Applied Thermal Engineering 70 (2014) 600–608

Contents lists available at ScienceDirect

Applied Thermal Engineering

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

Silicon carbonitride covered SiC composites for enhanced thermal conductivity and electrical insulation

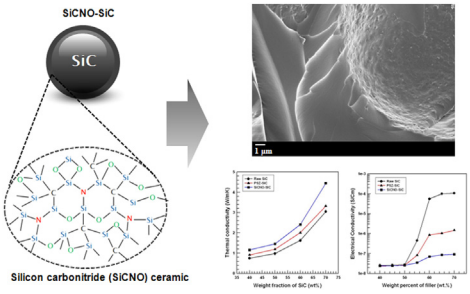
Yongseon Hwang, Kisang Ahn, Jooheon Kim*

School of Chemical Engineering & Materials Science, Chung-Ang University, Seoul 156-756, Republic of Korea

HIGHLIGHTS

- Silicon carbonitride covered SiC is fabricated with polysilazane.
- Surface-treated SiC composites result in an enhanced thermal conductivity.
- The measured thermal conductivity is correlated with theoretical models.
- Electrical conductivity results reveal the enhanced electrical insulation.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 20 March 2014
Accepted 3 May 2014
Available online 12 May 2014

Keywords:
Ceramic-matrix composites (CMCs)
Silicon carbide
Thermal properties
Electrical properties

ABSTRACT

Surface-treated silicon carbide (SiC) particles were prepared with polysilazane (PSZ) and its amorphous silicon carbonitride (SiCNO) ceramic coatings on the SiC surface using a dip-coating method. Moisture-crosslinking of PSZ on the SiC produced PSZ–SiC particles, and heat treatment of the PSZ–SiC at 800 °C converted the PSZ–SiCNO. The surface treatment of the SiC particles enhanced interfacial adhesion with the silicone-based matrix. The thermal transport properties of these composites were investigated and then, interpreted with Agari's model. An analysis of the coefficients of this model indicated that the surface treatment of SiC particles facilitates the formation of conducting paths. The electrical properties of the composites also demonstrated the effect of the amorphous Si–C–N–O network on the SiC surface.

1. Introduction

Despite the rapid progress in the field of electronic devices over the last few decades, the continued miniaturization of electronic device components faces significant problems associated with heat dissipation. These difficulties have emphasized the need for improved thermal interface materials (TIMs) for use in modern chip packaging [1–3]. The reliability of an electronic device is extremely sensitive to the operating temperature of the junction. A small difference between the actual operating temperature and the intended temperature of a device (10–15 °C) can result in a twofold reduction in its lifespan [4]. Therefore, it is crucial that the heat generated in the device is dissipated as quickly as possible to maintain the optimum operating temperature in the device.

In typical flip-chip assemblies of microprocessors, heat spreaders and heat sinks with large thermal conductivities (k) dissipate the heat generated in the die. However, surface asperities greatly limit the actual contact area at solid/solid interfaces (e.g., those between the die/heat spreader and heat spreader/heat sink), thereby reducing the effective thermal conduction [5]. TIMs fill the gaps between asperities in order to minimize the thermal contact resistance, and extensive research has been devoted to developing novel TIMs with improved performance [6,7]. To obtain TIMs with enhanced thermal conductivity, composites consisting of many

* Corresponding author. Tel.: +82 2 820 5763; fax: +82 2 812 3495.
E-mail address: jooheonkim@cau.ac.kr (J. Kim).

http://dx.doi.org/10.1016/j.applthermaleng.2014.05.015
1359-4311/

kinds of particles – metals, ceramics, and nanostructured carbon materials – in a thermosetting or thermoplastic polymer matrix have been developed.

Among the various thermally conducting fillers, ceramic particles with high thermal conductivity are attractive candidates because they provide the required thermal conductivity while maintaining the desired electrical insulation properties [8,9]. Polymers with ceramic fillers such as boron nitride (BN), aluminum nitride (AlN), silicon nitride (SiN), alumina (Al_2O_3), silicon carbide (SiC), silica (SiO_2), and diamond have emerged as cost-effective materials for thermal management applications. In these composites, a very high microfiller loading, normally 60 vol.% or even higher, is necessary to satisfy percolation threshold requirements and to obtain high thermal conductivity from continuously heat-conducting chains in the polymer.

Thermally conductive composites incorporating SiC have received some attention [10,11] because SiC possesses a high k and a low coefficient of thermal expansion. SiC has $k = 490\ W\ m^{-1}\ K^{-1}$, 3.3 times that of silica and 10 times that of either gallium arsenide or sapphire [11]. However, the electrical conductivity (σ) of SiC grown by most techniques is greater than that suitable for use as a TIM because of SiC's wide bandgap. Efforts have been made to reduce σ in SiC by adding a p-type (i.e., acceptor) dopant such as boron. In practice, however, SiC-based devices fabricated using boron to obtain high resistivity have exhibited unexpectedly poor performance at high power levels [12].

Polysilazanes (PSZ), polymers whose backbones consist of alternating Si and N atoms with pendent carbon-containing groups, are widely used in precursors, coating solutions, and blending applications [13,14]. PSZ coatings have good thermal stability, are electrically insulating, and provide oxidation and corrosion resistance. A unique and promising property of PSZs is that they are preceramic polymers and can be converted into SiCN ceramics with thermal treatment [14]. Currently, there is no published research on the surface modification of inorganic fillers by polymer-derived ceramics coating on the thermally conducting fillers as a method for improving the thermal and electrical properties of the composite system.

In this study, SiC composites were fabricated using both raw and surface-treated SiC particles. To enhance the interfacial interaction between the SiC particles and the silicone-based matrix, PSZ and silicon carbonitride (SiCNO) coatings were applied to the SiC particles by dip-coating before addition to the matrix. The properties of these modified composites were compared to those of the composites incorporating the raw SiC. The thermal conductivities of the SiC composites were measured and related to the SiC particle concentration. In addition, the effect of the surface treatments was investigated through an analysis of various thermal conductivity models. The electrical properties of the composites were also obtained to demonstrate the effect of the amorphous Si–C–N–O network on the SiC surface.

2. Experimental

2.1. Materials

The epoxy-terminated dimethyl siloxane (ETDS) was purchased from Shin-Etsu Silicon (KF-105, equivalent weight (E.E.W) = 490 g/eq, density = 0.99 g/cm^3) and used after being fully dried in vacuum at 50 °C for 24 h. 4,4′-Diaminodiphenylmethane (DDM) prepared by TCI Korea was used as curing agent without further purification. SiC particles (OCI Company Ltd. density = 3.1 g/cm^3) with a mean diameter of approximately 50 μm and regular spherical shape were used as filler. Hydrofluoric acid (HF, Aldrich, Seoul, Korea) was used as received. PSZ based coating resin (KiON HTT-1800) was purchased from Clariant GmbH, Germany.

2.2. Surface treatment of SiC particles

A native oxide layer of SiO_2 and O^{2-} ions exists on the surface of all kinds of SiC particles [15]. One bond connecting Si^{4+} and another bond form a hydroxyl (–OH) group when reacting with H_2O, according to the following chemical equation:

$$\equiv Si - O^- + H_2O \Leftrightarrow \equiv Si - OH + OH^- \quad (1)$$

SiC exhibits oxidation resistance at its surface by the formation of a passive thin and dense amorphous SiO_2 layer, which has extremely low oxygen permeability up to very high temperatures [15]. Therefore, the SiO_2 layer and metal oxide adsorbed on the surface of the SiC particles were removed by HF etching according to the following chemical equation:

$$SiO_2 + HF \leftrightarrow SiF_4 + 2H_2O \quad (2)$$

The process details are as follows: 20 g SiC particles and 300 mL 10% HF solution were placed in a 500 mL beaker, stirred for 1 h, and then leached with deionized (D.I.) water until the pH value of the leaching water reached 7–8. HF-etched SiC was dried at 100 °C for 1 h in vacuum.

PSZ was applied on the HF-etched SiC through dip-coating method. First, SiC particles were dipped and stirred in PSZ solution (SiC:PSZ = 1:1 w/w) at room temperature for 1 h. After that SiC dispersion was filtered to remove an excess PSZ solution, and then the filtered PSZ-coated SiC was placed in an oven at 160 °C to allow moisture-crosslinking of PSZ on SiC surface. During drying, PSZ-coated SiC was gently grinded every 20 min to prevent the aggregation for 2 h, and then kept in an oven for 24 h. Finally, PSZ–SiC was obtained. Then, SiCNO–SiC was carried out with the same procedure as the case of PSZ–SiC except, the heat treatment at 800 °C in air for 3 h was required to convert PSZ into SiCNO. This fabrication procedure is graphically illustrated in Fig. 1.

2.3. Composite fabrication

ETDS resin was added to raw SiC and surface-treated SiC (PSZ–SiC and SiCNO–SiC) particles, and the mixture was then heated to 50 °C via magnetic stirring for 2 h for achieving homogenization. The mixture was heated in a vacuum oven at 80 °C for 6 h to evaporate any residual solvents. DDM was mixed with an epoxy resin mixture in stoichiometric amounts at 100 °C for 15 min. The mixture was poured into PTFE molds, degassed in a vacuum oven at 80 °C for 30 min, and cured via the following cycles: 80 °C for 2 h, 120 °C for 6 h, and 160 °C for 6 h.

2.4. Characterization

Fourier-transform infrared (FT-IR) spectra were obtained at a resolution of 4.0 cm^{-1} on an FT-IR spectrophotometer (PerkinElmer Spectrum100, USA) at 25 °C in the wavenumber range of 4000–400 cm^{-1} to investigate the variation in the surface structure of the SiC particles. Thermogravimetric analysis (TGA) was conducted in the air atmosphere by using a CI Electronics microbalance (MK2–MC5). The sample was heated at a ramp rate of 10 °C/min to 800 °C, followed by an isotherm stage at that temperature for 30 min. Field emission scanning electron microscopy (FE-SEM, SIGMA, Carl Zeiss) was used to examine the SiC particles and morphology of the fabricated composites. The raw and surface-treated SiC particles were characterized by X-ray photoelectron spectroscopy (XPS, VG-Microtech, ESCA2000) using an Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer. During curve fitting, the Gaussian peak widths were kept constant in each spectrum.