

# High-Resolution Measurements of Water Permeability and Solubility in Microelectronic-Casing Made of a Hydrophobic Polymeric Composite

Tomer Zimrin,<sup>1</sup> Yaara Freeda Haruvy,<sup>2</sup> Shlomo Margel<sup>1</sup>

<sup>1</sup>Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel

<sup>2</sup>Soreq Nuclear Research Center, Yavne 81800, Israel

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**ABSTRACT:** Exposing the composite polymeric casing of integrated circuits (ICs) to water results in miniscule water absorption, followed by its permeation throughout the packaging, and component damage. Studying water penetration and solubility mechanisms in the IC casing is crucial for understanding water-related damage mechanisms and protection against them. The main analytical challenge, hereafter, stems from the need to study miniscule water amounts (<0.5 wt %) capable of penetrating the casing, despite its hydrophobic nature. In this article, a TGA has been employed to study the water uptake kinetics in the casing, and to decipher the related water penetration mechanisms. High-resolution measurements of water adsorption and desorption profiles were performed, followed

by calculations of the related activation energies and solubility enthalpies. These data were correlated with a relatively new model that assigned the primary locales of the adsorbed water to the compatible filler-polymer interface. Thus, water permeability is related to molecules hopping between these sites. Finally, we have shown that for the IC casing in our study, the activation energy of water permeation is related to the binding energy of H<sub>2</sub>O onto the Si-O-Si groups at the fused-silica-filler surface, where they desorb, hop, and reabsorb. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4523–4527, 2006

**Key words:** composites; diffusion; adsorption; thermogravimetric analysis; gas permeation

## INTRODUCTION

Integrated circuits (ICs) are currently encapsulated in polymeric casings, which, when compared with the ceramic-casing materials used prior to the 1980s, allow substantially faster production and lower prices.<sup>1</sup> From the 1990s, sophisticated molding materials and techniques facilitated the required performance and conquest of more than 97% of the market by polymer-encapsulated ICs.

Water impermeability is a crucial performance challenge for modern IC casing and its reliability requirements.<sup>2</sup> This challenge has been further complicated by the introduction of novel IC materials,<sup>3–5</sup> which are more water-sensitive. The ever-increasing density of device-features on a single chip,<sup>6,7</sup> as well as the ever-increasing reliability requirements,<sup>8</sup> implies an increasing exigency to address the challenge of studying the water permeability and the subsequent IC casing impermeabilization.

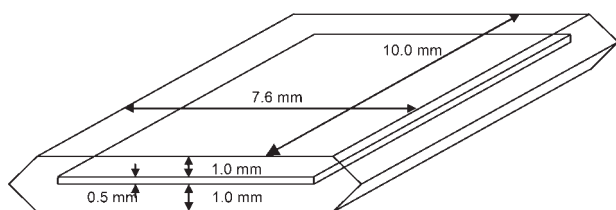
The currently employed IC casing materials, introduced in the late 1970s, are composite materials comprising a ceramic filler (65–80%), a crosslinked

polymeric matrix (up to 30%), and additives, such as flame retardants, etc.<sup>1</sup> These casing materials are characterized by very low water solubility and the diffusivity necessary for high performance reliability under moist conditions. Nevertheless, because of trace penetration of water through the casing, moisture-induced failures of the chip are detected in ultramodern ICs. Among these failures, the most prominent route was tracked to a strong interaction of penetrating water with the passivation layer, which hampers its dielectric characteristics and subsequently the entire IC performance.<sup>8</sup>

In view of such failures, the accurate analysis and clear modeling of water penetration into the casing of modern ICs have become increasingly important. Drozdov et al. recently suggested a fundamental mechanism for anomalous nearly-Fickian water permeability through hydrophobic composite polymers containing a mildly hydrophobic filler.<sup>9</sup> According to their model, water molecules hop between the residence sites at the hydrophilic filler moieties through the hydrophobic matrix. The water solubility in the composite casing material actually reflects the water molecules attached to the relatively hydrophilic surfaces of the filler. This was the foundation for our IC water penetration model.

Three analytical measuring strategies for solubility, diffusion, and permeability of fluids through poly-

Correspondence to: T. Zimrin (zimrint@mail.biu.ac.il).



**Figure 1** ICs' illustration: The submerged metal plate divides the wrapping composite polymeric casting of the integrated circuits into two similar separated parts. Other parts (such as the die, lead frame, etc.), because of their negligible dimensions, were omitted.

mers are well known. They are integral permeation, differential permeation, and the sorption rate.<sup>10</sup> However, the need to study the permeability of trace amounts of water in the hydrophobic casing extends these analytical techniques to their practical limits, and has not yet been performed on commercial ICs, where the poor signal-to-noise ratio has become a great analytical challenge.

Meeting this analytical challenge of high-resolution measurements of miniscule amounts of water in the casing material of real ICs at various stages is the primary objective reported and discussed in this article. Processing these data into the diffusion and sorption parameters, and the activation energies for the absorption and desorption stages, is another goal of this research. Molding all these findings, employing Crank's<sup>11,12\*</sup> and Arrhenius<sup>13</sup> equations, into a solid model of water permeability through ICs will also be described.

Finally, a fundamental understanding of the overall picture of the complex hopping of water molecules throughout the IC-casing composite material is discussed and assessed. Thus, specific chemical anchoring, owing to the high-resolution quantitative analysis of the water and the activation energies calculated for the water molecules, can be assigned.

## EXPERIMENTAL

### Materials

*Electronic integrated circuits:* SSC P111 PL Media Interface IC components, by Intellon, (IC no. 1) were selected for this study, as being representative of their kind. These are highly moisture-sensitive ICs

\*Most of the mathematical analyses used with experimental data are based on the assumption that the material under investigation is in the form of a plane sheet of infinite extent. Obviously, infinitely large plane samples cannot be obtained, but based on the investigated chip aspect ratio combined with the splitting metal plate effect, the area of the edges, which provide reasonable approximation, is relatively small when compared with the area of the plane surfaces.

(moisture sensitivity level 3 by JEDEC),<sup>14</sup> encapsulated in rectangular polymeric composite packaging split by a metal plate, as illustrated in Figure 1. A 54/74FCT244 Fast CMOS Octal Buffer/Line Driver by IDT (IC no. 2) was selected for this study, as durable reference ICs (moisture sensitivity level 1 by JEDEC)<sup>14</sup> because of their resemblance in dimension and the structure to IC no. 1. Storage of the components during the research period was carried out under vacuum ( $\sim 5.3$  Pa) at ambient temperature.

### Methods

Permeability studies of water penetration into the packaging were carried out by dipping the entire components or fragments of the casing material (mainly for DSC measurements) in water (ultrapure, liquid phase), at 50–150°C (under pressure above 100°C), for a few hours to 150 days. The soaked samples were wiped swiftly to remove surface water and immediately transferred for the TGA or DSC measurements.

TGA water out-permeation measurements of the water-soaked packaging material were done with a TG-50 (Mettler) system under N<sub>2</sub> (99.999%) atmosphere. The weight versus time data were recorded at constant temperature at the highest possible accuracies:  $\pm 0.5$  s,  $\pm 5$   $\mu$ g, and  $\pm 2^\circ$ C, respectively.

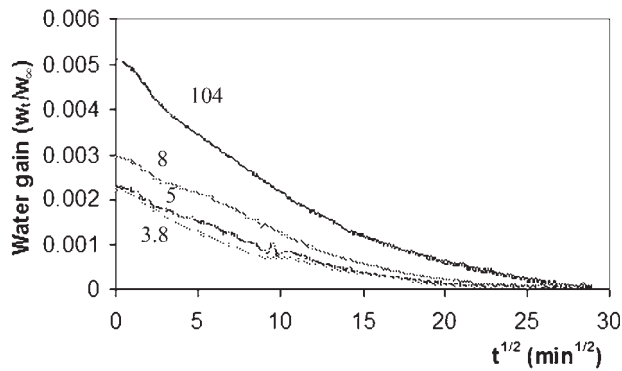
To maximize the signal-to-noise ratio in these experiments, the standard TGA alumina crucible (205 mg) was removed, leaving only the primary sample holder, which was found optimal for  $\sim 400$ –500 mg material samples. To eliminate noise from adsorbed water on the cell interference, prior to each measurement, the empty cell was dried at 250°C, and then cooled, while remaining under the dry nitrogen.

Vacuum combined with heat predrying process guaranteed the pristine chip packaging from residual measurable volatile materials. Repetitive TGA/DSC measurements with and without water exposure confirmed that the observed results generated were due to water permeation.

To assure the stability and accuracy of the measurements during prolonged desorption experiments, the ambient temperature was maintained at 16°C to allow the efficient cooling of the balance electronics.

## RESULTS AND DISCUSSION

The time profile of water absorption into the IC casing material was our foremost interest. Accelerated profile data of casing material soaked in water at 100°C for 3.75, 5, 8, and 50 h are shown in Figure 2 (similar curves to that shown were also obtained for studying longer soaking periods). As we can see, the water uptake increases with time up to a limit of  $0.53\% \pm 0.05\%$ , probably manifesting the absorption

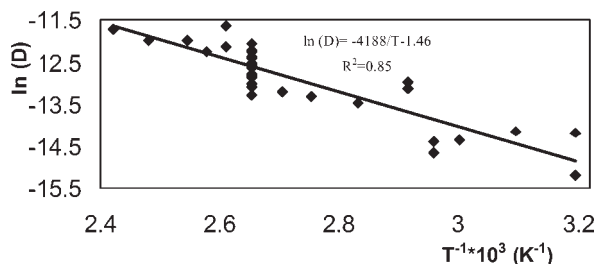


**Figure 2** Water desorption profiles (104°C) of the entire casing in boiling water (100°C) as they appear after different soaking periods (3.8, 5, 8, and 104 h). The weights presented here are after the reduction of the lead frame and silicon die weight.

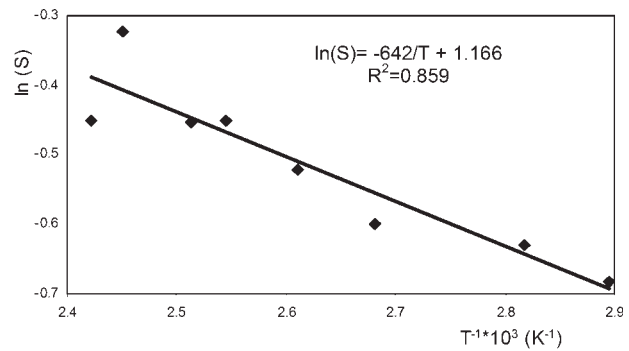
at a thermodynamic steady state. The very low water uptake is in accord with the hydrophobic nature of the casing material, which is composed of a Novolac epoxy matrix and fused silica microparticle filler.

The profiles of water desorption at 104°C vs.  $t^{1/2}$  shown in Figure 2 are apparently linear up to  $t^{1/2} \sim 12 \text{ min}^{1/2}$  ( $t \approx 2 \text{ h}$ ), and then approach the dry state exponentially. The diffusion coefficients [ $\text{mm}^2/\text{s}$ ] at various temperatures were calculated from Figure 2 slopes, employing Crank’s equation for plane sheets of infinite extent as presented in Figure 3.

The diffusion activation energy  $E_a(D)$ , calculated by the Arrhenius’ equation using the slope shown in Figure 3, was found to be 33.35 kJ/mol or 0.33 eV/molecule. The enthalpy of solution  $\Delta H(S)$ , similarly calculated using the slope shown in Figure 4, was found to be 1.93 kJ/mol or 0.02 eV/molecule. The activation energy for the permeability process, calculated by the energy balance [ $E_a(P) = E_a(D) + \Delta H_s$ ],<sup>15</sup> was thus found to be  $35.28 \pm 0.08 \text{ kJ/mol}$  or  $0.36 \pm 0.01 \text{ eV/molecule}$ . The less common eV/molecule scale is employed herein as well, since we are dealing with an electronic component in which the synergistic effects of chemical and electric potentials may take place.



**Figure 3** Arrhenius’ plot for water diffusion in the casing material as calculated by the permeability rate at different temperatures (50–150°C).

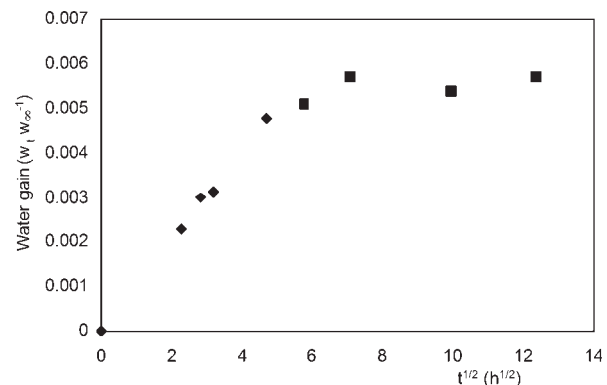


**Figure 4** Arrhenius’ plot for water solubility in the casing material, after reaching thermodynamic steady state, as measured at different temperatures (72.5°C–150°C).

The data of an isothermal absorption time profile, collected at 100°C, are displayed in Figure 5. The water absorption into the composite IC casing during the course of the first 23 h exhibits a linear profile ( $R^2 = 0.999$ ). The water absorption leveling off takes place after  $\sim 30 \text{ h}$ , probably manifesting the thermodynamic steady-state of the water in the composite.

An intriguing part of this study was to observe the differences between water absorption and water desorption processes, and the corresponding thermodynamic data. Hence, the activation energies of water permeability and diffusion in the course of the absorption process,  $E_a(P)$  and  $E_a(D)$ , respectively, were also determined. These data were calculated similar to the calculations performed for the desorption process. The comprehensive set of thermodynamic data is shown in Table I.

Despite the differences,  $\sim 33\%$ , between desorption and absorption  $E_a$  (c.f. Table I), which hint toward thermodynamic changes primarily due to sharp permeation rate changes observed through different sample dimensions (small DSC samples versus the pristine casting) such as plasticization, one should assume that the water permeation is mainly kinetic.



**Figure 5** Isothermal (100°C) water absorption and solubility in the casing material as measured after different soaking periods (0–150 h) followed by TGA desorption measurements.

TABLE I  
Measured and Calculated Thermodynamic Data of Water—IC-Casing Absorption and Desorption Processes

Sample	Absorption (kJ/mol) [eV/molecule]			Desorption (kJ/mol) [eV/molecule]		
	$E_a(D)$	$E_a(P)$	$\Delta H(S)$	$E_a(D)$	$E_a(P)$	$\Delta H(S)$
IC no. 1	$42.4 \pm 0.3$ [0.439]	$44.3 \pm 0.3$ [0.459]	$1.9 \pm 5.0$ [0.020]	$34.5 \pm 0.3$ [0.357]	$33.4 \pm 0.3$ [0.346]	$-1.1 \pm 5.0$ [-0.011]
IC no. 2	$58.0 \pm 0.3$ [0.601]	$65.0 \pm 0.3$ [0.673]	$7.0 \pm 5.0$ [0.072]	$54.7 \pm 0.3$ [0.567]	$59.5 \pm 0.3$ [0.616]	$4.8 \pm 5.0$ [0.050]

A puzzling finding for the hydrophobic IC casing studied was that the above-displayed absorption and desorption process activation energies (c.f. Table I) resemble those of hydrophilic polymer matrices:  $E_a(D)$  36 kJ/mol for poly(ethylene terephthalate)<sup>16</sup> or 34.22 kJ/mol for PVA,<sup>17</sup> as opposed to hydrophobic polymers such as polytetrafluoroethylene  $E_a(P) \rightarrow 0$ ,<sup>18</sup> polyethylene-acrylic acid (92:8)  $E_a(P)$  8 kJ/mol<sup>19</sup> or 9.2 kJ/mol for PMMA.<sup>18</sup>

On the other hand, the enthalpy of the solution  $\Delta H(S) = 1.93$  kJ/mol seems rather low when compared even with some hydrophobic polymer matrices: 0.95 kJ/mol for composite low density polyethylene.<sup>20</sup> It is noteworthy that the latter value is rather far even from the  $\Delta H(S)$  value found for polar matrices: 50 kJ/mol for chitosan<sup>21</sup> or 44.31 kJ/mol for the polyimide PMDA-50DDS/50ODA, which contains both polar carbonyls and nonpolar aromatic groups.<sup>22</sup> To verify this apparent mismatch, independent desorption enthalpy data employing DSC measurements were collected, as depicted in Figure 6.

The desorption enthalpy derived from the DSC plot, via peak integration, was found to be 33.7 kJ/mol or 0.35 eV/molecule. These data were similar to our  $\Delta H(S)$  data derived from the Arrhenius' plots ( $\sim 0.9\%$  difference).

The calculated and measured  $E_a(P)$  can be interpreted in terms of water-polymer binding energy. The  $E_a(P)$  of 0.334 eV/molecule thus manifests  $1.38 \pm 0.24$  hydrogen bonds (assuming OH—O bond types). These

hydrogen bonds probably attach protons of water molecules to Si—O—Si groups at the surface of the fused silica, and may be attached to the silanol groups therein. Water molecules may possibly also bond to the fused silica filler microparticles, relying on coordinative bonding between the well-fitted empty silicon d-orbital and oxygen nonoccupied full orbitals. It is also possible that miniscule water amounts are physically trapped in nanovoids at the polymer-filler interface, as schematically depicted in Figure 7. Thus, the apparent anomalies and discrepancies between measured and calculated data are resolved.

The relatively high  $E_a(P)$ , resembling hydrophilic polymers rather than hydrophobic ones, suggests that the water is primarily bound, in accordance with the hydrophobic nature of that matrix polymer, to the filler and not to the polymer. The importance, beyond its analytical merits, of this finding lies in its high practical value. Our finding suggests that in the composite casing material used for ICs, three, rather than two components, exist: the hydrophobic polymer (novolac epoxy), the mildly hydrophobic filler (fused silica), and the so-far-unnoticed filler surface, or the filler-polymer interface, which act as water absorption and diffusion moieties. These moieties are primarily interconnected, and thus allow water permeation through the IC casing, concurrent IC damage, and its functional failure thereafter.

In other words, whenever we attempt to produce a new composite polymer, to combine the properties

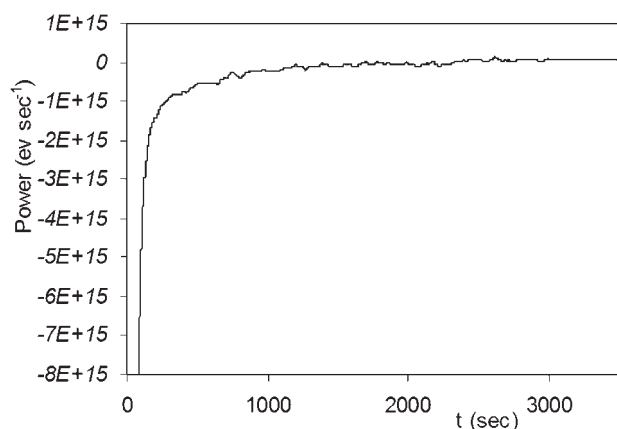


Figure 6 DSC water desorption from the casing material energy plot (1.72 g of water, 0.31 J).

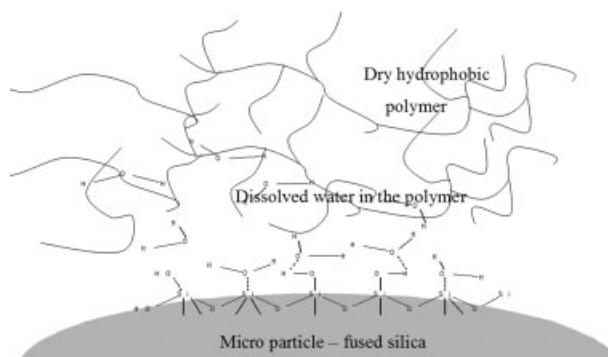


Figure 7 Water emplacement and bonding at the filler-polymer interface (fused silica microparticle, crosslinked novolac epoxy, respectively). The bonding to the package matrix are mainly hydrogen (and maybe coordinative) bonding to the silanol/silica surface groups.

of its components, we must carefully consider the properties of the third constituent: the interface, its unique properties, and their prospective effect on the overall performance of the composite. These considerations should be addressed when designing the next generations of IC casing to meet their ever-increasing performance and reliability requirements.

Our currently on-going research focuses on the synthetic side of the problem, and aims at nanoscale surface-modification of the current IC casing, with the objective of the substantial reduction of the water penetration therein. The consequent analytical challenge, relating to the modified as well as future IC casings, despite the improved IC water repellence features, will accurately assess the residual water-permeability features, and hence, the ever decreasing signal-to-noise ratios.

### CONCLUSIONS

With careful work, commercial TGA measurements could be successfully utilized to achieve high-resolution data of water absorption and permeation in relatively small samples (~400 mg) containing miniscule quantities of water (0.53 wt %).

The comprehensive data of diffusion and solubility coefficients and their activation enthalpies are in accord with a unique newly adopted permeability model for IC casings. According to this model, the water molecule penetration, absorption, hopping, and reabsorption take place primarily at the filler-polymer interface. This model adequately resolves all the mismatches related to the hydrophilic/hydrophobic nature of the casing composite as well as the higher than expected penetration rate of water into the IC and its failure thereby.

The extended analytical sensitivity attained, and the new understanding and model assignment pave the road to the current endeavor of surface-modified IC casings. These modifications aim at impeding

water penetration into the casing and, thus, enhancing the durability, against water-induced failures, of newly developed ICs of ever-increasing densities.

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