



Photochemical formation of palladium patterns on surface-modified polyimide resin

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Abstract

A simplified method for forming a palladium circuit pattern on polyimide resin substrate was proposed. The carboxyl group, as a cation exchange group, was formed on the polyimide resin surface by a potassium hydroxide treatment. Palladium(II) ion was then adsorbed onto the surface modified polyimide resin by ion exchange. Ultraviolet irradiation of this palladium(II) ion absorbed resin with sodium formate coated on its surface resulted in the formation of a palladium thin film. Irradiation through a metal-on-quartz mask onto the modified polyimide resin surface photoreduced the palladium ion into metallic palladium circuit patterns easily without using a plating resist.

1. Introduction

Electroless copper plating has been widely used in both negative and positive tone lithography for manufacturing circuitry via an additive metallization process [1]. In the additive metallization process, electroless copper deposition is catalysed by a palladium/tin colloid [2]. By this method, photolithography is required to define the pattern for metallization prior to the catalytic treatment and electroless copper deposition. The catalyst deposition for electroless selective metal plating was achieved previously by the u.v.-induced oxidation of Sn(II)colloids [3], photoreduction of Pd(II)-activated TiO [2, 4], ZnO films [5], or photochemical decomposition of Au(I)complex [6]. However, each of these methods only generated the catalyst required for the subsequent electroless plating of a conductive film; none generated a conductive film directly from the photoreduction.

Recently, much importance has been attached to the problem of environmental pollution. The use of the electroless copper plating has become more difficult because of the use of harmful formaldehyde and the difficulty in treating the spent chelating agents. The preparation of conductive films such as a palladium colloid, a conductive polymer, or graphite has been employed for manufacturing circuitry via an additive metallization processes [7]. The introduction of an ion exchange group into a plastic substrate, subsequent adsorption of Cu(II) ions, and the conversion of adsorbed ions to metals, would also be useful for

metallization on a plastic surface. Such a process has been reported by two of the present authors [8, 9, 10].

In this paper, a simplified method for forming a palladium circuit pattern on a polyimide resin through carboxylation of a polyimide resin followed by adsorption and selective u.v. photoreduction of Pd(II) ion was investigated.

2. Experimental details

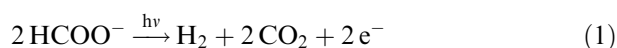
2.1. Carboxylation of a polyimide resin and adsorption of Pd(II) ion

Polyimide resin films, 50 μm thick were used (Toray-Dupont film 200-H film). Test samples of the polyimide resin were dipped in a 5 M potassium hydroxide solution at 50 °C for 5 min, neutralized thoroughly with 6 M hydrochloric acid, and then rinsed and dried. The degree of carboxylation was determined by ESCA (ULVAC-PHI model 5400 MC).

The carboxylated test samples were dipped in a 0.05 M palladium(II) chloride/0.4 M ethylenediamine solution at room temperature for 3 min to adsorb Pd(II) ions. The amount of Pd(II) adsorbed on the carboxylated polyimide resin was determined by eluting the Pd(II) ion from the carboxylated surface (2 cm \times 2 cm) with 5% nitric acid, and the Pd(II) ion content in the eluent was measured with a Seiko Instruments SPS7700 plasma spectrometer.

2.2. Formation of surface-selective palladium patterns

The carboxylated test samples were dipped in 5 M sodium formate solution for 1 min at room temperature, then dried at room temperature. The samples were irradiated with an Ushio Electric (UM-452) u.v. lamp (450 W high pressure mercury, with an irradiance of 35 mW cm^{-2}) for 1 min in the 200–500 nm wavelength range. The distance between the sample and u.v. lamp was 25 cm. Sodium formate as a secondary reducer was excited by u.v. irradiation, so that the reduction reaction for Pd(II) ion took place during irradiation. Thus,



The Pd nucleus can be produced by photochemical reduction of Pd(II) ion in the presence of formate. The main reaction is a reduction reaction by u.v. irradiation with sodium formate. Sodium formate is needed to increase the reduction efficiency. The sample was exposed to u.v. irradiation through either a metal-on-quartz glass mask or a PET lithographic mask. After irradiation, the surface electric conductivity of the palladium pattern was measured with a digital multimeter.

3. Results and discussion

3.1. Carboxylation of a polyimide resin and adsorption of Pd(II) ion

Figure 1 shows the process sequence for the formation of a palladium circuit pattern on a polyimide resin substrate.

Figure 2 shows the Cls XPS core level spectra of a polyimide resin surface untreated, and with the surface modified with 5 M potassium hydroxide solution at 50 °C for 5 min. Both samples were neutralized thoroughly with 6 M hydrochloric acid, then rinsed and dried. The potassium hydroxide treatment increased the C=O, O=C–NH and O=C–OH peaks, and simultaneously decreased the O=C–N–C=O peak. The O=C–OH content increased from 0% to 7%, and the content of C=O and O=C–NH increased from 0% to 7%. A decrease in the O=C–N–C=O peak means that there was degradation of imide rings in the polyimide resin by the potassium hydroxide treatment. From the Cls core level spectra, we conclude that a potassium hydroxide treatment leads to the formation of the O=C–OH peak, and also the degradation of imide rings in the polyimide resin. The polymer degradation and carboxylation reactions are shown in Figure 3. It is obvious, therefore, that the carboxyl group, which can act as a cation exchange group, was introduced onto the polyimide resin surface. The polyimide resin surface ($\sim 3 \mu\text{m}$) was only treated with 5 M potassium hydroxide

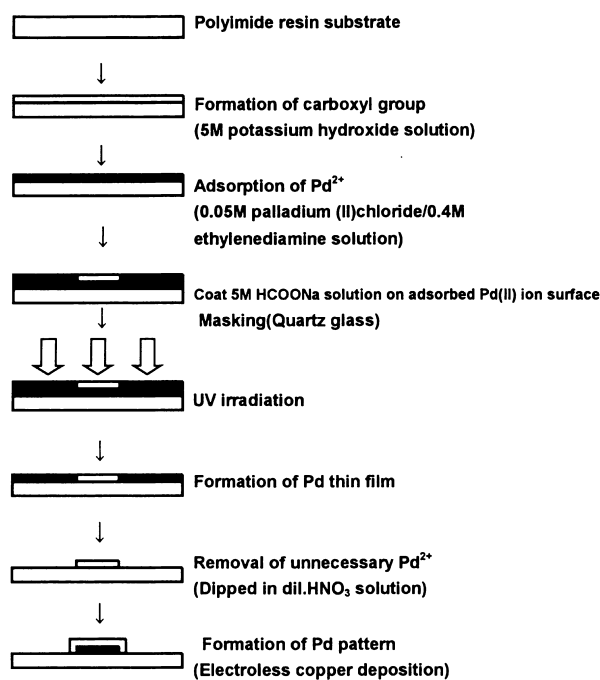


Fig. 1. Process sequence.

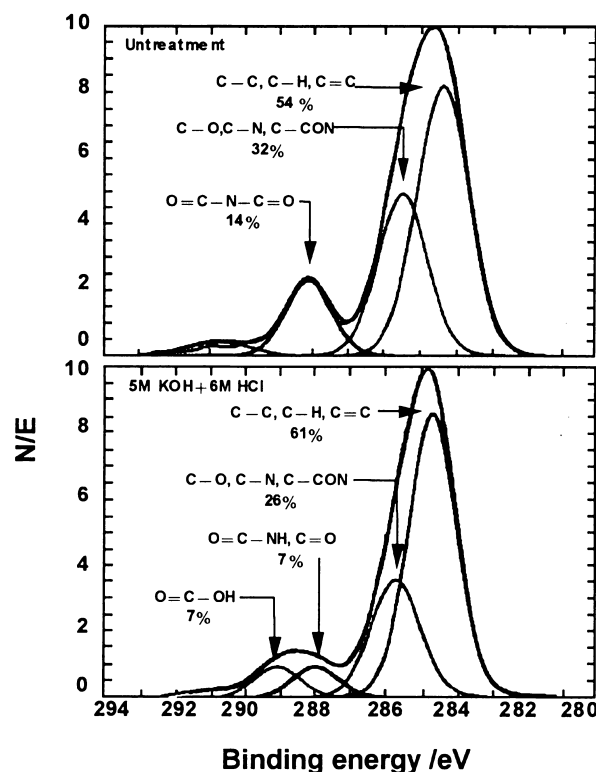


Fig. 2. Cls XPS core level spectra of a polyimide resin surface either untreated or modified with 5 M potassium hydroxide solution of 50 °C for 5 min and then neutralized with 6 M hydrochloric acid.

solution. Therefore, potassium hydroxide solution did not influence the bulk properties of the resin.

Figure 4 shows the effect of potassium hydroxide concentration (treatment at 50 °C and 5 min) on the amount of Pd(II) ion adsorbed, as a result of carboxyl group formation on the polyimide resin surface. In the

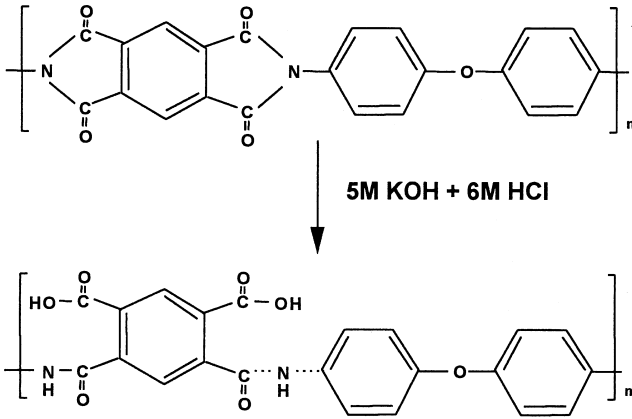


Fig. 3. Change in the structure of a polyimide resin surface modified with 5 M potassium hydroxide.

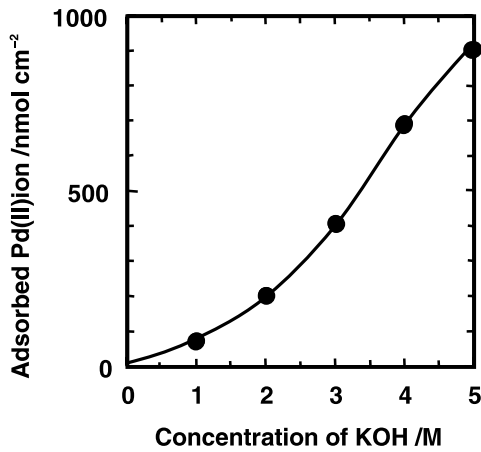


Fig. 4. Relationship between the amount of adsorbed Pd(II) ion and concentration of potassium hydroxide solution for carboxyl group formation on the polyimide resin surface.

non-potassium hydroxide treatment, there was no adsorption of Pd(II). The amount of adsorbed Pd(II) increased with increasing potassium hydroxide concentration, and then levelled off when Pd(II) reached 900 nmol cm^{-2} . Two carboxyl groups are needed to adsorb one Pd(II) ion. Using the palladium lattice constant of 0.389 nm [11], the maximum thickness of the average palladium thin film after the photochemical reduction process was estimated to be about 65 nm . Figure 5 shows the effect of potassium hydroxide treatment temperature (treatment at 5 M and 5 min) on the amount of adsorbed Pd(II); there was an increase in Pd(II) with increasing temperature. It was found that the polyimide resin was severely attacked when the treatment temperature exceeded $60 \text{ }^\circ\text{C}$. Figure 6 shows the effect of treatment time (treatment at 5 M and $50 \text{ }^\circ\text{C}$) on the amount of adsorbed Pd(II).

3.2. Creation of surface-selective palladium patterns

Figure 7 shows the relationship between the amount of adsorbed Pd(II) and the surface electrical conductivity of the palladium thin film formed by u.v. irradiation for

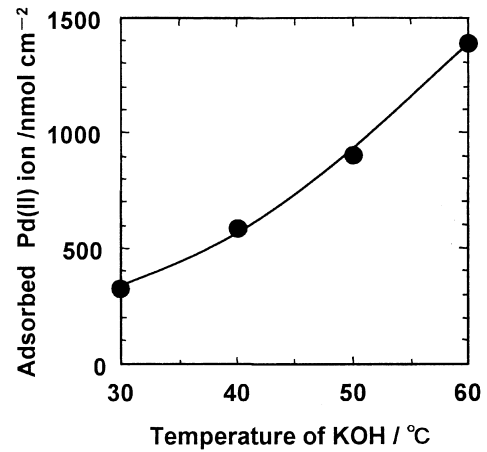


Fig. 5. Relationship between the amount of adsorbed Pd(II) ion and temperature of the potassium hydroxide solution for carboxyl group formation on the polyimide resin surface.

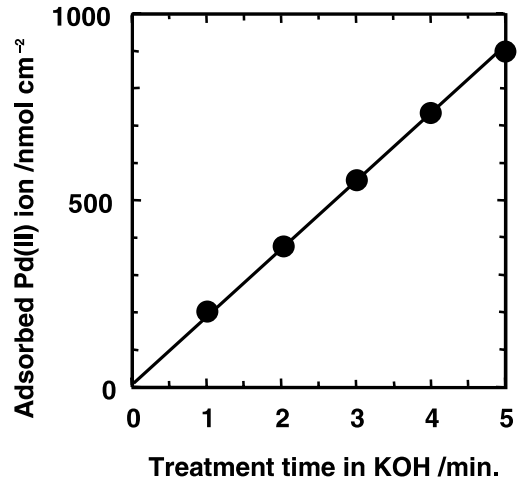


Fig. 6. Relationship between the amount of adsorbed Pd(II) ion and treatment time in potassium hydroxide solution for carboxyl group formation on the polyimide resin surface.

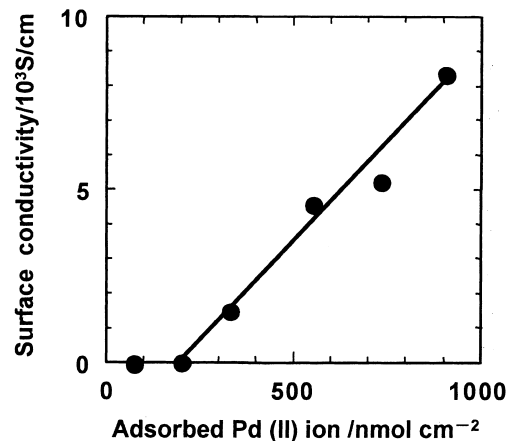


Fig. 7. The effect of the adsorbed Pd(II) ion content and the surface electrical conductivity of a palladium thin film deposited by u.v. irradiation for 1 min.

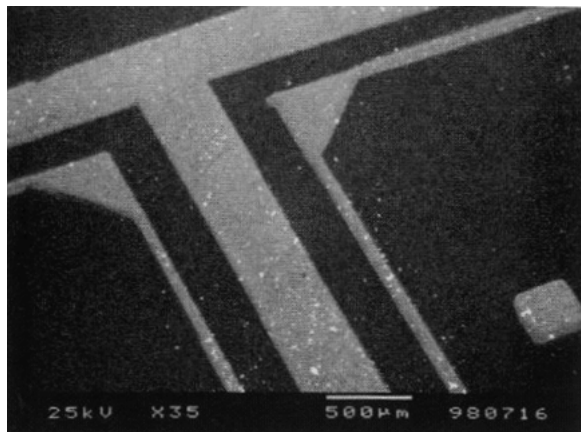


Fig. 8. SEM image of a u.v. enhanced palladium pattern on a polyimide resin.

1 min. The surface electrical conductivity increased with an increase in adsorbed Pd(II). After 1 min of u.v. irradiation, the surface had a bright metallic palladium appearance. The maximum electrical conductivity was $9 \times 10^{-3} \text{ S cm}^{-1}$ ($111 \Omega^{-1} \text{ cm}^{-1}$); an electrolytic copper deposit can be easily plated on such a thin film. When there was no potassium hydroxide treatment, the palladium patterns could not be formed on resin surface.

As shown in Figure 8, palladium thin patterns on a polyimide resin can be constructed easily through a metal-on-quartz lithographic mask with 1 min u.v. irradiation. With this process, it was possible to produce a high-resolution patterned image. The palladium patterns were smooth and uniform. Adsorbed Pd(II) between the lines, which was produced by u.v. irradiation, could be removed by 5% nitric acid solution. After samples were rinsed in 5% nitric acid solution, they were dipped in an electroless copper bath (Table 1). The electroless copper deposits were plated on only patterns; there was no deposit between the lines. According to these results, it was obvious that the adsorbed Pd(II) between the lines which was produced by u.v. irradiation could be removed by 5% nitric acid.

When using a PET (polyethylene terephthalate) lithographic mask, the deposition of palladium patterns was achieved with 10 min of u.v. irradiation. We believe that the poor resolution from the PET lithographic mask was caused by the heat release during irradiation.

The formation of palladium patterns by the photo-reduction process was studied as a function of irradiation wavelength. As shown in Figure 9, the quartz

Table 1. Electroless copper plating bath composition and condition

| | |
|--|--------------------------|
| CuCl ₂ · 2 H ₂ O | 0.05 mol l ⁻¹ |
| Ethylenediamine | 0.6 mol l ⁻¹ |
| Co(NO ₃) ₂ · 6 H ₂ O | 0.15 mol l ⁻¹ |
| Ascorbic acid | 0.01 mol l ⁻¹ |
| 2,2'-Bipyridyl | 20 mg l ⁻¹ |
| pH | 6.6 |
| Bath temperature | 50 °C |

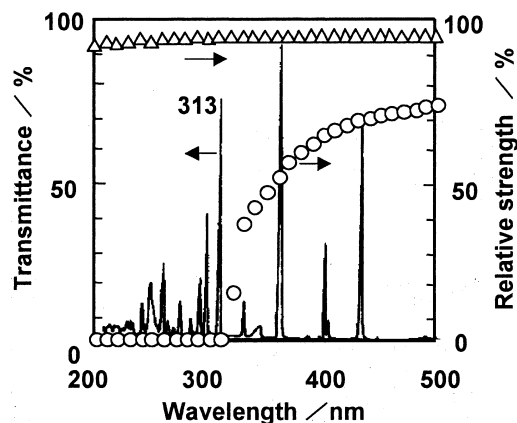


Fig. 9. Transmittance of the photomask and the relative strength of u.v. radiation. Key: (O) PET mask; (Δ) quartz glass mask.

transmittance was 90% at 313 nm. From this results it was concluded that circuit patterns could be formed easily on polyimide resin substrates without a patterned plating resist.

4. Conclusions

A simplified method for forming a palladium circuit pattern on a polyimide resin, through carboxylation of the resin followed by adsorption and selective u.v. photoreduction of Pd(II) ions is presented. The carboxyl group, as a cation exchange group, was introduced onto the polyimide resin surface by a potassium hydroxide treatment. Irradiation by u.v. of an adsorbed layer of Pd(II) that was treated with a sodium formate solution results in the formation of a palladium thin film. The maximum conductivity of the palladium film was $9 \times 10^{-3} \text{ S cm}^{-1}$ ($111 \Omega^{-1} \text{ cm}^{-1}$). Palladium circuit patterns were easily formed on the polyimide resin substrate, without a plating resist, by use of a metal-on-quartz lithographic mask.

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