Enhanced thermal conductivity of epoxy composites with core-shell SiC@SiO$_2$ nanowires

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Abstract: Electronic packaging materials and thermal interface materials (TIMs) are widely used in thermal management. In this study, the epoxy composites with core-shell structure SiC@SiO$_2$ nanowires (SiC@SiO$_2$ NWs) as fillers could effectively enhance the thermal conductivity of epoxy composites. The unique structure of fillers results in a high thermal conductivity of epoxy composites, which is attributed to good interfacial compatibility epoxy matrix and bridging connections of SiC@SiO$_2$ NWs. From neat epoxy to 2.5 wt% loading of SiC@SiO$_2$ NWs, the thermal conductivity is significantly increased from 0.218 to 0.391 W m$^{-1}$K$^{-1}$, increased by 79.4%. In addition, the composite with 2.5 wt% filler possess lower coefficient of thermal expansion and better thermal stability than that of neat epoxy. All these outstanding properties imply that epoxy/SiC@SiO$_2$ NWs composites could be the ideal candidate for TIM.

1 Introduction

In the present electronic age, the continued trend towards electronic device miniaturisation has obtained tremendous progress [1–3]. Electronic devices miniaturisation increases their portability and ease of handling nowadays [4–8]. Meanwhile, the power consumed by these compact electronic devices has been exponentially increasing from 50 W/cm$^2$ increasing over 1000 W/cm$^2$ [9]. Consequently, the heat generated by the working devices, resulting in reduced device life time and performance. Thus the selection of packaging materials and thermal interface material (TIM) is crucial for signal and power transmission, heat dissipation, and protection from moisture and contaminants [10–14]. However, low thermal conductivity of neat polymer ($\sim$0.1 W m$^{-1}$K$^{-1}$) limits its application for electronic packaging [15–17]. To solve this problem, epoxy composites, combining the advantages of matrix and filler component, are increasingly utilised for thermal management and microelectronic packaging because of its superior performances, remarkable processability well-defined coefficient of thermal expansion (CTE), and low cost [18, 19]. High filler loading is easily to obtain high thermal conductivity, which inevitably deteriorates mechanical property and process ability of the composites [20–23]. Therefore, preparation of high thermal conductivity at low loading is still a big challenge. In especially, fillers owning high aspect ratio and great interfacial affinity with matrix can effectively promote formation of thermally conductive pathways at relatively low loadings [10, 24]. It can maintain the epoxy properties, such as low permittivity, dielectric loss and thermal expansion, high strength and thermal stability [25, 26]. Moreover, traditional heat dissipating materials like copper and aluminium show CTE mismatch to silicon and insulating ceramics and cannot be used for direct device attachment without stress compensating interlayers [27, 28]. Silicon carbide (SiC) is on account of its particular crystal structure, usually used in new fixed abrasive lapping slurry [29], development of novel ceramic bond diamond wheels for grinding soft brittle [30–32], hard brittle crystals [33], and truing of new resin bond diamond wheels [34]. Not only the hardness property but also the high intrinsic thermal conductivity of SiC possesses. Thus, using new fillers like SiC nanowires (NWs) exhibits outstanding physical properties, it should be possible to obtain novel electronic packaging composites with extraordinary low CTE mismatch to silicon [19, 35–41]. Herein, SiO$_2$-coated SiC nanowires (SiC@SiO$_2$ NWs) with a novel core-shell structure was prepared by high-frequency heating and used as filler in order to obtain good interfacial compatibility between filler and epoxy matrix. The SiC@SiO$_2$ NWs were mixed uniformly with epoxy using ethanol as the solvent. Subsequently, the mixture was stirred in water bath and added in curing agent to obtain the epoxy composites. The epoxy/SiC@SiO$_2$ NWs composites may be utilised for effective thermal management in high-performance electronic and optoelectronic devices with long lifetimes [42, 43].

2 Materials

SiC NWs were produced by Changsha Sinet Advanced Materials Co., Ltd. China. Anhydrous ethanol was produced by Sinopharm Chemical Reagent Co., Ltd. Using as latent catalyst of neodymium (III) acetate/calonetrihydrate (Nd(III)acetac) was purchased from Aldrich Chemicals. Cycloliphatic epoxy resin (6105, DOW Chemicals) along with hardener of methyl-hexahydrophthalic anhydride ( Shanghai Liyi Science & Technology Development, China) is used in the present study. High-frequency induction heating furnace (XJH-15A) was produced by Chien Wah Induction Co., Ltd.
3 Preparation of SiC@SiO₂ NWs using high-frequency heating

For the preparation of core-shell SiC@SiO₂ NWs, required quantity of SiC NWs was added into a graphite crucible and placed in the high-frequency heating furnace in air to heat from room temperature to 1500°C in different time. The heating time was maintained for 15, 20, 25, and 60 s. The growth model for synthesising the core-shell SiC@SiO₂ NWs is shown in Fig. 1.

4 Preparation of epoxy composites

Epoxy composites with different loading SiC@SiO₂ NWs were prepared by the following procedures. Required quantity of Nd(III)acac was added into a cycloaliphatic epoxy resin and subsequently be stirred at 80°C in a three-necked flask for 2 h. The homogeneous solution was then cooled down to room temperature. A desired amount (0.5, 1.0, 1.5, 2.0, and 2.5 wt%) of SiC@SiO₂ NWs were dispersed in ethanol in an ultrasonic bath for 0.5 h and then added into the predetermined amount of epoxy resin with 0.5 h of ultrasonication. The uniform formed mixture was then placed in a beaker with vigorous mechanical stirring at 80°C in water bath until complete evaporation of ethanol. Curing agent was added at a ratio of 100:95 by weight (epoxy: curing agent) into the beaker and the mixture was stirred for 20 min. The obtained mixer was further degassed in the vacuum oven for 10 min to remove air bubbles. Finally, the mixture of epoxy with the homogeneously dispersed SiC@SiO₂ NWs was poured into the mould and be cured at 135°C for 2 h and 165°C for 14 h. After the curing process, the samples were naturally cooled down to the room temperature and then polished with emery paper for different characterisations. The preparation process of epoxy/SiC@SiO₂ NWs composites is illustrated in Fig. 1.

5 Characterisations

The microstructures of the samples were obtained from JEOL JEM-2100 (TEM, JEOL, Japan) instrument with an acceleration voltage of 200 kV. The fractured surface of the composites was examined by field emission scanning electron microscopy (FE-SEM, QUANTA FEG250, USA) at an acceleration voltage of 20 kV. Samples that were broken and the fractured surface was coated with a thin gold layer to avoid static electric charge-up in SEM. X-ray photoelectron spectroscopy (XPS) was carried out with a Kratos AXIS Ultra DLD spectrometer, using Al Kα excitation radiation (hυ:1253.6 eV). The Raman spectra were recorded using a Reflex Raman system (RENISHAW plc, Wotton-under-Edge, UK) with a laser wave length of 532 nm. The scanning was performed from 10⁰ to 80⁰ with a speed of 4° min⁻¹ at room temperature. Thermogravimetric analysis (TGA) was carried out using NETZSCH TG 209 F3 thermo-analyser. The temperature range was from 50 to 800°C at a ramp rate of 10°C/min in nitrogen atmosphere. Thermal conductivities of the composites were measured using the light flash apparatus LFA 447 NanoFlash® (Netzsch-Gerätebau GmbH, Selb, Germany). The infrared (IR) photos were captured by infrared camera (Fluke, Ti4000, USA). Differential scanning calorimetry was performed by a Pyris Diamond DSC (Perkin-Elmer, USA) at temperatures varies from 20 to 250°C at a heating rate of 10°C/min under a nitrogen atmosphere to find out glass transition temperature (Tg) of the composites. CTE measurements were performed on a thermal mechanical analyser (TMA 402F1/F3, NETZSCH, Germany). The samples mounted on TMA were heated from 310 to 460 K at a heating rate of 5 K/min. From the slope of the plot between thermal expansion and temperature the CTE values were determined.

6 Results and discussion

6.1 Characterisation of SiC@SiO₂ NWs

Figs. 2a and c show that an individual straight of SiC NW and SiC@SiO₂ NW on the copper grid, respectively. The NWs display smooth surface and very homogeneous diameter. From the TEM images, it clearly reveals NWs with a diameter range from 100 to 250 nm and the aspect ratio is approximately from 480 to 800. Figs. 2b and d exhibit the HR-TEM image of the NW. Fig. 2b displays the spacing distance between each parallel stripe (d = 0.25 nm) equal to interplanar crystal spacing of SiC cubic crystal structures, and the NW grow along the direction of [111] which is perpendicular to the parallel stripes. Along the axis of the SiC NWs we can observe the high density of stack-faults and twin crystal structure with about a few nanometres wide can be observed. Which reveals a typical crystal structure of β-SiC, with a clear edge indicate nothing on the surface of SiC NWs [44]. Fig. 2d can be observed a typical crystal structure of β-SiC in the core of NW and a layer of amorphous substance attach on the surface of SiC NWs, which is heated in air for 60 s in the high-frequency heating furnace. The thickness of attached amorphous substance is ~4 nm; therefore, the extremely thin of the shell can hardly be found in Fig. 2c. It declares that after 1500°C heating, the SiC on the surface of NWs was oxidised by oxygen in the air. In this reaction, the products are SiO₂ and CO₂. Then SiO₂ is deposited on the surface of NWs and the CO₂ is taken away by the air. The oxygen diffusion...
to 1500°C at 15, 20, 25, and 60 s. As shown in Fig. 3, the thickness change indicates that the transversal optic (TO) mode at 791 cm$^{-1}$.

Both peaks show a significant red shift of 5 cm$^{-1}$. First, it is reasonable to interpret this shift by a microcrystal model based on the size confinement effect. Furthermore, the stacking faults may also cause an additional size confinement effect. The difference thermal expansion coefficients between the SiC core and SiO$_2$ shell, this structure may result in internal stress within the SiC core when the temperature cool down to room temperature. These internal stresses may cause the red shift of the TO and LO phonon modes of SiC NWs [47–49].

Fig. 3 shows the HR-TEM images of SiC@SiO$_2$ NWs with different heating times (a) 15 s, (b) 20 s, (c) 25 s, (d) 60 s.

XPS analysis is employed to further verify the surface composition and investigate the functional groups. The binding energies obtained in the XPS analysis are standardised for specimen charging by using C$_1s$ as the reference at 284.6 eV. The high-resolution results of Si$_{2p}$, O$_{1s}$, and C$_{1s}$ are shown in Figs. 4b–d. The spectrum of C$_{1s}$ composes of four peaks centred at 284.60, 282.36, 286.14, and 288.59 eV which corresponds to C=C, C–Si, C=O, and O=C–O, respectively, as shown in Fig. 4b. The two-weak peaks of O=C and O–C=O can be attributed to the absorbed CO$_2$, and some organic molecules containing carbonyl functional groups [50].

6.2 Morphology of epoxy composites

To understand the relationship between the structure and properties of epoxy composites, the cross-sectional morphologies of neat epoxy and epoxy composites were observed using SEM, as illustrated in Fig. 5. Fig. 5a depicts a river patterns of layered structures with cracks, which is the typical microstructure of neat epoxy. In addition, the regions of the fracture surface are very smooth revealing that the composite is brittle thermosetting polymer. It can be clearly observed that all composites exhibit a wrinkled rough fracture surface with the increasing incorporation of the SiC@SiO$_2$ NWs, the fracture surfaces of the epoxy composites exhibit considerably different fracture graphic features and SiC@SiO$_2$ NWs are homogeneously dispersed in the epoxy matrix and no large bundles are observed, as shown in Figs. 5b–f.

Fig. 4 depicts a river patterns of striped shape and size, and interaction between the filler and epoxy matrix [52–54]. Meanwhile, in most solid materials the phonons play a major role in heat conduction. Neat epoxy cannot obtain an expected thermal conductivity since low crystallinity and phonon scattering of the randomly entangled molecule chains [55]. So clearly, the SiC@SiO$_2$ NWs provide substantially great thermal conductivity enhancement when embedded into epoxy, leading to low thermal interface resistance and low phonon mismatch. It suggests that phonon can easily be absorbed by crystalline structure in the procedure of transmission [56]. This result is in accordance with the aforementioned SEM results (shown in Fig. 5c).

6.3 Thermal properties of neat epoxy and its composites

As reported that thermal conductivity of a composite is affected not only by the thermal conductivity of the components but also by other factors such as the morphology, dispersion, porosity, filler shape and size, and interaction between the filler and epoxy matrix [52–54]. Meanwhile, in most solid materials the phonons play a major role in heat conduction. Neat epoxy cannot obtain an expected thermal conductivity since low crystallinity and phonon scattering of the randomly entangled molecule chains [55]. So clearly, the SiC@SiO$_2$ NWs provide substantially great thermal conductivity enhancement when embedded into epoxy, leading to low thermal interface resistance and low phonon mismatch. It suggests that phonon can easily be absorbed by crystalline structure in the procedure of transmission [56]. This result is in accordance with the aforementioned SEM results (shown in Fig. 5c). For obtaining the superior thermal conductivity of the composites, thermal resistance of interface, loading, and dispersion of fillers between the fillers and matrix are the critical factors [27, 57]. Usually, at a low filler loading, the heat-conductive particles (such as ceramic particles [58–60]) encapsulated by the epoxy matrix cannot touch each other which is analogous to the ‘sea-island' structure. However, according to literatures report that high aspect ratio or surface area fillers can form more continuous thermally conductive network in the polymer matrix. With the content of...
SiC@SiO\(_2\) is further increased, local chain and network would mutually bridge to generate the network. This network can also give the phonon a new path to transport, which leads to enhance the thermal conductivity of composites [61].

In order to assess the effect of SiC@SiO\(_2\) NWs on the thermal properties of composites, thermal diffusivity was measured first and then thermal conductivity was calculated, both as a function of SiC@SiO\(_2\) NWs loading content (0–2.5 wt%). Fig. 6a shows the thermal diffusivity and thermal conductivity of epoxy composites loading with different content of SiC@SiO\(_2\) NWs, ranging from 0 to 2.5 wt%. As can be seen, the thermal diffusivity of neat epoxy is around 0.108 mm\(^2\)/s. With the addition of 0.5 wt% SiC@SiO\(_2\) NWs, the thermal diffusivity of epoxy/SiC@SiO\(_2\) NWs composite increased to 0.124 mm\(^2\)/s, \(\sim 13\%\) enhancement. When the loading of SiC@SiO\(_2\) NWs was 2.5 wt%, the thermal diffusivity of the composite reached 0.173 mm\(^2\)/s, and the corresponding thermal conductivity was improved from 0.218 to 0.391 Wm\(^{-1}\)K\(^{-1}\). Comparing to neat epoxy, the composite loading with 2.5 wt% SiC@SiO\(_2\) NWs was improved significantly by 79.4% of the thermal conductivity. This result is higher than our previous research of epoxy composites with 2.5 wt% SiC NWs (0.356 W m\(^{-1}\)K\(^{-1}\)). Based on these results, it can be concluded that not only the outstanding large aspect ratio and intrinsic high thermal conductivity of SiC@SiO\(_2\) NWs but also the rigid linkage between SiC@SiO\(_2\) NWs and epoxy matrix which provides good interface compatibility that may reduce interfacial thermal resistance, and the good interface compatibility allows SiC@SiO\(_2\) NWs to disperse well in the epoxy matrix. All of these positive factors lead to an observed enhancement in thermal conductivity [62].

The effect of temperature from 50 to 150°C on thermal conductivity of neat epoxy and epoxy composite with 2.5 wt% filler was shown in Fig. 6b. In the shown pattern, this composite at a filler loading of 2.5 wt% exhibited a thermal conductivity of 0.346 W m\(^{-1}\)K\(^{-1}\) at 50°C (in comparison with 0.211 W m\(^{-1}\)K\(^{-1}\) in neat epoxy). For epoxy/SiC@SiO\(_2\) NWs composite, thermal conductivity was found to increase to 0.538 W m\(^{-1}\)K\(^{-1}\) with temperature over the temperature range investigated. Same trend of the thermal conductivity can be noted in neat epoxy with the increase of temperature (0.339 W m\(^{-1}\)K\(^{-1}\)). Under the temperature of \(T_p\) (shown in Fig. 6b), thermal conductivity is affected by the variation of phonon mean free path caused by structure scattering and chain defect scattering [63, 64], which refer to the propagation of lattice wave, independent of temperature, and the defects introduced by blending in the materials system, respectively. When temperature increases, the polymeric chain surrounding the fillers begins to vibrate and straighten out. Thus, the mean free path and phonon propagation length increased. The experimental results show that the longer phonon propagation length implies the higher thermal conductivity. The higher thermal conductivity of epoxy composites under the condition of raising temperatures can make it possible for efficient thermal transfer, which is expected to be very useful as the next generation TIMs [65].

Furthermore, the infrared camera is employed to demonstrate the effect on thermal performance of neat epoxy and epoxy composites. Before the tests, the surfaces of the samples and the platform were coated with a thin layer of amorphous carbon to ensure consistent emissivity of the surfaces and thermal radiation transfer between the hot platform and sample. The temperature profile evolution in time of two samples was captured using a calibrated infrared camera, as shown in Fig. 6c. Two samples were horizontally placed on the same heater in the order of neat epoxy and epoxy composites with 2.5 wt% SiC@SiO\(_2\) NWs. The surface temperature of hot platform was kept at room temperature at the beginning and the top heating temperature was set to 90°C. With the heating time increasing, it is obviously observed that the surface colour of two samples are becoming increasingly more brightly. The temperature as a function of heating time data indicated that heat penetrated further and temperature increased more quickly for the composite samples than the neat epoxy, resulting in a higher thermal conductivity. At first 15 s, the two samples exhibit different colour, the surface temperature of epoxy composite is \(\sim 41\)°C, but the neat epoxy is only \(\sim 38\)°C. Particularly after 40 s, the epoxy/SiC@SiO\(_2\) NWs composites display remarkable bright compare with neat epoxy, which the temperatures were 85 and 82°C. The results give us an interpretation that the better heat dissipation ability of epoxy composites which is in good agreement with the thermal conductivity values shown in Fig. 6a. To further demonstrate the effect on thermal performance, the system with a hot plate, a thermocouple element, and a versatile voltmeter were employed to get quantitative results of heating and cooling process. As shown in Fig. 6d, the heating and cooling trend of neat epoxy and epoxy composites can be noticed. From the curves, it can be seen that the
High Volt. was proposed in Fig. 7. The model of heat flow for neat epoxy filler, dispersed in the matrix, and better heat transfer is expected due to 581 s heating, the samples are shifted to a room temperature plate promising filler to enhance the thermal propagation of epoxy anisotropic and higher aspect ratio SiC@SiO$_2$ NWs composite. Fig. 8(a) shows the effect of SiC@SiO$_2$ NWs on the glass transition temperature ($T_g$) of the composites comparing to the neat epoxy, with the tested temperature range from 25 to 250°C. It is observed that the $T_g$ of epoxy/SiC@SiO$_2$ NWs shift to 196.1°C compare neat epoxy (191.7°C), increase by 4.4°C. This result indicating that a strong interface by reacting with matrix molecules during curing process, which creates more barriers to restrict the motion of macromolecular chain, leading to the higher $T_g$ and promoting thermal stability. TGA was further performed to evaluate the positive effect of epoxy compositions as shown in Fig. 8(c). It can be noted that all the samples display similar thermal behaviour and merely a one-step decomposition, indicating that the existence of the SiC@SiO$_2$ NWs did not significantly change the degradation mechanism of the epoxy matrix. Fig. 8(c) reveals the main weight loss in temperatures around 330 and 430°C. The chosen characteristic thermal parameters are 5% weight loss temperature ($T_{5\%}$), the $T_{5\%}$ of neat epoxy is 330.4°C. However, the $T_{5\%}$ of epoxy compositions with 0.5, 1.0, 1.5, 2.0, and 2.5 wt% SiC@SiO$_2$ NWs are 335.4, 322.9, 345.4, 345.8, and 347.9°C, respectively. Suggesting that SiC@SiO$_2$ NWs can partly enhance the thermal stability of epoxy composites. It can also be observed the char yields of all composites are increased in comparison with these of the neat epoxy. Moreover, the highest thermal degradation rate temperature, which is maximum degradation temperature ($T_{\text{max}}$), is shown in derivative thermogravimetric (DTG) curves in Fig. 8(d). The $T_{\text{max}}$ of neat epoxy is 373.5°C. However, the $T_{\text{max}}$ of epoxy compositions with 0.5, 1.0, 1.5, 2.0, and 2.5 wt% SiC@SiO$_2$ NWs are 373.5, 370.4, 377.9, 375.4, and 375.6°C, respectively. The patterns reveal that the $T_{\text{max}}$ of the epoxy compositions are also slightly improved by introduced the SiC@SiO$_2$ NWs compared to the $T_{\text{max}}$ of neat epoxy. These results suggesting that the SiC@SiO$_2$ NWs filled in epoxy matrix can restrict thermal motion of the polymer chains and the mobility of the polymer fragment at the interfaces of the epoxy [68].

### 7 Conclusions

In summary, the core-shell SiC@SiO$_2$ NWs were prepared as fillers into epoxy matrix. The thermal conductivity of 0.391 W m$^{-1}$ K$^{-1}$ was obtained for epoxy composites with 2.5 wt% SiC@SiO$_2$ NWs loading, 79.4% enhancement in comparison with neat epoxy. The results indicate that the thin interfacial SiO$_2$ layer could help to reduce the resistance to heat transfer. Meanwhile, high aspect ratio and intrinsic high thermal conductivity also play the critical factors to increase the thermal conductivity of epoxy improving the interfacial interaction between the SiC@SiO$_2$ NWs and epoxy matrix is observed to be another effective way to enhance the thermal conductivity. The CTEs of the neat epoxy and epoxy composite with 2.5 wt% filler were evaluated by TMA, as shown in Fig. 8a. It can be noted that samples in this work show non-linearity during thermal expansion as the temperature increases. The epoxy/SiC@SiO$_2$ NWs composite exhibit lower CTE values compare with neat epoxy. The CTE values are 31.6 ppm K$^{-1}$ at room temperature contrast with 40.1 ppm K$^{-1}$ of neat epoxy. In addition, among 360–460 K, the epoxy/SiC@SiO$_2$ NWs composite exhibits lower slope than neat epoxy. CTE values show a bigger difference from 40.0 ppm K$^{-1}$ of neat epoxy and 18.7 ppm K$^{-1}$ of neat epoxy/SiC@SiO$_2$ NWs. This consequence indicates that SiC@SiO$_2$ NWs in epoxy play a dominant role in effectively blocking the volume expansion. The SiC@SiO$_2$ NWs constrain the epoxy chain movements due to the interaction between SiO$_2$ with matrix. Moreover, the network formed by SiC@SiO$_2$ NWs can be served as framework to stabilise the molecular chains with the increasing temperature. It is believed that the decrease in coefficient thermal expansion is able to reduce the CTE mismatch with silicon and insulating ceramics on the basis of Hook's law and the Poisson ratio [67]. Materials with lower CTE value is expected to lower thermal strain, which will find extensive apply as TIM with improved thermal generated in electron devices [68–70].
composite. Furthermore, the epoxy composites possessed low coefficient of thermal expansion, high thermal stability and $T_g$. The epoxy composites with remarkable thermal properties are crucial in TIMs, electronic packaging, and other electrical devices applications.

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9 References


