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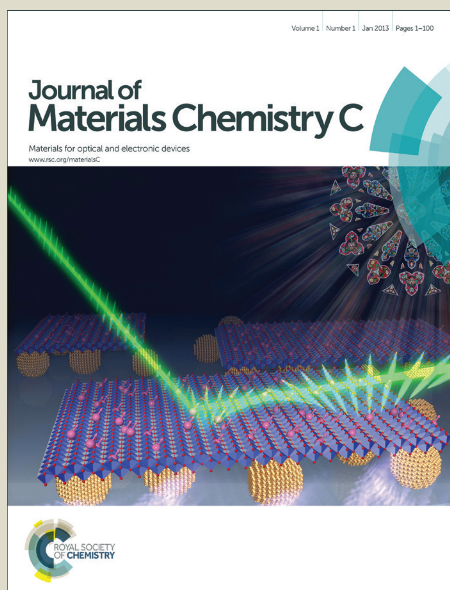

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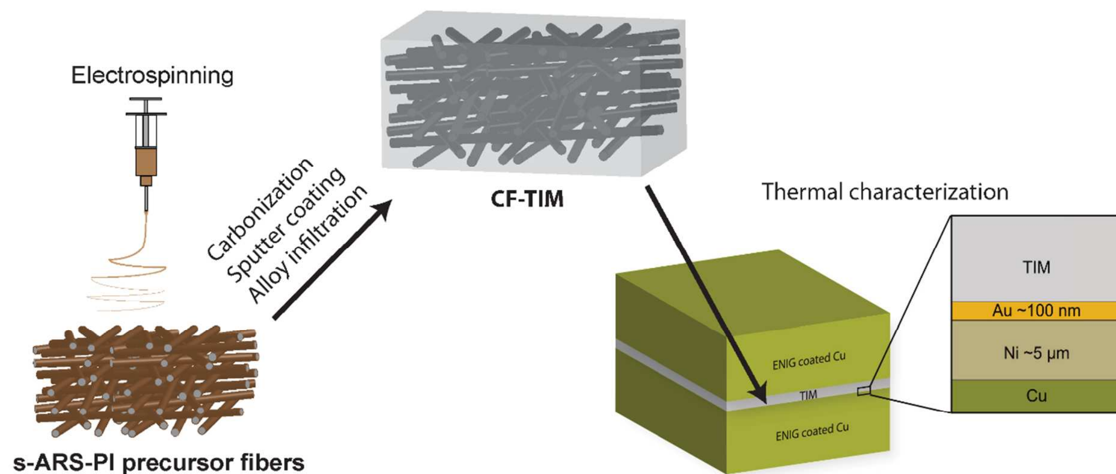
Novel carbon fiber solder matrix composite for thermal management of microelectronics



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COMMUNICATION

Carbon fiber solder matrix composite for thermal management of microelectronics

Cite this: DOI: 10.1039/x0xx00000x

Received May 2014
Accepted

DOI: 10.1039/x0xx00000x

www.rsc.org/

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A carbon fiber based tin-silver-copper alloy matrix composite (CF-TIM) was developed via electrospinning of mesophase pitch with polyimide and carbonization at 1000°C, followed by sputter coating with titanium and gold, and alloy infiltration. The carbonized fibers, in film form, showed a thermal conductivity ~4 W/mK and the CF-TIM showed an anisotropic thermal conductivity of 41±2 W/mK in-plane and 20±3 W/mK through-plane. The thermal contact resistance of the CF-TIM was estimated to be below 1 Kmm^2/W. The CF-TIM showed no reduction in effective through-plane thermal conductivity after 1000 temperature cycles, which indicates the potential use of CF-TIM in thermal management applications.

Continuous miniaturization of electronic devices leads to high power densities for the active components and intensifies the demands for efficient heat removal. Currently, the transportation of heat across interfaces is one of the main bottlenecks in the thermal management of high power electronic systems.[1,2] A major driving force to enable improved heat dissipation, is the development of advanced composite materials which can combine high thermal conductivity and low contact resistance with reliable mechanical performance, light weight and low production costs.[3–6]

Carbon based materials, such as carbon fibers (CFs), carbon nanotubes and graphene are attractive for thermal management applications due to their outstanding thermal and mechanical properties.[7,8,9,10] Owing to its special polynuclear ring structure, mesophase pitch can self-organize to form highly organized crystalline carbon structures via high temperature annealing. This makes mesophase pitch a promising alternative to polyacrylonitrile (PAN), in the development of advanced carbon based engineering composite materials.[11,12] Thermally conductive materials based on pitch have been reported by several groups; as aligned graphitic foams,[11] micro sized CFs [13], graphitic blocks [14], and a ribbon-shaped high aspect ratio fibers.[15] Generally, the measured thermal conductivities of such pitch based materials range from tens to hundreds W/mK.

Solder based thermal interface materials (TIMs) are often used in power electronic thermal management and are well known to offer very low contact resistance after reflow.[16,17] Combining the low contact resistance of solder alloy with the excellent properties of carbon based material, by forming composites, could thus be a very attractive solution for TIM applications. However, the use of continuous CF's to form composite solder for TIM applications has, to the best of our knowledge, not been reported in literature.

In this communication, we developed a new solder matrix composite material with mesophase pitch (ARS) derived carbon fibers via carbonization at 1000°C, aimed for thermal management applications. The CF's were formed via electrospinning of mesopitch[18] together with polyimide as a supportive carrier, followed by carbonization at 1000°C. The obtained CFs were then sputter coated with titanium (Ti) and gold (Au), followed by liquid phase infiltration of a tin-silver-copper (Sn-Ag-Cu) alloy matrix at elevated temperature, to form the final composite.[5] Measurements of the thermal conductivity and thermal interface resistance were performed after assembly in a sandwich structure. The thermo-mechanical reliability of the composite were also assessed by temperature cycling and repeated measurements of the thermal interface resistance.

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The flow chart in figure 1 shows the main steps in the preparation of the CF-TIM, via solvent extraction, electrospinning, stabilization, carbonization, sputter coating and pressure assisted liquid phase infiltration. In our initial experiments, the ARS was found to be very difficult to electrospin directly into fibers.[18] Instead, only the soluble portion of mesophase pitch (s-ARS) obtained from N,N-dimethyl acetamide (DMAc) solvent extraction was used. However, the s-ARS in DMAc also required the addition of polyimide (PI), to render a solution which could be electrospun.

From the electrospinning process, the resulting nonwoven fibers had diameters in the range of 1-2 micron with a uniform size distribution (Supporting Fig.1). The fiber mats were then preheated to 310°C (for stabilization), followed by carbonization at 1000°C in nitrogen atmosphere to form final CFs (Supporting Fig.2a-b). The carbonization treatment caused the fiber mats and individual fibers to shrink significantly.

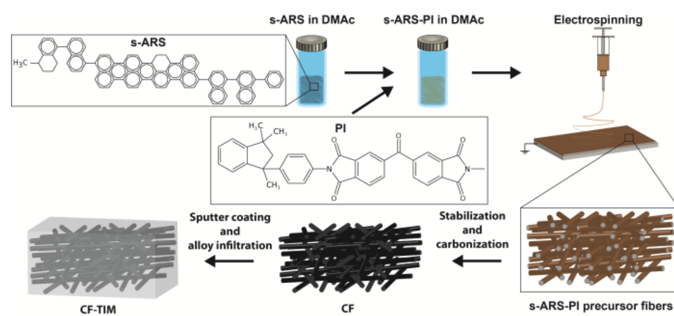

Figure 1. Schematic showing the various steps in the development of the mesophase pitch based carbon fiber tin-silver-copper alloy matrix composite. The preparation of the mesophase pitch based TIMs include solvent extraction, electrospinning, stabilization, carbonization, sputter coating with titanium and gold, and liquid alloy infiltration.

The chemical structural changes of the fibers before and after the heat treatments were studied using Fourier transform infrared spectroscopy (FTIR). Figure 1 shows the chemical structure of the PI and s-ARS samples. The PI used in this work was an aromatic polyimide, more precisely benzophenone-3,3´,4,4´-tetracarboxylic dianhydride 5(6)-amino-1-(4‘-aminophenyl)-1,3-trimethylindane. The electrospun pristine polyimide and s-ARS-PI fiber film was observed to exhibit similar spectral features (Supporting Fig. 2c). The absorption peak due to imide functional group was identified at 1722 cm^{-1} and the aromatic peak was observed at 3000 cm^{-1}. A peak due to the methyl ($-CH_3$) group co-appears with the aromatic C-H vibrations around 3000 cm^{-1}. From the collected FTIR spectra after annealing, it was also evident that most of the nitrogen and oxygen functional groups had disappeared and that only the carbon structure remained. Scanning electronic microscopy (SEM) analysis of the CF’s obtained from 1000°C carbonization processes shows fiber diameter just above one micron (Supporting Fig.2a-b). The fiber diameter was further confirmed using transmission electronic microscopy (TEM) as shown in Figure 2a-b.

Furthermore, the collected TEM images of the CFs indicate that each fiber has a disordered arrangement after the carbonization at 1000°C. The observed microstructure of the CFs (Figure 2a-b) is considered well known and is comparable to what has been reported for low temperature carbonization processes.[19, 20, 21, 22, 23, 23, 24]

The effect of annealing on the crystallinity was investigated using X-ray diffraction (Figure 2c). Both the pristine electrospun fibers (s-ARS) and the stabilized fibers (pre heated s-ARS fibers at 310°C) showed broad peak around $2\theta = 18^{\circ}$. However, after carbonization at 1000°C, the main peak was slightly shifted towards the (002) peak at $2\theta = 23^{\circ}$, and an emerging (10) peak was observed around $2\theta = 42^{\circ}$. This indicates the effects on the micro structure of the fibers from various processes occurring during the carbonization, such as dehydrogenation, condensation, hydrogen transfer and isomerization, and molecular rearrangements. The details of this process has been previously studied by several groups and reported in literature.[19, 20, 21, 23, 24]

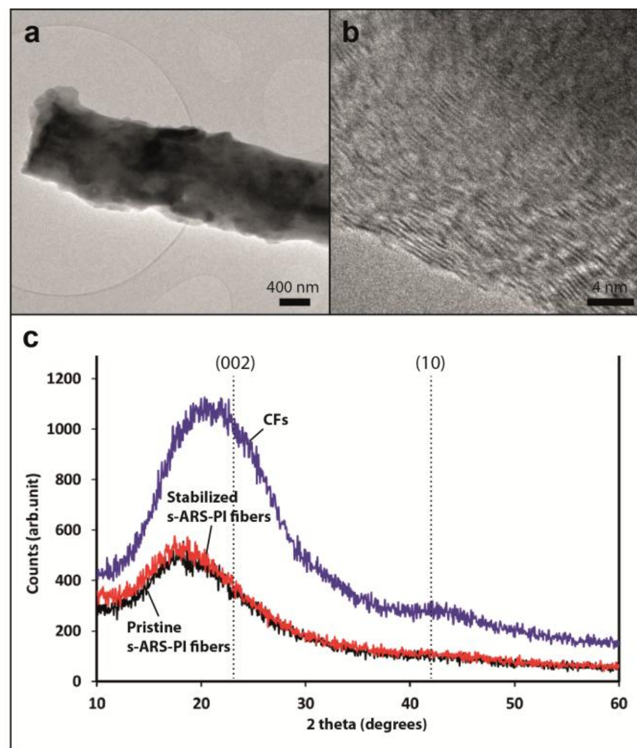

Figure 2: TEM images of CFs (a-b) and XRD profile of electrospun s-ARS-PI (black curve), stabilized s-ARS-PI fiber (pre heated s-ARS fibers at 310°C) (red curve), and CFs (blue curve) (c) obtained from 1000°C carbonization processes.

Raman spectra of CF sample annealed at 1000°C show both G band and D band at 1600 cm^{-1} and 1328 cm^{-1} respectively (Supporting Fig. 2d). The appearance of a D band indicates that the carbon structure has defects and is disordered in nature.[23]

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The intensity ratio of D band to G band (ID/IG) of the as prepared carbon nanofibers were found to be 1.46. These observations are consistent with literature results on the other CFs prepared at low temperature annealing processes.[27, 23, 28]

To measure the in-plane bulk thermal conductivity of CFs produced from 1000°C annealing, a transient in-plane measurement system (Hotdisk) was used. Using this technique, CF films with a thickness of 50±5 μm was measured to have a thermal conductivity of ~4 W/mK. This value is, as expected, considerably higher than the thermal conductivity of pure polyimide, reported in literature.[29] It should also be noted that the measured thermal conductivity is relatively low compared to other carbon based materials due to the high porosity of the carbon fibrous network. Nevertheless, the individual CF's can be expected to have significantly higher thermal conductivity than the measured 4 W/mK.

The measured thermal conductivity of mesophase pitch derived CFs can be compared to other CFs/carbon materials produced from 1000°C and reported in the literature. Wang et al. [30] found that the thermal conductivity of PAN-based CFs carbonized at 1000°C was 5 to 10 W/mK through measurements with the 3ω-method on individual fibers with a diameter of 7 μm. Ochanda et al. [32,33] studied the increase in thermal conductivity of PAN-based CFs by addition of metal nanoparticles during electrospinning. Using scanning thermal microscopy they measured a thermal conductivity of 55 W/mK for the PAN-based fibers produced at 1000°C, and claimed it was improved one order of magnitude by the nanoparticles. They also used these PAN based fibers to improve the thermal conductivity of an epoxy matrix. Li et al. reported the use of commercial PAN based CFs with a claimed thermal conductivity of ~4 W/mK for radiation shielding applications.[28] In summary, the thermal conductivity of CFs obtained by low temperature carbonization processes are typically found to be in the range of 5-50 W/mK, which is in agreement with our findings. The large variations in the measured thermal conductivity is likely due to varying quality and structure of the carbon material but also a consequence of whether the measurements are performed on a single fiber or a collection of fibers.[11, 13, 28, 30, 32, 33, 34, 35, 36, 37]

To form the final composite, and facilitate proper wetting during the liquid phase infiltration, the CFs were first sputter coated with 120 nm Ti and 60 nm Au. The coated CFs were then infiltrated with Sn-Ag-Cu matrix in molten stage under 30 MPa pressure, using a custom built infiltration equipment, to form the final composite.[5]

In order to study the anisotropic thermal conductivity of the CF-TIM, a Xenon flash instrument was used. The results are summarized in figure 3. The in-plane thermal conductivity was evaluated by measuring with an in-plane measurement fixture, and was found to be 41±2 W/mK. The through-plane thermal conductivity was evaluated by measuring the total thermal resistance of different thicknesses of the composite sandwiched and reflowed between electroless nickel and immersion gold (ENIG) coated copper plates. By measuring the total thermal resistance and knowing the thermal conductivity of the copper plates, the effective through-plane thermal conductivity of the composite could be determined. The effective through-plane thermal conductivity for CF-TIM was found to be 20 ± 3 W/mK over the range of 50 to 90°C at 65μm bond line thickness (BLT). The total thermal interface resistance was measured to be 2 - 7 Kmm^2/W at BLTs between 65 and 160 μm. Extrapolation of the results towards zero BLT indicate a contact resistance below 1 Kmm^2/W. For comparison, conventional polymer matrix based materials, such as high performance thermal grease, with thermal conductivities of around 4-5 W/mK, would result in total thermal interface resistance of 12 - 30 Kmm^2/W, at similar BLTs.[6] High performance thermal grease, are also known to suffer from reliability problems such as dry out, pump-out effects which can severely degrade the performance over time. Due to a much different material structure, the CF-TIM is not prone to these effects. Instead, the potential reliability issues of CF-TIM are expected to be more similar to that of solder joints.

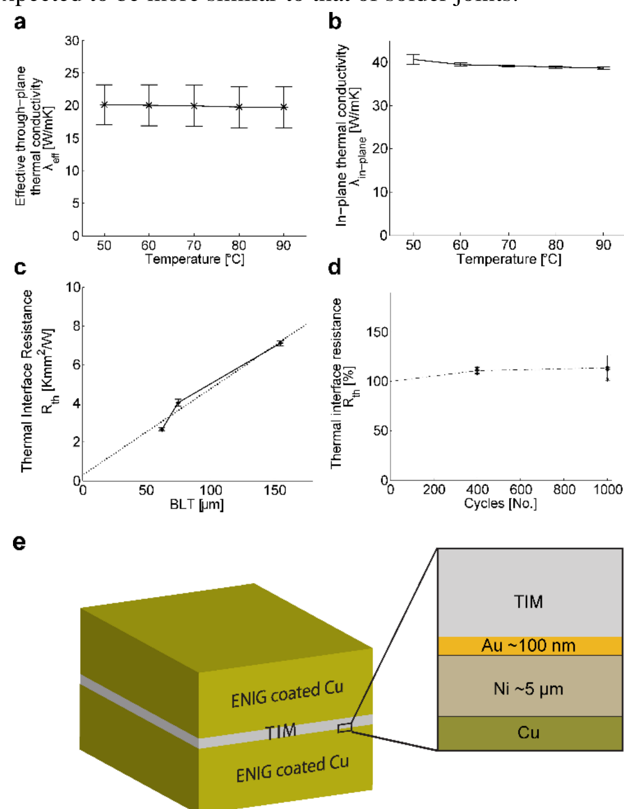

Figure 3: a) Effective through-plane thermal conductivity of CF-TIM between 50 to 90°C at a bond line thickness (BLT) of 65 μm. b) The bulk in-plane thermal conductivity CF-TIM. c) Total thermal interface resistance of CF-TIM at various BLTs. d) The relative change in thermal resistance of the CF-TIM after thermal cycling up to 1000 cycles. e) Schematic of CF-TIM test structure (8x8mm) used in the through-plane thermal conductivity measurements and thermal cycling.

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To assess the reliability of the joint formed with CF-TIM, thermal cycling of the test assemblies were carried out. The temperature was cycled between -40 to 115°C in accordance with global standards for microelectronics industry (JEDEC standard), for 1000 cycles while periodically evaluating the thermal resistance. It was found that the thermal resistances remain largely unaffected after 1000 cycles, indicating that reliable joints have been formed for all different sample thicknesses. The observable trend of a few percent increases in thermal resistance is below the accuracy of the measurements.

In conclusions, a new carbon fiber based tin-silver-copper alloy matrix composite (CF-TIM) with anisotropic thermal conductivity of 41 ± 2 W/mK in-plane and 20 ± 3 W/mK through-plane was developed. The in-plane bulk thermal conductivity of CFs produced from 1000°C annealing was found to be ~4 W/mK. After sputter coating and alloy infiltration into the carbon fibers, the resulting CF-TIM composite was assembled and evaluated as a TIM. Between ENIG coated Cu surfaces, the CF-TIM showed low total thermal interface resistances in the range of 2-7 Kmm^2/W for BLTs ranging from 65 to 160 µm. The contact resistance was estimated to be below 1 Kmm^2/W. Measurements after 1000 temperature cycles indicated high reliability, as no increase in thermal interface resistance was detected. Consequently, the developed CF based composite can be suitable for use as a TIM for thermal management of microelectronics.

Acknowledgements
The authors acknowledge European Union for the funding through programs “Smartpower”, “Eniac Nanoteg” and “Eranet Nano-TIM”. This work was also carried out within the Sustainable Production Initiative and the Production Area of Advance at Chalmers University of Technology. This support is gratefully acknowledged. We also acknowledge the funding from the SSF Funding within the “Material for energy program” regarding thermo-electric materials (Contract No EMII-0002.006). We also acknowledge the support from the Chinese National Science Foundation under the contract no 51272153 as well as the Shanghai Science and Technology Commission (STCSM) project under the contract No: 12JC1403900.

Notes and references

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Electronic Supplementary Information (ESI) available: [Supporting Information includes the experimental details of this work.]. See DOI: 10.1039/c000000x/

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