

Palladium-assisted Metal Patterning on Polyimide Surfaces

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Electronic Supplementary Information

Abstract A novel method of patterning high precision copper conductive micropatterns on flexible polymer substrate (polyimide) is developed. We utilized the coordination effect between palladium salts and pyridine structures to fix the palladium chloride (PdCl_2) on the surface of polymer film while the 2,6-dimethylpyridine structures formed in the specific areas under ultraviolet light guaranteed the resolution of final patterns. Simultaneous thermal reduction of PdCl_2 on the surface can be achieved in the process of thermal cyclization of the polymer substrate. As a consequence, the obtained polyimide (PI) film can be patterned with conductive copper micropatterns directly by electroless plating. In particular, we accomplished the deposition of high precision copper pattern with a minimum line width of 50 μm and minimum line spacing of 20 μm on PI thin films (thickness $\sim 10 \mu\text{m}$) by electroless plating. The prepared conductive copper micropatterns exhibit a low resistivity of 1.78 $\mu\Omega\text{-cm}$ the same as the pure block copper. And the relationship between the structures of the polymer chains and the physical properties of polymer substrates, such as the dimensional stability, mechanical and dielectric properties were also discussed in detail. This simple and novel method of patterning metal on the polymer surface does not need to achieve the catalytic metal adhesion required for electroless plating at the cost of destroying the substrate surface and avoiding the introduction of unstable interlayers. This patterning method is compatible with the current roll-to-roll production process and can be used to develop high-performance micro-integrated circuits.

Keywords Polyimide; Metal patterning; Electroless plating; Palladium chloride; Coordination effect

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INTRODUCTION

The methods of patterning conductive micropatterns on flexible polymer surfaces have widely aroused considerable interest on account of their great potential application in fabricating flexible displays,^[1] solar cell,^[2] and small intelligent wearable electronic devices.^[3] To achieve high-precision conductive metal patterns on flexible PI substrates, various advanced methods have been developed, such as lithography, printing, laser direct writing, etc.^[4–9] According to the way of forming conductive metal patterns, these methods can be divided into the subtractive method^[4,5,10] or additive method.^[6,7,11] Although it is a very mature commercial technology to prepare metal integrated circuits on PI substrates by the subtractive method, however, the steps involved in a typical subtractive method, such as a hot pressing composite of copper foil and PI films, complex lithography, and subsequent chemical etching are usually tedious and energy-consuming.^[12,13] At the same time, the adhesive layer of epoxy resin used in hot pressing is easy to be seriously delaminated with the metal layer because of the

mismatched linear coefficient of thermal expansion (CTE) problem in the high-temperature working environment.^[14,15]

The selective deposition of metals on PI substrates by the additive method can effectively reduce the complexity of the process and avoid the introduction of unstable interlayers. With the rapid development of materials and technology, and benefiting from the advantage of low cost, printing technology has become another popular new technology in large-scale manufacturing integrated circuit technology.^[6,7,16–19] However, the conductive line manufacturing realized by printing often has some problems, such as low line image resolution and poor metal adhesion, in which the incompatibility between the polymer substrates and inks is the main reason.^[20–22] Although the adhesion of inks to polymer substrates can be increased by some harsh treatment conditions, such as high temperature or plasma,^[23,24] it will inevitably cause irrecoverable damage to the flexible substrates. In addition, as another alternative simple and low-cost technology, electroless plating is often reported to be used to fabricate conductive metal lines on the PI surface.^[25–28] This method is especially suitable for manufacturing stannum (Sn), copper (Cu), silver (Ag), and nickel (Ni) metal lines because of their autocatalytic performance.^[22,29,30] The metal ions in the electroless plating bath can be deposited on the material surface in a zero-valent metal state under the action of reducing

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agents, in which the active catalytic sites on the material surface are essential.^[31,32] And the catalytic sites usually have absorbed ionic silver (Ag^+) or palladium (Pd^{2+}), and these ions need to be treated in special ways, such as laser,^[8,9,33] heating,^[34] plasma sintering,^[35] etc., to be reduced into the catalytic metals and further catalyze metal deposition on the interface between the plating bath and the film.

Although the metal ions on the catalytic sites can be fixed by surface modification or ion exchange techniques, the carboxylic acid groups commonly used for fixation of metal ions are mainly derived from hydrolysis of the surface imide ring structure of PI materials in alkaline solutions.^[26,27,36–39] Due to the uncontrollable surface hydrolysis of PI, metal ions tend to bind to the substrate surface without selectivity. Therefore, when the metal ions in one specific area are reduced, the rest of the metal ions need to be removed immediately to avoid affecting the subsequent electroless metal deposition,^[26] which will not only increase the process but also bring higher costs. Although the introduction of nitrogen-containing functional groups can also play a role in the fixation of metal ions, the indiscriminate adsorption for ions will also bring about the above problems.^[40,41]

Here, based on the coordination affinity of nitrogen to palladium, we propose to form the 2,6-dimethylpyridine structures on the polyimide precursor-polyamide acid (POP-PAA) films at the fixed regions to form specific active sites that can fix PdCl_2 . After fixing the PdCl_2 on the exposed region selectively, the PdCl_2 is synchronously thermally reduced to palladium metal, i.e., $\text{Pd}(0)$, in the process of thermal imidization of POP-PAA film. The $\text{Pd}(0)$ pattern integrated with PI film ensures the subsequent deposition of conductive metal copper patterns with high precision. In this study, the valence change of Pd^{2+} on the surface of the film during thermal imidization was characterized by X-ray photoelectron spectroscopy (XPS) combined with thermogravimetric (TGA) and Fourier transform infrared (ATR-FTIR) spectra analysis, and the profile of copper patterns after electroless plating was discussed in detail by atomic force microscope (AFM) analysis. The results show that the Cu patterns with a minimum line width of 50 μm , minimum line spacing of 20 μm and low resistivity of 1.78 $\mu\Omega\text{-cm}$ can be easily formed on the surface of thin PI films (thickness $\sim 10\ \mu\text{m}$) by this simple and convenient process, which is expected to be used in the preparation of micro/nano integrated circuits.

EXPERIMENTAL

POP-PAA Solutions Preparation (Taking POP-PAA-1 as an Example)

4,4'-Oxydianiline ether (ODA, 12.01 g) and the functional biphenylenediamine monomer (FDM, 11.09 g, the synthesis method refers to our previous work)^[25] were dissolved in *N,N'*-dimethylacetamide (DMAc, 153.5 g), and 1,2,4,5-benzenetetracarboxylic anhydride (PMDA, 15.27 g) was then added into the solution in batches. The solution was stirred at 10 $^\circ\text{C}$ for 24 h to obtain the POP-PAA-1 sample solution with a solids content of 20%. The monomers used for the synthesis of the other four POP-PAA solutions and their proportions are listed in Fig. S1 in the electronic supplementary information (ESI).

PI Samples for Routine Testing

Five kinds of POP-PAA solutions of the same volume (2.5 mL) were uniformly coated on five clean glass plates (12 cm $\times$ 12 cm) and then moved in a vacuum oven to begin the thermal imidization reaction at 80 $^\circ\text{C}/2\ \text{h}$, 125 $^\circ\text{C}/1\ \text{h}$, 165 $^\circ\text{C}/1\ \text{h}$, 200 $^\circ\text{C}/1\ \text{h}$, and 300 $^\circ\text{C}/1\ \text{h}$. When the temperature of the vacuum oven dropped to room temperature, the glass plates containing PI films were immersed in 80 $^\circ\text{C}$ deionized water. After 0.5 h, the PI films with a thickness of $\sim 10\ \mu\text{m}$ can be easily peeled off from the glass plates. Then, according to the requirements and specifications of each test, the PI films were cut into the appropriate rectangular shapes.

PI Samples for Surface Copper Deposition

POP-PAA solutions (100 μL) were uniformly coated on the clean cover slides (2.4 cm $\times$ 2.4 cm) then dried in a vacuum oven at 80 $^\circ\text{C}$ for 2 h. The obtained POP-PAA films were irradiated by UV light (24 W, 5 min) under a mask, and then the exposed films were immersed in a fresh ethanol solution of palladium chloride (0.1 mol/L) for 5 s. Finally, the POP-PAA films fixed PdCl_2 on the surface were carefully cleaned several times with anhydrous ethanol and then placed in a vacuum oven for thermal imidization.

Copper Electroless Plating

The PI samples containing $\text{Pd}(0)$ on the surface were placed in the 1 L of Cu electroless plating solution and the formaldehyde solution of 5 mL was then added under a continuous bubbling. After electroless plating for 10 min at 40 $^\circ\text{C}$, the PI samples surfaces were carefully washed with deionized water and then blow-dried with the compressed air. The composition of the Cu electroless plating solution can be found in reference.^[25]

Characterization

Photos and videos of all samples were taken by Sony camera (FDR-AX60). The micro-morphology of the samples surfaces was analyzed by the optical microscope (BKPOL, Optec), atomic force microscope (DimensionFastscan, Bruker), and the scanning electron microscope (S-4800, Hitachi). The thermal stability of the samples was determined by a thermogravimetric analyzer (TG209F1, NaiChi). The total reflection infrared spectra of the samples with different thermal imidization temperatures treatments were measured by a Fourier transform infrared spectrometer (Nicolet iS50, ThermoScientific). The transmittance of the PI thin films was measured by a UV-Vis spectrophotometer (Lambda950, PerkinElmer). The types, contents, and chemical states of elements on the surfaces of the samples were determined by X-ray photoelectron spectroscopy (XPS, ESCALab250). The linear thermal expansion coefficient and relative permittivity of PI samples below its glass transition temperature (T_g) were measured by the static thermomechanical analyzer (TA, TMAQ400) and impedance analyzer (Solartron, SI1260). The Young's modulus, tensile strength, and elongation at break of five kinds of PI samples were measured by a microcomputer-controlled electronic universal testing machine (ETM202A, WANCE). The electrical property of the copper patterns deposited on the surface of the PI films was measured by a multimeter (CHY, A830L).

RESULTS AND DISCUSSION

The developed fabrication process for the high precision

formation of copper conductive patterns on polyimide (PI) substrates by electroless plating is schematically shown in Fig. 1(a), which consists of steps 1–4 (the preparation of the functional substrates has been fully described in the experimental section): (1) the school badge pattern of Sun Yat-sen University was exposed on the functional POP-PAA films by mask method with UV light (365 nm). (2) Fixation of PdCl_2 at the exposed position. (3) The POP-PAA films experienced a programmed heating step of thermal imidization to become PI films. (4) Deposition of copper on the PI films' surface by electroless plating. Specifically, under UV irradiation, the structure of 1,4-dihydropyridines on the films' surface can be decomposed into 2,6-dimethylpyridinium structures, which can further fix the PdCl_2 in the ethanol solution due to the coordination of pyridines and subsequent formation of the red school badge pattern of Sun Yat-sen University. The POP-PAA films need to experience a thermal imidization in a vacuum oven to achieve the cyclization of molecular and then become high-performance PI films. At the same time, a fraction of PdCl_2 on the film's surface can be reduced to $\text{Pd}(0)$ and embedded in the substrates at high temperatures ($\sim 300^\circ\text{C}$). Finally, through the electroless copper plating process, continuous conductive Cu patterns with a minimum line width of $50\ \mu\text{m}$ and a minimum line spacing of $20\ \mu\text{m}$ can be deposited on the PI film's surface with high precision under the catalysis of $\text{Pd}(0)$ (Fig. 1b).

In this work, the $\text{Pd}(0)$ on the PI films' surface is an indispensable catalyst in the redox reaction between the Cu^{2+} and formaldehyde during the electroless plating process, and its content on the film surface will directly determine the final metal pattern quality. Although the high content of $\text{Pd}(0)$ on film surface can effectively catalyze the deposition of copper metal, it will also bring the problem of cost increase. On the other hand, Cu patterns cannot be formed or discontinuously formed on the PI films with a low content of $\text{Pd}(0)$. The content of $\text{Pd}(0)$ on the PI film surface depends on the fixation capacity of the initial POP-PAA film for PdCl_2 , which relies on the content of 2,6-dimethylpyridine structures contained in the

polymer chains. And the content of 2,6-dimethylpyridine structures can be regulated by adjusting the ratio of three required monomers (Fig. S1 in ESI), *i.e.*, five kinds of functional POP-PAA polymers were synthesized with three kinds of monomers of 1,2,4,5-benzenetetracarboxylic anhydride (PMDA), 4,4'-oxydianiline ether (ODA), and functional biphenylenediamine monomer (FDM). The comparison of the photos in Fig. 2(a) shows the appearance of the five materials in different stages in the metal patterning process. Although the exposed areas on the five kinds of POP-PAA films can well fix the PdCl_2 , after the same thermal imidization and subsequent electroless plating process, only the surface of the PI-5 sample cannot form the complete Cu pattern.

Although the POP-PAA-5 film still can exhibit a pattern consistent with the same dimensional accuracy of the mask pattern (Fig. 3a) by fixing PdCl_2 (Fig. 3b) at the exposed position after mask exposure, the sample surface after the thermal imidization process with low content of the $\text{Pd}(0)$ leads to a fragmentary Cu pattern formation. Figs. 3(c) and 3(d) show the surface profiles of POP-PAA-5 film after selective adsorption of PdCl_2 under the atomic force microscope (AFM) analysis. The unexposed areas still maintained flat geomorphology, while the exposed area formed a height difference of $\sim 120\ \text{nm}$ relative to the unexposed area due to the deposition of PdCl_2 (Figs. 3c and 3d). However, compared with the POP-PAA-4 sample, there were more defects and voids on the surface of the POP-PAA-5 film after adsorption of PdCl_2 due to the lower content of FDM (Figs. 3e and 3f).

Because the plating bath usually contains a large number of stabilizers to prevent or delay metal deposition,^[31] only when the Pd^{2+} on the PI film's surface is reduced to $\text{Pd}(0)$ can the Cu electroless plating be further realized on (Fig. S2 in ESI). To reveal the relationship between the thermal imidization process of the POP-PAA films and the synchronous reduction of PdCl_2 on their surface, the chemical structure as well as the surface element chemical state changes of these five samples during the thermal imidization process were further studied.

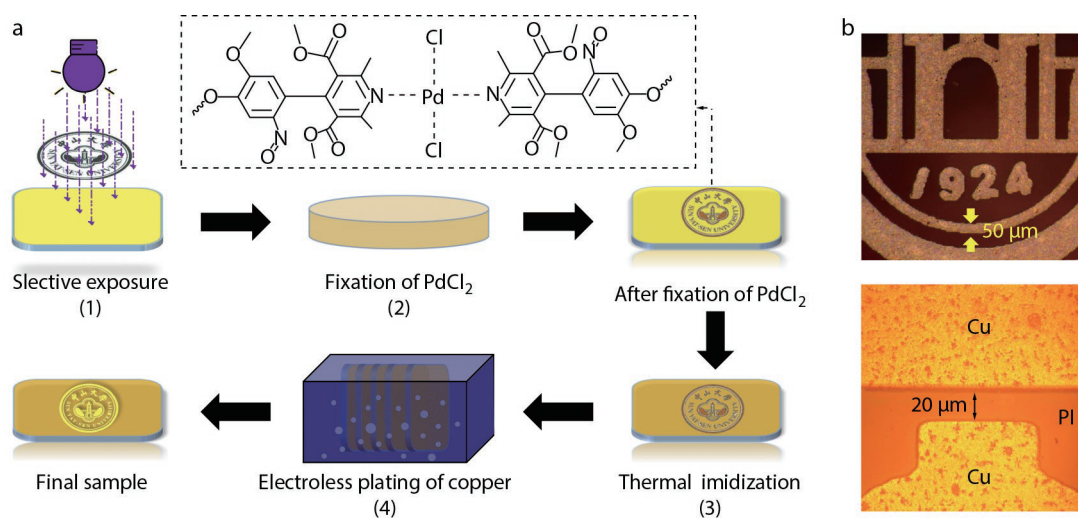


Fig. 1 (a) Schematic illustration of metal patterning on the surface of PI films: (1) mask exposure on POP-PAA films; (2) fixation of PdCl_2 on the exposed regions; (3) thermal imidization treatment; (4) Cu electroless plating. (b) Photos of Cu patterns on PI films.

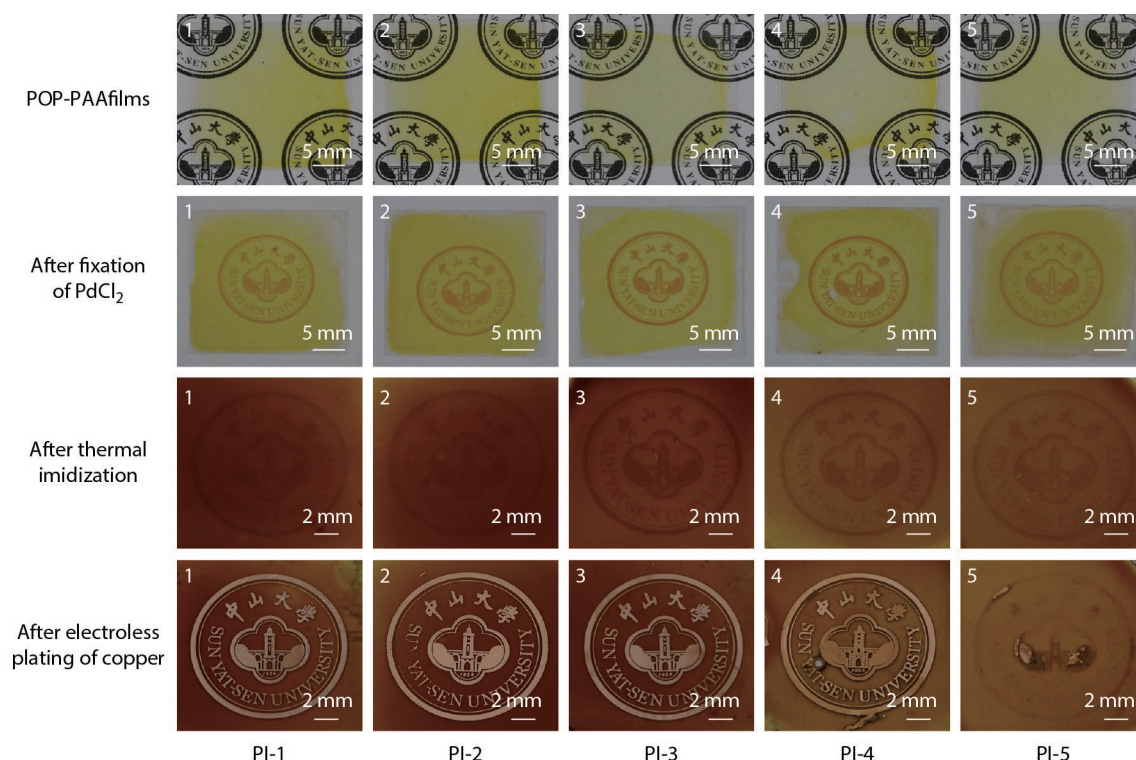


Fig. 2 Photos of five samples with different FDM contents in different stages of the metal patterning process (from top to bottom: after mask exposure, after fixation of PdCl_2 , after thermal imidization treatment, and after electroless plating).

Fig. S3(a) (in ESI) shows that the first obvious thermal weight loss appearance of five POP-PAA films occurred between 140 and 286 °C under the N_2 atmosphere. And the largest thermal weight loss rate of these films was at ~165 °C, which was mainly caused by the free residual solvent (N,N' -dimethylacetamide, boiling point ~165 °C) escaping from films. When free residual solvent volatilized completely, the molecular chains of the POP-PAA began to undergo dehydration and cyclization under further heating. Here, taking the POP-PAA-3 film sample as an example, the ATR-FTIR spectrum shown in Fig. 4(a) illustrates the chemical structure changes of its molecular chains after different temperatures treatments. Until the temperature reached 165 °C, the characteristic absorption bands of the imide ring are clearly shown on the ATR-FTIR spectrum, *i.e.*, the absorption bands at 1776 and 1716 cm^{-1} are classified as asymmetric and symmetrical stretching vibrations of carbonyl groups, at 1373 cm^{-1} is attributed to the stretching vibration of the C—N bond on the imide ring, and at 721 cm^{-1} is mainly caused by the out-of-plane bending vibration of the carbonyl group. And this is consistent with the changes in ATR-FTIR spectra of the other four POP-PAA films with different temperatures treatment (Fig. S4 in ESI). With the further increase of the temperature, the imidization reaction of the POP-PAA films was gradually completed, and the thermal weight loss rate of the films began to decrease. When the temperature reached 300 °C, the thermal weight loss rate of the film nearly became 0%, which indicated that the POP-PAA films had been completely converted into PI films.

In addition, compared with the programmed heating steps, the POP-PAA films under the TGA test environment can be re-

garded as experiencing a continuous heating process (the heating rate is 5 °C/min). TGA results at temperatures above 300 °C of the PI films obtained by programmed heating were almost the same as the films obtained by continuous heating (Fig. S3b in ESI). This indicates that the thermal imidization of the POP-PAA films only depends on the final imidization temperature, but has little to do with the heating rate and other factors, which may provide important reference information for reducing energy consumption in the future continuous production process. Moreover, the two results shown in Fig. S3 (in ESI) indicated that the first obvious thermal decomposition of the PI films occurred only when the temperature exceeded 340 °C, which was mainly due to the thermal decomposition of the functional side groups on the PI chains, and the thermal stability of the PI films could be significantly improved with the decrease of the FDM content in the polymer chains (Table S1 in ESI). It is worth noting that after the thermal imidization process, with the carbonization (Fig. 2, after thermal imidization process) caused by the thermal decomposition of the side chain groups in the polymers, the films with more FDM content appear dark brown and thus have lower light transmittance (Fig. 4b).

XPS results show that the content of PdCl_2 fixed on the exposed POP-PAA films decreased with the decrease of FDM content (Table S2 in ESI). Figs. 4(c) and 4(d) show the changes of surface element content and chemical state of the exposed POP-PAA-3 film fixed PdCl_2 on before and after experiencing the thermal imidization process. Prior to experiencing the thermal imidization process, the XPS results of the film surface showed that there were two single peaks of 337.7 and 343.0 eV between 335 and 346 eV, which was the position of

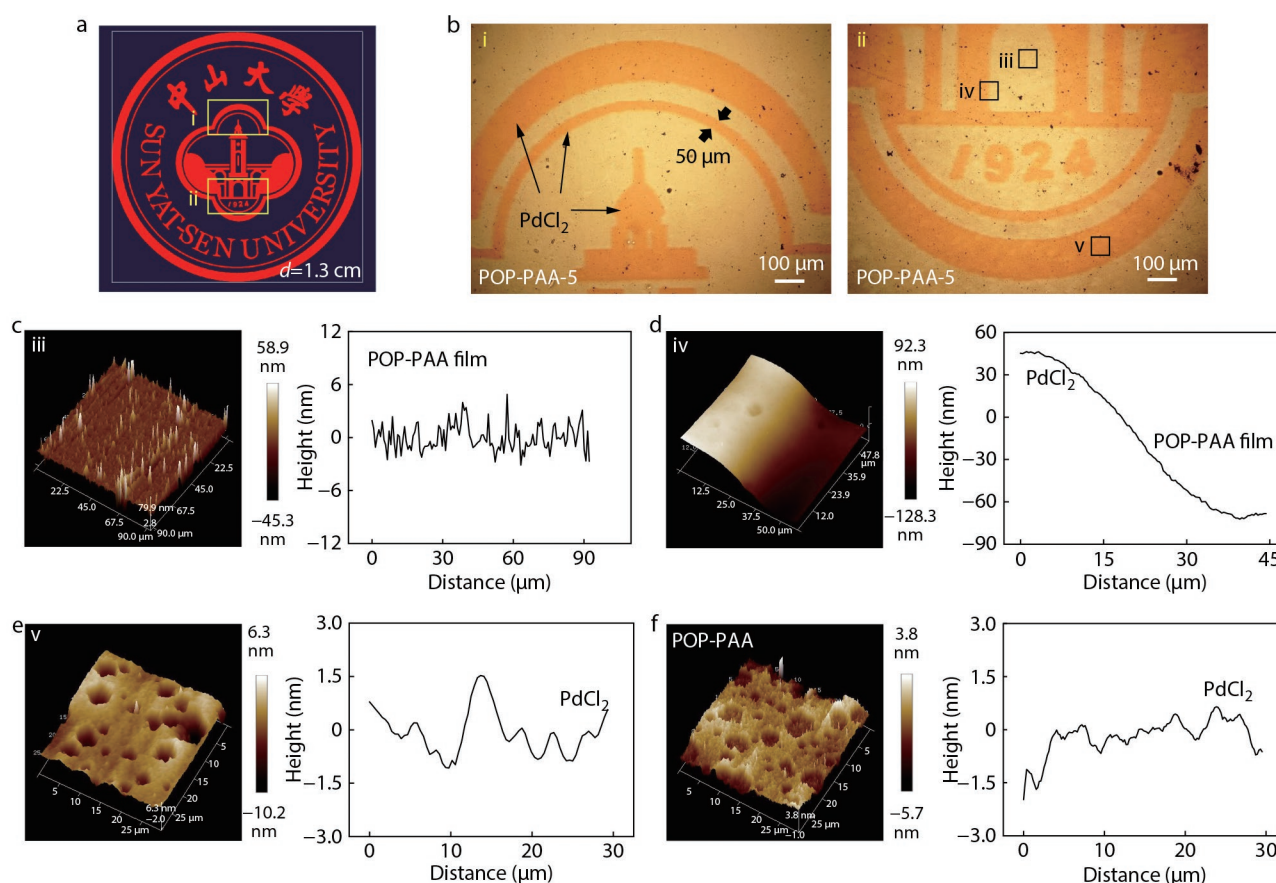


Fig. 3 (a) The mask pattern of the school badge pattern of Sun Yat-sen University (The red pattern with a diameter of 1.3 cm can be penetrated by UV light); (b) Photos of school badge pattern made of PdCl₂ on the surface of POP-PAA-5 film; (c–e) Profiles of different areas on the surface of POP-PAA-5 film after fixation of PdCl₂ analyzed by AFM; (f) Profiles of POP-PAA-5 film after fixation of PdCl₂ analyzed by AFM.

the bond energy peak of divalent palladium ion in typical PdCl₂. While after the thermal imidization process, the bond energy peak of chlorine was almost disappeared, and two double peaks appeared between 335 and 346 eV. The shoulder peaks at 340.4 and 335.4 eV are the bond energy peaks of Pd(0). Such results were also observed in the other four samples (Figs. S5–S8 in ESI). In addition, it is worth noting that the presence of Pd(0) was also found on the surface of PdCl₂ solid after the high-temperature treatment at 300 °C (Fig. 4e), which shows that the occurrence of thermal reduction reaction of PdCl₂ in the high-temperature environment might be only related to the heat treatment temperature rather than the PI substrate.

Fig. 5 shows the morphology and conductivity of Cu patterns on the surface of three kinds of films of PI-3/4/5 after undergoing the same Cu electroless plating process. Although complete copper metal patterns can be formed on both PI-3 and PI-4 films, there are more pit defects in the Cu pattern on the surface of the PI-4 sample compared with PI-3 (Figs. 5a–5d). Moreover, in the same plating time (10 min), the thickness of the copper layer (TCL) on the surface of PI-4 and PI-3 films are ~1.2 μm and ~2.5 μm, while the TCL of both PI-1 and PI-2 films can reach ~2.7 μm (Fig. S9 in ESI). The uneven distribution of low content Pd(0) on the surface of PI-5 film caused the sample could not form a complete Cu pattern on

the surface even with a long time (6 h) of electroless plating, and the thickness of the fragmentary copper layer was only ~70 nm (Figs. 5e and 5f). Meanwhile, coated by a thick copper layer made the micropatterned area difficult to show other chemical elements except for C, O, and Cu under the XPS analysis (Fig. S10 in ESI). However, the electroless plating process in the strongly basic solution resulted in forming the Cu(OH)₂ inevitably together with the copper layer that increased the pattern resistivity. The electrical conductivity of the copper layer (450 μm in width and 1.3 × π cm in length) on the surface of five kinds of PI films was also compared using a multimeter (Fig. 5g). The rings with the TCL of ~2.7 μm on PI-1 and PI-2 have a resistance value of ~0.6 Ω and a resistivity of 1.78 μΩ·cm, which is very close to that of pure block Cu. The Cu ring with a TCL of ~2.5 μm on PI-3 has a resistance value of ~0.7 Ω and a resistivity of 1.85 μΩ·cm. The resistance value of the Cu ring with a thickness of ~1.2 μm on PI-4 film was measured to be ~1.5 Ω, and its resistivity was 1.98 μΩ·cm. When the copper layers were connected to a closed circuit with a voltage of 1.5 V, the current values through the copper patterns decreased with the increase of the resistivity of the Cu patterns, and the measured current value of the PI-1/2 sample was ~2.5 A, and the current values for the Cu layers on PI-3 and PI-4 films were ~2.1 and ~1.0 A, respectively. The defect of the Cu layer on PI-4 film is the main reason for its high

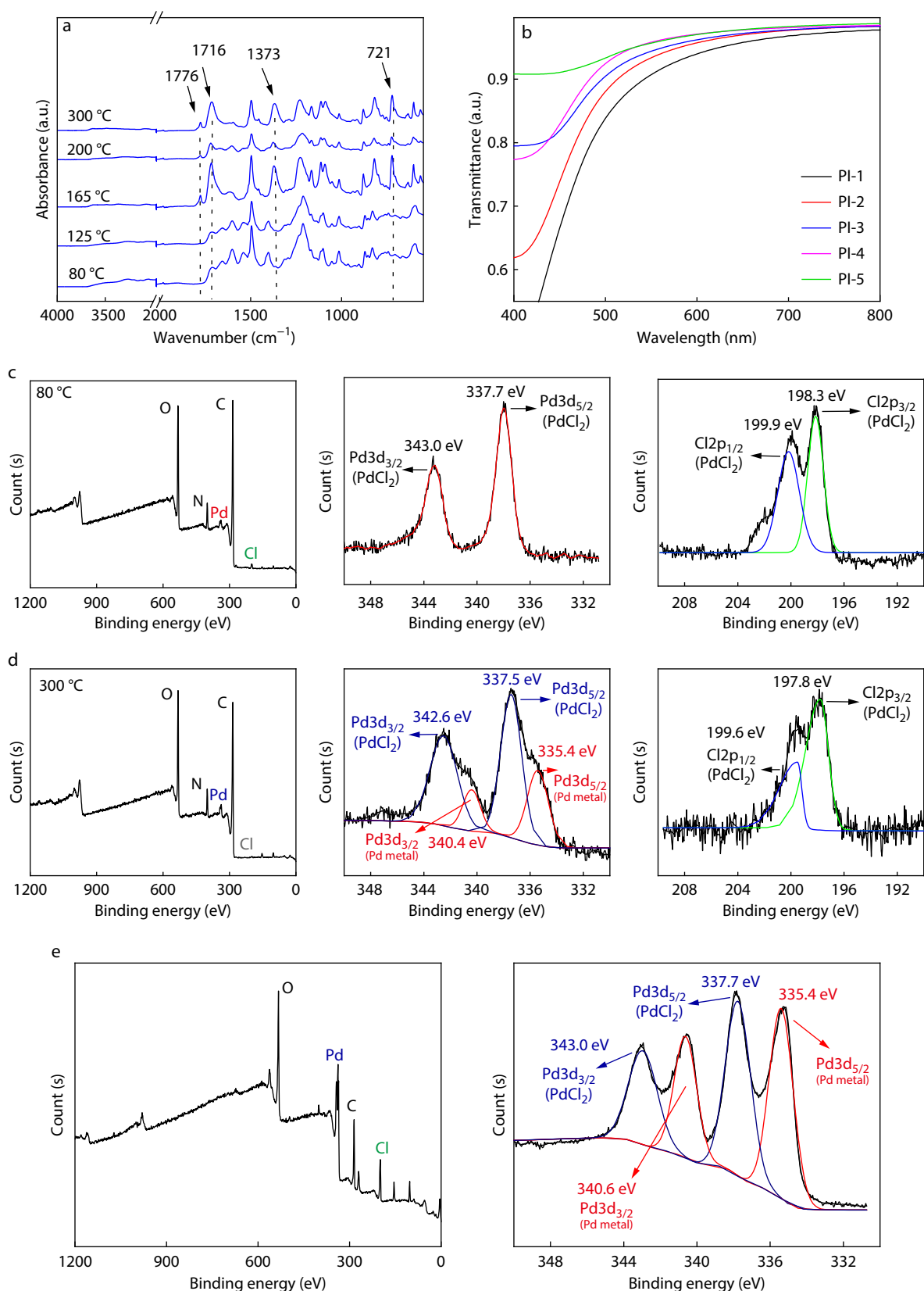


Fig. 4 (a) ATR-FTIR spectra of the POP-PAA-3 film after different temperature treatments; (b) Transmittance of five PI films in visible light range (film thickness is $\sim 10\ \mu\text{m}$); (c, d) XPS spectra of the exposed POP-PAA-3 film after fixation of PdCl₂ and then treated at different temperatures; (e) XPS spectra of PdCl₂ solid treated at 300 °C for 1 h.

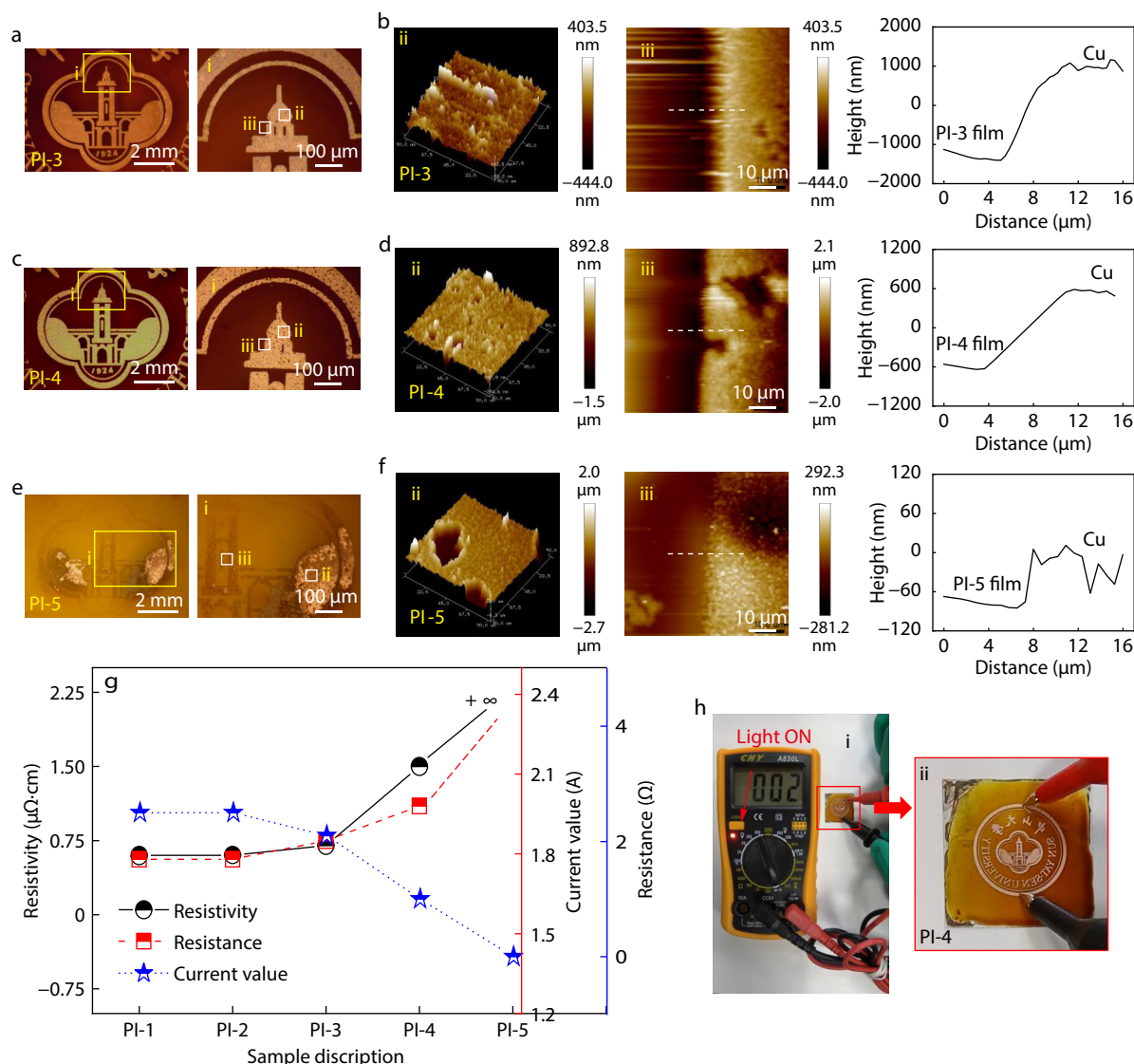


Fig. 5 (a–f) Photos and profiles of PI-3/4/5 films after electroless plating (i: photos; ii, iii: Cu layer and its boundary were analyzed by AFM); (g) Electrical property of the Cu layers on five kinds of PI films; (h) Metal continuity test of the Cu layer on PI-4 film.

resistivity. Nevertheless, the continuous conductive Cu layer on PI-4 film can still easily light on the LED lamp of the multimeter (Fig. 5h and Video S1 in ESI). As for the PI-5 sample, it showed infinite resistance due to its inability to form a complete copper pattern efficiently.

The dimensional stability and dielectric properties of flexible PI substrates should also be considered when metal wires are deposited on their surface by the electroless plating method. Static thermomechanical analyzer (TMA) and impedance analyzer test results show that as the content of FDM with large volume side groups decreased, the T_g and relative permittivity of PI films improved at the same time, their linear coefficient of thermal expansion (CTE) under T_g has been a marked decline (Fig. 6a, Figs. S9a and S9b in ESI). Among them, T_g of PI-5 film is the highest, which is $\sim 302^\circ\text{C}$, proving that the maximum temperature (300°C) in the programmed heating process suffices to meet the requirements of thermal imidization of the five POP-PAA films. Although the T_g of the

five samples relied on their polymer structures, the temperature of depositing PdCl_2 on the five kinds of POP-PAA films is 20°C (at least 250°C lower than the polymers' T_g), and the POP-PAA chains in this temperature are all in a 'frozen' state, so it can be considered that the content of PdCl_2 fixed on the surface of the POP-PAA films is only related to the content of 2,6-dimethylpyridine structures on the exposed regions, and is not greatly affected by the T_g of the polymers. The CTE of PI-3 and PI-4 films was $46.7 \times 10^{-6}/^\circ\text{C}$ and $44.4 \times 10^{-6}/^\circ\text{C}$, which were 33.9% and 37.1% lower than that of PI-1, respectively. In addition, the relative permittivity of PI-3 and PI-4 films showed little difference (~ 4.9), and the increase of molecular polarity caused by the decrease of FDM content may be the main reason for the increase of relative permittivity of PI films. In addition, although the CTE of PI-5 was the lowest ($40.8 \times 10^{-6}/^\circ\text{C}$), we could not ignore the fact that the formation of Cu on the surface of PI-5 film was ineffective.

In addition to the above properties, the reduction of FDM

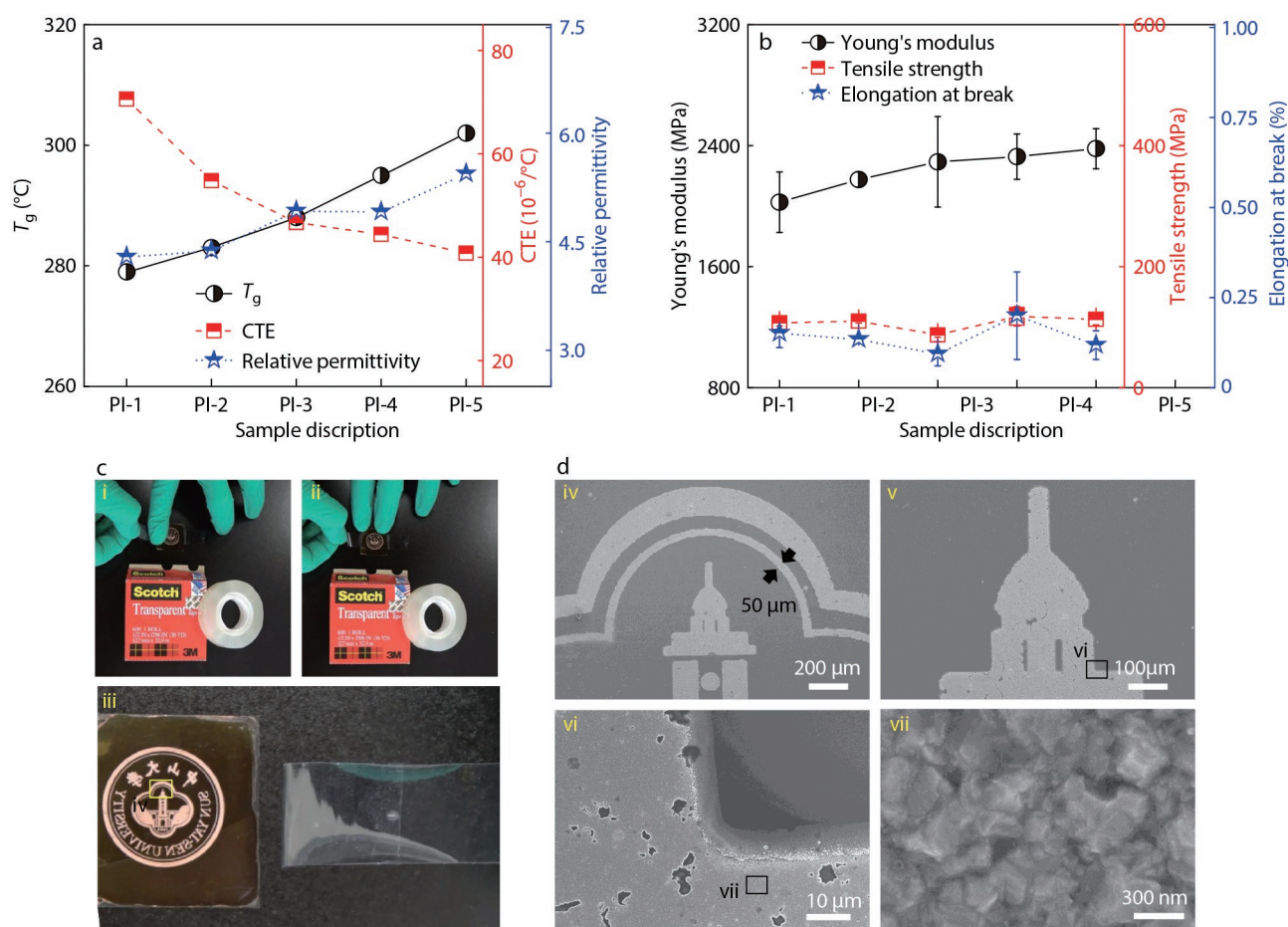


Fig. 6 (a, b) Comparison of thermoelectric properties and mechanical properties of five kinds of PI films; (c) Evaluation of the interfacial adhesion of Cu pattern adhered on the PI-3 film (i: attach Scotch tape on sample tightly, ii: peel of the tape rapidly, iii: no Cu appears on the Scotch tape); (d) Microstructures of Cu patterns on PI-3 film analyzed by scanning electron microscope.

content also affects the mechanical properties of PI films (Fig. 6b). The Young's modulus and tensile strength of both PI-3 and PI-4 films can reach ~2300 and ~100 MPa, respectively. On the other hand, great adhesion between Cu layers and PI substrate was crucial during the use of flexible electronic devices, so the interfacial adhesion of Cu patterns adhered on the PI-3 film was also evaluated by Scotch tape adhesion test (Fig. 6c and Video S2 in ESI). The test was performed by peeling the 3 M pressure sensitive tape attached to the sample quickly. The clean adhesive surface of the tape (Fig. 6c-iii) and consecutive copper patterns captured by the scanning electron microscope (Fig. 6d) indicated that the interfacial adhesion performance between Cu patterns and the PI-3 film had reached the highest adhesion classification of American Society of Testing Materials (ASTM). Meanwhile, it is obvious that the copper patterns have a clear and smooth edge without any obvious burr and remained the same size as the mask patterns as well as the PdCl_2 patterns (Figs. 3a and 3b). In general, the copper-coated sample with PI-3 film as the substrate has the best performance. For the manufacture of portable and miniaturized wearable electronic devices, flexible integrated circuits with high-performance quality make a good choice. The PI materials and the method of metal patterning

on their surface provided in this paper are expected to be applied to the fabrication of small-size integrated circuits devices in the future.

CONCLUSIONS

In conclusion, the PdCl_2 was fixed on the polymer surface under the coordination effect of the 2,6-dimethylpyridine structures in the exposed regions without destroying the substrate and introducing an unstable interlayer, and the high-resolution patterns of PdCl_2 assisted following deposition of conductive copper metal micropatterns. The results showed that a low-defect copper conductive metal pattern can be rapidly (<10 min) formed on the surface of polyimide film during electroless plating, and its resistivity can reach $\sim 1.78 \mu\Omega\text{-cm}$, which is similar to that of pure bulk copper. This simple and low-cost palladium-assisted metal patterning technique enables a conductive copper pattern with a minimum line width of $\sim 50 \mu\text{m}$ and a minimum line spacing of $\sim 20 \mu\text{m}$ on the polyimide substrate without requiring the expensive lithography machine and complex vacuum environments. This technology is compatible with the current roll-to-roll manufacturing process that meets the requirements of continuous production and has great application potential in manufacturing high-performance flexible micro-integrated circuits.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2778-1>.

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