Carbon 118 (2017) 1–7

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Synthesis and characterization of nitrogen-doped graphene nanosheets/copper composite film for thermal dissipation

Cheng-Che Hsieh, Wei-Ren Liu*

Department of Chemical Engineering, Chung Yuan Christian University, Chungli, 32023, Taiwan

ARTICLE INFO

Article history:
Received 18 December 2016
Received in revised form
12 February 2017
Accepted 9 March 2017
Available online 11 March 2017

Keywords:
Graphene nanosheets
Nitrogen doped
Composite film
Thermal dissipation

ABSTRACT

In this study, we propose a simple and cost-effective process to assemble composite film for thermal dissipation by combination of nitrogen-doped graphene nanosheets (N-GNS) and copper foil. We found that both nitrogen-doping contents and types of nitrogen bonding in GNS play important roles on heat dissipation performance. XPS results indicate that about 1.1–2.8 mol. % nitrogen atoms were successfully doped in GNS. The Raman analyses future confirm that D/G ratio could be efficiently reduced from 0.17 to 0.1 by N-doped healing process. For heat dissipation tests, we use both thermocouple measurement between two points and thermographic camera to distinguish performance of these samples. Laser flash analysis shows that the thermal conductivity (K) could be enhanced from 333.53 W/m K of Cu foil to 445.91 W/m K of GNS/Cu by GNS coating process. Furthermore, the thermal conductivity of N-GNS/Cu could approach to 542.9 W/m K, leading to 163% increase of thermal conductivity compared to the copper foil. These findings open up the thermal dissipation performance of our N-GNS/Cu composite film was superior to copper foil via nitrogen doping technique.

1. Introduction

In recent years, rapid development in miniaturization of modern electronics including smart phones, LED lamps and notebooks have increased hot-spot temperature, which motivates the development of thermal interfere materials (TIMs) with high thermal conductivity [1–6]. Effective thermal management is becoming increasingly important for high-power electronics and portables devices, which may find applications due to high thermal conductivity materials, e.g., copper, graphite paper and graphene.

Graphene, a novel material with merely a single layer of carbon atoms in two-dimensional lattice, has been intensity studied as a promising thermal conductive material for thermal management because of its particular advantages including the highest in-plane thermal conductivity, excellent mechanical strength, low density and thermal expansion coefficient [7–17]. Graphene nanosheets could combine with polymer TIMs or metal TIMs to fill the gaps between the heat sources and heat sinks, thus to increase the thermal transfer efficiency. Graphene composite film or graphene films paper then could be spread at x-y direction to remove hotspot by scattering the heat along the films plane.

Thermal management of electronic products by using thermal dissipation film could be carried out through several ways: (1) Nature graphite paper. It exhibits high quality, but it is harsh to decrease the film thickness and the nature graphite paper suffer from high processing cost due to high temperature of as high as 3000 °C. (2) Synthetic graphite paper (polyimide) can achieve more thin thickness film, but it needs high energy consumption during graphitization process. (3) Composite film based on combination graphene (or graphite) and metal foils can produce more large area thermal dissipation film by roll to roll process. For synthesis of graphene-based composite films, much efforts have been put, such as electrophoresis [18,19], dip coating [20], layer-by-layer assembling [21,22] and spin coating [22,23]. Lian et al. [7] investigated a novel approach to fabricate large area free-standing graphene paper sheets (GPs) of graphene films integrated with a continuous roll-to-roll process and simple water exfoliation from highly hydrophilic aluminum substrates. They applied thermal annealing to heal structural defects and removed functional groups in the graphene sheets and thus the thermal conductivity of graphene could be greatly improved [24–27]. Higher annealing temperature generally improves the thermal and electrical properties of the graphite paper (GP), and the optimized temperature is 2200 °C to deliver the defect-free,

* Corresponding author.
E-mail address: wrliu1203@gmail.com (W.-R. Liu).

http://dx.doi.org/10.1016/j.carbon.2017.03.025
0008-6223/

highly aligned, and light-weight (density ~2.1 g/cm^3) GPs. The annealed GPs at 2200 °C display superior properties with thermal conductivities of ~1238.3 W/m K, nearly 400% improvement as compared to the others. Hsieh et al. [28] reported to synthesize GNS as heat sink materials from artificial GP by mechanical cleavage. The method is composed of three main steps: GP isolation, GP exfoliation, and GN collection. The method is capable of preparing few layers of GNs repeatedly without using chemical oxidizing agents and costly deposition apparatus. The Hsieh et al. also demonstrated that the addition of GN onto Cu foil induces an improved capability for heat dissipation, as compared with original GP and Cu foil. According to the calculations of Fourier's law, the thermal conductivity of GN/Cu composite heat sink can reach as high as 2142 W/m K, leading to 26% increase of thermal conductivity compared to the GP heat sink. To enhance the thermal conductivity of graphene-based materials, some strategies have been reported such as doping [29], structure design [30] and thermal reduction [31] and so on. Doping is one of the most popular way that several methods have been developed to synthesize N-doped graphene, including arc-discharge [32], chemical vapor deposition [33], thermal annealing of graphite oxide (GO) in ammonia [34] and thermal annealing of GO with urea [35]. Wu et al. demonstrated that via doping nitrogen in the graphene network was identified the presence of three different types of nitrogen: pyridinic N, pyrrolic N and quaternary N [36,37]. N atoms that replace C atoms in hexagonal rings are termed quaternary nitrogen. These may lead to enhanced high performance electric conductivity [38], electrochemical properties [39–43] and thermal conductivity [44]. Gomes et al. [29] presented a new approach to synthesize N-doped graphene via thermal treatment of graphene oxide (GO) with amino-terephthalic acid under argon atmosphere. The effect and use of amino-terephthalic acid as a solid source of nitrogen for synthesizing N-doped graphene is yet to be reported in the literature. The synthesized N-graphene was finally evaluated for its energy storage capacitance in an electric double layer capacitors (EDLCs). Chung et al. investigated a simple and effective N-doping method to enhance the quaternary N doping and simultaneously decrease the atomic oxygen concentration in graphene is proposed. The strategy employed in this work was to modify graphene oxide (GO) prior to thermal annealing so as to provide a more efficient structure for quaternary N-doping. GO was first chemically reduced with hydrazine to substantially increase the formation of C=C bonds and simultaneously decrease the atomic oxygen concentration. The reduced graphene oxide (RGO) was then annealed in the presence of NH3. Although N-doping via the replacement of oxygen is preferred, the probability of carbon being substituted with N doping in the graphitic structure of RGO could increase due to the relatively higher content of C=C when compared to the atomic oxygen concentration.

To the best of our knowledge, there is no literature focus on N-doped GNS combines with copper to synthesis composite film using on thermal dissipation. Thus, in this study, we first report N-GNS coating on the copper with excellent thermal and electrical conductivity from N-GNS at low temperature of 800 °C using a solid-state reaction in the argon-containing atmosphere. We can change the nitrogen percentage to control the types of nitrogen binding of the pyridinic N, pyrrolic N and quaternary N in the graphene structure. On the basis of the experimental results, the N-GNS/Cu thermal dissipation film delivers superior thermal releasing ability with high thermal conductivity, as compared with Copper foil and GNS/Cu composite film by thermal infrared film imager and we set up a simulation device tests method to identify thermal difference of thermal dissipation film.

2. Experimental

2.1. Synthesis of graphene nanosheets (GNS)

Natural flake graphite with an average diameter of 500 μm was used for preparing the exfoliated graphite. Concentrated sulfuric acid and fuming nitric acid were used as chemical intercalate and oxidizer to prepare graphite intercalation compounds GICs. The resulting graphite intercalation compounds (GICs) was subjected to a thermal shock at 1050 °C for 15 s in a furnace to form exfoliated graphite. Exfoliated graphite exfoliated by ultrasonic vibration to form graphene nanosheets (GNS) (see Fig. 1).

2.2. Synthesis of nitrogen-doped graphene nanosheets (N-GNS)

N-doped graphene was prepared by thermal annealing process. In a typical experiment, 1 g of GNS was first finely milled with 1, 3, 5, 7 and 20 g of HMT (Hexamethylenetetramine) and then transferred onto a quartz boat. The boat with the mixture was put in the center of a tube furnace and heated to 800 °C under argon flow at a rate of 5 °C min^{-1} and kept at the temperature for 8 h to obtain the production N-GNS. To investigate thermal property, N-GNS powders were coated onto 35 μm Cu foil (purity: 99.9%) with a thickness of 20 μm. The N-GNS/Cu films were fabricated by mixing N-GNS powders, binder (Carboxymethyl Cellulose), SBR (Styrene Butadiene rubber) and conducting carbon black (Super-P) with the weight ratio of 89:6:3:2. The water based solvent, DI water, was employed to prepare the N-GNS slurry. The resultant slurry was uniformly pasted on Copper foil with a doctor blade, followed by evaporating the solvent, DI water, with an oven at 80 °C. Therefore the N-GNS/Cu films were adjusted to control a thickness of 20 μm (see Fig. 1).

2.3. Material characterization

The GNS and N-GNS powder were characterized by powder X-ray diffraction (XRD, Bruker D8 Advance Eco) with Cu Kα radiation (λ = 1.5418 Å). The X-ray Photoelectron Spectroscope (XPS, K-Alpha) measurements of the N-GNS were carried out nitrogen doped content and the detail of nitrogen bonding with carbon in graphene structure. The morphology and structure of the N-GNS/Cu were analyzed by scanning electron microscopy (SEM, Hitachi S-4100). The Raman spectra were carried out by a micro Raman spectroscopy system with laser frequency of 532 nm as the excitation source. The Scanning Probe Microscope System (AFM, Bruker Dimension Icon) of the GNS were identified the thickness. Thermal diffusivity (α) of the film was measured by laser flash thermal analyzer (LFA457 Micro Flash).

2.4. Heat transfer simulation details

Simulation tests of the N-GNS/Cu film were measured by Agilent 34970A. The testing fixture was regarded as a simulation of a tablet PC, then the heat dissipation of chips with the size of 1 cm (length) x 1 cm (width) x 1 mm (thickness) was 2 W, which were attached on substrates of 24.4 cm (length) x 16.3 cm (width) x 0.035 mm (thickness) with copper foil. The composite film was attached on the top of 24 cm (length) x 16.3 cm (width) x 2 mm (thickness) with acrylic plate with 2 mm gap between the substrates. The testing fixture had three sensing spots for temperature tests, as well as a spot on the heating chip, the first testing spot on the base material on top of the heating chip, and the second testing spot which was also on the base material and 0.5–5 cm apart from the first testing spot. The temperature testing method measures the gap between a temperature difference between T1 (point 1) and T2 (point 2).