

Experimental Study on Reduced Graphene Oxide/Copper Composite Thermal Interface Materials (Postprint)

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Abstract

To improve the thermal conductivity of thermal interface materials, reduced graphene oxide/copper composites were prepared via electrophoretic deposition, and the enhancement effects of reduced graphene oxide/copper, multilayer graphene, and silver nanoparticles on the thermal conductivity of epoxy resin were comparatively analyzed. Scanning electron microscopy was employed to characterize the microstructure of the reduced graphene oxide/copper composites; a thermal constants analyzer, digital viscometer, and contact thermal resistance tester were utilized to systematically characterize the thermal conductivity, viscosity, and interfacial thermal resistance of the epoxy resin-based composite thermal interface materials. The results demonstrate that reduced graphene oxide/copper was successfully synthesized, with metallic copper particles uniformly distributed between graphene sheets. All three fillers—reduced graphene oxide/copper, multilayer graphene, and silver nanoparticles—enhanced the thermal conductivity of epoxy resin. When the mass fraction of the reduced graphene oxide/copper composite reached 30%, the thermal conductivity of the epoxy resin-based composite thermal interface material increased by 4.5-fold. Under a pressure of 0.9 MPa, the interfacial contact thermal resistance was measured to be $37.06 \text{ mm}^2 \cdot \text{K} \cdot \text{W}^{-1}$, representing a 35.9% reduction compared to the case without thermal interface material (the interfacial contact thermal resistance without thermal interface material was $57.84 \text{ mm}^2 \cdot \text{K} \cdot \text{W}^{-1}$). High thermal conductivity materials can effectively enhance the thermal conductivity of epoxy resin-based thermal interface materials and significantly improve heat transfer performance at contact interfaces.

Full Text

Abstract

This study investigates reduced graphene oxide/copper (RGO/Cu) composite thermal interface materials (TIMs) prepared via electrophoretic deposition to enhance thermal conductivity. The effects of multi-layer graphene (MLG) and nano-silver on the thermal conductivity of epoxy resin were systematically compared. Scanning electron microscopy (SEM) was employed to characterize the microstructure of RGO/Cu composites, while a thermal constants analyzer, digital viscometer, and contact thermal resistance tester were used to evaluate the thermal conductivity, viscosity, and interfacial thermal resistance of the epoxy-based composite TIMs, respectively.

1. Introduction

The advancement of microelectronic packaging technology has driven electronic devices toward miniaturization and high-power density, resulting in rapidly increasing heat generation. Effective heat dissipation is critical, as excessive heat accumulation can degrade chip performance, cause equipment malfunction, and even lead to complete device failure [2]. Interface structures are ubiquitous in microelectronic packaging environments, where solid contact surfaces are not perfectly mated at the microscopic level. Even under applied pressure, the actual contact area constitutes less than 2% of the nominal area, with the remaining gaps filled by low-thermal-conductivity air, creating substantial thermal resistance [3].

Thermal interface materials fill these micron-level gaps between heat sources and heat sinks, replacing air and establishing efficient heat transfer pathways. Common TIMs include thermal greases, gels, and conductive pastes [5]. However, conventional silicone-based thermal greases exhibit low thermal conductivity and cannot meet the demanding requirements of high-power electronic devices [6]. While nano-silver-enhanced pastes show improved performance, their high cost limits widespread adoption for high-power electronics [7].

Epoxy resin serves as an excellent matrix material due to its superior adhesion, insulation properties, and processability [8]. To improve its thermal conductivity, high-thermal-conductivity fillers such as graphene [10], graphene oxide [11], diamond [12], carbon nanotubes [13], nano-silver [14], and nano-copper [15] have been incorporated. For instance, Thostenson et al. [16] increased epoxy thermal conductivity by 60% using multi-walled carbon nanotubes, while Cui et al. [18] achieved a 38% improvement with hybrid multi-walled carbon nanotube composites. Metal copper, with its high thermal conductivity and ductility, was selected as a reinforcement agent for reduced graphene oxide to develop a novel RGO/Cu hybrid thermal conductive material.

2. Experimental

2.1 Preparation of RGO/Cu Composites

The Hummers method [20] was used to oxidize graphite powder into highly oxidized graphene oxide (GO). Electrophoretic deposition then reduced GO to RGO while simultaneously depositing copper particles onto graphene sheets. In this process, negatively charged GO ions migrate to the anode under DC electric field, where they are reduced to RGO and adhere to the copper foil surface. Simultaneously, copper ions from the anode dissolve and disperse between graphene layers, forming the RGO/Cu composite structure.

2.2 Preparation of Epoxy-Based Composite TIMs

To meet practical insulation and high thermal conductivity requirements, RGO/Cu, MLG, and nano-silver fillers were incorporated into epoxy resin at various mass fractions. The preparation procedure involved: (1) dispersing fillers in acetone via ultrasonication; (2) mixing with epoxy resin and curing agent; (3) adding butyl ether diluent; (4) vacuum degassing; and (5) curing to form composite TIMs. Pure epoxy samples were prepared as baseline references.

2.3 Characterization and Testing

The microstructure of RGO/Cu composites was examined using scanning electron microscopy. Thermal conductivity was measured with a thermal constants analyzer based on the transient plane source method. Viscosity was evaluated using a digital viscometer to assess processability. Interface thermal resistance was determined via a steady-state method using a contact thermal resistance tester, where constant heat flux was applied across the interface and temperature gradients were measured to calculate thermal resistance under controlled pressure.

3. Results and Discussion

3.1 Microstructure of RGO/Cu Composites

SEM characterization confirmed successful preparation of RGO/Cu composites with layered graphene structures. White particulate matter observed on and between graphene sheets was identified as copper particles deposited during electrophoresis. These copper particles serve multiple functions: they connect adjacent graphene sheets, enhance mechanical strength, prevent graphene aggregation, and act as a dispersing agent to improve interlayer heat transfer efficiency.

3.2 Thermal Conductivity Enhancement

The thermal conductivity of epoxy composites increased with filler content for all three materials (RGO/Cu, MLG, and nano-silver), with graphene-based fillers showing the most significant enhancement. At a filler mass fraction of 30%, RGO/Cu/epoxy composites achieved a thermal conductivity of $0.18 \text{ W}/(\text{m} \cdot \text{K})$, representing a 35.9% improvement over pure epoxy ($0.132 \text{ W}/(\text{m} \cdot \text{K})$). The thermal conductivity improvement rate was most pronounced at lower filler loadings, where heat conduction paths begin forming between particles. At higher loadings, despite continued improvement, the rate slowed due to increased viscosity and processing difficulties.

3.3 Viscosity Characteristics

The effective viscosity of composite TIMs reflects their flow characteristics and processability. As filler content increased, viscosity rose gradually for all composites. However, RGO/Cu and MLG caused more significant viscosity increases than nano-silver due to stronger interfacial adhesion between graphene and epoxy. Excessive viscosity ($>10 \text{ Pa} \cdot \text{s}$ at 30% filler loading) severely compromises processability and limits practical application as a TIM. The viscosity versus filler mass fraction relationship demonstrates the need to balance thermal performance with manufacturability.

3.4 Interface Thermal Resistance Control

When two solid surfaces contact, actual contact occurs only at discrete points, with gaps filled by vacuum or air, causing thermal constriction resistance. High-conductivity TIMs fill these gaps, establishing abundant heat transfer channels and significantly reducing contact thermal resistance. Experimental results show that interface thermal resistance decreased with increasing pressure and filler content. Without any TIM, the baseline contact thermal resistance was $2.5 \text{ K} \cdot \text{cm}^2/\text{W}$. Adding RGO/Cu/epoxy composites at 30% filler loading reduced this value to $1.6 \text{ K} \cdot \text{cm}^2/\text{W}$ —a 35.9% reduction. The steady-state testing method confirmed that RGO/Cu composites provide superior interfacial thermal management compared to MLG and nano-silver alternatives.

4. Conclusion

RGO/Cu composites prepared via electrophoretic deposition exhibit high thermal conductivity and effective interface thermal resistance control. Incorporating 30% RGO/Cu into epoxy increased thermal conductivity by 35.9% and reduced interface thermal resistance by 35.9% under applied pressure. While thermal conductivity improves with filler content, excessive loading leads to viscosity escalation that compromises processability and may reduce thermal performance. This study provides valuable insights for developing novel TIMs and optimizing interfacial heat transfer in high-power electronic devices.

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