COPPER ELECTRODEPOSITION BY HYDROGEN EVOLUTION ASSISTED ELECTROPLATING (HEA) FOR WEARABLE ELECTRONICS

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ABSTRACT

A novel technique called hydrogen evolution assisted (HEA) electroplating, has dramatically shown enhancement to the deposition rate of copper compared to galvanostatic conventional electroplating methods, opening new venues for the direct integration of devices to fabrics leading to the development of useful wearable electronics. HEA can be used for both printing copper tracks on a multi-wall carbon nanotubes (MWCNTs) coated template tracks and soldering surface mount electronic devices (SMD) to such tracks, demonstrating its versatility to be used for specific applications in which fabric mutilation wants to be prevented. However, in this project we studied how copper deposition takes place at different voltage ranges using 1000 Denier Coated Cordura Nylon, Laminated Polyester Ripstop and 100% Virgin Vinyl in the constant presence of the hydrogen evolution technique. Cupric sulfate ($CuSO_4$) and sulfuric acid (H_2SO_4) were used as the medium to allow a lateral deposition over a multi-wall carbon nanotube track of 0.1mm by the application of a voltage ranging between -0.5V to -2.0V using a potentiostat to employ the cyclic voltammeter technique in order to achieve a uniform deposition. Structure of the fabrics and variation of the copper deposits with respect to the type of fabric used were observed using a scanning electron microscopy (SEM).

Key words: Hydrogen Evolution Assisted (HEA) Electroplating; Copper Electrodeposition; Wearable Electronics; Multi-walled Carbon Nanotubes; Fabrics.

INTRODUCTION

Along with advantages in the development of wearable and flexible electronics, there is an increasing demand for lightweight, flexible, and wearable human and environmental monitoring systems with countless applications [1]. Among different technologies and approaches, patterning a conductive template (i.e., circuit layout) on fabrics by copper electrodeposition wearable technology market, which has propelled itself as one of the most discussed topics in the field during past few years can lead to the development of different wearable and flexible electronics. Leading to a variety of technologies such as smart watches, health trackers, smart clothes, providing advances not only at the scientific level but developing a positive impact in areas of medicine, military advances among others. Since the market is predicted to develop from its present-day value of USD 40 billion to a full-size price of USD 160 billion through 2026, the ability for novel concepts of wearable technologies is surely visible [2].

With technology development, integrated circuits (ICs) have become more compact, lightweight, and low-power, well suitable for integration of ICs into fabrics for development of e-textile and wearable electronics. Currently, there is a huge interest in developing wearable medical devices for constant monitoring health status of patients, smart soldier vests for carrying more gadgets, and smart textiles for monitoring recreational activities [3, 4]. Although, the IC technology is well developed to address the needs in medical, military, and recreational applications, the lack of any practical solution to integrate devices to fabrics has limited the approach to the fabrication of printed circuit boards separately and using glue or a Velcro-type mechanism for the attachment, not suitable for truly e-textile applications. Developing e-textiles demands a fabrication method to integrate electronic components and circuits into fabric structures with the interconnect conductivity as high as that in copper (~6×10^7 S/m) [5] and a printing method with the feature size less than 1 mm to be compatible with the packaging of surface mount devices (SMDs). In addition, the adaptation of the current available devices and attachment-based wearables into integrated technology may involve a significant size reduction while retaining their functional capabilities [1]. The recently devised HEA method [6] is able to electroplate the surface of a conductive pattern with a growth rate of at least four orders of magnitude faster than the conventional galvanostatic electroplating speed and produces nanostructures for embedding the printed structure to the fabric fibers. More importantly, it is feasible to solder electronic components to the printed circuit board (PCB) at a low-temperature by the HEA method [7,8]. Surface modification of textiles with desired functionalities can be engineered by a considerable number of techniques ranging from traditional treatments to multifunctional approaches. Textiles, in fact, offer a challenging platform for functional modifications in order to meet additional strategic requirements for a large variety of applications [9].

Table 1. Different methods of fabricating e-textiles.

Method	conductivity	flexibility	cost	resolution	distributed*	soldering
Sewn (metallic wires)	✓	✗	✓	✓	✓	✗
woven/knitted (metallic wires)	✓	✗	✗	✓	✓	✗
woven/knitted (conductive yarns)	✗	✓	✗	✓	✓	✗
Silk screen	✗	✓	✓	✗	✗	✗
Inkjet	✗	✓	✓	✗	✗	✗
Attached PCBs	✓	✗	✓	✓	✗	✗
Proposed method	✓	✓	✓	✓	✓	✓

✓ = acceptable and ✗ = not acceptable for integration of SMDs into e-textiles.

* Suitable for fabricating e-textiles with distributed sensors and electronics all over a piece of clothing.

Wearable electronics consists of fabrics that feature electronics and interconnections woven into them, supplying physical flexibility and normal size that can't be performed with different existing electronic production strategies. The usage of e-textiles has shown a rapid adjustment and adaptation within the computational and sensing requirements of any particular utility. As shown in table 1, the fabrication of wearable electronics can lead us to obtain a numerous amount of characteristics and functions based on the approach used for its development. The main goal of using wearable electronic systems as our everyday outfits have to meet special requirements concerning wearability. Wearable systems will be characterized by their ability to automatically recognize the activity and the behavioral status of their own user as well as of the situation around her/him, and to use this information to adjust the systems' configuration and functionality. The convergence of textiles and electronics (e-textiles) can be relevant for the development of smart materials that are capable of accomplishing a wide spectrum of functions, found in rigid and non-flexible electronic products nowadays [10].

EXPERIMENTAL

Materials

Textiles. The 1000 Denier Coated Cordura Nylon, Laminated Polyester Ripstop and 100% Virgin Vinyl textiles were purchased from Rockywoods Fabrics. Each type of fabric was used placing conductive track of MWCNTS over them to conduct the experiments. The size of each sample of fabric used was of approximately 3.2 cm x 3.2 cm.

Interconnection Track. Multiwalled carbon nanotubes and Sodium dodecylbenzenesulfonate (SDBS) from Sigma Aldrich were used to develop an ink to be used as the interconnection track over the fabrics. The MWCNT ink was fabricated as mention by Aljafari et al. [11] by adding 300mg of MWCNTs and 150mg of SDBS into 30 mL of DI water. A desktop ultrasonic processor was used to make a homogenous mixture of the MWCNTs and SDBS. The solution was sonicated for 30 minutes at 30 W and 40 J. In order to make the interconnection track over each textile type a 5 mL disposable syringe was used. The fabrics were placed in the furnace for 5 minutes at 120 degrees Celsius, then removed and repeated for four times.

Electrolyte. To study the Hydrogen Evolution Assisted electroplating over the MWCNTs ink track, an aqueous solution containing 0.47 M $CuSO_4$ and 1.5 M H_2SO_4 (both from Sigma-Aldrich) was prepared by mixing them with 10mL of DI water for 5 minutes until completely dissolved.

Sample Preparation

To study the deposition of copper by the interaction of the hydrogen bubbles released while the deposition is taking place, a MWCNT ink track of 0.1 mm was made over each textile being studied. One of the main challenges of creating conductive patterns on fabrics [12] and soldering electronic elements is the damage it causes to use soldering paste or soldering wire with a heating tool (i.e., soldering iron or heat gun) which melts the solder (typical temperature of 300 °C) which then spreads into the fabric. The heat can damage the fabric, and the diffused solder changes significantly the stiffness of the fabrics at the soldering joints, and most of all, make a poor electric connection at the joint. For that reason, almost all the reported wearable electronics have used a form of a conductive paste (mainly silver pastes) for soldering. The low durability of pastes on flexible substrates can fail the entire integrated electronic system with only one poor soldering joint. To prevent the damage of the fabrics and to allow the variation of voltage interacting with the sample, two cables were sewed to the fabric to make a proper connection and to work as the working electrode using sewing thread and metallic thread as shown in figure 1.

Figure 1. A schematic of a piece of fabric with MWCNT track and connection cables properly sewed to provide continuous connection between the fabric and the instrument.

To allow the transport of Cu^{2+} ions in the aqueous solution a copper coil of 0.25 cm diameter was used as the counter electrode. Using an O-ring of 0.8 cm diameter, a small electrochemical bath was formed around the cathode. An aqueous based $CuSO_4 + H_2SO_4$ electrolyte and a copper wire anode (inserted into the bath) were used for the deposition. A microscope camera was set on top of the cell to record the process.

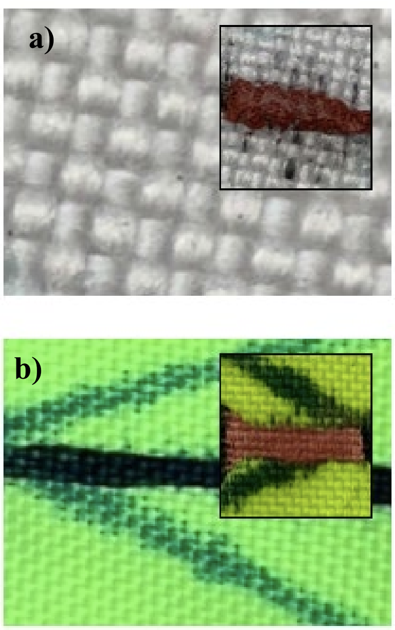

Figure 2. a) 1000 Denier Coated Cordura Nylon and b) Laminated Polyester Ripstop fabrics before and after copper electrodeposition takes place.

RESULTS

Applying a variation in voltage of -0.5 V to -2.0 V hydrogen bubbles appeared near the cathode, while a porous structure of copper started to grow as shown in figure 2. Variation of the voltage has been tested to understand the effect of the voltage and the conductivity of the copper deposition to find the best combination for the fastest electroplating growth with the lowest resistance of the final conductive structure on the surface. A constant and continuous growth was observed for both types of fabrics showing a proper adhesion of the copper deposits for 1000 Denier Coated Cordura Nylon and Laminated Polyester Ripstop as well as the presence of the hydrogen evolution assisted electroplating which helped in the fastest deposition of copper allowing a more wider agglomeration over the MWCNTs. As for the 1000 Denier Coated Cordura Nylon the agglomeration of copper deposits was significant, for the Laminated Polyester Ripstop the copper growth was more continue and less influenced by the hydrogen evolution which can be caused by the type of arrangement of the fabric's fibers. As shown in figure 3 the structure of the Laminated Polyester Ripstop fabric is very continuous.

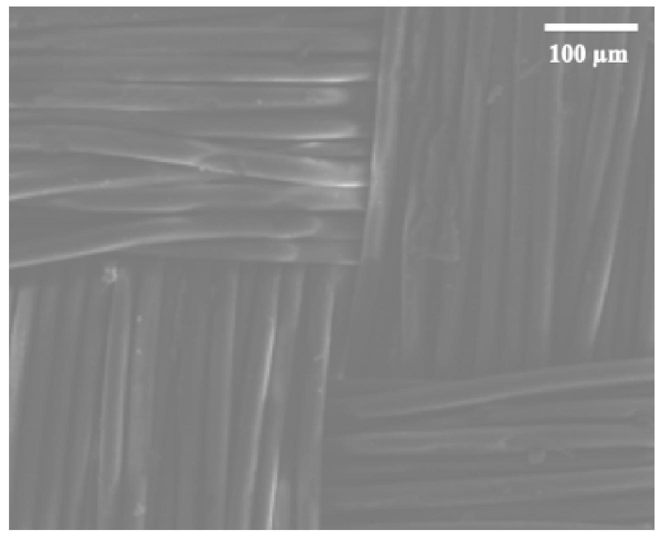

Figure 3. Structure of the Laminated Polyester Ripstop fabric at 100 µm.

The SEM image of the HEA grown copper (figure 4a and 4b) shows that the structure is highly porous and present nanoscale features for the 1000 Denier Coated Cordura Nylon fabric while for the Laminated Polyester Ripstop the copper deposition is more segregated creating a smoother structure. It is found that the shape of the nanostructures is a function of the concentration of the electrolyte and the applied voltage.

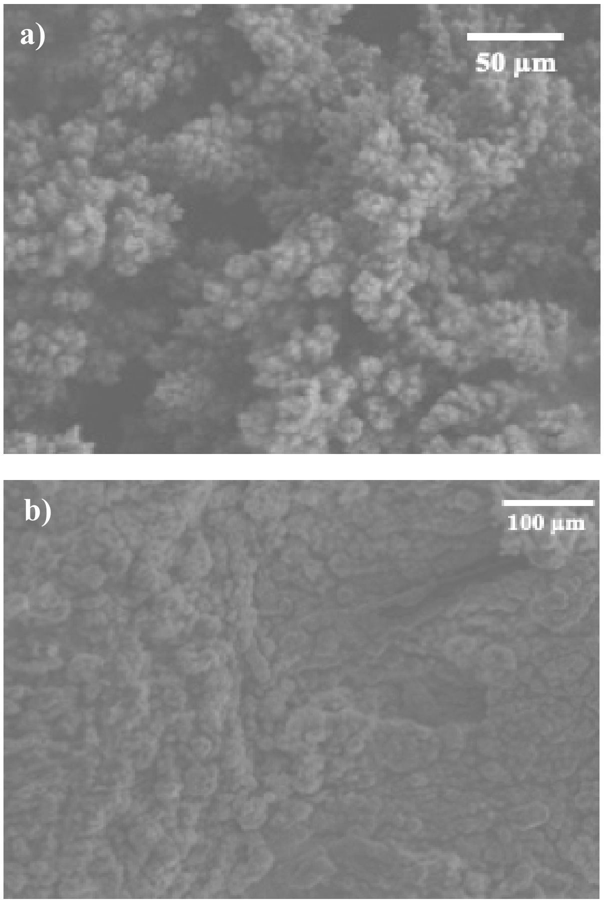

Figure 4. a) 1000 Denier Coated Cordura Nylon at 50 μm showing copper with a cauliflower structure after deposition and b) Laminated Polyester Ripstop fabrics after copper electrodeposition showing a more uniform structure with some copper agglomeration.

DISCUSSION

The proposed fabrication method aims to address some challenges in the current technologies by offering a relatively low-cost patterning of continuous high-resolution (suitable for SMDs) conductive interconnects at a high conductivity and a reliable method of soldering SMDs directly to the fabricated circuit layout. The HEA electroplating has an incredible speed of growing metals compared to the conventional electroplating generating structures of copper on the deposited area that can entangle the conductive pattern to the fabric for improving the adhesion of components and the integration of circuits. Localized HEA electroplating to develop a new approach for e-textile fabrication by integration of electronic circuits into fabrics to address the market need for smart textiles.

In a simple approach, also known as embroidered circuits, conductive yarns/threads are sewn for interconnecting the electronic elements [13]. In a more advanced level, conductive threads can be woven or knitted during the production of the fabric to make the conductive circuit layout [12,14]. Woven or knitted e-textiles are definitely more expensive and limited in the applications than additive methods for integration of electronics on already fabricated textiles. In all these approaches, the trade-off is between the flexibility of the final circuit and the conductivity of interconnects. Using metallic wires as the threads/yarns provide an excellent conductivity, but stiffness difference between wires and regular threads limits the flexibility of the final product. Using regular yarn materials, coated with conductive inks, maintains the flexibility of the fabric, but their low conductivity is not suitable for distributed electronics on fabrics; thus, the need for this work.

Many efforts have been put into fabricating wearable electronics by applying the circuit layout on fabrics with a printing method using conductive inks. Iron-on, silk screen, and inkjet printing methods have been demonstrated before [15-17]. In general, Iron-on and silk-screen patterns on fabrics have low printing resolutions not being suitable for patterning interconnects between terminals of SMDs with less than 1 mm spacing. Although the current inkjet printing technology offers high resolutions suitable for simple circuits, the conductivity of the printed patterns at high printing resolutions is too low for true e-textiles with may include embedded sensors, microprocessors, and wireless chips distributed all over the surface of a piece of clothing [15,18]. This is mainly due to the principle of printing patterns via printing droplets of ink containing metallic particles or conducting polymers. At the microscopic level, after drying the ink, only a high level of overlapping (above the percolation level [16] of the conductive particles can generate an electrically conductive pattern at the macroscopic level. In case of metallic nanoparticles, after printing, particles must be sintered [19]. Considering the dispersion of ink on the fabric fibers and a high porosity of fabrics, the yield of printing electrically continuous interconnects with high resolution is very low. For the same reason, even, at lower resolutions, the resistance of the interconnects is often too high for advanced electronics.

Localized HEA electroplating to develop a new approach for e-textile fabrication by integration of electronic circuits into fabrics has the potential to revolutionize the wearable electronics industry for production of miniaturized integrated electronics for medical, military, and recreational applications.

CONCLUSION

Copper electrodeposition assisted by the hydrogen evolution technique at voltage variation of -0.5 V to -2.0 V had shown a constant and uniform copper growth suitable for printing a circuit layout, soldering components and creating integrated circuits into fabrics. The hydrogen evolution effect was observed during the electrodeposition resulting in a dramatic increase of copper deposition while the electroplating was taking place. Due to the agglomerations of hydrogen bubbles a more porous copper structure was observed while using the 1000 Denier Coated Cordura Nylon fabric instead of a more compact structure as observed while using Laminated Polyester Ripstop fabric. Although the porous copper structure was not as uniform as we were expecting significant advantage of the HEA electroplating method can be gain from this structure. As it was shown copper electrodeposition over fabrics is a viable method which doesn't require any soldering machine to achieve a proper metal deposition facilitating the commercialization and development of several applications.

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