chemical integrity of the epoxy is altered and deteriorates as a result of (i) microcrack formation from hygromechanical stresses, (ii) polymeric bond degradation due to chain scission, (iii) reduction of the glass transition temperature (Tg) due to plasticization, and (iv) degradation of polymer interfaces resulting in de-adhesion (delamination). As interfacial voids or delaminations are potential nucleation sites for capillary condensation, these can then provide an easy path for moisture ingression, i.e., a path of least resistance, to any available ambient moisture. The nature of metal conductor surface also plays a role in determining the device susceptibility to ECM failure. Rough surfaces possess high-energy points that are ready targets for the migrating metal cations. In addition, metals that form tenacious metal oxides (e.g., Al₂O₃ and CuO) are certainly more protected against ECM than those having more soluble metal oxides (e.g., AgO). The flux residue is also one of the most deleterious process contaminants from the various assembly processes. Certain flux constituents, like the strongly hygroscopic polyglycols, greatly enhance the hydrophilicity of the epoxy. Polyglycol rapidly diffuses into the epoxy polymeric network at the assembly temperatures used and is retained within after the cleaning step. These become sites for water condensation and a significant amount of moisture absorption can result if the critical humidity level is exceeded. These flux residues act either by modifying the epoxy surface and altering their moisture absorption propensity or, through a degradation process, becoming the source of moisture itself [78].



Fig 6: A needle-like tin whisker.

Whisker growth is believed to proceed either via a dislocation mechanism or through a grain growth /recystallization mechanism. Various factors such as crystalline structure, plating thickness, electroplating current density, substrate, temperature, humidity etc are responsible for whisker growth. Whisker growth as shown in Fig.6 can takes place in various types of metal surfaces, such as tin, zinc, cadmium, and antimony. Whiskers can be straight, kinked, hooked or forked and lumpy. Harsh environments may aggravate the problem by causing thermal and/or mechanical stresses in metal coated surfaces, leading to the growth of whiskers and its induced failures. A common failure mode for whisker- prone electronic systems is whisker bridging, which causes electrical shorts. Whiskers often display a long (months and years) and unpredictable incubation period before significant growth occurs. High aspect ratio Sn whiskers are typically 1-5 µm in diameter and between 1-500 µm in length. The current worldwide initiative to reduce the use of lead (Pb) is driving the electronics industry to consider high tin alternatives to the widely used Sn-37Pb alloys used for plating and solder [83,84,85].

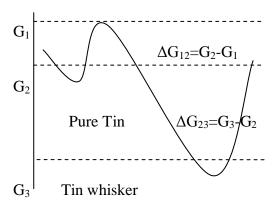


Fig 7: Relationship of Kinetics and Thermodynamics [86].

state of pure tin electroplate to the state of tin whiskers. This negative change of Gibbs free energy is the driving force of formation of tin whiskers. At the same time, Kinetic studies can provide the means to slow down the growth of tin whiskers, which are also helpful in dealing whiskers. The relationship between kinetics and thermodynamics is presented in Figure 7. Here, ΔG_{12} is activation energy, which is the Kinetic reason and determines the growth rate of tin whiskers, the growth rate can be expressed as

Growth Rate = N ln
$$\left(\frac{\Delta G_{12}}{RT}\right)$$
 (25)

Growth is highly variable and is likely to be determined by a complex relationship of factors including plating chemistry, plating thickness, substrate materials, grain structure, temperature, defects, diffusing coefficient, and environmental storage conditions. Growth rates from 0.03 to 9 mm/yr have been observed in an integrated circuitary. ΔG_{23} is the change of Gibbs free energy, the spontaneous nature implies that the formation of tin whisker on pure tin plate is thermodynamically favorable. Tin whiskers growth is generally believed to occur in order to relieve compressive stresses that exist within the pure tin plating. In general, growth is most likely induced by stresses such as those resulting from: residual stress within the tin plating, intermetallic compound formation, external stress, coefficient of thermal expansion mismatches, surface and particle irradiation. Residual stresses are directly related to electroplating process and the materials properties that inherent from other pre-treatment, hence, the various factors that may increase stresses within tin plating are electroplating current density, grain size and shape, interfacial stress level, substrate stress levels, co-deposited carbon or hydrogen. It was also noticed that the spontaneous development of compressive stress was responsible for diffusion of copper atoms from the substrate into the tin film and the formation of the intermetallic compound Cu₆Sn₅. Tin films with small grain size have more grain boundaries and provide diffusing species with more diffusion pathways. The amount of copper atoms diffused into tin grain boundaries per given time will increase with decreasing grain size, if given everything else same, compressive stress will build up more quickly in tin film with smaller grain and higher density of tin whiskers are expected (Figure.8). Moreover, the continuous growth of Sn whiskers must rely on grain boundary diffusion for mass supply [86]. Large number of the shape of grains tin whiskers grow from the grains having different orientation from the major orientation of the tin film.

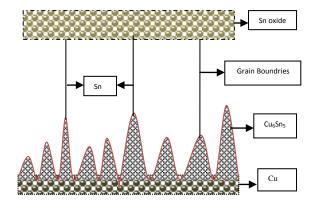


Fig 8: Cu₆Sn₅ Formed in Grain Boundaries within Tin. [86]

In this situation, the tin surface oxide film can be sheared along the boundaries of the grains. To release the compressive stress in the tin film,tin whiskers grow from the grain whose surface oxide is sheared [87]. It was inferred that with loosely packed grain boundaries, high angle have more dislocations to serve as diffusion paths, therefore, more prone to grow tin whiskers [88]. While other concluded low angle grain boundaries are more prone to whisker growth than high angle boundaries [89]. The formation of intermetallic compound of Cu₆Sn₅ reduces the specific volume and induces compressive stress within tin film. These intermetallic compound are considered as a flat layer formed between copper and tin, hence, it only give rise to compressive stress at the region near the interfaces. Several analyses are summarized as follows.

a) Diffusion via Grain Boundaries

If the intermetallic compound forms flatly in the interface between copper and tin, no stress will develop in the tin layer, regardless of the diffusion coefficients of species concerned. However, if the intermetallic compound layer forms in the tin grain boundaries, it will give rise to the compressive stress in the tin layer, because copper atoms are the dominant diffusing species. *B. Z.Lee* believes that the Cu₆Sn₅ layer is not flat and it penetrates into grain boundaries of tin film. This hypothesis is in agreement with the observation of tin whiskers only grow within tin film other than any interfaces [90].

Volume 16, Preprint 67

submitted 27 November 2013

Interstitial diffusion of copper atoms and the formation of intermetallic compound (Cu₆Sn₅) may alter the lattice spacing in the tin plating and generate compressive strain within tin lattice. *M.Endo* studied tin whiskers originated on a brass substrate where two diffusion species were found, zinc and copper. He believes that interstitial diffusion of copper into tin forms intermetallic compound and cause stress, while zinc atoms diffused toward the tin film surface and form oxide. This zinc oxide provides whiskers with sites to grow out of tin surface [91]. On the other hand, the atom radii of copper, zinc and tin are 1.57A, 1.53A and 1.72A which is comparable, thus huge strain will be created if copper or zinc "squeeze" into the small interstitial sites of tin lattice, which is not thermodynamically favorable. Therefore, it can be inferred that the interstitial diffusion of copper or zinc into tin crystals is very unlikely to occur if competing with grain boundary diffusion.

c) Diffusion and surface oxidation

When tin is deposited on a brass substrate, copper and zinc atoms from this substrate can both diffuse into tin film and forms Cu₆Sn₅ and zinc oxide as an intermetallic compounds [69]. Copper is more prone to stay within tin film and form intermetallic compound, while zinc atoms diffuse toward the tin film surface and bind there with oxygen to form oxide. More zinc atoms on the surface were found than that inside the tin film. *M. Endo* proposed that the formation of copper intermetallic compound may prevent further diffusion of zinc atoms from the brass substrate. Another study shows that zinc atoms have higher mobility than copper and could be more easily diffuse from brass substrate to tin surface than copper. The relatively solubility of zinc in tin implies that zinc atoms are the dominant and faster diffusing spices compared to tin [92].

d) Temperature

As the temperature rise the diffusion rate of copper into tin film can also increase which shows the quick build up of compressive stresses into the substrate material, and accelerates the tin whiskers growth. However, high temperature also helps relief internal stress within tin film and consequently oppresses the formation of tin whiskers. Based on literature research, the optimum temperature for whisker to form is around 50 C°, and most of researches were conduct at this temperature. Contradictorily, in a conformal coating

temperature ambient conditions (25 °C) than that on samples stored at 50 °C [93].

It was recommanded to use conformal coating or encapsulation that can protect electronic circuit. It was proposed that the part of the built-up compressive stress might come from the specific volume change on the tin surface. Alloying as little as 0.9% lead with the tin dramatically reduces the density and growth rate of tin whiskers, but both nodular and filament whisker were observed at the compressively stressed area even for a 10% lead-tin finish in Cunningham's experiments [94]. It was necessary to use Ni barrier effectively to reduce whisker growth, if the diffusion of copper species into tin films builds up internal stress eventually results in whisker growth, nickel barrier a barrierlayer may be an effective method to block the diffusion pathway and prevent whiskers. The nickel depositlower the initial stress between the interfaces and also act as an excellent barrier to copper diffusion, which hinders the formation of intermetallic compound [95]. Reflow is another effective process to minimise tin whisker, reflowing tin film with large grain size is less prone to grow whiskers, there is no compressive stress built up again in Sn film even after a long period of aging, e.g. 18 months, hence, no whisker growth observed [88].

9. Environmental effects on Corrosion

Environmentally humid condition results an accumulation of water and impurities on metal surfaces whereas heat and sunlight also decay the products and accelerate the process of corrosion and other harmful effects. Air velocity, temperature also has an effect on the rate of corrosion reaction and contamination of the surfaces. The Fig 9. shows the weather averages of temperates and relative humidity during various seasons in Mumbai, India during the calendar year-2010. The extremely significant factor to the corrosion risk is the relative humidity of the air exceeds 60% at all times. Corrosion and climatic effects increase the contact resistances of the joints, leakage currents between connectors and interconnects, increase in electromagnetic disturbances which can cause various operational faults of the circuit devices. At high temperature > 55°C, corrosion reactions accelerate even in dry conditions of use causing the decay of materials. Water, dust, gases and organic compounds cause leakage currents, short-circuits and mechanical changes. If the immediate environment of the device is relatively dust free and dry, relative humidity of the air is less than 40% then corrosion becomes so slow that it will not have much effect

on the device. The most common corrosion risk factor from environment is probably due to 185N 1466-8858

the soluble & insoluble salts from the sea water (chlorides) which can spread in the air as far as 50 km from the coasts.

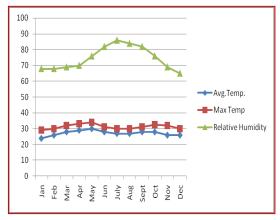


Fig 9:. Weather averages of temperates during various seasons (Climate graph 2010 Mumbai, India)

Considerable temperature variations can cause risk of water condensation on the surfaces whereby gases in the air and other impurities together with water form corrosive compounds, such as sulphuric, nitrogen and hydrochloric acids. These acidic substances on the surfaces of the components enhances corrosion reactions. Gaseous and ionic substances in the air and dust have basically spread evenly and everywhere in urban conditions. Concentrations exceeding the average considerably are only met in the vicinity of heavy traffic flows, industrial plants and power plants, which increase the risk for corrosion, form the usual. Electrical stress also speeds up corrosion, strong current can heat the solder joint and gradually weaken it. In dense wiring patterns the high field intensity between the wires increases leakage currents and accelerates corrosion on contaminated surfaces [96].In microcircuits where the wire widths are in micrometres, metallic migration may occur (wire breakage) due to high density of the current. and causes short malfunctions of the devices.

The graph statistic given below (Fig.10) shows that majority of faults in microelectronics are related to heat, humidity and vibration. When conditions change, the faults may also disappear. The temperature readings cold/hot, their fluctuation and humidity always affect the physical and chemical properties of materials and components. The material used in electronic devices is not completely inert (chemically passive) but the components,

Fig 10: Reasons for failure of micro electronic devices

component boards and metal parts and plastic structures can be made relatively inert to the corrosive effects with reasonable work In most electronics, high temperature of use naturally dries the inside of the device, but accelerates oxygnation and decay of material which results in corrosion surfacing in another form, such as decay of the solder connections or embrittlement of insulators. On the other hand, effective cooling with rough or humid outside air increases the gas contacts and relative humidity of the air inside, which results in more corrosion and contamination in the contacts in the component leads. The electrochemical cell created on the surface of a metal always has a voltage difference between the anode (the corrosion area) and the cathode. If the voltage difference is less than 0.3 V then the rate of corrosion is slow. The failure mechanisms have different effect on different materials, the most common failure of the components can be observed with, connectors, interconnects, and a gradual decay of solder connections especially in hot spot. New devices also noticed thermal fluctuation and mechanical vibration in their frame structure causing breaks in wire connections and connectors. There are various causes for occasional unidentified faults such as -reversible changing of component parameters due to change in the temperature, corrosion in the connections, leakage currents of surface of the component board in humid weather, leakage currents of soiled surfaces, breaks in connectors or wires due to thermal expansion, breaks due to vibration, contact faults caused by inferior contact spring material or design, stickiness of the keyboard due to chemicals of human origin, problems of the mechanical structure, software disturbance, disturbance in data transmission or power supply etc. These occasional faults are mentionaed in table 2. It was noticed that the operation of electronic components get affected even before the corrosion products are produced. In dry and dusty conditions the air going inside the respectively. The production of expect and nitrogen whereas carbon dioxide 2013 various nitrogen oxides, sulphuric compounds, sand dust, soot etc are also found in the low concentration. Such gases accumulate (adsorb) on the surfaces of the devices and also desorb (leave the surface) when the surrounding air flows across the surface and makes the surfaces conductive, which increases leakage currents and causes electricbreakdowns. Air pollutants such as sulphur dioxide, hydrogen sulphide, oxides of nitrogen, chlorides have also been found to contribute to atmospheric corrosion [97]. Acidic gases, such as hydrogen sulphide, sulphur oxides, chlorine, hydrogen fluoride (HF) and nitrogen oxides are the most harmful gases that can pose problems to sensitive electronic equipments. These corrosive gases are generated primarily from auto emissions, heavy industrial production and heat and power generation. Weather conditions play a major role in concentrating or dispersing external gaseous contaminants.

Table 2: Occasional failure of devices [125]

Table 2. Occasional randre of devices [125]					
Classification of corrosion effects					
Electrical functionality	Change of series resistance in contacts, Breaks of conductors, Change of insulation resistance, Leakage currents, soiled surfaces Change of dielectric constant of materials, Faults of component packages, Faults of component leads Short-circuits, Breaks of cable				
Mechanical Functionality	Increase of friction, Hindering of movement, Weakening of spring, Fault of contact mechanism, Fault of switch mechanism, Sudden breaks during heat and Mechanical Stresses				
Mechanical strength	Break of mechanical actuator, Break of supporting structure, Break of solder joint				
Appearance	Dusty appearance, Faults in outer surface, Color changes of platings, Soiled surfaces. Disappearance of markings				
Malfunction	Intermittent failure, Groundless change of new component Rejection of nearly intact device, Failure of oftware, Fault in electric supply				

Industrial smoke contains both particulate and gaseous contaminants is a source of nitrogen oxide. Microfiche systems are heavy producers of ammonia, while printers can discharge sulphur compounds and chlorides. Gases often present at such low levels, are in sufficient amount to damage the microelectronic devices, hence most of the odor threshold levels are maintained much higher than the levels needed to cause corrosive damage [98,99,100].

The complexity and diverse nature of the atmospheric pollutants make the prediction of the atmospheric corrosion difficult. Inorder to derive corrosion, a direct approach to the

problem is to measure the observed corrosion rates and the participating atmospheric parameters and correlate them. The most principal corrosives consist of moisture, relatively small amounts of sulphur oxides (SO_X), carbon dioxide (CO₂) from various combustion products and ammonia (NH₃), resulting from the decomposition of farm fertilizers. Rural environments generally are not aggressive towards metals. Urban atmosphere comprise of little industrial activity, characterized by pollution composed mainly of SOx and NOx variety, from motor vehicles and domestic fuel emissions which, with the addition of dew or fog, generate a highly corrosive wet acid film on exposed surfaces. Whereas industrial environment that spread sulphur oxides (SO_X) and nitrogen oxides (NO_X) produced by the burning of automotivefuels and fossil fuels in power stations are the major sources of corrosion. This contamination induces severe corrosion at relative humidities exceeding about 55%. This environment is characterized by proximity to the ocean and salt loded air that can produce severe corrosion damage of the metal alloys and accelerate deterioration of protective coating systems. Marine atmospheres are usually highly corrosive. The principal culprit in marine atmospheres is the chloride (Cl⁻) ion derived from sodium chloride [101,102,103]. Pollutants which are commonly present in an atmosphere and its influence on metallic devices are given in table 3.

Table 3: Outdoor air pollutants and their sources.

Pollutants	Source	Influence			
Sulphur dioxide(SO ₂)/ Sulphur oxide(SO _X)	Burning coal and oil.	Forms acidic surface. Attack many meals.Stress corrosion accelerator			
Nitrogen oxide(NO _X)/ Nitrogen dixide(NO ₂)	Burning fuel in cars and other industrial processes.	Attack metals like Co,Ni,& Fe.Nitrate particles cause failures at microelectronic interface.			
Carbon dioxide(CO ₂)	Volcanic activity and hot springs, combustion processes, cars and power plants.	Inhibit the NaCl induced carbonate containing corrosion products of zinc and copper			
Volatile organic compounds	Evaporates from sources such as vehicle exhausts, cleaning agents, furniture polish and fabric softener.	Destabilizes passive film by lattice impregnation & acid dissolution.			
Ammonia	Used to fertilise crops and emitted from this agricultural process and farm animals.	Complex with metal like Cu,Ni and Ag Forms basic surfaces			
Persistent organic pollutants (POP)	Produced through industrial processes and waste incineration.	Corrosion of metal at even at low concentration.			
Particulate matter (from sulphates and nitrates)	Fine particles which are either man made or natural.	Attack on metal like Co,Al increases with relative humidity.			
Ozone	Formed from the chemical reaction during sunlights	Degrades polymers & accelerate oxidation of H ₂ S,NO ₂ & SO ₂			

submitted 27 November 2013

Hydrogen sulphide (H₂S), elemental sulphur (S), and organic sulphur compounds such as mercaptans (RSH) rapidly attack copper, silver, aluminum, and iron alloys at low concentration of ppb level. The presence of NO₂ with H₂S greatly enhances silver sulfidation in presence of high humidity content. Active sulphur compound with inorganic chlorides as predominant a constituents are the causes of corrosion in process industries. Failures in printed circuit boards, integrated circuits, and other components have been known to occur due to the atmospheric exposure even in extremely low levels of these gaseous contaminants. Cuprous oxide protects copper from further attack by sulphur compounds in a dry atmosphere. In humid condition, cuprous oxide present as an adsorbed film, reacts with hydrogen sulphide to form Cu₄SO₄(OH)₆.H₂O a corrosion products [104].

Sulphur dioxide:

Corrosion-induced failures are frequent in electronic products used in sulphur dioxide environments. Oxidation of sulphur dioxide forms sulphate ions in presence of moisture.

$$SO_2 + O_2 + 2e \rightarrow SO_4^{2}$$
 (26)

The corrosion-stimulating sulphate ions are liberated during anodic dissolution leading to an auto-catalytic type of attack on the metal surface [105]. The acidification of the electrolyte also accelerates the corrosion rate, but this effect is likely to be of secondary importance because of the buffering effects of hydroxide and oxide corrosion products. At very high levels of sulphur dioxide, dissolution of protective layers and the formation of more soluble corrosion products is associated with higher corrosion rates. SO₂ pollutant substantially enhances the corrosion rates of metals exposed in the atmosphere. Rozenfeld [106]has suggested that, because of greater solubility (SO₂ is about 2600 times more soluble than oxygen), SO₂ might be reduced at cathodic sites more rapidly than oxygen, consequently increasing anodic dissolution rates. In solution, electro-chemical reduction of SO₂-3 competes with its oxidative conversion to SO₂-4. However, Seinfeld, [107] states that, in the absence of catalysts, solution phase oxidation of SO₂-3 by dissolved oxygen is slow. Under these circumstances SO₂ may persist for a sufficient length of time to act as a cathodic depolarizer in the manner as suggested by Rozenfeld. Corrosion can occur quite rapidly in humid environments in presence of atmospheric sulphur and chlorides results an

typical failure mechanism of electronic systems is the reaction of atmospheric sulphur with exposed metals – particularly copper and silver. These metals are found in PCB traces, integrated circuit (IC) leads and device terminations.

Silver creep corrosion (electromigration) readily occurs in humid environments in the presence of small amounts of sulphur and chloride. Sulphur-based corrosion failures increased dramatically upon introduction of immersion Ag surface finish on computer products (due to ROHS requirements). The corrosion rate distribution guidelines for copper in terms of environmental conditions necessary to protect their computer equipment is shown in fig.11. The majority of creep corrosion failures occurred on hard disk drives (HDD), graphic cards, and motherboards in desktop or workstation systems. Copper sulfide (Cu₂S) or silver corrosion products can grow and creep across surfaces such as IC packages and PCB substrates High amounts of Cu₂S typically indicate the presence of active sulphur compounds such as elemental sulphur (S), hydrogen sulphide (H₂S),or organic sulphur compounds such as mercaptans. Ag₂S can also be formed by these contaminants but can also be formed by exposure to sulphur oxide (SOx) contamination [108].

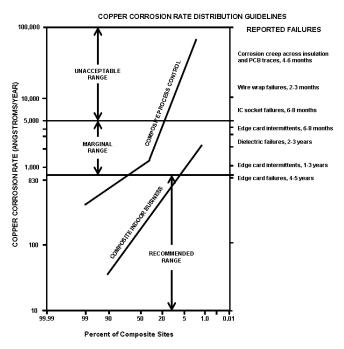


Fig11: Copper corrosion rate distribution guidelines. [108] (Courtesy: Digital Equipment Corporation 1985)

Volume 16, Preprint 67

submitted 27 November 2013

Nitrogen oxide compounds (NOx, NO₂, N₂O₄) have a major role in the formation of ozone in the atmosphere. Atmospheric oxidation of nitrous oxide to nitrogen dioxide and nitric acid takes place successfully with the following reaction,

$$2NO + O_2 \rightarrow 2NO_2 \tag{27}$$

$$2NO + H_2O + 3/2 O_2 \rightarrow 2HNO_3$$
 (28)

The NO₂/NO ratio in the atmosphere varies with time and distance from the source. NOx may be further oxidized to form nitric acid. Eriksson and Johansson [109] exposed copper to humid air containing NO₂. Simon, et al., [110] studied the corrosion products formed on copper exposed to humid air containing NO₂ identified cuprite (Cu₂O) and basic copper nitrate(Cu₂(OH)₃NO₃) on the surface usingXPS. The generalconclusion of these studies is that NO₂ in the ppm range has very slight corrosive effects on copper.

9.3 Inorganic chlorine compounds

Inorganic chlorine compound includes chlorine (Cl₂), chlorine dioxide (ClO₄), hydrogen chloride (HCl), etc.and reactivity will depend upon the specific gas composition. Presence of Cl₂ in humid conditions, disintegrate into hypochlorite and chloride, hypochlorite is a strong oxidant, and chlorine has a strong synergetic effect with hydrogen sulphide. Chloride has an ability to penetrate the oxides protecting metals and thus increases corrosion. Atmospheric salinity at low ppb react with metals like zinc, copper, tin, silver, and iron alloys accelerates corrosion. Feitnecht [111] carried out the major study of metals such as zinc, iron and copper which was exposed to HCl vapours at varying humidities between 50% and 95% RH, the value of which was approximately that of the vapor pressure over a saturated solution of the metal chloride formed during corrosion. The corrosion products found on zinc were 4 Zn (OH)₂. ZnCl₂, Zn (OH)₂ and ZnO.

9.4 Hydrogen peroxide

Hydrogen peroxide midsummer concentrations can be as high as 10-30 ppb and 10-100 μ m precipitation often greater than those of SO₂ or SO₂⁻⁴ concentrations [112]. In recent years increased emissions of oxides of nitrogen and hydrocarbons have resulted in increase in atmospheric H₂O₂. The interactions of metal surface with H₂O₂ produces HO_X radicals.

These oxidizing radiolytic products can have an inhibitive effect on the initiation of 2013 localized corrosion at potentials less than approximately +0.5 V vs. SHE, as are present in aqueous solutions exposed to the atmosphere [113].

9.5 Ozone

If the concentration of O₃ reaches to an extreme values in an urban areas, it can accelerate the sulphate and oxide formation in the atmosphere [114]. Later Graedel et showed that O₃ enhances the atmospheric sulphidation of copper. Eriksson [115] found a basic copper sulphate, Cu₂.5SO₄ (OH)₃. 2H₂O, when exposed to SO₂+O₃ with 90% relative humidity. Ozone promotes the oxidation of SO₂ to sulphate more efficiently than NO₂. A synergism proposed between SO₂ and O₃ includes oxidation of Sulphur dioxide by ozone and the capability of ozone to form oxides, hydroxides or other oxygen containing reaction products in the presence of smaller amounts of SO₂. Presence of ozone may lead to an increase the deposition of sulphur dioxide on metals. Accelerating effect of ozone on zinc appears to be limited, but with aluminum and copper distinct corrosion degradation was observed. SO₂ induced atmospheric corrosion of copper increases the formation rate of both Cu₂O and CuSO₄. x H₂O all over the surface [116,117,118].

9.6 Organic acids

Organic acids, such as acetic and formic acids, causes metal corrosion at very low concentrations. The presence of acetic acid and formic acids has been detected in the rain [119,120], where they increase the acidity. Acetic vapor from vinegar in the food processing industry also constitute about 0.1 to 1% of the total ion concentration in the copper exposed corrosion-products [119]

9.7 Saline particles

The amount of corrosion product formed increases with the amount of $(NH_4)_2SO_4$, particles, relative humidity (RH) and temperature [121,122,123]. At and above the critical relative humidity of $(NH_4)_2SO_4$, dissolution of Cu is followed by formation of Cu₂O, oxidation of Cu(I) ions to Cu(II) ions and precipitation of antlerite [Cu₃(SO₄)(OH)₄], brochantite [Cu₄(SO₄)(OH)₆], or posnjakite [Cu₄(SO₄)(OH)₆. H₂O]. Aluminum reacts with $(NH_4)_2SO_4$ particles only at or above the critical relative humidity (CRH) at either temperature. The corrosion rate increases with increasing RH and temperature [124].

submitted 27 November 2013

There are several techniques to minimise corrosion and improve the conditions of protecting electronic devices.

10.1 Fault-resistant technique

Connectors, switches, relays and connections of other components and displays as well as the wiring pattern of the circuit board always affected with a risk of corrosion degradation. If the electrical/mechanical functionality of the device requires very small tolerances in the signals, leakage currents or the size or quality of the impedances in the circuits (humidity affects the dielectric constant er), the device will be sensitive to corrosion, since corrosion of the surfaces, contamination and humidity affect not only the metal surfaces but the electrical properties of the surfaces of the insulators as well. These changes in the serial resistances of the joints (connectors, solder joints, switches), leakage currents between the wires and insulation resistances caused by corrosion should be included in the sizing of the electric circuits in the designing of the device. Minimising of the number of electromechanical connections, especially unprotected connections that can be opened, is a good means of reducing the corrosion risk.

10.2 Maintain dry atmosphere of the devices

A relatively tight device case is used to maintain the dry atmosphere in all situations since the presence of water always increases the risk for corrosion considerably and weakens the isolation of the surfaces. Heat from the device itself should be used to minimise the harmful effects of humidity in order to keep the device dry and to ensure the removal of possible moisture inside the device. If the various parts of device kept warmer than its surroundings it would be easy to minimise the failure. The cooling air inside the device provides a natural help in the removal of moisture but if the flow is based only on weak natural convection or ventilation through cracks in the seals, precautions must be taken against long term effects of internal moisture and the inside surfaces must be better protected.

10.3 To use compatible material at joints

There are various boundary surfaces of materials on the circuit board, wiring patterns, connectors, switches and microcircuits etc. If the device is subjected to the corrosive substances present in air and to water galvanic corrosion occurs. High temperature and

smallest risk of corrosion occur. If the metals are different, the least corrosion occurs between surfaces where the electric surface potentials are as close to one another as possible. If the materials differ much in this respect, the probability for corrosion is great, if there is water and if there are corrosive gases in the air and on the surfaces. It is rather difficult in electronics devices to avoid contacts between different materials. These are naturally in contact with various metals. When using tin-lead solder, it should be checked that the circuit board or the component wires do not carry excessively thick layers of gold which forms intermetallic alloys with tin. The mechanical strength of these alloys is weak and they corrode quickly in heat.

10.4 Air filtration technique

If the outer and inner surfaces of electronic devices are in constant contact with gasous impurities and undesirable dust particles with faster air flow then the probability of chemical reactions (corrosion, humidification) and contamination is higher. The reduction of polluted airflow inside the device can prevent corrosion. The most common technologies available to deal with gaseous contaminations are (1) particle removal filtration such as mechanical filters and electronic air cleaners and (2) gas-phase (dry-scrubbing) filtration. Particulate filters vary in their ability to remove particulate matter, depending upon the filter's material composition (typically cellulose, fabric. and glass-fiber materials) and the efficiency of the filters is typically 20 to 65 percent [98,99,100]. Most instrumentation air conditioning systems come with low- to mid-efficiency filters already built into the system. Electronic air cleaners, another form of particulate filtration, use the principle of electrostatic precipitation. Particles are charged and then captured on collecting plates. They are relatively efficient against particles of sub-micron size, but require regular cleaning. Additionally, the electronic air cleaners produce ozone which may prove hazardous to human health, as well as causing corrosive damage to electronic circuitry if they are not installed and maintained properly. In contrast to particulate filtration, gasphase air filtration uses the processes of adsorption, and/or chemical reaction to remove gaseous contaminants from an airstream. Oftentimes, these systems are used in tandem with particle removal filters for optimal filtration. Adsorption is the most common form of gas-phase filtration. The material most often used is carbon (activated and/or impregnated

surface area presented to the airstream and high removal capacity. Gas-phase filtration systems typically have gas removal efficiencies of 99.95 percent. To reach this level of efficiency, a system may employ multiple media beds for taking advantage of the strengths of the media to target specific gases. Gas-phase air filtration technology has been used to protect crucial process control systems operating in harsh, industrial environments, is available for the protection of today's commercial data processing center. Gaseous contaminants, both externally and internally generated, can be effectively removed down to the low parts per billion level to preclude any potential damage to electronic equipment.

11. Methods for testing devices due to corrosion

Corrosion tests are often accelerated tests. Humidity, elevated temperature and aggressive air born gaseous impurities are responsible accelerating factors to initiate corrosion. An examination of the combined effects of humidity, temperature and corroding gases by an accelerated test is a swift way of testing the durability of the circuit boards. The verification of the test conditions in the test chamber, the measurement of temperature and relative humidity, gas concentrations is a requirement for an accelerated test. The control of test conditions is limited by the analysing technique of gases. Various quick tests or more controlled standardised test gives fairly accurate information on the corrosion resistance properties of the products. This testing should be undertaken whenever the product is changed so that the changes may affect the tolerance for environmental conditions. When using new materials and components it should be checked that these actually function in the user conditions of the product. The testing and analysis methods listed in Table 4 are used for various coatings, component boards, components and entire devices. When the failure mechanisms are discovered it is possible to identify worthwhile corrective action for the next product generation [125]

submitted 27 November 2	2013	,
-------------------------	------	---

_	
Test	Analysis
Failure Analyse Methods	Visual inspection photography, Microscopy, Measurement of resistance, Measurement
	of coatings, Material analysis, SEM
Rapid test methods	Water, humidity, salt solution, acid fume, Scraping, tape adhesion test, Chemicals,
	perfumes.
Heat tests Dry	Heat and cold (short and long period), Change of temperature, Combined cold/heat and
	cyclic humidity.
Humidity tests	Cyclic damp heat, Long period humidity at high temperature, Accelerated tests for
	components e. g. 85°C/85% RH
Gas tests	Multigas tests, H ₂ S, SO ₂ , NO _x , Cl ⁻ , NH ₄ ⁺ etc
Salt mist tests Salt	Spraying salt solution mist
Tightness	Mechanical, dust and water tightness
Mechanical Tests	Vibration test, shock tests and fretting corrosion tests

12. Mixed Flowing Gas (MFG) Test

Mixed Flowing Gas (MFG) test is a method suitable for testing corrosion of electronic components caused by gaseous impurities in the air such as SO₂, H₂S, NO₂ and Cl₂. In flowing mixed gas test, a continuous flow of air including corrosive gases is directed through the test chamber and the various parameters such as temperature (°C), relative humidity (%RH), concentration of gaseous pollutants (ppb level), and other critical variables (such as volume exchange rate and airflow rate) are carefully defined, monitored and controlled. In this way, the repeatability of the test conditions can be guaranteed. The consciously chosen humidity level, 70...85% RH is essential in these tests, as is the simultaneous use of two or more gases.

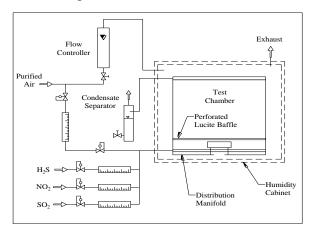


Fig.12:: Mixed Flow Gas Test Chamber

This method produces tests revealing certain failure mechanisms fairly well and tests 2013 copying certain environmental conditions. Test samples that have been exposed to MFG testing have ranged from bare metal surfaces, to electrical connectors, and to complete assemblies. For noble metal plated connector applications, MFG test has been widely accepted as a qualification test method to evaluate the performance of these connectors.

The operational environments for electronic equipments in atmosphere are divided into

four classes, from least corrosive (Class I) to most corrosive (Class IV). Class I means well-controlled office environment with continuous adjustment. Class II means light industrial environment, such as business offices without effective or continuous environment control. Class III means moderate industrial environment, such as storage areas with poor environment control. Class IV means heavy industrial environment, such as locations adjacent to primary sources of atmospheric pollutant gases. Since Class I indicate no precedent for environmental effects on reliability, there is no accelerated testing for Class I. The other three classes use a combination of corrosive gases such as NO₂, H₂S, Cl₂. SO_2 to accelerate corrosion [126,127]. Flowing mixed gas corrosion test, $(H_2S + SO_2)$ method, the predominant fault mechanism is pore corrosion, so it is suited for pore corrosion testing of gold and palladium coatings copying mild indoor conditions. The creep of corrosion products can be detected with humidity and heat tests and mixed gas tests. (H₂S, NO₂, Cl₂) method, can be used for corrosion product creep tests since the predominant fault mechanism in the test is the creep of corrosion products in addition to pore corrosion. These tests are also suitable for general reviewing of the corrosion sensitivity of the electronic components and simulating more demanding industrial conditions [125]. Since mixed flowing gas environment is an accelerated testing method, the determination of acceleration factor would be helpful to understand the reliability of the device [128].

13. Summary and Recommendations

This paper provides a comprehensive state of the art review of the corrosion induced degradation of electronic devices used in assembly processes. It also provides basic of atmospheric corrosion, influence of exposure parameters namely critical relative humidity, temperature, specific atmospheric corrodants (pollutants) and other atmospheric contaminant and airborne particles. It has been observed that more than 50% of microelectronic device failure is due to environmental conditions such as humidity or

condensation, contaminants, ionic or organic residuals, temperature, thermal stress and electrical bias in various atmospheres such as rural, urban, industrial, marine, or combinations of these. The aim of the paper was to describe the corrosion induced degradation of device structure and methods of use on the corrosivity of the products for solving the corrosion problems so that designer can verify the correctness of the used corrosion protection technique and also find new approaches for product reliability. Therefore, corrosion control of electronic devices and know-how of various protection methods have become a major field of design in order to ensure product durability and competitiveness on a demanding market. Corrosion essentially involves an electrochemical process and the driving force for this corrosion is the difference of electrochemical potentials between anode and cathode which may result from the dissimilar metals or alloys. Basic requirements for electrochemical corrosion includes the four condition such as (i) the metal anode, (ii) a cathode, (iii) electrolyte, usually condensate and salt or other contaminations, and (iv) a conductor to carry the flow of electrons from anode to cathode. The elimination of any one of the four conditions will stop corrosion. Because of wide temperature variations and high humidity, moisture tends to accelerate the corrosion and deterioration of the material can takes place. Under humid conditions serious problem such as fungus growth, changes in electrical characteristics and shortening can occur as a result of the accumulated moisture. Anodic, cathodic, and electrolytic reaction, uniform, galvanic, pitting and creep corrosion are the most common form of corrosion observed in electronics. The most commonly used metals and alloys such as aluminium, gold, silver, tin, lead, nickel and their alloys will be corroded rapidely if subjected to condition of corrosive environment and high humidity. There are several factors that would accelerate the corrosion process, which needs to be controlled in order to reduce the corrosion effect in electronic system. In a practical working environment it is only possible to control corrosion by developing the quality system and proper planing. Many corrosion problems encountered could be avoided by proper design. Since corrosion as a phenomenon is always a complex combination of situations resulting from the environment, materials and the method of use of the device, advance measuring techniques are necessary to eliminate the corrosive effects of the environment and the sensitivity to corrosion of the device. Basic recommendation to minimize corrosion such as,

component boards and metal parts which can be compatible and relatively inert.

2. To use fault tolerant technology to ensures the operability of the production even though corrosion results in for example increased contact resistances and leakage currents. Use large tolerances of the components in the electric design and maximize the allowed changes of series resistances and leakage currents on the signal paths.

- 3. Minimize the air flow and its velocity inside electronics and use mechanical protecting covers, avoid bare meal surfaces in direct contact with each other to avoid bimetallic (galvanic) corrosion.
- 4. To avoid dissimilar metal couples, the tendency towards galvanic corrosion is greater between widely separated groups than between adjacent groups. Metals from different groups may be placed in contacts where suitable protection against galvanic action is provided through use of barrier tape protective coatings or other methods of isolation. Consider system compalibility environment, avoid the use of alloys susceptible to stress corrosion cracking.
- 5. Use corrosion resistent materials including plastics and nonmetallics in severe environments where possible. Galvanised support should be specified during installation in neutral atmospheres and for inside installations where corrosive agents are present. Keep moisture away or provide for its removal.
- 6. Improve the environment by providing seals, dehumidification purges adquate ventillation, vapour phase inhibitors and air conditioning or by maintaining temperature above dew point. Protection of equipment against moisture, dust etc by use of storage in protected enclosure.

Corrosion control is of vital concern because corrosion of equipment and devices has a great effect on the operational and structural integrity of the system. A properly implemented corrosion programe will disclose corrosion attack in the early stages; minor maintenance can correct such corrosion. Preventive maintenance is the most cost effective method of controlling corrosion, including problem caused by poor design.

References:

- M.Datta, T.Osaka, J.W.Schultze, New trends in electrochemical technology, Microelectronic Packaging, CRC press 2005.
- 2. Mark White, Joseph B. Bernstein, Physics-of-Failure Based Modeling and, Lifetime Evaluation California Institute of Technology Pasadena, Microelectronics Reliability, California JPL Publication 08-5 2/08.
- Corrosion induced degradation of microelectronic http://www.tiscali.co.uk/reference/encyclopaedia/hutchinson/m0030289.html

submitted 27 November 2013

- 6. Microelectronics www.aboutmicroelectronics.com
- A.J. van Roosmalen and G.Q. Zhanga Reliability challenges in the nanoelectronics era, 1403–1414, Microelectronics Reliability 46 (2006)
- 8. Articlesource:http://www.Intel/webpage
- 9. Articlesource:http://www.Intel/webpage
- 10. Microeletroics, http://www.microelectronics.com/stateofart
- 11. Articlesource:http://www.Intel/webpage
- 12. Dr. Alan Doolittle, Georgia Tech ECE 6450 -Source:http://www.google.com
- Stamper AK, Fuselier MB, Tian X., Advanced wiring RC delay issues for sub-0.25-micron general CMOS. p. 62–8
 In:Proceedings of Int. Interconnect Tech. Conf. (IITC), (1998).
- Murarka SP, Low dielectric constant material for interlayer dielectric applications. Solid-StateTechnol(3):83–90 (1996).
- 15. Martin P. Electronic failure analysis handbook. USA: McGraw-Hill; (1999).
- Lau JH, Pao YH. Solder joint reliability of BGA, CSP, Flip Chip and fine pitch SMT assemblies. New York: McGraw-Hill; (1997).
- Tsukada Y. New era of electronics packaging and its technical difficulties. p. 1–4,In: Proceedings of ASME Advances in Electronic Packaging; (1999).
- 18. Blackwell GR. Direct chip attach, the electronic packaging handbook. Boca Raton (FL): CRC Press; (1999).
- 19. Clech J-P. Lead-free soldering., pb-free solder joint reliability, p145-172, New York: Springer Publications; (2006)
- 20. Dasgupta A, Pecht M., Material failure mechanisms and damage models. IEEE Trans Reliab; 40(5):531–6, (1991).
- 21. Lall P. Tutorial: temperature as an input to microelectronics reliability models. IEEE Trans Reliab 45(1):3–9 (1996).
- 22. Semiconductor devices-mechanical and climatic test methods-Parts 25: Temperature cycling. IEC 60749-25 ED. 1.0 B: (2003)
- 23. Semiconductor devices-mechanical and climatic test methods-Parts 34: Power cycling. IEC 60749-34 Ed. 1.0 B: (2005).
- 24. J. A. Mclinn, "Constant failure rate—a paradigm in transition?," Quality and Reliability Engineering International, vol. 6, pp. 237–241, (1990).
- 25. J. B. Bowles, "A survey of reliability-prediction procedures for microelectronic devices," IEEE Transactions on Reliability, vol. 41, pp. 2–12, March (1992).
- 26. W. Denson,"The history of reliability prediction," IEEE Transactions on Reliability, vol. 47, no. 3, pp. SP321–SP328, (1998).
- 27. J. A. Mclinn, "Constant failure rate—a paradigm in transition?" Quality and Reliability Engineering International, vol. 6, pp. 237–241, (1990).
- 28. J. B. Bowles, "A survey of reliability-prediction procedures for microelectronic devices," IEEE Transactions on Reliability, vol. 41, pp. 2–12, March (1992).
- 29. W. Denson, "The history of reliability prediction," IEEE Transactions on Reliability, vol. 47,no. 3, pp. SP321–SP328, (1998).
- 30. M. G. Pecht and F. R. Nash, "Predicting the reliability of electronic equipment," Proceedings of the IEEE, vol. 82, pp. 992–1004, July (1994).
- 31. E. Suhir, R.C.Cammarata, D.D.L.Chung, M.Jono,"Mechanical Behavior of Materials and Structures in Microelectronics", Materials Research Society Symposia Proceedings, vol.226, (1991).
- 32. Tu RH, Rosenbaum E, Chan WY, Li CC, Minami E, Quader K Berkeley, Reliability Tools-BERT. IEEE Trans Computer-aided Des Integrated Circuits Syst; 12:1524–34. (1993).
- 33. Electronic Materials Handbook," Vol. 1, pp 1-1140, ASM international, 1989.
- 34. Ying Zheng, Study of Copper Applications And Effects Of Copper Oxidation In Microelectronic Package, May 10, 2003 Articlesource www.google.com
- 35. W.A. Lanford, P.J. Ding, W. Wang, S. Hymes, S.P. Murarka, "Alloying of copper for use in microelectronic metallization," Materials Chemistry and Physics, Vol 41, pp 192-198 (1995).
- 36. J.R. Lloyd, Mat. Res. Soc. Symp. Proc. Vol. 239, pp.667-676, (1992)
- 37. C. Kittel, "Introduction to Solid State Physics", 7th edition, pp. 160, (1996).
- 38. ASM handbook, Corrosion, 9th ed. Vol. 13, pp 610-640 ASM international, (1987)

39. Z.E Horvath, G. Petò, Z.Paszti, E. Zsoldos, E. Szilagyi, and G. Battistig, "Enhancement of oxidation resistance in Cu ISSN 1466-8858 thin layer," Nuclear Instruments and Methods in Physics Research B 148, (1999) bmitted 27 November 2013

- 40. C.W. Tan, A.R. Daud, and M.A. Yarmo, "Corrosion Study at Cu-Al Interface in Microelectronics Packaging," Applied Surface Science 191, (2002).
- 41. G.L. Ang, L.C. Goh, K.W. Heng, and S.K. Lahiri, "Oxidation Of Copper Lead Frame," International Symposium on the Physical & Failure Analysis of Integrated Circuits, (1995).
- 42. O. Yoshioka, O. Okabe, R. Yamagishi, S. Nagayama, G. Murakami, "Improvement of moisture in plastic encapsulants MOS-IC by surface finishing copper lead fame," Proceedings-Electron Components Conference, pp 464-471, (1989)
- 43. www.synl.ac.cn/org/mic/english/index.htm
- 44. Robert S. Mroczkowski, Connector Design/Materials and Connector Reliability by: AMP Incorporated (1993).
- 45. J.A.Abys, Y.Okinaka, G.J.Russ and B.T.Kerns, 35th Meeting of International Society of Electrochemistry, Berkeley, CA (1984).
- 46. J.A.Abys, Connectors `87, Institute of metal Finishing, Coventry, England (1987).
- 47. J.A.Abys, J.J.maisano, C.Wolowodiuk and H.K.Straschil, Connectors `89, Institute of Metal finishing, Coventry, England (1989).
- 48. A.Abys, G.F.Breck, H.K. Straschil, I.Boguslavasky and G.Holmbom, Plating Surf. Finish, 86(1),108 (1999).
- 49. H.H. Manko, 159/151, Solder and Soldering, 2nd Edition, McGraw-Hill, New York, (1979).
- 50. R.E. Reed-Hill, Physical Metallurgy Principles, pp. 306-307. PWS Publishing Company, Massachusetts, (1994).
- 51. W.F. Smith, Principles of Materials Science and Engineering, p. 724. 2nd Edition, McGraw-Hill, New York, (1990).
- 52. M. Abtew, Corrosion of Solders Induced by Flux Residue and Ionic Contamination, Amdahl Corporation, Technical Bulletin, (1993).
- 53. J.H. Vincent and B.P. Richards, Alternative solders for electronics assemblies, Circuit World 19 (3) (1993) 33.
- 54. P.L. Key, T.D. Schlabach, Metals demand in telecommunication, 433-451 Mater. Soc. 10 (1986)
- 55. Xuan X, Chatterjee A, Singh AD, Kim NP, Chisa MT. IC reliability simulator ARET and its application in design-for-reliability, p. 19–22. In: Proceedings of the 12th Asian test symposium, 2003.
- 56. Yoram Shapira, Michael Talmor Electronic circuit reliability modelling Joseph B. Bernstein , 1957–1979 , Microelectronics Reliability(46), (2006).
- 57. M. Yunovich, Electronics, Appendix Z-ppZ1-Z72. articlesource-www.corrosioncost.com/pdf/electronic.pdf,
- McPherson, J., VLSI Corrosion Models: A Comparison of Acceleration Factors, Proceedingsof Third Intern. Symp. on Corrosion and Reliability of Electronic Materials and Devices, Electrochem. Soc., Vol. 94–29, 270 (1994).
- Comizzoli R B, Frankenthal R P, Milner P C and Sinclai J D, Corrosion of electronic materials and devices *Science* -340. (1986).
- 60. John W. Osenbach, Corrosioninduced degradation of microelectronic devices, *p*155-162, semicond.sci. Technol. 11(1996).
- 61. Iannuzzi M, Development and evolution of a pre-encapsulation cleaning process to improve reliability of HIC's with aluminium metallized chips p 228, 19th Ann Proc. Reliability Physics (New York: IEEE) (1981).
- 62. Iannuzzi M Bias humidity performance and failure mechanisms of non-hermetic SIC's in an environment contaminated with Cl2, IEEE Trans. Components Hybrids Manuf. Technol. (2) 191 (1983).
- 63. Paulson W M and Lorigan R P, The effect of impurities on corrosion of aluminium metallization 14th Ann. Proc. ReliabilityPhys. (New York: IEEE) p 112. Physics Symposium Proceedings, 44 (1986).
- 64. Andrew H. Rawwicz. "Stress induced corrosion of wire micro-joints in microelectronics a quantitative model", Microelectronics and Reliability, 34(5) 875-882 (1994).
- 65. Pecht M, Ko W. A corrosion rate equation for microelectronic die metallization. International Journal of Hybrid Microelectronics 13(2):41-52. (1990).
- 66. F.P. McCluskeya, Y.D. Kweona Method for assessing remaining life in electronic assemblies, 293-306, Microelectronics Reliability 40 (2000).
- 67. articlesource http://www.residues.com/
- 68. Fu-gin Chen and A. Jean Osteraas. "Electrochemical dendrite formation duringcorrosion of connector leads", Proceedings of ASM's third conference on electronic packaging: materials and processes and corrosion in microelectronics, 175-179 (1987).
- 69. Osenbach J W, Water-induced corrosion of materials used for semiconductor passivation, J. Electrochem. Soc. 140 3667 Michel Pecht. (1993).
- 70. A model for moisture induced corrosion failures in microelectronic packages, IEEE transactions on components, hybrids and manufacturing technology, 13(2), 383-389 (1990).

- 72. Schnable G L, Comizzoli B L, Kern W, and White L K A survey of corrosion failure mechanisms in microelectronic devices *RCA Rev.* 40 416 (1979).
- 73. Krumbein, S.J., "Tutorial: Electrolytic models for metallic electromigration failure mechanisms," IEEE Transactions on Reliability, 44, 539–549, (1995).
- 74. Katayanagi, H., Tanaka, H., Aoki Y., Yamamoto, S., "The effects of adsorbed water on printed circuit boards and the process of ionic migration," ESPEC Technology Report, 9, 15–20, (2000).
- 75. Chazalviel, J.N., "Electrochemical aspects of the generation of ramified metallic electrodeposits," Physical Review *A*, 42, 7355–7367, (1990).
- 76. Fleury, V., Rosso, M., Chazalviel, J.N., "Geometrical aspect of electrodeposition: the Hecker effect," *Physical Review A*, 43, 6908–6916, (1991).
- 77. Welsher, T.L., Mitchell, J.P., Lando, D.J., "CAF in composite printed circuit substrates: characterization, modeling and a resistant material," pp. 235–237, IEEE Proceedings of International Reliability Physics Symposium, (1980).
- 78. Reid, M., Punch, J., Rodgers, B., Pomeroy, M.J., Galkin, "Factors that influence ionic migration on printed wiring boards," pp. 300–304, IEEE Proceedings of International Reliability Physics Symposium, (2005).
- 79. X.J. Fan, E. Suhir (eds.), Moisture Sensitivity of Plastic Packages of IC Devices, 503 Micro- and Opto-Electronic Materials, Structures, and Systems, Springer Science+Business Media, LLC (2010).
- 80. Harsanyi, G., "Irregular effect of chloride impurities on migration failure reliability: contradictions or understandable?", Microelectronics Reliability, 39, 1407–1411,(1999).
- 81. Nieman, D.A., "Effect of contamination on copper migration in TAB tape structures," pp. 87–92, IEEE International Reliability Physics Symposium, (1994).
- 82. Apicella, A., R., De Cataldis, C., "Sorption modes of water in glassy epoxies," Journal of Membrane Science, 18, 211–225, (1984).
- 83. Luo, S., Wong, C.P., Leisen, J. "Fundamental study on moisture absorption in epoxy for electronic applications," International Symposium on Advanced Packaging Materials, pp. 293–298, (2001).
- 84. whisker, Articlesource "http://nepp.nasa.gov/WHISKER/background/index.htm
- 85. C. L. Rodekohr, G. T. Flowers, Influence of Quantifiable Extrinsic Stresses on Tin Whisker Growth ASME (2009).
- 86. C. L. Rodekohr, G. T. Flowers, Auger Electron Spectroscopic (AES) Measurements on High Aspect Ratio Sn Whiskers, p 232., Proc. 54th IEEE Holm Conference on Electrical Contacts, October (2008).
- 87. Qian Sun, Understanding and Minimization of Tin Whiskers Course MatE 234 800-14-0839 Spring (2003).
- 88. B.-Z. Lee and D.N. Lee, Spontaneous growth mechanism of tin whiskers, Acta mater, v46, n10, pp.3701-3714, (1998).
- 89. Chen Xu, Chonglun Fan, and Joseph A. Abys, Whisker prevention, APEX, proceedings of the technical conference, (2003).
- 90. A.Egli, W.Zhang, J.Heber, F.Schwager, M.Toben, New Orleans, LA. IPC (2002)
- 91. Chen Xu, Yun zhang, Chonglun Fan, and Joseph A. Abys, Understandingwhisker phenomenon-driving force for the whisker formation, pp. s06-1-1, APEX,proceedings of the technical conference, Jan (2002).
- 92. M. Endo, S. Higuchi, Y. Tokuda, Y. Sakabe, Elimination of whisker growth on tin plated electrodes, International Symposium for Testing and Failure Analysis proceedings, pp. 305-311, Oct (1997).
- 93. B. D. Dunn, A laboratory study of tin whisker growth, ISSN 0379 4067,(1987).
- 94. Jong S. Kadesch and Jay Brusse, "The continuing dangers of tin whiskers and attempts to control them with conformal coating," Tinwhisker Articlesource: www.google.com
- 95. Kathleen M. Cunningham and Michael P. Donahue, Tin whiskers: mechanism of growth and prevention, 4th International SAMPE Electronics Conference, June (1990).
- 96. Rob Schetty, Minimization of tin whisker formation for lead-free electronics finishing, IPC Works Conference Proceeding, Mami, (2000).
- 97. Naixin X, Zhao L, Ding C, Zhang C, Li R and Zhong Q, Corros. Sci., 44-163 (2002).
- 98. Brown P.W and Masters L.W, Atmospheric Corrosion, Wiley, New York (1982).
- 99. Standard: ANSI/ISA S71.04-1985, "Environmental Conditions for Process Measurement and Control Systems: Airborne Contaminants," Instrument Society of America, Research Triangle Park, NC, (1985).
- 100. Boonzaier, W.G. "Acid Gas Corrosion Protection," SA Measurement & Control, pp. 5-9, July, (1986).
- 101. Naeemi A.H and Albrecht P, Int. Cong. Metallic Corros., Toronto, Canada, 418. (1984)
- 102. Money K. L, Metals Handbook Corrosion, Metals Park, Ohio, ASM International, 204 (1987).

- 104. Abbott W.H, Proc. 16th Int. Conf, Electrical Contacts, Loughborough, England. (1992).
- 105. Barton K, Protection against Atmospheric Corrosion, John Wiley and Sons, London, (1976).
- 106. Rozenfeld I.L, Proc. 1st Int. Cong. Metallic Corros. Butterworth, London, 243. (1961).
- 107. Seinfeld J.H, The Atmospheric Chemistry and Physics of Air Pollution, Wiley, New York. (1986).
- 108. Paper- Proceedings of 2009 TAPPI Engineering, Pulping, Environmental Conference: Innovations in Energy, Fiber and Compliance October 11-14, 2009 – Memphis, Tennessee (USA) (2009).
- 109. Ericsson P and Johansson L.G, Proc. 10th Scandinavian Corros. Cong., Stockholm. (1986).
- 110. Simon D, Mollimard D, Perrin C and Bardolle J, Proc. 14th Int. Conf. Electric Contacts, Paris (1988).
- 111. Feitnecht W, 1952. Chimia, 6:3. [139] Barton K and Bartonova Z, Proc. 3rd Int.Congr. Metallic Corros. 4:403 (1969).
- 112. Graedel T.E, J. Electrochem. Soc., 133:2476 (1986).
- 113. Garrels R.M, Geochim. Cosmochim. Acta, 5:153 (1954).
- 114. Tidblad J and Leygraf C, J. Electrochem.Soc., 142:749. (1995).
- 115. Eriksson P, PhD Thesis. Chalmers University of Technology, Goteborg, Sweden. (1992).
- 116. Zakipour S, Tidblad J and Leygraf C, J.Electrochem. Soc., 142:757 (1995).
- 117. Oesch S and Faller M, Corros. Sci., 39:1505 (1997).
- 118. Aastrup T, Wadsak M, Schreiner M and Leygraf C, J. Electrochem. Soc., 147:2543. (2000).
- 119. Galloway J.N and Likens G.E, Water Air Soil Poll., 6:241 (1976).
- 120. Graedel T.E, McGrory-Joy C and Franey J.P, J. Electrochem. Soc., 133:452 (1986).
- 121. Lobnig R.E, Frankenthal R.P, Siconolfi D,J and Sinclair J.D, J. Electrochem. Soc., 140; 1902.(1993).
- 122. Sinclair J.D and Psota-Kelty L.A, Atmos. Environ. 24A:627. (1990).
- 123. Lobnig, R.E., Frankenthal R.P., Siconolfi J.D, Sinclair J.D and Stratmann M, J.Electrochem. Soc., 141:2935 (1994).
- 124. Lobnig, R.E, Siconolfi D.J, Maisano J, GrundmeierG, Streckel H, Frankenthal R.P., Stratmann M and Sinclair J.D, J. Electrochem. Soc., 143:1175 (1996).
- 125. Risto Hienonen & Reima Lahtinen, Corrosion and climatic effects in electronics VTT PUBLICATIONS 626 .ESPOO 2007.
- 126. American Society for Testing and Material, ASTM Designation B845-97: Standard Guide for Mixed Flowing Gas (MFG) Tests for Electrical Contacts, (1997).
- 127. Gore, R.R., Witska, R., Kirby, J.R., and Chao, J.L., "Corrosive Gas Environmental Testing for Electrical Contacts", IEEE Transactions on Components, Packaging, and Manufacturing Technology, vol.13, Issue 1, pp.27-32, March (1990).
- 128. Williams, D.W.; "The Effect of Test Environment on the Creep of Base Metal Surface Films over Precious Metal Inlays"; pp.36-42, IEEE Transactions on Components, Hybrids and Manufacturing Technology; vol.11, no.1, Mar. (1988).