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DOI
10.1109/ICEPT59018.2023.10492230

Publication date
2023

Document Version
Final published version

Published in
Proceedings of the 2023 24th International Conference on Electronic Packaging Technology (ICEPT)

Citation (APA)
Li, S., Jiang, J., Liu, X., Wang, S., Zhang, Z., & Ye, H. (2023). Analysis of Metallization Effects of Pressure-Assisted Cu Nanoparticle Sintering on DBC by Experiment and Nanoscale Simulation. In *Proceedings of the 2023 24th International Conference on Electronic Packaging Technology (ICEPT)* (2023 24th International Conference on Electronic Packaging Technology, ICEPT 2023). IEEE. https://doi.org/10.1109/ICEPT59018.2023.10492230

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Analysis of Metallization Effects of Pressure-Assisted Cu Nanoparticle Sintering on DBC by Experiment and Nanoscale Simulation

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2023 24th International Conference on Electronic Packaging Technology (ICEPT) | 979-8-3503-3881-2/23/$31.00 ©2023 IEEE | DOI: 10.1109/ICEPT59018.2023.10492230

***Abstract*—Substrate metallization is a crucial factor affecting the mechanical properties of sintered nanoparticles in microelectronics applications, as it is essential for ensuring good adhesion between the substrate and the sintered material. In this study, we investigated the influence of metallization on pressure-assisted nanocopper sintering and analyzed the related mechanism of interaction using experiments and molecular dynamics simulation. In the first session, we bonded dummy dies on various substrates, including bare Cu, and substrates with Ag or Au metallization by nanocopper pressure-assisted sintering. The mechanical properties of the bonding layers were estimated using shear strength and SEM image analysis of fracture and cross-section morphologies under different sintering conditions. We found that the group of Cu-bare Cu have better bonding strength as the sintering temperature or assisted pressure is not high enough. However, as more energy input to the bonding layer, such as higher temperature or larger sintering pressure, the mechanical performance showed a significant increase. In the second session, a sintering model, which contained a single nanoparticle and substrate, was built to illustrate the effects of metallization from the perspective of solid-state wetting. The contact angle was estimated using a creative method, and the crystallization structure evolutions under different sintering conditions were analyzed. We found that the lattice boundary generated as the Cu nanoparticle coalescence with Ag or Au substrate, which may decrease the bonding strength. However, for Ag and Au metallization, limited interface diffusion can be observed at the neck region, where a few numbers of substrate atoms transmitted toward Cu nanoparticle, and the contact area was larger than that of bare Cu substrate. Finally, a simple uniaxial stretching simulation was conducted to prove the results of sintering simulation. This study provides valuable insights into the effects of metallization on pressure-assisted nanocopper sintering, which can contribute to the optimization of mechanical properties of sintered nanoparticles in microelectronics applications.**

Keywords*—Sintering; Nano Copper; Metallization; Molecular Dynamics*

I. Introduction

The widespread use of high-power electronic devices has made reliable connection technologies in high-temperature environments increasingly critical[1]. Sintering technology has gained much attention in this regard due to its advantages of good bonding performance, high strength, low defects, and high reliability. However, traditional welding techniques suffer from issues such as insufficient bonding strength and susceptibility to electromigration. In recent years, nanocopper paste has emerged as a promising new connection material, offering advantages such as lower cost, higher bonding strength, and weaker susceptibility to electromigration, making it a potential ideal connection material for next-generation electronic devices.

Metallization plays a crucial role in the sintering process of metallic materials[2], particularly in the case of wide bandgap power devices. Research in this area has led to the development of various metallization layers, including Ti/Ag, ENPA, and E-ENPA, which have been shown to improve the thermal and mechanical properties of sintered joints[3]. However, the impact of these metallization layers on sintering properties remains an active area of research[4], particularly for nanoscale copper particles, which have shown great promise in the development of next-generation electronic devices[5]. Recent experimental and molecular dynamics simulation studies have explored the effects of metallization layers on the sintering behavior of copper particles, providing valuable insights into the role of metallization layers in enhancing the sintering properties of metallic materials.

Several studies have investigated the effect of different metallization layers on the properties of sintered joints. For example, one study found that the shearing fracture toughness of sintered Ag bonded joints increased with increasing sintering temperature, with the sintered Ag/Ag joint showing the highest shearing fracture toughness while

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the sintered Ag/Ni joint showed the lowest. Another study explored the effect of different surface finish metallization layers, including Cu, Ni, Au, and Ag, on the shearing fracture toughness of sintered Ag bonded joints[6]. The results showed that the shearing fracture toughness for different kinds of specimens all increased with the sintering temperature, with the main factors affecting the discrepancy of the shearing fracture toughness being the interface connection ratio and contact angle.

In addition to experimental studies, molecular dynamics simulations have also been used to investigate the effect of metallization layers on the sintering behavior of copper particles[7]. One study found that the use of a thin layer of Ag on the surface of copper particles significantly improved the sintering properties of the particles, due to the formation of a strong Ag-Cu interface[4]. Another study explored the effect of different surface metallizations on the sintering behavior of copper nanoparticles, finding that the use of a thin layer of Au significantly improved the sintering properties of the particles[8].

In this study, we explored the impact of metallization on pressure-assisted nano copper sintering and examined the underlying mechanisms of interaction through both experiments and molecular dynamics simulations. Furthermore, we assessed the degree to which sintering factors, such as temperature and NP diameter, influenced the process based on both simulation and experimental results.

II. METHOD

A. Experimental Method

The Cu nanoparticles were synthesized by the physical vapor deposition method. The average diameter of the nanoparticles was controlled to be in the range of 120-150 nm. After synthesis, the nanoparticles were coated with organic materials such as citric acid to prevent oxidation, and other organic solvents like alcohol were used to enhance their printability. The modified nanoparticles were then printed onto a substrate using screen printing, with a controlled thickness of approximately 100 μm. The printed layer was subsequently dried for 5 minutes to remove any residual organic solvents. The dried layer was then sintered in an inert atmosphere at a temperature of 230-270°C and a pressure of 5-20MPa to achieve a compact and uniform layer. For substrate (DBC), a metallization of Ag and Au with a thickness of 1μm was coated on its surface. The DBC with bare Cu was also used to sintering. Therefore, in this work, we have three types of substrates, DBC with Ag metallization, DBC with Au metallization and bare Cu DBC. The samples of DBC with different type of surface were shown in figure 1.

Figure 1 DBC with bare Cu surface, Ag metallization and Au metallization.

After the sintering process, the shear strength of the sintered layer was evaluated by a shear strength tester, Dage 4000 machine with a shear speed of 200μm/s. Following the shear strength testing, the microstructure and morphology of the sintered samples were examined using Scanning Electron Microscopy (SEM). This analysis provided valuable insights into the sintering process, the bonding mechanisms, and the factors influencing the shear strength of the samples.

B. Simulation Method

We first simulate the coalescence process of single NP with single substrate. The wetting behavior of the nanoparticles on the substrate was studied using the molecular dynamics simulation method. The size of the nanoparticles was set to be 4nm, 6nm, and 8nm, and the crystal orientation was set to be [100]. The substrate was also set to be [100] crystal orientation. The fix-part was set to fix the bottom three layers of atoms. Therefore, we only focused on the data of atoms not in fix-part. The simulation was first performed at a temperature of 300K for 500ps to reach a stable state. The two models were then combined with a distance of 0.3nm, and the simulation was continued for 500ps at a temperature of 300K. The system was then heated to 800K for 50ps and cooled down to 300K for 50ps to balance the system. The wetting area was calculated by statistically analyzing the coordinates of each layer of atoms and estimating the area of each layer.

The tensile strength of the sintered layer was studied using the molecular dynamics simulation method. The temperature was set to be 400K, 500K, 600K, and 700K. The annealing model was first obtained by simulation by performing decrease temperature process with a fixed decrease speed. And then we used the new model to conduct the single tensile simulation with the stretching speed of 0.02nm/ps. The tensile time was set to be 20 ps. During tensile process, the upper part of particle was fixed, where the z-axis strength was set to zero. The data of tensile strength was calculated based on interaction between upper NP and fix-part of substrate.

Since in tensile simulation, we cannot directly obtain the shear strength, to analysis the contribution of sintering factors with the same type of result, we tried to evaluate the shear stress based on tensile stress from simulation with The shear strength obtained from the simulation was used to estimate the shear strength of the sintered layer. The experimental shear strength obtained under different sintering conditions was compared with the simulated shear strength using the analysis of variance (ANOVA) method to determine the significance of each sintering condition on the shear strength.

III. RESULTS AND DISCUSSION

A. Experiment

The impact of temperature on the shear strength of bare copper, Ag-metallization, and Au-metallization substrates was investigated in this study as shown in figure 2. It was observed that at low temperatures (210°C), the shear strength of all substrates was significantly low. For bare copper, the growth rate of shear strength exhibited minimal change, with a slight decrease between 230-250°C, followed by a recovery between 250-270°C. In contrast, the Ag metallization showed a slower growth rate of shear strength before 250°C and an increase between 250-270°C. The Au metallization

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exhibited a similar growth trend as Ag, but with an earlier increase in the growth rate at 230°C.

The effect of metallization on shear strength at different temperatures was also examined as shown in figure 3. At 210°C, the shear strength of bare copper substrates was higher compared to Cu-Ag and Cu-Au, which exhibited similar shear strengths. At 230°C, the shear strength of Cu-Cu connections remained the highest, but the differences between Cu-Ag, Cu-Au, and Cu-Cu decreased. At 250°C, Cu-Au shear strength slightly surpassed Cu-Cu, while Cu-Ag remained marginally lower than Cu-Cu. Interestingly, at 270°C, both Cu-Ag and Cu-Au exceeded Cu-Cu, suggesting a possible relationship with interfacial diffusion.

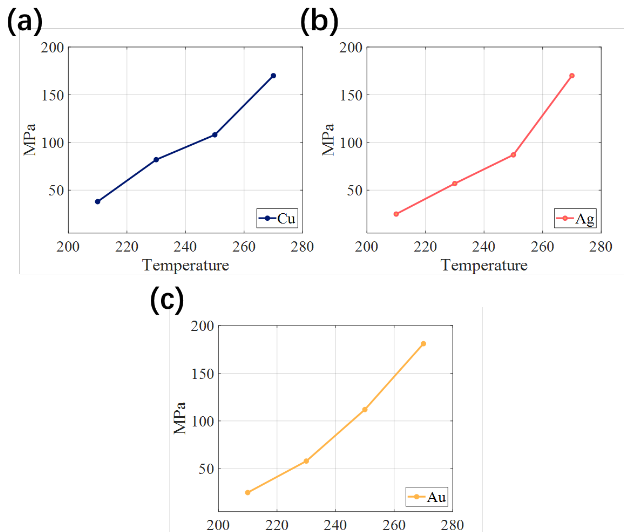

Figure 2 Impact of Temperature on Shear Strength for (a) Bare Cu (B) Ag-Metallization and (c) Au-Metallization

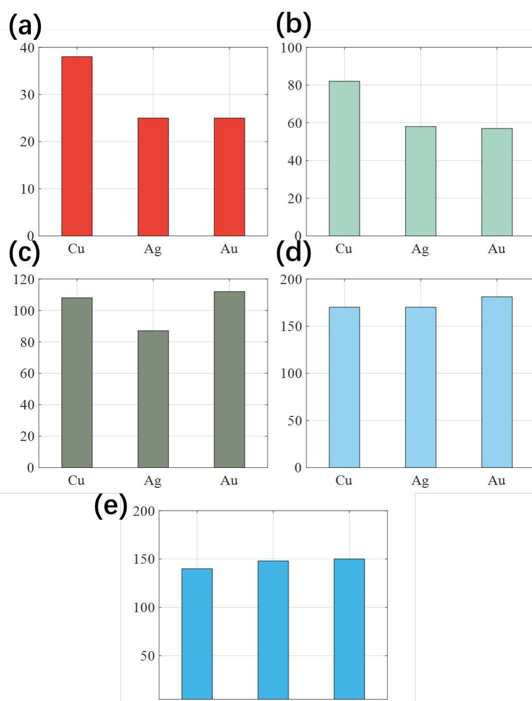

Figure 3 Impact of Metallization under different sintering environment, where (a)-(d) are sintered at 20 MPa 3min, under 210, 230, 250, 270 ˚C, (e) is sintered at 20MPa, 250˚C for 4min.

As the temperature increased, the interfacial diffusion rate also increased; however, at low temperatures, interfacial diffusion remained weak. The higher shear strength of Cu NP and bare copper could be attributed to their better crystal structure match under controlled oxidation conditions. To validate this hypothesis, a set of experiments was conducted at 250°C for 4 minutes, which demonstrated that Cu-Ag's shear strength was higher than Cu-Cu. Although diffusion had a more significant impact on sintering, the diffusion rate remained slow, necessitating a longer time to form stronger connections.

Cross-sectional SEM analysis of the metallization's impact on shear strength revealed larger voids in the cross-section between nanoparticle copper and the Au and Ag metallizations. A distinct cross-section was observed at the junction of Au metallization/Ag metallization and nanoparticle copper, whereas the connection on the bare copper substrate was more direct, without a clear connection cross-section. Despite no significant differences in porosity at 250°C-20MPa 3min, the color and other features of the cross-section exhibited noticeable disparities.

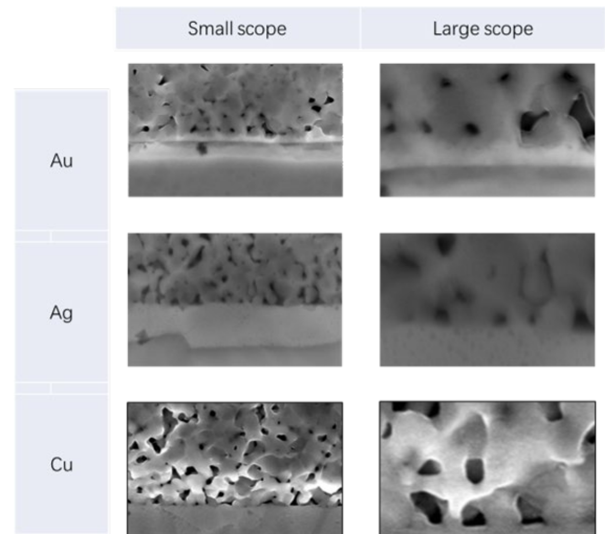

Figure 4 The SEM image of cross section morphology of Cu-Cu Substrate, Cu-Ag metallization and Cu-Au metallization

B. *Molecular Dynamics Study-coalescence process*

In this study, we investigate the coalescence process between a 4 nm Cu NP and an Ag metallization layer using molecular dynamics simulations. The crystal structures of the particles and the metallization layer are characterized by common neighbor analysis (CNA) and dislocation extraction algorithm (DXA). The snapshots were shown in figure 5.

At 5 ps, the Cu NP contacts the Ag metallization layer at the bottom. Both the Cu NP and the Ag layer maintain their crystal integrity, and no defects are generated. At 14 ps, a connection is formed between the Cu NP and the Ag layer. A significant number of atoms inside the Cu NP transform into amorphous and hexagonal close-packed (HCP) structures due to the lattice mismatch between the particle and the substrate. This mismatch results in the formation of grain boundaries at the interface. Dislocations are also generated above the amorphous atoms.

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At 20 ps, the bonding structure becomes more stable, and some atoms at the bottom of the Cu NP change from amorphous to HCP and body-centered cubic (BCC) structures. Although the proportion of amorphous atoms at the grain boundary decreases, the structure still remains non-crystalline. At 30 ps, the bonding structure stabilizes further as time progresses. To reduce the strain energy, dislocations expand, generating a large number of dislocations that move to the bottom of the structure and accumulate.

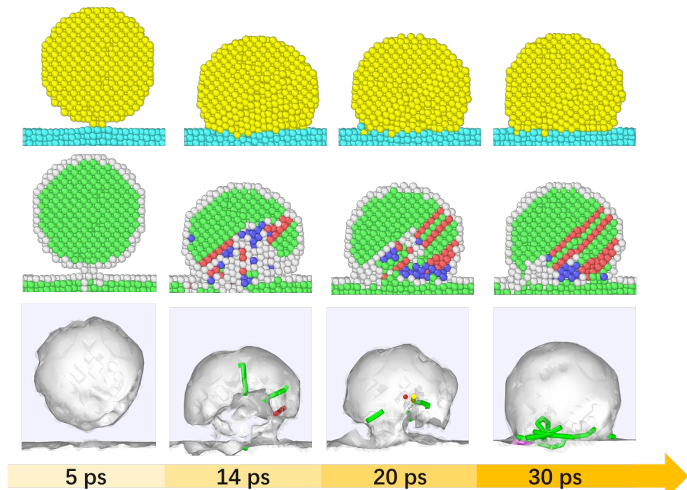

Figure 3 The snapshots of 4nm-Cu NP coalescence with Ag metallization from5 ps to 30 ps.

C. Molecular Dynamics Study-metallization effects

We also investigate the morphology and wetting of 8 nm Cu NPs on bare Cu substrate and Ag, Au metallization layers at different temperatures (500 K, 700 K, and 900 K) as shown in Figure 6. At 500 K, the wetting angle on the bare Cu substrate is large. Due to the absence of lattice mismatch, there is no tendency for interfacial diffusion, and only a few Cu atoms from the substrate move to the bonding interface.

At 500 K with Ag and Au metallization layers, the wetting angle is also large. However, due to lattice mismatch and surface energy effects, a significant number of atoms from the metallization layer move to the Cu NP. This phenomenon occurs even at low temperatures. At 700 K and 900 K, the spreading area of the Cu NP on the bare Cu substrate increases, with a few substrate atoms accumulating at the bonding interface. This accumulation appears to be driven by the reduction of the bonding interface surface area through diffusion.

On Ag and Au substrates, the spreading area increases more significantly with increasing temperature, and more atoms move to the bonding layer and above. This movement is a result of the combined effects of surface energy and diffusion energy. The wetting area of 8 nm Cu NPs on different substrates is further analyzed, with the simulation temperature range extended from 300 K to 1000 K.

At low temperatures, the wetting area of Cu NPs on the Cu substrate is larger than on Ag and Au metallization layers. Due to differences in surface energy and lattice constants, the wetting area of Cu NPs on the Au layer is slightly larger than on the Ag layer (at temperatures below 720 K). As the temperature increases, the diffusion area of Cu NPs on Ag and Au layers rapidly increases. When the temperature approaches 1000 K, the Cu NPs almost spread across the entire metallization surface. In contrast, the increase in the spreading area of Cu NPs on the bare Cu substrate remains relatively
small.

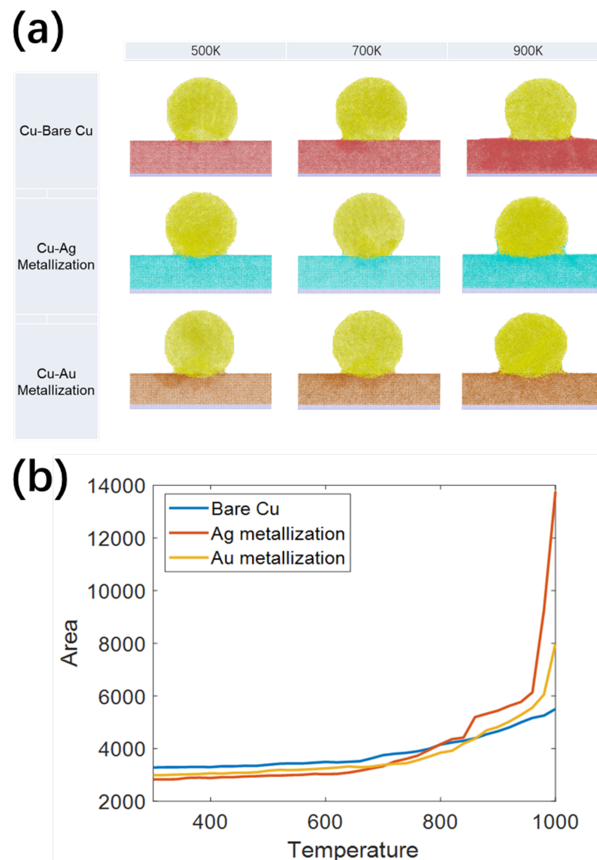

Figure 4 (a) The morphology of wetting state for 8 nm Cu NP and (b) is the wetting area evolution during heating process.

D. Shear stress Prediction Based on tensile

A simple tensile simulation was performed as , and although the results do not fully correspond to the real situation, some conclusions can be drawn through lateral comparison. To save simulation time and obtain the desired results, we only ensured that the simulation experienced the maximum stress point during the tensile process but did not break the connection between the particles and the substrate. The maximum stress point in this simulation is at the beginning of the tensile process. Since we are only concerned with the maximum stress value, a longer tensile time does not have much value.

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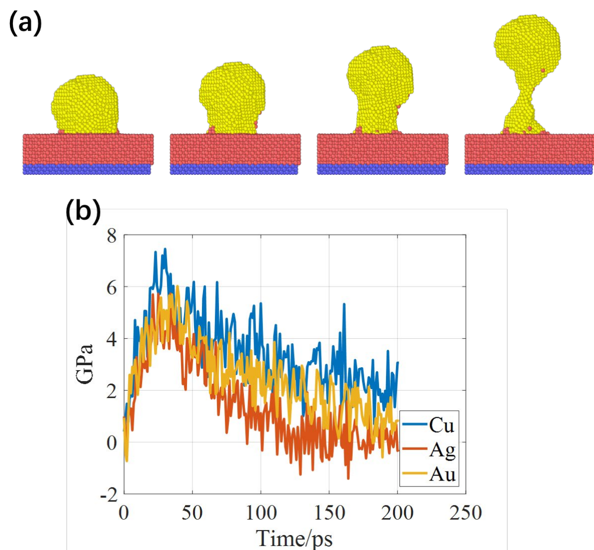

Figure 5 (a) The tensile simulation process for 8nm Cu NP and (b) is the tensile curves evolution during simulation for three types of simulation condition

This image shows the stress evolution during the tensile process of the 8nm-400K annealed model. It can be seen that the CuNP has the highest connection strength on the bare copper substrate. The maximum strength of CuNP on silver and gold plated substrates is similar, indicating that lattice mismatch has a significant impact on the connection strength. We also present a curve showing the strength changes with temperature in figure 8.

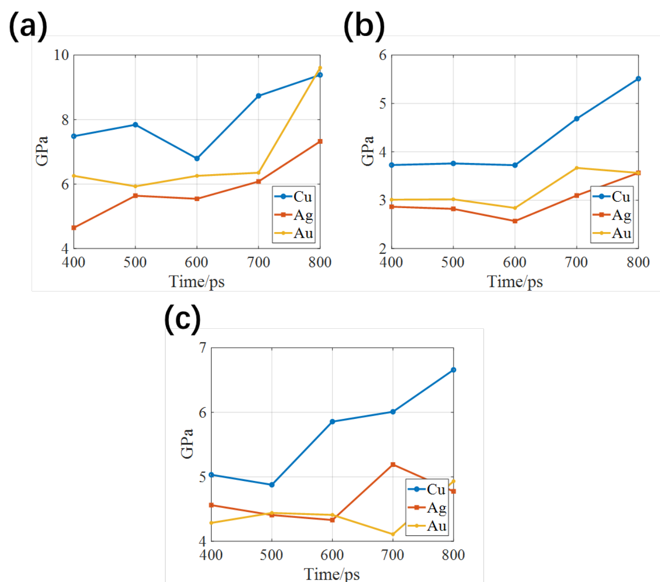

Figure 6 The Shear Strength obtained from simulation depend on temperature adn substrate surface, where (a) is 4nm NP, (b) is 6 nm NP and (c) is 8nm NP

To obtain more statistically significant results, we explored the degree of influence of various factors on shear strength using the full factorial experimental method. The results were shown in figure 9. Additionally, to form a comparison, we analyzed both experimental results and simulations results. The response of both simulation and experiment were set as shear strength. The factors in the simulation were particle size, metallization, and temperature, while the factors in the experiment were metallization and temperature.

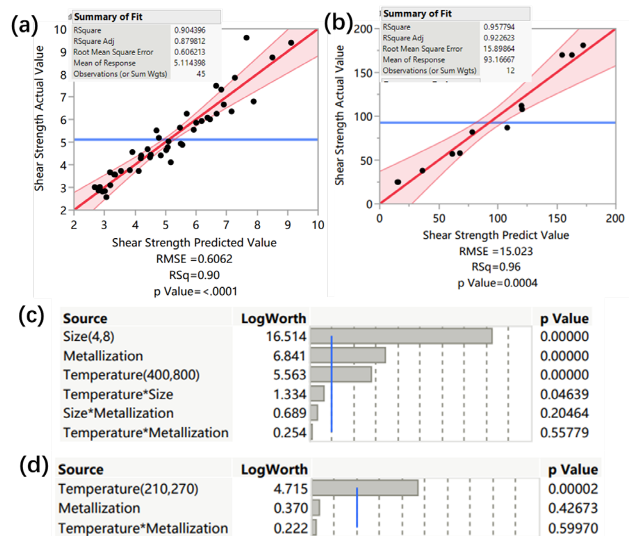

Figure 7 (a) and (b) were The Actual Value- predict Value curves for simulation and experiment respectively, (c) and (d) were the effect summary of simulation and experiment.

In the simulation, the RMSE of the predicted value is 0.6062, with a p-value <0.0001 and RSq=0.9, indicating that the predicted value is quite accurate. The significance of the three main effects of size, metallization, and temperature is considerable, with LogWorth values all greater than 2. Their interaction effects are all less than 2, indicating that the interactive influence is relatively small. The p-values of the three main effects are all equal to 0, indicating extremely high significance.

In the experimental results, the RMSE of the predicted value is 15.023, with a p-value =0.0004 and RSq=0.96, also showing that the predicted result is reliable. In the experiment, the influence of the metallization is relatively small, and the main effect is time. The p-value of this effect is 0.00002, indicating extreme significance. Combined with the simulation results, it can be seen that temperature plays a significant role in both cases, with small p-values and significance levels less than the specified 0.05. Therefore, the prediction accuracy of both temperature significance is extremely high, exceeding 85%, and the model fits the data very well, also large than the conventional request, 85%. Finally, we used the least squares method to predict the relationship between each factor and shear strength under experimental conditions. This approach allowed us to better understand the contributions of each factor and their interactions, providing valuable insights for further research and optimization of the tensile/shear process.

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$$
\begin{aligned}
&93.166666667 \\
&+71.2 \cdot \left(\frac{(\text{Temperature} - 240)}{30} \right) \\
&+\text{Match}(\text{Metallization}) \begin{pmatrix} \text{"Bare Cu"} & \Rightarrow 6.3333333333 \\ \text{"Ag"} & \Rightarrow -7.166666667 \\ \text{"Au"} & \Rightarrow 0.8333333333 \\ \text{else} & \Rightarrow . \end{pmatrix} \\
&+\left(\frac{(\text{Temperature} - 240)}{30} \right) \cdot \text{Match}(\text{Metallization}) \begin{pmatrix} \text{"Bare Cu"} & \Rightarrow -7.9 \\ \text{"Ag"} & \Rightarrow 0.8 \\ \text{"Au"} & \Rightarrow 7.1 \\ \text{else} & \Rightarrow . \end{pmatrix}
\end{aligned}
$$

IV. CONCLUSION

In conclusion, this study investigated the impact of temperature and metallization on the shear strength of bare copper, Ag, and Au substrates in contact with Cu nanoparticles (NPs) through molecular dynamics simulations and tensile simulations. The coalescence process between a 4 nm Cu NP and an Ag metallization layer was analyzed, providing insights into the structural changes and bonding mechanisms at the interface. The wetting behavior of 8 nm Cu NPs on bare Cu, Ag, and Au metallization layers at different temperatures was also examined, revealing the influence of lattice mismatch, surface energy effects, and diffusion energy on the spreading area of Cu NPs.

The tensile simulations were performed to predict the shear strength of Cu NPs on different substrates, considering particle size, metallization, and temperature as factors. The results demonstrated the significant impact of these factors on the connection strength, with temperature playing a crucial role in both simulation and experimental results. The least squares method was employed to predict the relationship between each factor and shear strength under experimental conditions, which allowed for a better understanding of their contributions and interactions.

Overall, this study provides valuable insights into the bonding mechanisms and shear strength of Cu NPs on various substrates, which can be useful in optimizing the tensile/shear process for practical applications. Future research could focus on exploring other factors that may influence the bonding strength, as well as investigating the long-term stability and reliability of these connections.

ACKNOWLEDGMENT

This research is supported by the Shenzhen Fundamental Research Program (JCYJ20200109140822796).

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