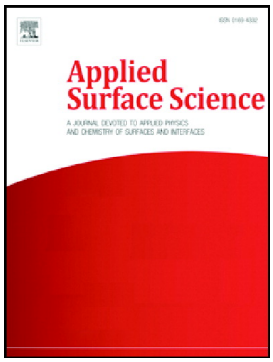

Surface modification with special morphology for the metallization of polyimide film

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Surface modification with special morphology for the metallization of polyimide film

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Abstract

Metallized polyimide (PI) film has great applications in the field of flexible electronics. Surface property adjustment is considered as an effective way to realize the metallization of PI film by chemical methods. In this work, we demonstrate a facile approach to fabricate metallized PI film *via* surface modification and electroless plating. Polyethyleneimine (PEI) cross-linked with glutaraldehyde (GA) is used as a modifier to act on the surface of alkali-treated PI film, and a special regular morphology is obtained. This PEI-modified PI film possesses not only functional groups for chemical bonding but also large surface roughness for mechanical locking with metallic copper layer. The resulting copper layer has low resistivity (2.30 μΩ·cm) and satisfactory adhesion to PI film (the highest score of 5B according to ASTM D3359), and the metallized PI sample exhibits reliable flexibility. These results demonstrate a promising potential of this approach in the field of PI film metallization with impact in wearables, light-weight, and flexible electronics.

Keywords: Polyimide film; Surface modification; Electroless plating; Special morphology; Flexible electronics

1. Introduction

With the development of information technology and materials engineering technology, future integrated circuit technology will develop along the directions of "More Moore", "More than Moore" and "Beyond CMOS" [1-3]. These trends will certainly put forward higher requirements for the spatial size of integrated circuits, three-dimensional interconnection between devices and functional diversification [4]. Flexible electronics with its good flexibility, ductility and structural features, gains more and more attention in the future development of large-scale integrated circuits [5]. In the field of flexible electronics, surface metallization of flexible substrates is an indispensable step in achieving three-dimensional interconnection among devices, rational wiring in a limited space, and multifunctional flexible electronic devices.

Among many flexible substrates, polyimide (PI) is one of the most important substrates for flexible electronics due to its excellent dielectric properties, heat resistance, mechanical properties and chemical stability [6-18]. It has been widely used in polymer film capacitors [6], liquid crystal alignments [7,8], batteries [9,10], flexible electronic sensors [11-13], electrode material [14-16], organic light-emitting devices (OLED) displays [17], molecular-scale transistor [18-21], and RFID tags [22]. The surface-metallized PI film enables simultaneous static and dynamic deflection. This advantage of bending deflection and being expandable into a three-dimensional space make the circuit design and mechanical structure design more flexible. Moreover, metallized PI film has low dielectric constant, loss angle tangent, and heat resistance, allowing the signal to be transmitted quickly at lower losses and

maintaining stable performance even at high temperature. However, PI molecules have poor polarity and the surface is usually very smooth, making it difficult to form an effective bond with surface metal layers [23], which greatly hinders its application and development in the field of flexible electronics.

At present, the technical routes for producing high-performance metallized PI in the industry mainly include coating, lamination, and sputtering. The copper film generated by these methods is uniformly dense and well bonded to PI substrate. However, metallized PI produced by coating and lamination usually results in a thick copper layer, which is difficult to meet the requirement of ultra-thin layers (less than 5 μm). Besides, sputtering is usually performed under high-vacuum requiring complicated and costly equipment. In order to achieve metallization of PI with desirable metal thickness, satisfactory adhesion, and low cost, the chemical deposition of copper on surface-modified PI has been developed. Physically changing the surface properties of PI film is a simple and useful strategy for surface treatment, such as immersing the PI film into an organic solvent to increase the surface roughness by swelling effect [24], or using an adhesive to achieve an effective combination of PI film and metal layer [25]. Also, chemical modification of PI film is considered as an effective approach to adjust its surface properties. Plasma is used to form a modified layer on PI film with free radicals such as hydroxyl groups and amino groups [26, 27]. Alkali treatment can hydrolyze PI molecules to form a surface layer with good hydrophilicity [28-31]. Also, the use of grafting agents to modify PI film is another efficient way to achieve PI film metallization [32-36]. Progress was made in these

efforts to obtain metallized PI film.

Here, we provide a facile approach to realize the surface metallization of PI film. We achieve a satisfactory adhesion between PI film and metal layer by a combination of physical effect and chemical bonding. Polyethyleneimine (PEI) was used to form a self-assembled layer with a special morphology and functional groups, which chemically modified the surface properties of PI film with high surface roughness. Electrical and mechanical properties of metallized PI were characterized. Our results demonstrate that this approach is very promising in the metallization of PI film with strong implications in the ongoing development of flexible electronics.

2. Experimental

2.1. Materials

PI film (thickness: 25 μm) is biphenyl type polyimide produced by Jiangyin Junyou Electronic New Material Co., Ltd. Ethanol, acetone, silver nitrate, potassium hydroxide, glutaraldehyde (GA), hydrochloric acid, potassium sodium tartrate, disodium EDTA, copper sulfate, nickel sulfate, 2,2'-dipyridyl, potassium ferrocyanide, sodium hydroxide, formaldehyde, and benzotriazole (BTA) were all analytical reagents (AR) purchased from Chengdu Kelong reagent factory. PEI (M.W. 10,000, AR grade) was obtained from Shanghai Aladdin Biochemical Technology Co., Ltd.

2.2. Surface modification of PI film

A 10 %wt potassium hydroxide solution was prepared as a hydrolysis agent to react with PI film. PEI (5 g) was put into a beaker containing deionized water (80 mL) and stirred at 25 °C until it was completely dissolved. Then, 0.25 vol% GA solution (5

mL) was added dropwise to PEI solution and stirred continuously for 60 min. Thus a solution containing branched PEI crosslinked with GA (denoted GA-PEI) was obtained.

Before performing the surface modification, PI substrate needed to be cleaned first in an ultrasonic bath with acetone for 10 min, followed by washing using ethanol and deionized water in sequence. Then, the substrate was dried at 100 ºC for 30 min to remove deionized water, ethanol, and acetone completely. Afterward, surface pre-modification was conducted by immersing the substrate into a potassium hydroxide solution at 50 ºC for 30 min. Finally, the surface-pre-modified PI substrate was immersed in the GA-PEI solution at 70 ºC for 30 min to obtain a self-assembled layer. This self-assembled layer could chelate metal ions for the subsequent deposition of a copper film. The substrate was thoroughly washed with deionized water after each step.

2.3. Copper metallization of PI film

The PI substrate with GA-PEI layer was activated by being soaked in an aqueous solution containing Ag^{+} (5 g L^{-1}) at 50 ºC for 30 min. After being rinsed by deionized water, the PI substrate was immersed in an electroless copper plating solution containing potassium sodium tartrate (24 g L^{-1}), EDTA disodium (2 g L^{-1}), copper sulfate (8 g L^{-1}), nickel sulfate (2 g L^{-1}), 2,2'-dipyridyl (10 mg L^{-1}), potassium ferrocyanide (20 mg L^{-1}), sodium hydroxide (10 g L^{-1}) and formaldehyde (12 mL L^{-1}). During the copper metallization process, silver ions are firstly reduced into silver nanoparticles by formaldehyde and then act as catalytic active sites for copper

deposition. After that, the initial deposited copper nanoparticles will act as self-catalysts for the further copper growth. The reduction reaction of Cu^{2+} is described in the following equation.

$$2HCHO+[CuL_x]^{2+xp}+4OH^- \rightarrow Cu^0+2HCOO^-+xL^p+2H_2\uparrow+2H_2O \quad (1)$$

In equation (1), L means ligand, x is the stoichiometric number of ligand and p stands for the electric charges carried by the ligand. Ligands provided by potassium sodium tartrate and EDTA disodium ensure the stability of Cu^{2+} in the electroless plating solution. The copper deposition temperature was maintained at 45 ºC. The resulting metallized PI sample was additionally treated in a BTA solution (2 g L^{-1}) to protect the surface from oxidization.

2.4. Characterization

Water contact angles on PI film were determined by sessile drop method with Dataphysics OCA 20 (POWEREACH, China) at room temperature. Surface morphologies were investigated by using Keyence VHX-500F optical microscope and JEOL JSM-6490LV scanning electron microscope (SEM). For SEM measurement, Au (1~2 nm of thickness) was sputtered onto the surface of non-conductive samples to improve image clarity. The chemical composition of deposited copper layer was analyzed using Genesis 2000 XMS energy dispersive X-ray spectroscopy (EDS). The surface roughness of PI substrate with GA-PEI coating was investigated by ICON2-SYS atomic force microscopy (AFM) in tapping mode. Fourier transform infrared (FT-IR) measurement was performed by Bruker Optics FT-IR spectrometer (Tensor 27). X-ray photoelectron spectroscopy (XPS) was conducted on an Escalab

250Xi system with Al Kα radiation (hv = 1486.6 eV). X-ray diffraction (XRD) spectrum was acquired with the help of Shimadzu XRD-7000 X-ray diffractometer. The sheet resistance of the copper layer was determined by a Model 280SJ automatic four point probe. Adhesion between the copper film and the PI substrate was tested according to the ASTM D3359 tape test.

3. Results and Discussion

The metallization process of PI film is schematically shown in fig. 1. Branched PEI is a highly water-soluble polymer, and the functional groups of primary amine, secondary amine and tertiary amine contained in PEI molecule endow it with unique properties and very high activity. Due to the presence of primary amine groups in the branch, PEI can form a network structure under the action of GA, and generate a stable chelate with heavy metal ions such as Ag^{+} and Cu^{2+}. Besides, it can also react with carboxyl groups to form stable amide groups. Pre-modification of PI substrate in alkali solution hydrolyzes PI molecule on the surface, providing carboxyl groups for the coating of GA-PEI on its surface. Strong bonding between PI substrate and copper layer is expected by this GA-PEI network structure.

FT-IR tests were conducted to investigate the structural changes in PI substrate before and after modification. Fig. 2a shows FT-IR spectra of original PI, surface-modified PI treated by KOH and further treated by GA-PEI solution. Compared with the original PI, the PI treated with KOH has a significant change in the FT-IR spectrum. An intense broad adsorption band from approximately 3200 to 3600 cm^{-1} can be observed in the spectrum of the KOH-modified PI film, which is

attributed to the stretching vibrations of O-H and N-H. The peak at 1650 cm^{-1} is due to the amide Ⅰ (C=O stretching), while the peak at 1552 cm^{-1} corresponds to the amide Ⅱ (N-H bending) modes of the amide bond. The band at 1598 and 1373 cm^{-1} are assigned to the asymmetric and symmetric stretching of carboxyl groups complexed with K^+ ions. These results demonstrate that the imide rings in PI surface molecule are cleaved, forming carboxylic acid potassium salts and amide bonds. Compared with the FT-IR spectrum of KOH-modified PI, the broad peak from 3200 to 3500 cm^{-1} in the FT-IR spectrum of the sample further treated by GA-PEI solution is inconsistent with the normal primary amine peak, which shifts to lower wavenumber. The strong absorption peak at this range indicates that there is not only an associated NH_2 structure on the substrate surface but also an NH structure that is attributed to the primary and the secondary amine structures in the backbone and branches of PEI molecule. The peaks at 2958 and 2840 cm^{-1} are attributed to the CH_2 asymmetric and symmetric stretching modes of PEI chain. No significant change is observed in the adsorption peaks in the range of 1200 to 2000 cm^{-1}, except for the peak at 1455 cm^{-1} with slightly higher intensity, which is attributed to the deformation of the primary amine groups ($-NH_2$). The FT-IR data indicate that a coating composed of GA-PEI layer has been successfully generated on the surface of the PI substrate.

Contact-angle measurements were carried out on the above-mentioned PI film to investigate the changes of surface properties further. The water contact angles on different PI film are presented in fig. 2b. The water contact angle of KOH-treated PI film (10.8°) is much lower than that of the original PI film (49.6°), which can be

ascribed to the hydrolysis of imide rings of PI molecule and the formation of hydrophilic potassium carboxylate under the alkali treatment. With GA-PEI layer forming on the surface of PI film, the contact angle of the PEI-modified PI film increases to 71.5°. This can be explained as follows. There are carboxyl groups existing on the surface of PI after being treated with KOH, while amine groups exist on the surface of PI being treated with GA-PEI further. The hydrogen bond between the oxygen atom in carboxyl groups and the hydrogen atom in water molecule is stronger than that formed between the nitrogen atom in amine groups and the hydrogen atom in water molecule, causing the hydrophilicity of PEI-modified PI to be weaker. Based on the FT-IR and water contact angles results, the amine groups were introduced to the PI film, acting as a linker between PI substrate and metal layer. This functionalization is possible thanks to the combination with the carboxyl group to form amide group and chelating with metal ions.

Comparisons between pristine and modified PI are assessed by SEM, AFM, and EDS results shown in Fig. 3. No difference in surface morphology is seen between the pristine and the KOH-treated PI substrate (Fig. 3a, b) except for a small increase of surface roughness from 4.1 nm (Fig. 3d) to 6.8 nm (Fig. 3e). The potassium element appears in the KOH-treated PI substrate with lower C/O ratio in Fig. 3h than that in Fig. 3g, indicating the hydrolyzation of the imide ring and the generation of potassium carboxylate. However, the surface morphology of PI drastically changes after being further treated with GA-PEI. As shown in Fig. 3c, the GA-PEI surface exhibits a regular network structure, and the roughness of the treated PI increases to 63.4 nm

(Fig. 3f). This roughness change may also contribute to an increase in water contact angle [37]. This unique morphology will not only provide a larger surface area to chelate with metal ions, but also support the mechanical locking for a metallic layer. Such mechanical anchoring improves the adhesion between copper layer and PI substrate. It can be observed from Fig. 3i that the atomic percentage of N in PEI-modified PI increases by about 8% compared with that of the original and the KOH-treated PI. These results further confirm the existence of the PEI-modified layer on PI substrate.

The pristine and the PEI-modified PI are soaked in the same Ag^+-bearing solution and then dried at room temperature for 30 min, followed by ultrasound washing in deionized water for 10 min. Fig. 4a, b shows the XPS spectra of Ag element for the pristine and the PEI-modified PI after the processing above. The strong Ag/PEI-modified PI interaction is evidenced by the fact that even after subjected to an ultrasonic bath, silver remains present in the film (Fig. 4b). The PEI-modified PI film with Ag^+ adsorbed on its surface was then immersed into an electroless copper plating solution to conduct metallization processing. In this process, silver ions were first reduced to silver atoms acting as catalysts for subsequent copper deposition. Then the copper metallization of PI film was obtained with the help of the autocatalysis of copper atoms. Typical SEM image and corresponding cross-sectional view of metallic copper layer are shown in Fig. 4c. The metallic copper layer displays a rather continuous morphology and compact packing. Sheet resistance and thickness of the metallic copper layer were investigated to control the metallization processing.

It can be clearly seen in Fig. 4d, the sheet resistance of the copper layer decreases dramatically at the beginning of the electroless deposition, and then gradually declines to a stable value. On the contrary, the thickness of the copper layer increases with deposition going on, and then a slow increase occurs after 30 min deposition. The resistivity of the copper layer deposited for 40 min is calculated to be about 2.30 μΩ·cm according to the equation of $\rho_s=R_s\cdot\tau$, where ρ_s is the resistivity, R_s is the sheet resistance and τ is the thickness of the copper layer. This is an outstanding result since it shows that our method allows obtaining a flexible copper film with a low electrical resistance of only 1.4 times that of bulk copper (1.68 μΩ·cm). For this metallic copper layer, no other elemental atoms are observed in addition to Cu atoms from EDS spectrum exhibited in Fig. 4e. Moreover, the crystalline structure of the copper layer on PEI-modified PI substrate is studied by XRD (Fig. 4f). Three strong characteristic diffraction peaks at around 43.3°, 50.5° and 74.1° are detected, corresponding to the (111), (200), and (220) planes of face-centered-cubic crystalline Cu, respectively. These sharp and protruding diffraction peaks indicate a good crystallinity of the copper layer.

The mechanical property of metallized PI film, which can be demonstrated by peel adhesion and bending reliability, is one of the most important performances for its practical application. The adhesion of metallic copper layer on PI substrate can be estimated by the standard peel adhesion test (ASTM D3359). The copper layer is scored into many 1×1 mm lattices, and then a standardized 3M tape is tightly adhered onto these squares. After that, the tape is quickly peeled off in the vertical direction.

As shown in Fig. 5a, the edges of squares are neat and almost no change occurred in the morphology after the peel adhesion test. This result meets well the highest adhesion rating (5B level) according to ASTM D3359, revealing the high adhesion of copper layer on PEI-modified PI substrate.

Flexibility of PI substrate with metallic copper layer is evaluated by bending samples according to given radii of curvature on both sides as depicted in Fig. 5b. R_1 and R_2 stand for the radii of curvature when bending inward and outward, respectively. A series of cyclical bending tests are conducted on PEI-modified PI substrate with the as-prepared copper layer. All the specimens used in these tests are fabricated in the same way and divided into 6 groups. Each group is bent for 500 times at radii of 6 mm, 4 mm, 2 mm, respectively. The ratio of G and G_0, representing the bended and the initial conductance respectively, is recorded every 100 times and exhibited in Fig. 5b. It shows that the conductance of copper layer changes barely even after 500 times bending when the radius of curvature is 6 mm, the conductance decreases at a relatively low speed at the curvature radius of 4 mm. Only when the radius of curvature is 2 mm, we observed significant changes in conductivity. And even in this case, after 500 times of outward bending, the electrical conductivity of metallic copper layer only reduced by half. These results show a realistic potential of metallized PI developed here for consumer applications based on flexible electronics.

4. Conclusion

In this paper, a convenient and efficient method to realize the double-sided metallization of PI film is developed. The self-assembled GA-PEI layer on

alkali-treated PI substrate exhibits a regular network structure, which not only provides functional groups for chemical bonding with metallic copper layer but also further enhances the adhesion of copper layer to PI film by mechanical locking. The metallic copper layer is well-crystallized, continuous, and densely packed with outstanding conductivity and remarkable adhesion strength, and the metallized PI sample exhibits reliable flexibility. This innovative approach for making double-sided metallization of PI film has promising potential in developing robust flexible electronic devices.

Acknowledgements

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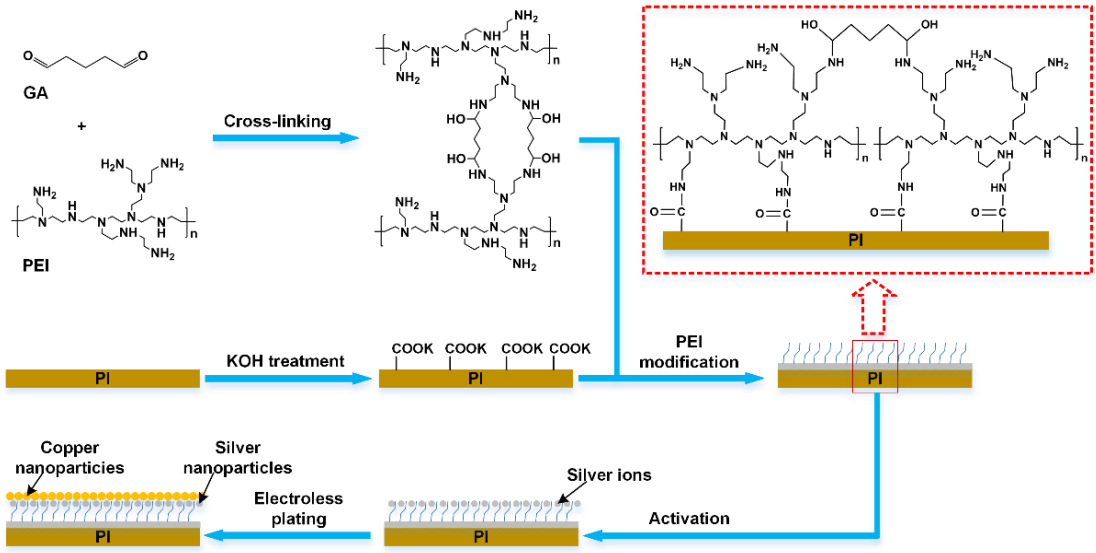

Fig. 1. Schematic diagram of the metallization process of PI film combined with the synthesis of GA-PEI, surface modification of PI substrate and copper deposition.

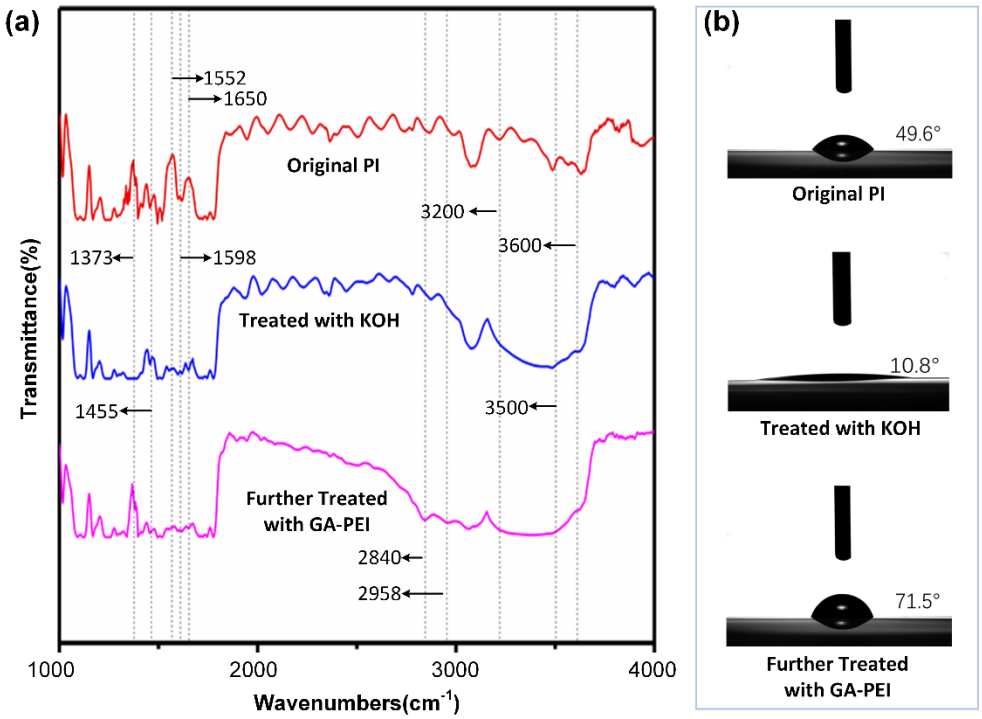

Fig. 2. (a) FT-IR spectra of pristine PI, surface-modified film treated by KOH and subsequently treated by GA-PEI solution. (b)Water contact angle on original PI, the pre-modified film with KOH solution and the PI film treated by GA-PEI solution after pre-modification.

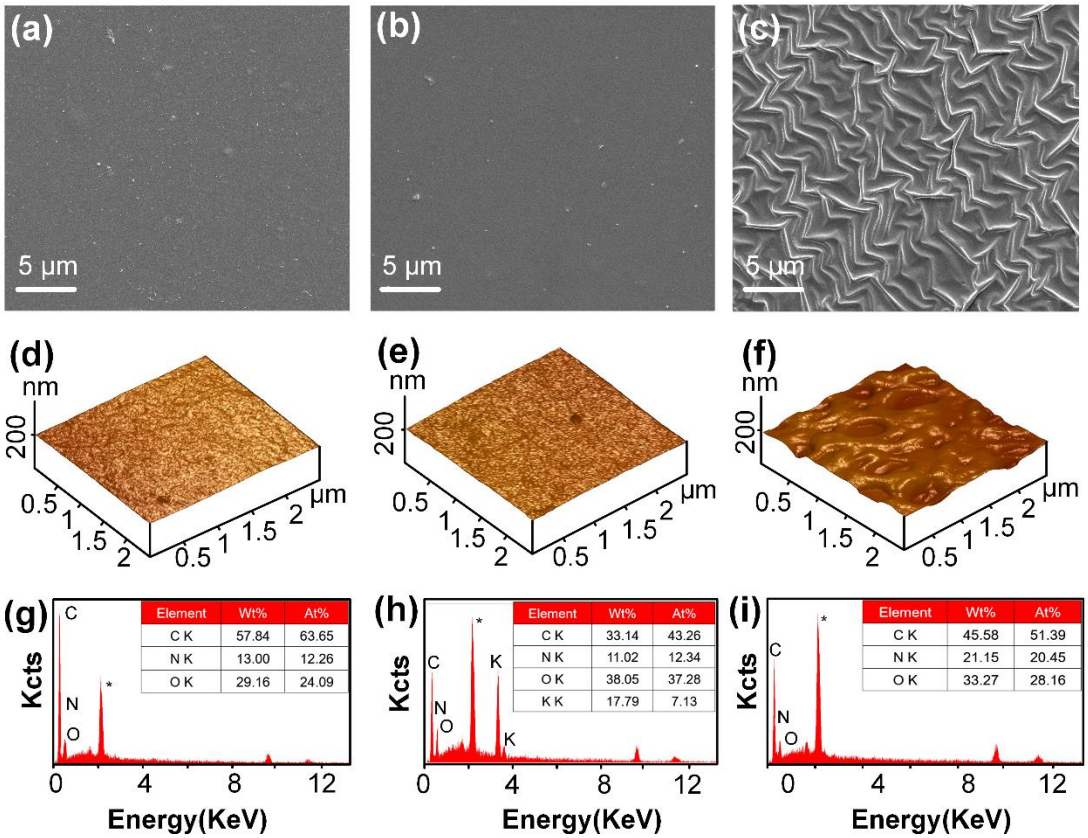

Fig. 3. SEM images, AFM images and EDS spectra of (a), (d), (g) original PI film, (b), (e), (h) pre-modified PI film treated with KOH and (c), (f), (i) PI film further treated with GA-PEI.

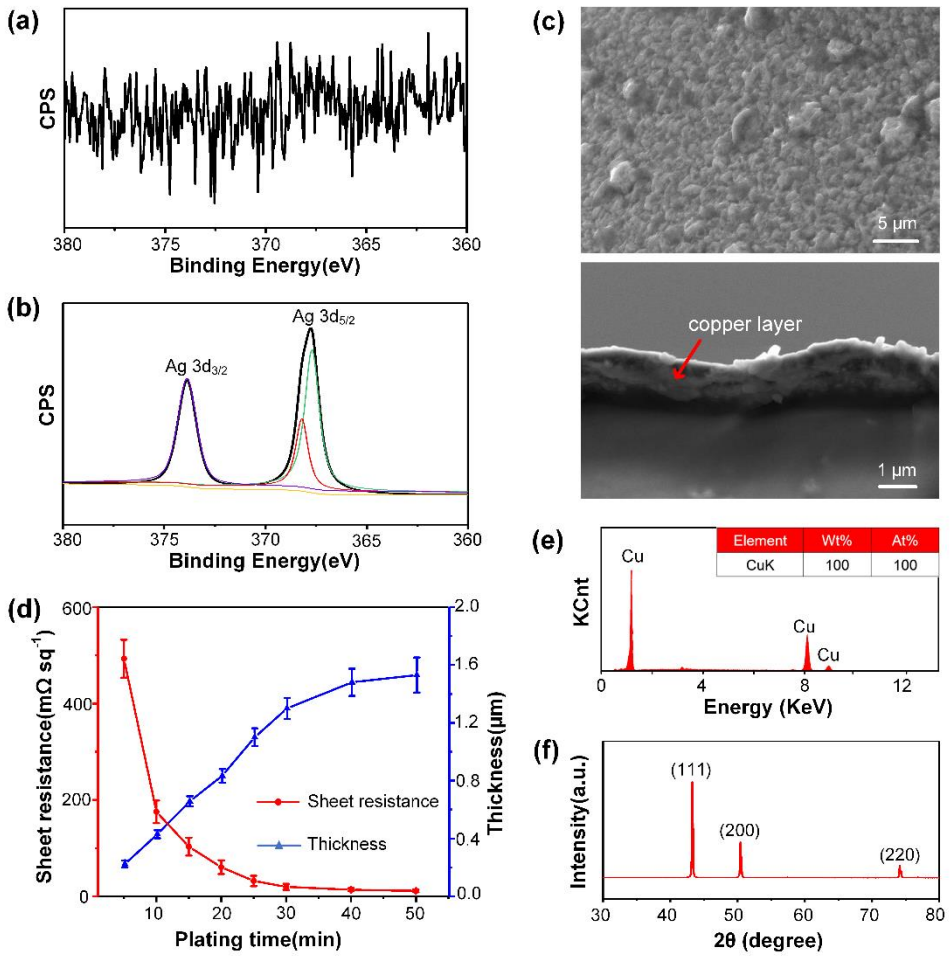

Fig. 4. XPS spectra measured with samples of (a) pristine PI and (b) PEI-modified PI after being immersed in Ag^{+}-bearing solution followed by ultrasonic cleaning. (c) SEM image and cross-sectional view of metallic copper layer on PEI-modified PI substrate. (d) Sheet resistance and thickness of copper layers varied with electroless plating time. (e) EDS spectrum and (f) XRD of the metallic copper layer.

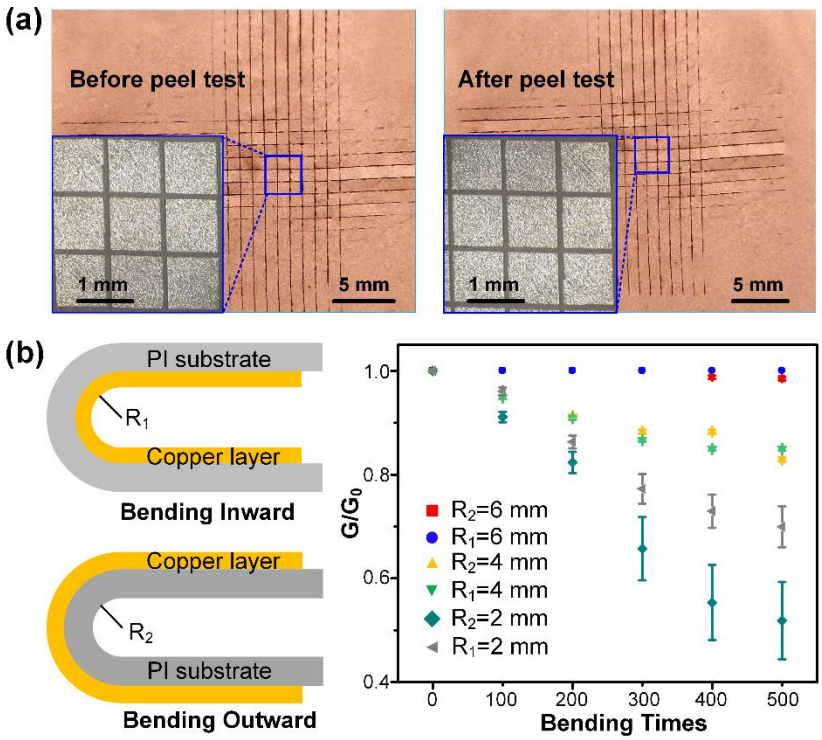

Fig. 5. (a) Optical images of the sample before and after adhesion test according to the standard peel adhesion test (ASTM D3359). (b) Schematic diagrams of bending test and changes in electrical conductivity of PEI-modified PI substrate with metallic copper layer.

Highlights

- Polyethyleneimine (PEI) cross-linked with glutaraldehyde was used for surface modification of polyimide (PI) films.
- The PEI-modified PI film possessed functional groups and a special regular morphology with high surface roughness.
- Metallic copper layer had good adhesion to PI film thanks to mechanical anchoring and chemical bonding.
- This facile approach for the metallization of PI film has great potential in developing flexible electronics.