

Transport of Corrosive Constituents in Epoxy Moulding Compounds

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Abstract

Epoxy moulding compounds are the leading encapsulating material in today's microelectronic packaging industry. These compounds are hydrophilic and absorb moisture when exposed to humid environments. As a result of the absorbed moisture, ions in the material will become more mobile. This, in combination with high electrical field strengths due to the continuously decreasing feature sizes of ICs, will result in a large flux of ions toward charged interfaces, such as aluminium bond pads. Hence, ion-related failure mechanisms, such as corrosion, might become more prominent. In this paper a method for obtaining the diffusion coefficients of the different ions at elevated temperatures in saturated moulding compounds is reported. This method is based on determining the total ionic content by ion chromatography after immersing a presaturated sample in a water bath containing the ions and fitting the data to a Fickian diffusion model. The measured diffusion coefficients of NaCl in a commercially available moulding compound at 30 °C and 60 °C are $2.9 \times 10^{-13} \text{ m}^2/\text{s}$ and $9.5 \times 10^{-13} \text{ m}^2/\text{s}$, respectively. These coefficients are used to compare experimental data for bond pad corrosion as function of humidity, time and bias with a multi-physics finite element model.

1. Introduction

Since the introduction of plastic-encapsulated microelectronics, corrosion has been one of the major reliability issues. To qualify the reliability of microelectronic products, lifetime tests are performed at accelerated conditions to reduce testing time. For these reasons, lifetime tests at elevated temperature and humidity are part of the total testing procedure. To extrapolate the lifetime obtained from these test to application conditions, empirical models, such as the well-known Peck model, are commonly used [1,2]. These models all assume that failure is accelerated by the applied temperature and humidity. The effect of electrical bias, however, is not yet clearly specified and is included in these models as an unknown function of bias voltage. The effect of the applied electrical bias is twofold, (1) bias directly influences the corrosion kinetics and (2) bias results in an electrical field that attracts the ions to the bond pads, which will eventually lead to a higher corrosion rate. The latter effect is controlled by the bias as well as the transport properties of the corrosive ions. In literature, however, not much has been reported on the transport properties of corrosive species, such as chloride and sodium in epoxy moulding compounds.

Lantz and Pecht [3] reported the diffusion of NaCl in a commercial biphenyl moulding compound to be slower than the diffusion of moisture. A diffusion cell was used to measure the diffusion coefficient of NaCl, while in addition Time-of-Flight Secondary-Ion-Mass-Spectroscopy (TOF-SIMS) was used to show the concentration profile of a cross-section of the sample. Due to the presence of water the mobility of the ions in a moulding compound will increase, and hence its electrical resistivity decreases. Rauhut [4] showed that after 1000 hours of exposure to steam at 103 kPa pressure, the volume resistivity decreases approximately by a factor of 100 for a highly filled biphenyl compound and by a factor of 300 for a regularly filled epoxy cresol novolac compound.

In this paper we present a method for determining the diffusion coefficients of water-soluble ions in epoxy moulding compounds. This method uses ion chromatography to determine the ion content of the sample after different exposure times to a water bath containing the ions. Next, a finite element model is used to show that there is a large difference between the bulk concentration of ions and their concentration at the bond pads due to the applied electrical field. Finally, the results of the finite element model combined with results from literature are used to show the effect of bias voltage on corrosion.

2. Background

In this section a general scheme for aluminium corrosion in the presence of chloride will be presented. However, the possible sources of corrosive ions that will contaminate the compound will be discussed first.

Small concentration of ions are always present in moulding compounds, examples of these are chlorine (Cl^-), sodium (Na^+), potassium (K^+) and bromine (Br^-). Some of these ions are due to the chemical synthesis of the subcomponents of the resins. Epichlorohydrin-based epoxy rings are typical resin components, since they readily react with alcohol and phenols. Functional groups are attached to these epoxy rings in the presence of NaOH. This will finally lead to the formation of NaCl. Although they are purified, a small concentration of NaCl always remains in the resin. Besides, processing steps such as etching of metallizations can introduce corrosive ions. Ions liberated from the die-attach glue at high temperatures might be another source of contamination.

Aluminium in a humid environment corrodes quickly, creating a protective oxide film. In case of an applied electrical potential a distinction can be made between corrosion at the anode and cathode.

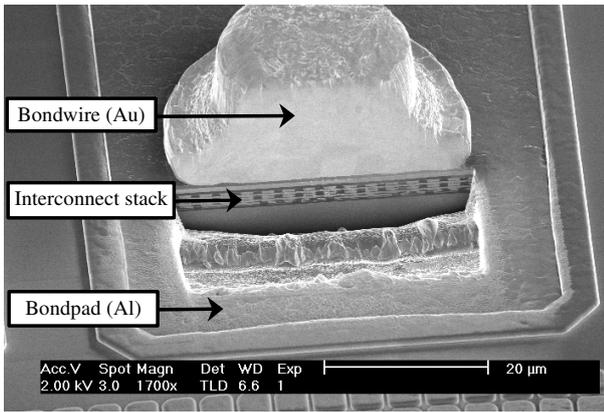
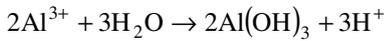
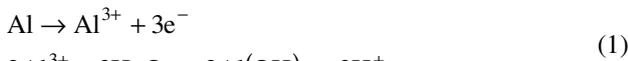
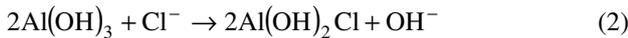


Figure 1: Cross section of the bond ball on an aluminum bond pad.

The chemical reactions occurring at the anode are given by [5,6]:



Dehydration of $\text{Al}(\text{OH})_3$ will lead to alumina (Al_2O_3). The anode attracts negatively charged ions, such as chloride and bromine. These ions will attack the protective oxide layer resulting in pitting corrosion. It is generally accepted that pitting is mainly caused by the attack of chloride, hence [5,7,8]:



After dissolution of the protective oxide film the bare aluminium corrodes according to:



The corrosion product now diffuses into the bulk solution and hydrolyzes yielding $\text{Al}(\text{OH})_3$ and Cl^{-} [5-9]. Note that a small concentration of chlorine ions can cause a large amount of corrosion since these ions are liberated during the process.

The corrosion scheme presented above assumes pure aluminium. The aluminium used for bond pads, however, contains amongst other materials a small amount of copper. The copper is present in the aluminium in the form of grains. This in combination with adsorbed electrolyte on the surface will result in a highly active galvanic cell, which will eventually lead to an increase of the corrosion rate [9].

3. Estimating the diffusion coefficient of ions

In this section a technique capable of measuring the mobility of ions will be described. In addition the mobility of sodium (Na^{+}) and chloride (Cl^{-}) ions in a commercially available moulding compound will be reported and discussed.

To obtain specimens a biphenyl-based compound has been moulded onto HVQFN lead frames. After moulding, the compound can easily be torn off the lead frames yielding 600 μm thick strips. These strips are cut into smaller parts with dimensions of 20, 10 and 0.6 mm for the length, width and thickness, respectively. These small

strips are then soaked in demi-water for 96 hours at 80 °C. Subsequently two sets of five strips are placed in separate beakers containing 200 ml demi-water at 30 °C and 60 °C. After equilibrating the specimens for 24 hours, NaCl was added to obtain a 0.15 M solution. The beakers are covered with aluminium foil to prevent the water from evaporating. The specimens are taken out of the salt solution at different times and were dried to remove any redundant solution from the surface. The specimens are transferred into separate pressure vessels where the ions are extracted from the moulding compound. The vessel consists of a PTFE (Teflon) inner shell with a metal jacket containing 20 ml ultra-pure water. The ultra-pure water extracts are finally analysed by ion chromatography. The results of this analysis are given in Fig. 2.

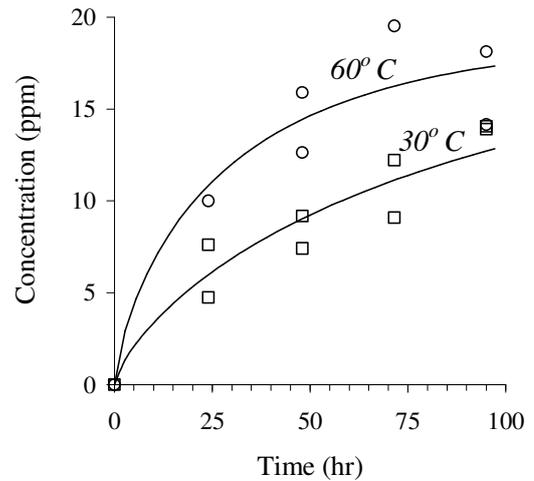


Figure 2: NaCl absorption of a biphenyl moulding compound in 0.15 M solution at 30 °C and 60 °C.

It is assumed that in the absence of an electrical field the diffusion of ions is governed by Fick's law. In this case the increase in concentration is approximately given by the expression [10]:

$$c(t) = c_{\text{sat}} \left\{ 1 - \exp \left[-7.3 \left(\frac{D \cdot t}{h^2} \right)^{0.75} \right] \right\} \quad (4)$$

where c is the concentration of species at the time t , D the diffusion coefficient and h the thickness of the specimen. Subscript sat denotes the saturation level. Fitting Eq. (4) to the results of Fig. 2 yields the following estimations for the diffusion coefficient, $2.9 \times 10^{-13} \text{ m}^2/\text{s}$ and $9.5 \times 10^{-13} \text{ m}^2/\text{s}$ for 30 °C and 60 °C, respectively.

The electrical conductivity of dry epoxy moulding compounds at room temperature (25 °C) is typically in the order of picoSiemens per meter. The ion conductivity of a material is given as:

$$\sigma = F \sum_i c_i \cdot z_i \cdot u_i \quad (5)$$

where F is Faraday's constant (96485 C/mol), z the valence number, c the concentration and u the mobility of ionic species i .

The Nernst-Einstein relation can be used to write the ionic mobility in terms of the diffusion coefficient, thus:

$$u = \frac{z \cdot F \cdot D}{R \cdot T} \rightarrow \sigma = \frac{F^2}{RT} \sum_i c_i \cdot z_i^2 \cdot D_i \quad (6)$$

where R is the universal gas constant (8.3144 J/(K·mol)). The conversion factor from mol/m³ to ppm depends on the mass density of the moulding compound and the atomic mass of the ions. The atomic mass of NaCl is 58.4 g/mol and the mass density of most commercial compounds is in the range of 2 to 3 g/mm², hence the conversion factor is approximately 25. Assuming the total amount of mobile ions in a compound to be 2 mol/m³ with z^2 equal to 1 yields an average diffusion coefficient in the order of 10⁻¹⁸ m²/s. This suggests that the presence of water has a significant influence on the transport properties of ions in epoxy moulding compounds.

4. Finite element model

A multi-physics finite element model is used to estimate the effect of an applied electrical bias on the local concentration of ions at the bond pad-moulding compound interface. The flux of ionic species is given by:

$$J_i = -\frac{D_i c_i}{RT} \text{grad}(\mu_i) \quad (7)$$

where μ_i is the chemical potential of species i given by:

$$\mu_i = RT \ln(c_i) + z_i \phi - RT \ln(1 - c_i c^*) \quad (8)$$

where ϕ is the electrical potential, c^* the reciprocal of the maximum concentration of species and e is the elementary charge (1.602×10⁻¹⁹ C). The chemical potential of the last term of Eq. 8 is in analogy with the potential for hard sphere mixtures reported by Bikerman [11]. Substituting Eq. 8 into 7 yields:

$$J_i = -D_i \left\{ \text{grad}(c_i) \left[1 + \frac{c^* c_i}{1 - c_i c^*} \right] + \frac{F c_i}{RT} \text{grad}(\phi) \right\} \quad (9)$$

where the concentration of species is given in mol/m³ and $\text{grad}(\phi)$ is the electrical field. Eq. 9 follows from the Nernst-Planck equation for the transport of ions, with an additional term to correct for the maximum concentration of species.

The electrical field is given by the Poisson equation:

$$\text{div}(\epsilon_r \epsilon_0 E) = F \sum_i z_i c_i \quad (10)$$

where ϵ_r is the relative permittivity and ϵ_0 the permittivity of vacuum (8.854×10⁻¹² F/m). At charged interfaces an electrostatic double layer of a few times the Debye length will be formed. In this layer the ions are distributed such that they screen out the electrical field. For monovalent ions the Debye length is given as [12]:

$$L_D = \sqrt{\frac{\epsilon_r \epsilon_0 RT}{2F^2 C_\infty}} \quad (11)$$

where C_∞ denotes the concentration of the bulk solution. It can be readily seen from Fig. 3 that in commercial moulding compounds the Debye length will be in the range of 1 to 100 nm.

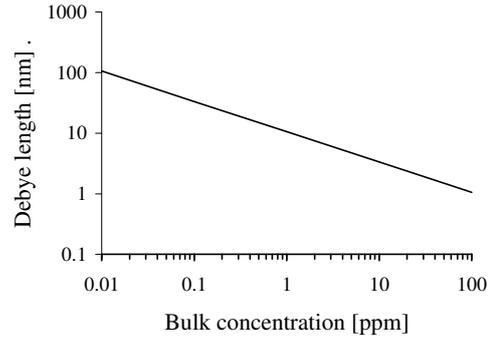


Figure 3: Debye length vs. bulk concentration of ions, $\epsilon_r=3.8$, $T=298$ K, ppm to mol/m³ ratio is 25.

Since the length in which the electrical field screens out is in the order of nanometers, an extremely fine grid is necessary at the electrode interface. This will increase the computing time tremendously. Therefore it becomes almost impossible to solve large three-dimensional models. In the absence of concentration gradients, however, the electrical field solely induces the transport of ions. Hence, initially, Eq. 10 remains to be solved without redistribution of ions. Therefore, the results of Eq. 10 will be used to simplify the geometry of the model as much as possible in such a way that the initial electrical field remains equivalent with the original model.

A three-dimensional model according to Fig. 6 is used as a starting point. Two times a quarter of a bond wire including a bond ball on a pad has been modelled using COMSOL Multiphysics 3.3 (fig. 6, left). The bond pads are placed on a 4 μm thick interconnect stack. Although this stack consists of a metal interconnect structure and a dielectric material it is modelled as a solid material with a relative dielectric constant equal to 1. It is assumed that the die underneath the interconnect stack results in a zero potential at the bottom of this stack. The relative dielectric constant of the moulding compound is set to 3.8. An electrical potential of +1 Volt and -1 Volt is set to the left and right bond wire, respectively. The electrical field ratio in z to x -direction of the area between the bond balls and under the dashed line of Fig. 6 is plotted in Fig. 4. It can readily be seen that the electrical field perpendicular to the plane of Fig. 4 is negligible compared to the electrical field parallel to this plane.

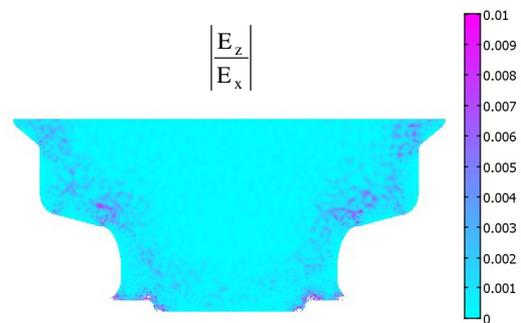


Figure 4: Norm of E_z/E_x for the area between the bond pads (fig. 6); $g=15$ μm , $\epsilon_{r,mould}=3.8$, $V=1$ Volt.

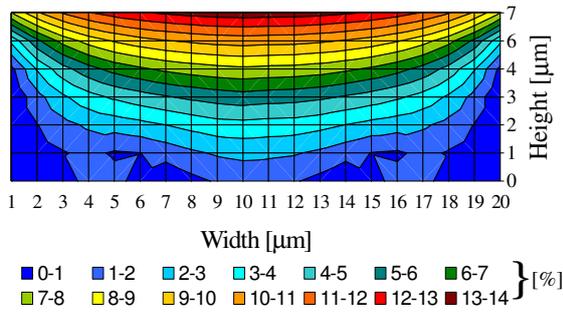


Figure 5: Difference in electrical potential between the original model (fig. 6, middle) and simplified model (fig. 6, right) for the dashed area; $V=1$ Volt; $\epsilon_r=3.8$.

Consequently, a two-dimensional model is created (Fig. 6, middle). Since the concentration of ions at the bond pad interface (indicated by P) are of interest in this research, the geometry of the two-dimensional model can still be simplified. Therefore straight lines have replaced all radii of the bond ball (Fig. 6, right). Furthermore, we have decreased the height as much as possible. To show that this model results in a sufficiently accurate estimation of the electrical field between the bond balls, the area indicated by the dashed lines has been analysed (Fig. 6 right). This area has been divided into squares of one by one micrometer. The electrical potential for both the original model (Fig. 6, middle) and the corresponding nodes of the simplified model is plotted in Fig. 5. It can be seen that around the points of interest the error in electrical potential is never larger than 5%. Therefore, we feel reassured in using the simplified model.

Now Eq. 9 is added to this model to include the transport of ions. All the boundaries of the model are set to insulating. Elements at boundaries where an electrical potential is applied are distributed such that their thickness is in the order of the Debye length (inset Fig.6).

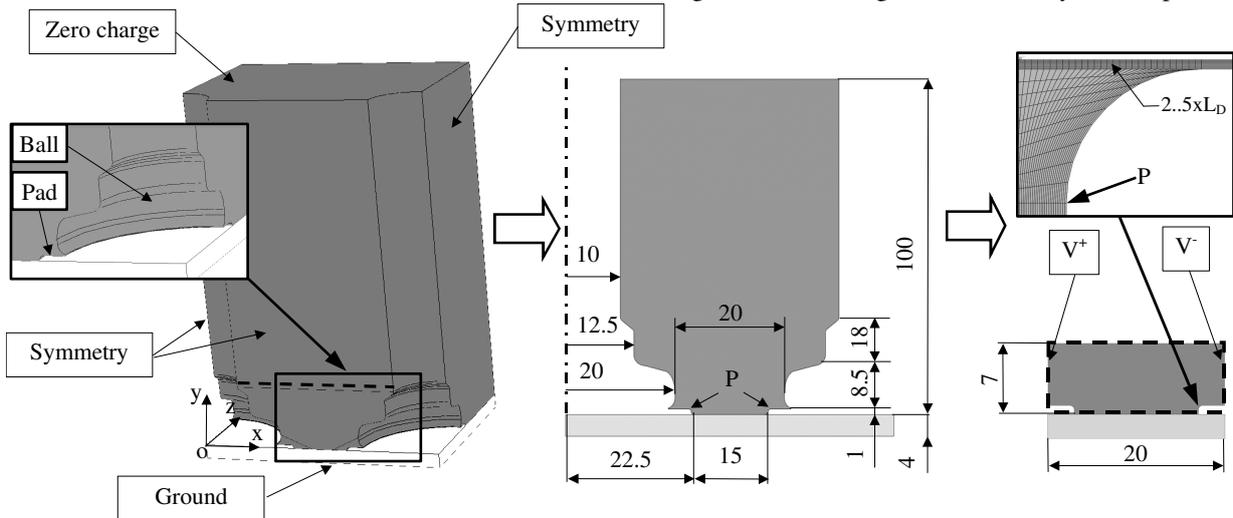


Figure 6: Reduction of the complexity of the FE model; left: 3-D model, middle: intermediate 2-D model, right: final 2-D model; moulding compound indicated by dark grey, interconnect stack by light grey; dimensions in micrometer.

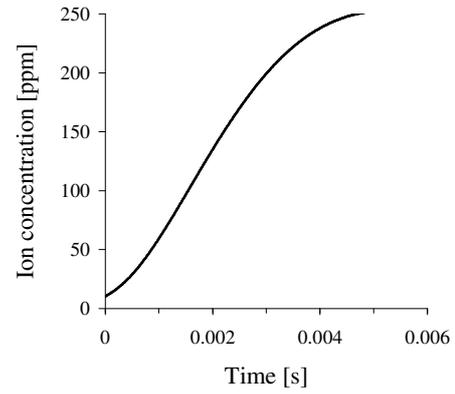


Figure 7: Concentration vs. time at P; $V=1$ Volt, $\epsilon_r=3.8$, $T=358$ K, $C_\infty=10$ ppm, $D=10^{-12}$ m²/s, $C_{max}=250$ ppm.

It is assumed that 5 M is the maximum concentration of ions that can be dissolved in water. The weight gain due to water uptake of a moulding compound is typically around 0.2%. Therefore the maximum concentration of ionic species is set to 10 mM (≈ 250 ppm). One species of anions and one species of cations are present in the moulding compound. The diffusion coefficients of both species are assumed to be equal. Next, the temperature is set to 85 °C and the ions are initially randomly distributed with a concentration of 10 ppm.

4. Results

A time-dependent solver has been used to calculate the increase in concentration. A typical plot of the increase in concentration versus time is given in Fig. 7. It can readily be seen that the concentration will reach the maximum concentration of 250 ppm. The time until this saturation level will be reached will decrease with an increase of the applied potential at the electrodes. Fig. 8 shows the decrease in time to saturation as a function of the applied potential. Determining the time to saturation is not completely unambiguous. Therefore not all the points in Fig 9 are on a straight line. Secondly, at low potentials

the concentration at the electrodes will not reach the maximum level. Therefore the relation between saturation time and low potentials differs from the relation of Fig. 8.

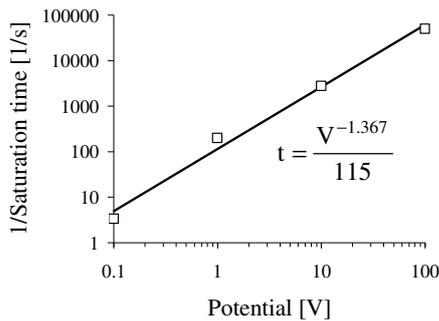


Figure 8: Reciprocal of the saturation time as a function of the applied voltage; $\epsilon_r=3.8$, $T=358$ K, $C_\infty=10$ ppm, $D=10^{-12}$ m²/s, $C_{max}=250$ ppm, $V=0.1..100$ Volt.

From Fig. 8 it can be seen that the time to saturation is negligible for typical applied potentials used during lifetime tests. However, for less mobile ions the time to saturation will increase, this is shown in Fig. 9. For a high diffusion coefficient the saturation level is reached almost instantaneously, whereas for low diffusion coefficients it will take days until this level is reached.

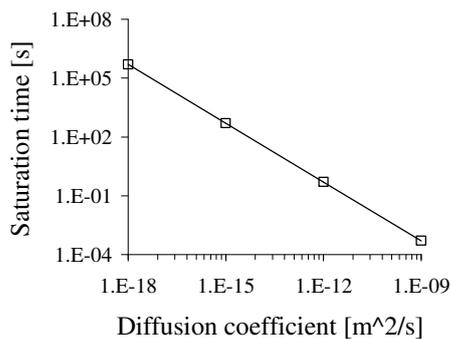


Figure 9: Saturation time as a function of the diffusion coefficient of the ionic species; $\epsilon_r=3.8$, $T=358$ K, $C_\infty=10$ ppm, $V=0.1$ Volt $C_{max}=250$ ppm, $D=10^{-18}..10^{-9}$ m²/s.

5. Conclusions

From literature and the observations reported here, it can be concluded that moisture has a significant influence on the transport properties of ions in epoxy moulding compounds. However, the time scale of the transport of ions in water-saturated compounds is negligible compared to the corrosion time scale. This is in contradiction with the model for the failure rate due to bond pad corrosion reported by Dunn and McPherson [5]. They assume that the corrosion is controlled by the transport of corrosive species. The data reported in this work suggest that there will be an induction time during lifetime test where the corrosion rate is very limited. This induction time finds its origin in the time needed for the moisture to ingress into the moulding compound and thus mobilizing the ions. This is in agreement with the failure rate model proposed by Pecht [6]. Next, in our model the concentration at the

bond pad interface will have a maximum, independent of the applied potential. This maximum concentration might increase significantly when there are flaws in the bonding of the moulding compound such that water can adsorb onto the bond pad. According to Paulson and Lorigan [8] the corrosion rate is proportional with $\log(c)$, where c indicates the concentration of corrosive species. So at these flaws the corrosion rate increases. Finally, in the model described above no fluxes of species due to chemical reactions are considered. Since the transport of species through the compound is much faster than the corrosion rate this is assumed to be a good approximation.

Acknowledgments

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