ABSTRACT

Moisture ingress in electronic packages can lead to catastrophic failures due to electromigration and corrosion. For space application, epoxy sealed CCDs are often used, and the risk due to moisture ingress during test and storage rarely assessed. This article propose a methodology to quantify the moisture ingress speed through a sealed joint and the evolution of the moisture amount inside the cavity.

In a first step, a characterization of the organic materials is carried out. The diffusion and saturation coefficient of the moisture inside the material are calculated. Then, a 2D finite element model is built using Fick diffusion laws, and taking into account the seal, the gas and each polymeric material inside the cavity.

In the next step, the moisture concentration inside the cavity of the CCD package is monitored by means of humidity sensors throughout the experiment. Changing the moisture level of the atmosphere surrounding the package bring changes to the internal moisture content. Both ingress and release of moisture have been observed over several months. The comparison between empty and fully equipped cavities showed the influence of the various materials used inside the cavity on measurable moisture.

Finally, the experimental results are correlated with the model.

INTRODUCTION

Since the beginning of the microelectronic development, moisture has always been a major factor to control. For some performances reason (leakage current) or reliability matter (corrosion or migration risks) a low moisture content inside the package of any microelectronic device had to be aimed. This demand was increased where a high reliability and a long ground storage exposure were required, typically for space applications. For this type of applications, hermetic packages were always used except for some CCD or programmable memories. Indeed, for these products, a widow has to be sealed on the package. This window is in most of cases glued on it. The use of organic material lead to a non hermetic package.

In that case, one has to know the moisture permeation mechanism to be able to qualify the package, and to calculate the moisture content of the cavity during its ground life.

This question is now well documented for plastic packages, but has not received a comparable attention for CCD packages. The problem is here not only to calculate the moisture diffusion through a seal, but also to take into account moisture absorption of all organic materials inside the cavity.

BASIC EQUATIONS GOVERNING MOISTURE DIFFUSION

The equations governing the moisture diffusion through the plastic materials are the Fick rules, as presented hereafter:

First Fick rule:  
$$ J = -D \nabla C $$  \hspace{1cm} (1)  

Second Fick rule:  
$$ \nabla D \nabla C = \frac{\partial C}{\partial t} $$  \hspace{1cm} (2)  

Where $D$ is defined as the diffusion coefficient, depending on the temperature as defined in the Arrhenius law hereafter:

$$ D = D_0 e^{-\frac{\Delta E}{kT}} $$  \hspace{1cm} (3)  

and $C$ defined as the concentration of the diffusing species in the material (e.g. water).

In this paper, we consider that the diffusion is reversible, and that no change due to the moisture in the material properties occur.

For the governing equation relating the equilibrium between moisture at the surface of the material and in the surrounding gas ($P_{\text{sat}}$), we can use the Henry’s law:  
$$ P_{\text{sat}} = S \cdot C $$  \hspace{1cm} (4)  

where $S$ is the saturation coefficient. This coefficient depends also on the temperature following an
Arrhenius law: \( S = S_0 e^{-\frac{\Delta E_a}{kT}} \) (5). This last assumption is a simplification and should be verified in the future.

**ORGANIC MATERIALS CHARACTERISATION**

As stated previously, the diffusion, and saturation coefficients are two types of data which depends on the material. For our package configuration, three different organic materials were used:

Material A: used as a sealing material was an epoxy

Material B: used as an insulating layer was a modified polyimide,

Material C: used as die and substrate attach was a silver filled epoxy.

Each of this material has been characterized at room temperature. First, plates of polymerized material of the following dimensions have been prepared: 2cm² area and about 1mm thickness. Then, the plates have been dried (120 hours under vacuum), and immersed in water at ambient temperature. It has been related [2] that the state of the water (vapor or liquid) does not significantly change the diffusion coefficient value for epoxies. The rate of moisture ingress in the material is then measured by periodic weights of the samples. At the end of the experiment, a moisture content measurement of the samples has been carried out using the Karl-Fisher method. The results are in agreement with the values calculated by weight measurement and are presented in the table hereafter.

In case of plates with a thickness much smaller than other sides, the samples can be considered as plane-sheets. In this case [1] gives one solution of the one dimension Fick equations:

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} e^{-\frac{n^2 D_t}{(2n+1)^2} \frac{l^2}{4}}
\]

were \( l \) is the plate thickness, \( M_t \) the weight gain at the time \( t \) and \( M_\infty \) the stabilized weight gain. If \( C \) of equation 4 is expressed in weight percentile, \( M_\infty \) is the saturation coefficient.

For times near to zero, equation (6) can be simplified:

\[
\frac{M_t}{M_\infty} = \frac{4}{\pi^2} \left( \frac{D_t}{l} \right)^{1/2}
\]

\( D \) and \( S \) (or \( M_\infty \) ) values calculated with equation (7) are as follows:

<table>
<thead>
<tr>
<th>Material</th>
<th>( D ) (cm²/s)</th>
<th>( M_\infty ) (% weight)</th>
<th>( M_\infty ) (Karl Fisher) (% weight)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5.3E-09</td>
<td>3.2</td>
<td>3.3</td>
</tr>
<tr>
<td>B</td>
<td>1.3E-08</td>
<td>1.9</td>
<td>1.8</td>
</tr>
<tr>
<td>C</td>
<td>2.6E-09</td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>

**Figure 1**

Some remarks can be drawn by this characterization. As expected [7], modified polyimide (B) absorbs much faster than epoxy materials, but this type of polyimide has a low saturation coefficient. As expected too, the filled epoxy absorbs less moisture than the filled ones. The diffusion coefficients are consistent with the published values ([2], [8]-[11]). For the filled epoxy (C), a correction of the measurements has been applied in order to take into account a loss of material during the test, due to its fragility.

**FINITE ELEMENT ANALYSIS**

**Analogy thermal/moisture diffusion**

In order to minimize the computation time, a known analogy between thermal conduction and diffusion of species in a material has been used. The thermal conduction equation can be written as follows:

\[
\nabla \cdot (k \nabla T) = \frac{\partial}{\partial t} (\rho C_p T)
\]

Where \( \rho \) = density, \( C_p \) = Specific heat and \( k \) = Thermal conductivity. This differential equation is the same as equation (2). Then if we consider:

- \( D \) as a thermal conductivity
- \( C \) as a temperature and
- \( \rho C_p \) as equal to 1, we can use any finite element thermal software to compute the moisture concentration in a material (provided that the temperature is kept constant). Nevertheless, in case of different materials (or gas and materials), a moisture concentration discontinuity exists at the interface. It is then convenient to use relative concentration (ratio concentration in the material/maximum concentration in the material) to overcome this difficulty. In this case, and in order to be compliant with the first Fick law, we have to consider that the material has an equivalent specific heat of \( M_\infty \), an equivalent density of \( d \) and an equivalent conductivity of \( K' \):

\[
d \text{ being the density of the material,}
\]
The second Fick law is then re-written:

$$\nabla \cdot (D \cdot M_{\infty} \cdot d) \nabla \left( \frac{C}{M_{\infty}} \right) = d \cdot M_{\infty} \frac{\partial \left( \frac{C}{M_{\infty}} \right)}{\partial t}$$

(9)

With this formulation, one can remark that the temperature (moisture relative concentration) can be more than 100%. In this case, the model is no longer valid, and condensation should be taken into account.

For simulating the moisture diffusion in atmosphere (assimilated to air), the following parameters have been used:

$$D=0.2 \text{cm}^2/\text{s}; \quad M_{\infty}=100\%; \quad d=8 \times 10^{-4} \text{ g/cm}^3$$

For each material, the calculated coefficients of equation 8 are:

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$</th>
<th>$\rho$</th>
<th>$C_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.1E-05</td>
<td>1200</td>
<td>3.32</td>
</tr>
<tr>
<td>B</td>
<td>2.9E-05</td>
<td>1200</td>
<td>1.83</td>
</tr>
<tr>
<td>C</td>
<td>5.3E-06</td>
<td>1800</td>
<td>1.14</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>16</td>
<td>0.8</td>
<td>100</td>
</tr>
</tbody>
</table>

Table II

2D simulation

The simulated package contains 2x10 CCDs and 10 detectors. These dice are glued on substrates which are assembled inside the package with the same epoxy (type C). The substrates are partly coated with an insulating layer made of material B. The package window is sealed on a cover with the epoxy A. The only simulated parts are each organic material and the outer and inner atmosphere. To save calculation time, a 2.5D model has been established and a rough mesh has been used. The length of each element has been introduced in the calculation to take into account the relative length of the seal and the attachment materials. At the end, we used the symmetry of the package. The mesh is presented hereafter; the letters represent the polymer material type.

Figure 2

An example of the calculation result corresponding to a 2600h exposure with the values provided in table II is given in figure 3. The boundary condition was a 100% relative humidity, and the initial condition was a 0% relative humidity of the seal and cavity. As can be seen, a large gradient is established inside the seal (from 100 to 15%). The dice adhesives show a reduced gradient (about 3%) and the substrate adhesive moisture concentration is maintained at 0% in its middle, due to the length of the path.

Figure 3

This figure show that it would be interesting to calculate the influence of the seal shape, and of the adhesive inside the cavity on the package moisture content.

Seal shape influence

As can be seen in figure 2, the seal shape is complex. Its final status depends on the process used to deposit the adhesive. The model allows us to perform a sensibility study, in order to quantify the impact of the shape of the seal. 4 shapes (presented in figure 4) have been modeled.

Figure 4

As expected, figure 5 shows that the seal shape has a dramatic effect on the internal moisture evolution. Here, the moisture ingress speed cannot be simply calculated with a resistance like calculation as described in [3], because the
interface surface is not taken into account. Indeed, figure 5 shows that seals B and D give comparable results although they have very dissimilar resistances (represented as the ratio average height/width). Seal D shows a slight longer response time than B, due to the amount of epoxy in the seal.

![Internal moisture evolution for different seals at 100% RH 3000h, and 0% RH 2200h](image)

**Figure 5**

**Adhesive influence**

The large gradient found in the adhesive under the substrate could indicate that the adhesive have an impact in case of long term exposure on moisture desorption. The figure hereafter shows that this effect is not higher than 10% of the total amount of internal moisture. This result is of course only valid for this type of package. In case of higher ratio cavity volume/adhesive volume, this effect could be much more important.

![Internal moisture evolution for seal D at 50% RH 4 years, and 0% RH 4 years with and without adhesive](image)

**Figure 6**

**EXPERIMENT**

The next part describes the experiment itself. Mixed Relative Humidity / Temperature sensors were implanted inside variously equipped CCD packages. These packages were then submitted to known ambient moisture concentrations while the internal moisture content was monitored.

**Moisture sensors**

The sensor selected for the experiment has the main advantage to incorporate a Relative Humidity (RH) sensor and a Temperature sensor on the same metal package (TO-5). This ensures that the measured temperature is identical to the one seen by the RH sensor.

The moisture content needs to be expressed in volume concentrations (ppmv) which does not depend on the temperature.

The following formula computes the Dew Point temperature (DP) from the RH and temperature:

If \( \text{DP} > 0 \)

\[
\text{DP} = \frac{\ln \left( \frac{\text{RH}}{100} \right) + 17.502 \cdot T}{2409 + T} - 240.9
\]  

If \( \text{DP} < 0 \)

\[
\text{DP} = \frac{\ln \left( \frac{\text{RH}}{100} \right) + 17.502 \cdot T}{2409 + T} - 240.9
\]

with

- \( \text{RH} \): Relative humidity (%)
- \( T \): Ambient Temperature (°C)
- \( \text{DP} \): Dew Point (°C)

Then the moisture concentration (ppmv) is obtained from the previously computed \( \text{DP} \):

\[
\text{ppmv} = \frac{10^6 \cdot \text{e(DP)}}{P - \text{e(DP)}}
\]

with

- \( P \): Total Pressure (mbar)
- \( \text{e(DP)} \): Vapor Pressure (mbar)

\( \text{DP} > 0 \)

\[
\text{e(DP)} = \left(1.0007 + 3.46 \cdot 10^{-6} \cdot P\right) \cdot 6.1121 \cdot \exp \frac{17.502 \cdot \text{DP}}{2409 + \text{DP}}
\]

\( \text{DP} < 0 \)

\[
\text{e(DP)} = \left(1.0007 + 3.46 \cdot 10^{-6} \cdot P\right) \cdot 6.1121 \cdot \exp \frac{17.502 \cdot \text{DP}}{2409 + \text{DP}}
\]

The existing CCD package leads were used to connect the sensors (see figure 1).
The CCD packages were baked and then sealed in a controlled atmosphere. The proper operation of the sensors was carefully checked before going further in the experiment.

**Experimental conditions**

The prepared packages were submitted to various humidity environments using the apparatus described in figure 7. Dry Nitrogen is circulated through a humidifier to get the proper moisture concentration, and then enters the chamber enclosing the CCD packages. The generated moisture concentration is measured by a Dew Point hygrometer. The purpose of the flowmeter is to ensure the proper gas flow (optimal for the Dew Point hygrometer).

The experiment was run on 4 different packages:

- Specimen 1 (Narrow seal, Equipped)
- Specimen 2: L88 (Large seal, Equipped)
- Specimen 3: A3-090 (Large and long seal, Empty)
- Specimen 4: A4-089 (Large and short seal, Empty)

The specimen 1 package was submitted to the following environments:

- 1 week: Cycle 50% RH (12 hours) / Dry (12 hours)
- 8 weeks: 50% RH
- 8 weeks: 100% RH
- 1 week: +5°C Vacuum
- 24 weeks: Dry

The Specimen 2 to 4 packages were submitted to the following environments:

- 13 weeks (8 weeks for the package A4-089): 30% RH
- 14 weeks: Dry

The experiment was run at room temperature. The Relative Humidity and Temperature were measured on a daily basis.

**Results**

The results are presented in Figure 8 (specimen 1) and figure 9 (other specimens).

The graphics represent the moisture concentrations (ppmv) inside the CCD packages against the time. The equations described above have been used to convert the Relative Humidity and Temperature to ppmv. The moisture concentration outside the packages have also been plotted on these graphics.
MODEL CORRELATION

The correlation (taking into account the seal shape of the package) between the results obtained with specimen 1 and the simulation is illustrated in the figure hereafter. To simulate the first surprising decrease in inner atmosphere moisture content, it has been stated that the gas inside the cavity was not as dry as the organic materials. This has been explained after the experiment by a control of the process. Then as initial condition, the inner atmosphere and interface relative concentrations were set to 1.6%. The rest of the organic material was set to 0%.
One can see that the model is able to give a 4%RH accuracy. But this error seems mainly due to a response time which is much longer than calculated. This effect can also been assessed with the correlation of the model specimens 2 and 4:

Three hypothesis could explain the differences between the model results and the measured values. The area between epoxy of attached components and inner atmosphere can be increased due to decohesion; the saturation coefficient of the organic materials could depend on the moisture concentration, and finally, the water adsorbed on the inner package surfaces could influence the total moisture inside the cavity. The first hypothesis can be easily canceled because comparable differences between model and experiment are found for empty and equipped packages. The third hypothesis can also be canceled, if we compare the curves of figure 11. We can see that the moisture difference at the end of the 33% RH external atmosphere sequence is much higher for the empty package than for the equipped one. The adsorbed water should be for both case nearly the same.

Then, the only explanation would be a moisture dependence of the diffusion coefficient of the epoxy A. If we analyze the curves, a threshold seems to be located at about 5%RH. This result should be verified by material characterization.

CONCLUSION

This paper proposed a methodology to assess the moisture ingress and evolution inside a non hermetic cavity such as a CCD package. This methodology is based on material characterization, package modeling, and measurement. Although this methodology based solely on diffusion modeling showed some limitations, it is accurate enough to simulate the on ground life of the device, and its behavior after the launch in case of space application.

The main results found in this study are the following:

- the moisture ingress inside the package have a minor effect on moisture evolution in our case, but could lead in other cases (where the ratio free volume/adhesive volume is smaller) to different results;
- the organic seals have to be accurately described in term of material property (for different relative humidity) and shape.

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REFERENCES