

Two Approaches of Study Cu/Epoxy Interface Enhancement with Benzenethiol Promoter

Peng He, Haibo Fan, and Matthew M.F. Yuan

Abstract Copper/epoxy interface is known as one of the most critical joints in electronic packages. However, due to its low adhesion, the Cu/epoxy interface is prone to delaminate. It will lead to the failure of electronic devices. To solve this problem, a thiol-based self-assembled molecular (SAM) treatment is introduced by our group in the Hong Kong University of Science and Technology. The benzene ring will give the hydrophobic characteristic to the surface by forming layer on top. The selected thiol functional group can react with copper substrate. The other end of benzenethiol materials are designed to react with an epoxy composite to build a chemical bridge between the copper and epoxy.

The focuses of this work are: (1) depicting the interfacial adhesion with the benzenethiol material treatment; (2) depicting the interface reliability under moisture condition. Three benzenethiol (BT) materials were studied with different functional groups, BT-1, BT-2, and BT-3.

In order to evaluate the candidate materials, two approaches are adopted: molecular dynamics (MD) simulation and interfacial fracture toughness test. Interfacial bonding energy is evaluated with MD simulation with and without moisture. The diffusion coefficient was then calculated from the mean square displacement. All MD simulations were performed using constant-pressure and temperature ensemble (NPT). The interfacial fracture toughness was also recorded with the Tapered Double Cantilever Beam (TDCB) test, and reliability test was conducted according to the MSL (Moisture Sensitivity Level) 1 (85 °C/85 % RH for 168 h). This work demonstrates two approaches, using MD simulation and TDCB test, to evaluate the BT materials as adhesion promoter for Cu/epoxy systems.

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1 Introduction

Due to its good thermal conductivity and electric properties, copper is selected as the leadframe material. But the Cu/epoxy interface is known as one of the weakest interfaces with delamination during reliability tests. One prime reason is the lack of adhesion between the copper and epoxy. The low adhesion, moisture ingress into the interface, and adhesion degradation are the main reasons for poor reliability [1, 2].

Previous studies demonstrated that adhesion could be improved with the oxidation method or the chemical coupling agent. Applying either acid, alkaline, or thermal treatment, oxidation of copper is built on the substrate to modify the surface morphology [3]. As reported by Lee [4], the interfacial adhesion strengthened from almost zero to 100 Jm^{-2} . Kim et al. reported the adhesion enhancement with black oxide treatment [5]. Adhesion dropped by 83.1 % from 7.5 to 1.27 MPa after pressure cooker testing ($121^\circ\text{C}/100\% \text{ RH}$) for 120 h.

A self-assembled monolayer (SAM) was suggested by Muller as an interfacial adhesion promoter for the copper and epoxy system [5]. The argument is that the covalent bonds have better adhesion than mechanical locks. Also, to fortify the reliability, Yee et al. recommended a hydrophobic component will impede moisture from diffusion into the interface [6]. Hence our group introduced the thiol-based self-assembled molecular (SAM) treatment with benzenethiol (BT) materials as the adhesion promoter, as the benzene ring is hydrophobic in nature. The thiol group is easy to build covalent bond with noble metals, such as Au and Cu. Thus the materials can form chemical linkages between the epoxy encapsulant and copper substrate.

In order to evaluate the candidate materials, molecular dynamics (MD) simulation was applied. MD models were built to investigate the interfacial adhesion with the molecular treatment, as well as the moisture diffusion inhibition and reliability improvement. This paper focuses on: (1) predicting the interfacial adhesion with the benzenethiol material treatment; (2) predicting the interface reliability under moisture condition. Three benzenethiol materials were studied with different functional groups. The MD simulation is conducted with the commercial software “Materials Studio” from Accelrys, Inc. The MD model was divided into three parts: constrained copper substrate, benzenethiol molecules that were attached to copper, and unconstrained epoxy molecules on the top. The molecular density of benzenethiol molecules was determined from the conformation run of MD simulation. The non-bonding cut-off distance was $12.5 \text{ \AA}$ and the simulation performed has an interval of 1 fs in each step. The interfacial adhesion energy of the interfaces was then calculated with the assumption that the interface failed along the SAM-epoxy interface.

To investigate the effects of moisture on interfacial adhesion, the mean square displacement of all water molecules were evaluated in each step to track the motion of the molecules. A diffusion coefficient was then calculated from the mean square displacement according to the Einstein equation, performed at a temperature of 85°C using the constant-pressure and temperature ensemble (NPT).

To benchmark the adhesion, the interfacial fracture toughness was also recorded with the Tapered Double Cantilever Beam (TDCB) test, and a reliability test was conducted according to the Moisture Sensitivity Level (MSL) 1 (85 °C/85 % RH for 168 h). This study, from a molecular dynamic perspective, helps to improve our understanding of the interfacial adhesion promotion with thiol-based self-assembled treatment of benzenethiol materials for copper and epoxy systems.

2 Experiment

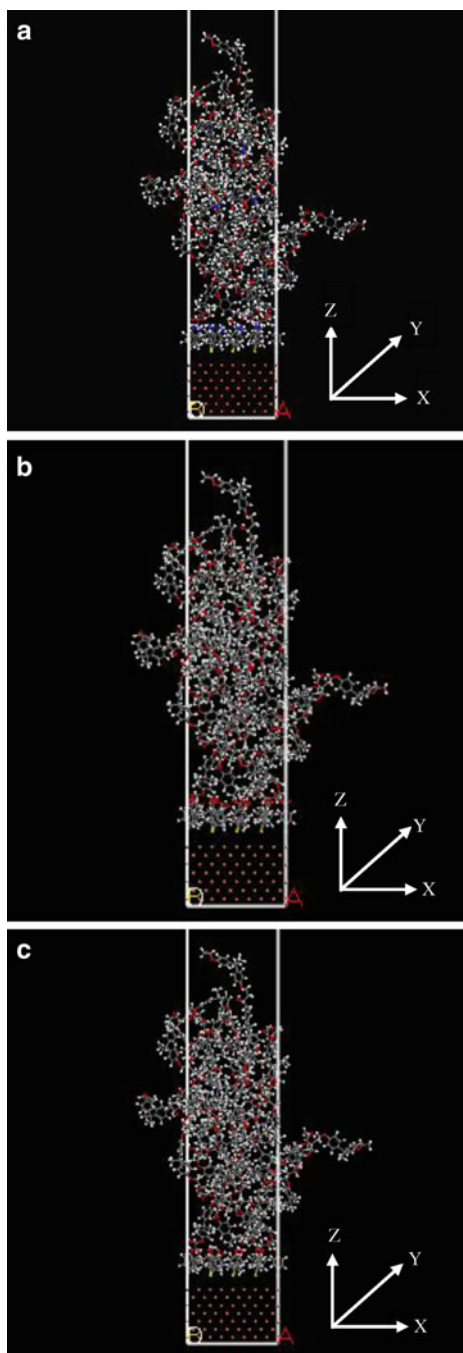
2.1 Molecular Dynamics Simulation

To understand the adhesion promotion with benzenethiol treatment, three benzenethiol materials are used, BT-1, BT-2, and BT-3. A commercial software package, Materials Studio, developed by Accelrys Software Inc., was employed. The condensed phase optimization molecular potentials for atomistic simulation studies (COMPASS) module in the Materials Studio software have been incorporated to conduct force field computations. The COMPASS force field was parameterized, tested, and validated for most common organic and inorganic materials [7]. The simulation calculated the interaction energy and predicted the structural, conformational, and thermal properties in both the isolated and condensed phases.

MD models are built according to the chemical structure of the BT materials with three layers: copper substrate, BT material, and epoxy. The substrate is a crystalline copper cleaved from the (001) plan with a thickness of 10 Å. According to Jackson et al. [8], the sulfur atoms were fixed 2.37 Å above the copper substrate along the z-axis. There are three types of BT materials built on top of the copper substrate, and it is assumed only one layer of the molecules are bonded. The unit cell is periodic in the X and Y axis to create a rectangular box of $2.54 \times 2.54 \text{ nm}^2$. MD simulation is carried out to find the optimized configuration of BT molecules on copper substrate. Conformation was performed at the temperature of 298 K, using a constant number of particles, constant-volume, and constant temperature (NVT).

With the chemisorbed BT material nanolayer, the epoxy will be directly linked with the copper substrate upon curing. Epoxy units cell were built using the major components of diglycidyl ether of bisphenol-A (DGEBA) epoxy and methylene diamine dianiline (MDA) curing agent. Based on the models presented by Fan et al. [9] and Wong et al. [10], interfacial bonding energies were estimated between the epoxy and BT material-treated copper substrate surface using MD simulation. One end of the BT molecule was linked with copper substrate to form thiolate, and the other end of the BT molecule of different functional groups was reacted with the oxirane ring. Applying the same method, models of three BT materials were built. All copper atoms in the simulation were held rigid and the BT molecules and epoxy molecules were free to move. Figure 1 illustrates the unit cell of the three BT materials treatment.

Fig. 1 Illustration of unit cells of (a) BT-1, (b) BT-2, and (c) BT-3. Sandwich structure of copper substrate, BT materials, and epoxy macromolecules on the top



2.2 Bonding Energy

In the simulation, it is assumed that fracture happened at the interface of the BT material and epoxy under fill since the copper–sulfur bond energy is quite high at 276 kJ/mol. Then bonding energy can be calculated using the energy difference, ΔE , in the following (1):

$$\Delta E = E_{\text{total}} - (E_1 + E_2) \quad (1)$$

where E_{total} is the total potential energy of the whole system, containing the substrate, BT molecules, and epoxy. E_1 is the total potential energy of the copper substrate and BT molecules, and E_2 is the potential energy of the epoxy. Then the interfacial bonding energy, γ , is calculated with (2) with a total area of A :

$$\gamma = \Delta E / 2A \quad (2)$$

2.3 Moisture Diffusion and Reliability

To estimate the reliability of this treatment under a moist environment, water molecules of 1.7 wt% of the EMC were inserted between the BT layer and epoxy. Figure 2 uses BT-3 as an example to show the water molecules in the model, which are labeled with an arrow.

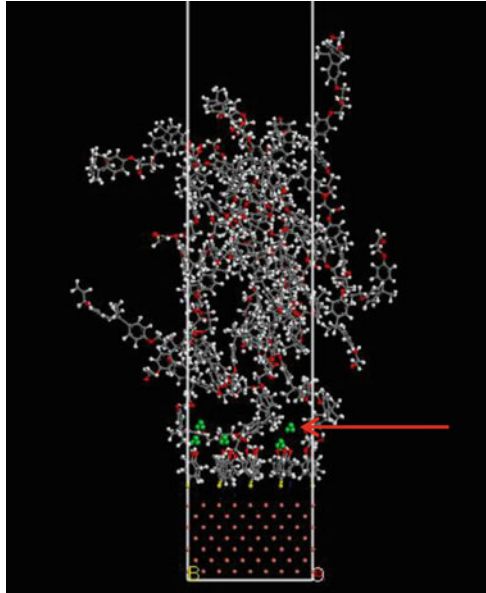


Fig. 2 MD model with water molecules

The moisture diffusion coefficient can be determined using the MD simulation of a polymer packing model. The mean squared displacement of water molecules will be used in (3),

$$s(t) = \left\langle |r(t) - r(0)|^2 \right\rangle \quad (3)$$

and the moisture diffusion coefficient D can be calculated by (4):

$$D = \frac{1}{6N} \lim_{t \rightarrow \infty} \frac{d}{dt} \sum_{i=1}^N (r_i(t) - r_i(0))^2 \quad (4)$$

where $r_i(t)$ is the coordinate of the center of the mass of the i th water molecule and N is the number of total water molecules in the model. By linear regression, the software will help to find the slope of the time vs. mean square displacement, which is $6D$, and then the moisture diffusion coefficient can be found.

The reliability of the copper and epoxy interface will also be estimated. Applying the same model and equations as that used for bonding energy calculation, the reliability is evaluated under 358 K with water molecules presented between the copper and epoxy.

2.4 TDCB Test

Beside MD simulation, experiments were also conducted to provide benchmark measurements. The experiments applied the TDCB setup and it is shown in Fig. 3.

The loading and displacement were recorded and the force during the stable crack propagation stage was applied to calculate the fracture toughness of the interface, G_{IC} , according to (5).

$$G_{IC} = \frac{4P^2 [3a^2 + h(a)^2]}{EB^2h(a)^3} \quad (5)$$

where P is the critical load for stable crack propagation, B is the specimen width, a is the crack length, h is the corresponding thickness of the jig at the crack front, and E is the plastic modulus of the copper jig. This calculation is based on the assumption of linear elastic fracture mechanics (LEFM).

A reliability experiment was conducted by applying accelerated moisture preconditioning using MSL 1. Samples were put into a humidity chamber of 85 °C and 85 % RH for 168 h, followed by the TDCB test.

Fig. 3 Experiment with TDCB setup



3 Results and Discussion

With the MD models, the interfacial bonding energies were calculated using the difference between the system potential energies by applying (1). Table 1 summarizes the interfacial bonding energy of different BT materials treatment.

As all three materials are similar in structure, it was expected that the results would be on the same scale, which is compliant with the MD simulation results. It also reveals that BT-1 has the least interfacial bonding energy, which is 0.58 J/m^2 , while BT-3 has the largest interfacial bonding energy, which is 0.73 J/m^2 .

To simulate the reliability of the BT materials treatment, a moisture diffusion model was built. Moisture diffusion coefficient was calculated with the mean squared displacement of water molecules between the copper substrate and epoxy. Figure 4 shows the mean square displacements of water molecules against time by the MD simulation with linear regression fitting, and the slope is $6D$, where D is the moisture diffusion coefficient.

The moisture coefficients for different cases are listed in Table 2. It is shown that with the BT-3 material treatment, the interface will have the least moisture diffusion rate, while with the BT-2 material treatment, the moisture diffusion is the most serious.

The interfacial adhesion enhancement was also measured with the TDCB experiment. Interfacial fracture toughness, G_{IC} , was recorded. To evaluate the effect on the reliability improvement and the moisture diffusion, samples were put into humidity chamber of 85°C and $85\% \text{ RH}$ for 168 h, and a TDCB test was

Table 1 Bonding energies for different BT treatments

Bonding energy	kJ/mol	J/m ²
BT-1	1,823	0.58
BT-2	1,949	0.62
BT-3	2,295	0.73

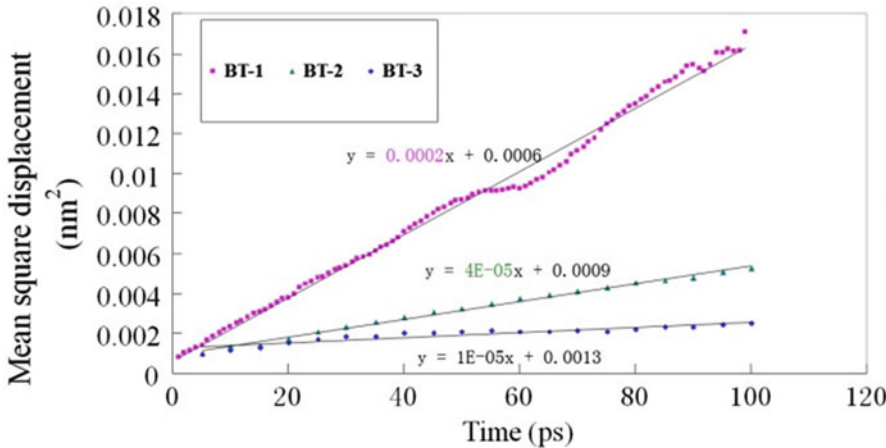


Fig. 4 Mean squared displacement of water molecules

Table 2 Moisture diffusion coefficients

	BT-1	BT-2	BT-3
Moisture diffusion coefficient (mm ² /s)	3.33E-5	6.67E-6	1.67E-6

conducted. To compare the changes after moisture preconditioning, the adhesion drop percentage was calculated. All TDCB experiment results are listed in Table 3.

From the experiment, BT-2 has the highest interfacial fracture toughness, and BT-1 has the lowest. For reliability after moisture preconditioning, BT-2 has the most significant drop in adhesion, and BT-1 has the lowest drop.

From the MD simulation results, the interfacial bonding energy decreased in the order of BT-3 > BT-2 > BT-1, and from the experiment results, the interfacial fracture toughness decreased in the order of BT-2 > BT-3 > BT-1. It can be noticed that the order of BT-2 and BT-3 are different between the simulation and experiment results. However, it was found that the surface of the copper surface was roughened after the BT-2 treatment, and this may be due to the etching by BT-2 solution. Since the surface roughness will improve the adhesion by some degree, the difference between the simulation and experiment result is acceptable.

For the reliability results, it is assumed that the reliability and degradation of the interface adhesion is mainly due to the diffusion of moisture into the interface. As shown in Table 2, the moisture diffusion coefficient decreased in the order of BT-1 > BT-2 > BT-3, and the low moisture diffusion rate may imply that the

Table 3 TDCB experiment results

	BT-1	BT-2	BT-3
Interfacial fracture toughness (J/m ²)	80.3 ± 9.1	244.4 ± 39.5	133.7 ± 7.8
Reliability test (J/m ²)	59.3 ± 3.4	115.7 ± 8.7	80.2 ± 15.9
Adhesion drop (%)	26.2	52.6	40.0

interface reliability should be higher, while, for the experiments the adhesion drop after moisture preconditioning deceased in the order of BT-2 > BT-3 > BT-1. The difference between the simulation and experimental values can be attributed to more complicated crosslink density of EMC, SAM structures on the Cu substrate and bonds between EMC and SAM. Moreover, voids or impurities inside the real samples will also affect the material performance to some extent.

Conclusion

In this study, we demonstrated the use of MD simulation as a tool to evaluate the interfacial adhesion enhancement with benzenethiol (BT) materials of different functional groups. Together, the interfacial fracture toughness was evaluated with TDCB experiment. Interfacial adhesion and reliability were estimated with interfacial bonding energy and moisture diffusion coefficient respectively. Although some deviation existed, the MD simulation and TDCB experimental results showed reasonable correlation.

As suggested by the simulation, BT-3 has the highest bonding energy, while from the experiment results it is found that due to the surface roughening effect, BT-2 treatment has a higher fracture toughness. For reliability, both the simulation and experiment results suggested BT-2, which has the lowest moisture diffusion coefficient and adhesion drop.

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