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Three-dimensional microstructuring of carbon by thermoplastic spacer evaporation during pyrolysis

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ABSTRACT

The three-dimensional microstructuring of carbon is useful for microelectromechanical devices and electrode arrays. A microstructure in the form of a microscale bridge (consisting of a girder and two adherent substructures) on an alumina substrate with a surface roughness of 1–2 μm (which allowed bonding by mechanical interlocking) was attained by using a novel low-cost process that involved thermoplastic spacer (paraffin wax) evaporation during pyrolysis of an epoxy-based film that coated the spacer and parts of the substrate. Fillers were chosen to reduce the shrinkage during pyrolysis and to increase the electrical conductivity. Multiwalled carbon nanotube as a filler was particularly effective for reducing the cracking tendency. Carbon black and silver nanoparticles as sole fillers were ineffective, producing cracked bridges. The total filler content (nanotube, optionally along with silver nanoparticles) had to exceed 3 vol.% in order to attain good control of the shape of the bridge. The method used a novolac epoxy resin in combination with an amine curing agent (without ultra-violet curing). The epoxy was chosen for low viscosity and strong bonding to the substrate. A bridge with a girder of length 90–300 μm, separated from the substrate by a height of 5–15 μm, was attained.

1. Introduction

Carbon is attractive for its electrical conductivity, thermal conductivity, low thermal expansion and chemical stability. The electrical conductivity is particularly important due to the use of the carbon as electrodes. Carbon in the form of films is suitable for miniaturized components that are formed on substrates as needed for electrical, electromechanical and electrochemical systems. Carbon films can be stand-alone films or adherent films on substrates. The preparation of adherent films is challenging due to the shrinkage of the precursor upon pyrolysis [1] and the difference in thermal expansion coefficient between the carbon and the substrate. Furthermore, adherent films serve as the basis for attaining artificial microstructuring. Both two-dimensional and three-dimensional forms of microstructuring are valuable. The latter, though more challenging, is particularly needed for microelectromechanical devices. Carbon can be made by the pyrolysis of polymers, thereby allowing the microstructuring to be performed on the polymer prior to conversion of the polymer to carbon.

Prior work on both two-dimensional [2–4] and three-dimensional [5–7] microstructuring of carbon mainly involves the lithography of resins (e.g., the novolac resin SU8 epoxy) that are cured by ultra-violet (UV) radiation exposure. Novolac SU epoxies are formulated with bisphenol A and high

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functionality, which provides relatively high chemical resistance compared to regular epoxies. The curing process involves numerous steps, namely mask application, UV exposure, development and pyrolysis. In case of three-dimensional microstructuring, additional steps are usually required. An example of an additional step is baking at a low temperature (e.g., 95 °C) after removal of the mask and before development in order to form a hard skin at the top of all regions of unexposed resin [5]. Another example of an additional step is the use of an electron beam to cure the top of selected regions of unexposed resin [6]. An alternative method of three-dimensional microstructuring involves controlling the spray direction of the developer, but this method does not allow three-dimensional microstructuring at specific locations [5]. A different approach of three-dimensional microstructuring involves the chemical etching of the part of the silicon substrate that is under a carbon film (made from a UV curable polyimide) and not under a silicon dioxide film [8]. Yet another approach of three-dimensional microstructuring involves spinning a polymer-based suspension of carbon nanotubes on a substrate, exposing the ends of a nanotube in the coating by electron beam lithography and development, and then sputtering a metal (niobium) to encapsulate the ends of the nanotube. The last step results in a suspended nanotube [9,10]. Due to the large number of steps in each of the processes mentioned above for three-dimensional microstructuring, the processing cost is high. Furthermore, the use of UV for curing in most prior work is more expensive and less versatile than the use of a curing agent for curing. But this work uses a curing agent for curing [11,12].

This paper provides three-dimensional carbon microstructuring by using a novel low-cost process that involves thermoplastic spacer evaporation during pyrolysis. A blend of a carbon precursor polymer (a novolac-type phenol–formaldehyde polymer) and a decomposable polymer (maleinic-acid modified low density polyethylene) that disappears completely upon pyrolysis was used in prior work to make porous carbon materials [13–16] and carbon nanotube [16]. However, the combined use (without blending) of a carbon precursor polymer and a decomposable polymer for carbon microstructuring has not been previously reported, other than [12]. This work uses a decomposable polymer (namely, a thermally decomposable paraffin wax) as a spacer for attaining three-dimensional microstructuring.

Pyrolysis tends to be accompanied by shrinkage [1]. As a consequence, the three-dimensional structures are distorted [5]. In spite of the use of a filler (iron oxide nanoparticles in the amount of 0.15% by mass of the resin), the distortion problem remains [5]. In contrast, this work uses multiwalled carbon nanotube as the filler for diminishing the shrinkage during pyrolysis. Carbon nanotube is attractive due to its high aspect ratio. In prior work, carbon nanotube or nanofiber was used to modify carbon–carbon composites [17] and two-dimensional carbon microstructures [18]. Carbon black is in the form of nanoparticles and is low in cost. For the sake of comparison, this work includes the use of carbon black in place of carbon nanotube.

The electrical conductivity of carbon increases with increasing heat-treatment temperature. Pyrolysis to form carbon films and their three-dimensional microstructures is conducted at relatively low temperatures, e.g., 700–1000 °C [1–8], since a high temperature is not suitable for some substrates and increases the propensity for oxidation of the resulting carbon. Due to the relatively low pyrolysis temperature, the resulting carbon is turbostatic and hence limited in the electrical conductivity.

Prior work on carbon microstructuring on substrates used the SU8 epoxy [3–6] as the carbon precursor. This epoxy is a solid at room temperature and is high in viscosity upon heating. Due to the high viscosity, the inclusion of a substantial amount of solid component is difficult, unless a solvent or a high temperature is used. Also, epoxy resin may not be cured enough especially behind the solid due to the masking effect of solid component even though it is exposed to the UV light [19]. In contrast, this work uses the epoxy SU 2.5, which is a liquid at room temperature. The low viscosity of SU 2.5 allows the inclusion of a substantial amount of filler. There is no prior report of the use of SU 2.5 in making carbon film or three-dimensional carbon microstructure.

The objectives of this paper are to provide a low-cost method of three-dimensional microstructuring of carbon and to improve the resulting three-dimensional microstructure by the use of fillers.

2. Experimental methods

2.1. Materials

The curing agent used in this work was 3234 (triethylenetetramine, abbreviated as TETA), as provided by Hexion Specialty Chemicals (Houston, TX), with specific gravity 0.98 at 20 °C and the amine hydrogen equivalent weight (HEW) approximately 24.5. The catalyst used in this work was 2-ethyl-4-methylimidazole, as provided by BASF Corp. (Florham Park, NJ), with specific gravity 0.97 at 40 °C. This product consists of 87–92 wt.% 2-ethyl-4-methylimidazole, 4–9 wt.% 4-methylimidazole, and 1–4 wt.% 2,4-dimethyl-1H-imidazole.

The epoxy used in this work was EPON SU2.5, as provided by Hexion Specialty Chemicals, with melt viscosity 2–6 Pa s at 52 °C, density 1.2 g/cm^3, and weight per epoxide (WPE) 180–200. This combination of curing agent and epoxy was chosen after a comparative evaluation of various combinations of curing agent and epoxy resin, as it provided carbon films of high quality [11,12].

The choice of the epoxy resin in relation to the viscosity is important. This is because of the need to mix the epoxy resin, curing agent and MWCNT at room temperature. The viscosity of the SU2.5 resin used in this work is sufficiently low at room temperature, although the reported viscosity of 20–60 P is not at room temperature but at 52 °C. The SU8 resin (viscosity = 10–60 P at 130 °C) is not suitable, due to the impossibility of mixing it with a solid component.

Multiwalled carbon nanotube (MWCNT), silver particles, and carbon black (CB) are used as fillers. Multiwalled carbon nanotube is from ILJIN (Korea), as prepared by chemical vapor deposition. The purity is higher than 95%, the length is >60 μm, and the average diameter is 50 nm. The density was taken to be 2.0 g/cm^3 [20,21]. Silver nanoparticles (Cat.# 47MN-0001) is from Inframat Advanced Materials. The purity

is 99.95%, the average particle size is around 150 nm, the melting point is 961.8 °C, and the density is 10.49 g/cm^3. The carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It is a powder with particle size 30 nm, nitrogen specific surface area 254 m^2/g, maximum ash content 0.2%, volatile content 1.07%, and density 1.7–1.9 g/cm^3.[2] In this work, the density was taken to be 1.8 g/cm^3. The substrates used are (i) alumina (96% Al_2O_3) of size 25 × 25 mm and thickness either 0.61 or 0.51 mm, and (ii) a glass-ceramic (64% SiO_2, 21% Al_2O_3, 4% Li_2O, and 2% TiO_2) [22], namely Robax from Schott North America Inc., (Louisville, KY) of size 25 × 25 mm and thickness 3.2 mm. The roughness (the average distance in level between the top of a hill and the bottom of a valley) is 1–2 μm for the alumina substrate and is less than 0.1 μm for the glass-ceramic.

2.2. Preparation procedures

2.2.1. Formulation of epoxy resin

The SU 2.5 epoxy was mixed with each of either TETA or imidazole. The combination of SU2.5 and TETA was formulated by considering the stoichiometric ratio, as obtained from the average WPE (the range mentioned in Section 2.1) of the epoxy and the HEW (the value mentioned in Section 2.1) of the curing agent. The mixing ratio of imidazol and SU 2.5 was 1 to 10 by weight.

2.2.2. Inclusion of a filler

In order to maintain the shape of the carbon precursor in the microstructured carbon, the precursor needs to be sufficiently high in viscosity. The addition of a filler increases the viscosity, although the viscosity depends on the type and amount of the filler. Furthermore, the filler serves to reduce the shrinkage during pyrolysis and increase the electrical conductivity of the resulting microstructured carbon.

The components SU 2.5 and TETA were mixed manually for 3 min. Then a filler (silver, carbon black or carbon nanotube) was added and mixed manually for 5 min. The curing was conducted at 121 °C for 4 h.

2.2.3. Pyrolysis

Each specimen in the form of a resin coated substrate was covered on the coating side by a flexible graphite sheet (GrafTech, Cleveland, OH), which was fastened to the specimen by wrapping with a continuous roving of carbon fiber. This assembly was placed in a steel box (167 × 116 × 63 mm) that was covered with a steel cover and had a steel inlet for a purging gas (nitrogen). The steel box was placed in a box furnace (0.004 m^3 in inside volume, Isotemp Programmable Muffle Furnace, Fisher Scientific Co.). Pyrolysis was thus conducted in nitrogen at 650 °C for 1 h, with a heating rate of 5 °C/min.

2.2.4. Carbon films for material characterization

Carbon films without microstructuring were prepared in order to characterize the film. Since the carbon films on glass-ceramic tended to crack, alumina was used as the substrate, unless stated otherwise. Bonding of the carbon film to alumina was better than that to glass-ceramic, due to the greater surface roughness of alumina [23], and probably also due to the surface functional groups on alumina.

2.2.5. Carbon yield determination

The carbon yield is defined as the mass of the carbon after pyrolysis to the mass of the epoxy resin prior to pyrolysis, with the mass of the filler(s) either included or excluded. The procedure involved first weighing the bare alumina substrate, followed by weighing the substrate with the carbon precursor film applied. After pyrolysis, the substrate with the resulting carbon film was weighed. The parts of the substrate surface on which the precursor film was applied (two strips of 25 × 8 mm each) were restricted by prior application of adhesive tape (thickness 60 μm, acid free Invisible Tape with matte finish, from Henkel Consumer Adhesives, Inc., Avon, OH) on the regions where the film was not to be applied. However, weighing of the substrate with film was performed after tape removal. An electronic balance (Mettler MT5, Mettler-Toledo, Inc.) was used for weighing. Two specimens of each composition were tested.

2.2.6. Three-dimensional microstructuring of carbon

The three-dimensional microstructuring of carbon is demonstrated by the forming of carbon bridges in the microscale. The decomposable thermoplastic is paraffin wax, as supplied by Crystal, Inc., PMC, Lansdale, PA, as Product CS-2032, with molecular weight exceeding 283 amu, specific gravity 0.90, melting temperature 52–56 °C, and viscosity (6.7–7.9) × 10^{-3} Pa s (at 99 °C).

Paraffin wax contained in an aluminum pan was heated in a furnace at 130 °C for melting the wax. The substrate with three strips of adhesive tape applied to selected regions to form two rectangular mold cavities, each of width ranging from 90 to 300 μm and thickness 60 μm (equal to the thickness of the tape). The mold cavity was actually just a channel, due to the presence of walls (tape) on two sides only. The substrate with the tape applied was heated in the same furnace at 130 °C for preheating. The molten wax was poured on the mold cavities (substrate) and excessive wax was removed by using a razor blade. Upon subsequent cooling to room temperature, the wax solidified. Upon peeling off the tape from the substrate, the molded solid wax remained as two strips on the substrate, as shown in Fig. 1a. Three other strips of the adhesive tape were applied on both the wax and substrate in a direction perpendicular to the wax strips in order to form two mold cavities, each of which having width ranging from 90 to 230 μm and two wax spacers at its base, as shown in Fig. 1b. The length of these cavities was not restricted. After this, a paste consisting of SU 2.5 epoxy, TETA curing and one or more fillers was applied to these mold cavities (substrate) and the excessive paste was removed by using a razor blade. The epoxy in the specimen was then cured at room temperature for 1 day. Subsequent removal of the tape resulted in the configuration of Fig. 1c. Then the epoxy in the specimen was further cured in air at 121 °C for 4 h at a heating rate of 3 °C/min, and then pyrolyzed using the procedure

[2] Material safety data sheet from Cabot Corp., "http://www.cabot-corp.com/cws/product.nsf/MSDSKEY/VXC72R~EN~North%20America/$FILE/VXC72R-NA-EN.pdf?OpenElement", as on December 19, 2007.

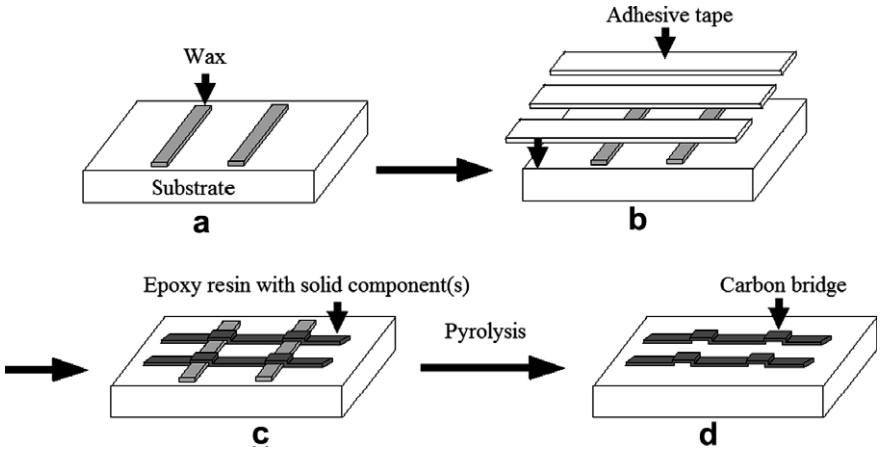

Fig. 1 – Schematic illustration of the process of carbon bridge formation. (a) Wax is poured between strips of adhesive tape. (b) The tape is removed, and other strips of tape are applied in a direction perpendicular to the wax strips in (a). (c) A paste consisting of the epoxy, curing agent and one or more fillers is cast between the strips of tape, and the tapes are removed. (d) The wax totally decomposes while the epoxy with one or more fillers remains. In the same heating step, the remaining epoxy is then pyrolyzed to form a carbon-matrix composite.

described in Section 2.2.3. During pyrolysis, the wax disappeared, due to its low thermal stability and low cross-linking upon degradation, resulting in the configuration illustrated in Fig. 1d.

3. Results and discussion

3.1. *Carbonization yield of carbonized film*

Table 1 shows the carbon yield of epoxy resin SU 2.5 in combination with TETA, with and without filler(s). The presence of the filler(s) increased the carbon yield when the mass of the filler(s) was included, as expected from the fact that the fillers did not participate in carbonization. When the mass of the filler(s) was excluded, the presence of the filler(s) had little effect on the carbon yield, except for the case of carbon black as the filler. The presence of carbon black reduced the carbon yield substantially, due to the cracks that were observed by SEM in this case only. The carbon yield in the range of 11–14% is similar to the prior report of around 17% for epoxy SU8 tested by thermogravimetric analysis during temperature scanning from 20 °C to 1100 °C [23].

Table 1 – Carbon yield of the epoxy resin on alumina, with and without filler(s)

Solid component(s)	Carbon yield (%)	
	Including filler(s)	Excluding filler(s)
None[a]	–	14 ± 1
MWCNT 3.6 vol.%	19 ± 0	13 ± 0
MWCNT 3.6 vol.% and silver 1.8 vol.%	30 ± 1	11 ± 1
Silver 10 vol.%	62 ± 1	12 ± 1
Carbon black 15 vol.%	30 ± 1	8 ± 1

The precursor was SU 2.5 in combination with TETA. The density is taken as 2.0 g/cm^3 for MWCNT and 1.8 g/cm^3 for the carbon black.
a Epoxy resin was diluted with 50 wt.% of toluene.

3.2. *Three-dimensional microstructuring demonstration*

Three-dimensional microstructuring of carbon was attained by the fabrication of a carbon bridge, which consisted of a girder, which was the beam of the bridge, and a substructure, which was in contact with the substrate (Fig. 2). The girder region shrank in the width direction relative to the substructure region upon pyrolysis. In the absence of a filler, the bridge collapsed, due to extensive shrinkage. In the presence of filler(s), the shrinkage was reduced, thus allowing the bridge to form without collapsing. Table 2 describes the bridge quality in terms of the extent of cracking in the girder and the well-controlled shape of the bridge for various fillers. Both the use of carbon black as a filler (15 vol.% relative to the precursor) and the use of silver nanoparticles as a filler (10 vol.% relative to the precursor) gave cracked bridges, although the bridge shape was good. The ability of MWCNT to resist cracking was superior to that of silver nanoparticles or carbon black (Table 2), because of the high aspect ratio of MWCNT. The amount of filler was intentionally limited, so that the viscosity of the carbon precursor was not too high for conformability to the substrate, though a high content of the filler would have been advantageous for reducing the shrinkage significantly. In the presence of MWCNT, no cracking occurred, although the total filler content had to exceed 3 vol.% in order to attain a good bridge shape. As shown in Table 2, a good bridge shape was attained by using MWCNT (3.6 vol.%), but it was not attained by using MWCNT (2.7 vol.%), unless silver nanoparticles (1.1 vol.%) was present as a second filler.

Fig. 3 shows a carbon bridge containing 2.7 vol.% MWCNT (relative to the precursor, i.e., SU 2.5 in combination with TETA) as the sole filler, with the glass-ceramic as the substrate. The girder was warped – an example of poor control of the bridge shape. Similarly poor control of the bridge shape was observed for the corresponding film on alumina (Table 2).

MWCNT was effective for decreasing the electrical resistivity, as recently reported by the present authors [11,12]. For

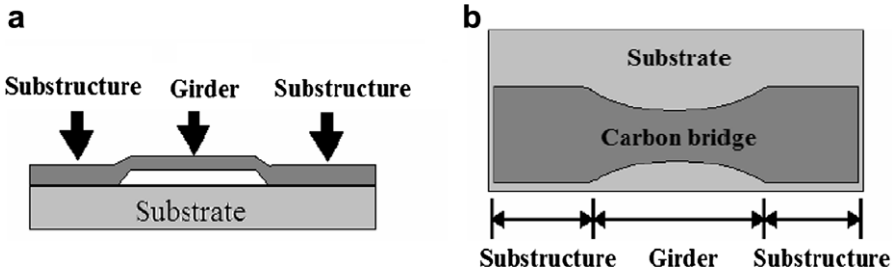

Fig. 2 – Geometry of a carbon bridge. (a) Side view. (b) Top view.

Table 2 – Effect of filler(s) on the carbon bridge quality, as described by the girder condition (extent of cracking) and the bridge shape control

Filler(s)	Girder condition	Bridge shape
No filler	Very poor[a]	Very poor[a]
Carbon black 15 vol.%	Poor	Good
Silver 10 vol.%	Poor	Good
MWCNT 2.7 vol.%	Good	Poor
MWCNT 2.7 vol.% + Silver 1.1 vol.%	Good	Good
MWCNT 3.6 vol.%	Good	Good
MWCNT 3.6 vol.% + Silver 1.1 vol.%	Good	Good

An example of a poorly shaped bridge is a warped bridge (Fig. 3). The precursor was SU 2.5 in combination with TETA.
a Girder collapsed.

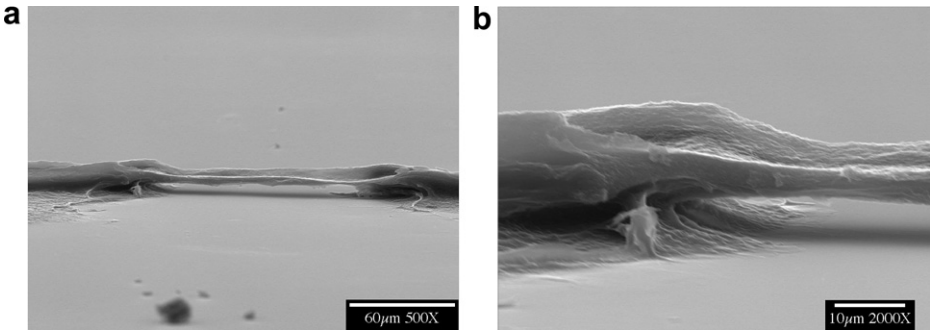

Fig. 3 – Carbon bridge made from a precursor consisting of SU 2.5, TETA, and MWCNT (2.7 vol.% relative to the precursor) on glass-ceramic. (a) Side view. (b) A magnified image of the substructure region in (a).

example, the resistivity of a carbon film containing MWCNT (3.6 vol.%) was $2 \times 10^{-2}\,\Omega\,\mathrm{cm}$. Although silver itself had high conductivity, the further addition of a small amount of silver nanoparticles (either 1.1 or 1.8 vol.%) did not give any further increase in the conductivity to the carbon-matrix composite [11,12].

Due to the bonding of the substructure to the substrate, the shrinkage during pyrolysis was greater for the girder than the substructure, thus resulting in the girder being narrower than the substructure, as shown in Fig. 4b for the case of the filler being 3.6 vol.% nanotube in the precursor, the resin being SU 2.5 in combination with TETA, and the substrate being alumina. When the filler was either carbon black or silver particles, the girder cracked, due to the inadequate reinforcing ability of these particles. In Fig. 4a, the girder was separated from the substrate, due to the decomposition of the wax, but the substructure of the bridge adhered to the substrate. The bottom of the girder was at a height of 5–15 μm from the substrate. Bridges on alumina were superior to those on glass-ceramic, as shown by a lower tendency for cracking at the substructure. This is probably due to better mechanical interlocking of the film to alumina, which had a rougher surface than the glass-ceramic.

One complication of the three-dimensional microstructuring method of this work relates to the viscosity of the spacer after melting. Since the viscosity of molten wax is low, the surface tension of molten wax may cause distortion of the resulting carbon bridge. The replacement of wax by other thermally decomposable polymers was investigated in this work, but polymers such as polyethylene glycol tended to result in a trace of carbon residue on the substrate after heating at 650 °C. The trace made the carbon bridge formation not perfect.

The combined use of the MWCNT (2.7 vol.% relative to the precursor) and silver nanoparticles (1.1 vol.% relative to the precursor) gave a bridge with better shape control than

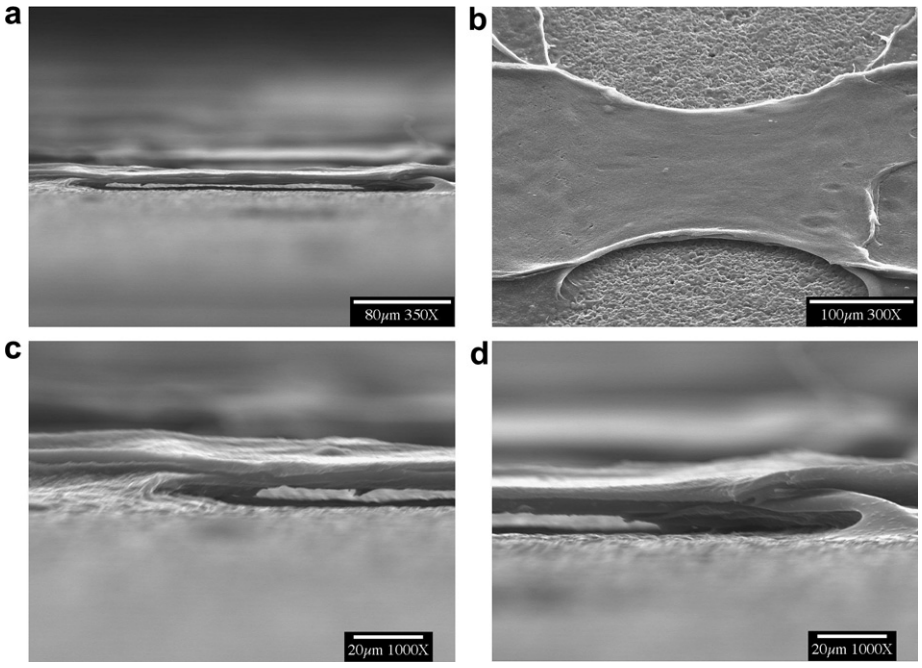

Fig. 4 – Carbon bridge made from a precursor consisting of SU 2.5, TETA, and MWCNT (3.6 vol.% relative to the precursor) on alumina. (a) Side view. (b) Top view. (c) and (d) Magnified images of the substructure region in (a).

the use of MWCNT (1.1 vol.%) as the sole filler. This is due to the higher total filler content for the former and the consequent reduction in shrinkage during pyrolysis.

The combined use of a higher content of MWCNT (3.6 vol.% relative to the precursor) and the same content of silver nanoparticles (1.1 vol.% relative to the precursor) did

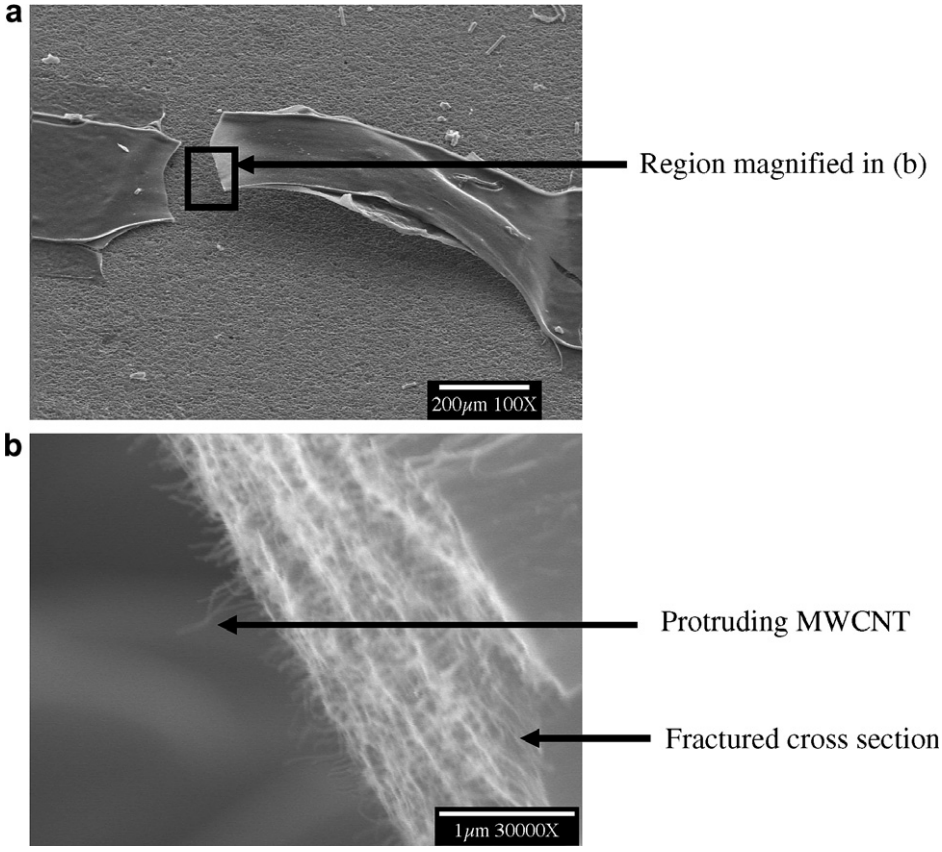

Fig. 5 – Carbon bridge made from a precursor consisting of SU 2.5, imidazol catalyst and MWCNT (2.3 vol.% relative to the precursor) on alumina. (a) Top view. (b) Cross-sectional fracture surface view.

not provide better shape control than the use of MWCNT at 3.6 vol.% as the sole filler. This is attributed to the high filler content in both cases. Apparently, when the filler content is sufficiently high, the use of silver as a second filler would not help.

Another curing agent (imidazol) was used in the presence of SU 2.5 to prepare a carbon bridge including MWCNT (2.3 vol.% relative to the precursor) on alumina. This bridge cracked all the way across its width, as shown in Fig. 5. Fig. 5a shows the top view of the cracked bridge, and Fig. 5b shows the fracture surface (cross section of the fractured girder) of the bridge of Fig. 5a. MWCNT protruded quite uniformly from the fracture surface, suggesting that MWCNT was quite well distributed. However, the extensive pull-out of MWCNT from the fracture surface suggests that the bonding of MWCNT with the carbon-matrix was weak. Surface modification of MWCNT may help to alleviate this problem.

The girder region shrank relative to the substructure, as shown in Fig. 4b, where the girder region is in the center part that occupies most of the photo. The shrinkage was most severe at the middle of the girder region and was least at the parts of the girder near the substructure regions. This transverse shrinkage was calculated using the equation

$$\text{Transverse shrinkage} = (W_s - W_g)/W_s$$

where W_s and W_g are the widths of the substructure and girder, respectively. The values for films of various compositions are shown in Table 3. These values are all around 45%.

The relatively large shrinkage of the epoxy upon pyrolysis may possibly be advantageous in providing partial alignment of the nanotube in the bridge, as illustrated in Fig. 6. Even with the low carbon yield of epoxy, MWCNT did not protrude out of the carbon bridge upon pyrolysis of the epoxy resin. This suggests that MWCNT may be partially aligned. For the substructure, which is in contact with the substrate, a degree of two-dimensional alignment of the nanotube in the plane of the substrate may possibly occur during pyrolysis, as the shrinkage primarily occurs in the direction perpendicular to the substrate. In case of the girder region, which is not in contact with the substrate and has its ends fixed by the substructure, the shrinkage occurs primarily in the direction perpendicular to the substrate as well as the direction along the width of the girder, thereby possibly resulting in a degree of one-dimensional alignment of the nanotube along the length of the girder. The lower the carbon yield is, the more the shrinkage is and the more the tendency to align is. Such alignment, though not demonstrated in this work, is attractive for the electrical and mechanical performance of the bridge.

Table 3 – Transverse shrinkage of the width of girder relative to that of the substructure of the carbon bridge

Filler (vol.%)[a]		Transverse shrinkage (%)
MWCNT	Silver	
2.9	0	48 ± 17
3.6	0	45 ± 4
3.6	1.1	43 ± 7

The precursor was SU 2.5 in combination with TETA.
a Filler content before pyrolysis.

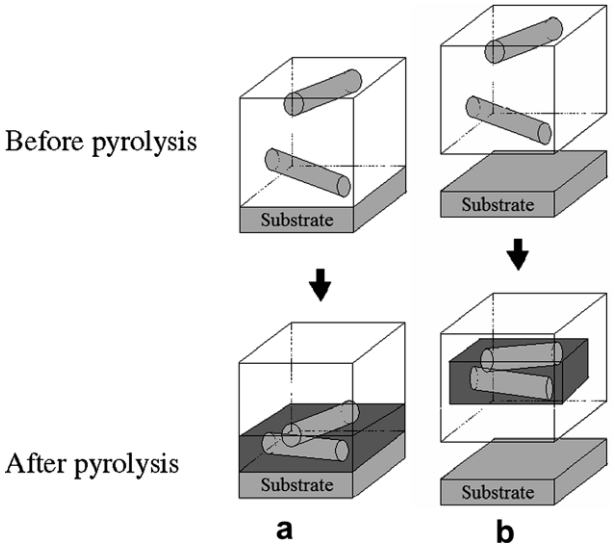

Fig. 6 – Schematic illustration of the possible partial alignment of two carbon nanotubes, due to the shrinkage of the epoxy resin upon pyrolysis. (a) The substructure, which touches the substrate, showing the two nanotubes having become closer together due to the shrinkage of the resin in the *z*-axis during pyrolysis. (b) The girder, which does not touch the substrate, showing the two nanotubes having a degree of one-dimensional alignment, due to the shrinkage of the resin in the *z*-axis and the *x*-axis during pyrolysis.

Although the three-dimensional microstructuring method demonstration in this paper is for a carbon bridge in the microscale, it is possible to reduce the size. The thickness of the carbon substructure or girder may possibly be smaller than about 500 nm. This thickness may be further reduced by using double-walled or single-walled CNT instead of MWCNT, which has a diameter of 50 nm. However, as the bridge becomes smaller, the effect of air voids becomes significant, and the air voids may cause cracks. Moreover, a small thickness of the carbon substructure helps reduce the shrinkage that accompanies epoxy pyrolysis.

Although the pyrolysis temperature used in this work is 650 °C, higher temperatures are expected to be feasible. A relatively low temperature is preferred for widening the applicability and decreasing the processing cost. The use of a furnace for pyrolysis in this work means that the technique is suitable for scale-up, so as to produce a large number of carbon microstructures at a time.

5. Conclusion

Three-dimensional microstructuring of carbon on alumina with a surface roughness of 1–2 μm (which allowed bonding by mechanical interlocking) was attained by using a novel low-cost method that involved the use of a spacer in the form of a decomposable thermoplastic, namely paraffin wax. The spacer disappeared during pyrolysis of the carbon precursor, thus resulting in a bridge that consisted of a girder and two

adherent substructures. The method used the SU 2.5 epoxy (lower in viscosity than the previously used SU8 epoxy) in combination with the TETA curing agent (in contrast to prior work that used UV curing instead of a curing agent). Microstructuring resulted in a bridge with girder length 90–300 μm, under-bridge spacing 5–15 μm, and 45% transverse shrinkage of the girder relative to the substructure. The use of MWCNT as a filler in the carbon precursor was particularly effective, due to the ability of MWCNT to resist cracking. Silver nanoparticles and carbon black as sole fillers gave cracked bridges. The total filler content (MWCNT, optionally along with silver nanoparticles) had to exceed 3 vol.% in order to attain good control of the shape of the bridge.

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