Supporting information for

Carbon fiber solder matrix composite for thermal management of microelectronics

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EXPERIMENTAL SECTION

Materials

Mesophase pitch (AR Resin; ARS) was obtained from Mitsubishi chemical company, Japan.[1] The ARS is an aromatic compound with a black colored pellet like appearance and has a softening point of 275 to 295^{o}C. The solvent *N, N*-dimethyl acetamide (DMAc) was obtained from Sigma-Aldrich with available highest purity. An aromatic polyimide (PI), more precisely benzophenone-3,3´,4,4´-tetracarboxylic dianhydride 5(6)-amino-1-(4‘-aminophenyl)-1,3-trimethylindane) (Matrimid 5218), was obtained from Huntsman Advanced Materials, USA. The alloy for infiltration (Sn95.5Ag3.8Cu0.7) was obtained from Indium Corporation, USA.

Methods:

N, N-dimethyl acetamide (DMAc) extraction: ARS powder was dispersed in a DMAc solvent and stirred for 24h at room temperature. The top layer was decanted in to a beaker and highly soluble fraction was collected by further centrifuging at 2000 rpm for 2 min. The DMAc solvent was subsequently removed and soluble mesophase pitch portion (s-ARS) was collected after drying.

Electrospinning process: A homogeneous s-ARS and PI mixture was prepared by stirring a 1.5g of s-ARS in 8g of DMAc for 12 to 24h, followed by addition of 1.5g PI and stirring for additional 24h. Finally obtained high viscous liquid was loaded into a 20 ml plastic syringe equipped with a 21G stainless steel cannula. For the electrospinning a voltage of 18 kV was applied to the cannula and the solution was feed at a rate of 2 ml/h. Grounded aluminum foils were used as collectors for the deposition of the resulting black electrospun fiber mats. The distance between the collector and cannula tip was 20 cm.

Carbonization process: The samples obtained from the electrospinning were pre heated in an air atmosphere to 310^{o}C with a 1^{o}C/min heating rate. After 20 min stabilization, the sample was cooled to room temperature. The stabilized fiber mat was then carbonized under N_2 at 1000^{o}C with a heating rate of 1^{o}C/min using a quartz tube furnace. After 120 min carbonization, the sample was cooled to room temperature under N_2 flow.

Sputter coating of carbon fibers: Prior to liquid phase infiltration of the alloy, and in order to enhance the wettability of the fibers, the CF networks were sputter coated with thin layers of titanium (Ti) and gold (Au). For the sputtering procedure, a standard metal sputtering system (FHR, Anlagenbau GmbH) was used at a chamber base pressure of 2*10E-7 mbar. The sputtering rate and time was adjusted to result in a thickness of approximately 120 nm and 60 nm for the deposited Ti and Au layer (thickness for deposition on a flat substrate). To enable coverage on both sides of the fibers the sputtering procedure was carried out twice, once from each side of the mesh.

Alloy infiltration: The CFs were infiltrated by pressure assisted liquid infiltration utilizing a system with custom design, and the process has been reported before.[2] Briefly, the CF mat is first placed in a cavity which is evacuated via a vacuum gate. Keeping the mold at elevated temperature, liquid alloy is let into the mold, surrounding the CFs from both sides. High pressure (30MPa) is

then applied to the liquid alloy to allow infiltration into the porous CF structure. Before cooling to allow solidification, the composite thickness is adjusted via a compressing piston.

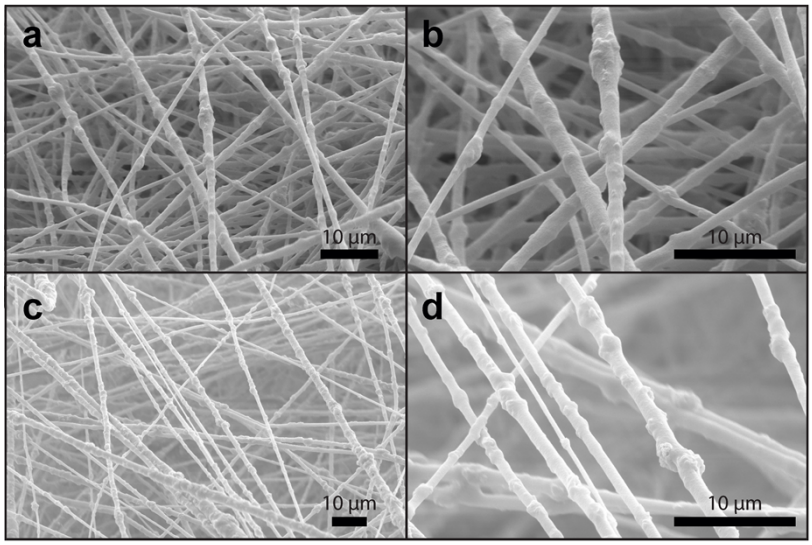
Characterization techniques: Infrared spectra were collected in an FTIR spectrophotometer (Spectrum two, Perkin–Elmer,) with UATR2 unit. Raman spectra of CF were collected on a standard Raman spectrometer (XploRA, Horiba Jobin Yvon) using a 100× objective lens with 638 nm laser excitation. Results are reported from the average of three scans to improve the signal-to-noise ratio. The surface morphology of the samples was characterized by using a scanning electron microscope (SEM) (Supra 60 VP, Carl Zeiss). The microstructure of the single fibers were observed by transmission electron microscope (TEM). In-plane thermal conductivity measurements for CF mats were performed using transient plane source equipment (Hot disk, TPS2500; (ISO 22007-2)). A slab module with a diameter of 4 mm was utilized and sandwiched between the samples being measured. Styrofoam was used as an insulator to minimize heat losses to the ambient.

The in-plane and through-plane thermal conductivity measurement of CF-TIM were conducted using xenon flash equipment (Nanoflash LFA447, Netsch) operating according to ASTM E1461. For through-plane measurements, samples were prepared by sandwiching composite preforms between two 8x8 mm electroless nickel and gold (ENIG) coated 1 mm copper plates. To ensure proper wetting of the surfaces and minimize the contact resistances, the stacked structure was subjected to reflow at elevated temperature and above the melting point of the alloy while being subjected to a 200 kPa compressive pressure.

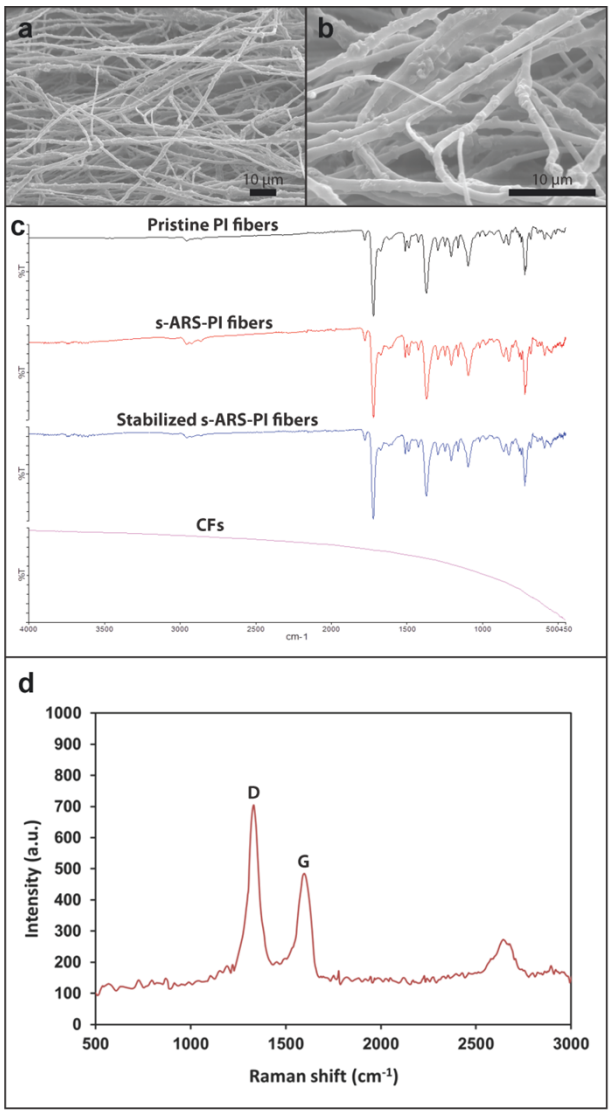
For the in-plane measurements, a standard in-plane fixture from the instrument manufacturer for the xenon flash instrument, was used. The in-plane fixture measurements are well suited for foils and thin films. The working principle is as follows: The fixture allows heat from the flash to be adsorbed only in the center on one side of the circular foil sample. The temperature increase of the sample is then detected on the opposite side of the foil at well-defined radius through openings in the fixture. For thin samples, the rise time for the temperature will be dependent on the in-plane

thermal diffusivity. The in-plane thermal diffusivity is then related to the in-plane thermal conductivity through specific heat capacity and density. The heat capacity of the CF-TIM was estimated by measuring the density of the composite, and from this acquiring the carbon and alloy weight ratios in the composite. The specific heat capacity was then calculated by using reference values for the respective material components.

Thermal reliability characterization: Thermal cycling of CF-TIM samples, mounted and reflowed between two 8x8 mm electroless nickel and gold (ENIG) coated 1 mm copper plates, was carried out in an environmental chamber (924E, Despatch) by adopting global standards for microelectronics industry (JEDEC standard) test condition I (soak mode 2), from -40°C to 115°C with 2 cycles/hour and 5 min soak time with heating rate of 15°C/min.



Supporting Fig 1. SEM images of electrospun s-ARS-PI fiber (a-b), and stabilized s-ARS-PI fiber (c-d).



Supporting Fig.2: SEM images of CFs obtained from carbonization at 1000°C (a-b) and (c) FTIR-ATR spectrum of electrospun pristine PI fiber film, electrospun s-ARS-PI fiber, stabilized s-ARS-PI fiber, and CFs (d) Raman spectra of CF recorded using 638nm laser excitation

References

1. AR (Aromatic Resin) http://www.mgc.co.jp/eng/products/abc/17.html
2. B. Carlberg, L.-L. Ye, and J. Liu, Mater. Lett., 2012, 75, 229–232.