Screen Printed Glassy Carbon: Applications in Printed Electronics and Sensors

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***Abstract*— Glassy carbon is a non-graphitizing carbon with unique properties including low electrical resistance, and high chemical and temperature resistance. This work demonstrates the use of glassy carbon for applications in printed electronics and sensors. Screen printing was adopted to pattern phenol formaldehyde as a precursor, which was subsequently thermally converted to glassy carbon, on an alumina substrate. The resulting glassy carbon printed patterns were characterized, demonstrating an electrical resistivity of around $2x10^{-4}$ Ohm-meter. A circuit using printed glassy carbon as a conductor and incorporating a LED was fabricated to functionally demonstrate the material. Finally, the printed glassy carbon was tested as a temperature sensor up to 140 °C, presenting a reliable temperature coefficient of resistance of around -0.0021 Ohm/Ohm/°C. These results demonstrate the viability of presented fabrication process by printing for novel integration of printed glassy carbon into printed electronics, as demonstrated for printed circuits and temperature sensing, with advantages in principle of suitability for harsh and chemical demanding environments.**

Keywords*— Glassy carbon, printed electronics, screen printing, temperature sensor

I. Introduction

Glassy carbon (GC) is a non-graphitizing isotropic carbon, a chemically stable fully sp^2 bonded carbon with locally ordered domains [1,2]. Its structure offers a host of important material properties including hardness, temperature resistance, impermeability to gases, low electrical resistance, chemical resistance, and biocompatibility [1–7]. Given these properties, there is potential for this material to offer enhanced benefits over traditional carbon materials used in printed electronics in applications such as sensors. Glassy carbon is typically produced via carbonization of a resole-type thermoset resin precursor [8, 9] either as a bulk material or as a film [10-13] and has also been demonstrated by the authors using rapid photonic treatment [14] but has not been presented in the form of discrete features such as those achieved by printing methods. This study therefore explores the patterning of resin precursor using screen printing, subsequent thermal conversion to glassy carbon, and then evaluation of electrical properties of printed features together with demonstration as a temperature sensor and incorporation into an electronic circuit to illuminate an LED.

II. Materials and Methods

A. Materials

Curaphen 40-852 B60 precursor, a phenol formaldehyde resin in a combination of solvents, supplied by Bitrez Limited (UK) was used to create glassy carbon. 96% alumina substrates with a thickness of 0.640 mm were purchased from Sigma Aldrich (UK).

B. Fabrication of Glassy Carbon Structures

Screen printing was selected as a deposition method due to its extensive application in printed electronics and crucially its suitability for the viscosity of the resin. Due to the hazardous nature of the material, screen-printing was performed by hand in an extracted environment. A polyester mesh with 77 threads per cm, 55 µm thread diameter and a 13 µm emulsion was used. The screen design consisted of a number of different features including straight lines of varying line width and a solid area measuring 40 by 40 mm. The manufactured screen and a photograph of printed precursor are shown in Figure 1. Conversion of the printed precursor resin to glassy carbon was performed in a two-stage process. Firstly, the printed resin was crosslinked by thermal curing at 220°C for 30 min in a ventilated convection oven (VTL 60/90 - Vötsch Industrietechnik GmbH). The substrates were then cut to fit in to alumina crucibles and in line with established procedures, the crosslinked resin samples were exposed to a temperature of 800°C for 2 hours following a ramp rate of 2°C per minute in a tube furnace (Carbolite GERO GHA 12/450) (10-13). An inert atmosphere in the furnace was achieved with a constant 1 litre/minute flow of nitrogen gas. Following the 2-hour cycle, the furnace was allowed to cool down to below 50 °C over a period of around 12 hours. This conversion process towards glassy carbon was demonstrated previously by the authors, spectroscopically showing the characteristic sp^2 dominant structure [14].

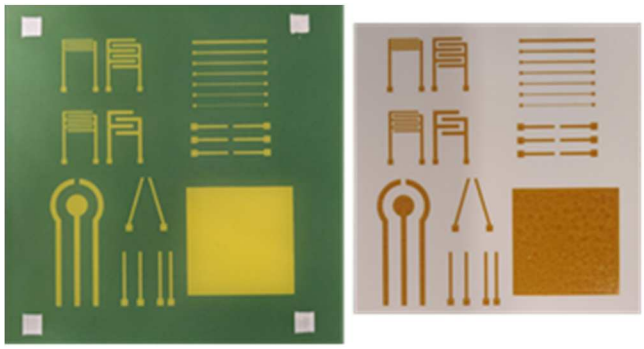

Fig. 1. Left: A photograph of the screen showing the structures to be printed, print image is 110 mm width by 120 mm height based on corner markers. Right: Photograph of printed resin precursor over alumina substrate

C. Print Topography and Resistivity Measurement

A series of samples were fabricated, of which three were used for electrical characterization, each containing printed lines of between 0.2 and 1 mm width and of length 27.2 mm, and one solid area of dimension 40 x 40 mm. Lines were measured with a 2-wire approach with three measurements per sample. The solid areas used sheet resistance measurement with five measurements per sample using an SDKR-13 4-point probe (NAGY Messsysteme GmbH) with a 1.3 mm gap between the pins followed by scaling by a geometric

correction factor of 4.512. Both approaches used a Keithley 2100 multimeter (Tektronix, US) using a moving average filter of 100 samples.

The edge layer thickness of the printed solid and the topography of the printed lines were measured using an Alpha-Step D-600) Stylus Profiler (KLA Instruments) at a scan rate of 0.05 mm/s and a stylus force of 10 mg. A Gaussian approximation was fitted to give the cross-sectional area of each line, with 6 measurements per line. The thickness of the printed solid areas was obtained by averaging 16 measurements per sample, 4 from each edge of the square. Using the thickness and resistance/sheet resistance values, the resistivity of the printed features was calculated.

D. LED Illumination Testing

After measurement of the electrical properties of the printed features, to demonstrate the conductivity of the printed glassy carbon lines and the potential use of the material as part of a printed electronics circuit, a green SMD LED was attached between two printed traces. The LED and conductive wires were bonded to the printed glassy carbon using a flexible silver paste (C2080415D2, Gwent Electronic Materials) which was cured at 120 °C for 20 minutes. Using a standard laboratory power supply, 3 V with current limit of 30 mA was applied.

E. Thermal Response Measurement

To measure the thermal response of glassy carbon structures, electrical connections were made between the end points of 0.7 mm printed lines and a Keithley 2100 multimeter. The sample was then placed in a VTL 60/90 convection oven with the temperature stepped from 20 to 140 °C in 10 °C increments whilst simultaneously logging the resistance. A photograph of the connections and placement in the oven is shown in Figure 2. Four separate samples were tested.

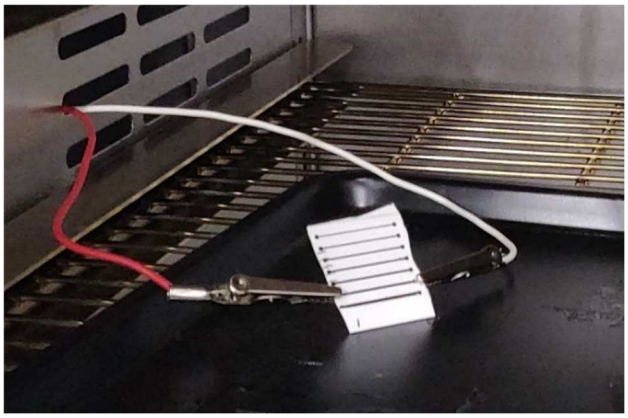

Fig. 2. A photograph showing a printed sample during thermal testing

III. RESULTS AND DISCUSSION

A. Printing and Carbonization Outcomes

The resulting printed and carbonized features are shown in Figure 3. Features were clearly defined and consistent with those of the screen and printed precursor (Figure 1).

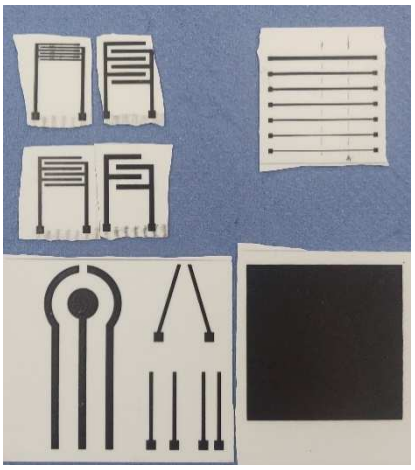

Fig. 3. Thermal carbonized screen-printed sample. Compilation of separate sections as the print was cut to fit the tube furnace for carbonization

B. Print Topography and Resistivity Measuraments

Measured resistances are presented for the printed carbonized lines (in kΩ) as well as the solid patches (in Ω/□) in Table 1. For lines the measured resistances fell from 11.4 to 2.0 kΩ when moving from a 0.2 mm to a 1.0 mm line width. Considering the dimensions of the features, these are converted to resistivity values. Slight variations were observed in both the cross-sectional area measurements of the printed lines and thickness of the solid areas. These can be attributed to the screen-printing process being performed by hand with inconsistencies in the squeegee force and angle, but the printed lines gave a broadly similar resistivities in the range 1.65 to 2.26 x 10^{-4} Ωm. For two of the solid patches, similar resistivities of 2.30 and 2.36 x 10^{-4} Ωm were recorded, which were close to the line resistivities, but one of the solid patches had a higher resistivity of 3.78 x 10^{-4} Ωm. For comparison a resistance of 2.90x10^{-4} Ωm was obtained for a conductivity optimized graphite-carbon black screen-printing ink (15), so apart from a single outlier, all the printed glassy carbon features were more conductive than the one achieved with the graphite-carbon ink.

TABLE I: RESISTANCE PROPERTIES OF PRINTED GLASSY CARBON FEATURES: PRINTED LINES OF VARIOUS WIDTH AND SOLID AREAS

Feature	Resistance	Cross-sectional Area or thickness	Resistivity (x10^{-4} Ωm)
Lines			
0.2 mm	11.43 ± 0.95 kΩ	526 ± 60 μm^2	2.21 ± 0.31
0.3 mm	6.88 ± 0.06 kΩ	743 ± 39 μm^2	1.88 ± 0.10
0.4 mm	5.26 ± 0.09 kΩ	853 ± 77 μm^2	1.65 ± 0.15
0.5 mm	4.43 ± 0.41 kΩ	1387 ± 116 μm^2	2.26 ± 0.28
0.6 mm	3.51 ± 0.11 kΩ	1476 ± 115 μm^2	1.91 ± 0.16
0.7 mm	2.79 ± 0.29 kΩ	1855 ± 110 μm^2	1.90 ± 0.22
1.0 mm	2.03 ± 0.03 kΩ	2779 ± 337 μm^2	2.07 ± 0.25
	n=3	n=3 x 6	
Solid 1	69.79 ± 5.31 Ω/□	3.30 ± 0.64 μm	2.30 ± 0.48
Solid 2	70.41 ± 3.33 Ω/□	3.36 ± 0.43 μm	2.36 ± 0.32
Solid 3	108.43±9.05 Ω/□	3.48 ± 0.39 μm	3.78 ± 0.53
	n=5	n=16	

C. LED Illumination Test

The LED was connected to the glassy carbon tracks using silver paste and was successfully illuminated as shown in Figure 4. This demonstrates that the conductivity of tracks was adequate and integrable for function in printed electronics. Attempts were made to directly solder to the glassy carbon, but this was not possible.

Fig. 4. Surface mount LED and metal wires installed on top of glassy carbon tracks using silver paste. LED is illuminated with a 3.0V potential and a current limit of 30mA.

D. Thermal Response Measurement

The resistance of the printed features decreased as the temperature of the samples was increased in the 20 to 140°C range. Resistance data is summarized in Table 2, with resistance at 20°C and 140°C compared as well as the change in resistance per degree Celsius, based on a linear trendline, and the temperature coefficient in terms of Ohms per Ohm per degree Celsius. To account for sample-to-sample variation in resistance, the change in resistance with temperature is also plotted in Figure 5, with resistance expressed as a ratio with respect to the resistance at 20°C (R/R0). All four samples exhibited a linear drop in resistance with temperature at similar gradients i.e. negative temperature coefficients in the range of -0.00199 to -0.00226 Ω/Ω/°C, averaging -0.002145 Ω/Ω/°C with a standard deviation of the sample of 0.000121 Ω/Ω/°C (<6%). For context, this can be compared against a commercial platinum resistance temperature device such as a Pt100 which has a resistance of 107.79 Ω at 20°C and 153.58 Ω at 140°C [16], which translates to an equivalent of + 0.0035 Ω/Ω/°C. In terms of change in resistance per 100°C (going from 20 to 120°C in this case) there is an average reduction of around 23% in resistance for printed glassy carbon vs. a 26% increase in resistance for a Pt100 sensor. This is a promising result in terms of sensitivity.

TABLE 1. CHANGE IN RESISTANCE WITH TEMPERATURE FOR 0.7 MM GLASSY CARBON LINES.

	Resistance at 20°C (kΩ)	Resistance at 140°C (kΩ)	dR/dT (Ω/°C)	Temp. coefficient (Ω/Ω/°C)
Sample 1	3.07	2.37	-6.1	-0.00199
Sample 2	3.50	2.60	-7.9	-0.00226
Sample 3	3.51	2.63	-7.8	-0.00222
Sample 4	2.70	2.07	-5.7	-0.00211

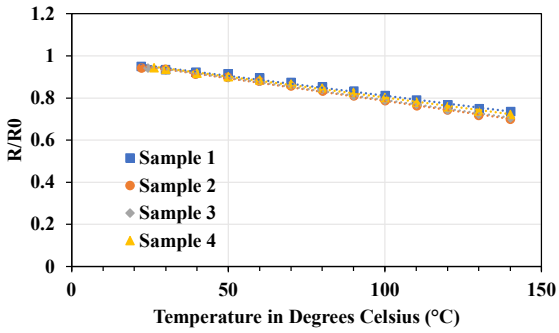

Fig. 5. Change in resistance with temperature of printed glassy carbon lines. Resistance is presented as ratio with respect to 20°C value using 0.7 mm width printed lines.

IV. CONCLUSIONS

This study presented the fabrication of discrete glassy carbon features deposited by screen-printing then converted by pyrolysis. This is a novel process that has not been reported previously and demonstrates potential for glassy carbon to be used in printed electronics, with comparable performance to an optimized conductive carbon ink, and sensors, with verification of a temperature sensor. There are potential benefits due to the natural chemical resistance and gas impermeability of glassy carbon, which could be desirable for electronics in harsh environments. In particular, glassy carbon can withstand much higher temperatures than carbon polymer inks, which degrade with heating. There are also benefits, from a printing perspective, in terms of the homogeneity of the material and lack of particles. Carbon inks are complex mixture of solvents, binders and multiple carbon morphologies , this can result in rough printed features, which leads to inconsistencies over the print run [15]; working directly with resin will alleviate these issues. Despite the potential benefits of using glassy carbon in printed electronics, a limitation of this production method is the extensive time and temperature required for carbonisation. This places limitations on the substrate which must be able to withstand the 800°C processing temperature. In this direction, glassy carbon has been recently demonstrated by the authors [14] as rapidly carbonizable using photonic treatment, taking a matter of seconds, opening opportunities for scale-up of the process. Further to this, photonic treatment, with its heat rapidly applied and dissipated [17], offers the potential for substrates that can tolerate intermediate lower temperatures.

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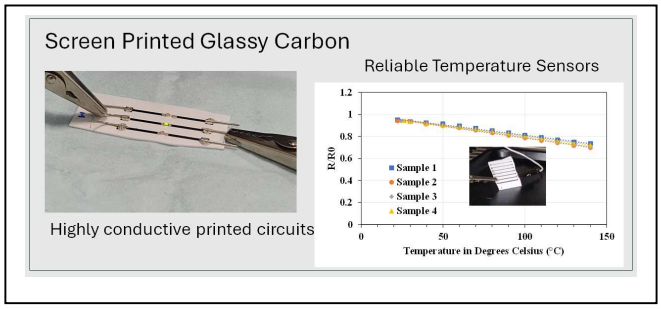

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