Inkjet Printing Involving Palladium Alkanethiolates and Carbon Nanotubes Functionalized with Single-Strand DNA

W. Boley,[1] T. Bhuvana,[2] B. Hines,[2,3] Robert A. Sayer,[1,2] G. Chiu,[1] T.S. Fisher,[1,2] D. Bergstrom,[2,3] R. Reifenberger,[2,4] G.U. Kulkarni[5]

[1] Purdue School of Mechanical Engineering, [2] Birck Nanotechnology Center. [3]Department of Medicinal Chemistry and Molecular Pharmacology, [4]Department of Physics, Purdue University West Lafayette, Indiana 47907 USA. [5]Chemistry and Physics of Materials Unit and DST Unit on Nanoscience, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064 INDIA.

Abstract

Pd hexadecanethiolate and Pd butanethiolate precursors as well as single-walled carbon nanotubes (SWCNTS) functionalized with single-strand DNA (ssDNA) were patterned using inkjet printing techniques to form metallic Pd interconnects upon thermolysis and circuit elements, respectively. Issues involved with printing these materials were addressed and overcome. Patterns with lateral dimensions of ≈50 μm were produced. The surface morphology of the Pd interconnects was examined using SEM. By printing 4-probe pattern of Pd alkanethiolates, the resistance as a function precursor concentration was determined, allowing estimates for the resistivity of the printed interconnects. A line trace containing an aqueous suspension of SWCNTs-ssDNA was inkjet printed for resistivity estimates and contacted with Pd pads.

Introduction

Since the early 1970's, inkjet technology has proven useful for the patterned deposition of liquid materials, including polymers and metal solutions in the fabrication of electronics and the functionalization of biomedical materials [1, 2]. Direct ink writing offers an attractive alternative for meeting the demanding design rules and form factors required in printed electronic and optoelectronic devices. Inkjet printing offers an attractive fabrication method because of its short processing time, low production cost, applicability to non-planar substrates, and diminutive environmental impact, particularly when compared to photolithographic techniques. For these reasons, it is generally recognized that inkjet printing is simpler, more environmentally friendly, and cost effective in contrast to vacuum-based methods [3].

Noble metals have been tested for inkjet printing applications, and the most commonly used inks are comprised of metal nanoparticles. An alternative is to print a metal salt and a reducing agent sequentially. In the case of nanoparticle inks, the printed patterns are subjected to sintering either by heating to 100-550°C [4, 5], by applying voltages [6], or by laser curing [7]. Allen *et al.* [6] used a nanoparticle ink containing 34.5 wt% Ag nanoparticles, with particle diameters of 10–20 nm, dispersed in triethylene glycol monoethyl ether. To obtain an electrical conductivity close to that of bulk, an external voltage was applied to sinter the nanoparticles. The use of silver nitrate with the reducing agent ascorbic acid to form Ag patterns has been demonstrated previously [8]. Chow *et al.* [9] used a mixture of two solvents to print uniform Au nanoparticles patterns on a glass substrate. Shah *et al.* [10] used inkjet printing on transparent plastic sheets to pattern Pt colloids as a catalyst for electroless Cu metallization. Printing Cu nanoparticles is difficult as the printed patterns easily oxidize. Cu nanoparticles have been mixed with Ag and printed as described by Woo *et al.* [3]. They developed a Cu-Ag-based mixed metal conductive ink by using Cu and Ag nanoparticles at varying volume ratios from 2:1 to 4:1, printed on a flexible plastic substrate and annealed at 175-210 °C to obtain conductive patterns. Li *et al.* [11] printed Cu/Ni patterns using an aqueous Cu/Ni salt solution and a reducing agent of sodium borohydride in two separate compartments.

There are a few reports on inkjet printing of Pd, which is often employed as a catalyst layer for the electrochemical deposition of other metals. Zabetakis *et al.* [12] used a commercial Pd-Sn electroless catalyst, Cataposit 44 (Rohm & Haas), to print a Pd catalyst on paper. Recently, Busato *et al.* [13] used ionic $PdCl_2$ as the source of Pd and printed a pattern on polyimide. The patterns were baked at 60 ºC for 15 minutes. Reduction of the surface-bound Pd(II) to metallic Pd(0) was accomplished by immersion into 0.1 M sodium borohydride at room temperature for 5 minutes.

In what follows, we report on the development of a new type of ink made from an organic precursor of Pd, namely Pd alkanethiolates. Previously, this precursor has been used as a highly sensitive resist for electron beam lithography. This chemical is soluble in most organic solvents and may form a new class of inks for printing [14]. A further advantage of this ink is that the precursor upon heating to 230 ºC forms a pure metal [15].

There are two issues related to the printing both Pd alkanethiolates and SWCNT-ssDNA. Firstly, if the concentration of the ink is too high, then the viscosity of the solutions becomes so large that the nozzles are likely to get clogged easily compared to lower concentration ink. Secondly, when printing these materials onto non-absorbing substrates, coalescence causes problems with printing continuous lines, thus detrimentally reducing the reliability and repeatability of the printed patterns. Another problem associated with Pd alkanethiolate ink was upon thermolysis, there was some shrinkage in the pattern causing discontinuity in the printed pattern. Particular to the SWCNTs-ssDNA is the issue with dissolving the SWCNTs into an aqueous medium. This paper addresses the aforementioned issues in order to realize successfully printing these two materials via inkjet for the first time.

Experimental Setup

Preparation of palladium alkanethiolates

Palladium alkanethiolate precursor was prepared by mixing an equimolar ratio of Pd acetate and alkanethiol (butyl or hexadecyl), both dissolved in toluene. Following the reaction, the solution became viscous, and the yellow color deepened to orange-yellow [14] indicating that hexadecanethiolate ($Pd(SC_{16}H_{35})_2$) or butanethiolate ($Pd(SC_4H_9)_2$) had formed. The obtained alkanethiolate was dissolved in toluene to make inks with different concentrations ranging from 50 - 600 mM. The substrates employed for the inkjet printing were oxidized silicon (SiO_2/Si) wafers. The patterns were thermolysed in an oven at 230 ºC under ambient atmosphere for 1 hour before further characterization.

Preparation of SWCNTs-ssDNA

The preparation of SWCNTs-ssDNA is described in detailed elsewhere [16, 17]. Briefly, SWCNTs were purchased from Unidym, Inc. and used as received. ssDNA was purchased from Integrated DNA Technologies, Inc. All other chemicals were purchased from Sigma-Aldrich. SWCNTs and ssDNA (1:1 wt/wt) were combined in phosphate buffered saline solution (PBS) (8 mL) and placed in a 15 mL polypropylene centrifuge tube. The mixture was placed on ice and sonicated for 120 minutes (Sonics Model VC 130) at 80% amplitude using a 6 mm diameter probe tip. The solution was then separated into seven 1 mL aliquots and centrifuged at 16,000 g for 90 minutes. The supernatant was carefully removed from each aliquot and combined into three Millipore Amicon® Ultra-4 centrifugal filter devices (molecular weight cut-off 100 kDa). The samples were desalted according to the manufacturer's protocol using ultra-pure water as the desalting solvent. The concentrated, desalted samples were collected, combined and stored at room temperature.

Inkjet printing of palladium alekanethiolates and SWCNTs-ssDNA

The inkjet system used for this study is shown in Figure 1. It contains an XY motorized stage with an encoder resolution of 0.5 μm, an HP TIPS thermal inkjet drop ejection system with pens containing up to 18 nozzles that can produce drops in the range of 1 – 220 pL per nozzle at an ejection frequency as high as 45 kHz, a CCD imaging system for viewing drop generation, and a laser registration system used for mapping out the position and orientation of substrates [18]. With this system, patterns can be easily formed, ranging from a periodic array of dots, to continuous lines, to complex patterns suitable for microelectronic applications. Printing times ranged from seconds to minutes, depending on the complexity and fidelity of the pattern desired.

While printing Pd alkanethiolate ink, to avoid clogging of nozzles, the concentration of solution was chosen such that it was ejectable from the nozzles in a reliable and repeatable manner. By controlling the concentration the viscosity was kept under control. For the Pd hexadecanethiolate, a concentration as high as 600 mM was printed while the more viscous ink, namely the Pd butanethiolate, was limited to less than 600 mM. In order to address the problem of coalescence, multiple-pass printing was invoked, more specifically, two-pass printing. For example, in order to print a continuous line all of the odd pixels of the line are filled with ink on the first pass, followed by the filling of the even pixels with ink on the second pass. A delay time of approximately 15 seconds between the two passes is sufficient time for the solvent to evaporate, thus reducing the surface tension enough so that coalescence does not occur. More on multiple-pass printing can be found elsewhere [19]. The issue of pattern shrinkage during thermolysis was overcome by using the printing technique of multiple layers [20]. The example of printing a line explained above is considered one layer. To make multiple layers, this process was simply repeated until the required number of layers is achieved. All results in this paper are reported with five layers unless otherwise mentioned. The shrinkage of patterns arises due to the phase change of Pd alkanethiolate during thermolysis to pure metal. Upon thermolysis, the solvent is evaporated followed by the decomposition of Pd alkanethiolate to release the hydrocarbon and leaving behind the Pd metal. If there was not enough material printed, then the printed pattern will appear discontinuous due to the loss of mass. Printing multiple layers of Pd alkanethiolate ensured that there is enough material so that forces causing this phenomenon are negligible.

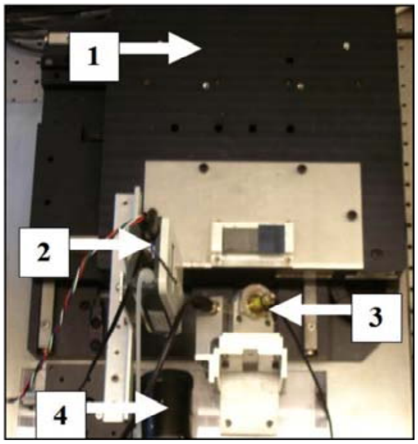

Figure 1*. Inkjet System used Including (1) XY Motorized Stage, (2) Drop Ejection System, (3) Laser Registration System, (4) Imaging System.*

The issues associated with printing SWCNTs in an aqueous solution are non-uniformity of SWCNTs in water, coalescence, and clogged nozzles. The methods for overcoming the coalescence and clogged nozzle issues are exactly the same as those mentioned with the printing Pd alkanethiolates. The ejectable concentration for the SWCNTs-ssDNA is less than 0.95 mg/mL. Non-uniformity of SWCNTs in water exists because of the hydrophobic behavior of SWCNTs. Functionalizing SWCNTs with ssDNA makes the material hydrophilic due to the sugar phosphate backbone of the ssDNA[16, 17].

Results and Discussion

The inkjet printed patterns of Pd alkanethiolates were thermolysed at 230 ºC to obtain metallic Pd. To characterize the electrical quality of the printed patterns, a four-probe resistivity measurement was performed on a five-layer inkjet-printed line pattern (190 μm wide) containing four integrated contact pads. A constant current in the range of 0.05 - 0.70 mA was applied across the outer two contact pads while the voltage drop was measured between inner two contact pads, which were 1.5 mm apart.

Figure 2 shows the variation in thickness as well as resistance as a function of precursor concentration for both precursors. As shown in Figure 2(a), thickness measurements using a profilometer (Alpha-Step IQ) revealed a systematic variation in line thickness for the different precursor concentrations of Pd hexadecanethiolate. The thickness was 413 nm for 600 mM and dropped to 66 nm for 50 mM concentration. The variation in resistance as a function of concentration is also plotted in Figure 2(a). The resistances were measured to be 103 Ω and 665 Ω for the highest (600 mM) and lowest (50 mM) concentrations, respectively. The highest concentration of butanethiolate that could be printed was 300 mM; attempts to use a 600 mM solution failed because the high viscosity prevented reliable inkjet drop formation. The results for the butanethiolate ink are given in Figure 2(b). The variation in thickness of the pattern for different concentrations reveals that for a low concentration of 50 mM, the pattern thickness is found to be 49 nm and for the highest concentration (300 mM), it is 186 nm. The variation in resistance follows the same trend observed for the hexadecanethiolate precursor. From the known geometry of the pattern, the resistivity is found to be (4.6 ± 0.8) x 10^{-6} Ω•m for hexadecanethiolate precursor and (2.5 ± 0.4) x 10^{-6} Ω•m for butanethiolate. The bulk resistivity of Pd metal is 1.05 x 10^{-7} Ω•m. The lower resistivity value for butanethiolate in spite of the particle connectivity being poorer may be due to the bigger particle size in comparison to hexadecanethiolate. Earlier studies of Pd hexadecanethiolate as a highly sensitive e-beam resist showed that the resistivity of an e-beam fabricated line pattern had a resistivity approximately 3 times greater than bulk [15]. Other studies involving patterning Pd by e-beam lithography have reported resistivity values of 100 x 10^{-6} Ω•m [21] and 417 x 10^{-6} Ω•m [22].

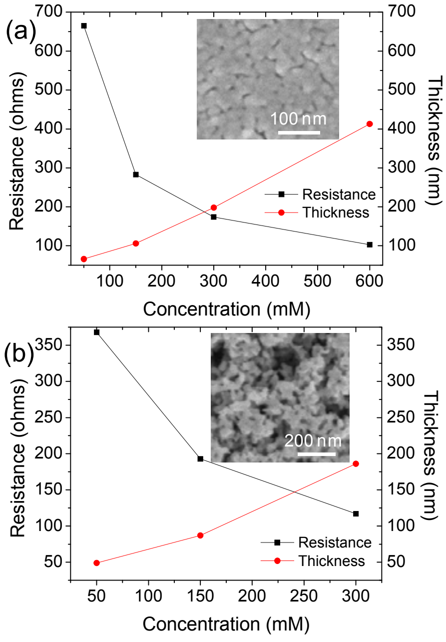

***Figure 2**. A plot showing the variation in thickness and resistance with concentration of the ink, (a) Pd hexadecanethiolate and (b) Pd butanethiolate. Inset showing respective SEM images.*

The morphology of a thermolysed pattern obtained from 150 mM concentration is shown in insets of Figure 2. SEM images (Hitachi S-4800 field emission scanning electron microscope) show that thermolysis of Pd hexadecanethiolate (see inset Figure 2a) leads to the formation of nanogranular smooth films with the nanoparticle sizes varying between 20 and 30 nm. In the case of butanethiolate (see inset Figure 2b), the pattern is somewhat rougher, with the particle size in the 35-50 nm range. The reason for the change in particle size is likely that the longer alkylchain length precursor forms a self-assembled bilayer while the shorter alkyl chain precursor cannot [14].

Energy dispersive spectroscopy (EDS) was performed on the patterns before and after thermolysis. These experiments showed that the carbon content in the hexadecanethiolate precursor before thermolysis was 70% and dropped to 7% after thermolysis. A similar trend was observed in the case of butanethiolate which had initially a 39% carbon content that dropped to 6% upon thermolysis. Initially, the sulfur content was found to be 12% and 15% for hexadecanethiolate and butanethiolate precursors respectively. These values drop below 1% after thermolysis. The results indicate that thermolysis is an important step to obtain metallic Pd patterns from a metal organic precursor.

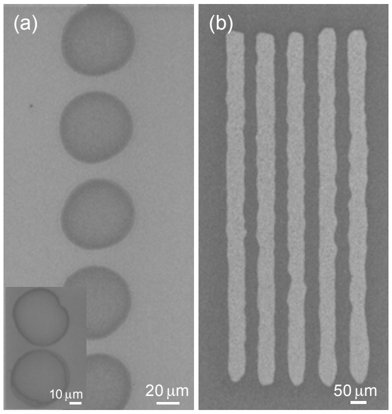

***Figure 3**. SEM images showing (a) smallest dot patterns printed using Pd hexadecanethiolate (150 mM); inset showing two close dots and (b) fine lines patterns.*

Figure 3 shows a few dot and line patterns generated by inkjet printing with 150 mM solution of the hexadecanethiolate precursor. Figure 3(a) shows uniform dots with 50-60 µm diameters. As illustrated in the inset, the separation between the dots is found to be 2.7 µm. Figure 3(b) shows that 50-60 µm thick continuous lines can be printed. To demonstrate the diverse applications of this Pd alkanethiolate ink, printing has also been successfully achieved on flexible Kapton® substrates.

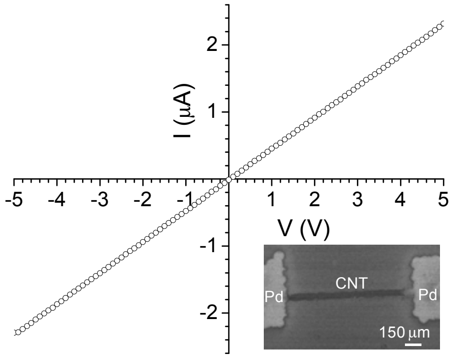

***Figure 4**. I-V plot showing the conducting nature of CNT across the Pd electrodes. Inset showing SEM image of a circuit printed by Inkjet printing, the contact pads are made of Pd and the active element across the pads is DNA wrapped CNTs.*

Separate experiments were performed to investigate the potential of inkjet printing for nanoelectronic applications. One of the many useful properties of single wall carbon nanotubes (SWCNTs) is their gage factor, which has been shown to be ~1000 or larger [23]. In our demonstration experiments, a network of SWCNTs was formed by printing two layers of an aqueous solution of SWCNTs wrapped with single-stranded DNA (ssDNA). Then, Pd alkanethiolate electrodes were printed to form electrical contact pads to either end of the SWCNT network. The thickness the SWCNTs-ssDNA pattern was found to be ~11 nm. The printed electrical circuit is shown as an inset in Figure 4. The contact pads made of Pd are 1 mm^2 in size and are printed 2 mm apart. These contact pads facilitate an electrical measurement of the 60 µm wide SWCNTs-ssDNA trace. I(V) measurements reveal the conducting nature of the randomly interconnected SWCNTs-ssDNA (see Figure 4). The I(V) plot in Figure 4 is linear and the resistance is found to be 2.14 MΩ. With the known dimensions of the pattern, the resistivity turns out to be 1.14 x 10^{-3} Ω•m.

Conclusion

Inkjet printing of Pd alkanethiolates and an aqueous solution of SWCNTs-ssDNA was achieved. The printing issues such as coalescence and nozzle-clogging with these materials were addressed and overcome by two-pass printing and concentration studies, respectively. Line separation of the Pd alkanethiolates was overcome by the printing of multiple layers while the hydrophobic behavior of SWCNTs in water is overcome by functionalizing the SWCNTs with ssDNA. The electrical properties of inkjet printed patterns of these materials have been investigated. The linear patterns of the Pd alkanethiolates obtained after thermolysis exhibit metallic conduction and have a resistivity value only one order of magnitude greater than the bulk resistivity of pure, bulk Pd. The resistivity of the SWCNTs-ssDNA is 1.18 x 10^{-3} Ω•m. Lines and dots of Pd alkanethiolates and SWCNTs-ssDNA with diameters of 50-60 µm can easily be printed. Insulating gaps between adjacent dots of Pd alkanethiolates can be as small as 2.7 µm. Future applications of Pd inkjet patterns range from circuit interconnects, the production of patterned surface-enhanced Raman substrates, or spatially printed catalysts for nanowire growth. Inkjet printed patterns of SWCNTs-ssDNA will be used for future electrical circuitry and strain gage applications.

References

[1] S. I. Zoltan, “Pulsed droplet ejection system,” U.S. Patent No. 3, 683, 212 (1972).

[2] P. Calvert, “Inkjet Printing for Materials and Devices,” Chem. Mater. 13, 3299 (2001).

[3] K. Woo, D. Kim, J. S. Kim, S. Lim, J. Moon, “Ink-Jet Printing of Cu-Ag-Based Highly Conductive Tracks on a Transparent Substrate,” Langmuir, 25, 429 (2009).

[4] S. B. Fuller, E. J. Wilhelm, J. M. Jacobson, “Ink-jet printed nanoparticle microelectromechanical systems,” J. Microelectromech. Syst., 11, 54 (2002).

[5] B. Y. Ahn, E. B. Duoss, M. J. Motala, X. Guo, S-I Park, Y Xiong, J. Yoon, R. G. Nuzzo, J. A. Rogers, J. A. Lewis, “Omnidirectional Printing of Flexible, Stretchable, and Spanning Silver Microelectrodes,” Science, 323, 1590 (2009).

[6] M. L. Allen, M. Aronniemi, T. Mattila, A. Alastalo, K. Ojanperä, M. Suhonen, H. Seppä, “Electrical sintering of nanoparticle Structures,’’ Nanotechnology, 19, 175201 (2008).

[7] N. R. Bieri, J. Chung, S. E. Haferl, D. Poulikakos, C. P. Grigoropoulos, “Microstructuring by printing and laser curing of nanoparticle solutions,” Appl. Phys. Lett., 82, 3529 (2003).

[8] S. M. Bidoki, D. M. Lewis, M. Clark, A. Vakorov, P. A. Millner, D. McGorman, “Ink-jet fabrication of electronic components,” J. Micromech. Microeng., 17, 967 (2007).

[9] E. Chow, J. Herrmann, C. S. Barton, B. Raguse, L. Wieczorek, “Inkjet-printed gold nanoparticle chemiresistors: Influence of film morphology and ionic strength on the detection of organics dissolved in aqueous solution,” Analytica Chimica Acta 632, 135 (2009).

[10] P. Shah, Y. Kevrekidis, J. Benziger, “Ink-Jet Printing of Catalyst Patterns for Electroless Metal Deposition,” Langmuir 15, 1584 (1999).

[11] D. Li, D. Sutton, A. Burgess, D. Grahamb, P. D. Calvert, “Conductive copper and nickel lines via reactive inkjet printing,” J. Mater. Chem., 19, 3719 (2009).

[12] D. Zabetakis, P. Loschialpo, D. Smith, M. A. Dinderman, W. J. Dressick, “Direct-Write Patterning Palladium Colloids as a Catalyst for Electroless Metallization for Microwave Composites,” Langmuir, 25, 1785 (2009).

[13] S. Busato, A. Belloli, P. Ermanni, “Inkjet printing of palladium catalyst patterns on polyimide film for electroless copper plating,” Sensors and Actuators B 123, 840 (2007).

[14] P. J. Thomas, A. Lavanya, V. Sabareesh, G. U. Kulkarni, “Self-assembling bilayers of palladium thiolates in organic media,” Proceedings of the Indian Academy of Sciences: Chemical Sciences, 113, 611 (2001).

[15] T. Bhuvana, G. U. Kulkarni, “Highly conducting patterned Pd nanowires by direct-write electron beam lithography,” ACS Nano, 2, 457 (2008).

[16] R. R. Lihiji, “Oligodeoxyribonucleotide Association with Single-walled Carbon Nanotubes Studied by SPM,” Small, 3, 1912 (2007).

[17] D. A. Heller, “Concomitant Length and Diameter Separation of Single-Walled Carbon Nanotubes,” J. Am. Chem. Soc. 126, 14567 (2004).

[18] N. J. Post, “Precision Micro – Deposition of Functional Layers Using Inkjet Drop – On – Demand and Applications to the Functionalization of Microcantilever Sensors,” Thesis, Purdue University, (2007).

[19] J. Yen, “Constraint Solving for Inkjet Print Mask Design,” Journal of Imaging Science and Technology, 44, 5 (2000).

[20] P. Calvert, “Multilayer inkjet printing of biopolymers, oleds and other devices,” Advanced Technology Workshop on Printing Intelligent Future, International Microelectronics And Packaging Society (IMAPS), 2002.

[21] T. J. Stark, T. M. Mayer, D. P. Griffis, P. E. Russell, “Electron Beam Induced Metallization of Palladium Acetate,” J. Vac. Sci. Technol. B, 9, 3475 (1991).

[22] M. T. Reetz, M. Winter, G. Dumpich, J. Lohau, S. F. Friedrichowski, “Fabrication of Metallic and Bimetallic Nanostructures by Electron Beam Induced Metallization of Surfactant Stabilized Pd and Pd/Pt Clusters,” J. Am. Chem. Soc. 119, 4539 (1997).

[23] D. Sickert, S. Taeger, I. Kühne, M. Mertig, W. Pompe, G. Eckstein, “Strain sensing with carbon nanotube devices, ” Phys. Stat. Sol. (b) 243, 3542 (2006).

Author Biography

John William Boley received a BS with a double major in Mechanical Engineering and Mathematics as well as an MS in Mechanical Engineering from the University of Kentucky. He is currently pursuing a Ph.D. degree in the School of Mechanical Engineering from Purdue University.