Research on the conductivity of circuit on fabrics based on inkjet printing and electroless deposition technology

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Abstract. Traditional silicon semiconductor substrate based electronic manufacturing has the shortcomings of non-bending, poor biocompatibility, and high cost. Fabric is more suitable for wearable electronic substrate due to its advantages of flexibility, air permeability, and skin-friendliness. We studied the manufacture of the conductive circuit based on inkjet printing and electroless deposition technology and got excellent conductivity and high dimensional accuracy circuit on fabric substrates. Three kinds of commonly used fabric materials cotton, polyester/cotton and polyester are selected to study the key work of surface pre-treatment, inkjet printing circuit pattern, and electroless deposition. The synergetic effect of SU-8 and P4VP (poly-4-vinylpyridine) on fabric ensures that the pattern retains its original size rather than diffusing. The distance between adjacent electric lines is no less than 0.3mm. With the extension of copper deposition time, the copper deposition layer becomes more and more uniform and dense. Sheet resistance reached 0.01Ω after 2 hours of copper deposition. The performance of all three kinds of fabric is similar. And cotton fabric had the best water lock performance. This technology has great potential for promotion and development in the application of intelligent textiles in the future.

1. Introduction

Traditional electronic manufacturing has a long history of the development and research. Although it has been applied into field of production and living, its inherent cannot bend, biological compatibility is poor, the defects of high cost, especially for the wearable activity monitoring equipment, limit the further development of the traditional non-flexible device. Flexible electronics are becoming a research hotspot in the world. To realize large-scale and low-cost manufacturing of flexible electronic devices and apply them to wearable devices, printing electronic devices on flexible substrates has become an increasingly concerning research field. At present, more flexible substrates have been studied, including paper, PU(polyurethane), PET(Polyethylene terephthalate), PDMS(Polydimethylsiloxane), Kapton film, fabric, and so on. Due to its advantages of flexibility, breathability, and skin-friendliness, fabric is more suitable for wearable electronic substrate, and more and more attention is paid to it, resulting in electronic textiles.

An important goal of electronic textiles [1] is to achieve conductive properties, which are textiles that can embed electronic components such as sensors, chips, batteries, screens, and electronic circuits.
into fabric and textile structures. [2] Traditionally, electronic textiles have been made through embroidery, weaving, sewing, etc. Although they have good electrical conductivity, reduce the mechanical flexibility of the fabric. Besides, traditional technologies are faced with limitations such as difficulty in obtaining uniform line width and clearance [3] and the significant skin effect that occurs at high frequency [4]. E-textiles are innovative fabrics that have been designed and fabricated to include technologies that provide users with increased functionality [5]. At present, E-textile [6] mainly used to make transistors, sensors [7-9], batteries, light, chips and small computers and electronic circuits [10] inductor, capacitor, energy management [11], memory [12], Flexible Sensors [13], electrochromic [14, 15], energy harvesting [16], nano-generator [17-19], battery [20], supercapacitors [21] and health monitoring [22].

Current methods of making conductive wires in electronic textiles include coating conductive polymers, carbon nanotubes, graphene, metal nanowires, and so on. Dip coating is easy and convenient, but physical adsorption is not as stable as chemical adsorption. Besides, dipping is not suitable for creating patterns, limiting its utilization. There has been a lot of studies on printing circuits on flexible substrates in the last decade. At present, many printing technologies for flexible substrates have been studied, such as inkjet printing [23-25], gravure printing [26-28], screen printing [29-32], transfer printing [33-35], extrusion printing [36], laser printing [37, 38], and aerosol jet printing [39-41]. The electroless deposition has been widely used and does not require expensive equipment or harsh working conditions. Yang's team has carried out a lot of research on the fabrication of conductive lines by ELD(electroless deposition) on flexible substrates, demonstrating the feasibility of the method. [42, 43] Based on this, this paper made a further study on the preparation of conductive lines on the fabric, including the width and spacing of conductive lines, fabric material and texture direction, ELD parameters, printing ink parameters, and other parameters on the performance of conductive lines. Three kinds of commonly used fabrics-cotton, polyester/cotton, and polyester are selected as the base materials. SU-8 is a good cross-linking agent for P4VP and fabric, making P4VP coating more uniform on cotton fabric. By inkjet printing, silver nitrate was printed on the fabric according to the design pattern, silver nitrate acted as an activator to start the ELD, and the copper continued to have an autocatalytic ELD reaction, forming a copper layer on the fabric surface. The pyridinyl group in P4VP has a strong affinity for metals and can form hydrogen bonds with polar substances. The mixing of SU-8, P4VP can also promote the polymerization of SU-8 epoxy groups, thus forming an interpenetrating polymer network between P4VP and SU-8 [23]. SU-8, as the cross-linking agent of P4VP and fabric, makes the silver ions and ELD layer adsorbed by P4VP stick to the fabric well and not easy to fall off. The influence of the ratio of SU-8 and P4VP on the conductivity of fabric conductive lines was studied. By selecting the appropriate ratio of Su-8 and P4VP, the appropriate deposition solution composition, and the reasonable ELD time, the excellent conductive circuit can be obtained.

2. Experimental

2.1. Materials
Poly (4-vinyl pyridine) (P4VP, Mw ~60,000), 1,4-dioxane (CH$_2$CH$_2$OCH$_2$CH$_2$O), anhydrous ethanol, silver nitrate (AgNO$_3$, 99%), sulfate pentahydrate (CuSO$_4$•5H$_2$O, 98%), potassium sodium tartrate tetrahydrate (C$_4$H$_4$KNaO$_6$•4H$_2$O, 99%), formaldehyde solution (HCHO, 36.5-38% in H$_2$O), 2,2-Dipyridyl (98%), and sodium hydroxide (NaOH, 97%), are from SIGMA-ALDRICH, SU-8 (Kayaku Micro Chem). All chemicals are used without further purification. The fabrics of cotton (100%), polyester/cotton (65%/35%), and polyester (100%) are from the Fabric market of Shanghai without any pretreatment.
2.2. Fabric preparation
Fabric pretreatment, first, cut the fabric into regular rectangles according to the need and ironed them. Then, prepared the solution with acetone and anhydrous ethanol in the ratio of 1:1, dipped the rectangular fabric in the solution, ultrasonic treatment for 20 minutes, and hanged them in the air for drying.

2.3. Surface treatment
At first, 5g P4VP was dissolved in 100ml anhydrous ethanol, got the solution I, 1.2g SU-8 was dissolved in 100ml 1,4-dioxane (CH₂CH₂OCH₂CH₂O), got the solution II. And then P4VP solution I was mixed with SU-8 solution II according to the ratio of 1:1, mixed adequately. Dipped the fabrics in the mixed solution, took them out after 30 seconds, to hang to dry in the air. Finally, the coated fabrics were treated in an oven at 120°C for 20 minutes and 30 minutes for a cross-linking reaction. [24]

2.4. Inkjet printing
Epson Stylus C88+ Inkjet Printer was adopted in this paper. According to the performance requirements of the Printer ink, With DI (deionized) water, glycerin and ethylene glycol as the main ingredients, Dynol 604 (0.5%) was added to prepare the basic ink vehicle, used for cleaning. For functional printing, we just dissolved the desired amount of silver nitrate (0.4g/ml) into it.

2.5. Electroless deposition copper
Copper deposition bath was a 1:1 mixture of freshly prepared solutions A and B. Solution A consisted of 13g/L CuSO₄·5H₂O, 12g/L NaOH, 29g/L KNa₃C₆H₅O₆·4H₂O, which were added into DI water in sequence. Solution B was 15ml/L HCHO in DI water. Once the metal deposition began, metal would grow first around the catalyst bonding with pyridine ligands and thus went into the inside of the modified layer to interlock with composite P4VP film and resulted in the formation of the highly adhesive copper layer. ELD time varied from 30 min to 3 hours depending on the resistivity (Figure 1).

2.6. Characterization
A Hitachi SU3500 field emission scanning electron microscope (SEM) and a Tabletop Microscope TM3030plus are used to observe the surface morphologies of the fabrics. A four-probe method using an RTS-8 tester is carried out to measure the sheet resistance.

3. Results and Discussion
Three samples of the fabrics, cotton (100%), polyester/cotton (65%/35%), and polyester (100%) were prepared. Each fabric was dipped in the coating solution respectively. A pattern of 20mm×20mm (Figure 2) was printed on every sample. Figure 2(a) was the cotton fabric before ELD, the pattern appears pale yellow, Figure 2(b) was after ELD for 30 min, the color was dark brown, had no obvious copper deposit, Figure 2(c) was after ELD for 60 min, appeared the copper color, Figure 2(d) was after ELD for 120 min, Shows a brighter color of copper, and the copper layer was very dense, and at this time the sheet
resistance was 0.01Ωsq⁻¹ (Figure 2d). Polyester/cotton and polyester fabrics behaved similarly, after ELD that gave them a darker color than cotton.

Because the fabric surface is rough and there is fiber direction, in the process of ELD with the increase of ELD time, some silver nitrate ions might diffuse a little bit. Here we changed the width of the lines and line space, according to the Figure 3 to design and print the pattern, and immersed the sample in copper deposition bath for 2 hours, to study the minimum interval without the short circuit of the lines and the electronic rate of different line width.

**Figure 2.** Digital images of different treatment stages of cotton fabric: a. After printing silver nitrate and before ELD; b. ELD for 30 minutes; c. ELD for 60 minutes; d. ELD for 120 minutes

**Figure 3.** Digital images of conductive lines after ELD for 2h obtained from different fabric substrates (line width = 0.5mm, length = 1mm): a. Polyester (100%); b. Polyester/cotton (65%/35%); c. Cotton (100%).
To study the influence of line width, line space, and line direction on conductive lines, we changed the line width and gap \((w=0.2 \, \text{mm}, \, g=0.25 \, \text{mm}; \, w0.25 \, \text{mm}, \, g0.3 \, \text{mm}; \ldots; \, w0.8 \, \text{mm}, \, g0.8 \, \text{mm})\) (Figure 3a). After 2 hours of ELD, it was found that when adjacent line space was 0.3 mm, there was no short circuit between adjacent lines (Figure 3b). The larger the line space, the less the short circuit was to happen. By changing the line width \((w=0.2 \, \text{mm}, \, 0.25 \, \text{mm}, \ldots, \, 1.0 \, \text{mm})\) we made the sample of Figure 3c, after ELD for 2 hours, and found that with the increase of line width, resistance decrease. When the width was 0.2 mm, and the length was 10 mm, it reached a good electrical conductivity, the resistance was 0.9 Ω (Figure 3d).

4. Conclusion
We presented a simple method to prepare conductive fabrics by combining inkjet printing technology with ELD. With P4VP and SU-8 mixture for fabric dip-coating decorate, made the fabric has good adsorption of silver ions and promoting the subsequent ELD, to guarantee inkjet printing pattern clear at the same time. When the adjacent line space is not less than 0.3 mm, that short circuit will not happen. Sheet resistance up to 0.01Ω can be obtained at 0.2 mm line width after 2 hours ELD. Based on these, we can conclude that this technology has wide application prospects and development potential in the future wearable smart fabrics.

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