Graphene/Copper Heterostructures for Thermal Management

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ABSTRACT

With the technological developments in the microelectronic systems used in military computers, the number of circuit elements per unit area increases enabling the production of faster and more efficient processors. To be able do this, these circuit elements are required to withstand higher current densities and thus higher temperatures are generated by Joule heating. Overheating (in general non-uniformly) at some specific areas in chips, adversely affects the performance and reliability of electronic devices. Therefore, it is critical to control temperature distribution within the chip and the efficient heat management is one of the most important issues for today's high power electronic devices and thus, every improvement in the area is very valuable. In this context, to increase the lateral heat conduction, the graphene-copper heterostructures (graphene-copper laminate structures for heat spreaders and graphene-copper porous structures for heat sinks/exchangers) are studied both experimentally and through computational studies. For the experimental studies, first graphene is synthesized on Cu via CVD. The thermal diffusivity measurements, which were performed through the laser flash method, show that the presence of graphene did not make a contribution to the thermal properties in graphene-copper laminate system. These results were also confirmed by the computational studies which showed that to see an increase in the thermal conductivity, the ratio of graphene/copper should be higher than 1/20. Within the scope of these findings, 3D graphene-Cu porous heterostructures are studied to increase the graphene's contribution to the thermal diffusivity. 3D graphene-Cu porous heterostructures showed an increase in the thermal diffusivity by 10% at the room temperature and 30% at 400 °C. Graphene's positive effect on the thermal properties is attributed to its high thermal conductivity and the protection of Cu structure against the oxidation at higher temperatures. Our studies show that the graphene-copper porous structures developed in this study can be a good lightweight candidate for a heat sink/exchanger with corrosion resistant and high thermal conductivity.

1.0 INTRODUCTION

High performance devices require the development of novel thermal management materials for more efficient spreading and dissipation of the heat generated. Schematic drawing of common integrated circuit configuration used electronic cards and top view picture of the circuit elements on PCB used in Aselsan's military computers are given in Figure 1-1. Two of the major heat management components in electronic devices are heat spreaders and heat sinks/exchangers. Development of a heat spreader with high thermal conductivity and producing a lightweight, corrosion resistant heat sink/exchanger with high thermal conductivity will be the important contributions towards heat management problem.

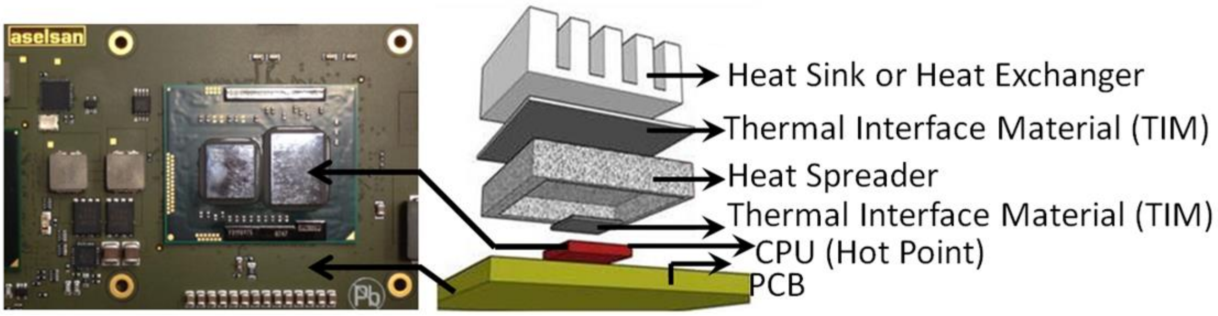

Figure 1-1: Top view picture of the circuit elements on PCB used in Aselsan's military computers and schematic drawing of common configuration of electronic cards

Recently, graphene which draws huge attraction in many applications in nanotechnology is proposed as a promising heat dissipating material, as its strong sp2 bonds result in ultrahigh thermal conductivity (~5300 W/mK) [1]. The first studies where graphene's application as a heat spreader material, include Barua's et al. work where graphene is applied on the top of a processor by using finite element analysis methods, the computational work of Grishakov et al. on the diamond and graphene heat spreader layers effect on the thermal and electrical properties of the high electron capability AlGaN/GaN transistors. Both studies showed that graphene heat spreader layers decreased the maximum temperature resulted from generated heat, increased the life cycle of the device and improved the current-voltage characteristics [2,3]. Parallel to these, Jagannadham's study in 2012 showed the thermal conductivity of electrolytic Cu in room temperature is improved from 387 W/mK to 460 W/mK by electrochemical deposition of 200 μm thick graphene onto Cu [4].

Yan et al. showed experimentally that the presence of few layer graphene (FLG) prepared through scotch tape method decreased the temperatures of the hotspots and increased the transistor life [5]. However, the graphene synthesized via scotch tape method is not appropriate for industrial applications considering the size and mass production. Gao et al. showed that graphene can be used as a heat spreader by synthesizing graphene via chemical vapor deposition (CVD) and transferring on the processor with a polymer. They reported that when single layer graphene is applied, the hotspot temperature decreased by 13 °C and when 6-10 layers of graphene is applied by 8 °C [1].

In a recent study, graphene is synthesized on 9 μm and 25 μm thick Cu foils via CVD and the synthesized graphene has improved the thermal conductivity of Cu foils compared to annealed Cu foils by 24% for 9 μm thickness and 16% for 25 μm thickness [6]. On the other hand, it was reported that the increase in the thermal conductivity results from the changes in the Cu morphology from the graphene synthesis via CVD process.

Patents are also present involving the graphene's application for the improvement of the heat dissipation in electronics. In these studies, graphene is usually applied as a nanoparticle-additive for thermal interface materials (TIM) [7–13]. Among the related patents about the graphene's application as a heat dissipater, the patent US 20100085713 A1 studies the application of graphene film as heat spreader for electronic and optoelectronic devices in "silicon-on-insulator" (SOI) technology and shows the overall thermal conductivity is improved; thus, the heat removal performance is improved as well [14]. In that study it is mentioned that the graphene can be synthesized via CVD or SiC decomposition technique and transferred to be used.

When the commercialized industrial products are investigated, the use of pyrolytic graphite as heat spreaders in the electronic cooling applications is quite common. The studies aiming the performance increase in the heat spreaders also involve geometrical improvements besides material studies such as the applications of laminate structures or sandwich structures [15–20]. The study conducted by Zweben et al. used a laminate structure which is composed of metal and polymer layers [15]. Kibler et al.'s patent produced a sandwich structure by placing pyrolytic graphite between two layers and showed the thermal conductivity of this hybrid structure reaches 1500 W/mK [20].

2.0 MATERIALS AND METHODS

Graphene Synthesis and Cu/Graphene Laminate Structure Formation: Graphene is synthesized on Cu foils (Alfa Aesar, 25 μm thickness, 99.8% purity) and via CVD. Cu foils (15 x 15 mm) are cleaned [21] before the synthesis and placed inside a graphite crucible. The furnace is heated up to 1010 °C with hydrogen (H_2) flow 20 sccm and annealed for 3 hours, then 0.5 sccm methane (CH_4) flow is fed into reactor for 30 minutes. After the synthesis of graphene, foils are stacked on top of each other and placed inside graphite molds. These molds are pressed between a graphite block and a quartz boat to ensure the foils are in contact with each other. Reactor is heated up to 500 °C with 20 sccm H_2 flow and annealed for 1 hour in order to produce graphene-Cu laminate heterostructures. The laminate structures are produced as 3 layers, 5 layers of graphene-Cu heterostructures and only H_2 annealed Cu laminate structures (without any CH_4 flow during process).

Modeling of heat dissipation in Graphene-Cu heat spreader system: In processor (heat source) and heat spreader laminate system, heat dissipation with respect to time is modeled both in 2-dimension and 3-dimension and required simulation and analysis programs (C++, Mathcad) are studied.

Cu/Graphene Porous Heterostructure Formation: -325 Mesh Cu powders with 99.99% purity were obtained from Nanografi. Cu powders have been placed inside a graphite crucible without pressing and the same graphene synthesis process used for the Cu foils is applied to Cu powders as well. At high temperatures simultaneous neck formation between Cu powders and graphene formation on the Cu surface result in Graphene/Cu Porous Heterostructures.

Characterization and Tests: The morphologies of the synthesized structures are investigated by optical microscope (OM), scanning electron microscopy (SEM) and Raman spectroscopy. The thermal diffusivity was measured by the laser flash method (LFA). For the 1 layer foil and the laminate structures the thermal diffusivity is measured in-plane direction and the measurements for the porous heterostructures are conducted in through-plane direction.

3.0 RESULTS AND DISCUSSION

3.1 Cu/Graphene Laminate Structures

In order to understand the morphology and the continuity of graphene, the graphene synthesized samples are oxidized in air to reveal the graphene domains. Since the graphene grown surfaces will be protected from the oxidation and uncovered regions will oxidize and change color, selective oxidation method is very effective to detect graphene domains and boundaries on Cu foils using OM without any chemical treatments. The OM images of the surfaces are shown the before oxidation step and after oxidation in Figure 3-1. After the oxidation of the samples, the graphene covered regions are protected from oxidation and uncovered Cu regions are exposed and oxidized revealing the coverage of graphene on Cu surface. The number of layers of the synthesized graphene is confirmed with Raman spectroscopy which is presented in Figure 3-1c. Raman study has shown that the 2D/G ratio is approximately 2.4 which indicates the synthesized graphene is mostly single layer [22].

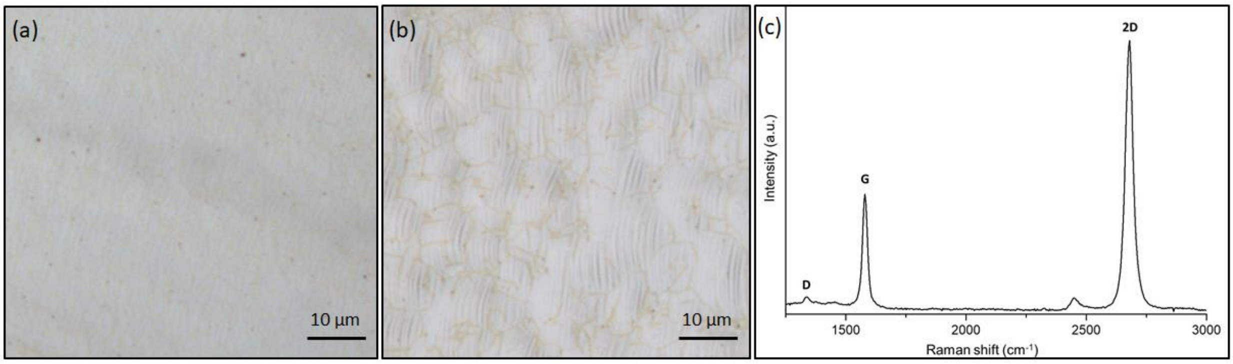

Figure 3-1: OM image of graphene grown Cu foil (a) before oxidation (b) after oxidation (c) Raman spectrum of transferred graphene on SiO_2.

After synthesizing graphene on copper foils, laminate structures (3 layers, 5 layers) are prepared as explained in the methods section. The laminate structures are prepared as only H2 annealed (without graphene) and with graphene to compare and investigate the effect of graphene. The thermal diffusivity results, which were performed at room temperature, are given in Table 3-1.

Table 3-1: Thermal diffusivity measurement results

Sample	Explanation	Thermal Diffusivity (cm^2/s)	
		Without Graphene	With Graphene
Bulk Cu	Ref. [23]	1.1	-
Cu Foil	1 Layer	1.0	1.0
	3 Layers	0.6	0.6
	5 Layers	0.5	0.5
Cu Foam	-325 Mesh Cu Powders	0.5	0.6

The measurements have shown that the in-plane thermal diffusivity values are decreased with the increased number of layers for both graphene-Cu and annealed Cu laminate (without graphene) structures. This can be explained with the interface scattering between the layers. Furthermore, the results indicate that the presence of graphene has not contributed to thermal diffusivity of the structures.

In order to investigate the graphene's contribution to thermal diffusivity in graphene-Cu laminate structures, heat dissipation with respect to time is modeled both in 2D and 3D for heat source (processor) and heat spreader (laminate structure) system. The 3-dimensional heat conduction equation given in equation 3.1 is solved for different boundary and initial conditions.

$$\frac{\partial T}{\partial t} = \alpha\left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right) + \frac{\dot{q}}{c_p \rho} \;;\; \alpha = \frac{k}{c_p \rho} \tag{3.1}$$

In in equation 3.1, T (K) is temperature, α (m2s-1) thermal diffusivity, k (Wm-1K-1) thermal conductivity, (Wm-3) heat generation, (Jkg-1K-1) specific heat and ρ (kgm-3) density. This equation is solved for each layer (graphene and Cu) and heat source (processor). All the dimensions and thermal diffusivity coefficients are normalized with layer thickness and thermal diffusivity of Cu (αCu). For the thermal diffusivity coefficients the following assumptions are made: for the in-plane direction $\alpha^{xy}_{graphene} \sim 20\ x\ \alpha^{xy}_{Cu}$, for the through plane direction $\alpha^{z}_{graphene} \sim \alpha^{zy}_{Cu}$. The system's geometry is presented in Figure 3-2.

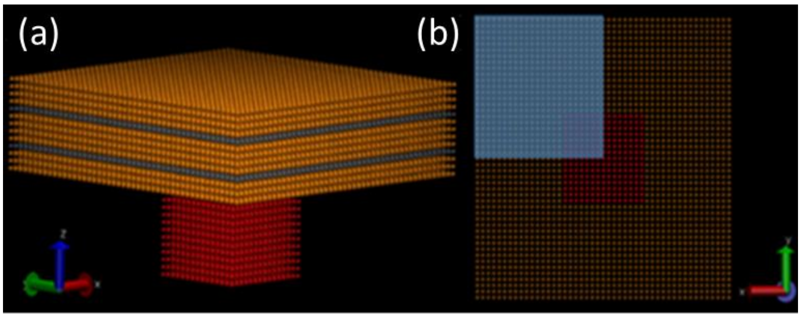

Figure 3-2: Mesh system constructed for the modeling of heat source (red) and heat spreader laminate structure (Cu: yellow, graphene: gray). (a) System's 3D image (b) System's top view (simulation area is shown in blue).

The system in this study is constructed by having 1 graphene layer for 25 μm thick Cu. In dimensional sense, this means 1 graphene layer on top of 25.000 Cu layers. Hence, in order to investigate the effects of graphene layers on the heat dissipation, the studies are conducted in other systems (Figure 3-3). The simulation results given in Figure 3-3a show that even in a system where graphene/Cu thickness ratio is 1/400, graphene does not have any contribution to heat dissipation. In order to observe graphene's positive effect on the heat removal, this ratio must be around 1/20 (Figure 3-3b).

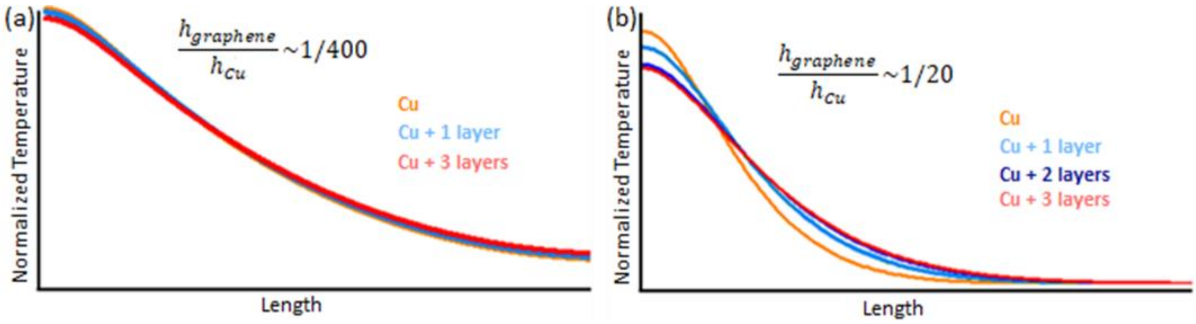

Figure 3-3: Simulation results of the system: Normalized Temperature vs distance from the center of the processor (heat source) when graphene/Cu thickness ratio is (a) 1/400 (b) 1/20.

3.2 Cu/Graphene Porous Heterostructures

Within the scope of theoretical and experimental studies a different design is also proposed to increase the graphene/Cu thickness ratio. Replacing Cu foil with Cu powders as a substrate material, it was aimed to increase the surface area of Cu and therefore increasing the thickness ratio. Graphene-Cu porous heterostructures has been synthesized in a cost effective and a simple way via using CVD. Cu powders are placed in CVD reactor as mentioned in Materials and Methods section and after the CVD process a porous network due to the necking between Cu powders has been synthesized successfully (Figure 3-4a). The SEM images of the synthesized porous network are given in Figure 3-4b. In a single process, a stable, porous, graphene grown Cu network has been successfully produced. The Raman spectroscopy is obtained after etching away the Cu network only to confirm the presence of graphene (Figure 3-4c). After the confirmation of graphene presence, the through-plane thermal diffusivities of the graphene-Cu and Cu porous heterostructures have been measured from room temperature to 400 °C (Figure 3-4d) by using LFA. The synthesized graphene successfully contributed to the system's thermal diffusivity. This contribution is explained with high thermal conductivity of graphene and protecting Cu network from oxidation at elevated temperatures. Moreover due to its porous and high surface area, graphene-Cu porous heterostructures are expected to have outstanding performance removing the generated heat via convection which will make them a promising alternative for the heat sink applications.

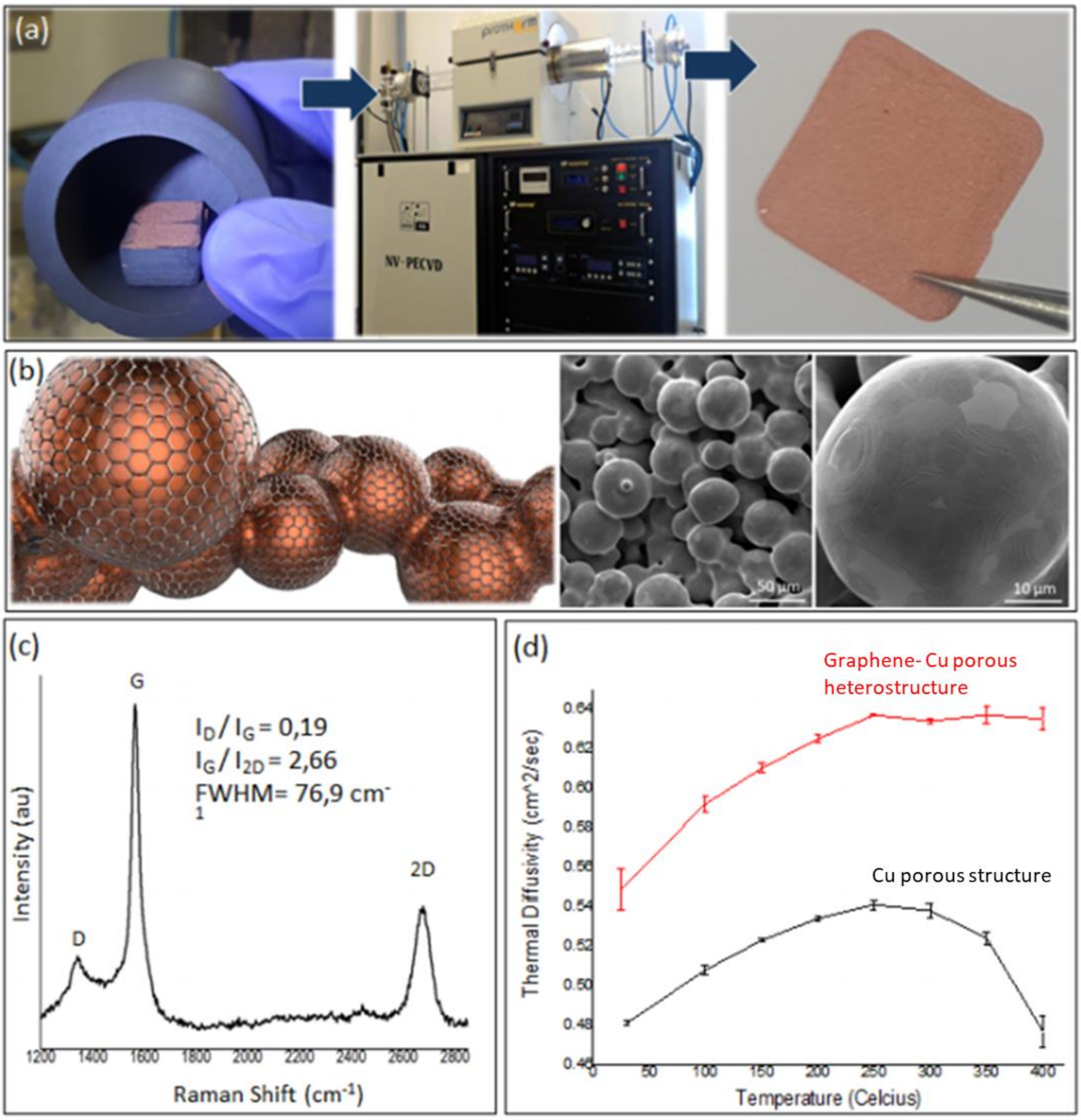

Figure 3-4: (a) Pictures of Cu powders before and after CVD process (b) The design of proposed structure and SEM images of graphene-Cu porous network (c) The Raman spectroscopy obtained from the graphene network (d) Through-plane thermal diffusivity results of porous structures from room temperature to 400 °C.

4.0 CONCLUSION

The laminate structures are produced from graphene-Cu and Cu foils in order to understand the effect of graphene on the thermal properties. The synthesized 1, 3, 5 layered Cu and graphene-Cu laminate structures' thermal properties are studied through LFA. It was concluded from investigation of these results that the graphene's presence has not contributed to thermal diffusivity experimentally. The reasons are further investigated by modeling studies. Within the scope of theoretical studies, in the heat source and heat spreader system, heat dissipation with respect to time is modeled both in 2D and 3D spaces and simulation and analysis programs (C++, Mathcad) are used to understand the system's behavior. The theoretical calculations suggested that the thickness of Cu layer is dominant in the thermal conduction against the graphene which has a high in-plane thermal conductivity and the decreased thickness ratio of graphene/Cu significantly lowers the systematical contribution of thermally high conductive graphene layers. The possible reasons for these are understood and to effectively harvest the thermal conductivity of graphene, a new heterostructure is designed and studied. Cu and graphene-Cu porous heterostructures' thermal diffusivities are measured from room temperature to 400 °C and the results showed that the graphene synthesized Cu porous structure has a higher thermal diffusivity value from the Cu porous structure (10% improvement at the room temperature and 30% at 400 °C). Graphene's positive effect on the thermal properties is explained with high thermal conductivity of the graphene and the protection of Cu structure against the oxidation at higher temperatures.

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