FACILE FABRICATION OF FLEXIBLE ELECTRONICS VIA DIRECT LASER WRITING OF CARBON-SILVER NANOCOMPOSITE

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ABSTRACT

In this paper, we demonstrate a facile method for the fabrication of porous-carbon/silver nanocomposites using direct laser writing on polymeric substrates. Our technique uses a combination of CO₂ laser-induced carbonization and selective silver deposition on a polyimide sheet to create flexible highly conductive traces. The localized laser irradiation selectively converts the polyimide to a highly porous and conductive carbonized film with superhydrophilic wettability. The resulting pattern allows for selective trapping of aqueous silver ionic ink solutions into the carbonized regions that are subsequently converted to Ag/C nanocomposite with sheet resistance as low as 0.02 $\Omega/\square$, upon annealing. The resulting patterns are flexible and electromechanically robust with less than 0.6 Ω variation in resistance after > 15000 flexion bending cycles. Furthermore, using this technique, we demonstrate the fabrication of a wireless resonant pressure sensor capable of detecting pressures ranging from 0 to 97 kPa with an average sensitivity of -26 kHz/kPa.

INTRODUCTION

Flexible and wearable electronics is an emerging field with a wide range of versatile applications, including flexible displays, health monitoring devices, and smart clothing [1]–[4]. Despite the high performance of conventional photo-masking and vacuum deposition processes, limitations such as small printing area, high cost, and high processing temperatures have restricted their use on flexible polymeric substrates [5], [6]. In recent years, many cost-effective direct-writing technologies such as micro contact printing, screen printing, laser-induced forward transfer, inkjet writing, and selective laser sintering (SLS) have been explored as alternative approaches to conventional clean-room processes. These provide attractive features including reduced material wastage and scalable manufacturing.

Among these techniques, inkjet printing and laser-assisted sintering have emerged as preferable approaches. Inkjet printing technology provides a unique non-contact and mask-less patterning process that has been widely used for depositing an extensive number of materials in solution form; these include conductive polymers, CNT, and various metallic nanoparticles [7], [8]. Despite its promise for fabricating flexible electronics, there are still important fabrication challenges associated with synthesis and printing conductive inks. Currently, most conductive inks are based on the suspension of metallic nanoparticles that often exhibit good levels of conductivity only after multiple printing cycles accompanied by high sintering temperatures at 200–350 °C [9], [10]. In addition, suspended nanoparticles tend to agglomerate over time, influencing the print quality and clogging of the equipment nozzle.

The SLS process of conductive metal nanoparticles (NP) has been explored as an alternative approach to inkjet printing. The NP sintering for typical inkjet printing processes is usually implemented by exposing the whole printed substrate to elevated temperatures; SLS is used to selectively localize the heat, thus enhancing the printing resolution and minimizing the substrate thermal exposure [11], [12]. Nonetheless, this method still faces challenges associated with formulation of the binder materials and

NP synthesis. Localized high temperatures induced by laser irradiation has also been utilized to selectively convert organic thermoset polymers into conductive carbon materials. This process can generate unique conductive carbon micro-patterns with highly porous micro/nano structures [13], [14]. The high porosity of the carbonized layer can be used to selectively trap precursor aqueous solutions. Despite the low cost of fabrication and stability of the laser carbonization process, previous reports have shown high electrical sheet resistance (typically between 15 $\Omega/\square$ to 1000 $\Omega/\square$) and sensitivity to mechanical deformations [15], limiting its use in flexible electronics, which often require highly conductive and robust interconnections.

In order to further advance the direct-writing laser-carbonization technique and overcome some of the above-mentioned shortcomings, we have developed a simple method to utilize the super-hydrophilicity of the carbon traces to selectively synthesize and trap silver nanoparticles into the carbonized regions, significantly enhancing the electrical conductivity and robustness of the flexible interconnects.

FABRICATION AND CHARACTERIZATION

The presented patterning technique relies on the laser pyrolysis of a thermoset polymeric substrate serving as the flexible support to create highly porous network of conductive carbon traces. These traces are later selectively coated with an aqueous reactive silver ink, as shown in Figure 1a-c. In this process, commercially available polyimide (PI) sheets (Kapton® HN, with a thickness of 60 μm) are used as the substrate for carbonization. The process begins by laser writing of highly porous carbon patterns into the surface of the PI sheet using a computer-controlled CO₂ laser cutting and engraving system (PLS6MW,

Figure 1: Fabrication process of carbon/silver nanocomposite using laser pyrolyzation and selective silver trapping.

Universal Lasers, Inc., Scottsdale, AZ). For maximum conductivity of the carbonized patterns, the laser is operated at 6.75 W with a scanning speed of 1.3 m/s. The laser modifies the surface of the polymer and creates porous super hydrophilic carbon patterns. The selective coating is carried out by loading the porous carbon traces with a reactive silver aqueous solution as shown in Figure 1b, followed by an annealing step at 90 °C for 10 min, Figure 1c.

Due to the hydrophilicity and wicking capability of the highly porous carbonized areas, the solution is only retained in the laser-ablated regions and rolls way from other areas on the polyimide substrate. The ionic silver ink is prepared by mixing 4 g of silver acetate with 10 mL of ammonium hydroxide. Next, under continuous magnetic stirring condition, 1 mL of formic acid is dropwise titrated into the mixture at room temperature. During the titration process, the solutions color changes from light yellow to a clear. Owing to low viscosity of the silver ink and the strong capillary force of the laser-carbonized traces the ionic silver ink can easily penetrate into the carbon network, allowing for the formation of a homogenous silver layer. Figure 2a-c shows examples of different carbon patterns before and after silver coating. Figure 2d shows an example of a simple flexible circuit made by conductive Ag/C-PI lines and used to light an array of LEDs.

Qualitative characterization

Optical and SEM images were used to evaluate the morphology of laser carbonized microstructures before and after silver deposition, Figure 3. Microscopic images show a clear change in the color from black to silver after the selective silver coating, Figure 3a,b. The SEM image shows the creation of a highly-porous network of carbon micro/nano structures generated by laser carbonization of the polyimide substrate. The alignment of

Figure 3: Magnified optical (a, b) and SEM (c, d) of carbonized polyimide and carbon-silver nanocomposite. All scale bars: 100 μm.

the carbon network is due to the scanning motion of the laser across the sample, Figure 3c. Figure 3d shows the top SEM image of the carbon trace after the precipitation of silver, illustrating a uniform deposition, forming a highly conductive silver/carbon nanocomposite.

Electrical characterization

Figure 4a shows the sheet resistance of the pristine carbonized polyimide and carbon-silver nanocomposite as a function of the annealing temperatures for samples of 3 cm length and 500 μm width (annealing time was fixed at 10 min). The pristine carbonized polyimide exhibits a maximum sheet resistance of 52 Ω/sq, which is consistent with previous laser carbonization reports [15]. As anticipated, the resistance of the silver-coated carbon traces decreases with increasing annealing temperatures. After drying the Ag/C nanocomposite at room temperature, the sheet resistance decreases slightly to 40 Ω/sq. Increasing the annealing temperature up to 90 °C improves the conductivity, with the sheet resistance decreasing to 0.026 Ω/sq. For temperatures above 90 °C, the effect of annealing on the conductivity is not significant (reactive silver ink is completely converted to bulk silver at 90 °C). Figure 4b, shows the change in the resistance of laser carbonized traces before and after silver coating at as a function of trace widths ranging from 200 μm to 2 mm at fixed annealing temperatures and times of 90 °C and 10 min. As can be seen, the composites traces show a resistance approximately three orders of magnitude lower than that of the pristine carbonized polyimide traces.

The electrical conductivity between the two ends of the carbonized PI is provided by the connection between carbon particles throughout the material. Mechanical deformation separates the connection points, resulting in an increase in resistance. However, the Ag/C nanocomposite has highly conductive Ag nanoparticles distributed in the carbon network, resulting in a higher conductivity and fewer disconnections between the particles in response to mechanical deformation. To assess the mechanical stability of the conductive traces upon bending, samples with different widths ranging from 200 μm to 2 mm were subjected to flexion at curvature radii (CR) of 50 mm to 2 mm. The mechanical stability of the conductive composite was characterized with samples subjected to the optimal annealing temperature of 90 °C. Figure 5a shows the change in the carbonized polyimide resistance as a function of CR. As can be

Figure 2: (a) laser carbonized traces before and after decorating with silver nanoparticles: (i) silver ionic solution, (ii) pristine carbonized trace, (iii) carbon/silver nanocomposite; (b, c) flexible traces before and after silver deposition; (d) array of lit LEDs with flexible interconnect. All scale bars: 1 cm.

Figure 4: (a) Electrical sheet resistance of carbon-silver composite after annealing at different temperatures, (b) carbonized polyimide and carbon-silver nanocomposite resistances as a function of line width

seen, for small traces (200 μm), the change in a resistance starts at 30 mm CR with a relatively linear sensitivity coefficient of 0.35 (R/R_0) per degree radius of curvature. However, with increasing width, the starting threshold decreases. For instance carbon traces 2 mm wide exhibit a resistance change starting at 10 mm of CR with a sensitivity of 0.04 (R/R_0) per degree radius of curvature. This observation can be explained by the fact that wider traces have more connecting points throughout the network, resulting in a higher conductivity and fewer disconnections between the particles in response to mechanical deformation.

In addition to a significantly lower resistance, the carbon-silver nanocomposite shows greater robustness and lower sensitivity to mechanical deformation, Figure 5b. For instance, after silver coating, a 200 μm -wide trace with an initial resistance of 7.5 Ω shows less than 12 % change in response to CR as small as 2 mm; this translates to a 900 % decrease in sensitivity to mechanical deformation as compared to a similar carbonized polyimide trace. Furthermore, for traces wider than 400 μm , carbon-silver nanocomposites have a high level of conductivity, with resistance smaller than 3 Ω and less than 9 % change in resistance at the maximum bending angles. This extreme level of conductivity and mechanical stability can be explained by the highly conductive Ag nanoparticles distributed throughout the carbon backbone structure. This structure provides multiple parallel electrical connections between particles, compensating for the change in the resistance of carbonized polyimide at high mechanical deformations.

Figure 5: Change in resistance as a function of radii of curvature for (a) carbonized polyimide and (b) carbon-silver nanocomposite with widths ranging between 0.2mm – 2mm.

WIRELESS PRESSURE SENSING APPLICATION

The described direct writing technology can be used to fabricate low-cost flexible sensors and actuators. As a proof-of-concept demonstration, we designed and fabricated a flexible passive wireless pressure sensor that can be used for wearable and implantable applications. Figure 6 shows the fabrication process and working mechanism of the LC passive pressure sensor. The device consists of a pressure-sensitive capacitor with a variable spacing between its two electrodes that is connected in series with a planar spiral inductor. In this design, the coil provides an inductively-coupled link between the reader antenna and the LC passive pressure sensor, allowing wireless powering and information transfer. When pressure is applied to the LC resonant circuit the gap between the two electrodes of the capacitor decreases, leading to an increase in the capacitance of the circuit. This change results in a reduction in the resonant frequency of the LC circuit that can be detected wirelessly by an external readout coil. We used a network analyzer to determine the resonant frequency of the sensor at various levels of pressure by measuring the location of the phase-dip in the impedance of the external coil.

Figure 6a shows the fabrication process using the presented conductive printing technique combined with a simple folding approach to make the inductor and capacitor used in the sensor. The inductor coil and the two capacitor electrode patterns were fabricated on a flexible polyimide substrate by using the aforementioned laser carbonized and silver deposition technique.

Figure 6: (a, b) Fabrication process experimental setup of wireless pressure sensor, (c) impedance phase versus frequency for several pressures, (d) sensor resonant frequency vs. pressure.

Next, a 50 μm -thick film of PDMS (Dow Corning Sylgard® 184, 10:1 ratio) was cast onto the conductive patterns and allowed to crosslink at 60 °C for 20 min. To fabricate the cavity needed for the pressure sensitive capacitor, a 300 μm -thick film of PDMS with predefined hole-punched openings was bonded to the PDMS coating. The bonding between the two layers of PDMS was achieved by a standard PDMS-to-PDMS bonding procedure using corona treatment (BD-10A High Frequency Generator, Electro-Technic Products, Inc.) followed by annealing on a hotplate at 90 °C for 2 h. Finally, the substrate was folded in half and bonded to create the final wireless pressure sensor with the PDMS cavity between the two conductive patterns. The change in the resonant frequency was characterized by measuring the dip in the impedance phase for gauge pressures ranging from 0 to 97 kPa, Figure 5c. As can be seen, increasing the pressure results in shifting the position of the dip to lower frequencies. The resonant frequency of the sensor as a function of applied pressure is shown in Figure 5d. As expected, the resonant frequency decreases linearly with pressures up to 97 kPa, with an average sensitivity of -26 kHz/kPa .

CONCLUSION

We have developed a facile method for fabricating highly flexible and robust electrical interconnects using direct writing of a carbon-silver nanocomposite on flexible polyimide (PI) substrates. The laser irradiation selectively carbonizes the surface of the PI substrate and converts it to a super-hydrophilic surface that is used to trap aqueous solutions of precipitating silver, resulting in improved conductivity and mechanical stability/robustness. As a proof-of-concept demonstration of the use of this technology, we demonstrated the fabrication of a flexible wireless LC resonant pressure sensor consisting of a pressure sensitive capacitor connected in series with a planar spiral inductor.

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REFERENCES

- [1] G. P. Crawford, *Flexible Flat Panel Displays*. Chichester, UK: John Wiley & Sons, 2005.
- [2] W. Honda, S. Harada, T. Arie, S. Akita, and K. Takei, "Wearable, Human-Interactive, Health-Monitoring, Wireless Devices Fabricated by Macroscale Printing Techniques," *Adv. Funct. Mater.*, vol. 24, no. 22, pp. 3299–3304, Jun. 2014.
- [3] A. Pantelopoulou and N. G. Bourbakis, "A Survey on Wearable Sensor-Based Systems for Health Monitoring and Prognosis," *IEEE Trans. Syst. Man, Cybern. Part C (Applications Rev.)*, vol. 40, no. 1, pp. 1–12, Jan. 2010.
- [4] A. M. Gaikwad, D. A. Steingart, T. Nga Ng, D. E. Schwartz, and G. L. Whiting, "A flexible high potential printed battery for powering printed electronics," *Appl. Phys. Lett.*, vol. 102, no. 23, 2013.
- [5] Y. Zheng, Z. He, Y. Gao, and J. Liu, "Direct desktop Printed-Circuits-on-Paper flexible electronics," *Sci. Rep.*, vol. 3, p. 1786, Jan. 2013.
- [6] W. Shen, X. Zhang, Q. Huang, Q. Xu, and W. Song, "Preparation of solid silver nanoparticles for inkjet printed flexible electronics with high conductivity," *Nanoscale*, vol. 6, no. 3, pp. 1622–8, Jan. 2014.
- [7] E. Song, R. P. Tortorich, T. H. da Costa, and J.-W. Choi, "Inkjet printing of conductive polymer nanowire network on flexible substrates and its application in chemical sensing," *Microelectron. Eng.*, vol. 145, pp. 143–148, Sep. 2015.
- [8] O.-S. Kwon, H. Kim, H. Ko, J. Lee, B. Lee, C.-H. Jung, J.-H. Choi, and K. Shin, "Fabrication and characterization of inkjet-printed carbon nanotube electrode patterns on paper," *Carbon N. Y.*, vol. 58, pp. 116–127, Jul. 2013.
- [9] M. Singh, H. M. Haverinen, P. Dhagat, and G. E. Jabbour, "Inkjet printing-process and its applications," *Adv. Mater.*, vol. 22, no. 6, pp. 673–85, Feb. 2010.
- [10] J. Weremczuk, G. Tarapata, and R. S. Jachowicz, "The inkjet printing humidity sorption sensor—modelling, design, technology and characterization," *Meas. Sci. Technol.*, vol. 23, no. 1, p. 014003, Jan. 2012.
- [11] S. H. Ko, H. Pan, C. P. Grigoropoulos, C. K. Luscombe, J. M. J. Fréchet, and D. Poulidakos, "All-inkjet-printed flexible electronics fabrication on a polymer substrate by low-temperature high-resolution selective laser sintering of metal nanoparticles," *Nanotechnology*, vol. 18, no. 34, p. 345202, Aug. 2007.
- [12] I. Theodorakos, F. Zacharatos, R. Geremia, D. Karnakis, and I. Zergioti, "Selective laser sintering of Ag nanoparticles ink for applications in flexible electronics," *Appl. Surf. Sci.*, vol. 336, pp. 157–162, May 2015.
- [13] J. Lin, Z. Peng, Y. Liu, F. Ruiz-Zepeda, R. Ye, E. L. G. Samuel, M. J. Yacaman, B. I. Yakobson, and J. M. Tour, "Laser-induced porous graphene films from commercial polymers," *Nat. Commun.*, vol. 5, p. 5714, Dec. 2014.
- [14] R. Rahimi, M. Ochoa, W. Yu, and B. Ziaie, "Highly Stretchable and Sensitive Unidirectional Strain Sensor via Laser Carbonization," *ACS Appl. Mater. Interfaces*, Feb. 2015.
- [15] S. Luo, P. T. Hoang, and T. Liu, "Direct laser writing for creating porous graphitic structures and their use for flexible and highly sensitive sensor and sensor arrays," *Carbon N. Y.*, vol. 96, pp. 522–531, Jan. 2016.

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