

Electrochemical Migration of Silver in Electronics Applications

Manolo G. Mena and Marie Stephanie S. Mena

*Department of Mining, Metallurgical and Materials Engineering,
University of the Philippines, Diliman, Philippines*

Abstract— Silver (Ag) filler is the most attractive choice among all the conductive fillers. However, silver electrochemically migrates in the presence of moisture and applied bias. In microelectronic devices, silver migration usually occurs between adjacent conductors/electrodes, which leads to the formation of dendrites and eventually results in short-circuit failure. An investigation for two types of fillers was done using the water drop test and a 1000-hour temperature-humidity-bias (THB) test. Four different bias voltages and six different distance spacings were used for each of the two fillers. The higher voltage requirement for Ag migration to occur for epoxy A than for epoxy C was attributed to the high volume resistivity of epoxy A. It was discovered that an electric field value of more than 1 volt/mm will start Ag migration.

Keywords— *Electrochemical Migration, Silver Migration,*

1. INTRODUCTION

1.1 Background of the Study

Electrochemical migration can be defined as the growth of conductive metal filaments under the influence of a DC voltage bias. This process takes place primarily when the local temperatures and current densities are low enough to allow water to be present on the surface since the actual mechanism is water-dependent. Silver is the most common metal that undergoes these effects under non-condensing, but humid conditions [1].

Silver and its alloy are commonly used as the noble metal components in thick film pastes. Silver is relatively an inexpensive material, which is easily soldered to, and bonds with high strength to the substrate. Its high frequency performance makes silver an attractive conductor material [2].

1.2 Significance of the Study

Silver (Ag) filler is the most attractive choice among all the conductive fillers because of its balanced properties and relatively low cost. However, a major problem of silver is that it electrochemically migrates in the presence of moisture and applied bias [3]. In microelectronic devices, silver migration usually occurs between adjacent conductors/electrodes, which leads to the formation of dendrites and eventually results in short-circuit failure.

The purpose of the research is to be able to understand the electrometallurgy of Silver electrochemical migration, i.e., to identify the minimum voltage, minimum spacing and other conditions required for electrochemical migration of silver to occur. With the acquired information, preventive measures can be done, thus decreasing the dilemma of silver migration in the microelectronics industry.

1.3 Silver Migration

Several studies have been conducted on silver migration: its mechanism, how it applies in the microelectronic devices, how to control or reduce the phenomenon, etc. Silver migration was initially reported as early as the 1930 time frame, as discussed by Kohman et. al. [4]. Silver surface migration is an electrochemical process. The pure silver electrochemical migration (ECM), or classical silver migration, proposed by Kohman et al. and summarized by Harsanyi [5] shown in Fig. 1, is described as a transport of silver ions from an anodic site, through an aqueous electrolyte, toward a cathodic site where the electrodeposition of the ions occurs to form silver dendrites. In the processes, hydrogen ions are collected around the cathodic site and discharged to maintain the electrical balances as shown in Fig. 2.

Figure 1. Diagram of silver migration [1]

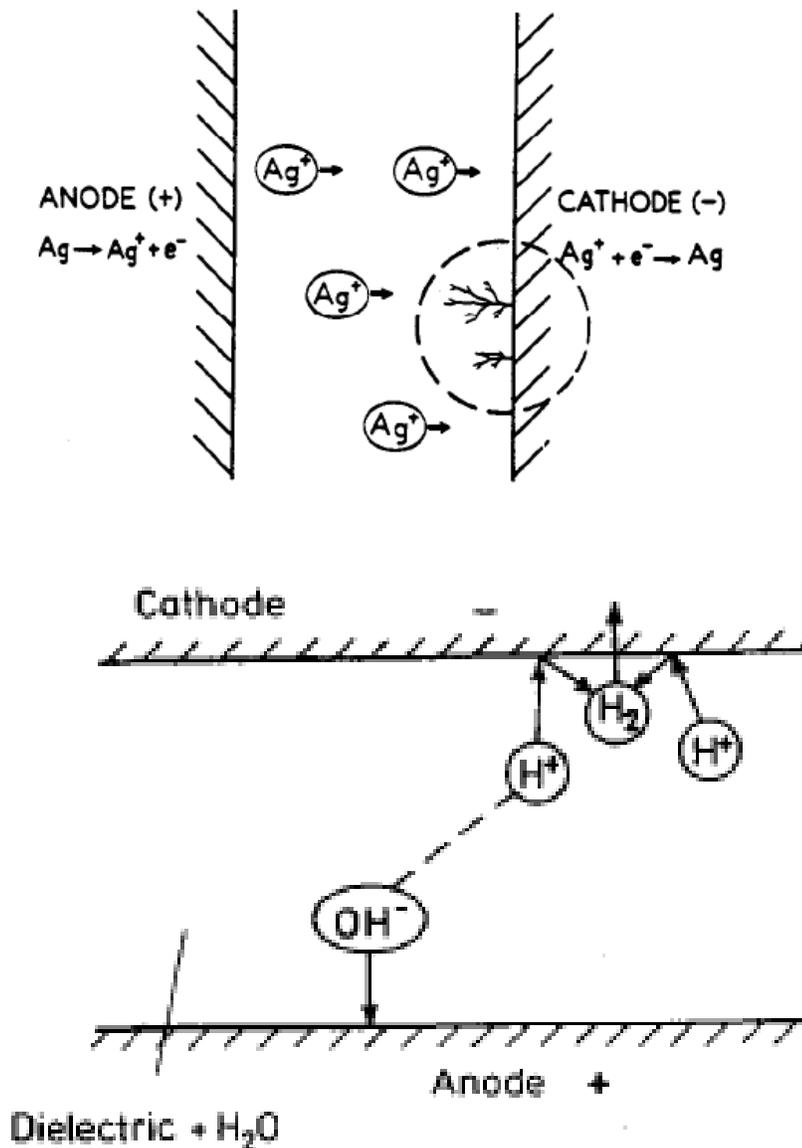


Figure 2. Water decomposition diagram (Harsayani, 1995)

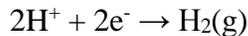
The Ag ECM process may be expressed through the following equations and steps (Krumbein, 1989, [6]):

- a. Silver oxidation and water ionization (at the anode)



- b. Silver ion migration from anode to cathode under an electric field

- c. Silver reduction and hydrogen evolution (at the cathode)



- d. Silver hydroxide formation and decomposition



Dendritic growth results from ion deposition at localized sites on the cathode in the form of needles or spikes as shown in Fig. 3. Once these nuclei have formed, the higher current density at their tips will greatly increase the probability of further deposition.

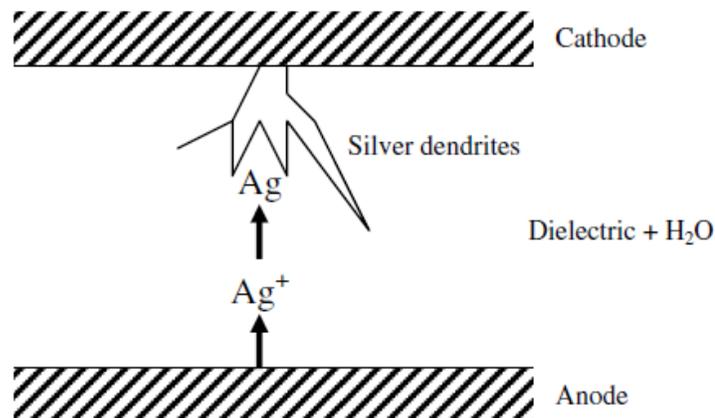


Figure 3. Dendrite growth [6]

1.4 Silver Migration Control

Several experimentations have been done to control silver migration. Vu [2] used silver palladium (Ag-Pd) alloy as the metal inclusion in conductive pastes. It was found that silver migration is reduced as the content of Pd in the formulation increases. The spacing between electrodes versus time-to-fail was also studied under a constant potential of 4 volts. It showed that as the gap between electrodes increases, time-to-failure also increases.

The experiment performed by Li and Wong (2006) involved adding a molecular self-assembled monolayer (SAM) passivated nano-Ag fillers to the conductive adhesive. The migration behavior was evaluated by measuring the leakage current-voltage (I-V) relationship at 0-5 volts. The untreated nano-Ag conductive adhesives showed a dramatic increase in leakage current with increasing voltage due to the high tendency for silver migration. On the other hand, the nano-Ag conductive adhesives incorporated with SAM showed much slower increase in leakage current.

The investigation of silver migration under THB conditions is similar to a study done by Yang et. al [6] in which they tested land grid array (LGA) sockets under highly accelerated stress test (HAST) conditions. The parameters used were 130°C, 85% RH and 5 volts. The time-to-failure was approximately 62 minutes when the temperature and humidity ramp-up time was included; 9 minutes if the starting point was when steady-state condition (130°C, 85% RH) was reached.

All the gathered literature stated that silver electrochemical migration can occur at high temperature, high humidity, high bias voltage and small spacing between electrodes. The lower limits of temperature, humidity, bias voltage and electrode spacing for silver electromigration have not been explored. This study aims to identify the minimum condition for migration to occur.

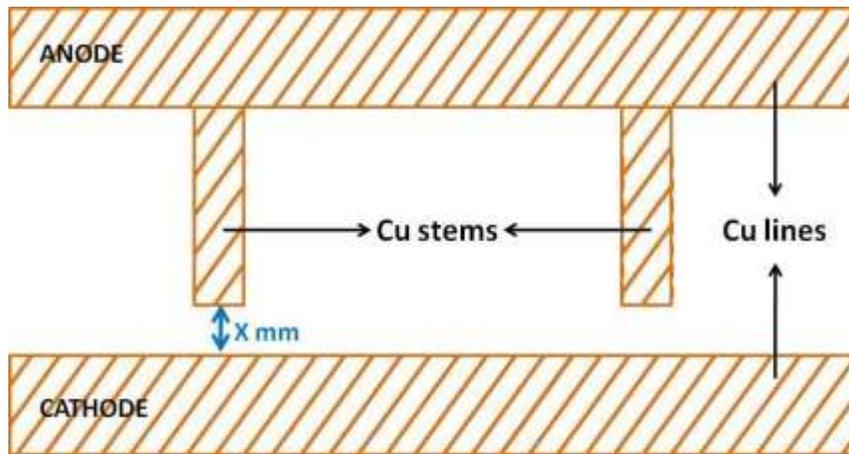


Figure 4. Diagram of PCB used for the experiment

2. METHODOLOGY

2.1 Set-up

Several printed circuit boards (PCBs) were designed including copper lines and stems (Fig. 4). The X values used were (average) 2.02 mm, 1.55 mm, 1.004 mm, 0.9532 mm, 0.9024 mm and 0.8516 mm. Copper stems were included in the design where the epoxy will be dispensed to make it easier for the data point to be severed/disconnected from the system once the point has shorted the circuit.

Table 1 shows some details and properties of the two (2) epoxy used in the experiment.

Table 1. Properties of Epoxy A and Epoxy C

	Epoxy A	Epoxy C
Silver Content	70-90%	70-80%
Epoxy Content	10-30%	10-30%
Solvent Content	1-10%	>5%
Glass Transition Temperature, Tg	38 °C	119 °C
CTE below Tg	81 ppm/°C	29 ppm/°C
CTE above Tg	181 ppm/°C	130 ppm/°C
Volume Resistivity	0.008 ohm-cm	0.00033 ohm-cm

After dispensing the epoxies on the copper stems, the PCB's were cured inside a drying oven at 150°C for one (1) hour.

2.2 Water Drop Test (WDT)

A drop of de-ionized water was placed to bridge the gap between the anode (die attach epoxy) and the cathode (opposite copper line) as shown in Figures 5 and 6. A bias was then applied to evaluate Ag migration. Bias voltages used were 2V, 3V, 4V and 5V. The time to fail (TTF) was taken from the moment of bias application, until the Ag connects the anode and the cathode. Once shorting has occurred, the power supply was turned off and the copper stem of the data point was severed.



Figure 5. WDT initial stage (50x mag)



Figure 6. WDT final stage (50x mag)

2.3 Temperature-Humidity-Bias (THB) Chamber Test

The temperature-humidity-bias (THB) chamber maintains a stable temperature and humidity environment. The conditions used were in accordance with JEDEC (Joint Electron Device Engineering Council) standards for MSL1 (Moisture Sensitivity Level 1) of 85°C and 85%RH. Using the same distance spacings and bias voltages, the PCBs were pulled out from the THB chamber after a certain number of hours to be inspected optically using a high-powered microscope and to measure resistance using a digital multimeter. In the event that a point has shorted, the copper stem was severed, after which, the PCB was placed back in the THB chamber to continue testing up to 1000 hours.

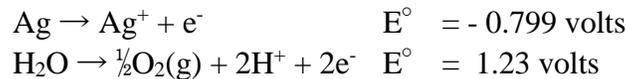
3. RESULTS AND DISCUSSIONS

3.1 Thermodynamics of Ag Migration

Several printed circuit boards (PCBs) were designed including copper lines and stems (Fig. 4). The X values used were (average) 2.02 mm, 1.55 mm, 1.004 mm, 0.9532 mm, 0.9024 mm and 0.8516 mm. Copper stems were included in the design where the epoxy will be dispensed to make it easier for the data point to be severed/disconnected from the system once the point has shorted the circuit.

For electrochemical migration to occur, an electrolytic solution and a DC voltage bias should be present between the anode and the cathode. The reactions at each electrode have corresponding effects on the total potential needed for silver to migrate, $E_{\text{migration}}$.

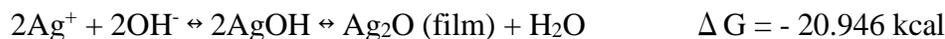
- At the anode, the following reactions as possible, with the dissociation of silver supplying the silver for electromigration. Decomposition of water can occur at a higher potential.



- At the cathode, reduction of silver ions results in the growth of dendrites. Hydrogen evolution is the secondary reaction that occurs at higher potentials.



- The presence of silver ions may also result in the redox reaction with generates a silver oxide film:



The total potential needed for migration of silver to occur may be calculated by using the equation below.

$$E_{\text{migration}} = E_{\text{rev}} + IR + E_{\text{irrev}} + E_{\text{ohmic}}$$

The reversible potential, E_{rev} is the sum of the reversible potentials at the anode and the cathode. Considering the that for silver, the anodic reaction is the opposite of the cathodic reaction, this results in an E_{rev} value of zero for the primary reaction:

$$E_{thermo} = E_{anode} + E_{cathode} = - 0.799 + 0.799 = 0$$

IR refers to the potential required to overcome electrolyte resistance. It is proportional to the resistivity of the electrolyte, separation distance between the electrodes and the current applied. For this study, it was assume to be negligible considering the small distance between the electrodes and the low current drawn, in the milliamperes observed in the experiments.

E_{ohmic} refers to the contact resistance between all the electrical connections in the system. This would include the contribution of the internal resistance of the epoxy.

E_{irrev} refers to the irreversible potential in the electromigration cell. This includes the overvoltages in the cathodic and anodic reactions. From the study conducted by Brusica et. al. [8], the cathodic overvoltage may be estimated to be 0.6v while the anodic overvoltage is 0.2 v.

Adding all the values above,

$$E_{migration} = 0.8 \text{ volts} + E_{Ohmic}$$

However, during migration, there were some cases where bubbles formed on the cathode surface. This phenomenon is called Hydrogen evolution. The hydrogen evolution overpotential on silver is in the range of 0.22 to 0.46 volts [7]. In this investigation, the upper limit is used. According to the standard electrode potential of hydrogen, the electromotive force required to reduce $2H^+$ to H_2 gas is zero (0). Thus, hydrogen evolution overpotential is 0.46 volt. When added to the migration potential equation, the value will now be

$$E_{migration} = 1.26 \text{ volts} + E_{Ohmic}$$

From the anodic reactions stated above, it is possible for oxygen to evolve on the anode surface. For oxygen to be liberated in the system, electrolysis of water should take place. The standard electrode potential for the electrolysis of water is 1.23 volts. The oxygen evolution overpotential, which is in the range of 0.6 to 0.91 volt [7], is then added to the standard potential. Adding the E_{rev} and overvoltage to the migration potential results into:

$$E_{migration} = 3.4 \text{ volts} + E_{Ohmic}$$

Hydrogen bubbles were observed when the applied voltage was about 4V and higher. No bubbles were observed at the anode for all the voltage applied. This would suggest that the E_{Ohmic} is a substantial value and that the potential required for oxygen evolution was not reached in the experiment.

3.2 Parameter Interactions

A three way ANOVA was performed to determine if the interactions of the three parameters have a significant effect on the TT,. From Table 2, it can be seen that all three main effects and the three first-order interactions have low P-values, all less than 0.05. This means that these terms have a statistically

significant effect on the TTF. However, the one second-order interaction has a P-value higher than 0.05. Thus, combining all three parameters does not affect the TTF significantly.

Table 2. Three-way ANOVA Parameter Estimates

PARAMETER ESTIMATES			
Term	Std Error	t Ratio	Prob> t
Paste	24.69307	7.31	<.0001*
Voltage	22.25531	-9.06	<.0001*
Distance	65.05173	9.60	<.0001*
Paste*Voltage	22.24662	-2.31	0.0222*
Voltage*Distance	57.54239	-3.30	0.0012*
Paste*Distance	65.03053	3.76	0.0002*
Paste*Distance*Voltage	57.80908	0.71	0.4767

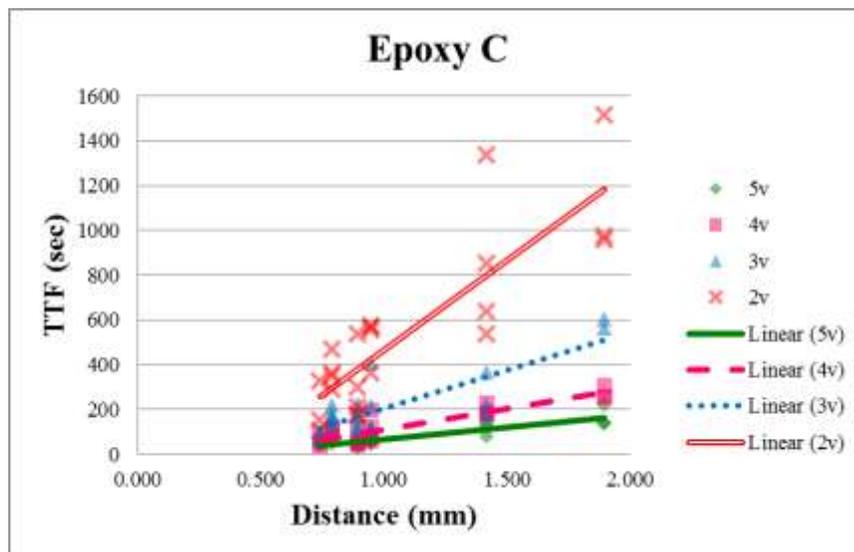


Figure 7. Linear trend line plot of TTF as a function of distance (Epoxy C)

3.3 Water Drop Test – Epoxy C

Epoxy C is a high-strength and low resistivity shield attach used in SMD interconnection formation. It has less solvent content as compared to epoxy A (see Table 1). Data analysis will start with epoxy C since it exhibited a more consistent data than epoxy A. Fig. 7 shows the linear trend line plot of time to fail (TTF) as a function of distance and Fig. 8 shows the linear trend lines of TTF as a function of voltage. The TTF is given in seconds, distance between the anode and the cathode is in millimeters and the bias voltage in volts. It can be seen that as the bias voltage applied increases, the slope of the lines decreases. Conversely, from the TTF vs. voltage plot, decreasing the distance spacing decreases the slope of the TTF vs. Voltage line. The slope of the lines represents the sensitivity of the TTF when changing the value of one parameter.

As observed in Fig. 7, the 2 volt trend line showed the largest slope, implying that at low voltages, a change in distance significantly affects the TTF. As the voltage increases, the dependence of the TTF to the change in distance decreases. On the other hand, decreasing the distance between the anode and the cathode decreases the slope of the trend line (Fig. 8). Similar to the analysis of increasing the voltage, the TTF is not considerably affected when the two electrodes are very close to each other. From Fig. 7 and 8, it can be stated that voltage inversely affects the TTF while distance has a direct effect.

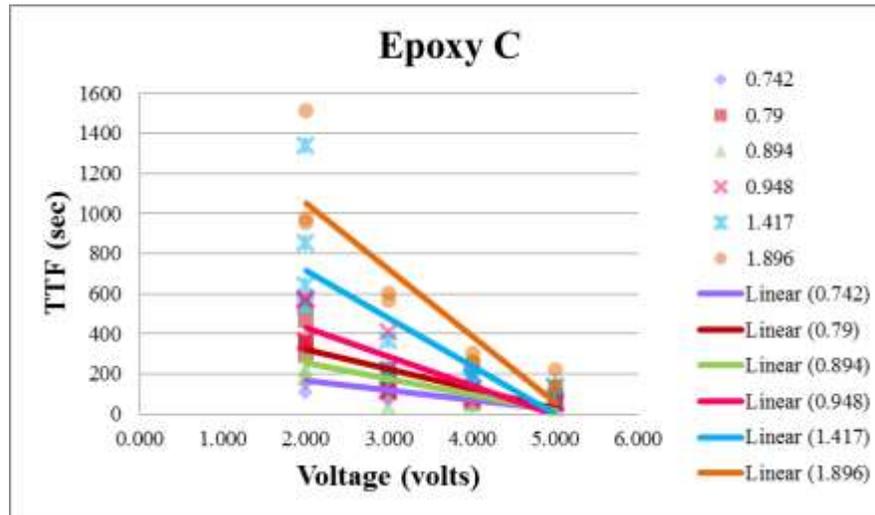


Figure 8. Linear trend line plot of TTF as a function of voltage (Epoxy C)

The effects of electric field was determined by replotting the data in Figure 8. Figure 9 shows an exponential relationship between electric field and TTF. As the electric field increases, the TTF exponentially decreases. The value of the electric field increases either by increasing the voltage or decreasing the distance spacing between the two electrodes. Therefore, the plot follows theoretical principles that increasing voltage applied and decreasing distance between electrodes decreases the time to short (TTF). From the equation of the power trend curve, if y is set at 1600 seconds, the corresponding x would be 0.91 volt/mm \approx 1 volt/mm. Thus, for this epoxy, the critical electric field is approximately one (1) volt/mm.

The curve also behaves asymptotically with respect to the x axis., i.e., the curve approaches zero (0) TTF as the electric field increases. It can also be seen that the curve is asymptotic, i.e., the curve approaches zero (0) TTF as the electric field increases. Beyond an electric field value of about three (3), there is no appreciable change in TTF.

3.4 Water Drop Test – Epoxy A

Epoxy A is a low-stress die attach epoxy, with a volume resistivity of 0.008 ohm-cm, which is more than 24 times that of epoxy C. Figure 10 shows the linear trend line plot of time to fail (TTF) as a function of distance at different voltages and Fig. 11 shows the linear trend lines of TTF as a function of voltage at various distances. The data for epoxy A has a higher level of scatter compared to data for epoxy C. As per the data sheet, Epoxy A is of one order of magnitude higher resistivity than Epoxy C. Thus, any variability in the arrangement of the silver filler in the dispensed epoxy could greatly affect the measured results.

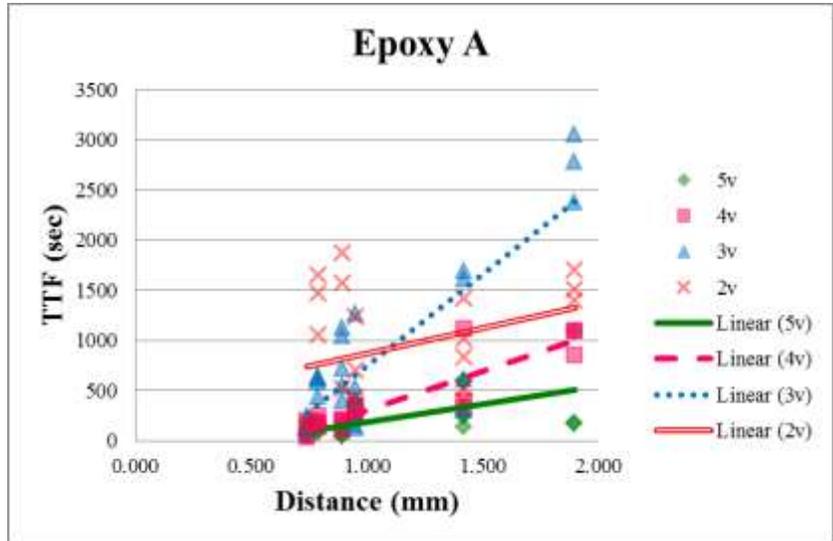


Figure 10. Linear trend line plot of TTF as a function of distance (Epoxy A)

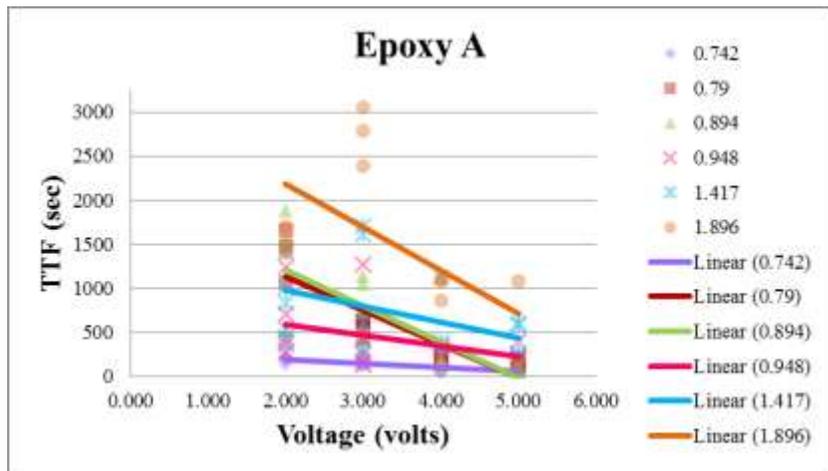


Figure 11. Linear trend line plot of TTF as a function of voltage (Epoxy A)

The trend should have followed an increasing voltage, decreasing slope behavior. But the slope of the 4 volts line is even higher than that of the 2 volts line, despite of it being lower than the 2 volts line. This can be explained by taking into account the high volume resistivity of epoxy A, as previously mentioned.

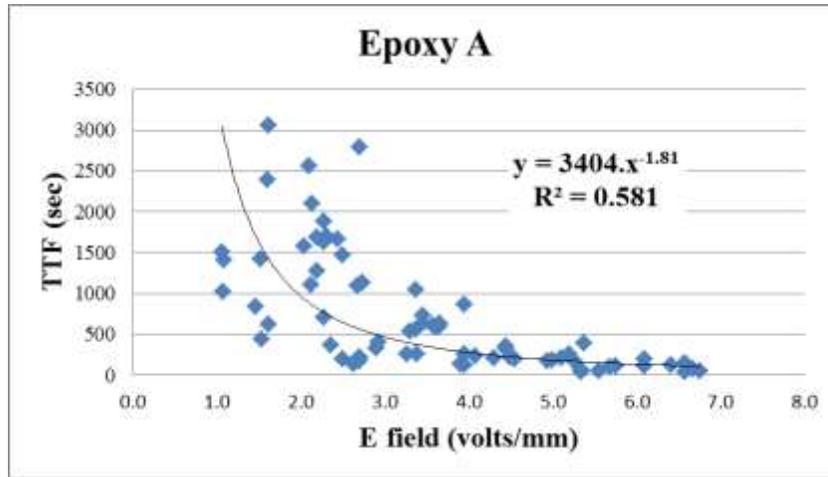


Figure 12. Plot of Electric Field vs. TTF With A Power Trend line (Epoxy A)

The electric field versus TTF was also acquired and shown in Fig. 12. Although the plot of electric field vs. TTF for epoxy A somewhat shows an exponential decay trend - which also follows theoretical principles - it is clearly seen that the data is very much scattered.

Setting the TTF to 3500, the corresponding electric field is 0.98 volt/mm \approx (1) volt/mm. This is similar to the minimum electric field obtained for epoxy C.

3.5 Dendrite Growth Rate

In order to determine dendrite growth rate, the instantaneous velocity was obtained by dividing the distance between the anode and the cathode into segments and recording the time it took as the dendrite travels from one segment to another, up to point of short, i.e reaching the anode. Fig. 13 shows a relatively linear increase in instantaneous velocity as the dendrite grows closer to the anode. Thus, dendrite growth has a constant acceleration.

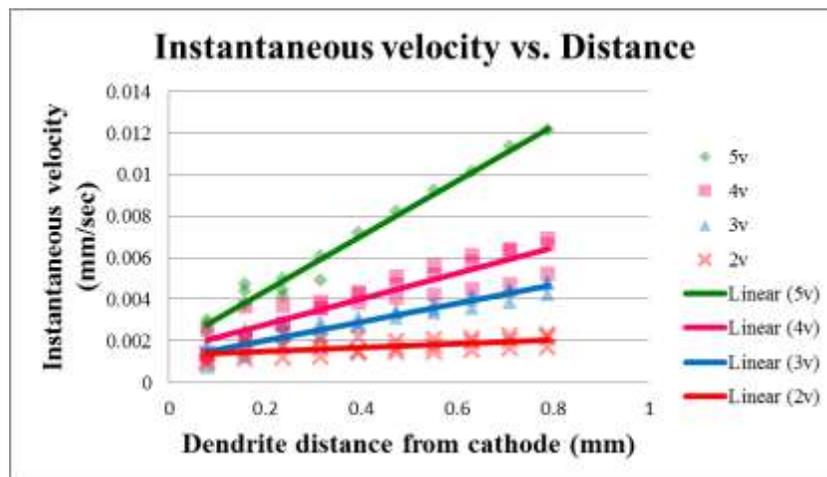


Figure 13. Plot of Instantaneous velocity vs. dendrite distance from cathode with linear trend lines

3.6 THB Test

The PCBs were subjected to temperature-humidity bias (THB) testing, in which a condition of 85°C and 85% RH was used and tested for 1000 hours. The PCBs were taken out of the THB chamber at fixed intervals (every 21-22 hrs) for optical and resistance inspection. From all the 576 data points, only two (2) failed or shorted during the 1000-hour THB testing. These points can be considered as outliers since they make up just 0.3% of the population data. This may be explained by recognizing that the die attach epoxy points on the PCBs were exposed and not enclosed in any package or encapsulant. The monolayer or film of water needed to commence migration could not form on the surface of the board since it can easily vaporize due to the 85°C temperature inside the chamber. The chamber is operated under non-condensing mode.

4. CONCLUSION

The data of epoxy C showed good behavior such that the plots and statistical analysis for the data revealed a coherent trend. It was found that the marginal value for Ag migration to occur when using epoxy C is 2 volts. At 2 volts, factors are present that impede Ag migration and deposition. The adequate bias voltage for migration to occur is 3 volts. Also, the minimum electric field was also computed and obtained a value of 0.91 volt/mm which was rounded off to one (1) volt/mm. Thus, a design rule can be proposed to prevent Ag migration. The ratio of voltage (in volts) to distance (in millimeters) should be less than the minimum electric field value of one (1) volt/mm in order to hinder Ag migration.

On the other hand, at 3 volts epoxy A still had a high spread of data, therefore, the sufficient voltage for Ag migration to occur when using epoxy A is 4 volts. The critical electric field calculated was 0.98 volt/mm \approx one (1) volt/mm, similar to the minimum electric field for epoxy C. Hence, the same design rule can be applied for epoxy A.

From the determination of the instantaneous velocity of the dendrite, it was discovered that velocity increases linearly with distance, making its acceleration to be at a constant. THB testing may not be the correct method for an exposed system because a film of water needed for Ag migration to occur is not able to condense on the surface of the PCB.

5. RECOMMENDATIONS

The determination of the additional potential to overcome the resistivity of the epoxy, E_{Ohmic} , is also suggested. Obtaining these values can result to a specific and more accurate estimate of the total potential needed to drive the Ag migration reaction forward. Other sources of the wider data variation for Epoxy A also needs to be identified.

A new THB condition recommended is to use 100% RH at 85°C. This is to ensure the condensation of of water on the PCB surface, which appears to be a requirement for electromigration to occur.

6. ACKNOWLEDGEMENT

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