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H₂S Pollution and Its Effect on Corrosion of Electronic Components

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Additional information is available at the end of the chapter

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1. Introduction

The microelectronic industry applies materials with good electrical and corrosion resistance properties for the manufacturing of the microelectronic devices. Silver and copper are materials with this characteristics used for that purpose. Some of their main applications are as high thermal conductive die attach paste that had silver flakes as conductive filler material, silver plated over copper frames, Sn-Ag and Sn-Cu alloys for solder paste used in Surface Mount Technology (SMT) process, conductive internal copper layers in printed circuit boards, copper wire bonding, and more. Other metals and alloys, widely used for support frames, heat diffusers and case wares in the electronics industry are tin, nickel, aluminum, carbon steel and galvanized steel.

Corrosion in microelectronics depends on several variants such as the package type, materials involved, assembly processes, moisture, inorganic and organic contaminants, atmospheric pollutants, temperature, thermal stress and electrical bias.(P. Roberge, 2000, J. Payer, 1990, M.Reid et al., 2007, M. Tullmin and P. Roberge, 1995, M. McNeil and B. Little, 1992, X. Lin and J. Zhang, 2004)

The plastic packages are the more widely used because of its size, cost and manufacturability advantages but, compared to other hermetic package systems like ceramics, are non-hermetic due to its polymeric materials that permit the permeation of moisture and corrosive gases, allowing in this manner the appearance of other problems associated with corrosion of the inside components. Therefore, the advances in the

microelectronics technology that have promoted the developing of devices with smaller and thin components, and the exposition of these devices to environments where temperature, humidity and atmospheric pollutants like chlorides, NO_x,, SO_x, COS and hydrogen sulfide (H_2S) which are not completely controlled, can favor atmospheric corrosion on their metallic components. Small quantities of corrosion products are enough to induce reliability issues and even catastrophic failures in the microelectronic devices due to the formation of insulating layers by the corrosion film.

In order to minimize the risk of corrosion failure it is important to be aware of corrosion damage during the design stage, reliability evaluations and qualifications, assembly processes, storage, shipping, and in the final use of the microelectronic devices.

Atmospheric contaminants such as H_2S and carbonyl sulfide (COS), that promote the corrosion of silver and copper, are dissolved in the thin layer of electrolyte over metals as a consequence of even low relative humidity (RH) and produce the HS^- ion which is their main reduced sulphur constituent at neutral pH. When silver is exposed in an environment containing a minimum concentration of these contaminants (<1ppm), the corrosion product formed is silver sulfide (Ag_2S). A similar process of sulphidation occurs when the exposed metal is copper that reacts with H_2S producing copper sulfide (Cu_2S). Several studies have been done on the indoor corrosion of silver and copper and revealed that silver sulfide is the main corrosion product on silver that had been exposed indoors. These corrosion films can form an insulating layer on the contact surfaces causing electrical failures on the microelectronic devices.

When silver alloys are exposed in a sulphur-rich environment, corrosion products of the most reactive metal are produced. That is the case of Ag-Cu, where the principal corrosion product is Cu_2S or in alloys of silver with palladium where the corrosion product is Ag_2S. (T. Graedel, 1992, D. Rice et al., 1981, C. Yang et al., 2007, H. Kim, 2003, M. Watanabe et al., 2006, C. Kleber et al., 2008, J. Franey et al., 1985, M. Watanabe et al., 2005, S,. Sharma, 1978, P. Vassiliou and C. Dervos, 1999, g. Russ, 1970, L. Veleva et al., 2008)

Corrosion kinetics depends on the type of metal and also is related to the nature of the electrolyte, atmospheric contaminants and corrosion products. Two kinetic corrosion laws are known for silver kinetics in indoor environments. Silver sulphide, which is a film with low corrosion resistance, obeys a linear corrosion law while AgCl a more protective corrosion layer presents a parabolic behavior. (L. Veleva et al., 2008)

Morphology of corrosion film on silver does not tend to be uniform because of the presence of dendrites or whiskers. Dendrites are fern-shaped and grow across the surface of the metal as a consequence of moisture capable of dissolving the metal and then the ions are redistributed by electro migration in presence of an electromagnetic field. When there is a thick layer of corrosion products, thin filaments projected at a right angle to the surface, called whiskers, begin to grow spontaneously even at room temperature and without an applied electric field. Several cases have been reported where tin whiskers caused failures. (B. Chudnovsky, 2002)

This chapter describes the more relevant results got from the study of silver corrosion at indoor conditions in companies dedicated to assembly and functional test of microelectronics devices. To achieve this, silver coupons and silver plated copper leadframes were exposed in two sites of the assembly process. In addition these materials were exposed in a test chamber that simulates indoor conditions of a plant with no controls for outdoor atmospherics contaminants.

On the other hand, in the electronics industry of Mexicali city located in the State of Baja California, Mexico, there are a variety of devices and electronic equipment inside the plants which are exposed to environments with no climate control and air pollution.

The electronics equipment suffers from corrosion, as humidity levels, sources emitting pollutants such as CO, NOₓ and sulphide penetrate thought cracks or air conditioning systems. Corrosion phenomena affect connections of electronic equipment (Frankel, 1995) and other electronics components protected with plastic or metallic materials. Atmospheric corrosion is an electrochemical phenomenon that occurs in the wet film formed on metal surfaces by climatic factors (Table I). The corrosion products form dendrites or whiskers in the metallic joints and connectors (Nishikata, et al 1995, Nishimura et al, 2000).

There are obvious differences in outdoor and indoor environments and consequent differences between outdoor and indoor corrosion behavior (Lyon et al, 1996). The corrosion of metals as copper in indoor environments may be viewed as a variation of outdoor atmospheric corrosion. In contrast to outdoor exposure, in an indoor environment the wet film on the metal surface is thinner and it is often governed by relatively constant controlled humidity conditions. Sometimes the indoor environment temperature and RH are controlled and as a consequence, the amount of adsorbed water on surfaces is minimal and is constrained within reasonably tight limits. Since atmospheric corrosion occurs when moisture is formed on the metal surface and depends on its duration and corrosion intensity increases (Veleva et al, 2008).

| Factors	Measuring instrument	Unit
Humidity	Hygrometer	%
Temperature	Thermometer	°C
Atmospheric pressure	Barometer	mmHg
Solar radiation	Pyranometer	W / m²
Pluvial precipitation	Rain gauge	mm
Wind direction	Wind vane	°Grade
Wind speed	Anemometer	m/seg

Table 1. Climatic factors and their measurement
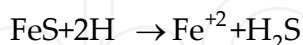
2. Chemistry of sulphidic corrosion

H₂S is a weak, reducing acid, soluble in water with a ionic dissociation:
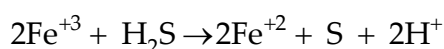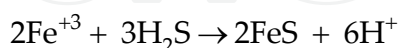
$$H_2S \leftrightarrow H^+ + HS^- \leftrightarrow 2H^+ + S^{2-}$$

H_2S attacks steel:

$$Fe + H_2S \rightarrow FeS + H_2$$
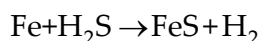
The FeS layer of steel is not stable, it is removed from the steel surface in an acidic environment, forming again H_2S, enhancing corrosion:
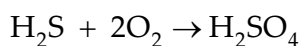
$$FeS + 2H \rightarrow Fe^{+2} + H_2S$$

H_2S reduces the Fe^{+3} present in rust: $Fe_2O_3 \cdot n\, H_2O$:

$$2Fe^{+3} + 3H_2S \rightarrow 2FeS + 6H^+$$

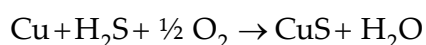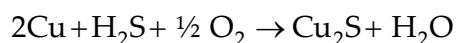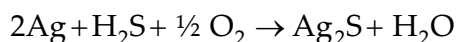$$2Fe^{+3} + H_2S \rightarrow 2Fe^{+2} + S + 2H^+$$

Other metals, applied an electronic device e.g. Ag, Cu, Sn, undergo similar reactions forming unstable metallic sulfides.

Under oxidizing conditions H_2S is converted into sulphuric acid, a strong corrosive agent:

$$H_2S + 2O_2 \rightarrow H_2SO_4$$

For silver and copper at atmospheric conditions, the general reaction are explained as follows:

$$2Ag + H_2S + \tfrac{1}{2} O_2 \rightarrow Ag_2S + H_2O$$

$$2Cu + H_2S + \tfrac{1}{2} O_2 \rightarrow Cu_2S + H_2O$$

$$Cu + H_2S + \tfrac{1}{2} O_2 \rightarrow CuS + H_2O$$

3. H2S toxicity

It is appropriate to report in the context of the present paper the toxicity of H_2S since this also affects quality of the environment and human health, central issues of modern society. H_2S gas emitted into the atmosphere from municipal sewage, industrial plants, animal farms, geothermal wells and polluted sewers and ports (M. Schorr and B. Valdez, 2005) causes inflammation of the eyes, skin burns and respiratory diseases such as rhinitis, bronchitis and pneumonia. When inhaled in small amounts, the gas produces headaches and nausea; a large amount produces paralysis. H_2S is very toxic, rapid death ensues from exposure to air containing > 1000 ppm H_2S owing to asphyxiation since it paralyses the Fe-phorphirin molecule in the human respiratory system. Lower doses cause dizziness and excitement because of damage to the central nervous system. Causes of the death of workers following the release of H_2S from sewage installations and from plant for the removal of sulphur from natural gas have been reported. (M. Schorr et al., 2006; S.E. Manahan, 1993)

4. Case studies

4.1. Corrosion behavior of silver and silver plated copper leadframes in H₂S polluted outdoor and indoor environments

In order to evaluate their corrosion behavior, metallic silver coupons and silver plated copper leadframes were displayed per triplicate during a period of 60 days between the summer months of July, August and September in three different sites. Two of the sites were inside and outside the clean room along the assembly process of a microelectronic company and the third one was on a sheltered test chamber (105 x 45 x 65cm in size of aluminum sheet 0.6mm thick material) to simulate indoor environment at uncontrolled flow of atmospheric contaminants O. Vargas et al, 2009).

The test chamber was located in a ventilated place at 10 m over the ground level. In parallel an exposition of metallic silver coupons was followed during a period of 12 and 24 months in the test chamber exposure site to study silver corrosion over a long period of time.

The exposure assembly was developed in Mexicali, Baja California, which is an urban semi-arid zone near to the Cerro Prieto geothermal power plant, the largest and oldest geothermal field in México.Prior to their exposure, the rectangular metallic silver coupons (99.95% pure and 10 x 5 x 1mm in size) were polished with silicon carbide (SiC) abrasive papers to 1200 grit, then were fine polished on a nylon cloth using a 3μm diamond suspension and finally were rinsed with deionized water and dried with nitrogen gas flow (Figure 1).

The leadframes materials, used for a wide range of microelectronics devices, consist in a copper frame with a silver electroplated die paddle and leads to provide mechanical support to the die during the assembly process and for external electrical connection. Dimension of silver plated area is 6x6 mm with a thickness of 6.5μm (Figure 2).
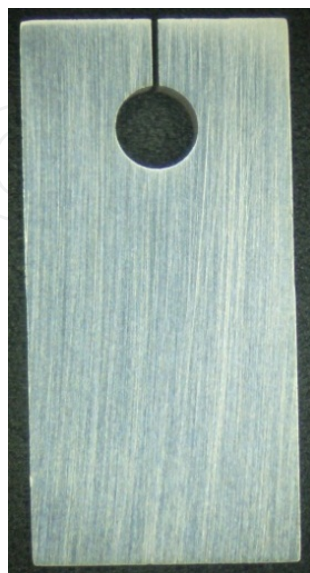

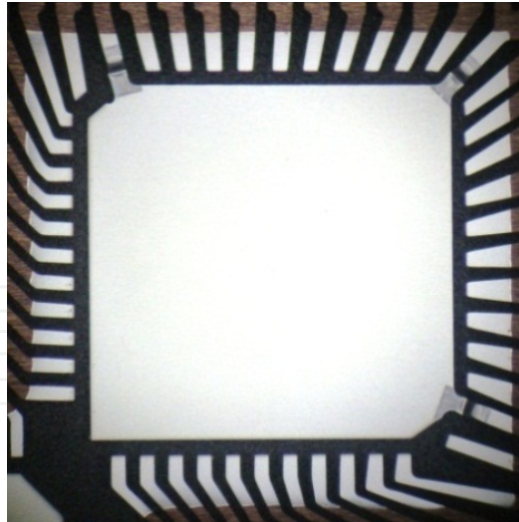
Figure 1. Metallic silver coupon

Figure 2. Silver plated on copper frame

The temperature, relative humidity (%RH) and main atmospherics contaminants were monitored and recorded during all the testing time. The morphology of samples was obtained with a JEOL JSM-6360 Scanning Electron Microscope (SEM) and the elemental microanalysis of corrosion products was performed using an EDAX brand Energy Dispersive X-ray Spectroscopy (EDS) detector attached to the SEM.

H_2S is a critical air pollutant in Mexicali. The formed thin AgS layer on the Ag surface in presence of H_2S prevents its adhesion toward the solder material thus making problematic the low resistance contact formation after the soldering process causing an increase of the device failure percentage. To determine the rate of corrosion provoked by H_2S of the silver frames used in microelectronics devices production, the Quartz Crystal Microbalance (QCM) technique was applied at controlled laboratory conditions simulating the indoor conditions. This technique allows the real time determination of the corrosion rate and the formed AgS layer average thickness. The mass gain is calculated applying the Sauerbrey equation:

$$\Delta F = -Cf \cdot \Delta m$$

with: ΔF = frequency change in Hz; Cf = sensitivity factor of the crystal in Hz/ng/cm2 ; Δm = mass change per unit area in g/cm2 . For 1 inch diameter 5 MHz quartz crystal Cf = 0.0566 Hz/ng/cm2 according to the data provided by QCM producer Maxtek (USA).

The Sauerbrey equation allows the real time determination of the mass gain and hence the corrosion rate of Ag provoked by H_2S as well as the thickness of the formed AgS layer. Family of curves in coordinates: QCM frequency - time was registered for different H_2S concentrations while the temperature was held constant and the relative humidity was monitored.

5. Corrosion process

Average values of temperature and RH during exposure of samples are shown in Table 2. These values were similar in the two sites inside the assembly process of the plant and were more aggressive in the test chamber used to simulate indoor conditions.

Atmospheric corrosion frequently occurs in the presence of a thin moisture layer that forms on the metal under certain environmental conditions. The layer may vary from monomolecular thickness to clearly visible water films. Above the critical value of 50% RH at room temperature, the metal is covered by physical adsorption with more than 3 molecular water monolayers (Table 3). This aqueous layer acts as an electrolyte and allows the incorporation of atmospheric contaminants. The critical RH for different metals in sulfur rich environments has been reported to be between 50 and 90%. (P. Marcus, 2002)

The time of wetness (TOW) is the period of time during which, due to the atmospheric conditions, is formed the moisture layer on the surface of metal and the corrosion process can occurs. When relative humidity raises the 90% and temperature is $0° \leq t \leq 25°C$ the dew point is reached and the humidity surface layer on metal becomes thicker. (ISO 9223, 1992)

According the RH registered data and temperature during the exposure, the three exposure sites presented the conditions for atmospheric corrosion of metallic silver coupons and silver plated copper frames.

Exposure Site	Temperature (°C)		Relative humidity (%)	
	Min	Max	Min	Max
Inside clean room	19.44	27.83	32.7	64.2
Outside clean room	19.16	27.33	36.5	65.3
Test chamber	24.36	46.46	10.83	89.9

Table 2. Temperature and relative humidity values during the exposition time

RH%	Water monolayers
90	8 on Ag
80	5-10
60	2-5
40	1.5-2
20	1

Table 3. Approximate number of water monolayers on different metals versus relative humidity

During the exposure time hydrogen sulfide (H₂S) was present, because the activities of vapor exploitation at Cerro Prieto geothermal power plant. When the geothermal fluid is processed to produce electricity, emissions of non-condensable gases are released into the atmosphere. The main involved gases normally are carbon dioxide (CO_2) at around 90%, followed by H₂S with only 2-3% by weight of total gases and, in lower proportion methane, ammonia, nitrogen, hydrogen, mercury and radon. H₂S is a pollutant with a characteristic odor of rotten eggs even at low concentrations, which affects the air quality, induces health damages and it is very corrosive. (H. Puente and L. Hernandez, 2005)

Anthropogenic activities in the region contribute to the increase of H₂S. An automatic air pollutant monitoring station that belongs to the California Environmental Protection Agency located in the nearest has shown an average concentration of 0.9 ppm during the

year. Other important atmospheric contaminants monitored by this station are listed in Table 3. (L. Veleva et al., 2008)

Indoor corrosivity indexes (IC2-IC3) for silver and copper has been reported for the Mexicali urban semi-arid environment in evaluations performed in a sheltered test chamber. (L. Veleva et al., 2008, ISO 11844-1, 2000)

Appearance of tarnish film on silver coupons and silver plated copper frames at the end of 60 days of exposure in the three sites can be appreciated in Figure 3 and are described in Table 5.

Contaminant	Average of Min. and Max. Concentration (ppm)
Carbon monoxide (CO)	8.39 to 12.04
Nitrogen oxide (NO)	0.029 to 0.061
Ozone (O$_3$)	0.03 to 0.10
Sulfur dioxide (SO$_2$)	0.029 to 0.086
Hydrogen sulphide (H$_2$S)	0.1 to 0.5

Table 4. Average of annual concentrations of atmospheric contaminants

Exposure Site	Silver Coupons	Silver plated over leadframe
Inside clean room	Royal blue coloration in the center and slightly surrounded by purple in the edges.	Light gold coloration surrounded by purple and blue in the edges.
Outside clean room	Gray coloration in the center and slightly surrounded by purple in the edges.	Purple and blue coloration in the center surrounded by squared shaped lines of purple and royal blue. Small stains were observed in the purple centered area.
In test chamber	Uniform gray coloration.	Gray coloration surrounded by royal blue in the edge. Several purple and dark stains were observed along the silver plated surface.

Table 5. Appearance description of samples after 60 days of exposure

The coloration of the tarnish film depends on its thickness. As the silver sulfide film becomes thicker it turns also darker. C. Yang et al, 2007)

After each exposure time, the samples were analyzed by SEM and EDS in order to observe the corrosion products morphology and chemical composition. In the case of metallic silver coupons, it was observed an uniform morphology with absence of dendrites or whiskers, and the presence of silver sulfide (Figure 4). For the case of silver plated on copper frames, they presented dendrites along the corrosion film (Figure 5). Punctual microanalysis was performed over representative areas with and without dendrites and was noted that, the

areas with dendrites presented just a little higher silver sulfide composition but in general composition in both areas was similar in the case of samples coming from inside and outside the clean room.
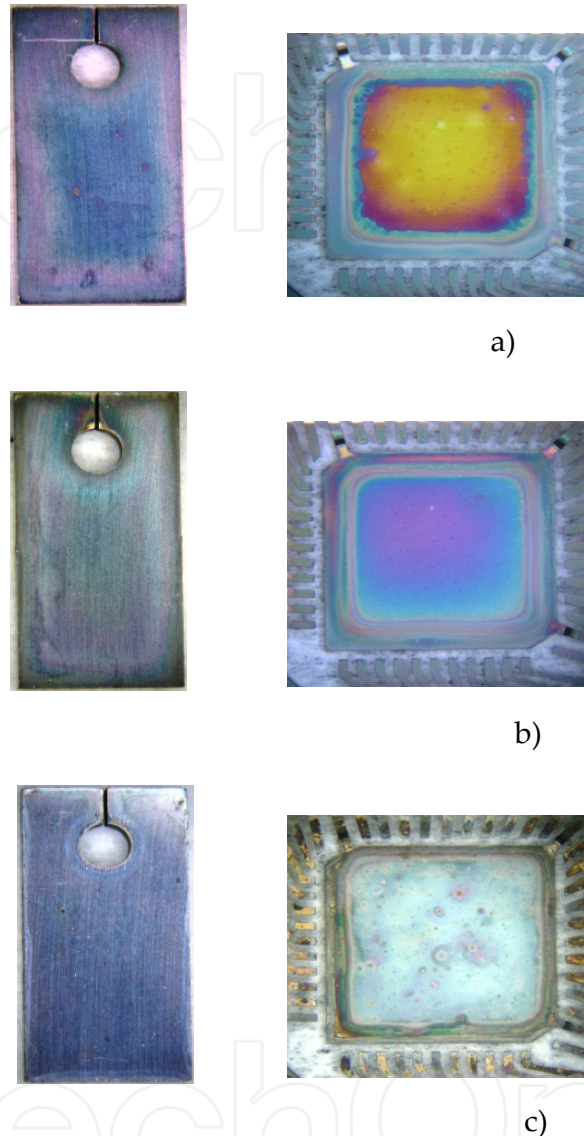

a)

b)

c)

Figure 3. Tarnishing appearance of silver coupons and silver plated copper frames, after 60 days of exposure: a) inside the clean room, b) outside the clean room and c) in test chamber.

Dendrites can cause failures in electrical equipment by short circuits when they bridge across components or between pads. Dendrite growth depends on the applied voltage, the quantity of contamination and surface moisture. This growth involves an anodic dissolution of the metal, electro migration of the ions and a subsequent cathodic deposition.

In the test chamber samples microanalysis it was detected in the corrosion film, the presence of copper sulfide in addition to silver sulfide. Figure 6 shows corrosion products of copper that comes from underneath the silver through the porosity of the plated layer. EDS microanalysis confirmed the composition of rich zones with corrosion products of copper. This could be
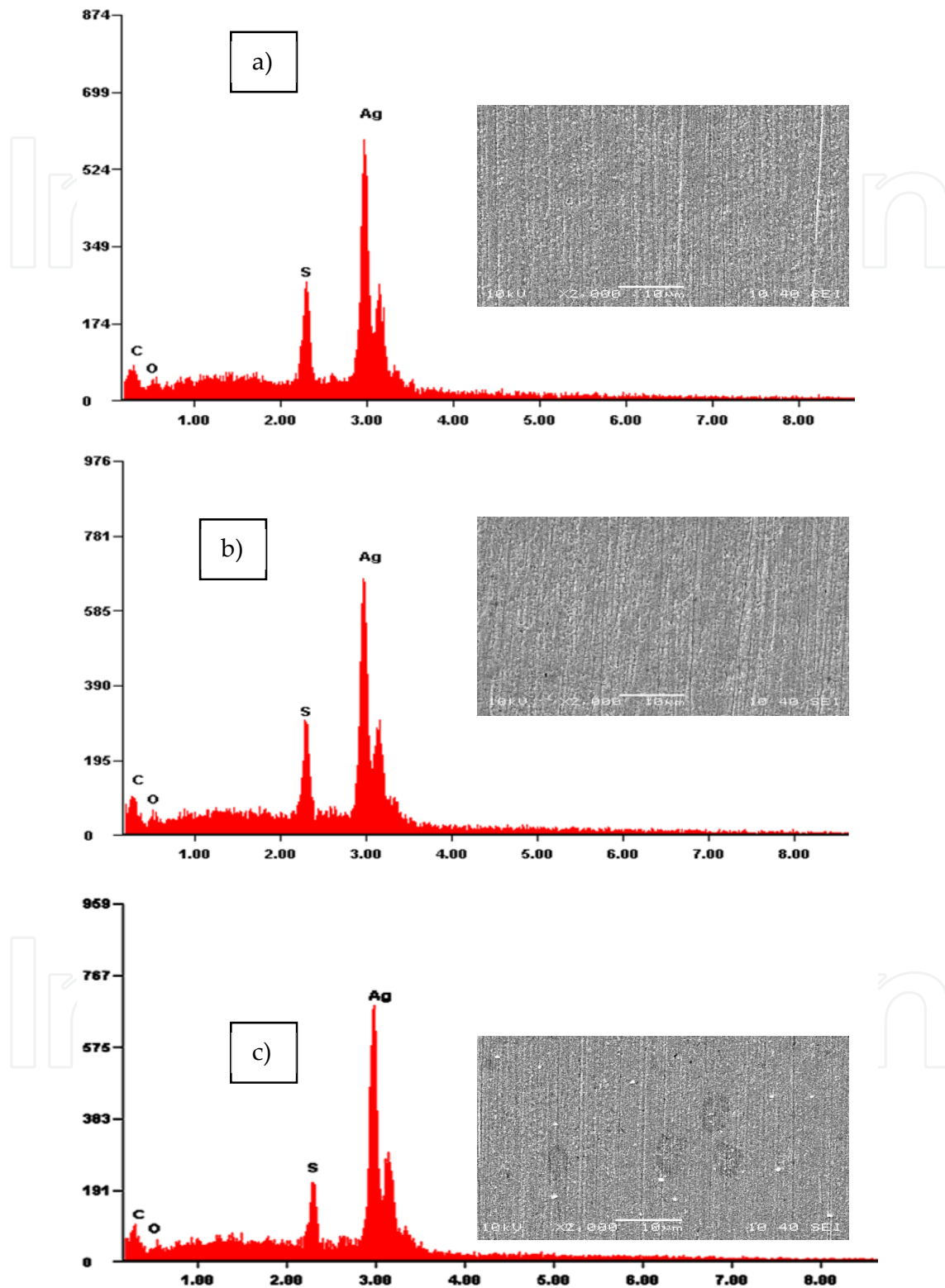
Figure 4. Results of SEM and EDS analysis of metallic silver coupons after 60 days of exposure: a) Inside clean room b) Outside clean room and c) Test chamber.
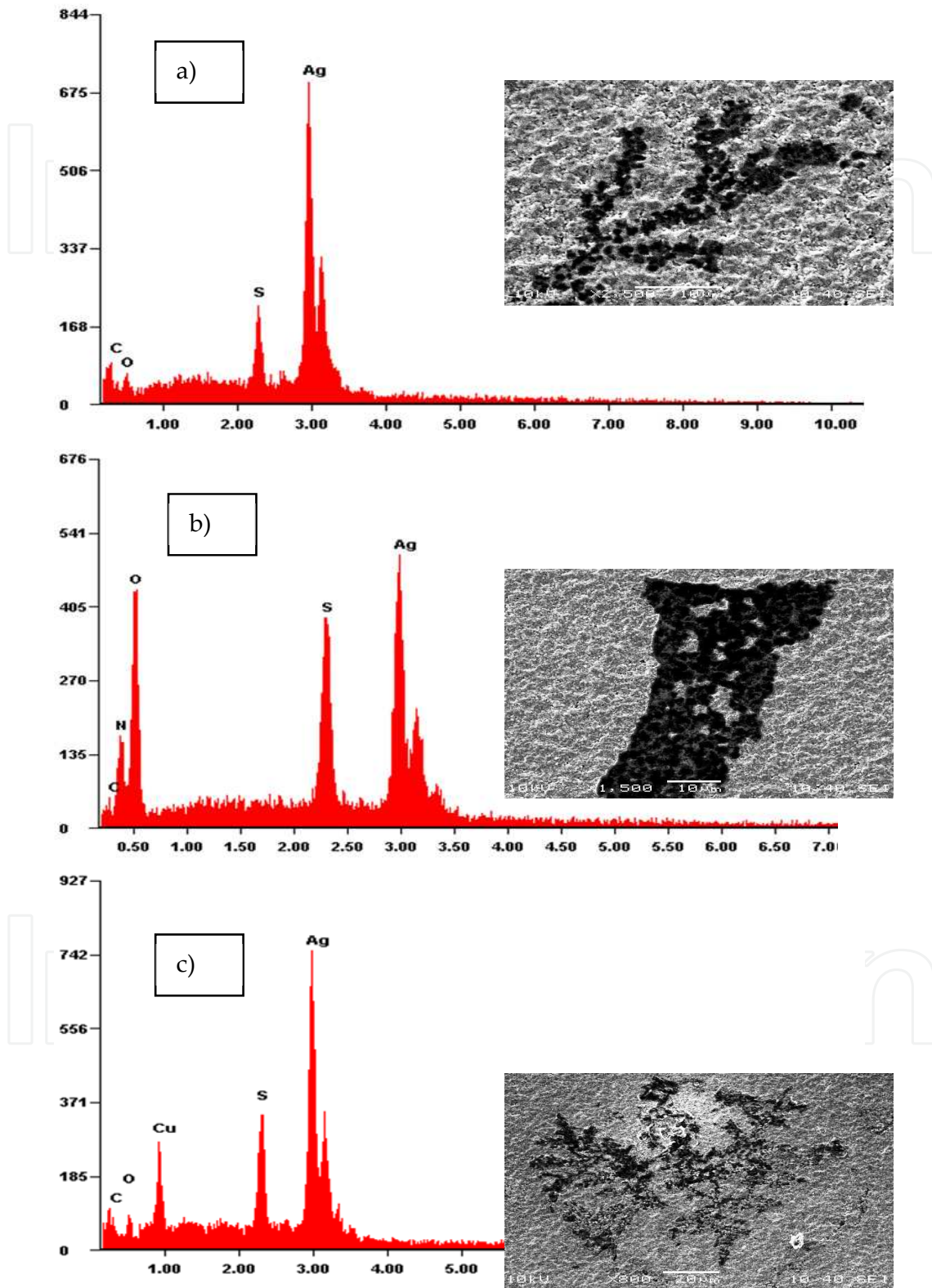
Figure 5. Results of SEM and EDS analysis of silver plated on copper frames after 60 days of exposure: a) Inside clean room b) Outside clean room and c) Test chamber.
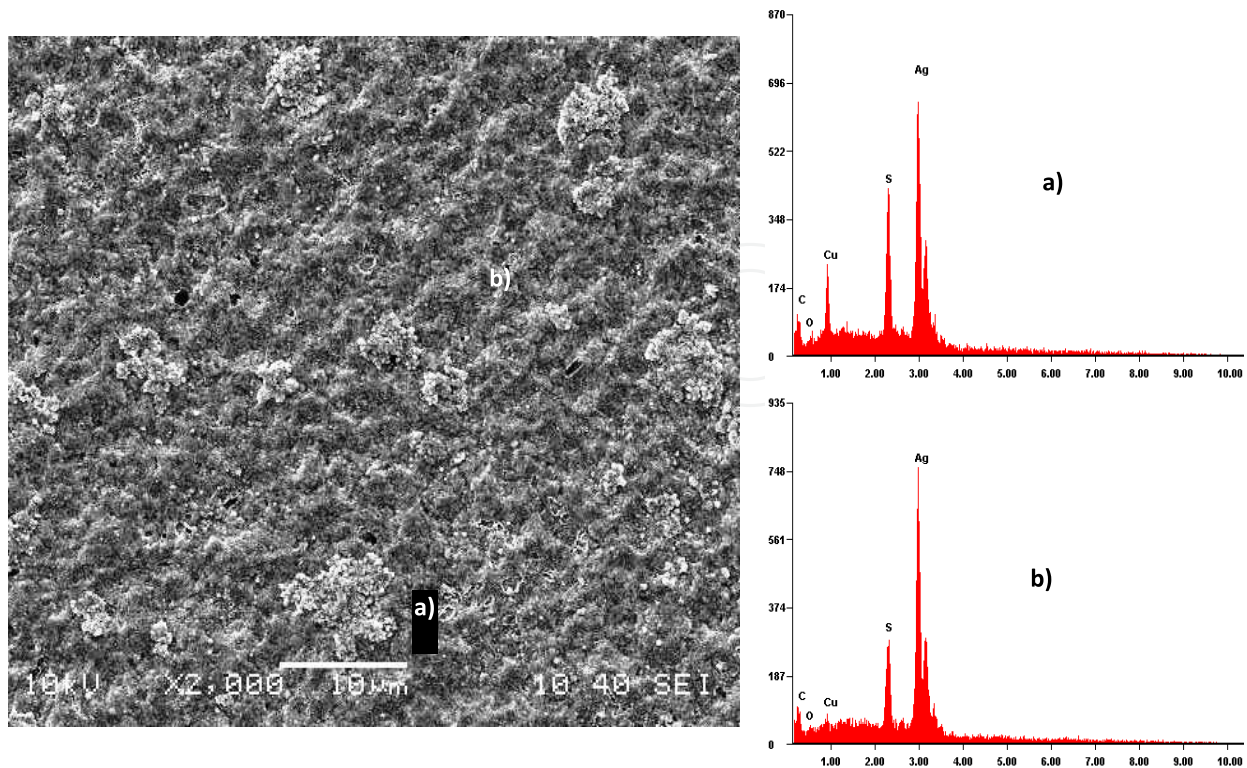
Figure 6. Corrosion products of copper in two different points (a and b) that comes from underneath the silver through the porosity of the plated layer.

happen in this site due to the higher conditions of RH and temperature. The thickness of the silver plated over copper is a very important factor in the reliability of microelectronics, when they are exposed in corrosive environments. A thick silver coating without porosity is highly recommended to avoid influences of the copper substrate on the corrosion mechanism for these materials.Regarding the exposure of metallic silver coupons to study silver corrosion over a long period of time, the presence of dendrites was observed after 12 months and after 24 months, thin branched whiskers were formed on the surface of silver (Figure 7 and 8).

Since whiskers are elongated single crystals of pure metal, they are highly conductive and can cause short circuits and arcing in the electronic and microelectronic devices. There are different shapes of whiskers, they can be straight, kinked, hooked, or forked, and some are reported to be hollow. High temperature and certain thickness of silver sulfide (Ag_2S) are factors that favor the rapid growth of whiskers. (B. Chudnovsky, 2002)

6. QCM technique application for mass gain

This QCM technique was applied for real time determination of the mass gain and hence the corrosion rate and the AgS layer average thickness. The specimens were Maxtek, 5 MHz, one inch in diameter polished quartz crystals covered by Ag on the active surface having a diameter of ½ inch. The temperature was held constant (25 °C) and the RH were monitored applying a Hygro-Thermometer Data logger during the experiment. The average registered RH value was 38.7 % with fluctuations during the experiment of +/-5.6 %.
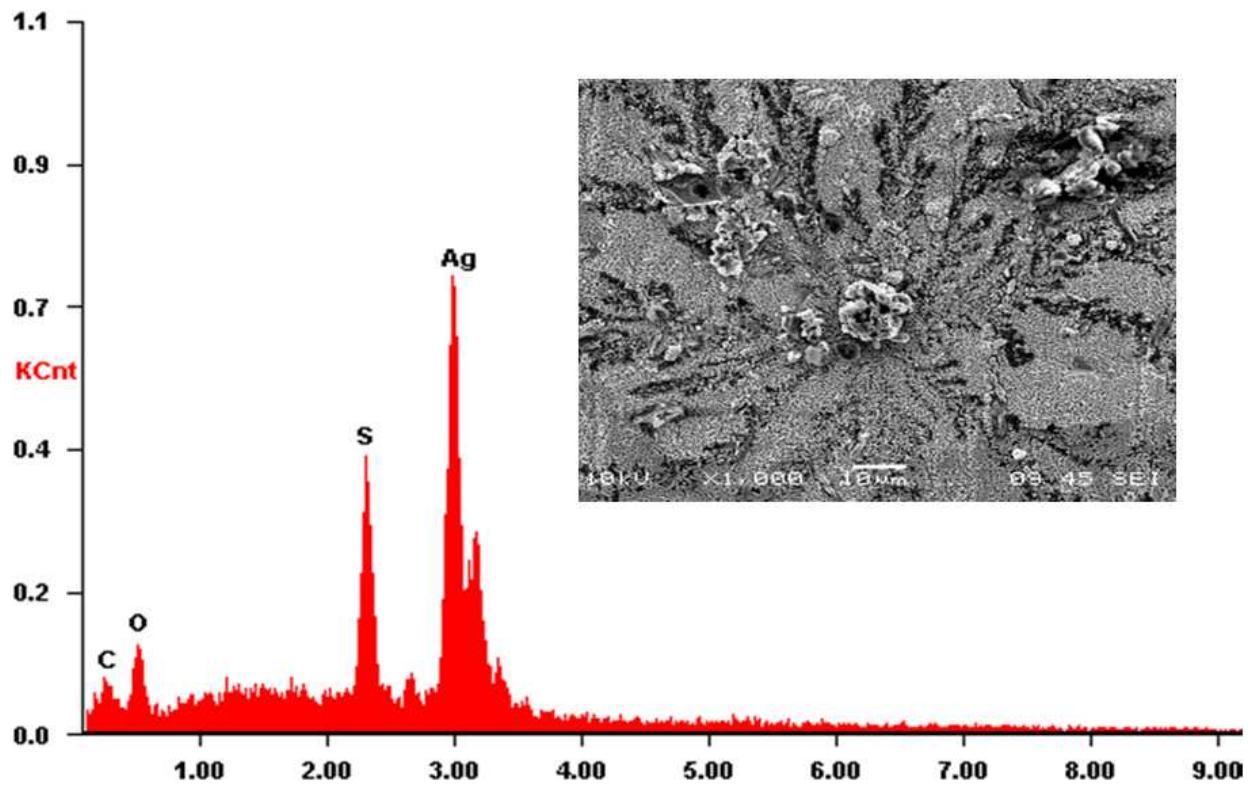
Figure 7. SEM and EDS analysis results for silver after 12 months of exposure in the test chamber.
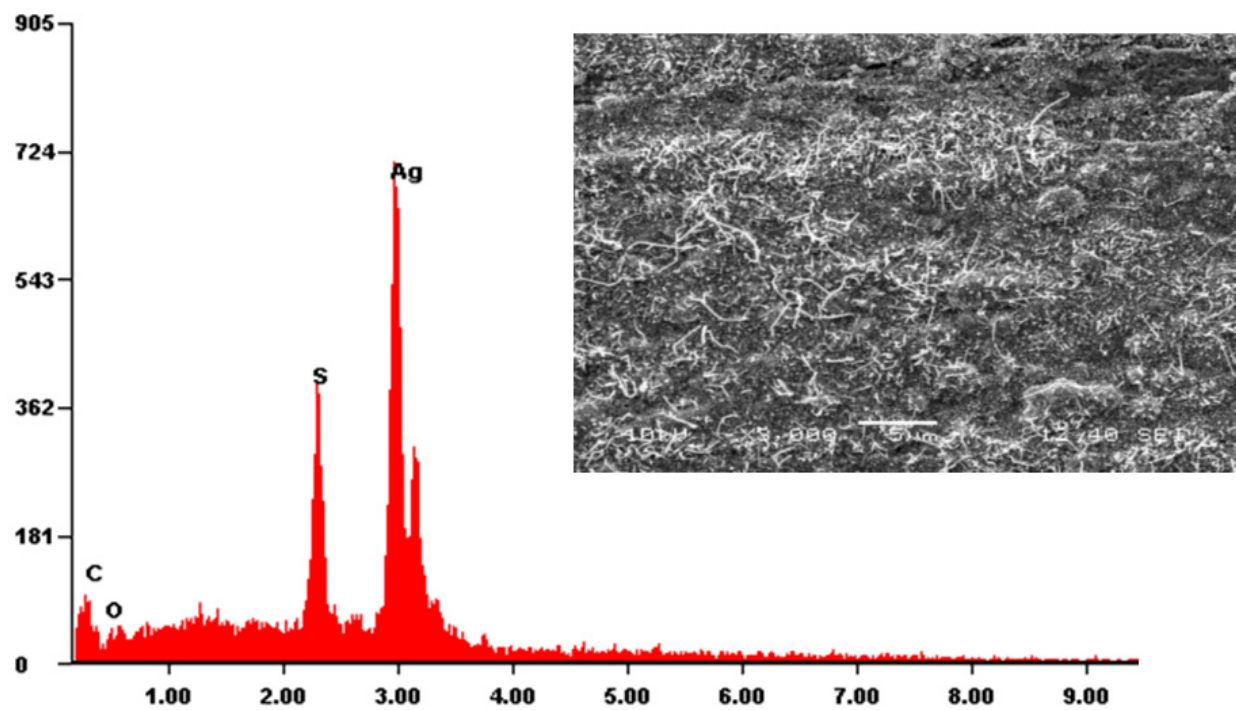

Figure 8. SEM and EDS analysis of metallic silver coupon after 24 months of exposure in the test chamber.

The controlled H_2S concentrations were achieved by additions of known volumes of H2S gas to the transparent plastic chamber containing, the covered by Ag one inch in diameter QCM quartz crystal serving as a specimen. A set of Frequency – Time curves were registered for H2S concentrations in the range 0.05 to 1 ppm which values represent the minimal and the maximal concentrations of this pollutant, while the average annual value for Mexicali was found to be 0.1 ppm (B.G. Lopez et al, 2007). The frequency – time curve for 0.5 ppm H_2S concentrations is shown on Figure 9. The change of the curve slope about the 1000th minute can be explained with the thickness increasing of the formed AgS layer, thus making difficult the further H2S gas diffusion through it in order to reach the fresh Ag surface. Using the curve shown on Figure 9 it was calculated that the rate of the AgS formation for the first 700 s represent 6.14 ng/cm.s while for the next part of the curve it falls almost twice to 3.27 ng/cm.s. The calculated rate of AgS thickness increasing is 6 nm/s, for the first part of the curve and 3.19 nm/s for the second part. These values showed that the AgS layer formation is very fast even at ambient temperature defining the need of measures to be taken for Ag surface protection.
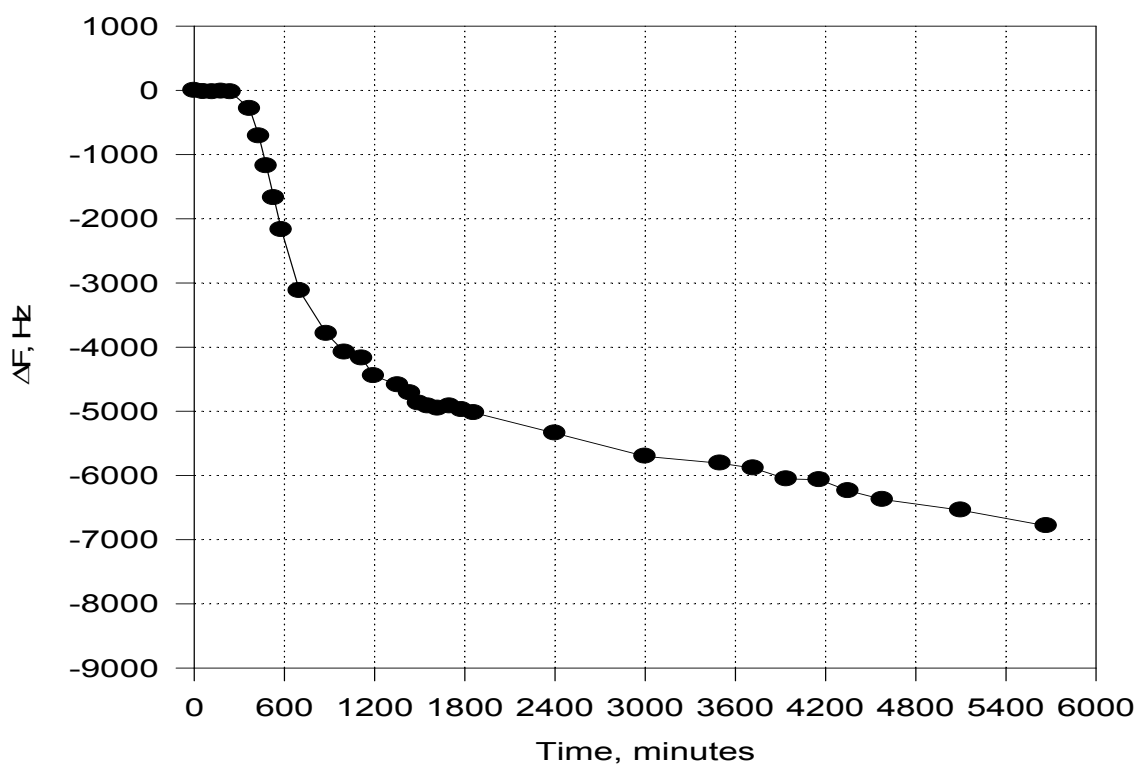

Figure 9. QCM Frequency – Time curve of active Ag surface at 25 °C, 38.7% RH and 0.5 ppm H_2S

Results of exposed silver coupons and silver plated copper frames during 60 days revealed that the indoor environment in the plant can induce silver corrosion, due to the presence of hydrogen sulfide high RH and temperature that favor the corrosion process. There was no difference between the corrosion behavior of samples inside and outside the clean room environment. In the two groups of samples a silver sulfide film was detected. Silver plated copper frame samples presented in addition, growth of dendrites in the corrosion film.

On the samples exposed in the sheltered test chamber corrosion products of copper were noted due to the porosity of the silver plated copper frame.

Regarding the silver coupons exposed in the test chamber used to study the corrosion behavior in a long period of time, growth of dendrites after 12 months and growth of whiskers after 24 months was observed.

The results obtained at the plant, where the study was carried out, indicate that it has not adequate controls to avoid the penetration of outdoor atmospheric contaminants into the assembly process, including the clean room.

7. Corrosion of copper, carbon steel, tin, nickel and silver in H₂S polluted outdoor and indoor environments

7.1. Exposure of metal specimens

Rectangular specimens with an approximate area of 6.45 cm² were prepared by polishing with silicon carbide paper to SiC 600 grit, cleaned in deionised water, degreased in ethanol, dried and stored in plastic bags and placed in a dessicator.

The specimens for corrosion tests were carbon steel, copper, tin, nickel and silver, with exposure periods of 1, 3, 6, 12 and 24 months in an upright position (ASTM G 1, G 4). An aluminum metal cabin, which allows free circulation of air, was built to simulate the conditions of indoor environments (J. Flores et al, 2006) (Figure 10), and installed 10 meters above the ground on the roof of a building. Subsequently the specimens were weighed on an analytical balance.

Figure 10. Simulation chamber for corrosion: left. Front view with installed specimens, Right. Side view with the ventilation device.

The classification of the corrosivity categories according to TOW was established following the standards ISO 9223, ISO 9224, ISO 9225, ISO 9226, ISO 1184-1 and ISO 1184-2 (Table 6). The deterioration of the metal specimens was evaluated by the gravimetric method; it was correlated with the minimum, average and maximum RH and outdoor temperature in different seasonal periods, which affect the plants indoor climate.

The electrical properties of a material are at least partially a function of the amount of humidity and pollutants present in the indoor environment, because the corrosive effect increases after moisture and ionic compounds are mixed G. Lopez, et al, 2007).

Categories ([a])	TOW ([b]) h/year
τ_1	≤10
τ_2	10 to 250
τ_3	250 to 2500
τ_4	2500 to 5500
τ_5	> 5500

Source. Environmental Deterioration of Materials, A. Moncmanova, WIT Press, 2007. [a] According to ISO 9223. [b]TOW. time of wetness; RH 80%, Temp > 0° C.

Table 6. Level categories of time of wetness in metals

7.2. Corrosion measurement

To determine the rates of indoor corrosion in the electronics industry and their relationship with outdoor conditions in a desertic region, a comparative measurement was performed exposing samples at indoor conditions and other metallic coupons in a test chamber. ASTM G50 was used to evaluate the corrosion rate in seasonal periods and in different environments (B.G. Lopez et al, 2007). The surfaces of the corroded metals were analyzed by scanning electron microscopy coupled to an electron disperse X-ray analyzer in order to characterize their morphology and chemical composition.

7.3. Gravimetric analysis

The corrosion test specimens were installed for periods of 1, 3, 6, 12 and 24 months and exposed to air pollutants from outside sources. After each exposure period the specimens were removed and weighed to obtain the weight gain due to the corrosion process.

The corrosion products morphology was observed in a optical microscope before being cleaned and reweighed to obtain the mass loss on an analytical balance to the nearest 0.0001 g. The simulation chamber was fabricated with pre-coated aluminum and had a volume of 0.1m^3 with two air inlets blinds coupled to metallic filters in order to permit the penetration of gases with the flow of air and to prevent the penetration of dust to avoid mistakes in the weightings. The Scanning Electron Microscope (SEM) was used and the chemical composition was determined by Electron Dispersive X-ray (EDS).

7.4. Numerical analysis

MATLAB a numerical computing environment and programming language, which allows easy matrix manipulation, creation of graphs of functions and data, implementation of algorithms, creation of user interfaces between operations and other program in different languages was utilized for the numerical analysis.

The analysis gives the correlation of climatic parameters, environmental and corrosion of metal specimens evaluated in the test chamber and in the companies. The graphics are of three-dimensions, which indicate areas of greater relationship between the variables of weather, air pollutants and corrosion rate, in order to determine the causes of the generation of corrosion in metallic materials used in the electronics industry and suggest methods of protection required to increase their lifetime.

The data were evaluated to determine the relationship between environmental parameters and corrosion rates. Linear regression analyses were performed to get the best fit models for experimental data and the trend of corrosion rate.

7.5. Corrosion of the metals at electronics plants conditions

Several techniques were used to obtain and organize information from the indoor environment, where mainly sulfates and chlorides were monitored and evaluated for TOW with RH levels and temperatures greater than 80% and 0 º C.

In the analysis data of RH higher than 70%, temperatures higher than 35 ºC and air pollutants such as CO, NO_X, O_3 and SO_2, in the periods that overpass the air quality standards in Mexicali, were considered (G. Lopez, 2008). In summer season the corrosion rate increased in the temperature range of 30 ˚ C to 42 ˚ C and RH levels of 35% to 65. Moreover, in the winter, with a range of temperature from 2 ˚ C to 12 º C and RH levels ranging between 35% and 70%, there was a higher incidence of water condensation on the metal surface.

The Figure 11 shows the evaluation of corrosion of copper at 2 ˚ C to 13 ˚ C and RH of 34% to 70% indicating that the corrosion rate diminishes. At temperatures of 23 ˚ C to 30 ˚ C, with RH levels of 30% and 75%, the corrosion rates increases. This methodology was applied for the corrosion behavior of the other metals tested and the results showed a very good fit in all the cases. Nevertheless, it is necessary to analyze data from several environmental monitoring stations in order to establish a map of the main pollutants behavior by season, zone, climate, economic activities, temperature and RH for at least 5 years. This map must be the most possible closer to the real conditions.

7.6. Corrosivity levels

The main sources of corrosive emissions in Mexicali are cars, fine dust from agricultural fields of an arid zone and the thermal and geothermal power plants (Valdez et al, 2006, J. Flores et al., 2003). Figures 12 and 13 show the corrosion rate values for both simulation chamber and industrial plants tests, it is clear that carbon steel is suffering an accelerated deterioration regarding to silver, copper, tin and nickel, in this order.
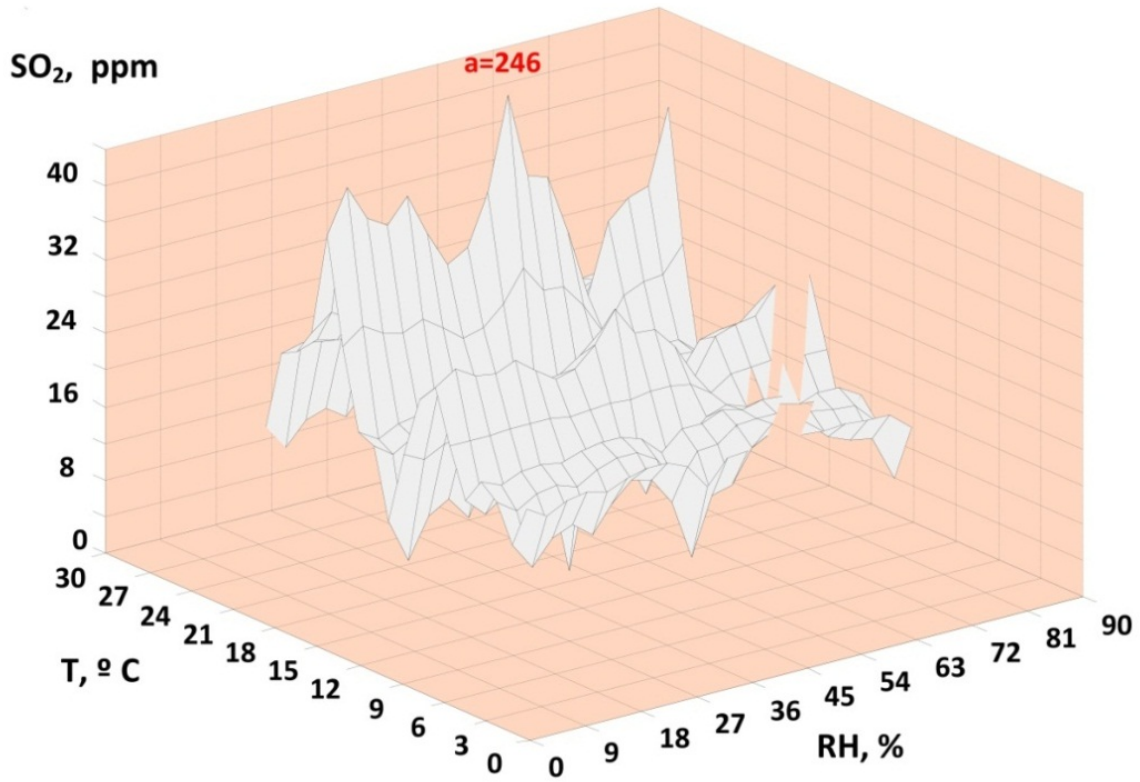
Figure 11. Correlation of temperature, RH and SO₂, a) represents, maximum corrosion rate (mg/m².year) of copper
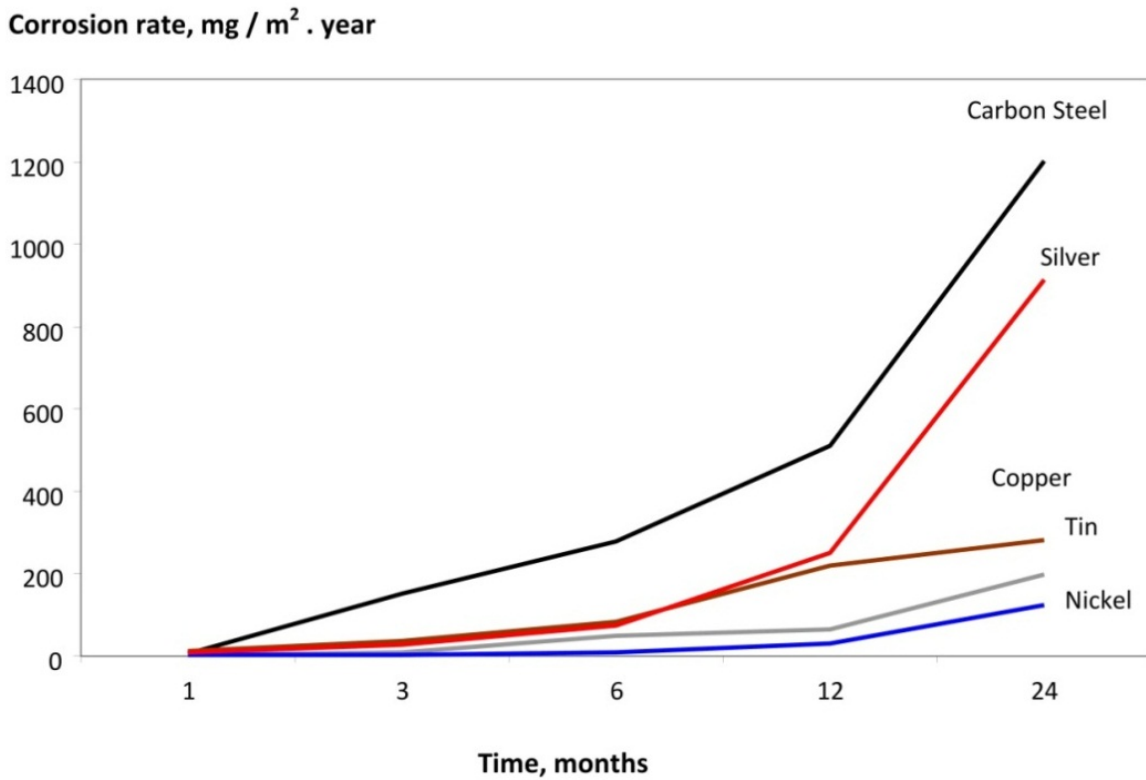

Figure 12. Corrosion rate of metals in the simulation chamber (2003 to 2005)
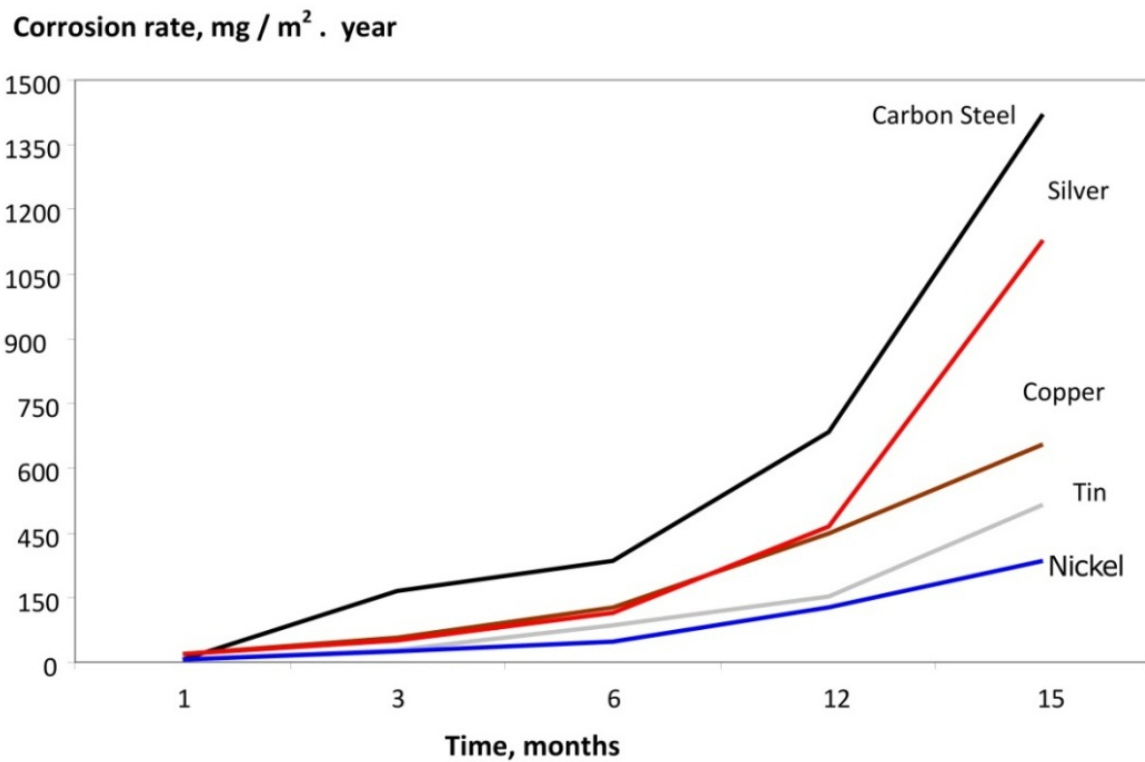
Corrosion rate, mg / m² . year

Figure 13. Corrosion rate of metals in industrial plants (2003 to 2005).

The exposure time in the chamber was 24 months and 16 months in the companies. The concentration of several atmospheric pollutants: CO, NOx, O₃ and SO₂ were monthly recorded by an automatic air pollutants monitoring station that belongs to the California Environmental Protection Agency-CALEPA network.

The electronic instruments used to monitoring air pollutants were equipped with filters to trap and detect gases and particles of air pollutants. To determine the concentration of sulfate in indoor of industrial plants the sulfatation plate technique was used inside industrial plants (ASTM G 91). Sulfates penetrate the plant environment by air currents, cracks, access doors and air conditioning systems that do not have special filters.

The exposure periods at indoor industrial plants conditions were determined according to the aggressiveness of the indoor environment, by day, week and month, seasonal and annual period. The wet candle method is applied to measure the speed of atmospheric deposition of chloride salts in a given area per unit time (ASTM G 140).

The information obtained from the deposition of chloride is used to classify the level of corrosivity of a specific area, such as conditions in the electronics industry. The standard is based in the ISO 9223 with reference to ASTM standards G 91 and G 140, measured in mg/m².year. This test is done because the levels of chlorides increase indoor atmospheric corrosion and is an important factor of corrosion phenomena. Sometimes the addition of chloride ions to metallic surfaces generate and increase the corrosion intensity, as in the case of copper and zinc, where these salts do not dissolve easily during corrosion in some areas of the metal causing pitting (Moncmanova et al, 2007).

In the beginning the corrosion rates were low for all the metals, with a variation of the RH from 40% to 60% and temperatures ranging from 25 ºC to 35 ºC (Zlatev et al, 2009). The surface spots presents on the surfaces of carbon steel, copper and silver were indicatives of an incipient corrosion process on these metals.

After 100 days exposure the weather turns warm and the temperature increases in the range from 30 ºC to 40 ºC and RH lower than 70%, the corrosion of copper, carbon steel and silver was pronounced, while nickel remains unaffected (G. Lopez et al, 2009).

The corrosion rate of all the metals was more severe after six month exposure. Ni and Sn show the best behavior compared with carbon steel, copper and silver which are covered with uniform layers of corrosion products. In this period the RH varied between 50% and 75 % and the average range of temperature was 30 ºC to 40 ºC and all the pollutants measured were higher than the permissible concentrations by the air quality standards. After one year the corrosion rate increases rapidly at approximately twice the value of to the previous period.

For specimens exposed during two years, the corrosion rate of copper coupons increases exponentially in a clear activated process. In general, all the metals showed corrosion damage and deterioration of their surfaces by the corrosion process effect. It was confirmed that SO_2 and NO_x were the predominant gaseous air pollutants. Fig. 14 shows the microstructures of corrosion products formed on the copper surface observing the presence of aggregates and pitting; the EDX analysis indicates that the main corrosion product is copper sulphide. Portable hydrogen sulphide monitors were used to measure the concentration of this gas at indoor conditions in different electronics industrial plants and in the interior of the simulation chamber. The H_2S was detected at indoor conditions with concentrations close to 1 ppm and an average value of 0.1 ppm (B.G. Lopez et al, 2007).
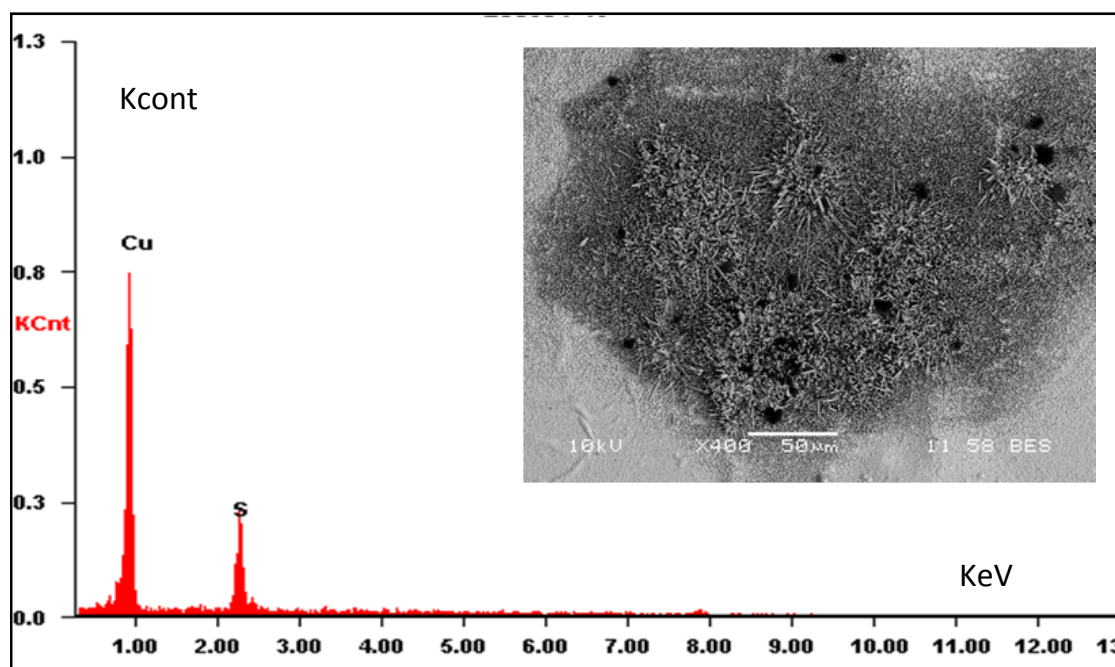

Figure 14. SEM microphotograph of copper after 6 months of exposure at indoors and EDX analysis.

8. Conclusions

All the metals tested used in the manufacturing of electronic devices, were deteriorated by atmospheric corrosion after two years exposure. Sulphide was the main component in the corrosion product layer, due the presence of SO_2 and H_2S produce by human activities and the geothermal field of Cerro Prieto, which promotes the contamination of indoor places.

Carbon steel, copper, nickel, silver and tin exposed to air pollutants reveal that an increase on their concentrations at outdoor conditions has a critical impact on the indoor corrosion process. Long exposure periods with RH values higher than 75 %, and concentrations of pollutants that exceeds those levels established in the regulations, promotes the corrosion of the metals evaluated.

In a descendent order, the most susceptible metals were carbon steel, copper, silver, tin and nickel. The use of 3D plots for multivariable systems generated by the MathLab software represents a useful tool for the monitoring of corrosion at indoor plants conditions. The 3D plots indicate the presence of pollutants in different levels of RH and temperature, and corrosion rates of the metallic probes. These plots and the Mathlab software constitute a very useful tool to study these phenomena.

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