The corrosion of silver in indoor conditions of an assembly process in the microelectronics industry

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Abstract

Purpose – The purpose of this paper is to evaluate the corrosion of silver due to hydrogen sulphide pollutant in indoor conditions at a microelectronics plant located in Mexicali, Baja California, a semi-arid zone in the northwest of Mexico.

Design/methodology/approach – Silver coupons and silver plated on to copper-lead frames are exposed in the assembly process building of a microelectronics company during a period of 60 days and also in a sheltered test chamber that simulates indoor conditions with ambient concentrations of atmospheric pollutants, temperature and relative humidity (rH). Other exposures are made in the test chamber to study the corrosion behaviour of silver coupons over a duration of 24 months. The corrosion products were analysed using the Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDS). Corrosion rates were measured by Quartz Crystal Microbalance (QCM) under laboratory-controlled conditions.

Findings – The presence of silver sulphide corrosion products, dendrites and whiskers is observed on the exposed samples using SEM and EDS analysis.

Practical implications – The paper is designed to establish whether the company, where the exposure is taking place, constituted an indoor environment with outdoor hydrogen sulphide pollutant in sufficient concentration to induce silver corrosion.

Originality/value – The methodology used in this work can be applied to study the indoor corrosion behaviour of other metals, which will be of interest to the microelectronics industry.

Keywords Corrosion environments, Silver, Copper, Electronic engineering, Assembly plants, Mexico

Paper type Research paper

Introduction

The electronics industry applies materials with adequate electrical and corrosion resistance properties for the manufacturing of the microelectronic devices, such as, silver and copper. Their main applications are as high thermal conductive die attach paste, that have silver flakes as conductive filler material, silver plated over copper frames, Sn-Ag and Sn-Cu alloys for solder paste used in the Surface Mount Technology (SMT) process, for conductive internal copper layers in printed circuit boards, for copper wire bonding, and more.

Corrosion in microelectronics modules 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.

The plastic packages are widely used because of their size, cost and manufacturability advantages but, compared to hermetic package systems like ceramics they are non-hermetic, due to the polymeric materials that permit the permeation of moisture and corrosive gases. This result in the appearance of other problems associated with corrosion of the internal components. Therefore, advances in the microelectronics technology have promoted the development of devices with smaller and thinner components. The exposure of these devices to environments where temperature, humidity and atmospheric pollutants such as chlorides, NO_x, SO_x, COS and hydrogen sulphide (H_2S), which are not completely controlled, can favour atmospheric corrosion of their metallic components. Small quantities of corrosion products are sufficient to induce reliability issues and even catastrophic failures in the microelectronic devices, due to the formation of insulating layers of corrosion films.

In order to minimize the risk of corrosion failure, it is important to be aware of corrosion risk during the design stage, reliability evaluations and qualifications, assembly processes, storage, shipping, and in the final use of the microelectronic devices (Roberge, 2000; Tullmin and Roberge, 1995).

Atmospheric contaminants such as H_2S and carbonyl sulphide (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, the main reduced sulphur constituent at neutral pH. When silver is exposed in an

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environment containing a minimum concentration of these contaminants (<1ppm), the corrosion product formed is silver sulphide (Ag_2S). A similar process of sulphidation occurs when the exposed metal is copper that reacts with H_2S producing copper sulphide (Cu_2S) (Graedel, 1992; Rice *et al.*, 1981).

Several studies have been done on the indoor corrosion of silver and copper revealing that silver sulphide is the main corrosion product on silver that had been exposed indoors (Yang *et al.*, 2007; Watanabe *et al.*, 2006). The corrosion films formed on copper and silver can act as insulating layer on the contact surfaces, causing electrical failures of 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 alloys, where the principal corrosion product is Cu_2S or in alloys of silver with palladium, where the corrosion product is Ag_2S.

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 (with a more protective corrosion layer) exhibits parabolic behaviour (Veleva *et al.*, 2008).

The structure of the corrosion film on silver tends not 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 absorbed moisture capable of dissolving the metal, and ions then are redistributed by electro migration in the presence of an electric field. When a thick layer of corrosion products is present, thin filaments project at a right angles to the surface; these are known as "whiskers", and they begin to grow spontaneously even at room temperature and without an applied electric field. Several cases have been reported where tin whiskers have caused failures (Chudnovsky *et al.*, 2002).

The objective of this work was the study of silver corrosion under indoor conditions in a company dedicated to the assembly and functional testing of microelectronic devices. To achieve this, silver coupons and silver plated over lead frames was exposed in two sites of the assembly process. Moreover, samples of the same materials were exposed in a test chamber that simulates indoor conditions.

Experimental procedure

Metallic silver coupons and silver plated copper lead frames were displayed in triplicate for 60 days during the months of July, August and September at three different sites. Two of the sites were inside and outside the clean room of the assembly process at the microelectronics company and the third one was in a sheltered test chamber (105 × 45 × 65 cm in size, fabricated from aluminium sheet 0.6 mm thick) to simulate the indoor environment with an uncontrolled flow of ambient atmospheric contaminants (Flores *et al.*, 2003). The test chamber was located in a ventilated place 10 m above the ground floor level (Figure 1).

In parallel, an exposition of metallic silver coupons was tracked over a period of 12 and 24 months in the test chamber exposure location, to study silver corrosion over longer durations.

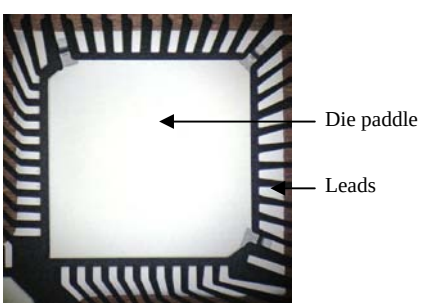
Figure 1 Rain-sheltered test chamber

The company where the exposure was developed is located 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 per cent pure and 10 × 5 × 1 mm in size) were polished with silicon carbide (SiC) abrasive papers to 1,200 grit, then fine polished on a nylon cloth using a 3μm diamond suspension and finally were rinsed with deionised water and dried with a nitrogen gas flow. The lead frames materials, used for a wide range of microelectronic devices, consist of 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 (Figure 2). The dimensions of the silver plated area were 6 × 6 mm with a thickness of 6.5 μm.

The temperature, rH (per cent) and main atmospherics contaminants were monitored and recorded during the entire testing period. Post-exposure sample morphology was evaluated using a JEOL JSM-6360 Scanning Electron

Figure 2 Silver-plated on copper frame



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.

Quartz cristal microbalance

H_2S is a crucial air pollutant in Mexicali. The thin Ag_2S layer formed on the Ag surface in presence of H_2S prevents the adhesion of the solder material, thus making it problematic to obtain a low resistance contact after the soldering process, thereby increasing the proportion of device failures. To determine the rate of corrosion provoked by H_2S on the silver frames used in microelectronic device production, the QCM technique was applied under controlled laboratory conditions simulating the indoor conditions. This technique allows real time determination of the corrosion rate and the formed Ag_2S layer average thickness. The mass gain is calculated applying the Sauerbrey equation:

$$\Delta F = -C_f \Delta m$$

where: ΔF = frequency change in Hz; C_f = sensitivity factor of the crystal in Hz/ng/cm^2; Δm = mass change per unit area in g/cm^2. For 1 inch diameter 5 MHz quartz crystal $C_f = 0.0566$ Hz/ng/cm^2 according to the data provided by QCM producer Maxtek (USA).

The Sauerbrey equation allows 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 Ag_2S layer. A family of curves with the coordinates: QCM frequency-time was registered for different H_2S concentrations while the temperature was held constant and the rH was monitored.

Results

Average values of temperature and rH during exposure of samples are shown in Table I. The outside clean room presents relatively higher rH values than those obtained inside the clean room atmosphere, but in both cases the maximum values (64.2 per cent – 65.3 per cent, at temperature below 20°C) create a possibility for monolayers of water to exist on the metal surface. The test chamber represented more aggressive conditions (rH average of 89.9 per cent at 24.4°C), and acts as a more accelerated test for the simulation of 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 per cent RH at room temperature, the metal is covered by physical adsorption with more than three water monolayers (Table II). It has been estimated that at 90 per cent rH eight monolayers of water are deposited on silver surface. This aqueous layer acts as an electrolyte and allows the incorporation of atmospheric contaminants. The critical rH for different metals in sulphur rich environments has been reported to be between 50 and 90 per cent (Marcus and Oudar, 2002; Dubus *et al.*, 2003).

The time of wetness (TOW) is the period of time during which, due to the atmospheric conditions, the moisture layer is formed on the surface of the metal and the corrosion process occurs. When rH (per cent) rises up to 90 per cent and temperature is $0° \leq t \leq 25$°C, the dew point can be reached and the humidity layer on the surface of the metal becomes thicker (Veleva and Kane, 2003).

According the registered data of rH and temperature during the exposure, the three exposure sites achieved the conditions for atmospheric corrosion of metallic silver coupons and silver plated copper lead frames. During the exposure time, hydrogen sulphide (H_2S) was present, due to the activities of vapour emissions from the Cerro Prieto geothermal power plant. When the geothermal fluid is being processed to produce electricity, emissions of non-condensable gases are released into the atmosphere. The main common gases are carbon dioxide (CO_2) at around 90 per cent, followed by H_2S with only 2-3 per cent by weight of total gases and, in lower proportion, methane, ammonia, nitrogen, hydrogen and radon. Hydrogen sulphide, a corrosive gas, is the one of most concern because of its characteristic odour of rotten eggs even at low concentrations, which affects the air quality and induces health damage (Puente and Hernández, 2005).

Anthropogenic activities in the region contribute to the increase of H_2S air concentration (Valdez *et al.*, 2009). An automatic air pollutant monitoring station, which belongs to the California Environmental Protection Agency, has measured a maximum average concentration of 1.5 ppm during the year. Other atmospheric contaminants monitored by this station are listed in Table III (Veleva *et al.*, 2008).

The concentration of H_2S in the tested electronics plant atmosphere was 0.9 ppm and in some areas of the assembly process it reaches 1.5 ppm, due to the operation of ovens used for the cure of epoxy resins as part of the manufacturing

Table I Temperature and rH values during the exposition time

Exposure site	Temperature (°C) Min	Max	Relative humidity (per cent) Min	Max
Inside clean room	19.44	27.83	32.7	64.2
Outside clean room	19.16	27.33	36.5	65.3
Indoor sheltered chamber	24.36	46.46	10.83	89.9

Table II Approximate number of water monolayers on different metals versus rH

rH (%)	Number of water monolayers
80	5-10
60	2-5
40	1.5-2
20	1

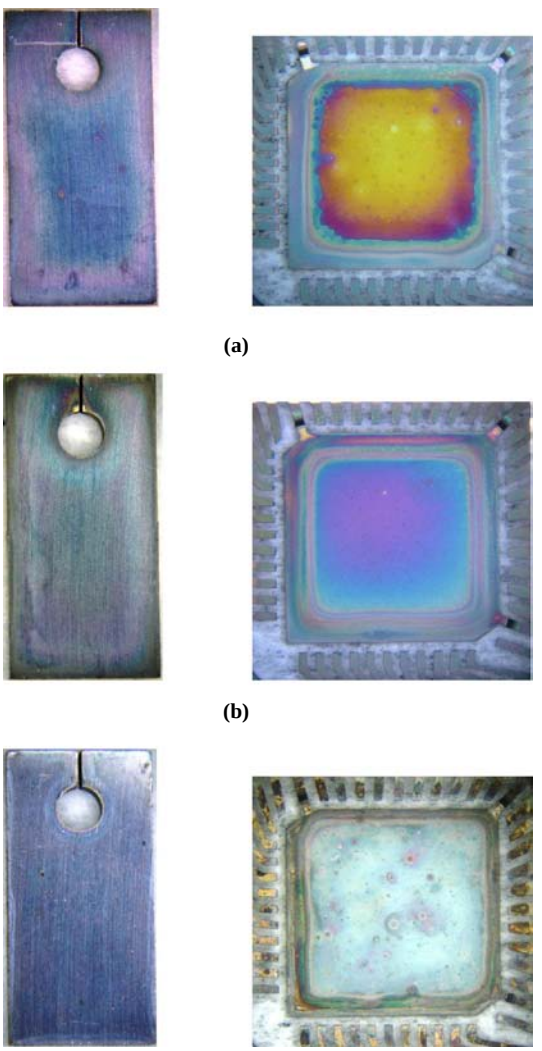
Table III Average of annual concentrations of atmospheric contaminants

Contaminant	Concentration (ppm) Min	Max
Carbon monoxide (CO)	8.39	12.04
Nitrogen oxide (NO)	0.029	0.061
Ozone (O_3)	0.03	0.10
Sulfur dioxide (SO_2)	0.029	0.086
Hydrogen sulfide (H_2S)	0.1	1.5

process. Indoor corrosivity indexes (IC2-IC3) for silver and copper have been reported for the Mexicali urban semi-arid environment in evaluations performed using the sheltered test chamber (Veleva *et al.*, 2008).

The appearance of tarnish films on the silver coupons and silver plated copper frames at the end of 60 days of exposure in the three sites is presented in Figure 3 and are described in Table IV. It has been reported that the colour of the silver tarnish film depends on its thickness and as the composition of the silver sulphide film, and as the (corrosion product) film becomes thicker, the tarnish becomes darker (Yang *et al.*, 2007).

Figure 3 Appearance of tarnish on 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



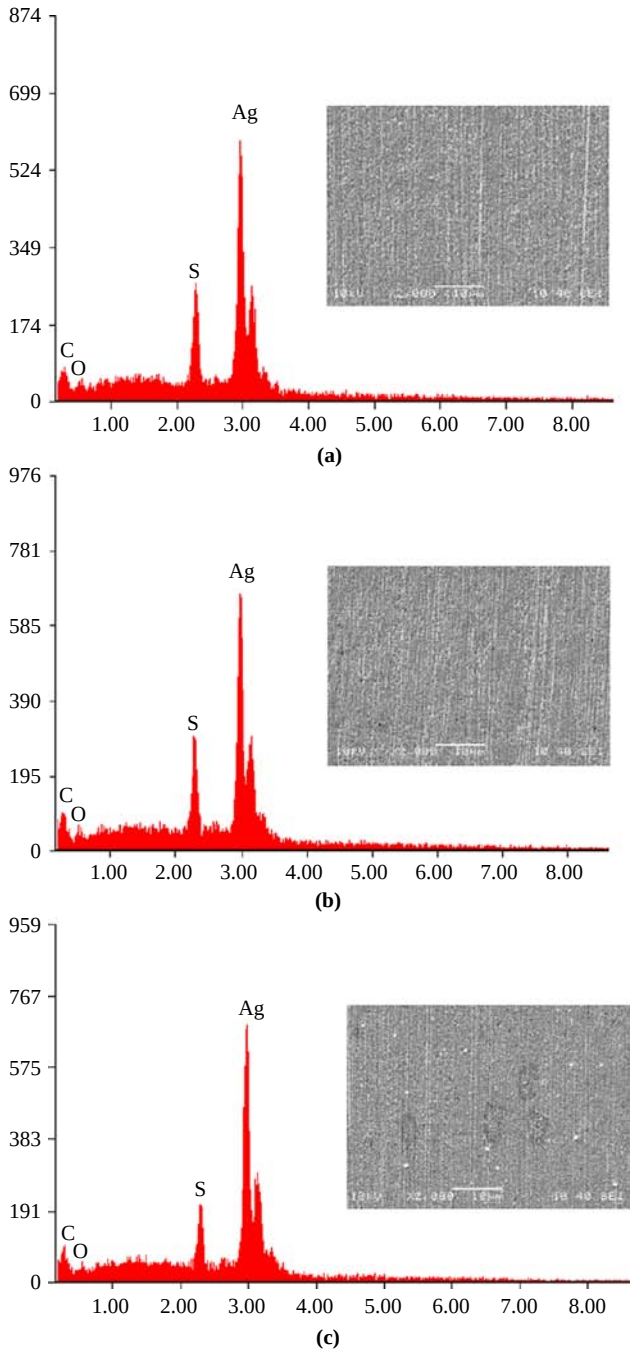
After each exposure time, the samples were SEM and EDS analysed to characterize the morphology and composition of the corrosion films formed on the samples surfaces exposed during 60 days in each tested environment. The tarnished corrosion films on the silver coupons showed a uniform morphology and the elemental microanalysis confirmed the presence of silver sulphide (Figure 4). The silver plated on copper lead frames exhibited dendrites within the corrosion film (Figure 5). The EDS microanalysis, performed in representative areas with and without dendrites, suggested that areas with dendrites have a quite higher amount of silver sulphide. In general, the composition of the corrosion film in both areas was similar and repetitive for samples exposed inside and outside of the clean room. It is reported that dendrites can cause failures in electrical equipment by causing short circuits when they bridge across components or between pads. Dendrite growth is dependent upon the applied voltage, the quantity of contamination and surface moisture. Their initiation involves an anodic oxidation of the metal, electro migration of its ions and subsequent cathodic deposition. Failures have been known to occur in less than 30 min, due to the growth of dendrites (Chudnovsky *et al.*, 2002). Moreover, the EDS elemental microanalysis results revealed also the presence of copper sulphide as corrosion product formed on silver plated on copper lead frames after their exposure in indoor chamber for 60 days (Figure 5(c)). Figure 6 shows a representative area of this sample where corrosion products of copper come to the surface through the pores of the plated layer. This could be happen at this host site due to the conditions of higher rH and temperature. The thickness and porosity of the silver plate over copper are very important factors in the reliability of microelectronics, when exposed in humid environments are aggressive for both metals. A thick silver coating without porosity is highly recommended to avoid the galvanic bimetallic corrosion of the typical copper substrate – silver coating. Through the pores of the silver coating, the copper can act as the anode (with more negative potential than silver) and, due to this fact, it corrodes when the indoor environment is humid.

The silver samples studied for longer durations showed the presence of dendrites after 12 months of exposure (Figure 7) and thin branched whiskers were formed on the surface of silver after 24 months (Figure 8). Because the 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. Different shapes of whiskers exist: straight, kinked, hooked, or forked; some are

Table IV Appearance description of samples after 60 days of exposure

Exposure site	Silver coupons	Silver plated over lead frame
Inside clean room	Royal blue coloration in the centre 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 centre and slightly surrounded by purple in the edges	Purple and blue coloration in the centre surrounded by squared shaped lines of purple and royal blue. Small stains were observed in the purple centred 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

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) sheltered test chamber

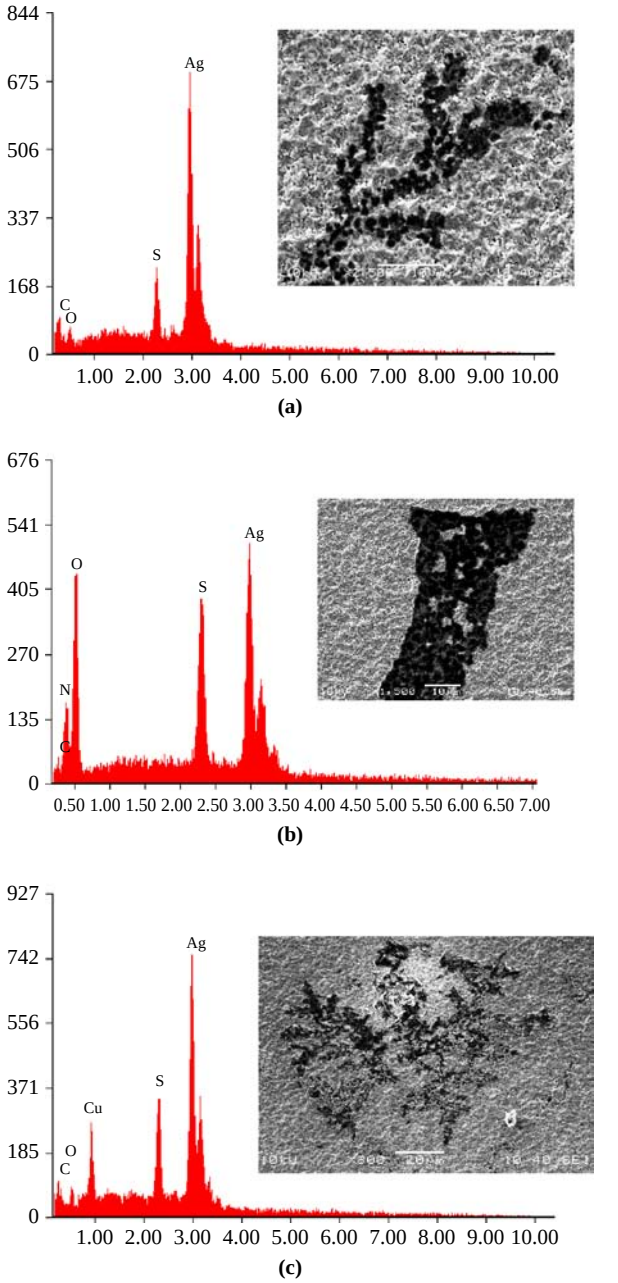


reported to be hollow. High temperature and certain thicknesses of silver sulphide film (Ag_2S) are factors that favour the rapid growth of whiskers (Chudnovsky *et al.*, 2002).

QCM technique application

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, and one inch in diameter, polished quartz crystals covered by Ag on the active surface having a diameter of $1/2\frac{1}{2}$ inch.

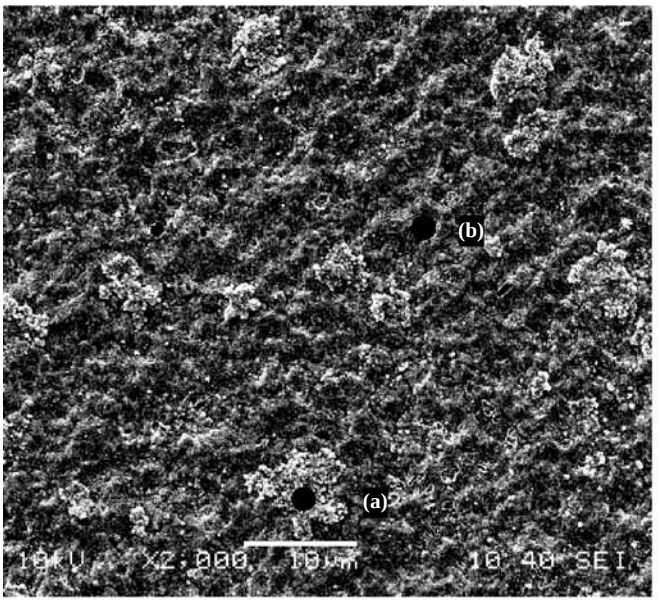
Figure 5 Results of SEM and EDS analysis of silver-plated on copper frames after 60 days of exposure: (a) inside clean room (b) outside clean room and (c) sheltered test chamber



The temperature was held constant at 25°C and the rH (per cent) was monitored applying EasyView 25 Hygro-Thermometer Datalogger (Extech, Taiwan) during the experiment. The average registered rH value was 38.7 per cent with fluctuations of ± 5.6 per cent during the experiment.

The controlled H_2S concentrations were achieved by additions of known volumes of H_2S gas to the transparent plastic chamber containing the Ag coated, one inch in diameter QCM quartz crystal serving as a specimen. A set of frequency – time curves were developed for H_2S concentrations in the range from 0.05 to 1 ppm, which represents the minimal and the maximal concentrations of

Figure 6 SEM and EDS analysis in area with corrosion products of copper (a,b), in silver plated on copper lead frame sample after 60 days of exposure in sheltered test chamber



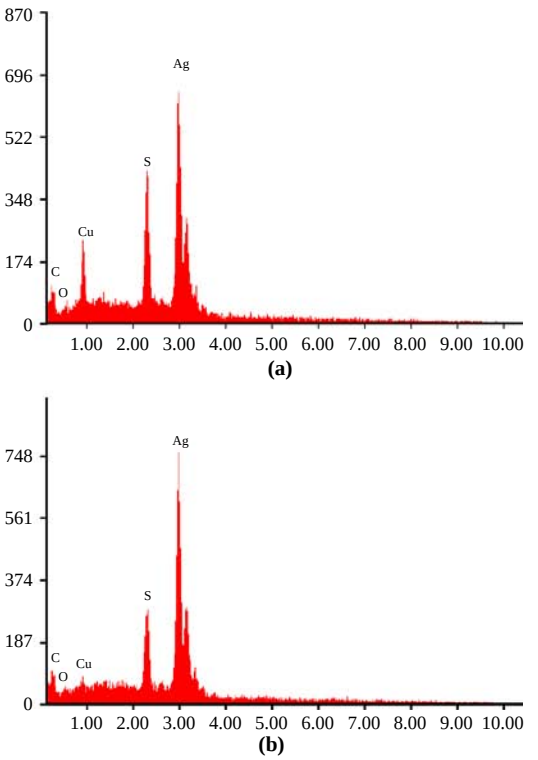


Figure 7 SEM and EDS analysis results for silver after 12 months of exposure in test chamber

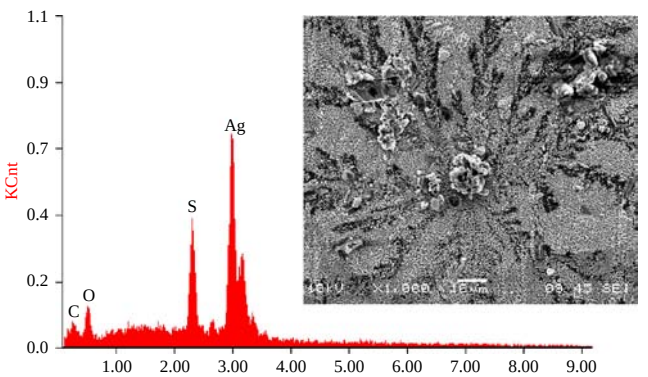
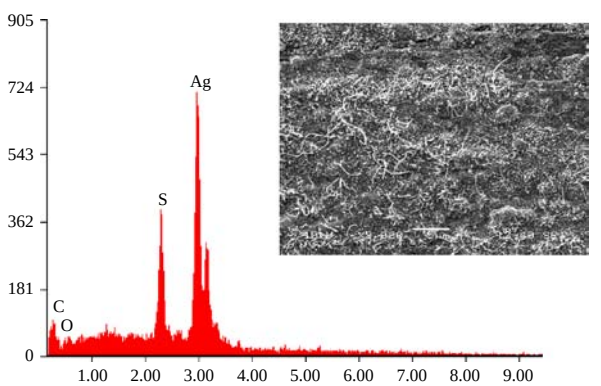
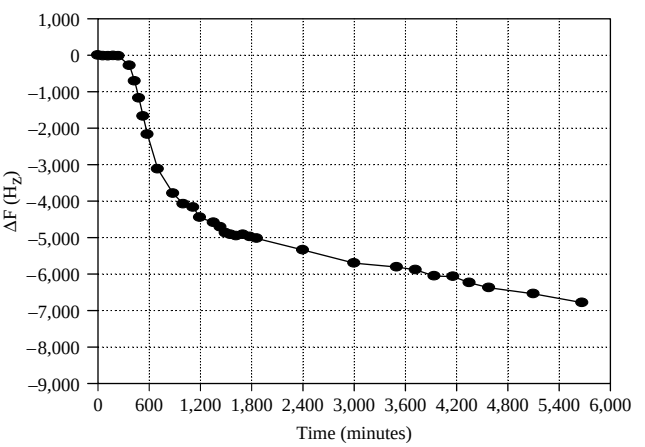


Figure 8 SEM and EDS analysis of metallic silver coupon after 24 months of exposure in the test chamber



this pollutant, while the average annual concentration for Mexicali was found to be 0.1 ppm (Lopez *et al.*, 2007). The frequency – time curve for 0.5 ppm H_2S concentrations is shown on Figure 9. The change of the plot slope about the 1000th minute is explained with the formed Ag_2S layer thickness increasing, thus making difficult for further H_2S gas diffusion through it, to reach the fresh Ag surface. Using the plot shown on Figure 9, the rate of the Ag_2S formation was calculated for the first 700 s representing 6.14 ng cm^{-1} s^{-1} while for the next part of the plot it falls almost twice to 3.27 ng cm^{-1} s^{-1}. The calculated rate of Ag_2S thickness increase is 6 nm/s for the first part of the plot, and 3.19 nm s^{-1}

Figure 9 QCM frequency–time plot of 1 inch 5 MHz quartz crystal with 0.5 inches active Ag surface at 25°C, 38.7 per cent rH and 0.5 ppm H_2S



for the second part. These values show that the Ag_2S layer formation is very fast, even at ambient temperature defining the need of measures for Ag surface protection.

Discussion

In the microelectronics industry, silver has been used for many applications, due to is physical properties and because of the cost savings over gold. However, reliability concerns regarding silver corrosion under certain atmospheric conditions must be not ignored. The main objective of this work was the study of silver corrosion at indoor conditions in a plant dedicated to assembly and functional testing of microelectronic devices. The clean room indoor environment is a critical stage during the assembly process of the microelectronic devices because the microcircuits are handled as it without encapsulation, when they are highly susceptible to atmospheric contaminants.

Conclusions

The results of silver coupon, and silver plated copper frame exposure tests for a 60-day duration revealed that the appearance of tarnish of different colours on the silver surface is the result of the formation of non uniform silver sulphide corrosion films, due to the presence of hydrogen sulphide pollutant and favourable high rH and temperature conditions. There was no difference between the corrosion behaviour of samples inside and outside the clean room indoor environment in the plant, due to very similar atmospheric conditions. Silver sulphide film was detected in both of the samples groups.

Silver plated over copper lead frames exposed in the test chamber for 60 days exhibited silver sulphide films, dendrites and also copper corrosion products, due to the porosity of the plated layer and the site atmospheric conditions.

Growth of dendrites on the pure silver samples also was observed when the samples were exposed for periods longer than 12 months in the indoor test chamber, and whiskers were evident after 24 months.

The results obtained during this study indicate that the electronic company must consider the control of several atmospheric factors, including lower air rH and temperature values, and the level of contaminants that correspond to the clean room indoor environment, in order to avoid silver corrosion and improve the reliability of electronic products.

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