

**Document Version**

Final published version

**Citation (APA)**

Zhu, Y., Wang, L., Wang, Y., Li, S., Zong, Q., Gao, C., Liu, X., & Ye, H. (2025). Molecular Dynamics Study on the Sintering Behavior and Mechanical Properties of Graphene-Doped Nano-Copper. In *Proceedings of the 2025 26th International Conference on Electronic Packaging Technology (ICEPT) (2025 ed.)*. IEEE.  
<https://doi.org/10.1109/ICEPT67137.2025.11157055>

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# Molecular Dynamics Study on the Sintering Behavior and Mechanical Properties of Graphene-Doped Nano-Copper

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**Abstract**—Graphene is widely used to reinforce metal matrix composites due to its excellent physical and mechanical properties. However, its poor interfacial wettability and dispersion problems in copper-based brazing filler metals still limit its application effect. This study explored the influence of graphene on the sintering behavior and structural properties of copper nanoparticles under different doping conditions through molecular dynamics simulation combined with experimental methods. The results show that an appropriate amount of well-dispersed graphene helps promote the densification process and improve the structural stability, while graphene in the agglomerated state may have an adverse effect on the mechanical properties. This work provides theoretical support and experimental basis for optimizing the application of graphene in copper-based brazing metals.

**Keywords**—Cu paste, sintering, graphene, molecular dynamics

## I. INTRODUCTION

In recent years, the growing demand for high-precision electronic devices has driven the rapid development of electronic packaging technologies, and the increasing output value of the packaging industry has attracted widespread attention. As chip manufacturing continues to advance, the feature size of fabrication processes continues to shrink, placing increasingly stringent performance requirements on packaging materials. Traditional Sn-based solders suffer from shortcomings such as short fatigue life, high melting

point, and brittleness, which can no longer meet the demands of modern high-power applications. As a result, researchers have shifted their focus to Ag-based and Cu-based materials, which offer superior electrical conductivity and ductility [1]. Compared to Ag-based solders, Cu-based solders exhibit better high-temperature resistance and cost-effectiveness; however, they are prone to oxidation at elevated temperatures and are susceptible to failure caused by thermal expansion mismatch. Therefore, researchers have attempted to incorporate graphene—known for its high thermal stability and excellent oxidation resistance—into Cu-based sintering pastes to enhance their electrical and mechanical properties [2, 3].

Graphene has a monolayer two-dimensional structure, which gives it exceptional physical and mechanical properties. It has been widely used in composite materials as a result. However, its poor interfacial affinity with metals limits its wetting behavior with copper, resulting in unavoidable degradation in both electrical and thermal conductivity in graphene-reinforced Cu composites [4]. Furthermore, the strong van der Waals interactions between graphene layers tend to cause aggregation, making it difficult to achieve uniform dispersion during processing [3, 5]. Numerous studies have confirmed the beneficial effects of graphene on Cu paste. Bashirvand et al. [6] investigated the influence of graphene/Cu interfacial interactions on the elastic constants of the composite and concluded that graphene is an excellent reinforcement for metal matrices.

Chu et al. [7] employed oxygen plasma treatment to modify the surface of graphene nanoplatelets and found that the oxygen-containing functional groups introduced by the treatment imparted good dislocation storage capabilities, effectively improving the ductility and fracture elongation of the composites. Lyu et al. [8] studied the sintering process of Cu nanoparticles (Cu NPs) and graphene-doped Cu nanoparticles (Gr-Cu NPs) via molecular dynamics simulations and concluded that the presence of graphene reduces the sintering rate of Cu.

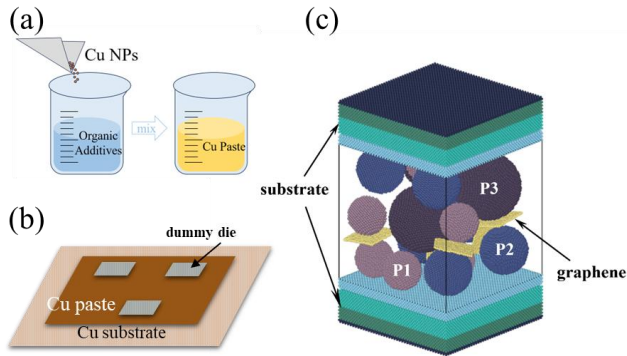


Fig. 1. (a) The fabrication methodology for Cu paste; (b) Cu paste and substrate structure; (c) model for LAMMPS simulation.

The microstructural evolution of metals during sintering occurs on the nanosecond timescale, making it difficult to capture these structural changes experimentally. Moreover, sintering outcomes are simultaneously influenced by multiple factors such as heating rate, pressure, and particle size, which adds to the difficulty of reproducing experimental results. Molecular dynamics (MD) simulation offers a way to directly observe microstructural phenomena such as defect evolution and interface formation during sintering, and it allows for precise control over each influencing factor. Therefore, in this study, MD simulations were employed to investigate the sintering mechanism of graphene-doped Cu paste at the atomic scale. A sintering model, as illustrated in Fig. 1(c), was constructed to analyze the effects of varying graphene content on the sintering behavior of Cu nanoparticles. Furthermore, experimental validation was performed to support the findings obtained from the simulations.

## II. METHODOLOGY

### A. Model Construction of Graphene-Doped Copper Nanoparticles

In this study, the simulation model was constructed using Python in conjunction with OVITO. In order to simulate the distribution of copper nanoparticles more realistically, a representative model as shown in Fig. 1(c) was designed with reference to the experimental design in Fig. 1(b). The system consists of three main components: pure copper substrates at the top and bottom, copper nanoparticles, and graphene nanosheets doped within the nanoparticle region. The upper and lower substrates are divided into four layers according to their distances from the interface, which are used for structural fixation, energy analysis and density reflection.

In the actual sintering process, copper nanoparticles do not exhibit regular arrangement. To more accurately reflect this behavior, a Python script was used to randomly generate

nanoparticles with varying sizes and positions. The simulation box was set to  $150 \times 150 \text{ \AA}^2$  in the xy-plane, and the particle radii ranged from  $20 \text{ \AA}$  to  $35 \text{ \AA}$ . In order to bring the atomic system to an energetically stable state, energy minimization was first performed using the conjugate gradient algorithm. Following minimization, the system was equilibrated under the canonical ensemble (NVT) using the Nose-Hoover thermostat to maintain a constant number of atoms (N), volume (V), and temperature (T). This was achieved via the `fix nvt` command in LAMMPS. During the sintering and cooling processes, the evolution of potential energy and atomic structure was analyzed.

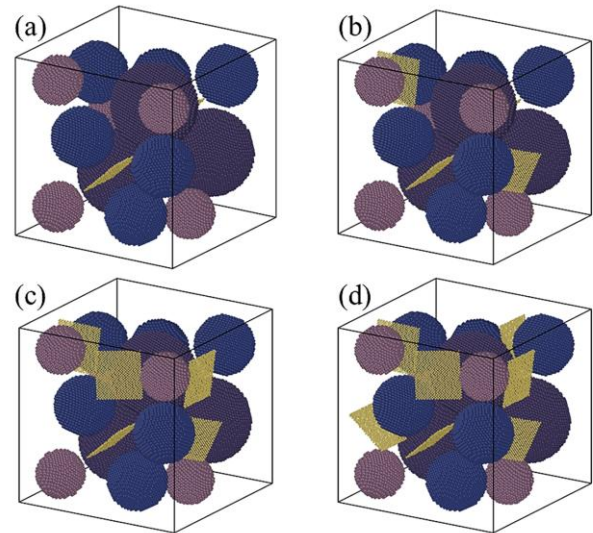


Fig. 2. Simulation models of graphene-doped copper particles (a) 0.253 wt%; (b) 0.505 wt%; (c) 0.754 wt%; (d) 0.996 wt%.

To investigate the effects of graphene doping in realistic conditions, randomly distributed graphene nanosheets ( $40 \times 40 \text{ \AA}^2$ ) were inserted into the void regions between copper nanoparticles. A surface fluctuation of  $0.5 \text{ \AA}$  was applied to simulate the natural wrinkling of graphene. The number of graphene sheets was used as a variable (Fig. 2), resulting in graphene mass fractions of 0.253%, 0.505%, 0.754%, and 0.996%, respectively. In the final model, the copper nanoparticles contained 96,129 Cu atoms, and each graphene sheet consisted of 1,292 carbon atoms.

### B. Simulation Details

The simulation was conducted in a three-dimensional Cartesian coordinate system. Periodic boundary conditions were applied in the x and y directions (p), while the z direction was set to be non-periodic (f), in order to simulate realistic sintering behavior between nanoscale substrates. The atomic style was set to atomic.

For the interatomic interactions, the embedded atom method (EAM) was employed to describe Cu-Cu interactions. The AIREBO (Adaptive Intermolecular Reactive Empirical Bond Order) potential was applied to describe both bonding and non-bonding interactions between carbon atoms. The heterogeneous Cu-C interactions were modeled using the Lennard-Jones (LJ) potential [9]:

$$V_{ij} = 4\epsilon_{CCu} \left[ \left( \frac{\sigma_{CCu}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{CCu}}{r_{ij}} \right)^6 \right]$$

With parameters set as  $\epsilon = 0.02578$  eV and  $\sigma = 3.0825$  Å [10, 11]. The chosen  $\sigma$  value was smaller than the initial minimum distance between Cu and C atoms in the system to avoid entering the strong repulsive regime of the LJ potential.

In terms of thermodynamic control, thermo output was performed every 1000 steps, including temperature, energy, and stress components. Additionally, atomic configuration data were dumped every 1000 steps for Common Neighbor Analysis (CNA) to monitor structural evolution and defect formation during sintering. The initial temperature was set to 300 K, and the system was gradually heated to 500 K at a constant rate over 200 ps. The system was then held at 500 K for 500 ps to ensure sufficient sintering. Subsequently, it was cooled linearly to 300 K over 200 ps under isothermal and isotropic conditions, to prevent the generation of non-uniform thermal stress. After sintering, the system was relaxed at 300 K for 100 ps to eliminate residual thermal stress and stabilize the microstructure.

### C. Experimental Process

The materials required for preparing the sintered samples include nano-copper particles, graphene, and an organic solvent. Figure 3 displays the SEM characterization of the doped graphene powder and Cu nanoparticles.

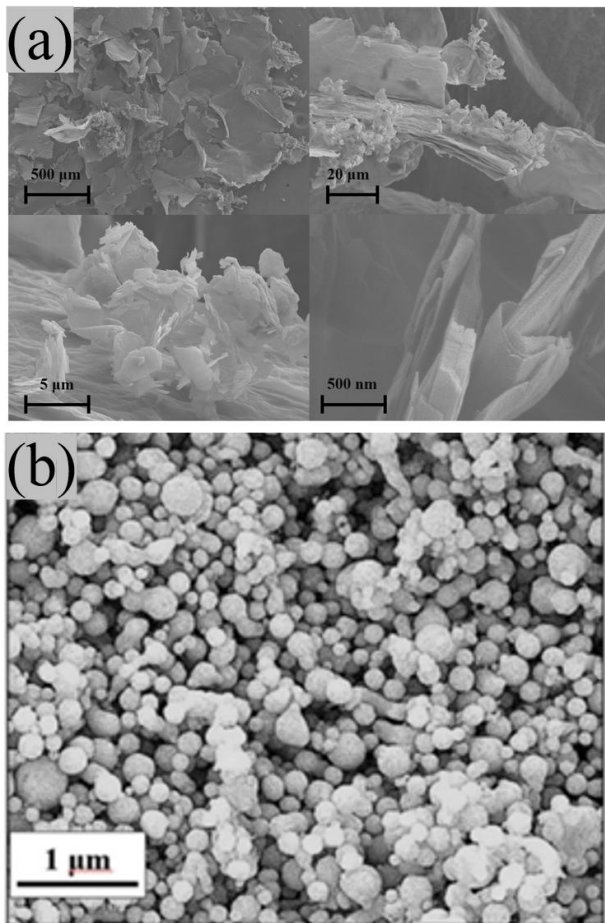


Fig. 3. Scanning electron micrographs of: (a) graphene powder; (b) Cu nanoparticles.

Two types of Cu pastes were formulated for sintering: one containing aggregated graphene and the other containing uniformly dispersed graphene. The solid content in both types of Cu pastes was maintained above 85%. For the

preparation of the aggregated graphene sample, untreated graphene sheets were directly mixed with copper nanoparticles to formulate the paste. In contrast, for the uniformly dispersed sample, graphene nanoplatelets were first subjected to ultrasonic dispersion and then added to a pre-prepared Cu paste, followed by thorough mixing to ensure homogeneous distribution.

After preparation, each paste sample was homogenized in a centrifuge for 2 minutes and then uniformly printed onto pure copper substrates using a stainless-steel stencil with a thickness of 100 μm. Three pieces of dummy dies were subsequently placed on top of the printed paste, as illustrated in Fig. 1(a). The printed substrates were then subjected to pressure-assisted sintering in a nitrogen atmosphere at 270 °C for 3 minutes under an applied pressure of 20 MPa.

## III. RESULT AND DISCUSSION

### A. Simulation Process

In the early stage of heating, the potential energy of all systems increases rapidly, which is attributed to thermal disturbance causing intense atomic motion, thereby driving the system from an initially lower energy state to a thermodynamically unstable configuration. Fig. 4(a) illustrates the evolution of potential energy during the sintering process for systems with varying graphene doping concentrations.

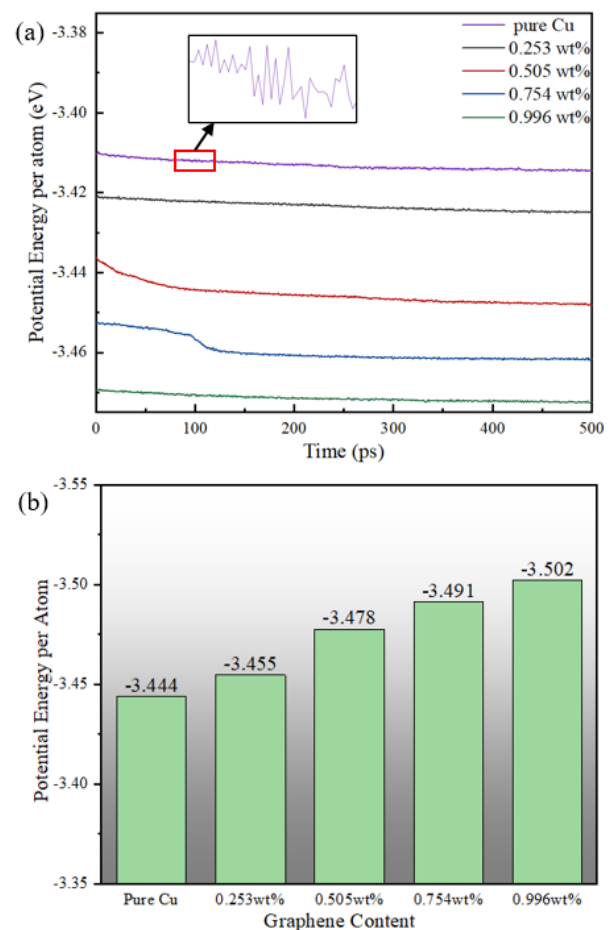


Fig. 4. (a) Potential Energy per Atom vs. Time Step; (b) Final potential energy per atom after sintering.

It can be observed that the potential energy gradually decreases and eventually stabilizes during the subsequent isothermal sintering phase, indicating that interparticle

interactions promote structural rearrangement and densification, leading the system toward a lower-energy, more stable state. Notably, as the graphene doping concentration increases, the average potential energy throughout the sintering process consistently decreases, and the final stabilized energy level is also comparatively lower. As shown in Fig. 4(b), the final average potential energy is highest in the pure copper system and declines progressively with increasing graphene content. This trend suggests that the introduction of graphene helps to reduce the total and per-atom energy of the system, thereby enhancing the stability of the atomic structure, improving thermal stability, and promoting a more effective sintering process.

This overall behavior can be attributed to the structural modulation effect imparted by graphene during sintering. On one hand, graphene's high thermal stability and large specific surface area facilitate interparticle adhesion and diffusion, thereby contributing to increased densification. On the other hand, the presence of graphene may suppress the formation of local grain boundary distortions and metastable structural configurations, leading to a lower overall energy state. These observations collectively demonstrate that appropriate levels of graphene doping play a positive role in improving sintering quality.

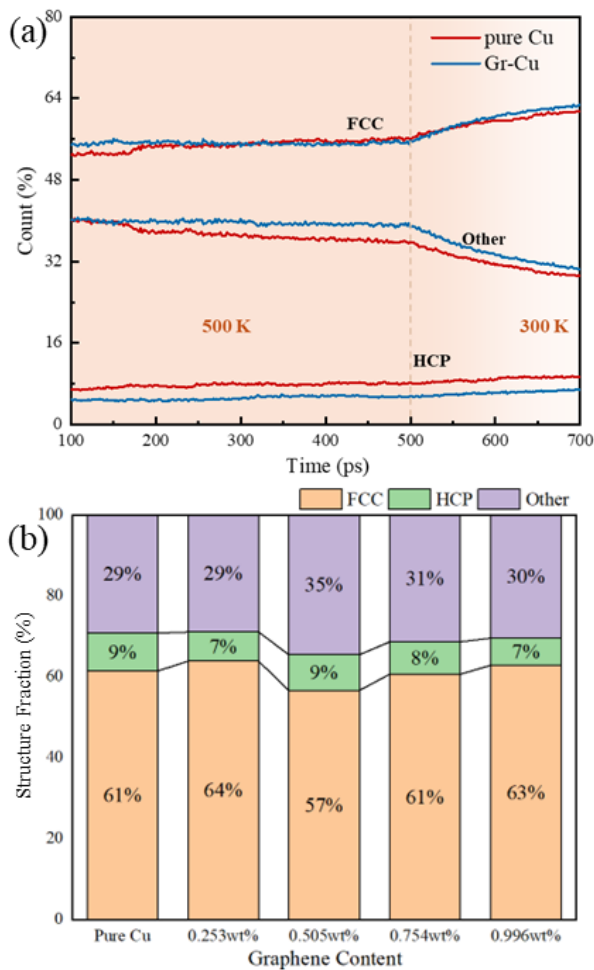


Fig. 5. (a) The evolution of phase content during sintering and cooling processes; (b) the structure fraction phase content of pure Cu, 0.253 wt%, 0.505 wt%, 0.754 wt%, and 0.996 wt% after cooling process.

After the cooling stage, the distance between the upper and lower substrates before and after sintering was compared.

It is evident that the volume of all sintered structures decreased. Furthermore, within the tested range of graphene mass fractions, systems with higher graphene content exhibited greater volumetric shrinkage. This indicates that the incorporation of graphene nanosheets contributes to improved densification of copper nanoparticles during sintering. Such densification is beneficial to the continuity and structural integrity of the sintered materials.

CNA analysis was performed during the sintering and cooling processes to compare the phase evolution between pure Cu and the 0.996 wt% graphene-doped system under isothermal sintering at 500 K followed by uniform cooling to 300 K, as shown in Fig. 5(a). It was observed that during the sintering stage, the difference in FCC (face-centered cubic) phase content between the pure Cu and Gr-Cu systems was minor, although the HCP (hexagonal close-packed) content in pure Cu remained slightly higher than that in the graphene-doped counterpart. However, after the completion of the cooling process, the phase compositions of the two systems became nearly identical.

During the isothermal sintering and uniform cooling processes, the variation in total dislocation line length closely followed the trend of HCP phase content, both exhibiting a gradual increase. Moreover, the total dislocation line length in the pure Cu system was significantly greater than that in the Gr-Cu system.

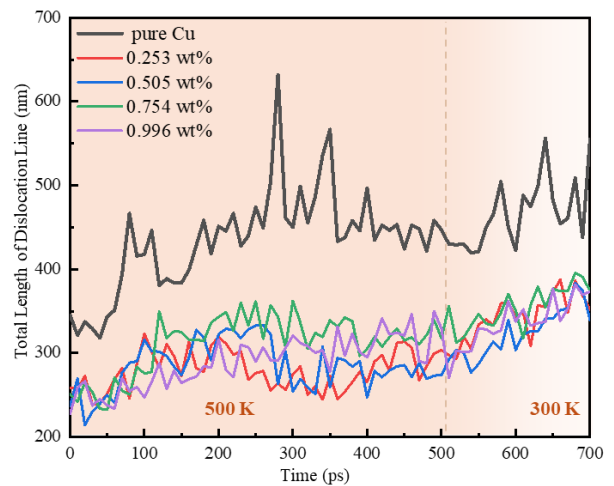


Fig. 6. The evolution of total length of dislocation line for pure Cu, 0.253 wt%, 0.505 wt%, 0.754 wt%, and 0.996 wt% during sintering and cooling processes.

Fig. 7 shows the evolution of HCP structures and dislocation lines in the model during the isothermal sintering process. A detailed examination of the distributions reveals that in the pure Cu system, HCP structures gradually form at the interfaces between particles and remain largely unchanged once established. In contrast, in the Gr-Cu system, HCP structures exhibit continuous rearrangement at the boundaries between different copper particles, indicating a more dynamic structural evolution.

This contrast suggests that the presence of graphene alters the local structural stability and stress distribution during sintering. In pure Cu, stable HCP phases tend to emerge due to localized stacking faults at particle junctions. However, in the graphene-doped system, the presence of graphene affects the packing and bonding configurations

between particles, possibly introducing local disturbances or inhibiting the stabilization of grain boundaries. As a result, HCP structures remain in a state of continuous adjustment throughout the sintering process. These observations imply that graphene plays a regulatory role in microstructural evolution, potentially suppressing structural locking at grain boundaries and promoting dynamic rearrangement mechanisms during densification.

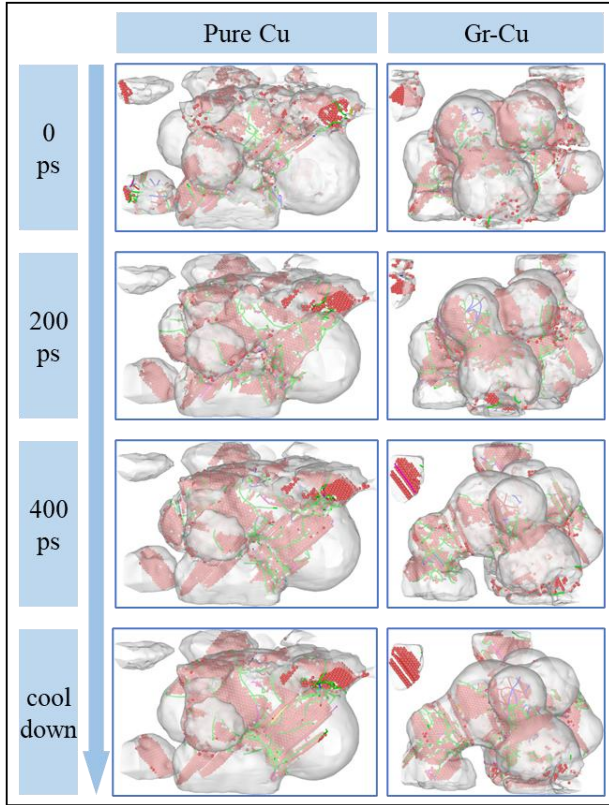


Fig. 7. The evolution of total length of dislocation line for pure Cu, 0.253 wt%, 0.505 wt%, 0.754 wt%, and 0.996 wt% during sintering and cooling processes.

Fig. 8 provides an intuitive visualization of the spatial distribution of graphene sheets, HCP structures, and dislocation lines in the 0.996 wt% Gr-Cu system after the isothermal sintering process. It is evident that the graphene sheets predominantly adhere to the surfaces of copper particles and rarely penetrate their interiors. The copper particles encapsulated by graphene exhibit a stable FCC structure, with almost no dislocations forming inside them; most dislocation lines are concentrated at the interfaces between adjacent copper particles.

This observation indicates that the role of graphene in structural regulation is primarily interfacial rather than interstitial. The interaction between graphene and copper is governed by relatively weak van der Waals forces, which limits graphene's ability to embed into the copper lattice. As a result, graphene acts more as a surface barrier, stabilizing the outer atomic layers and suppressing internal lattice rearrangement or defect formation, thereby creating a multiphase structure with distinct stress distribution characteristics.

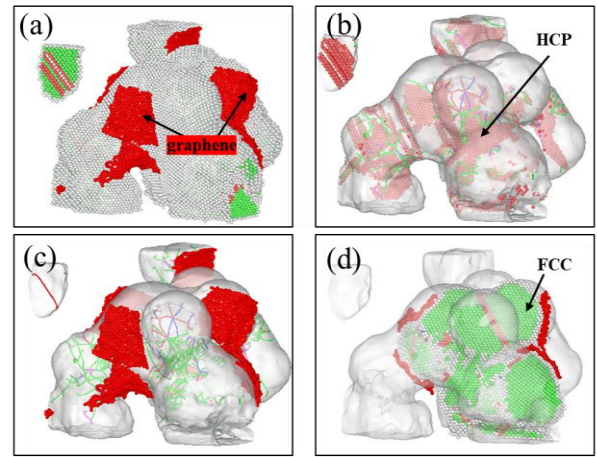


Fig. 8. (a) CNA analysis with graphene highlighted; (b) DXA analysis; (c) DXA analysis with graphene highlighted; (d) 5 Å wide slice of CNA.

The analyses of Fig. 7 and Fig. 8 demonstrate that the incorporation of graphene significantly influences the microstructural evolution during the sintering of copper nanoparticles. On one hand, graphene alters the structural evolution at particle interfaces, enabling more dynamic rearrangement of HCP phases in the Gr-Cu system and preventing local structural locking. On the other hand, graphene acts as a surface encapsulant that stabilizes the internal fcc structure of copper particles and suppresses dislocation formation within them, leading to stress localization at particle junctions. Collectively, these effects highlight graphene's dual role in enhancing densification while modulating structural stability and stress distribution.

### B. Experimental Verification

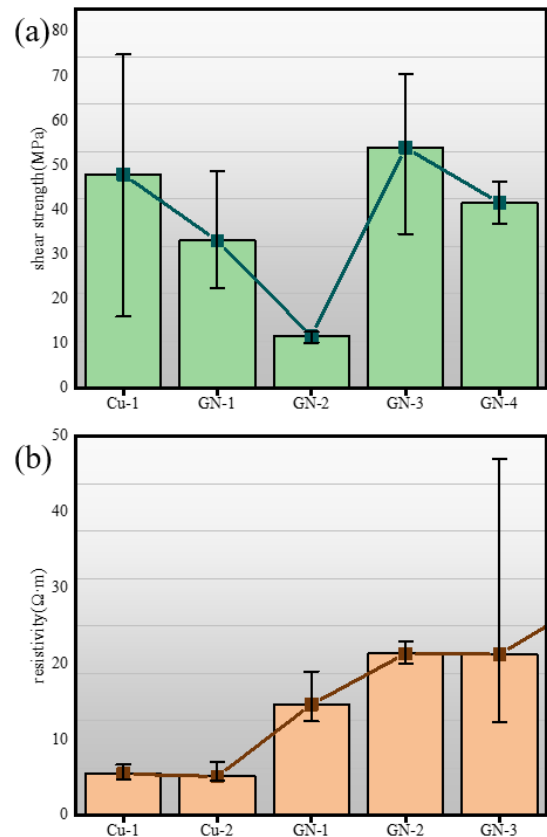


Fig. 9. Copper paste with different graphene contents: (a) Shear strength; (b) resistivity.

Fig. 9 presents the measured shear strength and electrical resistivity of samples containing aggregated graphene after sintering. It is found that while aggregated graphene shows limited enhancement in mechanical strength, as evidenced by the lack of significant increase in shear strength, it notably reduces electrical conductivity. In contrast, Cu pastes doped with discrete, monolayer graphene sheets exhibit improved mechanical properties after sintering, outperforming those containing aggregated graphene.

#### IV. CONCLUSION

By comparing the simulation and experimental results, it can be concluded that under well-dispersed conditions, the presence of a small amount of graphene can promote the densification of the sintering process, reduce the potential energy of the system, and enhance the structural stability of the copper paste. Graphene effectively inhibits the formation of internal dislocations and promotes the dynamic structural rearrangement at the particle interface.

In contrast, polymerized graphene offers limited mechanical improvements and significantly reduces electrical conductivity. These findings indicate that the dispersion quality and concentration of graphene are key factors in optimizing the performance of graphene-doped copper paste. When graphene is unevenly dispersed and tends to agglomerate, its effect may be counterproductive. Agglomerated graphene has limited ability in enhancing mechanical properties (with little change in shear strength), and its electrical conductivity drops significantly due to the disruption of the continuous conduction path of copper. This phenomenon highlights the key role of the dispersion degree of graphene in its enhancement effect.

#### ACKNOWLEDGEMENT

This research was supported by Grant No. 2023TQ07C475, YIXINXINXI Technology Advanced State Perception Joint Lab, the ENMICRO Precision Electronics Advanced Packaging and Testing Technology Joint Lab, and Shennan Circuits Sky Chip Interconnection Advanced Packaging Technology Joint Lab.

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