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Molecular Dynamics assisted Corrosion-resistant Evaluation of Encapsulation Materials on Copper used in Power Electronics Packaging

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***Abstract*—Corrosion protection is one of the most important issues when copper is applied in power electronics packaging as bonding wire, die attachment, interconnection, and DBC substrate. Covering a layer of corrosion-resistant encapsulation material is a worthy consideration to protect copper. In this paper, the corrosion-resistant effects of two organic encapsulation materials, polydimethylsiloxane (PDMS) and hexamethyldisiloxane (HMDSO), on the copper surface were performed by molecular dynamics simulations. Firstly, the Cu-coating bilayer models were constructed, and the binding performances of the encapsulation material/copper interface were evaluated through calculating their interaction energy, proving that the organic coatings can form interconnection on copper surface. Then, the diffusion processes of corrosive gas molecules (H_2S, H_2O and O_2) into the copper layer under different coating conditions were simulated, and both coatings exhibited good corrosion protection performances. The above results indicate that both PDMS and HMDSO have promising potential for copper corrosion protection in power electronics packaging. This may provide some guidance for corrosion protection of copper material used in power electronics packaging.**

Keywords—Power electronics packaging; Corrosion-resistant encapsulation; Corrosion protection; Copper; Molecular dynamics simulation

I. INTRODUCTION

Compared to traditional semiconductor materials like silicon (Si) and gallium arsenide (GaAs), wide bandgap (WBG) materials such as silicon carbide (SiC) and gallium nitride (GaN) have gained increasing applications in the field of power electronics due to their higher breakdown voltage, thermal stability, and comparable carrier mobility [1][2]. The higher operating voltage and temperature of devices bring challenges to the reliability of packaging materials. Copper (Cu), with its excellent electrical and thermal conductivity, exhibits remarkable advantages among various packaging materials. It is widely spread in the field of power device packaging, often used for manufacturing bonding wires, die attachment, interconnections, and DBC substrates. However, similar to other metals, exposure to high humidity and corrosive gases can lead to Cu degradation, accelerating the failure of packaging structures. Therefore, corrosion protection of Cu has always been a consideration in packaging processes.

Hydrogen sulfide (H_2S) is one of the main corrosive gases that cause metal corrosion. It originates from various sources such as industrial and agricultural waste, marine environments, and sulfur-containing mineral springs, exacerbating the corrosion challenges faced by power electronic devices in specific regions [3]. Currently, some studies have been made to reveal the corrosion mechanism of Cu in hydrogen sulfide atmospheres [4][5]. Tran *et al.* [4] studied the growth of corrosion layers on Cu surfaces under different H_2S concentrations, temperatures, and relative humidities using coulometric titration. They found that under conditions close to real indoor/outdoor H_2S concentrations and temperature-humidity levels, the corrosion layer on Cu surfaces consists of a mixture of copper sulfide and copper oxide, with the reaction rate get accelerated with the increases in these three influencing factors. Chen *et al.* [5] analyzed the corrosion behavior of bulk Cu and sintered Cu induced by H_2S through experiments and molecular dynamics simulations, summarizing and comparing the effects of corrosion on the mechanical, thermal, and electrical properties of the two materials.

In order to enhance the corrosion resistance of metals in packaging, some research in processing technology has been conducted. Some organic materials, led by epoxy resins, have shown potential in corrosion resistance [6][7]. Jung *et al.* [6] studied the influence of doped epoxy resin solvents on the mechanical and electrical properties of nanosilver particle (NP) pastes, finding that pastes with higher epoxy resin content exhibited better bonding strength, while the resistance increased as well. Subsequently, Wang *et al.* [7] investigated the impact of epoxy resin solvents on the corrosion resistance of sintered Cu and sintered silver in high humidity-H_2S environments. They found that the addition of epoxy resin significantly improved the corrosion resistance of sintered Cu, while although the corrosion level of sintered silver did not decrease significantly, its shear strength notably increased. In addition to epoxy resin, some silicon-

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containing organic materials, such as polydimethylsiloxane (PDMS) and its shortest unit hexamethyldisiloxane (HMDSO), can also be involved in the packaging of power devices through certain processing techniques. PDMS can form elastomers through a thermal cross-linking process, serving as protective materials for chip or in the manufacturing of flexible integrated circuits [8]. HMDSO can be used as a material for plasma treatment to enhance the performance of metal defects in packaging structures [9]. However, researches on whether these two materials can improve the corrosion resistance of internal metals are barely reported.

In this study, we utilized molecular dynamics simulations to analyze the interaction between the different coatings and Cu substrate at the atomic and molecular scales, and calculated the barrier effects of the two coatings against H_2S. The models were constructed and the binding performances of encapsulation material/copper interface were calculated in Materials Studio (MS). While the diffusion processes of corrosive gas molecules under different conditions were simulated via the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS). The simulation results may provide some guidance for corrosion protection of Cu material used in power electronics packaging.

II. METHODOLOGY OF SIMULATION

A. Generation of Coating Structure

Construction of the Cu-coating bilayer model was completed in the MS. The molecular models of PDMS and HMDSO were established based on some previous works [8][9]. Their molecular structures are shown in Fig. 1 (a) and (b). Considering the processes required for coating with two materials (PDMS for thermal crosslinking and HMDSO for plasma jet), we can modify the initial models to obtain the final molecular structures of the two materials after processing, and use these modified molecules to construct the encapsulation model. The new models include the crosslinked PDMS molecules as well as fragmented HMDSO molecules. Former one requires connecting two types of molecules: PDMS molecules and cross-linker molecules. The structure of cross-linker was referenced from the work of Heine *et al.* [10]. And for the latter one, in order to confirm the structure of the HMDSO fragment, the main components of the thin film were detected experimentally. Infrared spectroscopy after plasma treatment was done on Cu surface. Fig. 1 (c)-(e) show the structure of cross-linker, HMDSO fragment and crosslinked PDMS molecular, respectively.

After modeling the initial molecules for each coating layer, the construction of the encapsulation model started. In this step, by using the "construction" task in the Amorphous Cell module, a three-dimensional periodic structure containing a specific number of molecules can be obtained. The PDMS coating and HMDSO coating were composed of 1 and 25 corresponding molecules, respectively. Their initial densities were set to 0.98 g/cm^3 and 0.764 g/cm^3, respectively, referencing some existing works [8][11]. Then, the organic coating layer was placed on a (1 0 0) Cu substrate. The Cu substrate consisted of a total of 900 atoms in five layers, with a thickness of approximately 10.46 Å. A vacuum layer of 3 Å was placed between the substrate and coating model, while a 30 Å one above the coating model. The purpose of the large vacuum layer at the top was to avoid the effects of periodic boundary. The final size of the simulation cell was 28.92 Å × 28.92 Å × 81.95 Å for Cu-crosslinked PDMS coating model and 28.92 Å × 28.92 Å × 72.18 Å for Cu-HMDSO coating model.

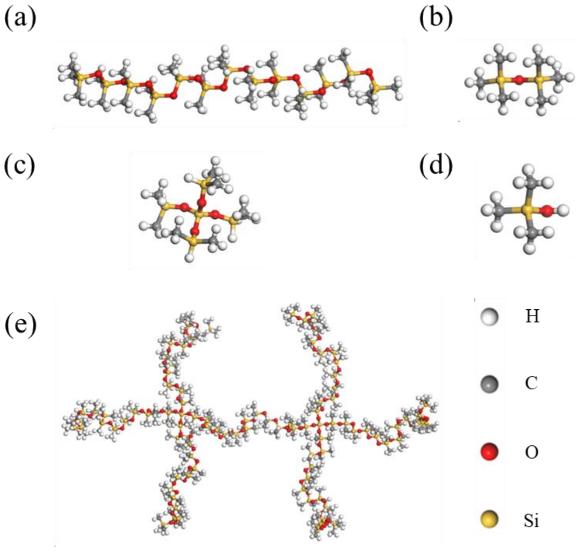

Fig. 1. The molecular structures of (a) PDMS, (b) HMDSO, (c) cross-linker, (d) HMDSO fragment and (e) crosslinked PDMS

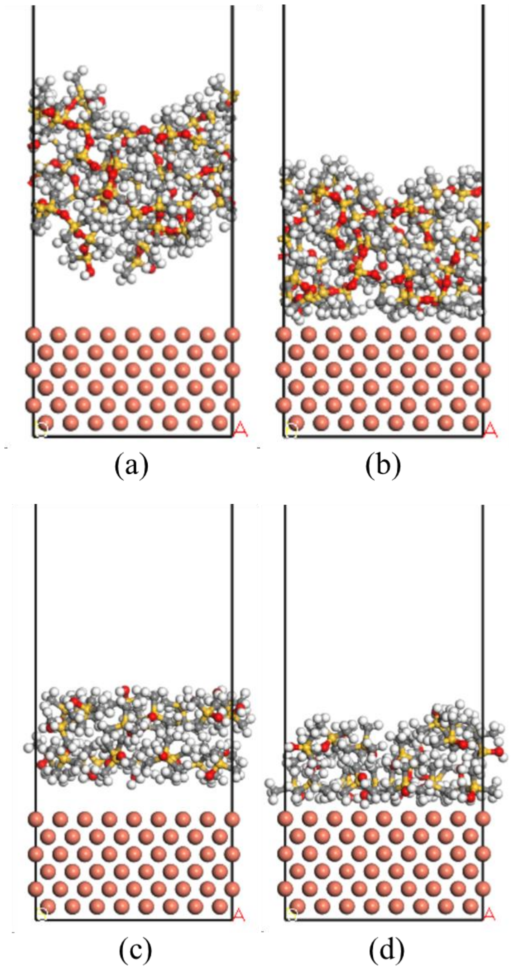

Fig. 2. Schematic of Cu-PDMS interfaces (a) before and (b) after optimization; Cu-HMDSO interfaces (c) before and (d) after optimization.

Before proceeding with subsequent simulations, it is necessary to perform energy minimization on the initial coating-Cu bilayer model, which can be completed with the "Geometry Optimization" command in Forcite module. This process optimizes the system's structure and facilitates the smooth progression of molecular dynamics simulations. Considering that no chemical reactions would occur between the organic coating and the underlying Cu atoms, and the temperature set for the entire simulation process was 300K, the deformation of Cu layer was neglected. Therefore, the positions of the Cu atoms were fixed before conducting energy minimization in order to simplify the calculations. The smart algorithm was used during this step, and the energy convergence tolerance, maximum force, maximum displacement and maximum iterations were set to 1.0e-4, 0.005, 5e-5 and 5000, respectively. Fig. 2 shows the schematic of coating-Cu models before and after energy minimization.

B. *MD Simulation of Corrosion Process*

To investigate the protective effect of the two coatings in corrosive atmosphere, corrosive gas molecules were introduced into the system for analyzing the coatings' isolation effect through molecular dynamics simulations. The corrosive gas layer was also built in MS. The layer consisted of three types of molecules: H_2S, H_2O, and O_2, which were the main participants in the corrosion process caused by H_2S. In the gas layer, the number of molecules for each of the three types was set to 50, with an overall density of 0.5 g/cm^3. Due to time and computational constraints, simulating with actual H_2S concentration and gas density would significantly increase the simulation time. Therefore, the density we set was much higher than the reality. The gas layer was put on three different models: Cu substrate only, Cu-crosslinked PDMS coating, and Cu-HMDSO coating. The model construction and optimization methods were the same as those mentioned in previous section. Due to the complexity of the Cu-coating bilayer models, we deleted some Cu atom layers to simplify the calculating process. Since we found that the gas molecules were unable to diffuse deeply into Cu substrates, thinning of the Cu layer would not affect the simulation results.

The following molecular dynamics simulations towards the diffusion process were conducted using LAMMPS. The Reactive Force Field (ReaxFF) was employed to simulate the chemical reactions during the corrosion process, enabling the generation and statistical analysis of reaction products. Considering the different types of elements in models with and without coatings, different ReaxFFs were utilized. The one referenced in ref [12] was used for the model without a coating, while the force field for models with coatings was based on ref [13]. The system energy E_{system} can be divided into multiple parts according to the following equation:

$$E_{system}=E_{bond}+E_{over}+E_{under}+E_{lp}+E_{val}+E_{tors}+E_{conj}+E_{vdW}+E_{Coulomb} \tag{1}$$

the terms on the right side represent bond energy, over-coordination energy, under-coordination energy, lone pair energy, valence energy, torsional energy, conjugate energy, van der Waals energy, and Coulomb energy, respectively. Overall, they can be categorized into interactions determined by bond order, covalent interactions, and non-bonding interactions [5][14].

Here are some details of the simulation. All models underwent energy minimization using the conjugate gradient algorithm (CGA) before the MD simulations. Units and atom types were set as real and charge, respectively. System temperature was set to 300K, and the canonical ensemble (NVT) was used to fix the number of atoms, volume, and temperature of the system. The time step was set to 0.001 fs, with a total of 1,000,000 steps, equivalent to a simulation time of 1000 ps.

III. RESULTS AND DISCUSSION

A. *Interaction Energy*

This section presents the calculation results of the interaction energies (Einteraction) between two organic coatings and the Cu substrate. After obtaining the optimized Cu-coating bilayer model in MS, the $E_{interaction}$ between different coatings and the Cu substrate were calculated using the energy task in the Forcite module, in order to examine the bonding strength of the two organic coatings with the Cu surface. The calculation of interaction energies was based on the following formula:

$$E_{interaction}=E_{total}-(E_{Cu}+E_{coating}) \tag{2}$$

where E_{total}, E_{Cu} and $E_{coating}$ respectively refer to the total system energy, the energy of the Cu substrate, and the energy of the coating layers. Calculation results of the interaction energies between the two coatings and the Cu surface were shown in Table I. The interaction energy of the HMDSO coating was -377.78 kcal/mol, and the interaction energy of the PDMS coating was -357.8 kcal/mol. Noticing that the interaction energies of both coatings were negative, indicating that they can form a certain strength of interconnection with the Cu surface, showing potential as corrosion-resistant materials for Cu surfaces in practical applications. The bonding strength of the HMDSO coating is slightly higher than that of the PDMS coating.

TABLE I. ENERGY OF EACH PART OF THE MODEL

	E_{total} ***(kcal/mol)***	E_{Cu} ***(kcal/mol)***	$E_{coating}$ ***(kcal/mol)***	$E_{interaction}$ ***(kcal/mol)***
HMDSO	-1915.57	0	-1537.79	-377.78
PDMS	-8479.10	0	-8121.30	-357.80

B. *Corrosion Process Analysis*

This section presents the molecular dynamics simulation results of the corrosion process in a high humidity-H_2S atmosphere for three models (Cu substrate, Cu-HMDSO coating, Cu-PDMS coating).

Fig. 3 illustrates the simulation results of the Cu substrate model after 1000 ps of reactive molecular dynamics simulation. Fig. 3(a)-(b) depict the overall atomic distribution of the system before and after the simulation, with different atoms represented by distinct colors in the figures. After a period of simulation, gas molecules gradually diffuse into the surrounding vacuum, with some gas molecules adsorbing onto the surface of the bulk Cu and undergoing dissociation. This results in the observation of independent S, O, and H atoms on the Cu surface. Some S and O atoms react with the surface Cu atoms, leading to the formation of copper oxide (CuO) and copper sulfide (CuS).

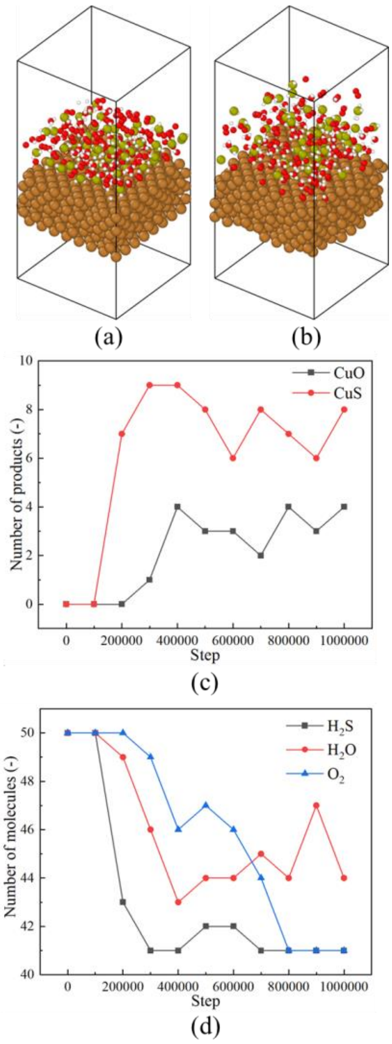

Fig. 3. Atomic distributions in Cu substrate model (a) before and (b) after corrosion. The number of (c) corrosion products and (d) gas molecules during the simulation

Figures 3(c)-(d) show the variation of the number of products and gas molecules during the simulation process. Within the first 100000 steps, the diffusion stage of the gas layer started, but the corrosive gas molecules haven't contacted the Cu surface yet, resulting in no production of reaction products and a constant number of gas molecules. The reaction stage mainly occurs between 100000 and 300000 steps, with a decrease in the number of all the three kinds of gas molecules and the generation of the corresponding products. Comparing the two product generation curves, it is noted that the formation of CuS precedes CuO, indicating that the sulfidation reaction of Cu is easier to occur compared to oxidation. Additionally, in a humid environment, water mist may form a water film on the Cu surface, facilitating easier contact of H_2S with Cu, due to its higher solubility compared to O_2, leading to preferential reactions. Furthermore, CuO formed earlier in the process may react in the presence of H_2S in the humid environment, ultimately producing sulfides. Possible reactions involved are as follows:

The basic reactions of Cu reacting directly with H_2S and O_2 to produce CuO and CuS:

$$Cu + H_2S \rightarrow CuS + H_2 \tag{3}$$

$$2Cu + O_2 \rightarrow 2CuO \tag{4}$$

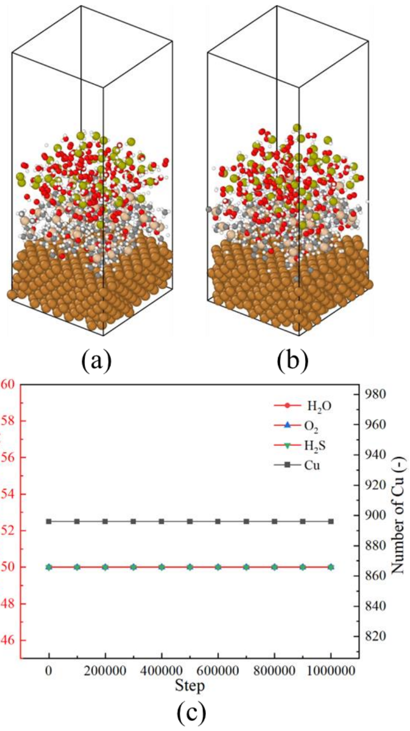

Fig. 4. Atomic distributions in Cu-HMDSO coating model (a) before and (b) after corrosion. (c) The number of gas molecules.

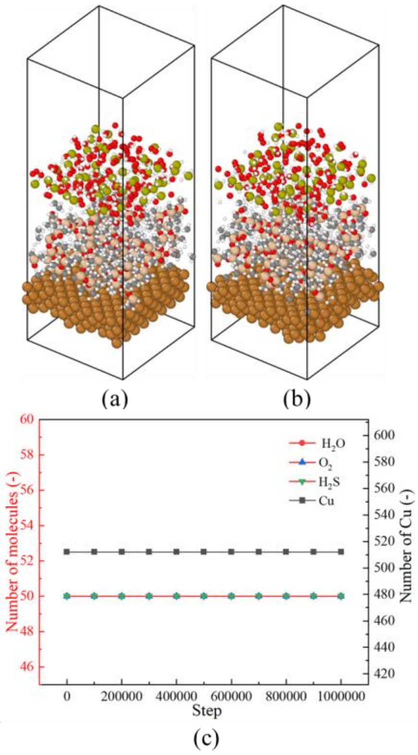

Fig. 5. Atomic distributions in Cu-PDMS coating model (a) before and (b) after corrosion. (c) The number of gas molecules.

When the Cu surface contains water, on one hand, H_2S dissolves in water to generate dissolved H^+ ions and S^{2-} ions, creating a weakly acidic environment. On the other hand, a small amount of oxygen dissolves in water, leading to oxygen-absorbing corrosion on the Cu surface, with the mechanism as follows [7]:

$$2Cu + O_2 \rightarrow 2CuO \tag{4}$$

$$\text{Cathode electrode: } 4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad (5)$$

$$\text{Anode electrode: } Cu - 2e^- \rightarrow Cu^{2+} \quad (6)$$

Then the dissolved Cu^{2+} ions can form CuS precipitates with S^{2-}:

$$Cu^{2+} + S^{2-} \rightarrow CuS \downarrow \quad (7)$$

Some of the initially formed CuO will also react with H_2S or sulfide ions in the environment, ultimately producing CuS:

$$CuO + H_2S \rightarrow CuS + H_2O \quad (8)$$

$$CuO + 2H^+ + S^{2-} \rightarrow CuS + H_2O \quad (9)$$

As for the other two models with coatings, their MD simulation results are shown in Fig. 4 and Fig. 5, respectively. Fig. 4 illustrates the simulation results of the model with the HMDSO coating. From the schematic of atomic distribution, it can be observed that the gas molecule layer underwent some diffusion during the simulation. However, within the 1000 ps simulation time, due to the hindrance of the coating, corrosive gas did not effectively diffuse into the coating layer, which avoided the close contact between the corrosive gases and Cu surface. Fig. 5 shows the simulation results of the model with the crosslinked PDMS coating. Similar to the previous model, the coating effectively blocked the diffusion of corrosive gas. The variation of the quantities of gas molecules during the diffusion process are shown in Fig. 4 (c) and 5 (c). No reaction products were observed in either model throughout the simulation process, indicating that both coatings provide good corrosion protection to the Cu surface. If we want to further compare the protective effects of the two coatings under long-term corrosion conditions, we need to conduct longer molecular dynamics simulations. However, due to the restriction of time and computing power, longer simulations could not be conducted at the moment.

It should be noticed that in some previous experiments, we found that plasma coatings formed with HMDSO have exhibited better hydrophobicity compared to crosslinked PDMS coatings. Since water plays a significant role in the H_2S corrosion process, the question arises whether this characteristic could enhance the corrosion resistance, leading to HMDSO coatings providing better protection than PDMS coatings. Further research from both experimental and simulation perspectives is needed to investigate this potential enhancement in corrosion resistance.

IV. CONCLUSION

In this study, molecular dynamics simulation was used to study the corrosion resistance of two coatings, including HMDSO formed by plasma treatment and crosslinked PDMS, on Cu surfaces in a high humidity and H_2S environment. Firstly, the interaction energies between the two coatings and the Cu surface were calculated in MS, demonstrating that the coatings can form good interconnection on the Cu surface, making it a feasible surface treatment option. The connection strength between the HMDSO coating and the Cu surface was found to be higher. Then, using LAMMPS, molecular dynamics simulations of three different models were conducted to analyze the protective effect of two coatings. The results indicated that both coatings have good blocking effects against corrosive H_2S, H_2O and O_2 gases, showing good corrosion protection to the Cu surface. Further research is needed to check their long-term corrosion protection conditions as well as the effect of hydrophobicity on corrosion resistance performances.

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