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Low-temperature sintering of silver nanoparticles on paper by surface modification



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Abstract

Ultralow-temperature sintering plays a vital role in the development of flexible printed electronics, which improves flexibility and reduces energy consumption. This study investigates the ultralow-temperature sintering of large-sized silver nanoparticles (Ag NPs) by laser modification of the substrate surface. Ag NPs in conductive ink were sintered at only 60 °C. Designing the appropriate size of modified regions, the sintered Ag layer exhibits a sheet resistance of only 0.274 Ω and withstands 10 000 folding cycles. Energy-dispersive x-ray spectroscopy showed that TiO₂ formed by laser ablation promotes the sintering of Ag NPs and joining with the substrate. A paper-based flexible integrated circuit board was also prepared.

Supplementary material for this article is available online

Keywords: paper-based flexible printed electronics, low-temperature sintering, laser modification, silver nanoparticles, TiO_2

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, flexible electronics have drawn considerable attention owing to potential developments in wearable electronics and flexible displays [1–15]. Advances in flexible electronics have created a large demand for flexible substrates, such as polyimide, polyether ether ketone, and polyester films [16, 17]. Flexible electronics markets have thus searched for thin, eco-friendly, low-cost, and easy-to-print print substrates with improved performance [18, 19].

Paper is particularly ideal because it is low-cost, wellestablished in printing, biodegradable, and can be bent or folded [20–28]. Electronic patterns can be fabricated onto the paper substrate by printing. Meanwhile, printing of deposited materials can be improved using several methods, including coating [29] and electroless deposition of metals [30]. In the current study, pre-coated commercial paper, also referred to as high-temperature resistant paper, is selected as the flexible electronic substrate.

Most studies have focused on metal ink that can be directly printed on paper. Printed patterns are then sintered to achieve improved conductivity. The ignition point of paper is about 130 °C; thus, a low sintering temperature for metal ink is needed [31]. Metal nanoparticle (NP) inks, such as the Cu

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NP ink [32], Au NP ink [33], and Ag NP ink [34], exhibit considerably high conductance and enhanced antioxidation. Compared with Cu, Ag possesses higher conductivity and thermal stability; in addition, Ag has an advantage over gold with respect to cost. Thus, the present study was aimed at preparing Ag NP ink by synthesizing Ag particles (the size of Ag NP is about 50 nm) and mixing the particles with ethylene glycol.

To reduce the sintering temperature of the Ag NP ink printed onto a paper substrate, numerous methods have been developed, such as particle size reduction (smaller than 10 nm) [35–39], changing the chemical component of the paper surface [40, 41], infrared sintering [42], microwave sintering [43], and pressure-assisted sintering [44]. However, these studies may involve complex processes and alteration of the components of paper substrate. They do not efficiently reduce the sintering temperature, and no breakthrough in flexibility is observed.

In the current study, we adopt a method for modifying the paper substrate by surface treatment, using an ultraviolet (UV) laser marking machine to form multiple-size patterns. This method does not require different materials and only changes the chemical component of the paper substrate by physical means. The sintering temperature of the synthesized Ag NP ink based on the modified paper can be as low as 60 °C, and the conductivity of the sintered pattern developed using the aforementioned technique can remain stable after 10 000 folding cycles. This finding indicates that the flexibility of samples is significantly increased.

2. Experimental

2.1. Pulsed UV-laser surface modification

High-temperature resistant paper with a layered structure (figure 1(b)) was used as the substrate. The application of a pulsed UV laser for surface modification has become commercially viable in various fields. Periodic linear and circular patterns arrays were generated on the paper surface by using a moving table for expansive coverage. These diffraction arrays with patterns of varying sizes were formed by controlling the parameters of the pulsed UV laser, including the densities of current, speed, frequency of laser, and pulse width. These patterns were used to adjust the distribution of the composition on the substrate surface. Figure 1(d) shows the fieldemission scanning electron microscopy images of the patterns, which consist of patterns with varying diameters (d) and a space between the patterns (D). In this study, we prepared six kinds of patterns with the following parameters: $d = 10 \,\mu\text{m}$ with $D = 30, 50, 70 \,\mu\text{m}$ and $d = 20 \,\mu\text{m}$ with $D = 50, 70, 90 \,\mu\text{m}.$

2.2. Preparation of silver nanoparticle ink

We synthesized Ag particles in an aqueous solution by reducing the Ag nitrate in the presence of hydrazinium hydrate and polyvinylpyrrolidone (PVP). An illustration of the detailed preparation process is provided in our previous study [45]. Using a multistep procedure, we first mixed these components to create a population of Ag NPs. The particles were coated with organic capping molecules (PVP). PVP not only facilitates the dispersion of Ag NPs but also prevents the aggregation of Ag NPs under normal storage conditions. The reaction products were then centrifuged at 4000 r for 5 min to achieve high solid loading. The Ag particles were subsequently redispersed in ethanol to remove the PVP capping agent and were again concentrated by centrifugation. This process was repeated three times, thereby reducing the thickness of the capping agent. Although the PVP coating could prevent severe agglomeration of Ag NPs, the process of cleaning the PVP coating plays an important role in lowtemperature sintering, considering that PVP is difficult to remove at 60 °C to initiate sintering. The Ag particles were ultimately set in a drying oven to remove the residual ethanol and water. Figure 1(f) presents the bright-field scanning electron microscopy (SEM) image of the as-prepared Ag NPs, which mostly exhibit a spherical shape with a mean size of 50 nm. The Ag NP ink was composed of Ag NPs and ethylene glycol, and their weight rate ranged between 1:3 and 1:4.

2.3. Preparation of the electrodes

Silkscreen printing was used as the coating method although no silk screen was applied. Before the coating process, the conductive ink was oscillated by ultrasound to achieve uniform dispersion. The as-prepared ink was coated on the modified substrate by silkscreen printing, followed by drying in the oven to allow the evaporation of ethylene glycol and sintering of Ag NPs. At 60 °C, 90 °C, and 120 °C, the corresponding times were 4, 3, and 2 h. After the evaporation of ethylene glycol, the Ag NPs were sintered together and then joined with the substrate.

2.4. Cycling folding test of the electrodes

The experimental setup for the cyclic bending test is illustrated in figures 1(h) and (i). By fixing one end (right) and moving another side (left) in a cyclic motion, the same bending radius is maintained.

2.5. Electrical resistance measurements

Electrical resistivity measurements were conducted using a four-probe method (Automatic Four-Point Probe Model 280SI). The electrical resistivity of each sample was measured four times, and the averages were used as the sheer resistivity of the samples.

2.6. Characterization

The microstructures and maps generated by energy-dispersive spectrometry (EDS maps) of the samples were systematically investigated by field-emission SEM. Sintering of different zones on the samples before and after bending was assessed based on the SEM image. The percentages of different



Figure 1. Schematic diagrams (a)–(g) of the fabrication process. (a) Original paper substrate and (b) its cross-sectional structure. (c) Laser ablation on the surface of the paper and (d) SEM image of the array of black patterns after ablation. (e) Coating layer of Ag NP ink on the modified substrate, and (f) SEM image of the ink. (g) Heat treatment and sintering of the sample. Optical images of the electrode before (h) and after (i) the folding test. (j) Schematic showing the A-type region and B-type region on the surface. SEM images of the entire Ag layer, A-type region, and B-type region when $d = 20 \,\mu\text{m}$, $D = 90 \,\mu\text{m}$, and $T = 60 \,^{\circ}\text{C}$ are shown in (l), (k), and (m), respectively. The SEM images of the entire Ag layer and the B type region when $d = 20 \,\mu\text{m}$, $D = 90 \,\mu\text{m}$, and $T = 120 \,^{\circ}\text{C}$ are shown in (n) and (o). (p) The initial sheet resistance of the 19 electrodes with different *d*, *D*, and *T*. (q) The percentage of well-sintered A-type region and B-type region when $T = 120 \,^{\circ}\text{C}$.

modified regions were calculated by analyzing the pixels with graphics processing software.

3. Results and discussion

3.1. Characterization and structure of the electrodes

The composition and structure of a flexible electrode sintered at low temperatures are shown in figure 1. The high-temperature-resistant paper (figure 1(a)) was used as the electrode substrate; its cross-sectional structure is shown in figure 1(b). The top layer and the middle layer mainly consisted of carbon and titanium, respectively, and the bottom layer consisted of polyimide. The ignition point of this layered structure reached $300 \,^{\circ}$ C. The surface of the paper was ablated with a laser in accordance with the preset points array, as shown in figure 1(c).

The SEM image of the modified paper are given in figure 1(d), and these dark patterns were the ablative area. The heat generated by the laser causes the temperature at the array position to rise at an extremely high rate, resulting in the oxidation of surface components. The conductive ink was then coated on the modified substrates, as shown in figure 1(e). The SEM image of the Ag NPs in the conductive ink is presented in figure 1(f). The diameter of Ag NPs was \sim 50 nm, and many of the gaps between these particles were smaller than 10 nm. After coating, the sample was stored in a drying oven (figure 1(g)), and the residual ethylene glycol completely evaporated. These Ag NPs were sintered together, and a flexible electrode was obtained.

The optical image of the electrode is shown in figure 1(h), with the sintered Ag layer as the central square area. Notably, the method used during flexible property testing was folding, indicating that the deformation angle of the electrode was 180° , as shown in figure 1(i). High-reliability joining between the Ag layer and the substrate ensured that the electrode could withstand the rigorous folding test.

Sintering and joining Ag NPs showed different states in the modified region (dark patterns) and the unmodified region. Not all dark patterns resulted in reliable joining with the Ag layer. The same occurrence was true for the unmodified region. The patterns that joined reliably with the wellsintered Ag layer were defined as the A-type region, and the unmodified regions that joined reliably with the well-sintered Ag NPs were defined as the B-type region, as shown in figure 1(j).

Figure 1(1) presents the SEM images of the entire sintered Ag layer with the diameter of the dark patterns (d) equal to 20 μ m, the central distance of two round patterns (D) equal to 90 μ m, and the sintering temperature (*T*) set to 60 °C. For the A-type region (figure 1(k)), Ag NPs were sintered together and joined with the particles in the modified substrates, thereby achieving the desired conductivity and reliable joining. For the B-type region (figure 1(m)), the Ag particles were sintered into a weak network. Such a slightly continuous Ag layer damaged the electrical conductivity.

Figure 1(n) presents the SEM images of the entire sintered Ag layer when $d = 20 \,\mu\text{m}$, $D = 90 \,\mu\text{m}$, and $T = 120 \,^{\circ}\text{C}$. Ag NPs could be sintered into a highly continuous Ag layer without other modifications because the sintering temperature was considerably higher than the previous treatment. Therefore, the B-type region showed an Ag layer with low porosity, as shown in figure 1(o).

The electrical properties of the prepared electrodes are shown in figure 1(p). The initial sheet resistance (R_0) of all electrodes were lower than 7Ω , suggesting the superior conductivity of flexible electrodes in this study. However, the size of the patterns largely affected the resistance. Regardless of the sintering temperature, the sheet resistance values were consistently the lowest, $<1 \Omega$, when $d = 20 \mu \text{m}$, $D = 70 \mu \text{m}$, and 90 μ m. Even though the sintering temperature was only 60 °C, the resistance was as low as 0.274 Ω . By contrast, the values of the resistance were highest at any sintering temperature when $d = 10 \,\mu\text{m}$, $D = 50 \,\mu\text{m}$, and $70 \,\mu\text{m}$. When T = 60 °C, the highest initial resistance of the electrodesthat is, $6.745 \,\Omega$ —was achieved. For the electrode with an unmodified substrate, the Ag particles could only be sintered at 120 °C, and the electrical resistance was higher than that of all electrodes with the modified substrates. These results indicated that the electrode could be sintered at a low temperature with the best conductivity when $d = 20 \,\mu \text{m}$ and $D = 70 \,\mu \text{m}$ or 90 μm .

A small number of patterns and unmodified regions were not joined with the Ag NPs and thus could not contribute to the conductivity. Therefore, the percentage of the A region in all patterns and the percentage of the B-type region in all unmodified regions were valuable parameters for measuring the electrical conductivity of the electrodes. The resistance of the electrodes is shown in figure 1(q) when $d = 10 \,\mu\text{m}$ and $D = 70 \,\mu\text{m}$. As the sintering temperature decreased, the percentages of the A and B regions decreased monotonically. At the same temperature, the percentage of the A region was always higher than that of the B region, which proved that laser modification significantly improved the sintering performance. The resistance of the electrodes when $T = 120 \text{ }^{\circ}\text{C}$ is shown in figure 1(r). For all pattern sizes, the percentage of the A region was always higher than that of B. The increase in pattern diameter contributed more to Ag NP sintering. Therefore, the percentage of the A region with a diameter of 20 μ m was always higher than that with a diameter of 10 μ m.

3.2. Folding test

To evaluate their flexibility, electrodes with patterns of varying sizes and sintering temperatures were subjected to extreme folding cycle test, as shown in figure 2. Figure 2(a) shows the ratio of the sheet resistance (R_s) of the electrodes to R_0 during the folding cycles when $d = 10 \,\mu\text{m}$ and $D = 30 \,\mu\text{m}$. The resistance of the electrode sintered at 60 °C increased rapidly during the initial 100 folding cycles, and R_s/R_0 reached 7.092. In the subsequent 1900 cycles, the ratio fluctuated within the 2.093–3.925 range and reached 3.062 until failure occurred. For the electrode sintered at 90 °C, R_s increased rapidly during the initial 50 folding cycles, and



Figure 2. Electrical property testing of samples with patterns of varying sizes and sintering temperatures during thousands of bending and folding cycles (a)–(f).

 $R_{\rm s}/R_0$ reached 7.395. In the subsequent 1950 cycles, the ratio fluctuated within the 3.844–5.267 range and reached 3.896 after 2000 folding cycles. For the electrode sintered at 120 °C, no significant change in $R_{\rm s}$ occurred after 2000 folding cycles. The $R_{\rm s}/R_0$ fluctuated within the 1.000–1.383 range and reached 1.073 after 2000 folding cycles. Therefore, the flexibility and electrical properties of the electrode sintered at 60 °C were higher than those of the electrode sintered at 90 °C. Although the sintering temperature could be reduced to lower than 120 °C at this pattern size ($d = 10 \,\mu$ m and $D = 30 \,\mu$ m), the electrical properties deteriorated.

Changes in R_s/R_0 during the folding cycles when $d = 10 \ \mu\text{m}$ and $D = 50 \ \mu\text{m}$ are shown in figure 2(b). For the electrode sintered at 60 °C, resistance increased to 12.806 after only 3 folding cycles and then failure occurred. For the electrode sintered at 90 °C, R_s increased rapidly during the first 70 folding cycles, and R_s/R_0 reached 6.883. In the subsequent 1930 cycles, the ratio fluctuated in the 4.193–6.089 range and reached 6.089 after 2000 folding cycles. For the electrode sintered at 120 °C, R_s/R_0 reached 4.396 during the first 50 folding cycles. In the subsequent 1950 cycles, the ratio fluctuated within the 1.974–2.845 range and reached 2.823 after 2000 folding cycles. Therefore, the flexibility and electrical properties of the electrode with these pattern sizes, sintered at 60 °C, were inferior.

The resistance values of the electrodes sintered at 90 $^{\circ}$ C and 120 $^{\circ}$ C were also relatively high.

Changes in R_s/R_0 during the folding cycles when $d = 10 \,\mu\text{m}$ and $D = 70 \,\mu\text{m}$ are illustrated in figure 2(c). For the electrode sintered at 60 °C, failure occurred after only 1 folding cycle. Meanwhile, the electrode sintered at 90 °C achieved R_s/R_0 equal to 3.590 after 3 folding cycles. The electrode sintered at 120 °C achieved R_s/R_0 equal to 7.559 during the first 50 folding cycles. In the subsequent 1950 cycles, the ratio sharply fluctuated within the 3.333-5.036 range and reached 4.765 after 2000 folding cycles. Thus, electrodes with this pattern size ($d = 10 \,\mu\text{m}$ and $D = 70 \,\mu\text{m}$) could hardly lower the sintering temperature of Ag NPs. Predominant flexibility and resistance of electrodes were not achieved when the sintering temperature was set to 120 °C. Therefore, when the diameter of the patterns was 10 μ m, the electrodes could only withstand up to 2000 folding cycles. With an increase in distance at the center, the paper-based flexible electrodes became more difficult to prepare at considerably low sintering temperatures.

By increasing the diameter of the patterns to 20 μ m, prominent flexibility was achieved, and the electrodes could withstand 10 000 folding cycles. Figure 2(d) shows R_s/R_0 during the folding cycles when $d = 20 \,\mu$ m and $D = 50 \,\mu$ m. For the electrode sintered at 60 °C, the resistance increased slowly, and R_s/R_0 reached 3.137 after 10 000 folding cycles. Notably, no sharp fluctuations occurred in the early stages of the folding cycle, indicating that excellent sintering of Ag NPs and high reliability of joining with the substrate were achieved under such conditions. For the electrode sintered at 90 °C, R_s increased rapidly during the initial 90 folding cycles, and R_s/R_0 reached 7.056. In the subsequent 9910 cycles, the ratio fluctuated within the 4.159–10.177 range and reached 6.541 after 10 000 folding cycles. For the electrode sintered at 120 °C, R_s increased sharply during the initial 200 folding cycles, and R_s/R_0 reached 8.850. In the subsequent 9800 cycles, R_s/R_0 fluctuated within the 4.153–8.737 range and reached 8.737 after 10 000 folding cycles. Therefore, for electrodes with the aforementioned pattern sizes, the sintering temperature could be reduced to 60 °C, and electrodes with predominant flexibility, cyclic stability, and electrical conductivity could be successfully obtained.

 $R_{\rm s}/R_0$ during the folding cycles when $d = 20 \,\mu{\rm m}$ and $D = 70 \,\mu\text{m}$ is shown in figure 2(e). For the electrode sintered at 60 °C, the resistance increased slowly, and R_s/R_0 reached 7.182 after 10 000 folding cycles. No sharp fluctuations and occurred in the early stages of the folding cycles. For the electrode sintered at 90 °C, R_s fluctuated during the initial 35 folding cycles, and R_s/R_0 reached 4.147. In the subsequent 9965 cycles, the ratio increased slowly, and after 10 000 folding cycles, the ratio reached 5.790. For the electrode sintered at 120 °C, R_s increased sharply during the initial 70 folding cycles, and R_s/R_0 reached 8.238. In the subsequent 9930 cycles, R_s/R_0 fluctuated and reached 21.276 after 10 000 folding cycles. For electrodes with the aforementioned pattern sizes, the sintering temperature could also be lowered to 60 °C; however, electrodes sintered at 90 °C exhibited predominant flexibility, cyclic stability, and electrical conductivity.

 $R_{\rm s}/R_0$ during the folding cycles when $d = 20 \,\mu{\rm m}$ and $D = 90 \,\mu\text{m}$ is shown in figure 2(f). For the electrode sintered at 60 °C, the resistance increased markedly during the initial 90 folding cycles, and R_s/R_0 reached 4.772. Subsequently, $R_{\rm s}/R_0$ fluctuated, reaching 8.927 after 2500 folding cycles, and then failure occurred. For the electrode sintered at 90 °C, the resistance increased rapidly during the initial 130 folding cycles and $R_{\rm s}/R_0$ reached 4.227. In the subsequent 9870 cycles, the ratio increased slowly and reached 6.115 after 10 000 folding cycles. For the electrode sintered at 120 °C, R_s increased during the initial 130 folding cycles, and R_s/R_0 reached 2.664. In the subsequent 9870 cycles, R_s/R_0 fluctuated within the 2.148-6.028 range and reached 5.368 after 10 000 folding cycles. For electrodes with the aforementioned pattern sizes and sintered at 120 °C, fine flexibility and electrical conductivity were achieved. Therefore, the increase in d and decrease in D resulted in a well-sintered Ag layer and reliable joining with the substrate, obtaining highly flexible conductive electrodes. The optimal values of the pattern sizes were $d = 20 \,\mu\text{m}$ and $D = 50 \,\mu\text{m}$.

3.3. Joining mechanism between the silver and substrate

The joining of the Ag layer to the substrate before and after folding cycles are presented in figure 3. For the six electrodes sintered at 60 °C (figure 3(a)), the percentage of the A region ranged from 70.87% to 98.15%. Electrodes with $d = 20 \,\mu\text{m}$ showed a high percentage of the A region (>93.33%). When $d = 10 \,\mu\text{m}$, this percentage was reduced to 70.87%. For the



Figure 3. Initial percentage of the A region (a) and B region (c). Decrease in percentage of the A region (b) and B region (d) after thousands of folding cycles.

six electrodes sintered at 90 °C, the percentage of the A region ranged from 79.29% to 100.00%. Electrodes with $d = 20 \,\mu \text{m}$ showed a high percentage of the A region (>97.77%). When $d = 10 \,\mu$ m, the aforementioned percentage was lowered to 79.29%. For the six electrodes sintered at 120 °C, the percentage of the A region was higher than 94.67%. Sintering and joining were slightly reduced by lowering the sintering temperature and decreasing the pattern diameter. The percentage of the A region after thousands of folding cycles is shown in figure 3(b). For the six electrodes sintered at 60 °C, the remaining percentage of the A region ranged from 45.83% and 98.14%. The electrode with pattern sizes equal to $d = 20 \,\mu \text{m}$ and $D = 50 \,\mu \text{m}$ exhibited strong joining, considering that the percentage of the A region slightly decreased from 97.98% to 95.96%. For the six electrodes sintered at 90 °C, the percentages of the A region ranged from 65.04% to 93.93%. The electrode with pattern sizes equal to $d = 20 \,\mu\text{m}$ and $D = 50 \,\mu\text{m}$ also exhibited strong joining because the percentage of A region slightly decreased from 97.77% to 93.93%. For several electrodes sintered at 120 °C, the percentage of the A region decreased from 96.11% to 36.89%, indicating that the flexibility of the electrode deteriorated as the sintering temperature increased. For the electrodes sintered at low temperatures, only a small number of A region joinings were destroyed during the folding test.

The initial percentage of the B region is shown in figure 3(c). For the six electrodes sintered at 60 °C, the percentage of the B region ranged from 20.64% to 51.29%. Electrodes with $d = 20 \,\mu$ m achieved a higher percentage for the B region (>46.59%). This percentage was reduced to 20.64% when $d = 10 \,\mu$ m. The percentage of the B region was lower than that of the A region because the regions of the substrates between the patterns were unmodified. For the six

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Figure 4. (a) SEM images of the modified position and its vicinity. (b)–(d) show the EDS map of C, Ti, and O in regions C, D, and E. SEM images of the silver (Ag) layer before (e) and after (f) folding cycles. The wetting angles of the Ag NP ink on the modified (g) and original (h) surface of the paper.

electrodes sintered at 90 °C, the percentage of the B region ranged from 58.14% to 74.52%. The highest percentage of the B region was observed on the electrodes with pattern sizes $d = 20 \,\mu\text{m}$ and $D = 50 \,\mu\text{m}$ when $T = 60 \,^{\circ}\text{C}$ and $90 \,^{\circ}\text{C}$. For the six electrodes sintered at 120 °C, the percentage of the B region exceeded 68.78%. Sintering was slightly easier at increased temperatures. The percentage of the B region after thousands of folding cycles is shown in figure 3(d). For the six electrodes sintered at 60 °C, the remaining percentage of the B region ranged from 20.64% to 49.52%. For the six electrodes sintered at 90 °C, the percentage of the B region ranged from 44.44% and 59.69%. For the electrode with pattern sizes equal to $d = 20 \,\mu\text{m}$ and $D = 50 \,\mu\text{m}$, the percentage of the B region slightly decreased from 51.29% to 49.52% when $T = 60 \degree C$ and from 74.52% to 58.34% when T = 90 °C. For several electrodes sintered at 120 °C, the remaining percentage of the B region ranged from 54.17% to 69.92%, which was the highest percentage achieved under the three sintering temperatures. As to the unmodified substrate, the electrode was sintered at 120 °C, and the percentage of the B region was reduced from 40.52% to 37.17%, which was lower than those of the electrodes with modified substrates. For electrodes sintered at low temperatures, only few instances of B region joining were destroyed during the folding test.

The results in figures 2 and 3 demonstrated that the adhesion of the silver layer was indeed significantly optimized by the modified paper substrate. More reliable adhesion leads to lower resistance and higher flexibility. By contrast, the unmodified substrate did not allow the electrode to exhibit excellent electrical properties in the flexibility test.

In general, the increase in d and the reduction in D could lead to significant percentage increases in the A and B regions, which promoted the sintering of Ag NPs and enhanced the joining between the Ag layer and the substrate. Thus, the electrodes exhibited predominant flexibility and stable electrical conductivity.

3.4. Surface morphology

The effect of laser modification on the substrate was evaluated; the SEM image is presented in figure 4(a). The area directly ablated by the laser was defined as the C region. The location adjacent to the Area C was a heat-affected zone, defined as Region D. The gray area above Region D was the original surface of the substrate, defined as Region E. The distribution of carbon, titanium, and oxygen in these three regions is illustrated using EDS maps, as shown in figures 4(b)–(d). The titanium was mainly distributed in Region C, and the carbon was mainly distributed in Region E. Region D was affected by the intense heat of the laser; thus, the carbon and titanium coexisted here. Oxygen was mainly distributed in Regions C and D. A schematic cross-section of the substrate is presented in figure 1(b). The titanium of the intermediate layer was covered by carbon on the top layer; thus, the EDS map of the unmodified region (Region E) mainly consisted of carbon. Laser ablation induced the oxidation of carbon and titanium. Carbon dioxide was volatilized, leaving titanium dioxide (TiO₂) in Regions C and D. The presence of TiO₂ effectively lowered the sintering temperature of the Ag NPs, and strong joining between the well-sintered Ag layer and the substrate was achieved. Therefore, Ag NPs were sintered at 60 °C, achieving sheet

resistance of only 0.274 Ω , and the electrode withstood more than 10 000 folding cycles.

The excellent sintering of the electrodes was mainly attributed to the TiO₂ caused by surface modification rather than by the incidentally rougher surface. In sintering processes, transport of atoms (ions) across grain boundaries is very important. The N-type Schottky barrier is formed at the grain boundary interface between the TiO₂ layer and the Ag layer [46]. The work function of Ag (4.3 eV) is larger than that of TiO₂ (3.2 eV) [47, 48]; thus, electrons are transferred from the TiO₂ layer to the Ag layer. Therefore, Ag particles have negative potential, whereas TiO₂ particles have positive potential. The electric field is then established. Negative particles and positives particles transfer to each other because of the electric field thereby obtaining low-temperature sintering and high-strength interfaces between the Ag coating and the substrate.

The SEM images of the initial Ag layer sintered at 60 °C are shown in figure 4(e). Some gaps were found in the layer. After thousands of folding cycles, more gaps appeared in the A-type and B-type regions, as shown in figure 4(f). The increase in number of gaps did not indicate that the Ag layer fell off the substrate but that the Ag and the joined TiO₂ were displaced during folding. Owing to the poor flexibility of the Ag itself, these gaps provided a space for the deformation of the Ag layer. Notably, the total number of gaps was considerably small. Therefore, in the initial stages of the folding cycles test, resistance increased quickly. sharply fluctuated, and then stabilized. For the electrode sintered at 120 °C, the Ag layer exhibited excellent continuity and low electrical resistance. Consequently, a large number of cracks appeared during folding, resulting in unstable resistance and poor flexibility. The wetting angles (figures 4(g) and (h)) of the conductive ink on the modified and original surface of the substrate were 83.1° and 50.3°, respectively. Wetting angles of less than 90° allowed the Ag particles to spread more evenly over the surface of the substrate, facilitating sintering and joining.

When $d = 20 \,\mu\text{m}$ and $D = 50 \,\mu\text{m}$, the spacing between the edges of the patterns was 30 μm . Owing to the presence of the heat-affected zone (Region D), the width of Region E between the patterns was less than 30. Moreover, the lower wetting angle of region E (50.3°) was more conducive to ink distribution. Therefore, a strong bond between Ag and the modified substrate was prepared, and excellent flexibility was achieved.

3.5. Cross-section and thickness

Loss of carbon content in the Ti+C layer results in a rougher surface. Contact angle pinning induces higher contact angles with modified areas, leading to a smaller silver layer thickness than those of the unmodified areas. Figure 5(a) shows the silver thicknesses of the modified and unmodified regions. Although the silver layer thickness ($22 \mu m$) is larger because of the smaller contact angle, the silver layer is not sintered well in the unmodified region and cannot exhibit lower resistance. During bending and folding, numerous cracks and



Figure 5. SEM images show the thickness of the Ag coating layer. (a) Cross-section of the electrode with modified and unmodified regions. (b) and (c) Cross-section with modified regions. (d) EDX map of the Ag layer corresponding to the SEM image in (c).

considerable shedding of the silver layer occurred. By contrast, the rougher surface of the modified region and the higher contact angle did not affect the flexibility and electrical properties of the electrodes.

Figure 5(b) shows the cross-section of the electrode with a modified surface. The thickness of the well sintered silver layer is 13 μ m, as evaluated by the SEM and EDX map in figures 5(c) and (d). Slightly undulating thickness and flatness resulted from the uneven Ti+C layer and the knife. Regardless, the silver layer is tightly attached to the paper substrate owing to surface modification and the action of TiO₂.

To verify the thickness effect of the A regions and B regions on sheet resistance, the cross-section of the electrode was characterized. The SEM images (figure 5) demonstrate that the differences in thickness between the A regions and B regions exert less effect on sheet resistance. On the one hand, the use of laser light can remove the carbon element in the localized portion of the Ti+C layer, and the removal of a certain amount of carbon cannot induce a significant change in thickness in the modified paper substrate. On the other hand, minor changes in paper thickness caused by surface

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Figure 6. Screen-printed paper-based flexible integrated circuit board. (a) Optical photographs of surface-modified paper substrates. (b) Microscopic optical photographs of surface-modified regions. (c) Optical image of the prepared flexible circuit. (d) Schematic showing all components and placement of LEDs. (e) Circuit on operation and 'H I T' arrays of red LEDs. (f) The circuit board remains in operation during bending.

modification are almost obscured by the original roughness of the paper surface because the paper substrate itself does not exhibit absolute flatness. Therefore, the silver layer in the A region does not exhibit a greater thickness than the B region, as shown by the SEM images in figures 5(a)–(c).

3.6. Flexible circuit board

A paper-based flexible integrated circuit board was prepared. The surface modification region exhibited the same pattern as that of the circuit (figure 6(a)). The line width of the circuit pattern was 1.2 mm, and all lines were composed of pattern arrays. More than 106 patterns were prepared in this substrate. Figure 6(b) shows the microscope optical photos of the pattern arrays. Commercial silver pulp was used as conductive substances. After silkscreen printing, the device was sintered at 40 °C for 8 h. The optical image of the prepared flexible circuit is shown in figure 6(c).

The circuit design is shown in figure 6(d). A total of 15 red LEDs were arranged in the 'HIT' pattern. These LEDs were connected by a common anode, and the anode lines were marked in red. The cathode of the LED was connected in series with a fixed resistor and then connected to the pin of the chip; in addition, the associated lines were marked in green. The oscillator circuit was marked in blue. The power supply used was 5 V DC. Figure 6(e) shows an optical photo of the flexible board in operation, with 15 red LEDs showing

the 'HIT' pattern. The microcontroller continued to operate during the bending test, as shown in figure 6(f). A support video showing the work procedures of a single-chip microcomputer (SCM) is provided. First, 15 LEDs alternately turned on and off, and the alternating frequency gradually increased. The three letters (H, I, T) were then displayed alternately. HIT is short for Harbin Institute of Technology. A 'HIT' array of all LEDs were simultaneously in operation. The program was then completed. The second time we ran the program, the bending performance of the SCM circuit board were tested. The program was not affected by the bending test, proving the excellent flexibility of the circuit board.

4. Conclusion

In this study, reducing the sintering temperature of Ag NPs by laser modification of the substrate surface was studied. Six sizes of modified pattern arrays were prepared on paper substrates, and their electrical and flexible properties when the sintering temperature was set at 60 °C, 90 °C, and 120 °C were evaluated. Designed with the appropriate pattern diameter and central distance, the sintered Ag layer exhibited a resistance of only 0.274Ω and withstood 10 000 folding cycles. Compared with the original surface of the substrate, the Ag NPs in the modified region were more susceptible to sintering. The EDS maps demonstrated that TiO₂ formed by laser ablation promoted the sintering of Ag and joining with the substrate. Moreover, a paper-based flexible integrated circuit board was investigated. With predominant sintering flexibility and energy savings owing to reduced sintering temperatures, this low-temperature sintering process can be used in flexible printed electronics.

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