Hydrophobic Self-Assembly Monolayer Structure for Reduction of Interfacial Moisture Diffusion

H. B. Fan, Cell K.Y. Wong, and Matthew M.F. Yuen
Department of Mechanical Engineering,
Hong Kong University of Science and Technology
Clear Water Bay, Kowloon, Hong Kong SAR, China

Abstract
Interfacial delamination is one of the primary concerns in electronic packaging design. Pop-corning during the solder reflow of plastic-encapsulated IC packages is a frequently occurred defect due to moisture penetration into the packages. Moisture absorption has a detrimental effect on the EMC/Cu interfacial adhesion and drastically reduces the reliability of plastic packages. To improve package reliability and to prevent interfacial delamination, it is important to design the EMC/Cu interface for high hydrophobicity and good adhesion.

The object of this paper is an investigation of both adhesion and moisture absorption at the EMC/Cu interface using MD simulations. Three kinds of models containing SAM1, SAM2 and a mixture of SAM1 and SAM2, have been used to evaluate the bonding energy and moisture absorption between EMC and SAM coated Cu substrate in this study. In each model, SAM1 or SAM2 or mixture of SAM1 and SAM2 chains were aligned on the copper substrate. MD simulations were performed at a given temperature using the constant-volume and temperature ensemble (NVT). Non-bond interactions cut-off distance of 1.25 nm with a smooth switching function was used in all simulations. The simulations were performed with an interval of 1 femto second (fs) in each MD simulation step. Moisture distribution and binding energy were calculated from simulation for each model. MD simulation results showed that the SAM1 has the higher bonding energy, while SAM2 has the higher hydrophobicity. It was also found that a mixture of SAM1 and SAM2 has both a higher bonding energy and a higher hydrophobicity which can be used as an interface promoter for adhesion and moisture inhibitor in electronic packages. This study shows that MD simulation can be an efficient tool for optimization of SAM to create a hydrophobic interface, which can provide useful pointers of the selection of the SAM structure.

Introduction
Moisture induced reliability concerns have been extensively studied in a package design. Pop-corning in plastic-encapsulated IC packages is a defect frequently occurring during solder reflow due to moisture penetration into the packages. Moisture absorption has a detrimental effect on the EMC/Cu interfacial adhesion and drastically reduces the reliability of the encapsulated package. Factors governing the interfacial delamination are mainly the moisture content and adhesion strength of the epoxy/copper interface at the target temperature. The loss of interfacial adhesion due to moisture is governed by the moisture diffusion rate combined with vapor pressure generated at the interface. Understanding interfacial adhesion subjected to different levels of moisture content is of significant interest to the electronic packaging industry.

Yee et al [1] have recommended the hydrophobic component in an epoxy system can hinder moisture uptake of the bulk epoxy. It implies that a hydrophobic interface may reduce the moisture content at an interface. Kinloch [2] suggested that the long alkyl chain of an vinyl silane with 20 carbons might impede water and improve bond durability. The argument is that the middle alkyl chains which are highly hydrophobic can obstruct water penetration and can thus improve the interface. Although these studies showed that a hydrophobic surface can reduce moisture absorption for interfacial joint, design of a hydrophobic interface with higher bonding energy for electronic devices still cannot be completely achieved. Moreover, as material properties at the interface are different from those of bulk materials, such as, moisture diffusion along the EMC/Cu interface, it is important to better understand moisture diffusion at a molecular level.

Molecular modeling represents molecular structures numerically and simulates their behavior with the equations of quantum and classical physics and it is one of the fastest growing fields in science. The molecular dynamics (MD) method was first introduced by Alder and Wainwright in the late 1950’s to study the interactions of hard spheres [3]-[4]. Mitsuhiro Fukuda and Satoru Kuwajima [5] used MD simulations to estimate diffusion of water cluster in amorphous polyethylene, which showed good agreement with the experimental values. The diffusion of water in mixture of water and poly was investigated using MD simulation by Muller-Plathe [6]. He concluded that water diffusion undergoes a pronounced change with the concentration and temperature when pure water mixed with high polymer concentration. Yarovskyi, et al. [7] used MD simulations to investigate the diffusion constants for water molecules in the crosslinked polymer network composed of the epoxy resin of polymerization and different curing agents. Fan et al. [8] conducted MD simulations to investigate moisture diffusion into the epoxy molding compound (EMC) and the EMC/Cu interface. The MD results showed that the seepage along the EMC/Cu interface was more prevalent than moisture diffusion in the bulk EMC, and thus rendering it a dominant mechanism causing moisture induced interfacial delamination in plastic packages. However, not much research effort has been dedicated to the investigation on design of hydrophobic interface with higher interfacial bonding energy.

In this study, MD simulations were conducted to investigate wettability and the interfacial moisture diffusion at the EMC/Cu interface. Three kinds of models containing SAM1, SAM2 and a mixture of SAM1 and SAM2, were built. The MD simulation results show that SAM1 has the higher bonding energy, while SAM2 has the higher hydrophobicity. The MD results also revealed that optimized SAM on Cu substrate for higher interfacial energy and more...
hydrophobicity can be achieved by the mixture of SAM1 and SAM2.

**Molecular Dynamics Simulation**

**Wettability of SAM coated Cu substrate**

In order to design a hydrophobic interface for reduction interfacial moisture diffusion, contact angle of water droplet on the SAM coated cooper surfaces was investigated using MD simulation. MD simulations are carried out for Cu surface coated with SAM1, SAM 2 and mixture of SAM1 and SAM2. Two SAM candidates are involved in this study and their chemical structures are shown in Figure 1.

![Chemical structures of (a) SAM 1 (b) SAM 2](image1.png)

Figure 1: Chemical structures of (a) SAM 1 (b) SAM 2

In this simulation, the copper surfaces were cleaved from a crystal copper structure, corresponding to the (001) plane. As the non-bond cut off distance in the force field setting is 9.5Å, the depth of copper surface used in the simulation was about 10Å. A layer builder was used to build a sandwich and a large vacuum spacer was positioned at the top of the copper surface in order to avoid interaction across the mirror image in the z direction in the calculations. The unit cell was extended in the x and y directions to create a rectangular simulation box (50.22 x 50.22Å²), periodic in the plane parallel to the surface. The SAM chains were initially placed on the copper substrate. Normally each sulfur atom in the chains should be covalently bonded to a copper atom. All simulations were carried out at the temperature of 298K, using the ensembles of the constant number of particles, constant-volume and constant temperature (NVT). MD simulations were performed to obtain optimized structure on the Cu substrate.

After the optimization of SAM on the copper substrate, a freely relaxed water droplet consisting of 670 molecules was centered on top of the SAM surfaces. The interactions among water molecules and between water molecules and SAM surface consist of van der Waals force and Coulombic force. The parameters used in the simulations are from the polymer consistent force files (PCFF) Accelrys Inc. San Diego CA, USA). A cutoff distance of 12.5Å was used for these nonbonding interaction forces. All the simulations were conducted at 25°C using NVT for about 500ps with an interval of 1 femtosecond (fs) in each MD simulation step.

Figure 2 shows the final configurations of water droplets on the two SAM-coated substrates. Water droplets on the two substrates were spread finally with different spheric shape of droplet cap. It is obviously seen that water contact angle for SAM2 coated Cu substrate is larger than that for SAM1 coated substrate. The stronger wettability of SAM1 coated substrate results from hydrophilic group N₂ in SAM1. While the hydrophobic group in SAM2 results in less interaction between water molecules and SAM 2, making the larger contact angle.

![Final configuration of water droplets on (a) SAM1 coated Cu substrate (b) SAM2 coated Cu substrate](image2.png)

Figure 2: Final configuration of water droplets on (a) SAM1 coated Cu substrate (b) SAM2 coated Cu substrate

**Interfacial moisture diffusion and bonding energy**

Due to different wettability of SAM, optimized SAM structures on the Cu substrate should be designed to achieve a higher adhesion and lower interfacial moisture diffusion for the EMC-Cu interface. Considering the wettability of SAM and its ability to react with epoxy, three kinds of models containing SAM1, SAM2 and a mixture of SAM1 and SAM2, have been used to evaluate the moisture absorption and bonding energy between the EMC and SAM-Cu in this study.

In this study, the system consists of SAM, a fragment of Epoxy Molding Compound (EMC) and a Cu substrate. SAM solvent develops a thin monolayer on the Cu surface that allows direct linkage between Cu and epoxy resin. The fully cured epoxy network is composed of diglycidyl ether of bisphenol-A (DGEBA) epoxy and methylene diamine diaminle (MDA) curing agent and the model is same as that presented by Fan et al. [8]. Wong et al. [9] estimated interfacial bonding energy between the EMC and the SAM modified Cu substrate using MD simulations. They presented a method on how SAM was adsorbed on the Cu substrate and connected the EMC and the Cu substrate. Based on the same method, three models were built. For the model with SAM1, it was connected to the EMC by the covalent bonds formed between oxraine rings in the EMC chains and nitrogen atoms in SAM1 chains. For the model with SAM2, there is no any bonding between the EMC and SAM2. While for the third model, there is a mixture of 50% SAM1 and 50% SAM2, in which EMC was connected to SAM1 by the chemical bonds formed between them.

All MD models were built with a rectangular simulation box 2.54 x 2.54 nm² in the x and y directions, periodic in the plane perpendicular to the EMC-Cu interface. A large vacuum space was positioned at the top of the epoxy chains in order to avoid interaction across the mirror image in the z direction in the calculations. All the copper atoms were held rigid, while all the EMC chains and SAM molecules were allowed to move freely in all simulations. Water molecules were inserted in to the EMC/Cu interface. The mass ratio of water...
molecules to the EMC in both MD models is around 1.7%. Given the humidity condition, all the simulations were then carried out at a temperature of 85°C with a presumed moisture concentration value, using the using the ensemble of the constant-pressure and temperature (NPT) under 1 bar. All the system was equilibrated for about 100ps under 1 bar at 85°C with an interval of 1 femto second (fs) in each MD simulation. MD calculations were performed using the Discover module in Materials Studio software to find the thermal stable morphology and achieve a conformation with minimum potential energy for the whole system. Figure 3 shows the morphological configuration with the minimum potential energy for different SAM-coated substrates.

![Morphological Configuration](image)

Figure 3: Morphological configuration of (a) SAM1 coated Cu substrate (b) SAM2 coated Cu substrate (c) Mixture of SAM1 and SAM2 coated Cu substrate.

Constants of moisture diffusion can be obtained in principle from diffusion trajectories $r(t)$ of water molecules determined during a MD simulation of a polymer packing model. The diffusion coefficients for the water molecules can then be calculated from the mean squared displacement, $s(t) = \langle [r(t) - r(0)]^2 \rangle$, of the water molecules averaged over time as follows:

$$D = \frac{1}{6N} \lim_{t \to \infty} \frac{d}{dt} \sum_{i=1}^{N} (r_i(t) - r_i(0))^2$$  \hspace{1cm} (1)

where $D$ is the moisture diffusion coefficient, $r_i(t)$ is the coordinate of the center of the mass of the $i$th water molecule and $N$ is the number of water molecules in the system.

Figure 4 shows the mean square displacement of water molecules against time calculated from MD simulations. The graphs were fitted using linear regression, $y = ax + b$, and the slope of the line, $a$, can be obtained (labeled in red in the figure). Since the value of the mean square displacement is already averaged over the number of atoms, $N$, the equation (1) can be simplified to:

$$D = \frac{a}{6}$$  \hspace{1cm} (2)

Figure 4: Mean square displacement of water molecules against time and the fitted line.

Normally, the interfacial energy is evaluated from the energy difference, $\Delta E$, between the total energy of the whole system and the sum of the energies of individual parts as follows:

$$\Delta E = E_{\text{tot}} - (E_{\text{EMC}} + E_{\text{Cu+SAM}})$$  \hspace{1cm} (3)

where $E_{\text{tot}}$ is the total energy of the whole system, $E_{\text{EMC}}$ is the energy of the EMC without the substrate, $E_{\text{Cu+SAM}}$ is the energy of the SAM coated substrate without the EMC. The interfacial bonding energy, $\gamma$, is evaluated using the interfacial energy, $\Delta E$, and the contact area, $A$, between the EMC and cuprous oxide substrate:

$$\gamma = \frac{\Delta E}{2A}$$  \hspace{1cm} (4)

Results and Discussion

In this simulation, mean square displacement was used to analyze the moisture diffusion coefficient. Based on the slope of the linear regression fitting line for different mass ratio of water molecules to the EMC, the moisture coefficients for different cases are obtained by equation (2), and are listed in Table 1. From the above MD simulations, the interfacial moisture diffusion in three kinds of SAM coated Cu substrates are predicted. It is anticipated that moisture diffusion decreases when the substrate changes from SAM1, mixture of SAM1 and SAM2 to SAM2, which matches their wettability of these SAM-coated substrates. The reason is that the non-polar group in SAM can hinder interfacial moisture diffusion and water residence at the interface.
We also experimentally measured water contact angle on SAM1 and SAM2 treated Cu substrate. The contact angle for the SAM1 treated substrates was $50\pm1^o$, while the contact angle for SAM 2 is around $112\pm4^o$. These experimental results show the consistence with MD simulation results.

Based on equations (4), the interfacial bonding energy between the EMC and SAM coated substrate was calculated and the results were also listed in table 1. It shows that the interfacial bonding energy for the SAM 1 is the largest and that for SAM 2 is the smallest. The highest energy for SAM1 results from the covalent bonds formed between the SAM1 and EMC. The mixture of SAM1 and SAM2 still can provide a higher interfacial energy comparing with SAM2.

Table 1: Interfacial moisture diffusion coefficients and bonding energies for different SAM coated Cu substrates

<table>
<thead>
<tr>
<th></th>
<th>SAM1</th>
<th>SAM1 &amp; SAM2</th>
<th>SAM2</th>
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<tbody>
<tr>
<td>Moisture diffusion coefficient at the EMC/Cu interface (mm²/s)</td>
<td>3.33e-5</td>
<td>1.0e-5</td>
<td>5.0e-6</td>
</tr>
<tr>
<td>Interfacial bonding energy (J/m²)</td>
<td>0.58</td>
<td>0.49</td>
<td>0.17</td>
</tr>
</tbody>
</table>

We also used tapered double cantilever beam (TDCB) test to evaluate fracture toughness the tensile adhesion between the EMC and SAM coated copper substrate under tensile mode. Experimental results showed that interfacial fracture toughness ($G_{IC}$) for SAM1, mixture of SAM1 and SAM2 and SAM2 only are 159 Jm^{-2}, 112 Jm^{-2} and 5 Jm^{-2} respectively. These experimental results are all consistent with the results from MD simulations in this study confirming that optimized SAM on the Cu substrate can improve adhesion between EMC and Cu substrate.

Both experimental and simulation results shows that mixture of SAM1 and SAM2 can not only improve adhesion by covalent bonds formed between EMC and SAM1 but hinder interfacial moisture diffusion by non-polar group in SAM2. These studies suggest a hydrophobic copper-epoxy interface can improve the long term reliability of an interfacial joint in electronic packages.

The results from MD simulations demonstrated moisture diffusion and bonding energy between the EMC and SAM coated substrate. Optimization of SAM on the Cu substrate can not only give higher adhesion but a hydrophobic copper-epoxy interface to reduce moisture absorption. Although MD simulations could not be directly compared to the experimental measurements, MD simulations are capable of generating in depth insight into the local molecular interactions and can be used as a guide for further researches.

Conclusions

The paper is focused on wettability, interfacial moisture diffusion and bonding energy for different SAM coated Cu substrates using molecular dynamics simulations. MD simulation results show that the SAM1 has the higher binding energy, while SAM2 has the higher hydrophobicity. A mixture of SAM1 and SAM2 has both a higher bonding energy and a higher hydrophobicity which can be used as an interface promoter for adhesion and moisture inhibitor in electronic packages.

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