Epoxy-based carbon films with high electrical conductivity attached to an alumina substrate

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ABSTRACT

Carbon-based films (0.8–13 μm thick) with good bonding to the substrate and high processability were produced at 650 °C on an alumina substrate, using SU 2.5 bisphenol-A type novolac epoxy (plus triethyleneteramine curing agent) as the carbon precursor. This precursor gave crack-free and scratch resistant carbon films. Interconnected filamentary nickel nanoparticles were more effective for conductivity enhancement than silver nanoparticles or multiwalled carbon nanotubes at 5 vol.% or below, in spite of the high conductivity of silver and the high aspect ratio of nanotubes. The carbon film with 2.5 vol.% nickel showed resistivity 6×10^{-3} Ω cm.

Electrically conductive films are useful for microheaters (Joule heating) [1,2], electrodes (such as those for microelectromechanical devices) [1,3], electrical interconnections, electromagnetic interference (EMI) shielding and related applications. They are commonly in the form of films attached to substrates that are electrically insulating, with film thickness in the micrometer range. These films are referred to as "thick films". By patterning a film on a substrate, various geometric configurations of electrically conductive lines can be obtained. The patterning can be extended from two to three dimensions, thus providing three-dimensional microstructures [1–3].

Prior work on carbon thick films on substrates (except those prepared by sputtering) [4] used either the SU8 epoxy [5] or pitch [6] as the carbon precursor. In contrast to carbon coatings prepared by sputtering, carbon films prepared by the carbonization of a polymer precursor tend to be inadequate in the hardness and adhesion, because the precursor shrinks and generates gas upon carbonization. Prior work utilizing the SU8 epoxy involved UV curing [5], which suffers from partial curing of SU8 due to the masking of UV by a filler present in the resin [7]. Previously reported silver particle carbon–matrix composite films suffer from poor bonding, high porosity, high silver volume fraction, and large film thickness (>28 μm) [6]. The bonding of a carbon film to its substrate depends on the carbon precursor, the substrate [8] and the thickness of the carbon film [5,9]. No quantitative mechanical evaluation of carbonized SU8 or carbonized pitch on substrates has been reported, but this work includes a quantitative evaluation of the mechanical properties, as indicated by scratch testing, because of the correlation between wear and adhesion [4]. This paper addresses the development of epoxy-based carbon thick films that exhibit no crack, good bonding to an alumina substrate, and high electrical conductivity, using a low carbonization temperature.

The epoxy used in this work (Fig. 1) is bisphenol-A type novolac epoxy (EPON SU2.5) with weight per epoxide 180–200 and average functionality 3.4. The curing agent is EPIKURE 3234 (triethylenetetramine or TETA) with amine hydrogen equivalent weight 24.5. Both epoxy and curing agent were provided by Hexion Specialty Chemicals (Houston, TX). Nickel, silver, and multiwalled carbon nanotube (MWCNT) were used as conductive fillers. Nickel nanoparticle (Inco 210 H, Inco Ltd.,Wyckoff, NJ) was in the interconnected filamentary form, with particle size 200–500 nm and purity 98.7%. Silver nanoparticles (Product no. 47MN-0001, Inframat Advanced Materials, Farmington, CT, had purity 99.95% and average particle size around 150 nm. MWCNT (ILJIN Nanotech Co., Ltd., Seoul, South Korea), as prepared by chemical vapor deposition, had purity above 95%, length exceeding 60 μm, and average diameter 50 nm. The substrate used was 96% alumina with roughness (the vertical distance between the hill top and the valley bottom) 1–2 μm, except that it was 0.1 μm when the film thickness was less than 3 μm. All substrates were ultrasonically cleaned in acetone and then ethanol prior to use.

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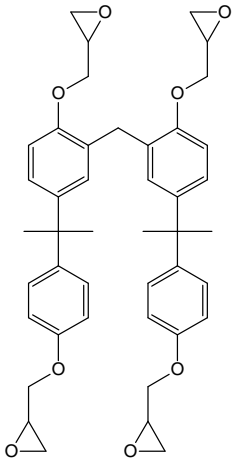

Fig. 1 – Chemical structure of bisphenol-A type novolac epoxy (SU 2.5).

The epoxy resin was formulated by considering the stoichiometric ratio. In case that no filler was used, the mixture of epoxy and solvent (either ethyl acetate or toluene, used to help form a thinner film) was subjected to sonication and TETA was added. In case that either a filler or a combination of fillers was used, the solvent was not added. The mixture was applied to a 25×8 mm region of an alumina substrate, and the film surface was made flat by using a razor blade. The film was cured at room temperature for 1 day and then at 121 °C for 4 h, followed by pyrolysis in nitrogen at 650 °C for 1 h, with a heating rate of 5 °C/min. Scratch testing after pyrolysis was conducted using a Model 139-B shear/scratch tester (Teledyne Taber, North Tonawanda, NY) at a speed of 0.1 m/min and a load of 50 g (0.49 N). The diamond tool had a 90° cone shape, with a round tip of radius 127 μm. The wear rate R (m^3/N m) was obtained by calculating the cross sectional area of the wear track from the scratch width and the dimension of the tip [4], using the equation $R = A/F$, where A is a cross-sectional area (in m^2, as obtained from the measured scratch width and the scratch tip dimensions) of the wear track, and F is the force applied. The DC volume electrical resistivity of the carbon films was measured using the four-probe method and a multimeter (Model 2002, Keithley Instruments, Inc., Cleveland, OH). The outer two contacts were 20 mm apart, whereas the inner two contacts were 10 mm apart.

The SU 2.5/TETA resin formed carbon film with the shape of the carbon precursor maintained and without substantial cracks. The minor cracks present in the carbonized film were eliminated by adding either a solvent (either ethylacetate or toluene) or filler(s) to the precursor. The solvent served to enable the resulting precursor film to be thinner (less than 8 μm), thereby reducing the shrinkage during pyrolysis and alleviating the cracking problem. In spite of the generation of a large amount of gas upon carbonization, the film (without filler) did not have any pore of size greater than about 1 μm, as shown in Fig. 2. Fig. 3 shows the fracture surface of the carbon film that contained 1.5 vol.% nickel. Bright spots observed within the carbon film (Fig. 3) were of typical size less than 500 nm (the same as the nickel particle size) and were identified by energy dispersive X-ray spectroscopy to be nickel. The rather uniform distribution of these dots suggests that the nickel was relatively well dispersed without agglomeration.

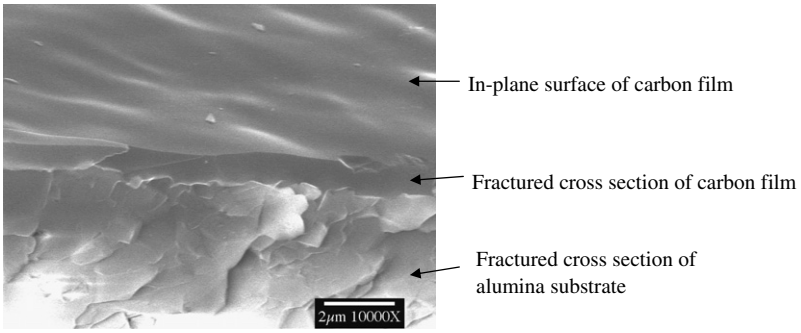

Fig. 2 – SEM image of the fracture cross section of a carbon film without any filler.

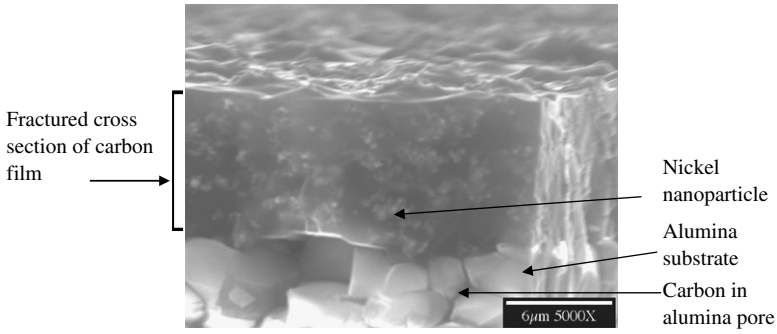

Fig. 3 – SEM image of the fracture cross section of a carbon film containing 1.5 vol.% nickel.

Table 1 – Thickness and electrical resistivity of carbon films

Filler	Thickness (μm)	Average resistivity (Ω cm)	Range of resistivity (Ω cm)
None (with 75 wt.% ethyl acetate)	0.8 ± 0.2	3.5	1.4–5.6
None (with 50 wt.% toluene)	4.5 ± 3.6	3.4	0.7–6.1
Silver (2.5 vol.%)	5.9 ± 1.2	2.6	1.1–4.1
Silver (5.0 vol.%)	4.9 ± 1.4	2.0×10^{-1}	$(0.9–3.1) \times 10^{-1}$
Silver (10 vol.%)	5.6 ± 2.5	3.8×10^{-4}	$(1.6–6.0) \times 10^{-4}$
Nickel (0.5 vol.%)	6.7 ± 2.0	6.8	5.0–8.6
Nickel (1.5 vol.%)	8.7 ± 2.4	2.5×10^{-1}	$(0.30–6.0) \times 10^{-1}$
Nickel (2.5 vol.%)	8.7 ± 1.7	5.7×10^{-3}	$(0.86–1.3) \times 10^{-3}$
Nickel (5.0 vol.%)	9.0 ± 2.0	5.3×10^{-3}	$(0.89–10) \times 10^{-3}$
Nickel (7.5 vol.%)	11 ± 1	5.7×10^{-4}	$(0.70–13) \times 10^{-4}$
Nickel (10 vol.%)	13 ± 1	6.2×10^{-4}	$(0.70–16) \times 10^{-4}$
MWCNT (3.6 vol.%)	4.3 ± 2.8	2.3×10^{-2}	$(1.0–3.6) \times 10^{-2}$
MWCNT (3.6 vol.%) + silver (1.1 vol.%)	6.8 ± 1.1	2.2×10^{-2}	$(0.5–3.9) \times 10^{-2}$
MWCNT (3.6 vol.%) + silver (1.8 vol.%)	4.5 ± 2.1	2.1×10^{-2}	$(0.8–3.4) \times 10^{-2}$
Carbonized pitch film[a]	28	5×10^{4}	$(1–9) \times 10^{4}$
Carbonized pitch film (10 vol.% silver)[a]	203	2×10^{4}	2×10^{4}
Carbonized pitch film (15 vol.% silver)[a]	140	7×10^{-3}	$(6–8) \times 10^{-3}$

a Pyrolyzed at 650 °C for 30 min [6].

Table 1 shows the thickness and resistivity of the epoxy-based carbon films of this work in comparison with pitch-based carbon films of prior work [6]. In the absence of a filler, epoxy-based carbon film showed lower electrical resistivity than pitch-based carbon film, due to its small thickness (consequent low residual stress) and absence of cracks or microscopic pores. Table 1 also shows the thickness and resistivity of carbon films with and without nickel, silver or MWCNT at various volume fractions. At lower filler volume fractions (<5 vol.%), the nickel-filled film exhibits lower resistivity than the silver-filled film at the same filler volume fraction. Although nickel (6.8×10^{-6} Ω cm [10]) is higher in resistivity than silver (1.6×10^{-6} Ω cm [10]), its filamentary morphology makes it more effective than silver as a filler for enhancing the conductivity. Moreover, nickel is advantageous in its good oxidation resistance and low cost compared to silver. In spite of its high aspect ratio, MWCNT was less effective than nickel nanoparticles for enhancing the conductivity, though it was more effective than silver nanoparticles. The addition of silver to MWCNT essentially did not affect the resistivity, in spite of the increase in the total filler volume fraction. The percolation threshold could be roughly estimated as 2 vol.% for nickel and 7 vol.% for silver. For pitch-based carbon films containing silver particles of size 3 μm in prior work, the percolation threshold is 12% [6].

Table 2 shows the measured scratch width and calculated wear rate of carbon films with and without fillers at various volume fractions. Carbon films showed a small scratch width and a low wear rate either in the absence of a filler or in the presence of up to 5 vol.% nickel. For the same filler (either nickel or silver), the scratch width and wear rate increased with increasing filler volume fraction. This trend was due to the increased air void content, the decreased hardness of the film, and the increased viscosity of the epoxy resin (hence greater difficulty of penetration of the substrate by the epoxy resin and a lower degree of mechanical interlocking between the film and the substrate). This trend gives an additional reason for minimizing the filler content in practical use. At the same filler volume fraction of 7.5 vol.%, nickel and silver as fillers gave similar values of the scratch width and wear rate. Nickel at 5 vol.% gave a higher scratch resistance than MWCNT at only 3.6 vol.%. The addition of silver to MWCNT increased the scratch width and wear rate, due to the increase in the total filler volume fraction.

In summary, carbon-based films were prepared by carbonizing a mixture of bisphenol-A type novolac epoxy, triethylenetetramine, and optionally solvent or conductive fillers on an alumina substrate at 650 °C. The addition of solvent or filler(s) to this precursor gave carbon films without cracks. Interconnected filamentary nickel nanoparticles were more effective for conductivity enhancement than silver nanoparticles (not filamentary) and multiwalled carbon nanotube (filamentary) at the same volume fraction (5 vol.% or below) in spite of the high conductivity of silver and the high aspect ratio of carbon nanotubes. By using 2.5 vol.% nickel, a carbon film of resistivity 6×10^{-3} Ω cm was attained. This filler vol-

Table 2 – Scratch width and average wear rate of epoxy-based films with and without filler

Filler	Scratch width (μm)	Calculated wear rate[b] (10^{-12} m^2/N)
None[a]	§	§
Nickel 2.5 vol.%	§	§
Nickel 5.0 vol.%	§	§
Nickel 7.5 vol.%	21 ± 7	12 ± 17
Nickel 10 vol.%	27 ± 7	26 ± 26
MWCNT 3.6 vol.%	11 ± 2	2 ± 1
Silver 7.5 vol.%	20 ± 5	11 ± 10
Silver 10 vol.%	31 ± 3	40 ± 13
Silver 15 vol.%	36 ± 6	63 ± 37
MWCNT 3.6 vol.% and silver 1.8 vol.%	17 ± 1	7 ± 1

§No trace or slight trace was observed for the scratch by optical microscopy, so the scratch width or wear rate was too small to be determined, indicating good scratch resistance.

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

b The wear rate was calculated from the average value of the scratch width.

ume fraction and electrical resistivity is much lower than those in prior related work at the same carbonization temperature. Although any of the fillers diminished the scratch resistance of the carbon film, carbon film including nickel showed higher scratch resistance than carbon film including the MWCNT at a similar filler volume fraction.

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Easy deposition of amorphous carbon films on glass substrates

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ABSTRACT

The easy fabrication of amorphous carbon films on glass substrates is described. The films are obtained by a simple gas phase deposition technique that takes place in air under mild conditions (400 °C, ambient pressure). The experimental set-up is straightforward and can be routinely applied for the large-scale fabrication of high quality carbon films, while, the carbon source is a decomposable polymer precursor (polyvinylpyrrolidone, PVP).

Carbon thin films contain predominately carbon and moderate amounts of property-influential heteroatoms such as H, N or O. They are usually amorphous with a mixture of sp^2 and sp^3 carbon atoms and are deposited in the form of granular thin films with thicknesses of a few micrometers. For a number of years, the technologically attractive properties of carbon films have drawn an almost unparalleled interest [1–6], which include high hardness, low friction, electrical insulation, optical transparency, smoothness, protection and resistance to wear.

Carbon thin films on glass substrates are mainly produced using chemical vapour, plasma, pulsed laser, electron gun, ion beam or sputtering deposition techniques [1–6]. These methods are largely preferred over simply coating a substrate with an organic precursor and subsequent carbonization [7] because gas phase deposition techniques ultimately lead to

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