Investigating Coalescence Kinetics in Cu Nanoparticle by Molecular Dynamics and 3D Reconstruction

Du, Leiming; Ji, Xinrui; Liu, Kai; Fan, Jiajie; Zhang, Guoqi

DOI
10.1109/ICEPT63120.2024.10668699

Publication date
2024

Document Version
Final published version

Published in
Proceedings of the 25th International Conference on Electronic Packaging Technology, ICEPT 2024

Investigating Coalescence Kinetics in Cu Nanoparticle by Molecular Dynamics and 3D Reconstruction

Leiming Du *
Department of Microelectronics
Delft University of Technology
Delft, Netherlands
L.Du@tudelft.nl

Xinrui Ji
Department of Microelectronics
Delft University of Technology
Delft, Netherlands
x.ji@tudelft.nl

Kai Liu
Department of Materials Science and Engineering
Delft University of Technology
Delft, Netherlands
k.liu-3@tudelft.nl

Jiajie Fan
Academy for Engineering & Technology
Fudan University
Shanghai, China
jiajie_fan@fudan.edu.cn

Guoqi Zhang
Department of Microelectronics
Delft University of Technology
Delft, Netherlands
g.q.zhang@tudelft.nl

2024 25th International Conference on Electronic Packaging Technology (ICEPT) | 979-8-3503-5380-8/24/$31.00 ©2024 IEEE | DOI: 10.1109/ICEPT63120.2024.10668699

***Abstract*—This study presents a dual approach combining molecular dynamics simulations and experimental analysis to explore the sintering behavior of copper (Cu) nanoparticles. Our simulation model comprises 240 nanoparticles, through which we systematically examine the coalescence kinetics during the sintering process. The simulations provide a detailed view of the particle interactions, structural evolution, and the mechanisms driving nanoparticle fusion at the atomic level. Complementing the simulations, we conducted 3D reconstructions using Focused Ion Beam Scanning Electron Microscopy (FIB-SEM) to characterize the microstructure of the sintered nanoparticles. This hybrid approach not only deepens our understanding of the fundamental processes governing the sintering of Cu nanoparticles but also bridges the gap between theoretical predictions and experimental observations, offering insights into the optimization of sintering processes in practical applications.**

Keywords—sintering, Cu nanoparticles, molecular dynamics simulation, coalescence kinetics, 3D reconstruction

I. INTRODUCTION

As the demand for higher performance in power electronics continues to escalate, the development of materials capable of operating under extreme conditions has become crucial. Third-generation wide bandgap power semiconductors, like silicon carbide (SiC) and gallium nitride (GaN), have set new standards for devices that can efficiently perform at elevated temperatures [1]. These semiconductors are pivotal in sectors that require robust performance, such as in electric vehicles, renewable energy systems, and high-power electronics. However, the full potential of these materials is often limited by traditional interconnect technologies, which cannot withstand the high operational temperatures. This challenge has led to the exploration of novel sintering materials, particularly metal nanoparticles, due to their superior thermal and electrical conductivities. Among these, Cu nanoparticles (Cu NPs) have garnered significant interest, which presents an intriguing alternative to traditional solder materials, such as Sn-Ag and Sn-Ag-Cu. These conventional solders, with melting points ranging from 482–493 K, are ill-suited for the high-temperature environments necessitated by next-generation semiconductors. On the other hand, Cu NPs can be sintered at temperatures significantly lower than their melting point (1358 K), offering a robust solution that maintains structural integrity and connectivity under high thermal conditions.

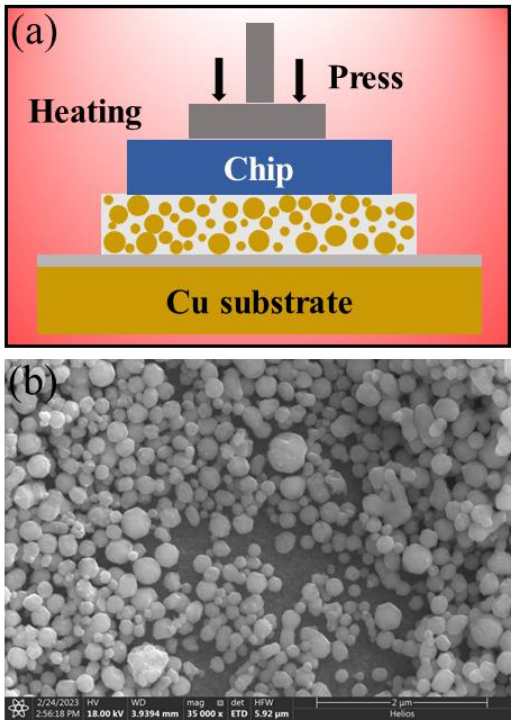

Fig. 1. (a) Schematic of thermal-compressive sintering process; (b) SEM image of the Cu nanoparticles.

Some researchers have investigated the effect of sintering process parameters on the microstructure of sintered Cu NPs [2-5]. For example, Liu et al. [2] studied the effect of sintering temperature, pressure and time on the microstructure and bonding strength of Cu NPs sintered with a protective atmosphere. In their study, an optimal combination of sintering process parameters (250 ℃, 20 MPa and 3 min) was proposed and the die shear strength of more than 100 MPa was achieved. The Cu NPs can be easily oxidized in air because the surface Cu oxide is more stable than pure Cu from the viewpoint of thermodynamics [6]. When using Cu NPs for low-temperature interconnections, it

is important to consider that the favourable formation of surface Cu oxide could lead to an increased sintering temperature, which is a serious concern. Zhang et al. [3] demonstrated that it was feasible to create high bonding strength of Cu NPs with an average die shear strength above 40 MPa by pressure sintering under air atmosphere. Meanwhile, they revealed the positive effect of pressure and temperature on promoting necking growth, and sintering networking formation accounts for the higher bonding strength. In addition, some studies have reported the application of Cu NPs for 'all-Cu interconnects' [7-9], which has been a promising technology to fulfil the requirements of higher interconnection densities and power capacities. There are several methods for transferring the Cu NPs to achieve all-Cu interconnects, such as photolithographic stencil printing [7], dip-transferring [8], and pulsed laser deposition [9]. Our previous study [7] employed the photolithographic stencil printing (LSP) method to provide a high-throughput solution for Cu NP bumps patterning in the flip chip integration. The relationship between sintering parameters, microstructure and mechanical properties was established and an optimal combination of sintering parameters (260 ℃, 25 MPa and 15 min) was proposed for Cu NPs in all-Cu interconnects. esides, some researchers have investigated the microscale mechanical properties and deformation mechanism of sintered Cu NPs by using molecular dynamics (MD) simulation [10-13]. According to their studies, significant neck contraction is seen in the neck area before fracture when subjected to a tensile load, which eventually leads to fracture along the tensile direction and a fracture tip. However, in the current MD simulation, the limited number of atoms and particles are only capable of revealing the deformation of certain grain boundaries due to computational constraints. This limits our capability of statistically addressing the effects of porous distribution and sintered neck quality on bulk mechanical properties in a larger model.

In this study, we present a comprehensive investigation into the sintering process of Cu NPs using MD simulations. Through our simulations, we aim to elucidate the atomic-level interactions and structural transformations that occur during sintering, contributing to a deeper understanding of the underlying mechanisms. Complementing our simulation work, we employed FIB-SEM for 3D reconstruction to characterize the microstructure of sintered Cu NPs. This experimental technique provides a detailed view of the morphological and structural changes occurring during the sintering process, offering valuable insights that validate and enrich the findings from our simulations.

II. METHODOLOGY

A. Model Construction for Molecular Dynamics Simulation of Sintering Cu Nanoparticles

The MD simulation model for studying the sintering of Cu NPs was constructed by incorporating a random distribution of particle diameters to accurately reflect the natural variability found in experimental systems. Initially, a log-normal distribution was selected to represent the diameters of the nanoparticles. Using this distribution, particle sizes were generated randomly. These particles were then randomly positioned within a simulation box, ensuring no initial overlaps or unphysically close distances between them. The simulation box dimensions were chosen to accommodate all particles with sufficient space for their interactions during sintering. The system was equilibrated at the desired temperature using a thermostat to ensure thermal stability before commencing the sintering simulation. This setup allowed for a realistic simulation of the coalescence kinetics and structural evolution of the Cu NPs during the sintering process.

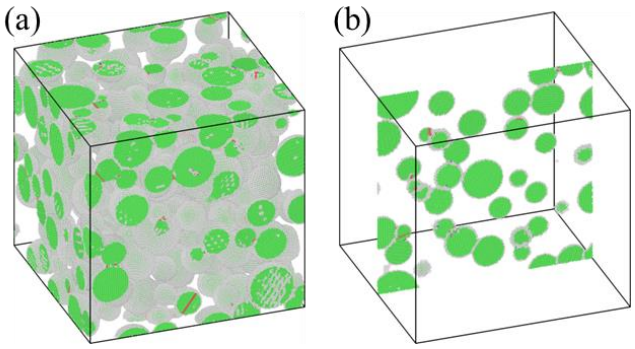

Fig. 2. (a) 3D particle model for MD simulation; (b) cross-section of the 3D model.

B. Development of the sintering model

Using MD simulation, we simulated the sintering process of Cu NPs leading to the formation of a porous structure. In this study, we utilized the large-scale atomic/molecular massively parallel simulator (Lammps) as our MD simulation software platform. Interatomic interaction potential is depicted by the potential function of the Embedded Atom Method (EAM). This potential has been successfully applied in simulating various mechanical properties and microscopic phenomena in Cu, such as diffusion and grain boundary migration (see references). The melting point Tm of bulk Cu with this potential is 1273 ± 30, aligning well with the experimentally observed value of 1358 K. In the EAM potential, the total potential energy of the system is broken down into two components: the interaction potential between atoms and the embedded atomic energy. The total potential energy, which is used to simulate Cu atoms, is the sum of the embedding energy and the pair potential energy, as expressed in the following manner [13]:

$$E = \sum_{i}^{N} F_i\left(\rho_i\right) + \frac{1}{2}\sum_{j\neq i}^{N} \Phi_{ij}\left(r_{ij}\right)$$

Where r_{ij} represents the distance between atom i and j, Φ_{ij} is the short-range pair potential function between atoms i and j, F_i is the embedding energy function of electron density, ρ_i denotes the sum of electron cloud densities generated at i by other atoms except for the i th atom, ρ_j is a function of the electron density generated by atom j at the position of atom.

C. Reconstruction of Sintered Cu Nanoparticles Using FIB-SEM

To investigate the microstructure of sintered Cu NPs, we conducted a detailed 3D reconstruction using Focused Ion Beam (FIB) and Scanning Electron Microscopy (SEM) combined with Avizo software. Initially, the sintered Cu NPs were prepared and mounted for FIB-SEM analysis. The FIB was employed to systematically mill the sample layer by layer, while SEM captured high-resolution images of each newly exposed surface. These sequential SEM images were then imported into Avizo software, where they underwent precise alignment and stacking to build an accurate 3D model. Avizo's advanced image processing and visualization tools facilitated the detailed analysis of the 3D

microstructure, enabling us to examine features such as particle size distribution, neck formation, porosity, and grain boundaries. This comprehensive approach provided critical insights into the sintering behavior and structural evolution of Cu nanoparticles.

III. Results and Discussion

A. Sintering process

The MD simulations provided detailed insights into the sintering process of Cu NPs, particularly focusing on the effects of increasing pressure. Fig. 3 shows the sintered structures at different deformation. As the strain increased, the microstructure of the sintered nanoparticles exhibited significant densification. Initially, the nanoparticles, with a random distribution of diameters, began to form necks at their contact points. These necks grew progressively under the influence of pressure, enhancing the overall connectivity between particles.

As shown in Fig. 3e and f, the MD simulations revealed the formation of stacking faults within the sintered necks. Stacking faults are planar defects that occur due to the improper stacking sequence of atomic planes. As the pressure increased, the density of these stacking faults also increased, indicating a higher degree of atomic misalignment in the sintered structure. This phenomenon is attributed to the increased atomic mobility and diffusion rates under high-pressure conditions, which facilitate the rearrangement of atoms into energetically favorable configurations despite the presence of defects. Additionally, the presence of voids was observed during the initial stages of sintering. These voids, resulting from incomplete coalescence and packing of nanoparticles, gradually decreased in size and number as the pressure was increased. The high pressure promoted the diffusion of atoms into the voids, effectively reducing porosity and leading to a more compact and uniform microstructure.

B. 3D reconstruction

To complement the MD simulations, a detailed 3D reconstruction of the sintered Cu NPs was performed using FIB-SEM and Avizo software. This technique provided a comprehensive view of the microstructural evolution and morphological characteristics of the sintered nanoparticles.

The FIB-SEM analysis involved systematically milling the sample layer by layer and capturing high-resolution SEM images of each exposed surface, as shown in Fig. 4a and b. These sequential images were then imported into Avizo software for precise alignment and stacking, resulting in an accurate 3D model of the sintered structure.

The 3D reconstruction revealed several key features of the sintered Cu NPs. FIB-SEM 3D reconstruction revealed that the restructured structure has a similar distribution of voids compared to the sintered model for MD simulation. This proves the validity of mechanical simulations using molecular dynamics.

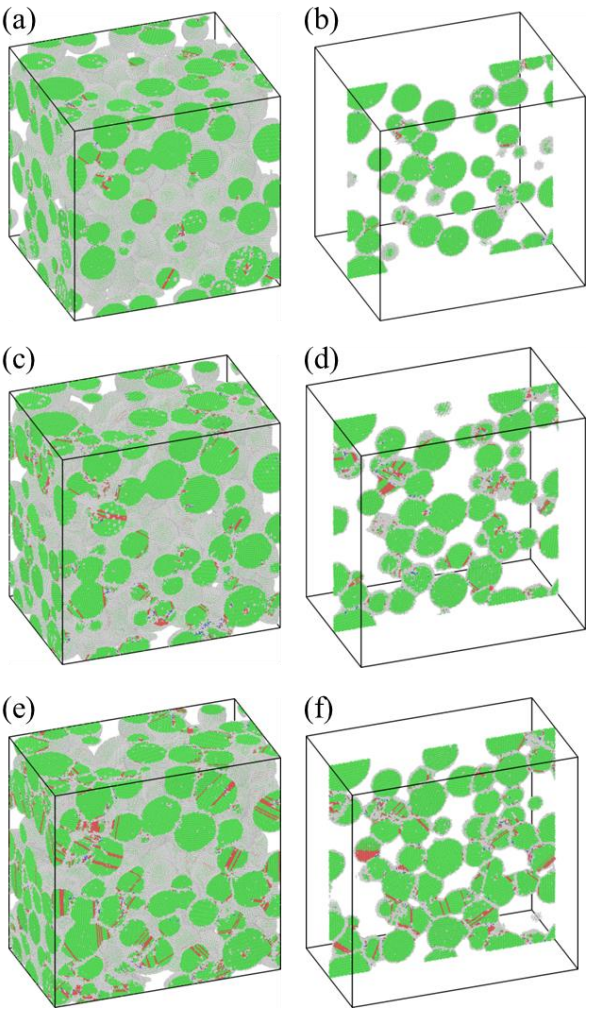

Fig. 3. Sintered structure at (a), (b) 10%, (c), (d) 20% and (e), (f) 40% strain.

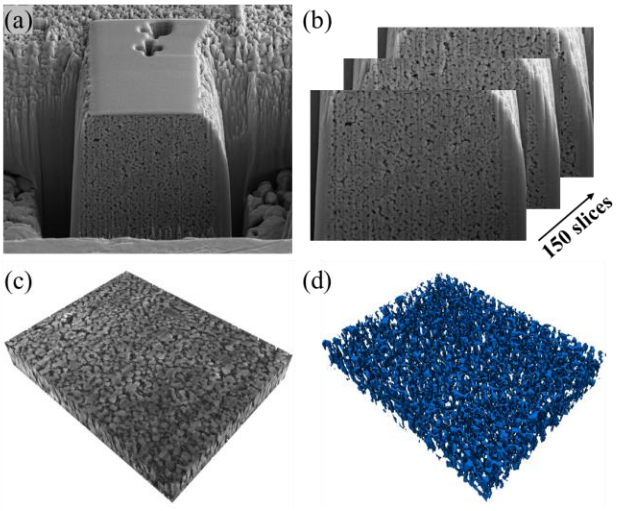

Fig. 4. (a) Image of slicing area under FIB-SEM tomography; (b) SEM slices; (c) sintered Cu domain and (d) voids domain.

IV. Conclusion

In this study, we employed a combination of molecular dynamics (MD) simulations and experimental 3D reconstruction techniques to investigate the sintering process and mechanical properties of Cu nanoparticles. The MD simulations provided a detailed understanding of the

coalescence kinetics and structural transformations occurring at the atomic level during sintering. Key findings from the simulations revealed that increasing pressure significantly enhances the densification of the sintered structure, promotes the formation of well-defined necks between particles, and increases the density of stacking faults and dislocations, leading to a more compact and defect-rich microstructure.

ACKNOWLEDGMENT

The authors would like to acknowledge the financial support from the ECSEL Joint Undertaking (JU) under grant agreement No 876659. The JU receives support from the European Union's Horizon 2020 research and innovation program and Germany, Austria, Slovakia, Sweden, Finland, Belgium, Italy, Spain, Netherlands, Slovenia, Greece, France, and Turkey.

REFERENCES

[1] Y. Yorozu, M. Hirano, K. Oka, and Y. Tagawa, "Electron spectroscopy studies on magneto-optical media and plastic substrate interface," IEEE Transl. J. Magn. Japan, vol. 2, pp. 740–741, August 1987 [Digests 9th Annual Conf. Magnetics Japan, p. 301, 1982].

[2] X. Liu, S. Li, J. Fan, J. Jiang, Y. Liu, H. Ye, G. Zhang, "Microstructural evolution, fracture behavior and bonding mechanisms study of copper sintering on bare DBC substrate for SiC power electronics packaging," J. Mater. Res. Technol., vol. 19, pp. 1407-1421, 2022.

[3] B. Zhang, A. Damian, J. Zijl, H. Zeijl, Y. Zhang, J. Fan, G. Zhang, "In-air sintering of copper nanoparticle paste with pressure-assistance for die attachment in high power electronics," J. Mater. Sci. Mater. Electron., vol. 32, pp. 4544-4555, 2021.

[4] Y. Gao, J. Jiu, C. Chen, K. Suganuma, R. Sun, Z. Liu, "Oxidation-enhanced bonding strength of Cu sinter joints during thermal storage test," J. Mater. Sci. Technol., vol. 115, pp. 251-255, 2022.

[5] N. K. Roy, C. S. Foong, M. A. Cullinan, "Effect of size, morphology, and synthesis method on the thermal and sintering properties of copper nanoparticles for use in microscale additive manufacturing processes," Addit. Manuf., vol. 21, pp. 17-29, 2018.

[6] J. Liu, H. Chen, H. Ji, M. Li, "Highly Conductive Cu−Cu Joint Formation by Low-Temperature Sintering of Formic Acid-Treated Cu Nanoparticles," ACS Appl. Mater. Inter., vol. 8, pp. 33289–33298, 2018.

[7] X. Ji, L. Du, S. He, H. Zeijl, G. Zhang, "Microstructural and micromechanical characterization of sintered nano-copper bump for flip-chip heterogeneous integration," Microelectron. Reliab., vol. 150, pp. 115180, 2023.

[8] L. D. Carro, J. Zürcher, U. Drechsler, I. E. Clark, G. Ramos, T. Brunschwiler, "Low-temperature dip-based all-copper interconnects formed by pressure-assisted sintering of copper nanoparticles," IEEE Trans. Compon. Packag. Manuf. Technol., vol. 9, pp. 1613–1622, 2019.

[9] S. Wang, G. Zou, Y. Wu, Z. Deng, R. Du, L. Liu, "Patterned Cu Nanoparticle Film for All-Cu Interconnection Without Chemical Mechanical Polishing Pretreatment," IEEE Trans. Compon. Packag. Manuf. Technol., vol. 13, pp. 604-614, 2023.

[10] S. Yang, W. Kim, M. Cho, "Molecular dynamics study on the coalescence kinetics and mechanical behavior of nanoporous structure formed by thermal sintering of Cu nanoparticles," Int. J. Eng. Sci., vol. 123, pp. 1-19, 2018.

[11] D. Hu, Z. Cui, J. Fan, G. Zhang, "Thermal kinetic and mechanical behaviors of pressure-assisted Cu nanoparticles sintering: A molecular dynamics study," Results in Phys., vol. 19, pp. 103486, 2020.

[12] A. Malti, A. Kardani, A. Montazeri, "An insight into the temperature-dependent sintering mechanisms of metal nanoparticles through MD-based microstructural analysis," Powder Technol., vol. 386, pp. 30-39, 2021.

[13] J. Liu, W. Lv, C. Chen, Y. Kang, "Atomic insight in fusion mechanism of heterogeneous and homogeneous sintering: Cu and Ag nanoparticles," Results in Phys., vol. 57, pp. 107411, 2024.