# Silver Migration – The Mechanism and Effects on Thick-Film Conductors

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## ABSTRACT

Hybrid microelectronics utilizes conductive pastes to interconnect different discrete devices on a common substrate, which is usually Alumina. Silver Palladium (Ag-Pd) alloy is widely used as the metal inclusion component in conductive pastes. Positive characteristics of Ag include low cost and low sheet resistivity. However, Ag migration in un-desired areas is its major drawback. Anodic dissolution rate of Ag can reach $10^{-1}$A/cm$^2$ that corresponds to a catastrophic removal rate of 35.6 nm/s [5]. Silver migration can be classified as electromigration and ionic migration depending upon the environmental conditions of occurrence. The second migration is the utmost failure mode in thick film systems whenever the insulator separated the conductor acquires sufficient moisture from the ambient. The mechanism of Ag migration can be viewed as three steps process: electro dissolution, ion transport and electro deposition. Detail discussion on Ag migration mechanism is addressed in this paper.

Silver migration is reduced as the content of Pd in the formulation increases. Water drop test showed that the rate of Ag migration decreased by approximately 100 times as the Pd concentration in the conductors was increased from 10 to 19% [4]. The formation of PdO that requires a lower potential energy anode explains for the decrease in Ag migration with Pd content. The sufficient amount of Pd to inhibit Ag migration was reported 30%. At 5-15% Pd concentration in Ag-based alloy, Ag migration was still observed in the test structures. Optical micrograph for the Ag migration indicated three forms of silver compounds- dendrite, dark cloud like and the mixed of the two found on anodes and cathodes. The conductivity of the dendrite was $6.8 \times 10^7$ sm$^{-1}$ while the cloud like was varying from $2.5 \times 10^5$ to $7.6 \times 10^6$ sm$^{-1}$ depending on the Pd content in alloys.

Effects of electrode spacing and type of encapsulant on Ag migration are also addressed in this paper. Silver migration altered the dielectric properties, and reduced the insulation resistance. Silver migration causes short circuits and promotes devices failure especially under the high humid environment.

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# 1. INTRODUCTION

Thick films are used extensively in hybrid microelectronics for combining two or more semiconductor devices on a common interconnect substrate. In hybrid thick film circuits, discrete circuits elements such as monolithic integrated circuits, transistors, diodes, resistors, capacitors, and inductors are mounted on an insulating substrate by screening and firing layers of high viscosity pastes (Figure 1).

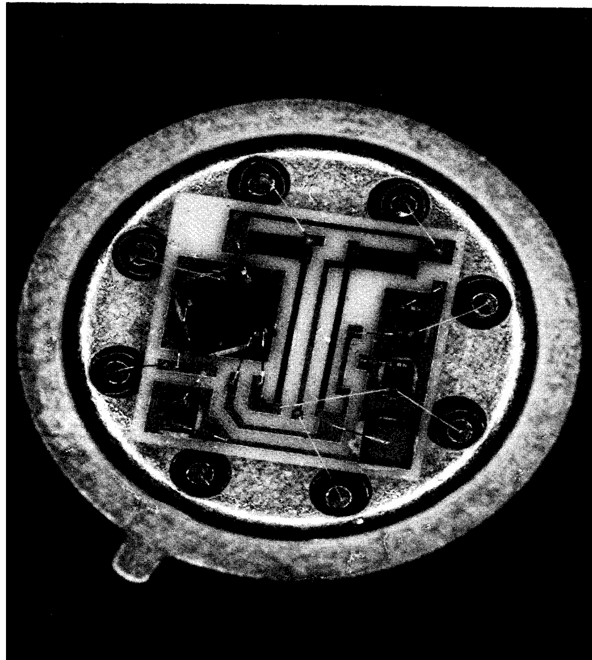


Figure 1: Thick film hybrid circuit from Intersil, Incorporated [1].

Thick film hybrid microcircuits are relatively easy to design and less expensive in terms of capital equipment, circuit development, and production cost. This technique of devices bonding performs better in high frequency, high voltage, and high power applications. Three typical thick film materials are conductors, resistors and dielectrics. This paper will focus on the conductor thick film, particularly the ones relating to silver (Ag) and its migration phenomenon.

The quality of the conductor paste depends on manipulating its three components consisting of:

[a] A metal or alloy to provide conductance and join ability

[b] A flux or frit to adhere the land to the substrate

[c] A vehicle to provide screen ability

Silver and its alloy are commonly used as the noble metal components in thick film pastes. Silver is relatively inexpensive material, which is easily soldered to, and bonds with high strength to the substrate. Silver has a very low sheet resistivity in the range of $10^{-3}$ (⃠/⊗). Its high frequency performance makes silver an attractive conductor material.

However, electrochemical migration is a major problem for Ag bearing thick films especially under high humidity conditions. Silver migration causes short circuits failures in different devices such as changing the dielectric properties in crossover structures and MLCC packages. Palladium (Pd) additive in pure Ag can minimize the migration phenomenon. Detail discussion on Ag migration can be found in section 3 below.

## 2. SILVER AS A PASTE CONDUCTOR INCLUSION:

Thick film conductors play an important role in hybrid microelectronics and electronic packaging. As the devices dimensions have become smaller and high-speed devices are required; the material requirements are even much more demanding. One of the challenges is to search for conductor materials that are subjected to a broad number of processing conditions with low failure rates.

The primary function of a thick film conductor is to provide an electrically conducting path from one location on the circuit to another. Properties of thick film conductors [2] include:

- Resistivity
- Solderability and solder leach
- Line resolution
- Physicochemical compatility with other components such as resistors, dielectrics and the substrate.
- Long term stability in hostile environments such as heat, humidity and thermal cycling
- Migration resistance
- Cost
- Wire and die bondability

Ag and its binary, ternary alloys seem to satisfy the stringent requirements for conductor pastes usage in a wide range of applications; except for the negative feature of electro migration. As in element forms, the comparison of relative cost and physical

properties was made by Sergent et al. [2] to show the positive features of using conductive Ag. See Table 1.

Table 1: Elements Used in Thick Film Conductors [2].

| **Element** | **Density ($g/cm^3$)** | **Electrical Resistance (③⦸.cm)** | **Sheet Resistivity (⦸/⊗)** | **Melting Point ($^{o}C$)** | **Linear Thermal Expansion Coefficient ($ppm/^{o}C$)** | **Thermal Conductivity (W/m K)** | **Cost** |
|---|---|---|---|---|---|---|---|
| **Ag** | **10.5** | **1.6** | **0.64** | **961** | **19.7** | **429** | **1** |
| Au | 19.3 | 2.3 | 0.92 | 1063 | 14.2 | 317 | 70 |
| Pt | 21.4 | 10.5 | 4.2 | 1769 | 9.0 | 72 | 100 |
| Pd | 12 | 10.8 | 4.3 | 1552 | 11.7 | 72 | 30 |
| Cu | 8.96 | 1.7 | 0.68 | 1083 | 16.5 | 401 | 0.02 |
| Mo | 10.2 | 5.2 | 2.04 | 2610 | 5.1 | 138 | 0.07 |
| W | 19.3 | 5.6 | 2.24 | 3410 | 4.6 | 174 | 0.06 |
| Ni | 8.9 | 6.8 | 2.72 | 1453 | 13.3 | 91 | 0.03 |

Metal phase in a thick film paste is utilized in powder form that is mixed in an organic medium or vehicle as mentioned in the introduction. The size distribution of particles suitable for solder paste ranges from 45 to 74 microns in diameter. Typical constituents in Ag thick film systems consist of a silver, carbon, or Ag and C mixture phase dispersed in a thermoplastic or thermosetting polymer and solvent [3]. Table 2 [1] exhibits Ag characteristics in thick film conductor hybrid packages samples. Ag has very low resistivity and adheres well with the commonly used alumina substrate.

Table 2: Material characteristics of representative silver thick film conductor pastes [1].

| Type | Sheet Resivitity (⊘/ ⊗) | Printing and Drying | Firing Peak | Thinner | Shelf Life | Adhesion | Solder ability |
|---|---|---|---|---|---|---|---|
| Silver (ESL-5964) | 0.005 | 200 mesh. 100-125C for 15 min. | 750-850C for 10-15 min. | Butyl cellosolve ESL 404 | 1 year | Excellent to alumina, beryllia | Soft solder w/ 3% Ag |
| Silver (Owen-IL 06103) | 0.003 | 220-325 mesh. 100-125C for 15-20min. | 600-900C for 5-15 min. | OI thinner 06999 | --- | >2000 psi 100mil diameter test pad | Good with Sn/Pb/Ag Solder. |

In manufacturing, binary Ag alloys are used extensively to reduce Ag migration. The most popular Ag-based alloy is Ag-Pd. Ag and Pd exhibit complete solid solubility, which is found in many established phase diagrams. Moreover, the addition of Pd to pure Ag improves solder leach resistance and reduces Ag migration because of the solid solution formation. In thick film conductors, the Ag to Pd ratios of 3:1, 4:1, and 6:1 are commonly used.

## 3. SILVER MIGRATION

Silver migration phenomenon is discussed below in terms of its mechanism and effects focusing on thick film conductor systems.

### 3.1 Silver Migration - The Mechanism:

Electro migration is the flow of ions in a conductor due to the electric current. When the applied voltage is off, ions undergo the random thermal diffusion. The migration mechanism is influenced by temperature, voltage gradient, and the distance between electrodes. Other migration parameters considered of primary importance in hybrid thick film packages are the conductor composition, the state of the moist environment, and the type of encapsulant.

Migration of an electronic component has two types depending on the environmental conditions of occurrence. Electromigration is the solid-state type of migration that involves in electron momentum transfer at relatively high temperature (150$^{o}$C) in the dry environment. On the other hand, ionic migration occurs at ambient temperatures (<100$^{o}$C) in moisture condition. The second migration is the utmost failure mode in thick film systems whenever the insulator separated the conductor acquires sufficient moisture from the ambient. Naguib et al [4] through their series of experiments confirmed that ionic migration of Ag is the main failure mode in cross over dielectric structures. Anodic dissolution rate of Ag can reach $10^{-1}$A/cm$^{2}$ that corresponds to a catastrophic removal rate of 35.6 nm/s [5]

Silver surface migration is an electrochemical process. When Ag is in contact with insulator in high humid condition and under an applied electric field, it leaves its initial location in ionic form and re-deposits at another location. Electrolytic migration

can be viewed as three steps process including: electro dissolution, ion transport and electro deposition. Ionic Ag migration mechanism [6] can be explained as:

[a] Water from the ambient moisture under the applied electric potential is ionized:

$$Ag \rightarrow Ag^{+} \quad \text{[Equation 1]}$$

$$H_2O \rightarrow H^{+} + OH^{-} \quad \text{[Equation 2]}$$

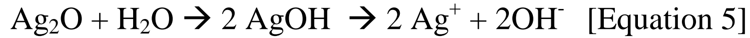
[b] The hydrogen ion migrates to the cathode and discharges as hydrogen gas; while the hydroxyl ion moves towards the anode and encounters $Ag^{+}$ moving from anode to form colloidal precipitate close to the anode:

$$Ag^{+} + OH^{-} \rightarrow AgOH \quad \text{[Equation 3]}$$

[c] The unstable AgOH decomposes on anode to form a dark deposit ($Ag_2O$) around the anode:

$$2\ AgOH \rightarrow Ag_2O + H_2O \quad \text{[Equation 4]}$$

[d] A hydrate reaction takes place



$$Ag_2O + H_2O \rightarrow 2\ AgOH \rightarrow 2\ Ag^{+} + 2OH^{-} \quad \text{[Equation 5]}$$

Figure 2 indicates the presence of $Ag_2O$ dendrite on anode when using Ag-15% Pd powers (15 A and 15 M) in distilled water test at a bias of 5 V for 2200s [7]. Notice that A stands for alloy of Ag-15 %Pd and M stands for mixture of Ag and 15% Pd. The binding energies reported for $Ag_2O$-$3d_{5/2}$ and $Ag_2O$-$3d_{3/2}$ were 367.8 eV and 373.8 eV respectively. The intensity peaks for $Ag_2O$ is greater in 15A than 15M that mean samples preparation methods have effects on blocking Ag migration.

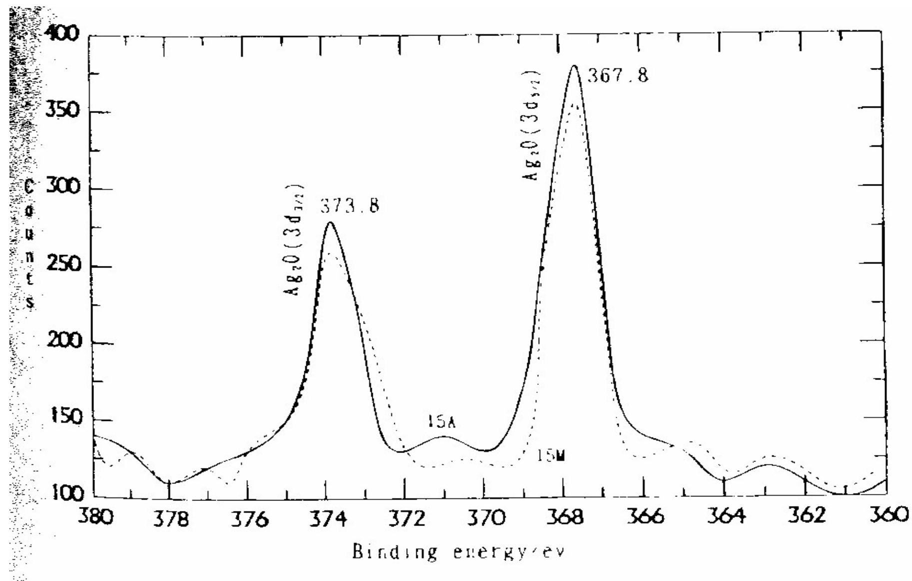



Figure 2: ESCA of $Ag_2O$ anodic films prepared from alloyed and mixed Ag-15% Pd powders [7].

Silver tends to be more susceptible to migration than other metals because it is anodically very soluble and requires low initiate activation energy. Dryzek reported Ag activation energy for vacancies was 0.67 $\pm$ 0.02 eV using positron annihilation [8]. Hornung [9] proposed a mathematical model for silver migration as:

$$t_{50} = (\alpha G/V).\exp(\Delta H/kT) \qquad \text{[Equation 6]}$$

where $t_{50}$ is the median life (time required for 50% cumulative failures, $\alpha$ is the proportionality constant, V is the applied voltage, G is the gap between two bias electrodes, $\Delta H$ is the activation energy for Ag migration, k is Boltzmann's constant, and T is the absolute temperature. More details on FCC Ag migration activation energy can be found in references [10] and [11]. As a result of Ag migration, dendrites growth is found either on the surface of insulator or through the insulator and ultimately cause shorting in the circuit.

## 3.2 Silver Migration Tests:

Two common methods to observe Ag migration are the water drop (WD) and temperature-humidity-bias (THB) tests. In WD test, a drop of de-ionized water is placed to bridge the electrodes gap. A bias is applied to between these conductor electrodes lines to evaluate Ag migration. The WD is not considered the normal devices operation test. The later THB test is performed in a controlled environmental chamber to maintain a stable temperature and humidity. Naguib et al [4] on their experiments to evaluate binary Ag-Pd conductor pastes performance showed that the rate of the Ag migration in a THB condition is approximately $10^4$ times slower than in WD conditions. Different methods such as SEM, EDX, EPMA, ESCA, FTIR and electrical measurement are used to analyze the Ag migration results from these tests.

## 3.3 Parameters Effect Silver Migration:

Voltage gradient, applied bias time, conductor composition, electrodes distance, moist condition and type of encapsulant are typical parameters affecting to Ag migration.

### 3.3.1 Conductor Composition:

Binary Ag-Pd system is widely used to reduce migration. In the presence of Pd, most of the current in the cell is consumed to produce hydrogen gas at the cathode and only a small portion is used for the deposition of the Ag. The resistance to silver electrolytic migration increases with the Pd concentrations in the films. See Figure 2.Water drop test showed that the rate of Ag migration decreased by approximately 100 times as the Pd content in the conductor was increased from 10 to 19% [4].

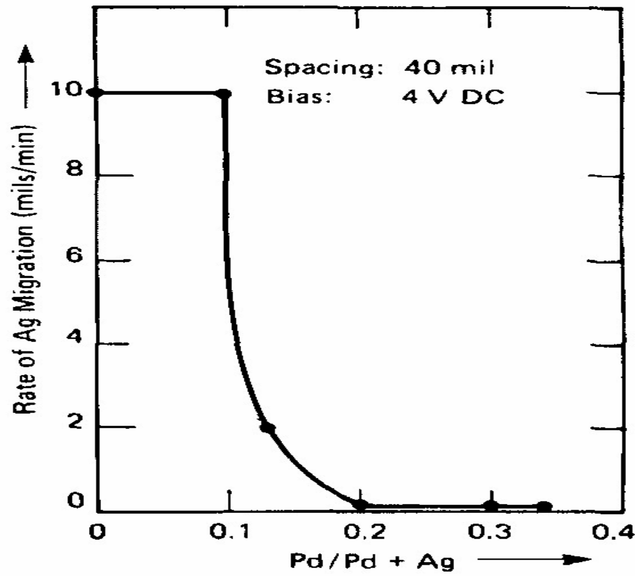



Figure 3: Rate of Ag migration versus ratio Pd/(Pd+Ag) in conductor ink [4].

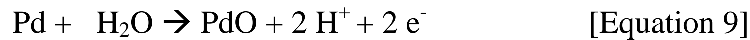
The reduction in Ag migration can be explained by the formation of PdO at the anode. The dependence of potential energies on pH values [7] can be described as:

$Ag + ½ H_2O \rightarrow ½ Ag_2O + H^+ + e^-$ [Equation 7]

- With $E^o = 1.173 – 0.0591$ pH

$Ag_2O + H_2O \rightarrow Ag_2O + 2 H^+ + 2 e^-$ [Equation 8]

- $E^o = 1.398 – 0.0591$ pH



$Pd + H_2O \rightarrow PdO + 2 H^+ + 2 e^-$ [Equation 9]

- $E^o = 0.896 – 0.0591$ pH

The formation of PdO occurs more easily than that of $Ag_2O$ and AgO due to lower equilibrium potential required in calculated from equations 7,8 and 9. The passive PdO anodic film retards the dissolution of the Ag-Pd alloying in the humid environment. Lin et al [12] reported that the PdO anode coverage is not sufficient in blocking Ag migration when the Ag-Pd thick films containing 5-15% Pd. Optimized concentration of

Pd in the alloy varies from 20 to 30%. See Figure 4 for the inhibition mechanism of Ag migration by PdO. Figure 4(a) shows that the naked Ag is more reactive than Pd atom and dissolves the Ag-Pd alloy easily under humid and electric field effects. Figure 4(b) displays Pd atom forming a shield layer to prevent the dissolution.

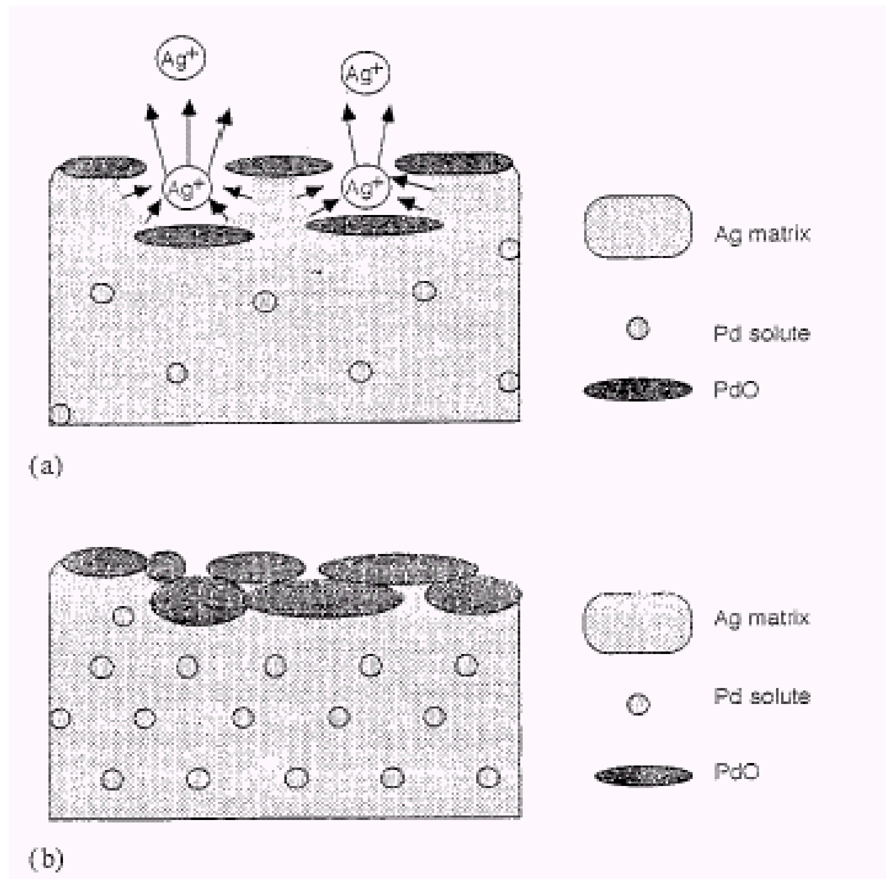



Figure 4: Models for the Ag migration in the Ag-Pd thick film with (a) Pd [ 15% and (b) 20% [ Pd [ 30% [12].

Figure 5 shows the morphology of Ag-Pd thick films at various Pd compositions on alumina substrates. Ag migration depends significantly on the Pd amount in the Ag-based pastes. No de-alloying dissolution of Ag from Ag-Pd occurs when increase the Pd content to more than 30% as seen in Figure 5 XC4.

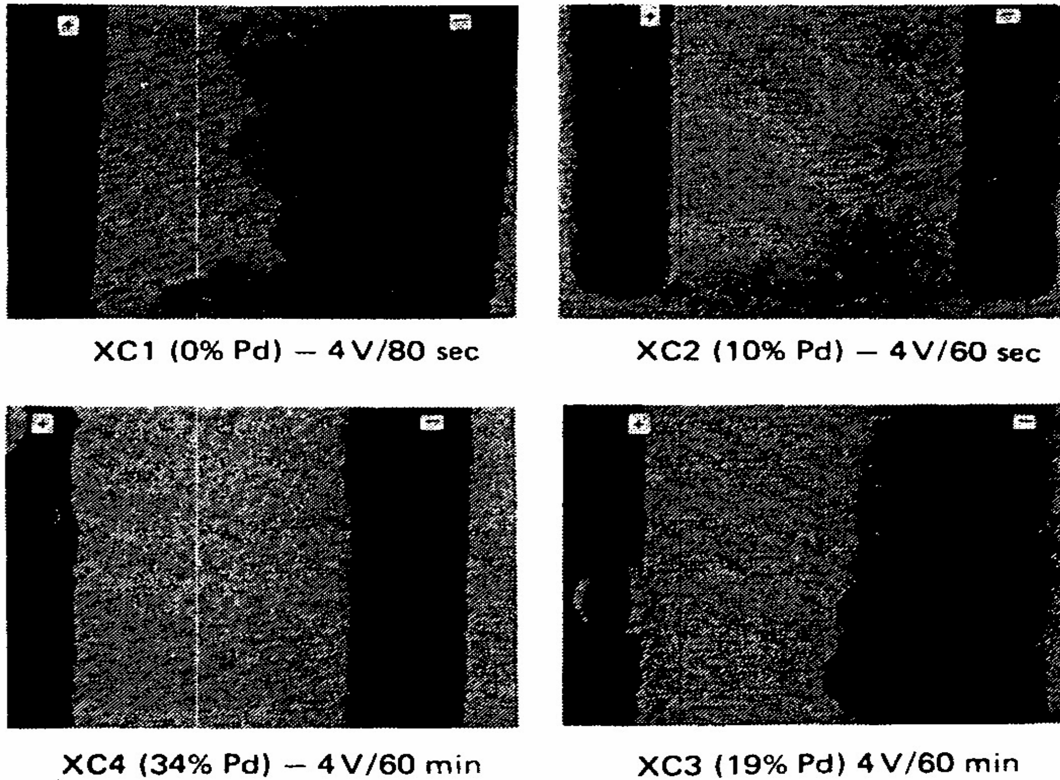



Figure 4: Ag migration varies with Pd/Ag compositions [4].

The resistance of Ag migration can be enhanced at optimal thick film preparation method. At the same Pd concentration of 15%, alloying or mixing Pd onto the Ag based thick film can alter the amount of $Ag_2O$ formation at anode as exhibited in Figure 2 previously. Ag migration is more pronounced in alloys than in mixed Pd – Ag thick paste.

Ternary alloy of Ag-Pd-Au (60%-20%-20%) is found to have higher migration resistance than the Ag-Pd binary one [12] on alumina substrate. The comparison indicates that better reliability in the ternary alloys may be due to the presence of Au. The Au forms an alloy with Ag; thereby reducing the amount of free Ag available to cause migration [13]. See Figure 5 with the vertical axis expressing the time in unit of hours.

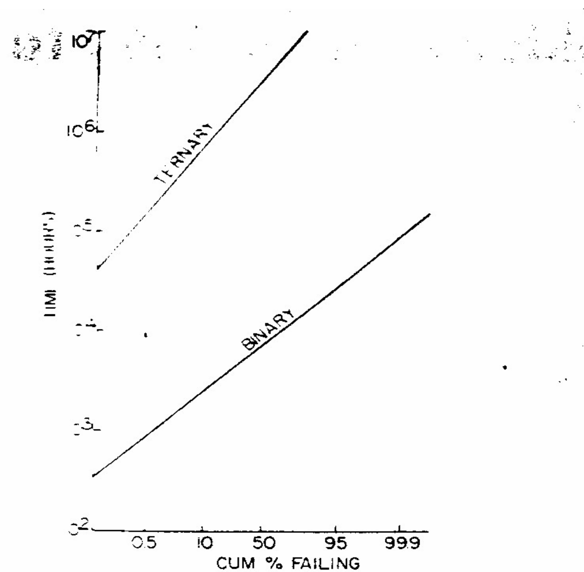



Figure 5: Lognormal life distribution of binary and ternary conductors tested at 120C, 5V [13].

The films appearance on anodes due to Ag migration can be dendrites, cloud like or existing in both forms depending on the type of thick films. Dendrites, cloud like layers, and dendrites together with cloud like layers were found on the pure Ag, the Ag-30% Pd and the Ag-15% Pd films respectively [6].

3.3.2 <u>Time Duration under Potential Applied:</u>

The rate of Ag migration is increased by an increase in the time of the applied voltage. A sample of Ag-10 Pd was tested at 5 V for 1300 and 1500s [12]. The in situ microscope observation confirmed that the growth rate of cloud like product in Figure 6 is more rapid than that of the dendrite. Dendrites in Figure 6(b) appeared to be denser than ones in Figure 6(a) that means higher migration current was found as increasing the applied potential duration time. Two solid films- dendrite and dark cloud like and bubble $H_2$ were found on the cathode. The bubbles were identified as Hydrogen.

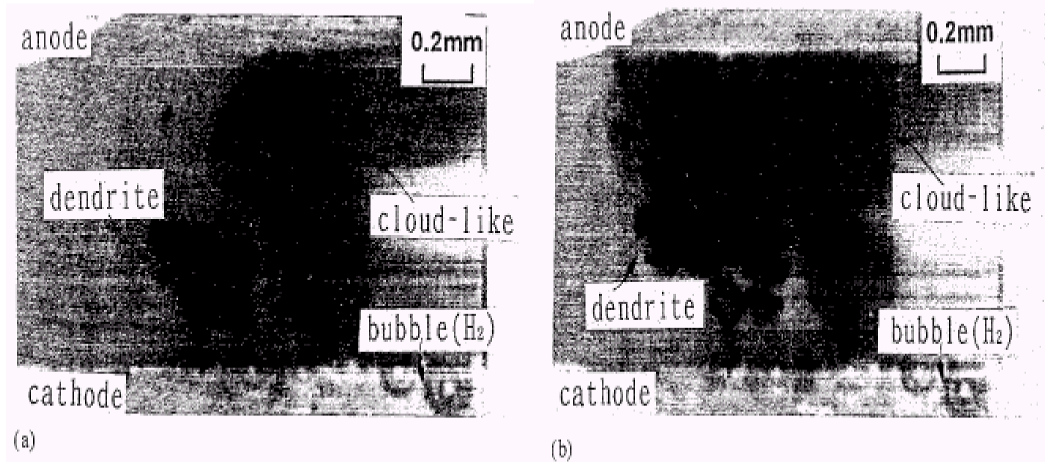



Figure 6: Optical micrograph for the Ag migration in situ observation of Ag-10% Pd in distilled water at 5V after (a)1300s and (b) 1500s.

The conductivity of the dendrite (6.8 x $10^7$ $Sm^{-1}$) is greater than that of the cloud like solid (varying from 2.5 x 105 to 7.6 x $10^6$ $Sm^{-1}$ depending on the Pd content) [12]. Thus, electrical current resulted dendrite connection is greater than that of the cloud like.

3.3.3 Electrode Spacing:

The demand for smaller devices has led to the reduction in spacing between conductors lines in hybrid thick film packages; that means the time to failure is further shortened due to the enhancement in Ag migration. The capacitance is mathematically inversely proportional to the distance of the electrode. Silver dioxide appearing as either dendrites or cloud-like are more susceptible to form. Time to failure due to migration as a function of electrode gap distance is shown in Figure 7 below.

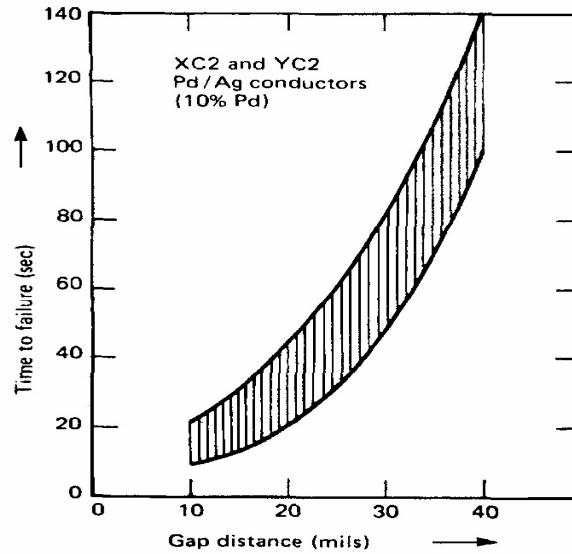



Figure 7: Time to failure versus gap distance at 4 V DC [4].

### 3.3.4 Type of Encapsulant:

The Ag migration is higher on the surface of bare alumina substrates than on the ones covered with dielectric layers. The Du Pont 9137 glass encapsulant was found to be effective in inhibiting Ag migration under THB tests as reported by Naguib et al [4]. Suitable low dielectric materials covered substrates provide good isolation between small dimension conductor spacing lines; hence aids the Ag migration reduction.

## 4. RELIABILITY ISSUES IN SILVER BASED CONDUCTORS

The most common effect of Ag migration on devices performance is to short the circuits and promotes the devices failures. Silver migration can change the dielectric strength of the sandwich material between conductor lines. Zuo et al [14] showed that

the content of Ag added to the relaxor ceramic altered its dielectric properties. Increase in silver concentration in mol % leads to the reduction in insulation resistance as shown in Figure 8 below.

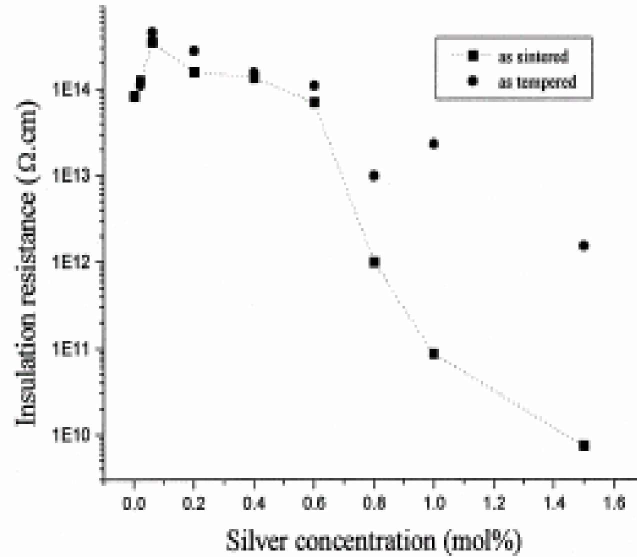



Figure 8: Insulation resistance of silver-doped relaxor ceramic for different heat treatment[14].

Silver migration also cause grain growth, and change dielectric properties. Literature on the effect of Ag migration on grain growth and grain boundary can be found in reference [15].

Silver is utilized in other applications in micro electronic packaging including wire bonding, die attachment and etc… Even though silver has outstanding properties and is cheap, Ag migration is still its main limitation.

## 5. CONCLUSION

Silver is the inclusion metal component in thick film conductors that is used extensively in hybrid microelectronics. Silver is a high conductive and inexpensive metal. It also provides a good bonding to different substrates. However, ionic migration is a major problem for the Ag-based thick films under humid condition and low Pd content. Addition of Pd up to 30 weight percent to Ag either by mixing or alloying can inhibits Ag migration that results in high cost material.

General trends to control silver migration in thick film conductor lines are:

[a] The Ag migration reduces when the Pd content increase

[b] Ternary alloy of Ag-Pd-Au is more effective in Ag migration prevention as compared to binary alloy of Ag-Pd

[c] The Ag migration enhances as the spacing between conductor lines reduces

[d] The Ag migration is more pronounced as potential applied time as well as the duration time increase.

Silver migration alters the dielectric properties and lower insulation resistance. It causes short circuits and device failure in hybrid microelectronics.

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