Published in final edited form as:

IEEE Sens Lett. 2019 January 17; 3(2): . doi:10.1109/LSENS.2019.2893741.

Fabrication of a Silver-Based Thermistor on Flexible, Temperature-Sensitive Substrates Using a Low-Temperature Inkjet Printing Technique

Yongkun Sui^{1,*}, Loren P. Kreider², Kath M. Bogie^{3,4}, Christian A. Zorman^{1,**}

¹Department of Electrical Engineering and Computer Science, Case Western Reserve University, Cleveland, OH 44106 USA

²Department of Biomedical Engineering, Indiana Institute of Technology, Fort Wayne, IN 46803 USA

³Advanced Platform Technology Center, Louis Stokes Cleveland Veterans Affairs Medical Center, Cleveland, OH 44106 USA

⁴Department of Orthopaedics, Case Western Reserve University, Cleveland, OH 44106 USA

Abstract

Inkjet printing has been identified as a cost-effective method to fabricate sensors on polymeric substrates. However, substrate materials suitable for printing are limited by the annealing temperature required by conventional inks. In this article, we describe the fabrication of an inkjet-printed thermistor on polyethylene and cellophane substrates that are not thermally compatible with the conventional inkjet printing processes. Fabrication on these substrates is made possible by a novel plasma-based postprint treatment step that limits the substrate temperature to $<50^{\circ}\text{C}$. The sensors exhibited a temperature sensitivity of $0.25\ \Omega^{\circ}\text{C}^{-1}$ that was independent of substrate material. The utility of the fabrication process was demonstrated by fabricating thermistors for common indoor and outdoor applications.

Index Terms

Thermal sensors; flexible sensors; inkjet printing; low-temperature printing; plasma reduction; thermistor

I. INTRODUCTION

Inkjet printing is a leading fabrication method for printed electronics [1], and is now being developed for related technologies such as micro-electro-mechanical systems (MEMS) [2], photovoltaics [3], and sensors [4]. Inkjet printing has several key advantages over conventional subtractive fabrication methods based on photolithography. As a layer-by-layer, direct-write technique, inkjet printing is able to achieve complex geometries that would

Corresponding author: C. A. Zorman (caz@case.edu).

*Student Member, IEEE

**Senior Member, IEEE

require several processing step using photolithography. Inkjet printing is also more environment-friendly and potentially less expensive, because it generates significantly less waste. Unlike vacuum-based vapor-phase deposition systems, printing does not inherently rely on sophisticated tooling, therefore enabling rapid prototyping in small laboratory settings [5].

In the field of flexible devices, inkjet printing is particularly attractive on account of its compatibility with a wide range of substrate materials. Flexible substrates are attractive for use in electronics and sensor applications owing to the wide variety of available materials and compatibility with large area fabrication approaches [6]. In the case of the temperature sensor, which is the most widely employed among all sensors [7], the most commonly used flexible substrates are polyethylene terephthalate [8] and polyimide [7]. These substrate materials are chosen because of their relatively high thermal stability, which is a requirement for inkjet printing electrically conductive metallic materials due to the thermal annealing step that is typically required after printing.

Metallic inks for inkjet printing are typically divided into two classes, namely, nanoparticle inks and metallo-organic decomposition (MOD) inks [9]. Nanoparticle inks contain metal nanoparticles encapsulated by organic capping groups that must be thermally removed after printing [10]. MOD inks are made of MOD complexes that can be thermally decomposed into metal and gaseous byproducts [11]. Both inks typically require a high-temperature post-print annealing step to be activated, therefore the use of temperature-sensitive substrates is limited. As many flexible sensors are advancing toward disposable [12] and/or degradable designs [13], there is a demand for developing inkjet printing processes for more environment-friendly substrate materials, such as polyvinyl alcohol [14], polylactic acid [15], and polycaprolactone [13]. However, all these polymers have melting temperatures below the typical thermal annealing temperature ($> 150\text{ }^{\circ}\text{C}$) of nanoparticle inks and MOD inks.

In this letter, we report on the development and preliminary testing of a silver-based thermistor on flexible, degradable, and temperature-sensitive polymer substrates using a low-temperature inkjet printing technique. The printing technique utilizes a unique Ag salt-based ink and a plasma reduction method to convert the ink to Ag [16]. The highest substrate temperature in our printing process was $42\text{ }^{\circ}\text{C}$, which is significantly lower than the annealing temperature ($\sim 150\text{ }^{\circ}\text{C}$) used to fabricate thermistors from nanoparticle inks [7], [8]. The thermistor in this work was fabricated on two temperature-sensitive substrate materials: 1) a modified polyethylene (PE) film that significantly shrinks at $90\text{ }^{\circ}\text{C}$ and 2) commercial cellophane tape that softens at $130\text{ }^{\circ}\text{C}$. The measured temperature sensitivity of our printed thermistors is independent of substrate material and is comparable to that of the thermistors printed using nanoparticle inks. To demonstrate the utility of our printing process, we performed field tests on thermistors fabricated on each of the two substrates. The thermistor fabricated on the cellophane tape was adhered to a bathroom faucet and used to measure the water temperature. The thermistor was able to provide a reasonably fast response to temperatures within the residential water temperature range. The thermistor fabricated on the PE film, which is marketed as synthetic mulch, was used to measure soil temperature. Compared to commercially available soil temperature sensors which are mostly

IC-based, the printed thermistor can potentially reduce the cost of fabrication and implementation by direct integration of the sensing element into the material. The measured soil temperature was 0.1–1 °C higher than the air temperature but follows the same profile over a 16-hour period. These field tests show that our printing process can be used to fabricate thermistors on common substrates that are not temperature compatible with the currently used inkjet printing technologies.

II. MATERIALS AND METHODS

A. Thermistor Fabrication

The thermistor was fabricated by the inkjet printing and plasma treatment process illustrated in Fig. 1(a) and first described in [16]. The Ag ink was prepared by dissolving 0.5 M (1.7 g) silver nitrate (AgNO_3 , 98% purity, Alfa Aesar) in a mixture of 4 ml de-ionized water (Millipore), and 16 ml ethylene glycol (Fisher Scientific). The viscosity of the ink was 10.8 cP (measured by a Brookfield DV-E viscometer) and the surface tension of the ink was ~ 27 dynes/cm (measured by a Kruss K100 tensiometer).

Inkjet printing was performed by a Dimatix DMP 3000 material printer with 16 piezoelectric nozzles (DMC-11610). The sensor was comprised of the serpentine pattern, as shown in Fig. 1(b). The width of the lines was 1 mm. The length of the lines in the longitudinal directional was 10 mm, and the length of the lines in the latitudinal direction was 4 mm. The size of the contact pads was $2 \times 2 \text{ mm}^2$.

The substrates used in this study were a PE-based biodegradable mulch film (Agfabric) and a cellophane tape (Scotch brand). The PE film was treated using a 50-W O_2 plasma for three minutes before inkjet printing to enhance ink wettability. The serpentine pattern was printed on the two substrates at room temperature. The printed ink was then treated with a 150-W Ar plasma for ten minutes to convert the printed structures to metallic Ag. The background pressure of the Ar plasma was 630 mTorr. Two copper wires were attached to the contact pads by silver epoxy to make electrical connection to the sensor.

B. Benchtop Sensor Testing

A custom-built oven was constructed to characterize the temperature sensitivity of the sensors. To construct key components of the oven, a 1/8 ft thick acrylic sheet was laser cut into $8 \times 8 \text{ cm}^2$ squares for the outer shell of the oven and $5 \times 5 \text{ cm}^2$ squares for the inner shell. Circular feed-throughs were cut into each of the squares. The squares were assembled into two boxes. The smaller box was placed inside the larger box, and the volume in between the two boxes was filled with cotton for thermal insulation. A $1 \times 6 \text{ in}^2$ flexible silicone rubber strip heater (Tempco SHS80333) was mounted along the walls of the inner box.

The printed thermistor was mounted on a stack of $1 \times 1 \text{ cm}^2$ acrylic squares that was attached to the bottom of the inner box to position the sample in the center of the oven. A thermocouple (Omega L0044 K, 0–1250 °C, ± 2.2 °C, or 0.75%) was placed above the printed thermistor. The thermocouple and the silicon rubber strip heater were connected to a proportional-integral-derivative (PID) controller (Omega CN32PT-220) to control the temperature of the oven. The PID controller was controlled by a custom Lab VIEW virtual

instrument (VI) program. The resistance of the thermistor was calculated by measuring the current-voltage (I - V) characteristics using a voltage source (Keysight E3631A) and a current meter (Keithley 6485). The voltage source and the current meter were also controlled by the custom Lab-VIEW VI program. A schematic illustration and an optical image of the test setup is shown in Fig. 2(a) and (b).

III. RESULTS AND DISCUSSION

The relationship between the measured resistance as a function of temperature follows a third-order equation [7]. For a change in temperature over a small range, this equation can be approximated to a first-order expression

$$\alpha_T = \frac{1}{R(T)} \frac{\Delta R}{\Delta T} \quad (1)$$

where α_T is the temperature coefficient of the material (sensitivity), $R(T)$ is the resistance at a reference temperature T , ΔR is the change in resistance, and ΔT is the change in temperature. The temperature coefficient is an intrinsic property of the material. In practice, to achieve high sensitivity, the resistance of the thermistor at the reference temperature must be large. With the inorganic Ag-salt ink, in addition to the serpentine design, the resistance of the printed Ag line can be tuned by varying the plasma treatment time [16]. We found that for a line thickness of $\sim 1 \mu\text{m}$, plasma treatment at 150 W for 10 min yields Ag with a resistivity of $2 \times 10^{-6} \Omega\cdot\text{m}$. For a thermistor that is 1 mm wide, the length has to be >50 mm to achieve a resistance of $>100 \Omega$. To minimize the sensor footprint, we chose serpentine geometry so that the thermistor fits within an area of $10 \times 12 \text{ mm}^2$. It is noted that the substrate temperature during plasma treatment rose from room temperature to 42°C over the 10-min period. This temperature is far below the temperature rating of the substrates used in this work, which is 90°C for PE and 130°C for cellophane tape.

To characterize the temperature sensitivity of our printed thermistors, we fabricated five thermistors on each substrate material and tested each of them in the custom-built oven. The resistances of these thermistors at room temperature ($\sim 22^\circ\text{C}$) were derived from the I - V curves. The resistances, as shown in Table 1, range from 117.65 to 133.33 Ω . The average resistance of the thermistors printed on cellophane is 128.35 Ω with a standard deviation of 5.66 Ω , and the average resistance of those printed on PE is 130.39 Ω with a standard deviation of 2.63 Ω . We found from microscopic measurements that the width of the printed lines varies by $\sim 4.1\%$. The difference resistance values in Table 1 are most likely due to the dimensional variation of the printed thermistors caused by local variations in the substrate surface, such as surface roughness, contamination, and surface defects. This fabrication tolerance can be improved if substrate materials with high surface quality are used. However, the resistance data suggest that the resistance of the printed thermistors is independent of substrate material. This is likely because the plasma conversion of the AgNO_3 -based ink to Ag is limited to the near surface region of the printed structure where plasma interaction is most intense [16]. For the printing process used in this study, the printed structure was not likely completely converted to metallic Ag, but rather consisted of

a multilayered structure consisting of a textured Ag layer sitting atop a crystalline AgNO₃ layer [16].

The temperature coefficient of the printed thermistors was also assessed using the customized oven. The silicon strip heater, regulated by the PID controller, was used to heat the oven from 25 to 50 °C at intervals of 0.5 °C. For each thermistor, an I - V curve was measured at each temperature using the customized Lab VIEW program, and from each I - V curve, the resistance was calculated. Plots of resistance versus temperature for thermistors on PE and cellophane substrates are shown in Fig. 3(a) and (b), respectively. Without exception, the resistance-temperature curves are linear with very similar slopes. By linear curve fitting, the sensitivities of the thermistors are derived and shown in Table 1. The average sensitivity is 0.246 Ω°C⁻¹ with a standard deviation of 0.022 Ω°C⁻¹ for thermistors printed on PE, and the average sensitivity is 0.248 Ω°C⁻¹ with a standard deviation of 0.024 Ω°C⁻¹ for thermistors printed on cellophane tapes, indicating that the temperature sensitivity does not dependent on substrate material. The thermistor printed using the plasma-conversion technique has an average temperature coefficient of 1.91×10^{-3} °C⁻¹, which is comparable to the thermistors that are made by inkjet printing using nanoparticle inks, however, with a much lower processing temperature.

To demonstrate a potential application of the inkjet-printed thermistor, we performed field tests for thermistors fabricated on the cellophane tape and the PE film. A thermistor printed on cellophane tape was attached to a curved metal faucet and used to measure the temperature of residential tap water being discharged through the faucet. The temperature of the faucet was simultaneously measured by a thermocouple (Omega JTSS-HH). The resistance of the thermistor was measured using a digital multimeter. Silver epoxy was used to connect the printed contact pads to copper wires that were connected to the multimeter. A photograph of the measurement setup is shown in Fig. 4(a), and a graphical representation of the test procedure and associated test results are shown in Fig. 4(b). At the beginning of the test, the hot water tap was opened. The temperature measured by the thermistor quickly rose from ~25 to 45 °C within 40 s and then stabilized at 45 °C. The temperature measured by the thermocouple rose at a slower rate to 45 °C. The cold water tap was opened 60 s after the hot water was opened and remained open for 60 s. The temperature measured by the printed thermistor decreased over the next 50 s and stabilized at ~31 °C, while the temperature measured by the thermocouple decreased during the entire 60 s to ~31 °C. The hot water tap was closed at the 120 s mark and the temperature measured by both the thermistor and thermocouple slowly decreased from ~31 °C to ~25 °C over the next 60 s. The measured results show that the thermistor was able to track the temperature of the water flowing through the faucet and provide a faster response to the temperature change than the commercial thermocouple. This demonstration shows that our printed thermistor, which was conveniently fabricated on an adhesive-backed, temperature-sensitive substrate using our low-temperature printing technique, can potentially be used as a disposable temperature sensor for indoor temperature measurement on curved surfaces.

A thermistor printed on a PE-based mulch film substrate was used to measure the temperature of outdoor soil. In this test, the PE substrate on which the thermistor was printed was covered by a larger piece of PE, providing a moisture-proof covering for the thermistor.

The gap between the two PE layers was sealed by a water-proof epoxy. The thermistor was deployed in a backyard garden in the evening of a rainy autumn day. The soil was moist but not saturated. The resistance of the thermistor was measured hourly by a multimeter during the next day between 6:00 am and 10:00 pm. Photographs of the measurement setup and the mulch film during the soil test are shown in Fig. 4(c). The temperature of the outdoor air was measured during the same time points by a commercial temperature sensor. The hourly soil and the air temperatures are plotted in Fig. 4(d). The soil temperature measurements were always higher than the air temperature measurements. The difference between the temperatures increased after sunrise and reached a maximum at 4:00 pm, presumably because the black mulch film traps heat in the underlying soil as well as absorbing heat from sunlight. The temperature difference expectedly decreased after sunset. Because Ag is generally not considered as an environmental risk, printed thermistors on PE-based mulch film can potentially be used as a degradable sensor for outdoor temperature measurement.

IV. CONCLUSION

An Ag-based thermistor fabricated on temperature-sensitive substrates using an inkjet printing technique based on a postprint plasma treatment process was demonstrated. The use of temperature-sensitive substrates that is not compatible with conventional inks enable printing of disposable and degradable temperature sensors for many common indoor and outdoor applications. The resistance-based thermistor also has a potential of being developed into a wireless sensor by integration of a chipless radio-frequency identification (RFID) design [17]. The use of biocompatible Ag also enables sensor printing for smart biomedical applications.

ACKNOWLEDGMENT

This work was supported in part by the National Science Foundation under Grant CMMI-1246715 and Grant DMR-1559708 and in part by the VA Rehabilitation Research and Development Service Merit Award RX002166.

REFERENCES

- [1]. Kamysny A, Steinke J, and Magdassi S, "Metal-based inkjet inks for printed electronics," *Open Appl. Phys. J.*, vol. 4, pp. 19–36, 2011.
- [2]. Chung S, Karim MAU, Kwon H-J, Scheideler W, and Subramanian V, "A high-speed inkjet-printed microelectromechanical relay with a mechanically enhanced double-clamped channel-beam," *J. Microelectromech. Syst.*, vol. 26, no. 1, pp. 95–101, 2017.
- [3]. Krebs FC, "Fabrication and processing of polymer solar cells: A review of printing and coating techniques," *Sol. Energy Mater. Sol. Cells*, vol. 93, no. 4, pp. 394–412, 2009.
- [4]. Ando B and Baglio S, "All-inkjet printed strain sensors," *IEEE Sensors J.*, vol. 13, no. 12, pp. 4874–4879, Dec. 2013.
- [5]. Campbell I, Bourell D, and Gibson I, "Additive manufacturing: Rapid prototyping comes of age," *Rapid Prototyping J.*, vol. 18, no. 4, pp. 255–258, 2012.
- [6]. Wang Y et al., "Paper-based inkjet-printed flexible electronic circuits," *ACS Appl. Mater. Interfaces*, vol. 8, no. 39, pp. 26112–26118, Oct. 2016. [PubMed: 27582243]
- [7]. Dankoco MD, Tesfay GY, Benevent E, and Bendahan M, "Temperature sensor realized by inkjet printing process on flexible substrate," *Mater. Sci. Eng. B*, vol. 205, pp. 1–5, Mar. 2016.
- [8]. Molina-Lopez F, Quintero AV, Mattana G, Briand D, and de Rooij NF, "Large-area compatible fabrication and encapsulation of inkjet-printed humidity sensors on flexible foils with integrated thermal compensation," *J. Micromechanics Microeng.*, vol. 23, no. 2, pp. 025012–025022, 2013.

- [9]. Cummins G and Desmulliez MPY, "Inkjet printing of conductive materials: A review," *Circuit World*, vol. 38, no. 4, pp. 193–213, 2012.
- [10]. Niittynen J, Abbel R, Mäntysalo M, Perelaer J, Schubert US, and Lupo D, "Alternative sintering methods compared to conventional thermal sintering for inkjet printed silver nanoparticle ink," *Thin Solid Films*, vol. 556, pp. 452–459, 2014.
- [11]. Wünscher S, Abbel R, Perelaer J, and Schubert US, "Progress of alternative sintering approaches of inkjet-printed metal inks and their application for manufacturing of flexible electronic devices," *J. Mater. Chem. C*, vol. 2, no. 48, pp. 10232–10261, 2014.
- [12]. Yang M et al., "Flexible and disposable sensing platforms based on newspaper," *ACS Appl. Mater. Interfaces*, vol. 8, no. 51, pp. 34978–34984, Dec. 2016. [PubMed: 27976864]
- [13]. Annese VF, De Venuto D, Martin C, and Cumming DRS, "Biodegradable pressure sensor for health-care," in *Proc. IEEE 21st Int. Conf. Electron., Circuits Syst*, pp. 598–601, 2014.
- [14]. Jang JH and Han JI, "Cylindrical relative humidity sensor based on poly-vinyl alcohol (PVA) for wearable computing devices with enhanced sensitivity," *Sensors Actuators A: Phys*, vol. 261, pp. 268–273, 2017.
- [15]. Oliveira JE, Mattoso LH, Medeiros ES, and Zucolotto V, "Poly(lactic acid)/carbon nanotube fibers as novel platforms for glucose biosensors," *Biosensors*, vol. 2, no. 1, pp. 70–82, Feb. 2012. [PubMed: 25585633]
- [16]. Sui Y, Ghosh S, Miller C, Pappas D, Mohan Sankaran R, and Zorman CA, "Tunable resistivity in ink-jet printed electrical structures on paper by plasma conversion of particle-free, stabilizer-free silver inks," *J. Vacuum Sci. Technol. A*, vol. 36, no. 5, 2018, Art. no. 051302.
- [17]. Borgese M, Dicandia FA, Costa F, Genovesi S, and Manara G, "An inkjet printed chipless RFID sensor for wireless humidity monitoring," *IEEE Sensors J*, vol. 17, no. 15, pp. 4699–4707, Aug. 2017.

Fig. 1.

(a) Schematic illustration of the inkjet printing and plasma reduction process, (b) Optical images of the printed thermistor on the biodegradable PE mulch film (left) and cellophane tape (right).

Fig. 2.

(a) Schematic diagram and (b) an optical image of the thermistor characterization setup.

Fig. 3. Measured resistance as a function of temperature for thermistors printed on (a) PE and (b) cellophane substrates.

(a)

(b)

(c)

(d)

Fig. 4.

(a) Measurement setup and (b) test results for the thermistor used as a water temperature sensor, (c) Measurement setup and (d) test results for the thermistor used as a soil temperature sensor.

Table 1.

Resistance, Sensitivity, and Temperature Coefficient of the Thermistors Printed on PE and Cellophane Substrates.

Sensor	Substrate	Resistance at 22°C (Ω)	Sensitivity ($\Omega \cdot ^\circ\text{C}^{-1}$)	Temp. Coeff. ($10^{-3}/^\circ\text{C}$)
1	PE	133.33	0.26	1.98
2	PE	128.21	0.26	2.01
3	PE	117.65	0.21	1.78
4	PE	129.87	0.23	1.77
5	PE	132.68	0.27	2.06
6	Cellophane	133.14	0.26	1.95
7	Cellophane	131.31	0.27	2.06
8	Cellophane	125.76	0.27	2.15
9	Cellophane	129.43	0.21	1.62
10	Cellophane	132.33	0.23	1.74