ELECTRICALLY CONDUCTIVE CARBON FILMS AND THEIR THREE-DIMENSIONAL MICROSTRUCTURING

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Abstract

Electrically conductive carbon-based films and their three-dimensional microstructuring are useful for microelectromechanical devices and electrode arrays. Three-dimensional microstructuring to form bridges was attained by using a novel low-cost process that involved thermoplastic spacer (wax) evaporation during pyrolysis of the epoxy film (filled with multiwalled carbon nanotube, optionally together with silver nanoparticles) that coated the spacer and parts of the substrate. The nanotube was necessary for reducing the cracking tendency. The method used epoxy in combination with a curing agent (no UV curing). Microstructuring resulted in a bridge with the girder of length 90-300 μm, separated from the substrate by a height of 5-15 μm. The combined use of the nanotube (2.7 vol.% of precursor) and silver nanoparticles (1.1 vol.% of precursor) gave a bridge with better shape definition than the use of the nanotube (2.9 vol.% of precursor) in the absence of particles, due to the higher total solid content in the former and the consequent greater reduction of the shrinkage during pyrolysis. Carbon black was an ineffective solid component, as it resulted in cracked bridges and films of low scratch resistance. Silver also served to enhance the electrical conductivity. On the other hand, any of the solid components diminished the scratch resistance of the carbon film.

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. Furthermore, films are attractive for the possibility of microstructuring them. In particular, 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. Both two-dimensional and three-dimensional forms of microstructuring are valuable. The latter, though more challenging, is particularly needed for microelectromechanical devices.

Prior work on both two-dimensional (Schueller et al., 1999; Seidemann et al., 2002; Malek, 2002) and three-dimensional (Wang et al., 2005; Malladi et al., 2006) microstructuring of carbon has mainly involved lithography of resins (e.g., the epoxy novolac resin SU8) that are cured by ultra-violet light exposure. The 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 (Wang et al., 2005). Another example of an additional step is the use of an electron beam to cure the top of selected regions of unexposed resin (Malladi et al., 2006). 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 (Wang et al., 2005). 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 (Naka and Konishi, 2005). 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 (Lee et al., 2002a, 2002b). 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 (this work).

This work 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 has been used in prior work to make porous carbon materials (Patel et al., 2002; Ozaki et al., 1997; Hulicova and Oya, 2003) and carbon nanotube (Sandou and Oya, 2005). However, the combined use (without blending) of a carbon precursor polymer and a decomposable polymer for carbon microstructuring has not been previously reported. 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 (Park et al., 2005). As a consequence, the three-dimensional structures are distorted (Wang et al., 2005). In spite of the use of a solid component (iron oxide nanopowder in the amount of 0.15% by mass of the resin), the distortion problem remains (Wang et al., 2005). In contrast, this work uses multiwalled carbon nanotube as the solid component for diminishing the shrinkage during pyrolysis. Carbon nanotube is attractive due to its high aspect ratio. In prior work, carbon nanotube or nanofiber has been used to modify carbon-carbon composites (Lim et al., 2002) and two-dimensional carbon microstructures (Wang et al., 2006). 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 is conducted at relatively low temperatures, e.g., 700-1,000°C (Park et al., 2005; Naka and Konishi, 2005), as the detrimental effect of slight oxidation of the carbon to form gases is larger for films than bulk carbons. Furthermore, a high temperature may not be suitable for the substrate. Due to the relatively low pyrolysis temperature, the resulting carbon film is turbostratic and hence limited in the electrical conductivity. The electrical resistivity is 10^{-2} Ω.cm for a pyrolysis temperature of 1,000°C and is 1 Ω.cm (or above) for a pyrolysis temperature of 700°C (Park et al., 2005). The electrical resistivity is 10^{-2} Ω.cm for a pyrolysis temperature of 900°C and is 10 Ω.cm for a pyrolysis temperature of 700°C (Naka and Konishi, 2005).

In order to increase the conductivity of carbon films produced at a low pyrolysis temperature, this work includes the use of silver particles as a solid component. The silver particles may be used in combination with carbon nanotube. There is no prior work on the combined use of silver and carbon nantube in a carbon matrix. Prior work on silver particle filled carbon (in either bulk form or 100-μm thick

film form) has attained an electrical resistivity of 10^{-5} Ω.cm at a silver particle content of 40 vol.% (Hsu and Chung, in press; McNab and Johnson, 1979). There is no prior work on silver particle filler carbon films that are thinner than 100 μm. Furthermore, the silver particles in prior work are large in size (e.g., 3 μm (Hsu and Chung, in press)). The large size is not suitable for films of thickness in the micrometer range. In contrast, this work uses silver nanoparticles.

Prior work on carbon films mainly used the epoxy SU8 (Seidemann et al., 2002; Malek, 2002; Wang et al., 2005; Malladi et al., 2006) as the carbon precursor. This epoxy resin 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. 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 solid component. There is no prior report of the use of SU 2.5 in making carbon films.

The adhesion of the carbon film to the substrate is of practical importance. This adhesion depends on the carbon precursor and the substrate (Singh et al., 2002). However, no quantitative evaluation of the adhesion has been reported. This work includes a quantitative evaluation of the adhesion of the carbon film, as indicated by scratch testing.

The objectives of this paper are (i) to develop a low-cost method of three-dimensional microstructuring of carbon, (ii) to improve carbon films by the use of fillers (carbon nanotube for decreasing the shrinkage during pyrolysis, and silver particles for increasing the electrical conductivity), and (iii) to investigate the scratch resistance of carbon films with and without fillers.

Experimental methods

Materials
The curing agents used in this work are EPIKURE 3115 (polyamide), 3010 (amidoamine) and 3234 (triethylenetetramine or TETA), as provided by Hexion Specialty Chemicals (Houston, TX). The viscosity of polyamide is 50-75 Pa.s at 40°C, the density is 0.97 g/cm^3 at 25°C, and the amine hydrogen equivalent weight (HEW) is approximately 156. The viscosity of amidoamine is $(2-5) \times 10^{-1}$ Pa.s at 25°C, the density is 0.96 g/cm^3 at 25°C, and HEW is approximately 95. The viscosity of TETA is 25×10^{-3} Pa.s at 20°C, the specific gravity is 0.98 at 20°C, and HEW is approximately 24.5.

The epoxies used in this work are EPON SU2.5, EPON 862 and EPON HPT 1050, as provided by Hexion Specialty Chemicals. The viscosity of EPON 862 is 2.5-4.5 Pa.s at 25°C, the density is 1.2 g/cm^3, and the weight per epoxide (WPE) is 165-173. The melt viscosity of EPON HPT1050 is 31-40 Pa.s at 52°C, the density is 1.22 g/cm^3, and WPE is 176-181. The melt viscosity of SU 2.5 is 2-6 Pa.s at 52°C, the density is 1.2 g/cm^3, and WPE is 180-200.

Carbon black (CB), silver particles, and multiwalled carbon nanotube (MWCNT) are used as solid components. The carbon black is Vulcan XC72R GP-3820 from Cabot Corp., Billerica, MA. It is a powder with particle size 30 nm, a 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. Silver nanopowder (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. Multiwalled carbon nanotube is from ILJIN (Korea), as prepared by chemical vapor deposition. The purity is higher than 95%, the length is >60 micrometer, the average diameter is 50 nm. The substrates used are (i) Robax, which is a glass-ceramic (64% SiO_2, 21% Al_2O_3, 4% Li_2O, and 2% Ti_2O) (Guedes et al., 2001) from Schott North America., Inc. (Louisville, KY), of size 25 x 25 mm and thickness 3.2 mm, and (ii) alumina (96% Al_2O_3) of size 25 x 25 mm and thickness either 0.61 or 0.51 mm. All substrates were ultrasonically cleaned in acetone and then ethanol.

Preparation procedures
Formulation of epoxy resin

Various combinations of epoxy resin and curing agent were used for the sake of comparison. The epoxy SU 2.5 was mixed with each of three curing agents (polyamide, amidoamine and TETA) for comparing the effects of the various curing agents. In addition, the curing agent TETA was mixed with each of three epoxy resins (EPON SU2.5, EPON 862 and EPON 1050) for comparing the effects of the various epoxies. Thus, a total of five formulations were studied.

Each combination of epoxy and curing agent was formulated by considering the stoichiometric ratio, as obtained from the average WPE (the range mentioned in the last section) of the epoxy and the HEW (value mentioned in the last section) of the curing agent. For the formulation development and film material characterization, each combination of epoxy and curing agent was mixed manually for 5 min and then applied manually on a 25 x 8 mm region (defined by masking the remaining part of the substrate by adhesive tape (thickness 62 μm; acid free Invisible Tape with matte finish, from Henkel Consumer Adhesives, Inc., Avon, OH), which was removed after the curing of the resin at room temperature for 1 day) of an alumina substrate. After the application, the top surface of the film was leveled by using a razor blade.

Curing of epoxy resin

The epoxy-TETA mixture was cured in air at 121^oC for 2 h, with a heating rate of $3^oC/min$. The epoxy-polyamide mixture was heated in air at 150^oC for 2 h, with a heating rate of $3^oC/min$. The epoxy-amidoamine mixture was heated in air at 145^oC for 2 h, with a heating rate of $3^oC/min$. These curing conditions were determined beforehand by use of differential scanning calorimetry (DSC, Series 7, Perkin-Elmer Corp., Norwalk, CT) to monitor the curing reaction at a heating rate of $10^oC/min$. The curing reaction depends more on the type of curing agent rather than the type of epoxy. The temperature at which the curing reaction ceases, as shown by the completion of evolution of the heat of reaction, is taken to be the suitable curing temperature for the particular combination of epoxy and curing agent.

Pyrolysis

Each specimen in the form of a resin coated substrate was covered on the coating side by a graphite sheet, which was fastened to the specimen by wrapping with a continuous roving of carbon fiber. This assembly was placed in a steel box (167 x 116 x 63 mm) that was covered and had an 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^oC for 1 h, with a heating rate of $5^oC/min$.

Inclusion of a solid component

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

SU 2.5 and TETA were mixed manually for 3 min. Then a solid component (silver, carbon black or carbon nanotube) was added and mixed manually for 5 min. The rest of the process is as described above, except that the curing was conducted at 121^oC for 4 h.

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 for all of carbon films prepared for material characterization. Adhesion of the carbon film to alumina was better than that to glass-ceramic, due to the greater surface roughness of alumina, and probably due to the surface functional groups on alumina.

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 solid component(s) either included or excluded. In this work, the carbon yield was determined by measuring the weight of the substrate containing the film, but without the adhesive tape, before and after pyrolysis, using an electronic balance (Mettler MT, Mettler-Toledo, Inc.). Two specimens of each composition were tested.

Microscopy of carbon films

The fracture surface (cross-sectional) and the top surface of the film (on a substrate) after pyrolysis were observed by scanning electron microscope (SEM).

Scratch testing of carbon films

Scratch testing of a film (on a substrate) after pyrolysis was conducted using a Model 139-B shear/scratch tester, which was manufactured by Teledyne Taber (North Tonawanda, NY). The diamond tool used to scratch a specimen has a 90° cone shaped and a round tip of radius 127 μm. The specimen was mounted on a horizontal plate that could be rotated. The tool was attached to a finely balanced scale beam calibrated in grams. The load was 50 g. The scratch width was observed by using an optical microscope (EPIPHOT, Nikon, Japan) equipped with image analysis software (Buehler Omnimet/ Image Capture and Report Generation System, Buehler Ltd. Lake Bluff, IL). The smaller is the scratch width, the higher is the shear strength, which relates to both the bond strength of the thick film to the substrate and the shear strength within the thick film. Two specimens with two scratches per specimen were measured for each composition.

Electrical resistivity measurement of carbon films

The DC volume electrical resistivity of the carbon films was measured by using the four-probe method. Four electrical contacts were used. The outer two contacts were for passing current, whereas the inner two contacts were for voltage measurement. Two specimens of each composition were tested. A multimeter (Keithley Instruments, Inc., Cleveland, OH, Model 2002) was used for resistance measurement.

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 (Product CS-2032, with molecular weight exceeding 283 amu and specific gravity 0.90 and melting temperature 52-56°C, and viscosity $(6.7-7.9) \times 10^{-3}$ Pa.s at 99°C.

Paraffin wax contained in an aluminum pan was heated in a furnace at 130°C for melting. The 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 62 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. 1(a). 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. 1(b). The length of these cavities was not defined. After this, a paste consisting of SU 2.5 epoxy, TETA curing and one or more solid components 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. 1(c). 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 described in the section on Pyrolysis. During pyrolysis, the wax disappeared due to its low thermal stability and low cross-linking upon degradation, resulting in the configuration illustrated in Fig. 1(d).
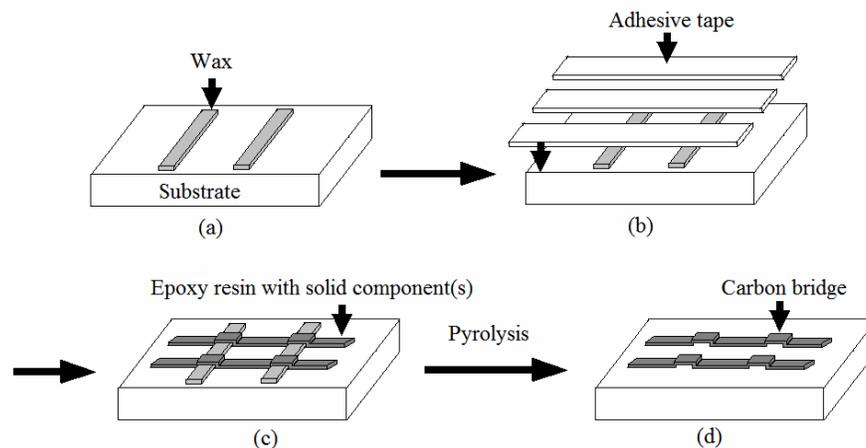
Figure 1. Schematic illustration of the process of carbon bridge formation. (a) Wax is poured between strips of adhesive tape. (b) The tape is removed, and other strips of tape are applied in a direction perpendicular to the wax strips in (a). (c) A paste consisting of the epoxy, curing agent and one or more solid components is cast between the strips of tape. (d) The wax totally decomposes while the epoxy with one or more solid components remains. In the same heating step, the remaining epoxy is then pyrolyzed to form a carbon-matrix composite.

Results and discussion

Formulation of epoxy resin

The epoxy SU 2.5 was mixed with each of three curing agents (polyamide, amidoamine, and TETA). Only the combination of TETA and SU 2.5 formed carbon with the shape of the carbon precursor maintained. Other combinations resulted in resins that migrated on the substrate upon pyrolysis. This difference in behavior among the various combinations is due to differences in the degree of cure (Potter, 1970) and cross-linking density. In particular, the cross-linking density is high for TETA, due to the high content of amine groups. Additional curing at 200 or 250°C for 2 h did not alleviate the migration problem.

Among the three epoxies, only SU 2.5 (in the presence of TETA) formed a carbon film, though the film contained a few cracks when no solid component was included. The cracks were eliminated by adding either a solvent (either ethylacetate or toluene, for dissolving the resin) or a solid component (carbon nanotube, carbon black or silver nanoparticles). The solvent served to enable the resulting carbon film to be smaller in thickness, thereby reducing the shrinkage during pyrolysis and alleviating the cracking problem.

Carbon film characerization

Table 1 shows the carbon yield of epoxy resin with and without solid component(s). The presence of the solid component(s) increases the carbon yield when the mass of the solid component(s) is included, as expected. When the mass of the solid component(s) is excluded, the presence of the solid component(s) had little effect on the carbon yield, except for the case of carbon black as the solid component. 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% to 14% is similar to the prior report of around 17% for epoxy SU8 tested by thermogravimetric analysis during temperature scanning from 20 to 1,100°C at a heating rate of °C/min (Singh et al., 2002).

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Table 2 shows the thickness and the electrical resistivity of carbon films with and without solid component(s). Addition of any of the solid components reduced the resistivity. Addition of 5 vol.% of silver had little effect compared to the addition of 10 vol. % of silver. This is because of percolation threshold is between 5 and 10 vol.% of the silver, as shown by the abrupt drop in resistivity between these two silver volume fractions. For films containing silver particles of size 3 μm, the percolation threshold is 12% (Hsu and Chung, in press).   It is expected that the percolation threshold is lower when the particles are smaller.

Table 1 Carbon yield of the epoxy resin on alumina, with and without solid component(s). The density is taken as 2.0 g/cm^3 for the nanotube and 1.8 g/cm^3 for the carbon black.

Solid component(s)	Carbon yield (%)	
	Included solid component(s)	Excluding solid component(s)
None*	-	14 ± 1
3.6 vol.% (or 6.0 wt.%) nanotube	19 ± 0	13 ± 0
3.6 vol.% (or 5.3 wt.%) nanotube and 1.8 vol.% (or 14 wt.%) silver	30 ± 1	11 ± 1
10 vol.% (or 50 wt.%) silver	62 ± 1	12 ± 1
15 vol.% (or 22 wt.%) carbon black	30 ± 1	8 ± 1

*Epoxy resin was diluted with 50 wt.% of toluene.

Table 2 Electrical resistivity of carbon films on alumina, with and without solid component(s).

Solid component(s)	Thickness (μm)	Electrical resistivity (Ω.cm)
None*	0.6 - 0.9	3.5 ± 2.1
3.6 vol.% (or 6.0 wt.%) nanotube	1.5 - 7.1	$(2.3 \pm 1.3) \times 10^{-2}$
3.6 vol.% (or 5.3 wt.%) nanotube and 1.8 vol.% (or 14 wt.%) silver	2.3 - 6.5	$(2.1 \pm 1.3) \times 10^{-2}$
5.0 vol.% (or 33 wt.%) silver	3.5 - 6.2	$(2.0 \pm 1.1) \times 10^{-1}$
10 vol.% (or 50 wt.%) silver	3.1 - 8.1	$(3.8 \pm 2.2) \times 10^{-4}$

*Epoxy resin was diluted with 75 wt.% of ethylacetate.

Table 3 shows the scratch width of carbon films with and without solid component(s). Addition of solid component(s) increased the amount of pores in the film. In case of carbon black, it also increased the amount of cracks. Furthermore, the solid component(s) increased the viscosity of the carbon precursor, thereby reducing the conformability of the precursor to the surface topography of the substrate and increasing the air void content at the interface between the film and the substrate. The more was the amount of solid component(s), the worse was the scratch resistance.

Table 3 The scratch width (µm) of thick films with and without solid component.

Solid component(s)	Scratch width (μ m)
None[*]	§
3.6 vol.% (or 6.0 wt.%) nanotube	11 ± 2
3.6 vol.% (or 5.3 wt.%) nanotube and 1.8 vol.% (or 14 wt.%) silver	17 ± 1
10 vol.% (or 50 wt.%) silver	31 ± 3
15 vol.% (or 22 wt.%) carbon black [†]	36 ± 6

[*]Epoxy resin was diluted with 50wt.% of toluene
§No trace was found by optical microscopy.
†The substrate was also scratched.

Three-dimensional microstructuring demonstration

Three-dimensional microstructuring of carbon has been attained by the fabrication of a carbon bridge, which consists of a girder, which is the beam of the bridge, and a substructure, which is in contact with the substrate. Without a solid component, the demonstration failed. The nanotube is particularly valuable as a solid component for reducing the shrinkage during pyrolysis and for reinforcing the carbon bridge. The reinforcing ability is superior to that of particles, such as silver or carbon black. This is because of the high aspect ratio of the nanotube. The amount of solid component should be limited so that the viscosity of the carbon precursor is not too high for conformability to the substrate, though a high content of the solid component is advantageous for reducing the shrinkage significantly. Due to the adhesion 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. 2 for the case of the solid component being 4.9 wt.% nanotube, the resin being SU 2.5 in combination with TETA, and the substrate being glass-ceramic. When the solid component is either carbon black or silver particles, the girder cracked, due to the inadequate reinforcing ability of these particles.
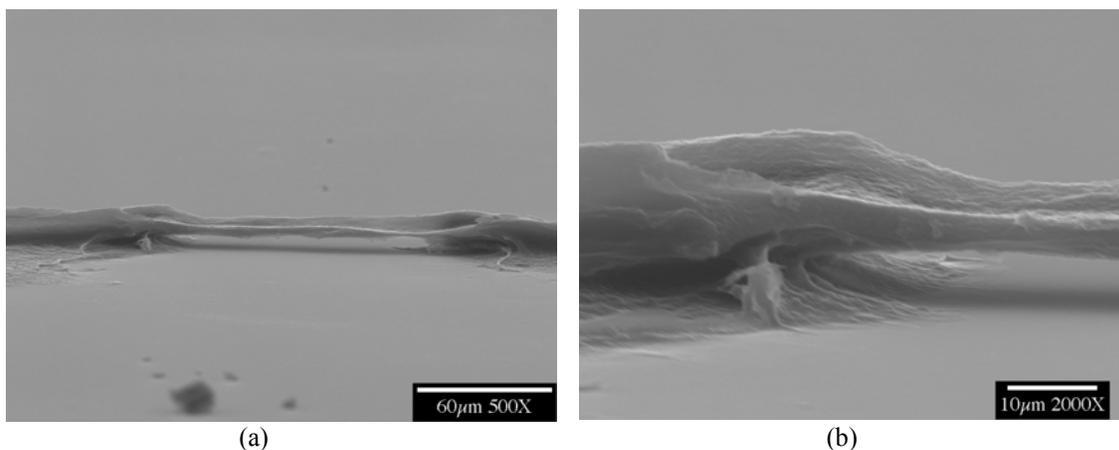

| (a) | (b) |

Figure 2. Carbon bridge made from a precursor consisting of SU 2.5, TETA and nanotube (2.9 vol.% of precursor or 4.9 wt.% of precursor) on glass-ceramic

Due to the tendency for the nanotube to increase the viscosity of the precursor significantly, a high nanotube content is not possible. Thus, a high solid component content, which is attractive for decreasing the shrinkage, is attained by the combined use of nanotube and silver particles, as shown in Fig. 3. The bridge obtained by this combined use (Fig. 3) is better defined in shape than that involving nanotube as the sole solid component (Fig. 2). In both Fig. 2 and 3, the bottom of the girder is at a height of 5-15 µm from the substrate.

Bridges on alumina are superior to those on glass-ceramic, due to better adhesion on alumina. The superiority is indicated by a lower propensity for cracking at the substructure.
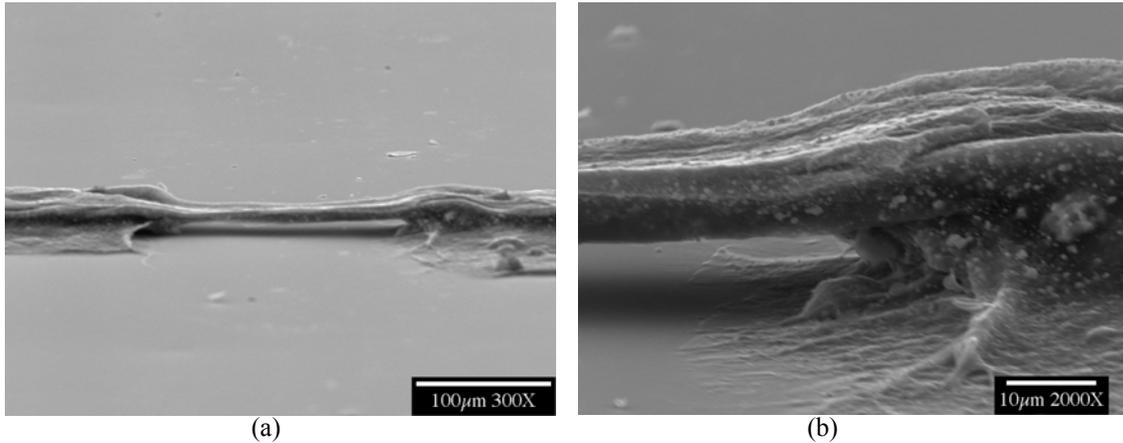

<div align="center">(a)   (b)</div>

Figure 3. Carbon bridge made from a precursor consisting of SU 2.5, TETA, nanotube (2.7 vol.% of precursor or 4.2 wt.% of precursor) and silver (1.1 vol.% of precursor or 8.8 wt.% of precursor) on glass-ceramic

The relatively large shrinkage of the epoxy upon pyrolysis may be advantageous in providing partial alignment of the nanotube in the bridge, as illustrated in Fig. 4. 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 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 is the carbon yield, the more should be the tendency to align. Such alignment, though not demonstrated in this work, is attractive for the electrical and mechanical performance of the bridge.
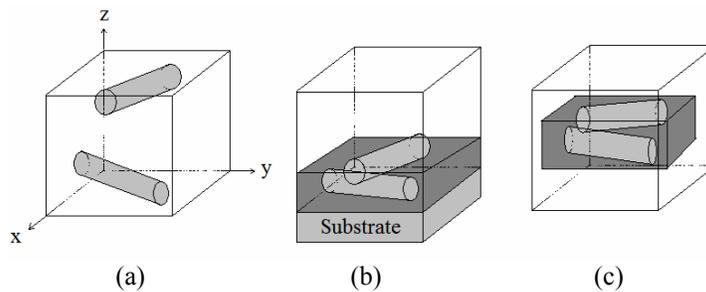

<div align="center">(a)   (b)   (c)</div>

Figure 4. Schematic illustration of the partial alignment of 2 carbon nanotubes, due to the shrinkage of the epoxy resin upon pyrolysis. (a) Before pyrolysis. (b) After pyrolysis for the substructure, which touches the substrate, showing the two nanotubes having become closer together due to shrinkage of the resin in the z-axis. (c) After pyrolysis for the girder part, 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- and x-axis.

<div align="center">9</div>

Conclusion

Three-dimensional microstructuring of carbon has been attained by using a novel low-cost method that involves the use of a spacer that is a decomposable thermoplastic, namely wax. The spacer disappears during pyrolysis of the carbon precursor. The method uses epoxy in combination with a curing agent, in contrast to prior work that used UV curing. Microstructuring has resulted in a bridge with the girder of length 90-300 μm, separated from the substrate by a height of 5-15 μm. The use of multiwalled carbon nanotube as a solid component in the carbon precursor was necessary, due to the reinforcing ability of the nanotube. However, the combined use of the nanotube (2.7 vol.% of precursor) and silver nanoparticles (1.1 vol.% of precursor) gave a bridge with better shape definition, due to the higher total solid content, which helped reduce the shrinkage during pyrolysis. Carbon black was an ineffective solid component, as it resulted in cracked bridges and carbon films of low scratch resistance. Silver also served to enhance the electrical conductivity. The percolation threshold was 5-10 vol.% for the silver nanoparticles. On the other hand, any of the solid components diminished the scratch resistance of the carbon film. The carbon yield was essentially unaffected by the presence of any of the solid components, unless the film was cracked.

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