Microheater with Copper Nanofiber Network via Electrospinning and Electroless Deposition

Geon Hwee Kim (geonhwee.kim@chungbuk.ac.kr)
Chungbuk National University

Na Kyoung Kim
Chungbuk National University

Kanghyun Kim
Pohang University of Science and Technology

Hansol Jang
Chungbuk National University

Hyun-Joon Shin
Chungbuk National University

Taechang An
Andong National University

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Abstract

In this report, we present the development of a copper nanofiber network-based microheater, designed for applications in electron microscopes, gas sensing, and cell culture platforms. The seed layer, essential for electroless deposition, was crafted through the electrospinning of a palladium-contained polyvinylpyrrolidone solution followed by a heat treatment. This process minimized the contact resistance between nanofibers. We successfully fabricated a microheater with evenly distributed temperature by controlling the electrospinning time, heat treatment conditions, and electroless deposition time. We assessed the electrical and thermal characteristics of the microheater by examining the nanofiber density, sheet resistance, and transmittance. The microheater's performance was evaluated by applying current, and we verified its capacity to heat up to a maximum of 350 °C. We further observed the microheater's temperature distribution at varying current levels through an infrared camera. The entire manufacturing procedure takes place under normal pressure, eliminating the need for masking or etching processes. This renders the method easily adaptable to the mass production of microdevices. The method is expected to be applicable to various materials and sizes and is cost-effective compared to commercially produced microheaters developed through microelectromechanical system processes, which demand complex facilities and significant expenditure.

1. Introduction

Microheaters have found utility in a variety of applications such as gas sensors, where they elevate the temperature to facilitate the reaction between the gas and the sensing material [1]–[3]. They are also used in cell culture platforms [4], microfluidic chips [5], wearable devices [6], and as infrared sources [7]. Miniaturizable heating mechanisms typically include ultrasonic heating [8], radiative heating [9], the Peltier effect [10], and the Joule heating principle [11]. Of these, Joule heating, which involves a current flowing through a resistive wire, is the simplest.

Micro-Joule heaters necessitate high electrical resistance for efficient heating, making the selection of a suitable material crucial [9]. Frequently used metal materials include platinum [12], titanium [13], tungsten [14], gold [15], and copper [16]. Microheater substrates are primarily ceramic. For efficiency, the substrate in contact with the ground should possess low thermal conductivity, while the intermediary substrate sandwiched between the heating layer and the heat transfer material should exhibit high thermal conductivity [17].

Microheaters employing the Joule heating method typically use processes such as physical vapor deposition (PVD) [18], chemical vapor deposition (CVD) [19], and electrochemical vapor deposition (EVD) [20] to pattern elongated electrodes onto the substrate. PVD processes, including sputtering [21] and electron beam evaporation [22], are integral to semiconductor fabrication. These processes form a thin metal film on a substrate via the bombardment of ionized gas atoms on the targeted deposition material. They offer the advantage of depositing most metals and alloys in a thin layer [22].
Meanwhile, CVD involves forming a thin film on the substrate through a chemical reaction that produces the deposition material in gaseous form. Given its high adhesion to the target substrate and its applicability to most surfaces, it is a highly versatile technology [24].

EVD is a metallization method that leverages the electrolysis phenomenon, where anions move to the anode and cations to the cathode. It has recently been demonstrated to be applicable to insulators [25]. However, both PVD and CVD processes are typically conducted under vacuum [26] and to fabricate a heater, a microelectromechanical system (MEMS) process is required. While EVD requires an external power source, it suffers from the limitation of poor uniformity [27].

In certain applications, microheaters are required to be transparent. For instance, they are used in scanning transmission X-ray microscopes to heat particles loaded on a substrate to analyze their properties as a function of the annealing temperature [28]. Devices integrating a gas sensor, an LED, and a microheater have also been fabricated [29].

Transparent electrodes, boasting high transmittance and electrical conductivity, find application in displays [30] and solar cells [31]. The most widely used material for transparent electrodes is indium tin oxide (ITO). However, the increasing prominence of wearable and flexible devices has driven up the cost of ITO [30], and its high brittleness [33] is a concern. As a result, transparent electrodes can now be fabricated using carbon-based materials such as carbon nanotubes [32] and graphene [35], conducting polymers [36], composite materials [37], and metals such as gold [38], silver [39], and copper [38] in nanowire form.

Nanowires, including those made of gold [41], silver [42], and copper [41], can undergo electroless plating through oxidation–reduction reactions on the surface without any external current. The thickness and particle shape of the metal layer deposited using this method depend on factors such as pH [42], temperature [43], and deposition time [46]. The catalyst seed necessary for electroless deposition can be applied using electrospinning, a process that uses high voltage to produce micro- to nano-scale-diameter fibers from a polymer solution, driven by the repulsive force between electrical charges. The shape of the electrospun fibers can be controlled by manipulating parameters such as the viscosity of the electrospinning solution, spinning time, distance between the solution discharge and collector, and solution flow rate [45]. After seed layer application, fiber electrodes with diameters ranging from several nanometers to micrometers can be efficiently formed through electroless deposition [48], [49].

In this study, we fabricated a low-cost, transparent microheater by sequentially executing electrospinning and electroless deposition on thin silicon nitride, which is typically used in X-ray evaluation experiments. Polyvinylpyrrolidone (PVP) fibers containing palladium were electrospun, and then the PVP was removed via pyrolysis to form a seed layer. Subsequently, palladium was electrolessly plated with copper—a material gaining attention for its use in microheaters and transparent electrodes—to achieve a highly transmissive microheater. Each fabrication method can be quantitatively controlled by adjusting the process time. After applying a DC current to the fabricated microheaters, we confirmed a successful
temperature increase using an infrared camera. This fabrication method, which does not require a separate MEMS process, is anticipated to be adaptable for various materials and sizes.

2. Experimental Section

Materials

A 5-µm-thick silicon nitride membrane (Si$_3$N$_4$; frame size: 5 mm × 5 mm, membrane size: 0.5 mm × 0.5 mm) was procured from Silson Ltd. (United Kingdom), while PVP (AR grade; molecular weight, 1,300,000) powder was sourced from Alfa Aesar (USA). Copper(II) sulfate pentahydrate (CuSO$_4$·5H$_2$O; special grade, 99.5%), N,N-dimethylformamide (DMF; special grade, 99.5%), sodium hydroxide (NaOH; special grade, 98.0%), ammonium tetrachloropalladate(II) ($\text{NH}_4\text{H}_2\text{PdCl}_4$; 99.998% metal basis), and potassium sodium tartrate tetrahydrate (KNaC$_4$H$_4$O$_6$·4H$_2$O) were procured from Sigma-Aldrich (USA). Formaldehyde solution (HCHO; 36.0–38.0%) was acquired from Wako Pure Chemical Industries, Ltd. (Japan). All reagents were used as received, without any purification.

Characterization

The morphology of the nanofbers at different process stages was observed using an optical microscope (ECLIPSE LV150N; Nikon, Japan) and a field emission scanning electron microscope (FE-SEM; Ultra Plus; ZEISS, Germany). The properties of the nanofbers were analyzed with an energy dispersive X-ray spectrometer (FlatQUAD; Bruker, USA). The linewidth and area fraction of the fabricated nanofbers were measured using the ImageJ software (NIH, USA). The transmittance of the nanofber structures, as a function of copper deposition time, was measured in the spectral mode of an ultraviolet–visible spectrophotometer (OPTIZEN POP-V; JASCO, Japan), using a bare silicon nitride membrane as the reference. The surface resistance of the heat-treated/metallized nanofber structure was measured using a four-point probe method (CMT-SR2000 N; AIT Co., Korea). To verify the performance of the fabricated microheater, a current was applied from a current source (2231A-30-3 Triple Channel DC Power Supply; Keithley, USA), and the resulting heating temperature was determined. The temperature distribution was observed using an infrared camera (FLIR A655sc 25°; Teledyne FLIR, USA) and the FLIR ResearchIR Max software (Teledyne FLIR, USA).

Palladium seed layer deposition by electrospinning

An electrospinning solution was prepared by adding 0.3 g of ammonium tetrachloropalladate(II) and 3 g of PVP to 10 mL of DMF. This mixture was stirred at 300 rpm for 24 hours using a vortex mixer. The silicon nitride membrane was used as a substrate and attached to the collector. Electrospinning was performed by applying 10 kV for 30 seconds, while maintaining a 10-cm distance between the syringe tip and the collector. During this process, relative humidity was kept between 40–50% and the temperature was controlled at 25–30 °C (Fig. 1A). Subsequently, the electrospun fibers were heat treated at 300 °C for 30 minutes to consolidate the intersection junctions and degrade the PVP gradually, forming a palladium seed layer (Fig. 1B).
Copper nanofiber formation by electroless deposition

Following seed layer deposition, a copper conductive layer was grown on the palladium-embedded seed layer. The copper electroless deposition solution was prepared by dissolving formaldehyde, sodium hydroxide, potassium sodium tartrate tetrahydrate, and copper(II) sulfate pentahydrate in deionized water at concentrations of 0.1 mL/mL, 40 mg/mL, 140 mg/mL, and 30 mg/mL, respectively. In this mixture, formaldehyde served as a reducing agent to supply electrons, sodium hydroxide was used to adjust the pH, potassium sodium tartrate tetrahydrate functioned as a complexing agent, and copper(II) sulfate pentahydrate supplied copper metal ions. The chemical equation for copper electroless deposition is as follows:

\[
\text{Cu}^{2+} + 2\text{HCHO}^+ + 4\text{OH}^- \rightarrow \text{Cu}^{+2}\text{HCOO}^- + 2\text{H}_2\text{O} + 2\text{H}_{\text{ads}}
\]

The copper electroless deposition process underwent the Cannizzaro reaction for 2 minutes on a digital shaker at 50 rpm, at room temperature (Fig. 1C). A conductive wire was gently placed on a silicon nitride membrane and an electrical connection was established with a macroelectrode and silver paste (Fig. 1D-1F).

3. Results and Discussion

Analysis of morphological, electrical, and optical properties of the microheater

Electrospun nanofibers are subsequently metallized via an electroless deposition process and transformed into microheaters. These microheaters operate on the principle of Joule heating, where thermal energy is produced upon the application of external electrical energy [50]. High performance in microheaters can be evaluated by their ability to generate high temperatures under low power [53]. Dense geometry in the nanofibers is beneficial for thermal stability and heat transfer, as an increase in the percentage of the metal fiber network deposited on the substrate results in a higher generation of thermal energy [52]. Figure 2 depicts an optical microscope image that shows the distribution of PVP-palladium nanofibers collected on a silicon nitride membrane as a function of electrospinning time. Since the quantity of fibers collected varied with the electrospinning time, we compared them to ascertain optimal conditions. The optical image was digitized with a threshold to compute the fiber distribution ratio. As demonstrated in Fig. 2C, a sufficient number of nanofibers were efficiently collected at 30 seconds.

Figure 3 presents the electrical and optical characteristics of fabricated microheaters. Figure 3A shows the variation in surface resistance of the microheater with respect to heat treatment time on a logarithmic scale. From 3 to 10 minutes, the surface resistance of the microheater decreased rapidly with increasing heat treatment time, eventually saturating at 5.71 Ω/sq, representing an 89.9% decrease. This trend was attributed to the elimination of intersections between nanofibers during heat treatment, and the formation of a seed layer with stably embedded palladium as the PVP component in the fibers decomposed due to heat.
Figure 3B displays the variation in surface resistance of the microheater with respect to heat treatment temperature and time. The blue and red dots represent heat treatment times fixed at 30 and 60 minutes, respectively, with the heat treatment temperature rising from 200°C to 350°C. For 30 minutes at 200–300°C, the microheater’s surface resistance decreased from 12.42 to 5.5 Ω/sq as the annealing temperature increased, before increasing to 6.38 Ω/sq at 350°C. Similarly, for 60 minutes at 200–300°C, the microheater’s surface resistance decreased from 13.39 to 8 Ω/sq as the annealing temperature increased, but then rose to 9.98 Ω/sq at 350°C. This suggests that overlaps between nanofibers and PVP components are effectively removed and decomposed as the heat treatment temperature rises, but the resistivity gradually increases beyond a certain temperature.

Figure 3C shows the variation in surface resistance of the microheater with respect to the copper electroless deposition time. From 30 to 90 seconds, the microheater’s surface resistance gradually decreased from 1.36 to 1.34 Ω/sq with increased deposition time, and then sharply fell to 0.22 Ω/sq after 120 seconds. As the electroless deposition time increases, the thickness and linewidth of copper growing on the palladium-embedded seed layer increase, leading to enhanced electrical conductivity [53].

Figure 3D presents the transmittance of the microheater as a function of copper electroless deposition time, across a wavelength range of 300–900 nm. When electrospun nanofibers of the same density were electrolessly plated for 30, 60, 90, 120, 150, or 180 seconds, the microheaters exhibited average transmittance of 98.09%, 94.44%, 77.2%, 49.8%, 38.61%, and 14.50%, respectively. As the electroless deposition time increased, the quantity of copper deposited increased, resulting in a gradual decrease in transmittance. From Figs. 3C and D, it is evident that the surface resistance of the microheater and the transmittance in the visible region can be controlled by adjusting the electroless deposition time.

Figure 4 presents the changes in nanofiber morphology during the fabrication stages of the microheater. Figure 4A, A’ displays the morphology of PVP-palladium nanofibers electrospun onto a silicon nitride membrane. Figure 4B, B’ presents the seed layer with a reduced linewidth due to the thermal degradation of PVP. The intersections occurring between nanofibers were also eliminated [53]. Figure 4C, C’ illustrates the nanofiber network fabricated through 2 minutes of electroless deposition, with a significant increase in linewidth. Figure 4D demonstrates the variation in nanofiber linewidth according to the microheater fabrication steps. The PVP-palladium nanofibers fabricated by electrospinning averaged 505.45 nm, which decreased to 183.25 nm after heat treatment due to PVP decomposition. After 2 minutes of copper electroless deposition, the linewidth expanded to 1296.57 nm. Figure 4E displays the variation in nanofiber linewidth with copper electroless deposition time. The linewidth increases with increasing electroless deposition time.

Performance evaluation of microheater

Figure 5 presents an evaluation of the final microheater performance. Figure 5A displays the temperature of the microheater as a function of current. When a constant current was applied, the temperature rose and then remained stable within less than 5 seconds; the average temperatures recorded were 70 °C, 130 °C, 200 °C, and 350 °C when the current of 0.2 A, 0.4 A, 0.6 A, 0.8 A was applied, respectively. The
microheater reached a maximum temperature of 353 °C at a current of 0.8 A, after which the silicon nitride membrane melted and the microheater broke. Figure 5B displays the final temperature distribution across each section during current application, captured using an infrared camera. In Fig. 5B I, II, III, and IV, final temperatures of 70 °C, 130 °C, 200 °C, and 350 °C were achieved in each section at a current of 0.2, 0.4, 0.6, and 0.8 A, respectively. The infrared temperature distribution from I to IV gradually shifted from purple to white, confirming the high uniformity of heating. This process enabled the fabrication of a high-efficiency microheater with a fast thermal response and high heating temperature, even at low power.

4. Conclusion

In this study, we fabricated a microheater with a nanoscale pattern on a thin silicon nitride membrane through three steps: electrospinning, heat treatment, and electroless deposition. Given that all three steps are carried out at atmospheric pressure, this method is simpler than conventional metal patterning techniques such as PVD and CVD. The process is also well-suited for mass production due to the large-area applicability of electrospinning. Notably, the nanofiber web generated by electrospinning undergoes metallization via an electroless deposition process, which is performed without the need for a separate power source. This offers a major advantage as it eliminates the need for separate masking, etching, and control technologies.

Additionally, the formation of a web structure by fibers with nanoscale diameters endows the microheater with superior electrical efficiency and high mechanical strength compared to commercial microheaters that feature a single conductor structure. We found that the electrical and optical properties of the microheater could be easily modulated by controlling factors such as the nanofiber density, electrospinning duration, heat treatment time and temperature, and electroless deposition duration. The final microheater exhibited rapid thermal response characteristics and high heating performance, with a maximum temperature of approximately 350 °C as determined by comparing temperature changes under various currents.

In the future, we anticipate that microheaters for various applications will be fabricated by modifying the geometry of the electrospun nanofiber web, possibly by introducing a method such as passivation masks, or enhancing the performance of the microheater through the application of different metals like gold, silver, or tungsten. The microheaters and fabrication process discussed in this study hold promise for use in applications requiring localized heating such as gas sensors, electron microscopes, fuel cell heat sources, and electronics heating. We expect that these applications could further extend to advanced areas such as solar cells, displays, and wearable devices when deployed on flexible transparent substrate materials.

Declarations

Data availability
The datasets generated during the current study are available from the corresponding author on reasonable request.

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References


Figures

Figure 1

Schematic of the microheater fabrication process. (A) Electrospinning of PVP-palladium nanofiber onto a silicon nitride membrane. (B) Creation of a palladium-embedded seed layer through heat treatment. (C) Copper electroless deposition on the palladium-embedded seed layer using a chemical reaction. (D) Placement of a conducting wire on the copper-deposited nanofibers. (E) Application of pressure via a resin stone to firmly bond the conducting wire to the copper-deposited nanofibers. (F) Final, fabricated microheater.
Figure 2

Comparison of fiber density against the electrospinning time: (A) 5 seconds, (B) 10 seconds, (C) 30 seconds, and (D) 60 seconds. The small numbers and images illustrate the mean ratio of the area occupied by the nanowire to the total area, and the black-and-white image (n = 5).
Figure 3

Analysis of the electrical and optical properties of the microheater. (A) Correlation between sheet resistance and heating time (log scale). (B) Correlation between sheet resistance and heating temperature. (C) Correlation between sheet resistance and transmittance in the visible range of 300–900 nm. (D) Correlation between sheet resistance and electroless deposition time. n = 5. Error bars represent the standard error.
Figure 4

Analysis and morphologies of the nanofibers depending on the overall fabrication steps. (A, A') Optical and FE-SEM image of the electrospun PVP-palladium nanofibers. (B, B') Optical and FE-SEM image of the palladium-embedded seed layer heated at 300°C for 30 minutes. (C, C') Optical and FE-SEM image of electroless Cu-deposited nanofibers. (D) Copper nanofiber width at each process step. (E) Correlation between electroless deposition time and copper nanofiber width. n = 5. Error bars represent the standard error.
Figure 5

Performance evaluation of the microheater. (A) Correlation between the duration of applied current and microheater temperature. Various currents were applied to the microheater and the resulting temperature changes were recorded. The dotted line represents the time of constant current change. (B) Infrared imaging camera observation of the microheater at 70 °C (I), 130 °C (II), 200 °C (III), and 350 °C (IV).