Ionic Migration on Printed-Circuit Boards

ESPEC CORP.

CONTENS

1. Introduction
2. About ionic migration
3. Test methods
4. Insulation resistance test
   (Copper and silver migration)
5. Solder alloy migration
Migration occurring on electronics components

(a) Copper migration on PCB

(b) Copper migration on telephone connector
Failure on PCB and environmental stress

winter

Connected deterioration

Humi.

Temp. cyclic

Temp.

Solder crack

summer

Insulation deterioration

Dew condensation

Migration occurring

(a) Temperature and humidity in automobile

(b) Failure on PCBs
Factors of failure on PCB

Failure phenomena

Connected deterioration
- Fatigue – solder clack
- Oxidation – contact defective
- Abrasion

Insulation deterioration
- Corrosion – migration
- Adhesion – water absorption
- Transform – decrease in insulation distance

Failure mode | Factor | phenomena | result
---|---|---|---
Increase of contact resistance | Fatigue – solder clack | Connected deterioration
Breakdown | Oxidation – contact defective

Decrease in insulation resistance | Corrosion – migration | Insulation deterioration
Breakdown | Adhesion – water absorption

Transform – decrease in insulation distance
About ionic migration
## Classification of migration phenomenon

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Classification</th>
<th>Phenomenon</th>
<th>Failure part</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrochemistry</td>
<td>Ionic migration (electrochemical migration)</td>
<td>The metal ionizes, a metallic ion migrates by the electric field.</td>
<td>Between wiring for PCBs</td>
</tr>
<tr>
<td>Physical</td>
<td><strong>Electro migration</strong></td>
<td>Interaction of metallic atom and electron</td>
<td></td>
</tr>
<tr>
<td></td>
<td><strong>Stress migration</strong></td>
<td>A metallic atom migrates by the mechanical stress.</td>
<td>Aluminum wiring of semiconductor</td>
</tr>
<tr>
<td></td>
<td><strong>Thermal migration</strong></td>
<td>A metallic atom migrates by the thermal stress.</td>
<td></td>
</tr>
</tbody>
</table>

(a) Ionic migration (electrochemical migration)  

(b) Electro migration  

(c) Stress migration

Reference (b) (c): Tsuneo Ajiki: “reliability of semiconductor device”, Nikkagiren, 1988
The forms of Ionic Migration

(a) Dendrite

- Anode (+)
- Cathode (-)
- Dendrite
- Dew or moisture

Phase 1: Metallic dissolution
Phase 2: Metallic ion migrate
Phase 3: Metallic deposition

Solder dendrite on PCB

(b) CAF (Conductive Anodic Filament)

- Anode (+)
- Cathode (-)
- CAF
- Resin
- Moisture

Copper CAF in PCB

0.1mm

0.5mm
Reaction mechanism of Ionic Migration

**Anodic reaction**

\[ M \rightarrow M^{n+} + ne \quad \cdots \cdots \cdots \cdots \cdots (1) \]
\[ H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e \quad \cdots \cdots \cdots \cdots \cdots (2) \]
\[ M + H_2O \rightarrow MO + 2H^+ + 2e \quad \cdots \cdots \cdots \cdots \cdots (3) \]

**Cathodic reaction**

\[ M^{n+} + ne \rightarrow M \quad \cdots \cdots \cdots \cdots \cdots (4) \]
\[ O_2 + 2H_2O + 4e \rightarrow 4OH^- \quad \cdots \cdots \cdots \cdots \cdots (5) \]
\[ 2H_2O + 2e \rightarrow H_2 + 2OH^- \quad \cdots \cdots \cdots \cdots \cdots (6) \]
\[ 2M^{+} + 2OH^- \rightarrow M_2O + H_2O \quad \cdots \cdots \cdots \cdots \cdots (7) \]
\[ M^{2+} + 2OH^- \rightarrow M(OH)_2 \quad \cdots \cdots \cdots \cdots \cdots (8) \]

**Reaction between electrodes**

\[ 2M^{+} + 2OH^- \rightarrow M_2O + H_2O \quad \cdots \cdots \cdots \cdots \cdots (9) \]
\[ M^{2+} + 2OH^- \rightarrow M(OH)_2 \quad \cdots \cdots \cdots \cdots \cdots (10) \]
# Acceleration factor of Ionic Migration

<table>
<thead>
<tr>
<th>Factor</th>
<th>Acceleration condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>(Fast) Ag &gt; Cu &gt; Pb &gt; Sn-Pb Solder &gt; Sn &gt; Au (Slow)</td>
</tr>
<tr>
<td>Temperature</td>
<td>High Temp</td>
</tr>
<tr>
<td>Humidity</td>
<td>High humidity</td>
</tr>
<tr>
<td>Voltage</td>
<td>High voltage</td>
</tr>
<tr>
<td>pH</td>
<td>Acidity</td>
</tr>
<tr>
<td>Ionic impurities</td>
<td>Halogen material (Chlorine, Bromine)</td>
</tr>
<tr>
<td>Printed-circuit board material</td>
<td>Paper phenol &gt; Glass epoxy &gt; Polyimide &gt; Ceramic</td>
</tr>
</tbody>
</table>
Acceleration factor : materials (Pourbaix potential - pH diagrams)

Silver (Ag)

Copper (Cu)

Lead (Pb)

Tin (Sn)

immunity  corrosion

passivity
### Acceleration factor: materials (Energy of oxide-film)

**Gibbs free energy change of metal oxide-film**

<table>
<thead>
<tr>
<th>metal oxide-film</th>
<th>$\Delta G_f^\circ$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$</td>
<td>-515.47</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>-496.64</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>-321.92</td>
</tr>
<tr>
<td>ZnO</td>
<td>-321.92</td>
</tr>
<tr>
<td>SnO</td>
<td>-257.32</td>
</tr>
<tr>
<td>PbO</td>
<td>-189.33</td>
</tr>
<tr>
<td>CuO</td>
<td>-127.19</td>
</tr>
<tr>
<td>Ag$_2$O</td>
<td>-10.75</td>
</tr>
</tbody>
</table>
**Acceleration factor**: Humidity *(water–film and corrosion)*

(a) Relative humidity and corrosion of metal (iron)

(b) Thickness of water-film and corrosion speed

Reference (a): varon, w. : Trans, faraday soc., 23, 113(1927)
(b): Tomashov, N D.: corros., 20, 7t(1964)
Acceleration factor: Voltage

(a) Quantitative characteristics of elution: voltage and copper ions

(b) The relationship between applied voltage and migration occurrence
Test methods
### Test standards for Insulation evaluation

<table>
<thead>
<tr>
<th>Test Standards</th>
<th>Test Category</th>
<th>Test Result</th>
<th>Test Description</th>
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</thead>
<tbody>
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</table>
Migration test pattern on PCB

(a) IPC test pattern

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>导体径</td>
<td>0.165</td>
<td>0.318</td>
<td>0.635</td>
</tr>
<tr>
<td>导体間隔</td>
<td>0.165</td>
<td>0.318</td>
<td>0.635</td>
</tr>
<tr>
<td>重ね代</td>
<td>15.75</td>
<td>15.75</td>
<td>15.75</td>
</tr>
</tbody>
</table>

(b) IPC multi-purpose test board
Test methods: Simple migration test

(a) Water drop test

(b) Filter paper test
Test methods: Environmental migration test

Temperature / humidity chamber

Dew condensation cyclic chamber

HAST

Temperature / humidity cyclic chamber

(a) Evaluation by absorption

(b) Evaluation by dew
measurement method: Manual measurement

(1) specimen

(2) High Temp/High Humi. test

(3) Insulation resistance meter (HP4329)

(4) Insulation resistance meter (HP4339)
Insulation resistance test of PCBs
Results of Water Drop test (Cu and Ag, 2V/DC bias)

**Change in current**

Copper (Cu)

![Graph showing change in current for Copper (Cu)]

Silver (Ag)

![Graph showing change in current for Silver (Ag)]

**External appearance after testing**

- **Copper migration**
  - Image of copper migration with an arrow indicating the direction.

- **Silver migration**
  - Image of silver migration with an arrow indicating the direction.

- **Anode (+)**
- **Cathode (−)**
### Surface insulation resistance (SIR) test for PCB

**(a) Test condition**

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>40 °C, 87%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>60 °C, 87%</td>
</tr>
<tr>
<td></td>
<td>85 °C, 85%</td>
</tr>
<tr>
<td></td>
<td>1000Hr</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>PCB material</th>
<th>Glass-cloth epoxy (FR-4)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>IPC-B comb pattern</td>
</tr>
<tr>
<td></td>
<td>(Gap=0.3mm)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Applied voltage</th>
<th>50V / DC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mesurement intervals</td>
<td>1 Hr</td>
</tr>
</tbody>
</table>

**(b) Specimen**

Grass-epoxy PCB

Ionic migration evaluation system (ESPEC)

Wiring situation
Results of SIR test (Copper pattern PCB, 50V/DC bias)

Change in insulation resistance  
Change in absorption characteristic

![Graph showing change in insulation resistance and absorption characteristic over time for different conditions.](image-url)
Results of SIR test (Copper pattern PCB, 50V/DC bias)

External appearance after testing (2000Hour)

40 ㎛, 87%
No migration

60 ㎛, 87%
No migration

85 ㎛, 85%
No migration

anode (+)
cathode (-)
Example: Results of SIR test (Paper phenolic PCB)

External appearance after testing

85 °C, 85%, 50V/DC, 2000Hr

110 °C, 85%, 5V/DC, 300Hr

CAF growth

anode (+)
cathode (-)

CAF growth

CAF
Example: Results of SIR test (Flux and Dew test)

Evaluation of soldering flux
(85% 85%, 50V/DC bias)

Dew cyclic test
(5%/25 90%, 5V/DC bias)
Life estimated formula of insulation failure

IPC-9201 (Surface Insulation Resistance Handbook)

\[ t_2 = t_1 \times \exp\left(\frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \times \exp\left[b\left(\frac{1}{RH_1} - \frac{1}{RH_2}\right)\right] \times \left(\frac{A2V_2}{A1V_1}\right) \]

The Institute of Electrical Engineers of Japan (Report No. 772)

\[ AF = \exp\left(\frac{E_a}{R}\right) \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \times \left(\frac{RH_2}{RH_1}\right)^r \times \left(\frac{V_2}{V_1}\right)^n \times \left(\frac{D_1}{D_2}\right)^m \]

Ea = Activation energy (Glass Epoxy PCB = 1eV)
R = Boltzmann’s Constant (8.63 × 10⁻⁵ eV/k)
T1, RH1, V1, D1, t2 = Practice use Temp., Humi., Voltage, Electrode Distance, Time
T2, RH2, V2, D2, t1 = Accreted test Temp., Humi., Voltage, Electrode Distance, Time
B, A1, A2, r, n, m = constant (r=3, n=2)
Life estimated formula of insulation failure

\[ AF = \exp\left(\frac{Ea}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \times \left(\frac{RH_2}{RH_1}\right)^r \times \left(\frac{V_2}{V_1}\right)^n \times \left(\frac{D_1}{D_2}\right)^m \]

- \(Ea\) = Activation energy
  (Glass Epoxy PCB = 1eV)
- \(R\) = Boltzmann’s Constant (8.63 \(\times\) 10\(^{-5}\) eV/k)
- Practice Temp.(T1)=45\(^\circ\)C, Humi.(RH1)=85%
  Voltage(V1)= 5V
- Test Temp(T2)=85\(^\circ\)C, Humi.(RH2)=85%
  Voltage(V2)=5V, 2000Hr
- \(r, n\) = constant ( r=3, n=2)

\[ AF1 = \exp[1.16 \times 10^4 \times (1/318-1/358)] \]
\[ = \exp(4.1) = 59 \]
\[ AF2 = (85/85)^3 = 1 \]
\[ AF3 = (5/5)^2 = 1 \]
\[ AF = 59 \times 1 \times 1 = 59 \]

Life Time \(=\) 2000Hr \(\times\) AF
\[ = 118000Hr = 13.4\text{ years} \]

Reference: The Institute of Electrical Engineers of Japan (Report No. 772)
Solder alloy migration
Factors of Solder alloy migration

(a) SEM image of solder surfaces

(b) Standard potential of solder composition materials

<table>
<thead>
<tr>
<th>Element</th>
<th>Reaction</th>
<th>Standard Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc</td>
<td>(\text{Zn}^{2+} + 2e^- = \text{Zn})</td>
<td>-0.763</td>
</tr>
<tr>
<td>Tin</td>
<td>(\text{Sn}^{2+} + 2e^- = \text{Sn})</td>
<td>-0.138</td>
</tr>
<tr>
<td>Lead</td>
<td>(\text{Pb}^{2+} + 2e^- = \text{Pb})</td>
<td>-0.126</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>(2\text{H}^+ + 2e^- = \text{H}_2)</td>
<td>0.000</td>
</tr>
<tr>
<td>Bismuth</td>
<td>(\text{Bi}^{3+} + 3e^- = \text{Bi})</td>
<td>0.215</td>
</tr>
<tr>
<td>Copper</td>
<td>(\text{Cu}^{2+} + 2e^- = \text{Cu})</td>
<td>0.337</td>
</tr>
<tr>
<td>Silver</td>
<td>(\text{Ag}^+ + e^- = \text{Ag})</td>
<td>0.779</td>
</tr>
</tbody>
</table>
Electrochemical characteristics (Static characteristic)

Rest potential of each type solder (in 0.1M KO₃ aqueous solution)
**Electrochemical characteristics (Dynamic characteristic)**

**Simple metals**

- **Zn**
- **Pb**
- **Sn**

**Solder Alloys**

- **Sn-37Pb**
- **Sn-9Zn**
- **Sn-3.5Ag**

Current - potential curves = dissolution characteristic (in 0.1M KO₃ aqueous solution)

*Dissolution is easy*
Water Drop test - 1 (6V/DC bias)

Change in current

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Current (mA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Process of migration deposits

Sn-Pb
- 10 sec
- 20 sec
- 30 sec

Sn-Ag
- 20 sec
- 90 sec
- 123 sec

Sn-Zn
- 250 sec
- 332 sec
- 350 sec

cathode (-)
**Water Drop test - 2 (SEM analysis)**

**SEM image of migration deposits**

**Compositional analysis of migration deposits**

<table>
<thead>
<tr>
<th></th>
<th>Sn-Pb</th>
<th>Sn-Ag</th>
<th>Sn-Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
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<tr>
<td>C</td>
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</tbody>
</table>

**Sn-Pb**
- **anode (+)**

**Sn-Ag**
- **cathode (-)**

**Sn-Zn**
- **200 µm**
Surface insulation resistance test (50V/DC bias, 85% RH)

Change in insulation resistance

Sn-37Pb

Resistance (Ω) vs. Time (Hour)

Breakdown

Migration occurring

Sn-Ag-Cu

Resistance (Ω) vs. Time (Hour)

No migration

Solder migration

Migration occurring
Evaluation using mounting PCBs (THB Testing, 5/DC bias, 80 ~ 90%)

Terminal of QFP (spacing: 0.5mm)

No migration

Chip capacitance (spacing: 0.8mm)

No migration

Sn-Ag-Cu solder

END