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Effects of oxidation curing and sintering temperature on the microstructure formation and heat transfer performance of freestanding polymer-derived SiC films for high-power LEDs

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ABSTRACT

Effects of oxidation cross-linking and sintering temperature on the microstructure evolution, thermal conductivity and electrical resistivity of continuous freestanding polymer-derived SiC films were investigated. The as-received films consisting of β-SiC nanocrystals embedded in amorphous SiO_xC_y and free carbon nanosheets were fabricated via melt spinning of polycarbosilane (PCS) precursors and cured for 3 h/10 h followed by pyrolysis from 900 °C to 1200 °C. Results reveal that nanoscale structure (β-SiC/SiO_xC_y/C_{free}) provides an ingenious strategy for constructing highly thermal conductive, highly insulating and highly flexible complexes. In particular, the 3 h-cured films sintered at 1200 °C with satisfying thermal conductivity (46.8 $W m^{-1} K^{-1}$) and electrical resistivity (2.1×10^8 Ω m) are suitable for the realization of high-performance substrates. A remarkable synergistic effect (lattice vibration of β-SiC nanocrystals and close-packed SiO_xC_y, free-electron heat conduction of β-SiC and free carbon, and supporting role of oxygen vacancy) contributing to thermal conductivity improvement is proposed based on the analysis of microstructure, intrinsic properties and simulations. Eventually, the SiC films without additional dielectric layers are directly silk-screen printed with high-temperature silver paste and used as heat dissipation substrates for high-power LED devices via chip-on-board (COB) package. The final devices can emit bright light with low-junction temperature (52.6 °C) and good flexibility owing to the mono-layer SiC substrate with low thermal resistance and desirable mechanical properties. This work offers an effective approach to design and fabricate flexible heat dissipation ceramic substrates for thermal management in advanced electronic packaging fields.

1. Introduction

Light emitting diodes (LEDs), as the most promising solid-state lighting devices, are replacing traditional incandescent and fluorescent lamps owing to their unparalleled advantages such as long lifetime, energy saving and quick startup, etc. [1–9]. However, only 20–30% of input electrical energy is used for light emitting, and the remaining energy is mostly converted into heat [2–4]. The consequent temperature increment of LED chips has been eventually linked to quantum efficiency reduction, emission wavelength shifts and devastating device failures [2–5]. Therefore, thermal dissipation has become a crucial issue for LED devices with increasing power densities.

Several reports have proposed reasons for unsatisfactory thermal dissipation of high-power LEDs: high thermal resistance of thermal interface materials (TIM), large mismatch of thermal-expansion coefficients, and improper design of package structures, etc. [5–7]. Indeed, finding appropriate heat dissipation materials and effective thermal management solutions has still remained a major challenge. Heat dissipation substrates should possess several advantages such as high thermal conduction with electrical insulation, suitable thermal-expansion coefficients matching with chips, excellent mechanical strength and high flatness [6–9]. Although commercial metal substrates (aluminum, copper) are cost-effective with high thermal conductivities, thermal stress generated from mismatch of thermal-expansion

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coefficients between substrate and chip would lead to catastrophic failures [9–11]. The heat dissipation performance of metal substrates is also severely affected by an additional dielectric layer. To avoid these problems, expensive ceramic substrates like Al_2O_3 and AlN are commonly used for high-power LEDs [12,13]. Despite low thermal expansion property and high electrical resistivity, it is difficult to manufacture flexible devices using these thick and rigid ceramic substrates. In fact, flexible electronics usually utilize polymers as substrate, but their thermal conductivities are generally lower than 10 $W\,m^{-1}\,K^{-1}$ as discussed in some papers [14–16]. Therefore, flexible ceramic substrates with both excellent thermal conduction and electrical insulation are desired for electronic applications.

Silicon carbide (SiC) films have drawn great attention owing to their high thermal conductivity (320–490 $W\,m^{-1}\,K^{-1}$), low thermal-expansion coefficient ($3.3 \times 10^{-6}\,K^{-1}$), desirable mechanical properties, chemical inertness and thermodynamic stability [17–20]. As reported previously, β-SiC nanocomposites provide a profound potential to manufacture flexible heat dissipation ceramic substrates for their unique combination of high thermal conductivity and high electrical resistivity [19,20]. So far, SiC films can be prepared by multiple methods: magnetron sputtering, ion implantation, liquid phase epitaxy (LPE) and chemical vapor deposition (CVD). In particular, an elegant approach to synthesize SiC developed by Yajima et al. [21], namely polymer precursor pyrolysis, offers many advantages compared with above techniques such as free of substrates, low processing temperature, and high flexibilities in shaping process. In our previous work, freestanding SiC films capable of avoiding coating/substrate interaction problems have been successfully prepared in this easy and economic manner. The films consist of β-SiC nano-crystals embedded in amorphous SiO_xC_y and free carbon cluster [22,23]. This composite structure may endow the films with desirable material properties including high thermal conductivity, high electrical resistivity, low thermal-expansion coefficient matching with chips, and excellent chemical stability, which is suitable for potential applications in heat dissipation substrate fields.

In this present study, continuous freestanding polymer-derived SiC films with different nanoscale composite structures were produced by pyrolysis of polycarbosilane (PCS) precursors. PCS were melt spun into freestanding green films and subsequently oxidation cross-linked for different time and finally sintered at different temperatures. Morphology, microstructure, composition and physical properties of the as-received products were characterized to provide an elaborated understanding toward their nanoscale composite structures. Meanwhile, molecular dynamics simulations were further carried out to support the experimental results. Principle and pathways to enhance thermal conductivity of the films would be proposed based on the microstructure analysis, comparison of intrinsic properties and related simulation results. The films with optimum combination of good thermal conductivity, excellent electrical resistivity and high flatness among all specimens were selected to be silk-screen printed with high-temperature silver paste. Afterwards, the silk-screened films were used as heat dissipation substrates for high-power LED devices via chip-on-board (COB) package. Furthermore, heat dissipation performances of the final devices including thermal resistance and junction temperature were evaluated by transient thermal measurements. All these works are devoted to exploring an ideal candidate for heat dissipation ceramic substrates (even for flexible substrates) of high-power LEDs, micro-electromechanical systems (MEMS), integrated circuit (IC), and so forth.

2. Experimental section

2.1. Preparation of polymer-derived SiC films

Transparent solid PCS precursors (Si: 41.03 wt%, C: 43.24 wt%, O: 1.05 wt%) with a melting point of 215 °C employed in this study were synthesized in our laboratory via thermal decomposition of polydimethylsilane (PDMS). Their number average molecular weight is 1426 determined by gel permeation chromatography (GPC) through an Agilent 1100 system (Agilent, Santa Clara, CA, USA). PCS were deaerated for 3 h in a vacuum deaeration furnace under 290 °C, and then melt spun into green films using a melt spinning machine (MMCH05, Chemat, Northridge, CA) at 265 °C in pure N_2. Thickness of green films was controlled by adjusting spinning speed or size of spinneret mouth. The green films were cross-linked in air (flow rate: 200 ml min^{-1}) at a heating rate of 3 °C min^{-1} to 190 °C, and then separately maintained for 3 h/10 h to get oxidation-cured films with different oxygen content. Subsequently, the cured films were presintered in pure Ar (flow rate: 200 ml min^{-1}) at a heating rate of 4 °C min^{-1} to 900 °C and maintained for 1 h. During the process, the translucent oxidation-cured films were converted into glossy black ceramic films. Finally, the films were sintered in pure Ar at a heating rate of 5 °C min^{-1} and maintained for 10 min at 900 °C, 950 °C, 1000 °C, 1050 °C, 1100 °C and 1200 °C, respectively, to possess different nanoscale composite structures.

2.2. Fabrication of high-power LED devices with polymer-derived SiC films via COB package

These obtained continuous freestanding polymer-derived SiC films were used as heat dissipation ceramic substrates of high-power LEDs by the following steps. Firstly, the electrodes were prepared with high-temperature sintered silver paste (GW-02, UV TECH, China) placed over the films via a silk-screen printing technique, followed by heat treatment at 650 °C in Ar (flow rate: 200 ml min^{-1}) for 30 min to yield ceramic substrates. The width of silver electrode line is 0.2 mm, and the spacing between adjacent silver electrode lines is controllable. Afterwards, high-power LED chips (APT4040B, APT Electronics, China) were bonded onto the substrate between two electrodes by silver-epoxy adhesive, and then baked for 45 min at 135 °C. Subsequently, electrodes of the chips were connected to silver electrodes by bonding gold wires using a wire bonder (WT-2310, Baixiangyuan, China). Phosphor silicone matrix was dispersed onto the surface of chips and bonding wires to form a phosphor layer. After baking for 1 h at 150 °C, the high-power LED device was finally manufactured.

2.3. Analysis and characterization

PCS green, cured and pyrolyzed films were examined by Fourier transform infrared spectrometer (Nicolet Avatar FT-IR 360, USA). Polymer-derived SiC films with different curing time and pyrolysis temperature were characterized by the following ways. Their composition and microstructure were analyzed by electron probe micro-analysis (EPMA, JXA-8100, JEOL, Japan), X-ray diffractometer (XRD, X′pert PRO, Panalytical, Netherlands), Raman spectrometer (LabRam I, Dilor, France), and transmission electron microscope (TEM, Tecnai F30, Philips-FEI, USA). Microscopic structure of β-SiC/SiO_xC_y interface were studied by electron paramagnetic resonance (EPR) using a Bruker ER 200D-SRC X-band spectrometer, and morphology was investigated by scanning electron microscope (SEM, Model 1530, LEO, Germany). Thermal analyses for the polymer-derived SiC films were performed using thermal gravimetric analysis (TGA, SDT Q600, Netzsch STA, Germany) under N_2 (flow rate: 40 mL min^{-1}). Thermal conductivity of specific films (10 mm × 10 mm × 0.5 mm) produced with the same process was determined by transient laser flash technique using laser thermal conductivity analyzer (LFA-457, Netzsch STA, Germany) with density measured by a pressure-of-floatation method and specific heat obtained from differential scanning calorimetry (DSC 204C, Netzsch STA, Germany). Electrical resistivity of the films was directly tested by ground resistance tester (ZC25A-4, Kanghai, China). Thermal resistance and junction temperature of the high-power LED devices based on polymer-derived SiC films were measured and calculated in a transient thermal tester (T3ster, MicReD Ltd., Hungary).