Using an Office Inkjet Printer to Define the Formation of Copper Films on Paper

Sushant Kumar, Vijayashree Bhat, Kalarickaparambil J. Vinoy, and Venugopal Santhanam

***Abstract*—A low-cost fabrication process for forming conductive copper lines on paper is presented. An office inkjet printer was used to deposit desired patterns of silver nitrate and tannic acid solutions sequentially on paper. Silver nitrate was instantaneously reduced *in situ* on paper by tannic acid at room temperature to form silver nanoparticles, which acted as catalysts for the subsequent electroless deposition of copper. The copper films were 1.8 μm thick, and the sheet resistance of the copper film on paper was 9 $\Omega/\square$. A dual monopole ultrawide band antenna was fabricated on paper and its performance was equivalent to that of a similar antenna fabricated on a copper-film covered Kapton substrate using conventional lithographic processes. The paper-based conductive copper films fabricated using the facile process presented herein will aid the development of low-cost flexible circuits and sensors.**

***Index Terms*—Copper, flexible structures, nanoparticles, printing, radio frequency identification (RFID) tags.**

I. Introduction

THE development of flexible and portable electronic circuits in a cost-effective manner relies on the fabrication of conductive films in desired patterns [1]. In particular, there is a need to develop fabrication processes that are compatible with roll-to-roll processing, to facilitate large-scale manufacturing of RFID-based tags/sensors for diagnostic devices [2] and for "ubiquitous" sensor networks [3]. The use of paper as a low-cost and "green" alternative to flexible polymer substrates for fabricating electronic circuits has been actively pursued for the last two decades [4]. Conductive patterns on paper-based substrates have been fabricated using techniques such as physical vapor deposition [5], chemical modification [6], rod coating [7], screen printing [8], spray painting [9] etc. However, all these techniques require an additional subtractive process to remove unwanted material and form desired patterns.

The use of inkjet printing, an additive technique, for fabricating conductive patterns is actively pursued, especially to meet the requirements of low-cost, high-volume applications such as RFID tags, as it offers the added advantage of being compatible with roll-to-roll processing [10]. Using nanoparticle-based ink solutions necessitates tedious and expensive processing during nanoparticle ink formulation to ensure ink-stability during storage [11], and also requires subsequent thermal [12] or chemical annealing [13] steps to eliminate organic components and become conductive. The need for such complicated processing renders inkjet printing of nanoparticle inks unsuitable for cost-effective production of conductive patterns on paper. Alternatively, the use of a reactive inkjet printing technique, wherein precursor solutions are sequentially printed and react *in situ* on a substrate to form nanoparticles, can help overcome issues with ink formulation, thereby, paving the way toward low-cost applications [14]. However, conductive features can only be formed after several hundred repetitive cycles of printing precursor solutions and intermittent drying, hindering its adaptation as a large-scale manufacturing process [15].

To overcome the requirement for sintering of nanoparticle inks, conductive features have been fabricated on plastic substrates using a combination of inkjet deposition of nanoparticle inks and electroless deposition [16], [17]; wherein, the nanoparticles act as catalytic sites for electroless deposition. However, material and capital costs, associated with nanoparticle ink formulation and use of specialty printers, are still prohibitive for development of ubiquitous sensors or low-cost diagnostics. A simpler approach of forming catalyst patterns for electroless deposition by using a desktop printer to deposit palladium salt solution and then dipping the substrate in a bath of reducing agent to form palladium nanoparticles was reported earlier [18]. However, challenges related to material costs, precursor stability, hazardous nature of the reducing agent used, and losses due to detachment of colloidal particles during reduction have to be overcome for using such an approach to fabricate low-cost, paper-based circuits. To surmount this barrier, we formed silver nanoparticles by reactive inkjet printing of stable and nonhazardous reagents, used them as catalysts for electroless deposition of conductive and thick copper films on paper, and further demonstrated their utility as RF antennas.

This communication describes the rapid, *in situ* formation and characterization of silver nanoparticles on paper at room temperature using stable, nonhazardous reagents, and their subsequent development into conductive copper films using an electroless plating process. The results of characterization of RF antennas fabricated on paper and their performance comparison with similar antenna designs on a copper-clad Kapton substrate, fabricated using conventional lithographic processes, are presented next. To our knowledge, this is the first successful demonstration

Manuscript received June 30, 2013; accepted December 17, 2013. Date of publication December 20, 2013; date of current version January 6, 2014. This work was supported in part by the Department of Science and Technology, New Delhi; the Joint Advanced Technology Programme, and Space Technology Cell of IISc. The review of this paper was arranged by Associate Editor E T. Yu.

S. Kumar and V. Santhanam are with the Department of Chemical Engineering, Indian Institute of Science, Bangalore 560012, India (e-mail: sushant@chemeng.iisc.ernet.in; venu@chemeng.iisc.ernet.in).

V. Bhat and K. J. Vinoy are with the Department of Electronics and Communication Engineering, Indian Institute of Science, Bangalore 560012, India (e-mail: bvjshree@ece.iisc.ernet.in; kjvinoy@ece.iisc.ernet.in).

Color versions of one or more of the figures in this paper are available online at http://ieeexplore.ieee.org.

Digital Object Identifier 10.1109/TNANO.2013.2295765

of the use of an office inkjet printer to fabricate paper-based RF antennas.

II. Materials and Methods

All the chemicals used were of analytical grade or higher, and used as received. Deionised (DI) water, from a MilliPore MilliQ system, was used to prepare the required solutions. Printer and black cartridges were procured from an HP retail outlet in Bangalore, India.

A. Fabrication of Conductive Copper Patterns

An inkjet printer (HP deskjet 1000 J 110 series, Rs. 1100/-), using thermal inkjet technology, and black cartridges (HP 802) were used in these experiments. After prying open the lids of the cartridges, the ink and sponge used for ink storage were removed, and the cartridges were thoroughly rinsed with tap water. The cartridges were then used to print "black" pages using DI water and isopropanol a few times to flush ink solution out of the channels and aid in drying of the channels within the cartridges, respectively. Printing was carried out in grayscale mode using a resolution of 600 dpi $\times$ 600 dpi. The amount of water deposited varied from 4 to 5 μL/cm^2 per print. As a precaution, all precursor solutions were printed three times to overcome nonuniformities in spatial deposition. Overall, a line resolution of 0.3 mm and positioning accuracy $<$ 0.5 mm, for manual duplex printing, could be routinely achieved using this printer.

Silver nanoparticles were formed on paper (A4 size commercial printer paper, 80 g/m^2) by sequential printing of silver nitrate (470-mM solution, metal precursor) and tannic acid (25-mM solution, reducing agent) from two separate cartridges, to avoid inadvertent contact within a cartridge. The pH of the tannic acid solution was adjusted to 10, just prior to printing. The process conditions are based on a rapid, room temperature synthesis protocol that was developed earlier in our group using tannic acid, an environmentally benign reagent derived from plants, [19]. The desired patterns were created and saved as .pdf files with appropriate resolution and printed from a standard computer. The amount of silver deposited was $\sim$ 0.7 mg/cm^2 of printed area. The silver nitrate printed paper was allowed to dry under ambient conditions and then manually placed in the feed tray before printing the tannic acid solution. The formation of silver nanoparticles was evident as the paper reached the output tray of the printer. The same process could be repeated to form silver nanoparticles on both sides of the paper.

Copper films were formed on paper using the silver nanoparticles as catalyst for the electroless deposition. A standard recipe [20] was modified to increase the rate of deposition. Briefly, the printed paper was placed in a plastic tray and immersed in 60 mL of copper plating solution containing $CuSO_4.5H_2O$ (3 g), Ethylenediaminetetraacetic acid (EDTA, 6.5 g), NaOH (4.2 g), formaldehyde (2 mL), and Potassium ferrocyanide ($K_4Fe(CN)_6.3H_2O$, 2.5 mg). The pH of the electroless plating solution was maintained between 12.5 and 13. Potassium ferrocyanide acts as a stabilizer preventing the formation of copper oxide as the reaction begins, but it also lowers the deposition rate. The reported recipe was modified to avoid blistering and increase the rate of deposition, by adding 0.5 mL of formaldehyde to the plating solution at a regular interval of 2 min. For the samples reported here, the plating solution was maintained at 60 °C for 8 min and then the paper was rinsed in DI water and dried. These conditions were determined to be optimal for forming copper films, which remained conductive even after prolonged exposure to ambient conditions. Further increase in plating rates by adding more formaldehyde led to fragile powdery deposits, which were easily dusted off and rendered the patterns nonconductive. Copper-clad Kapton films were coated with a photoresist film that was patterned using photolithography. The exposed copper film was then etched away and the photoresist stripped off to form the flexible antennas needed for performance comparison.

B. Characterization Techniques

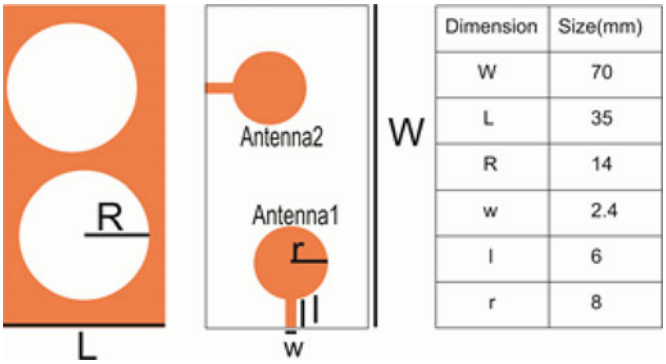
Field emission scanning electron microscope (FESEM) (Ultra 55, Zeiss GmbH) operated at 2 kV was used for structural and morphological characterization of the samples on paper. An optical profilometer (Zeta 20, True color 3-D) was also used to measure the thickness of the copper film deposited on paper fiber. X-ray diffraction (XRD) spectra were recorded using a Siemens Diffractometer (AXS D5005, Cu source). X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Thermo Scientific Multilab-2000 instrument with Al-Kα (energy of 1486.6 eV) as the X-ray radiation source. The antenna performance was characterized using a vector network analyzer from Agilent (2-port PNA-N5320 A).

C. Ultrawide Band (UWB) Antenna Design

The design of the dual monopole RF antenna was adapted from Wang and Huang [21]. Since substrates used were thin and had relatively similar values of dielectric constants (Kapton substrate: $\varepsilon_r = 3.85$, (loss tangent) "tan δ" ≤ 0.004 [22], thickness $= 1.1$ mm; b) Paper substrate: $\varepsilon_r = 3.2$, tan $\delta = 0.07717$ [23], thickness $= 1.2$ mm), antenna design parameters were first optimized for paper based on simulations carried out using CST microwave studio, and used in both cases. The dimensions and the layout of the UWB antenna used for printing are shown in Fig. 1.

III. Results and Discussions

Fig. 2 shows digital photographs of the UWB antennas fabricated on paper using the proposed process and on Kapton using conventional lithographic processing. To ensure good mechanical and electrical contact between the RF connector and the printed antenna structure, the patterns corresponding to the two sides were printed on different areas of a sheet of paper; after copper deposition the two patterns were cut and glued onto opposite sides of a cardboard support (1-mm thick). Similarly, two sheets of Kapton were pasted onto another cardboard. The photograph clearly shows that copper film is deposited only on the areas defined during inkjet printing of the silver nanoparticle precursor solutions. Also, the electrodeposited film has a



Dimension	Size(mm)
W	70
L	35
R	14
w	2.4
l	6
r	8

Fig. 1. Design layout of the fabricated antenna structures along with antenna dimensions.

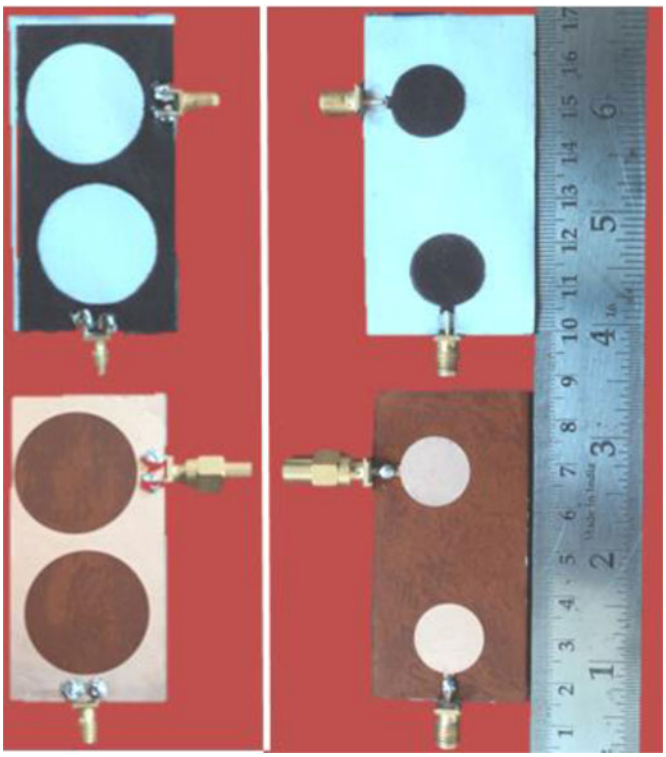


Fig. 2. Digital photographs of the two sides of UWB antennas fabricated on paper (top) by using reactive inkjet printing and electroless deposition, and on Kapton (bottom) by using lithographic processes. The electrodeposited copper has a much rougher microstructure and appears black in color, while the copper cladding on Kapton has a lustrous metallic sheen.

rough microstructure (*vide infra*) and appears black, while the commercially available copper cladding has a lustrous sheen. The copper patterns deposited on the paper substrate are robust and adhere well even after being flexed or rubbed using fingers.

A. Structural Characterization

Microscopic (FESEM) and spectroscopic characterization (XPS, XRD) of a paper-based sample after reactive inkjet printing, and after electroless plating confirmed the reduction of silver salt *in situ* on paper to form silver nanoparticles, and the formation of uniform copper plating over the paper-fibers,

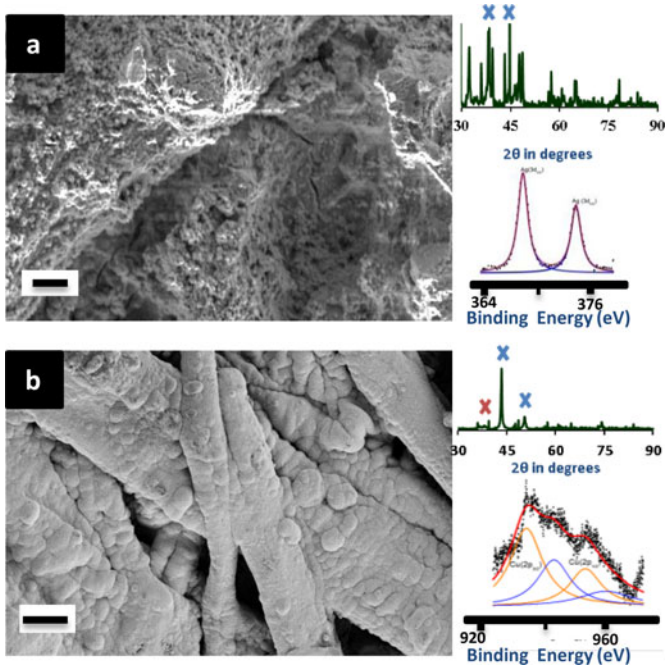


Fig. 3. Structural characterization of paper samples (a) after silver nanoparticle formation—FESEM image shows that silver nanoparticles are uniformly distributed over the fibers along with some organic matrix (presumed to be excess tannic acid). Scale bar corresponds to 1 μm. XPS analysis [bottom-right in (a)] shows the presence of silver in reduced form only and XRD [top-right in (a)] further confirms the presence of metallic silver. Peaks corresponding to FCC (111) and (200) planes of silver are marked with a blue "x." (b) after copper plating—FESEM image shows that all fibers are uniformly coated with copper and that copper film is interconnected at the microscopic scale. Scale bar corresponds to 10 μm. XPS analysis [bottom-right in (b)] shows the presence of copper in oxidized form along with reduced copper. XRD [top-right in (b)] confirms the presence of both copper ((111) and (200) planes-blue "x") and copper oxide (red "x") phases.

respectively (see Fig. 3). XPS, being a surface-sensitive technique with a penetration depth of $\sim$10 nm [24], indicated that 30% of copper was in oxidized state after exposure to air. XRD, with a penetration depth of $\sim$0.2 μm [25], also showed the presence of copper oxide phases, but the extent was only 5% suggesting that oxide phases were formed mainly at the exposed surface. XRD measurements on the silver nanoparticle film also indicate the presence of other metal-organic complexes, presumably silver atoms dispersed in a matrix of tannic acid residues. The presence of cracks in FESEM images of silver nanoparticle coated paper is also suggestive of the formation of such complexes.

The thickness of the deposited copper film was estimated to be 1.8 μm based on cross-sectional FESEM images, and this estimate was further corroborated by optical profilometer measurements (see Fig. 4). The cross-sectional FESEM image shows that the electroless film is composed of nanoparticles, which are uniformly spread over the depth of the film.

Together, the results of structural characterization clearly demonstrate that silver nanoparticles formed *in situ* using an office inkjet printer catalyzed the formation, by electroless plating, of copper films on paper.

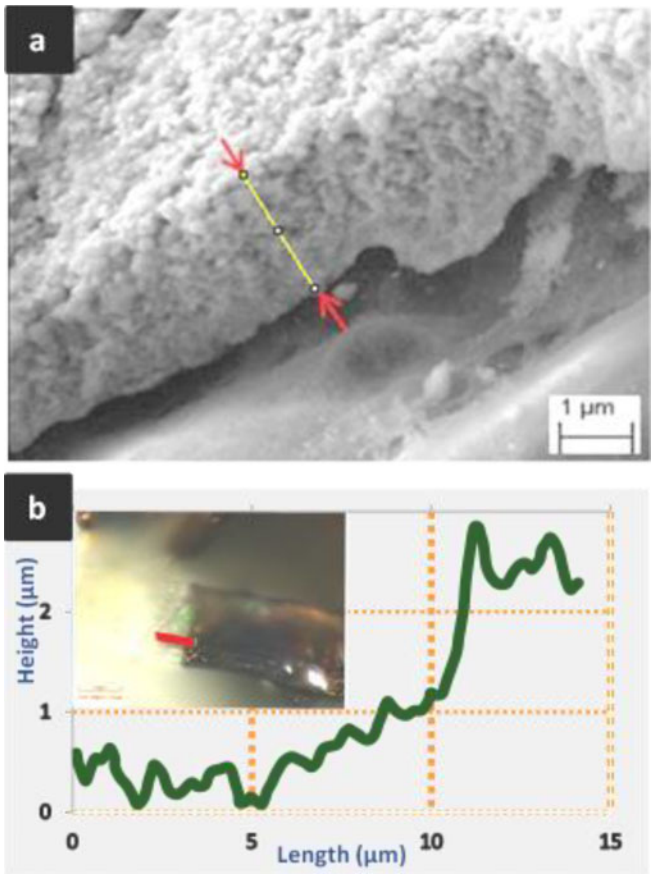


Fig. 4. Thickness of electrodeposited copper film. (a) Cross-section FESEM image shows that copper nanoparticles have aggregated to form the film. The thickness of the film was estimated to be 1.8 μm. (b) Height profile, using an optical profilometer, along a paper-fiber and across the edge of the copper film (corresponding to the red line in the inset). The average thickness estimated from this profile corresponds well with FESEM measurements.

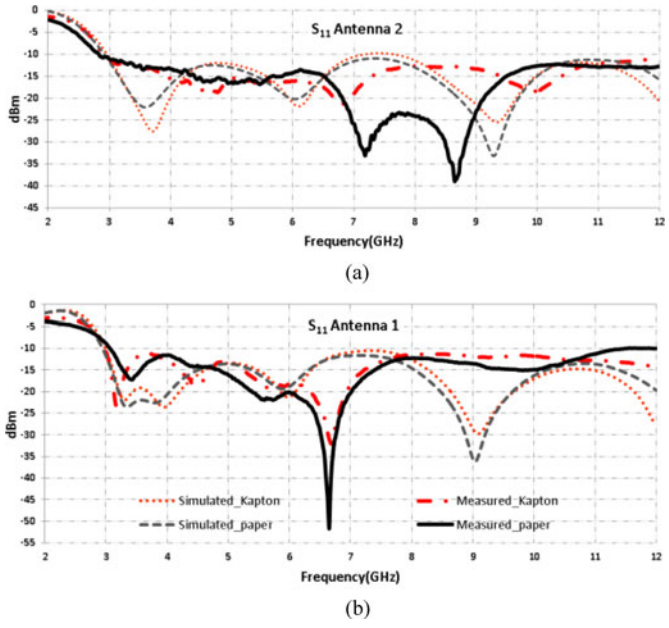


Fig. 5. Measured transfer characteristics (S_{11}) of fabricated antennas. (a) Antenna 2 and (b) Antenna 1. The –10-dB bandwidth of both antennas on paper span from 3 to 11 GHz, covering the entire UWB spectrum. The performance of paper and Kapton-based antennas are comparable.

B. Electrical Characterization

The sheet resistance of the copper film deposited on paper was measured to be 9 $\Omega/\square$ using four-point probe measurements. This corresponds to a resistivity of 4.5×10^{-5} Ω·m, considering paper to have 70% porosity. This resistivity estimate is $\sim$1% of typical values reported, and reflects the absence of a thermal annealing step to sinter the deposited copper nanoparticles. The transfer characteristics (S_{11}) of the two antennas in the design were measured and compared with simulations for both paper-based antennas as well as those fabricated on a Kapton substrate (see Fig. 5). The measured and simulated characteristics are similar for both substrates, deviations are attributable to contact impedance variations. The performance of paper-based antennas was comparable to that of antennas fabricated on a Kapton substrate, thereby, demonstrating the capability of fabricating low-cost RFID tags using an office inkjet printer.

IV. Conclusion

Silver nanoparticles were formed *in situ* on paper using a simple office inkjet printer. Electroless plating of copper on these silver nanoparticles was used to fabricate conductive copper patterns on paper. The performance of UWB antennas fabricated using the proposed process was found to be equivalent to that of similar antennas fabricated using conventional lithographic processes. These results are promising for low-cost, high-volume manufacturing of RFID tags, as both inkjet printing and electroless plating are amenable for roll-to-roll processing [26]. The simplicity of using an office inkjet printer for defining conductive patterns should enable the advent of flexible, low-cost devices for applications in diverse areas, such as biomedical diagnostics, flexible electronics, ubiquitous sensing platforms etc.

References

[1] J. Perelaer, P. J. Smith, D. Mager, D. Soltman, S. K. Volkman, V. Subramanian, J. G. Korvink, and U. S. Schubert, "Printed electronics: The challenges involved in printing devices, interconnects, and contacts based on inorganic materials," *J. Mater. Chem.*, vol. 20, pp. 8446–8453, 2010.

[2] A. N. Sokolov, M. E. Roberts, and Z. Bao, "Fabrication of low-cost electronic biosensors," *Mater. Today*, vol. 12, pp. 12–20, 2009.

[3] T. Sekitani, M. Takamiya, Y. Noguchi, S. Nakano, Y. Kato, T. Sakurai, and T. Someya, "A large-area wireless power-transmission sheet using printed organic transistors and plastic MEMS switches," *Nat. Mater.*, vol. 6, pp. 413–417, 2007.

[4] G. Shaker, S. Safavi-Naeini, N. Sangary, and M. M. Tentzeris, "Inkjet printing of ultrawideband (UWB) antennas on paper-based substrates," *IEEE Antennas Wireless Propag. Lett.*, vol. 10, pp. 111–114, Jan. 2011.

[5] A. C. Siegel, S. T. Phillips, M. D. Dickey, N. Lu, Z. Suo, and G. M. Whitesides, "Foldable printed circuit boards on paper substrates," *Adv. Funct. Mater.*, vol. 20, pp. 28–35, 2010.

[6] J. Lee, J. Ryu, and H. Youn, "Conductive paper through LbL multilayering with conductive polymer: Dominant factors to increase electrical conductivity," *Cellulose*, vol. 19, pp. 2153–2164, 2012.

[7] L. Hu, J. W. Choi, Y. Yang, S. Jeong, F. La Mantia, L.-F. Cui, and Y. Cui, "Highly conductive paper for energy-storage devices," *Proc. Nat. Acad. Sci.*, vol. 106, pp. 21490–21494, 2009.

[8] Y.-S. Song, G. Muthuraman, Y.-Z. Chen, C.-C. Lin, and J.-M. Zen, "Screen printed carbon electrode modified with poly(L-Lactide) stabilized gold nanoparticles for sensitive as(III) detection," *Electroanalysis*, vol. 18, pp. 1763–1770, 2006.

[9] N. Singh, C. Galande, A. Miranda, A. Mathkar, W. Gao, A. L. M. Reddy, A. Vlad, and P. M. Ajayan, "Paintable battery," *Sci. Reports*, vol. 2, 2012.
[10] W. S. Wong and A. Salleo, *Flexible Electronics: Materials and Applications*. vol. 11, New York, NY, USA: Springer, 2009.
[11] P. Calvert, "Inkjet printing for materials and devices," *Chem. Mater.*, vol. 13, pp. 3299–3305, 2001.
[12] S. P. Chen, Z. K. Kao, J. L. Lin, and Y. C. Liao, "Silver conductive features on flexible substrates from a thermally accelerated chain reaction at low sintering temperatures," *ACS Appl. Mater. Interfaces*, vol. 4, pp. 7064–7068, 2012.
[13] M. Layani, M. Grouchko, S. Shemesh, and S. Magdassi, "Conductive patterns on plastic substrates by sequential inkjet printing of silver nanoparticles and electrolyte sintering solutions," *J. Mater. Chem.*, vol. 22, pp. 14349–14352, 2012.
[14] P. J. Smith and A. Morrin, "Reactive inkjet printing," *J. Mater. Chem.*, vol. 22, pp. 10965–10970, 2012.
[15] D. Li, D. Sutton, A. Burgess, D. Graham, and P. D. Calvert, "Conductive copper and nickel lines via reactive inkjet printing," *J. Mater. Chem.*, vol. 19, pp. 3719–3724, 2009.
[16] Y. C. Liao and Z. K. Kao, "Direct writing patterns for electroless plated copper thin film on plastic substrates," *ACS Appl. Mater. Interfaces*, vol. 4, pp. 5109–5113, 2012.
[17] D. Zabetakis, P. Loschialpo, D. Smith, M. A. Dinderman, and W. J. Dressick, "Direct-write patterning palladium colloids as a catalyst for electroless metallization for microwave composites," *Langmuir*, vol. 25, pp. 1785–1789, 2009.
[18] S. Busato, A. Belloli, and P. Ermanni, "Inkjet printing of palladium catalyst patterns on polyimide film for electroless copper plating," *Sens. Actuators B*, vol. 123, pp. 840–846, 2007.
[19] S. K. Sivaraman, I. Elango, S. Kumar, and V. Santhanam, "A green protocol for room temperature synthesis of silver nanoparticles in seconds," *Current Sci.*, vol. 97, pp. 1055–1059, 2009.
[20] F. Hanna, Z. A. Hamid, and A. A. Aal, "Controlling factors affecting the stability and rate of electroless copper plating," *Mater. Lett.*, vol. 58, pp. 104–109, 2004.
[21] L. Wang and B. Huang, "Design of ultra-wideband MIMO antenna for breast tumor detection," *Int. J. Antennas Propag.*, vol. 2012, art. ID 180158, 7 pp., 2012. doi:10.1155/2012/180158.
[22] W. M. Fathelbab, F. Khoury, J. J. Kellar, and K. W. White, "Ultra-wideband (UWB) hairpin-comb filters with broad stopband performances," in *Proc. IEEE Radio Wireless Symp.*, 2008, pp. 451–454.
[23] L. Yang, A. Rida, R. Vyas, and M. M. Tentzeris, "RFID tag and RF structures on a paper substrate using inkjet-printing technology," *IEEE Trans. Microw. Theory Tech.*, vol. 55, no. 12, pp. 2894–2901, Dec. 2007.
[24] C. J. Powell and A. Jablonski, "Surface sensitivity of X-ray photoelectron spectroscopy," *Nucl. Instrum. Methods Phys. Res. A, Accel. Spectrom. Detect. Assoc. Equip.*, vol. 601, pp. 54–65, 2009.
[25] T. Blanton, C. Barnes, and M. Lelental, "The effect of X-ray penetration depth on structural characterization of multiphase Bi-Sr-Ca-Cu-O thin films by X-ray diffraction techniques," *Physica C: Supercond.*, vol. 173, pp. 152–158, 1991.
[26] T. Koch, D. Hill, M. Delos-Reyes, J. Mabeck, J. S. Yeo, J. Stellbrink, D. Henze, and Z. L. Zhou, "Late-news paper: Roll-to-roll manufacturing of electronic skins," in *Proc. SID Symp. Dig. Tech. Papers*, 2009, pp. 738–741.

Authors' photographs and biographies not available at the time of publication.