

electron generation and injection properties including these additive and binder effects will be presented in a further publication. The spectral response of the best photoreceptor obtained in this work is shown in Figure 8. The photoreceptor exhibited a high and flat sensitivity of about $1.2 \text{ cm}^2/\mu\text{J}$ in the absorption region of the TiOPc (600–850 nm). At present, these are the best data for all-organic double-layered photoreceptors that can work in the positive charging mode and are on a practical level.³⁵

Conclusion

We have developed a new class of electron-transporting compounds, unsymmetrically substituted diphenoquinones. The unsymmetrical substitution remarkably

enhanced not only the solvent solubility but also polymer dispersibility of diphenoquinone derivatives. High electron mobilities over $10^{-6} \text{ cm}^2/\text{V s}$ were obtained for the first time in organic amorphous films with transport-active molecules dispersed in common binder polymers. Moreover, it has been found that electrons can be injected from TiOPc pigment into the diphenoquinone-doped polycarbonate, demonstrating the possible application to xerographic photoreceptors that can work in the positive charging mode.

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Photoselective Catalysis of Electroless Copper Solutions for the Formation of Adherent Copper Films onto Polyimide

Thomas H. Baum* and Delores C. Miller

IBM Almaden Research Center, 650 Harry Road, San Jose, California 95120-6099

Terrence R. O'Toole

IBM Watson Research Center, P.O. Box 218, Yorktown Hts., New York 10598

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The photoreduction of potassium iron(3+) oxalate in the presence of palladium(2+) chloride results in the selective formation of palladium metal, which can catalyze copper plating from an electroless bath. This process is characterized by a rapid photospeed at several ultraviolet wavelengths, and selective electroless deposition of copper occurs only in the irradiated regions. A chemical treatment of the polyimide film, prior to treatment with the photocatalytic mixture results in excellent adhesion of the copper-plated pattern to polyimide. In an attempt to understand the mechanism for both adhesion and the photoformation of the active catalyst, an in situ X-ray photoelectron spectroscopic study was initiated. The results indicate base hydrolysis of the Kapton to form the disodium salt of polyamic acid, cation exchange at the polyamic acid groups, the rapid photoreduction of Fe^{3+} to Fe^{2+} and the slower reduction of Pd^{2+} to Pd^0 . Mechanisms for copper-Kapton adhesion and for the photoformation of palladium metal are proposed based upon the results of this surface study. The described process utilizes aqueous solutions and thus is attractive for both manufacturing and environmental reasons. The simplicity of this method for creating selective copper circuit patterns and for producing highly adherent films of copper onto polyimide is highlighted.

Introduction

The metallization of dielectric materials is critical to the production of high-density microelectronic packaging components. The requirements placed upon the dielectric media have become increasingly stringent. Many microelectronic applications require low dielectric constants, thermal stability at elevated temperatures, a high degree of flexibility, and good tensile strength. Polyimides derived from pyromellitic dianhydride and oxydianiline (PMDA-ODA) have been extensively utilized because they meet the above requirements, are resistant to chemical attack, and are readily available as solutions, suspensions, and free-standing films.¹ Although several chemical and physical techniques for polymer metallization are available, these methods require polymer lithography to define the metal circuits.² Efforts to reduce the costs associated with the fabrication of multilayered packaging modules have stimulated research into alternate techniques for selective

metallization. Photoselective metallization of polyimides via electroless plating offers several advantages including the elimination of lithographic steps, reduced fabrication costs, and simplicity.

Additive metallization via electroless deposition is initiated by a noble-metal catalyst.³ Several techniques have been explored for achieving selectivity of the active catalyst, which in turn provides selectivity of the plating process. Selective metal plating from electroless solutions was previously achieved by the UV-induced oxidation of tin(2+) colloids,⁴ by the photoreduction of palladium-(2+)-activated TiO_2 films,⁵ by photoinhibition of active palladium-tin catalyst,⁶ by the laser-induced decomposi-

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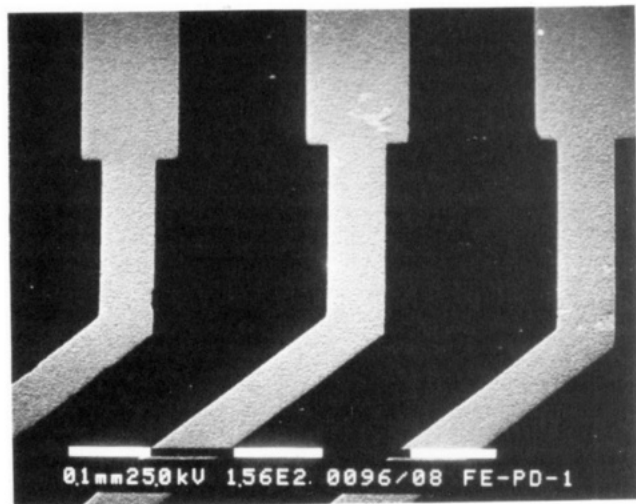


Figure 1. Section of an electrolessly plated copper circuit pattern on a free-standing Kapton film. The pattern was produced by the method described using 30 s of UV irradiation (0.84 J/cm^2 at 365 nm), plated for 5 min in the electroless copper solution, baked to 125°C for 2 h and electroplated to a thickness of $2 \mu\text{m}$. The pattern displayed minimum line widths of $30 \mu\text{m}$ and good adhesion.

tion of palladium(2+) β -diketonates,⁷ and by the photochemical formation of a gold catalyst.⁸ In all of these approaches, light is used to define the regions of catalytic activity, thereby achieving selectivity of the metal plating process.

In this paper, an alternate technique for the photoselective metallization of polyimide films is described. Base hydrolysis⁹ of the Kapton films provides excellent copper-Kapton adhesion and was used in tandem with a photoreactive iron-palladium catalyst¹⁰ to achieve selective copper plating. X-ray photoelectron spectroscopy (XPS) was utilized to study the chemistry occurring on the Kapton surface. At high energy resolution, shifts in the binding energies (BEs) can be generally correlated with the chemical environment of a specific atom. In particular, both $\text{Fe}(2p_{3/2})$ and $\text{Pd}(3d_{5/2})$ emissions were monitored to elucidate a probable mechanism for the formation of palladium metal, the active catalyst for electroless copper plating. This simplified approach for selectively forming copper circuit patterns (Figure 1) displays great potential for microelectronics applications as a result of the rapid photospeed, excellent copper-polyimide adhesion, and the high degree of spatial resolution from conventional exposure sources.

Experimental Section

Potassium ferric oxalate trihydrate, $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3 \cdot (\text{H}_2\text{O})_3$, was purchased commercially from Alfa Chemicals: 4.00 g (0.008 mol) was dissolved with vigorous stirring into 100 mL of deionized water. Tetraamminepalladium(2+) chloride hydrate (0.20 g, 0.00076 mol, Aldrich Chemical Co.) was dissolved in the aqueous iron oxalate solution to prepare the catalyst. A 1.0-L aqueous solution containing 100 g (2.50 mol) of NaOH (Aldrich Chemical Co.) and 20.0 g (0.0685 mol) of N,N,N',N' -tetrakis(2-hydroxy-*n*-propyl)ethylenediamine (Aldrich Chemical Co.) was prepared and used to hydrolyze the Kapton surface. Polyimide films (Kapton) were purchased from Du Pont and were 2 mils ($50 \mu\text{m}$) thick. The free-standing films were cut into approximately 2-in. squares and

used as received. Base hydrolysis of the polyimide⁹ was achieved by immersion of the Kapton film into the basic ethylenediamine solution for 5–10 min. The polyimide film was then rinsed in flowing deionized water (30 s), immersed into the Fe-Pd solution for 10 min, and spun-dry on a lithographic spinner for 60 s at 2000 rpm.

XPS analyses were performed on a Surface Science Instruments SSX-100 model 05 spectrometer, equipped with a monochromatized Al $K\alpha$ source. A $600\text{-}\mu\text{m}$ spot was used throughout. For survey data, the analyzer pass energy was 150 eV; for high-resolution spectra, a 50-eV pass energy was used. System base pressure was $\sim 8 \times 10^{-10}$ Torr. Neutralizing low-energy electrons were supplied as necessary to counteract charging. θ , the angle between the sample plane and the analyzer, was 35° and translates into giving an analysis depth of about 50 Å.

We took 1000-eV survey spectra after high-resolution scans for major constituents (C(1s), O(1s), N(1s), $\text{Pd}(3d_{5/2})$, $\text{Fe}(2p_{3/2})$) as applicable. The samples were examined after a prolonged pump-down period to remove residual water from the substrates. Kapton films were analyzed as received, after 5 and 10 min of immersion into the basic ethylenediamine solution. Analyses were performed on Kapton films that had been immersed into the potassium iron oxalate-palladium chloride solution (10 min) after immersion into the basic ethylenediamine solution (10 min). Two other films, one immersed in $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ and the other in $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$, were also analyzed and used as control samples for the study. Lastly, $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ and $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ crystalline solids were pressed into indium metal and analyzed as references.

The iron/palladium-treated Kapton films were irradiated with an Optical Associates Inc. exposure tool (Model 780) equipped with a 500-W Hg-Xe deep-UV lamp (Advanced Radiation Corp.). The power was measured using an Optical Associates (Model 270) power meter equipped with several broadband probes and found to be 8 and 28 mW/cm^2 at 254 and 365 nm, respectively. The UV radiation was passed through either a chrome-on-quartz or chrome-on-Pyrex lithographic mask to achieve the desired circuit pattern. For the in situ XPS irradiations, the output of the lamp was directed through the window of the antechamber on the XPS instrument (base pressure $\sim 8 \times 10^{-8}$ Torr). To calculate the UV exposure dose during in situ radiation of the films, a correction for the optical losses at the vacuum window was necessary; it was experimentally determined that the window was 90% transmitting. The UV doses reported throughout this paper correspond to the dose at 365 nm. For the XPS studies, the samples were exposed in the antechamber and then moved to the main chamber for analysis; this procedure was repeated for prolonged irradiation experiments. The iron($2p_{3/2}$), palladium($3d_{5/2}$), potassium(2p), and carbon(1s) spectra were collected as a function of irradiation time.

The X-ray sensitivity of the iron oxalate complex during the analysis was of concern, as was its sensitivity to the neutralizing electrons. Therefore, several control runs were performed on the Kapton films that had been coated with the Fe-Pd mixture, with $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$, and with $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ to determine the extent of decomposition upon X-ray exposure. The Fe^{3+} in $\text{K}_3\text{Fe}(\text{C}_2\text{O}_4)_3$ was found to reduce under the X-ray beam over a period of several minutes, still slow enough to monitor changes induced by the UV exposure. However, Pd^{2+} in $\text{Pd}(\text{NH}_3)_4\text{Cl}_2$ was reduced only after hours under the X-ray beam. No chemical change in the Fe^{3+} or Pd^{2+} complexes was observed after prolonged exposure to the neutralizing electrons. We concluded that the best way to minimize the X-ray beam decomposition, which could complicate the mechanistic interpretation, was to move to a fresh site on the sample for each analysis. Thus, measurements were made in one area, the film blanket UV irradiated and subsequently monitored in a region that had not been X-ray beam exposed. The iron spectrum was always taken first, and the analysis time was kept to the feasible minimum. This method allowed the X-ray decomposition during the analysis to be minimized but adds uncertainty due to lateral inhomogeneity.

Surface atomic concentrations, C_i , were estimated from the survey data with

$$C_i = 100 \frac{I_i / \sigma_i}{\sum_{i=1}^n I_i / \sigma_i}$$

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Table I. Surface Atomic Concentrations, Estimated from XPS Survey Data with^a

$$C_i = 100 \frac{I_i/\sigma_i}{\sum_{i=1}^n I_i/\sigma_i}$$

sample	C	O	N	Si	Na	Fe	Pd	Cl	K
Kapton, as recd	75.0	17.0	4.8	2.9					
NaOH soln, 5 min	71.0	20.0	4.8		4.5				
NaOH soln, 10 min	72.0	18.0	5.3		4.1				
NaOH soln + Fe-Pd cat. soln	44.0	36.0	6.2			1.6	1.5	0.73	10.0
NaOH soln + Fe soln	36.0	48.0	1.4			2.5			13.0
NaOH soln + Pd soln	54.0	17.0	16.0				4.6	8.8	
PMDA-ODA (theory)	75.9	17.2	6.9						
polyamic acid Na salt (theory)	66.7	21.2	6.1		6.1				
ethylenediamine (theory)	70.0	20.0	10.0						
K ₃ Fe(C ₂ O ₄) ₃ (theory)	27.3	54.5				4.5			13.6
Pd(NH ₃) ₄ Cl ₂ (theory)			57.1				14.3	28.6	

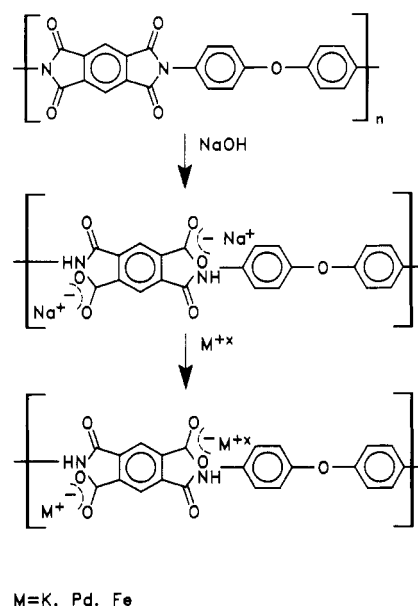
^a I_i and σ_i are the signal intensities and elemental cross sections⁹ for the i th element, respectively.

where I_i and σ_i are the signal intensities and elemental cross sections¹¹ for the i th element, respectively. This calculation assumes uniform elemental distribution versus depth. High-resolution binding energies were referenced to the lowest peak fit carbon 1s line taken as 284.6 eV.

After UV exposure, the Kapton samples were plated in an electroless copper solution (Dynachem, 835 medium copper solution). This commercial bath operates at room temperature with a pH of 12 and utilizes formaldehyde as a reducing agent. The plating of a thin, copper film was achieved in 3–10 min after immersion into the above solution. A copper film (0.5 μ m thick), as defined by the lithographic mask pattern, was selectively plated onto the exposed regions of the substrate. Other copper and nickel plating baths were observed to produce metal deposits under similar process conditions. The metallized polyimide film was rinsed in deionized water. A thermal bake step was used to ensure good copper-to-polyimide adhesion; this consisted of heating the sample for several hours (temperatures ranged from 125 to 400 °C). Copper to polyimide adhesion was quantified by pull testing lines that were electroplated to a thickness of 15–25 μ m. A Selrex acid copper plating solution was used to electrolytically plate copper. Copper-Kapton adhesion was determined by pull-testing with an Instrumentors Inc. slip/peel tester at a 90° angle to the substrate and a peel rate of 0.25 in./min.

Results and Discussion

Base Hydrolysis and Surface Modification. Base hydrolysis of Kapton (Figure 2) occurs upon immersion of the film into the NaOH solution⁹ containing tetrakis-(2-hydroxy-*n*-propyl)ethylenediamine.¹² XPS was utilized to examine the Kapton films; high-resolution spectra of C(1s), O(2p), and N(1s) were monitored for the "as received" films, after 5 and after 10 min of immersion into the NaOH-ethylenediamine solution. As shown in Table I, the "as-received" surface of the Kapton is contaminated relative to the theoretical stoichiometry. The base hydrolysis results in a modification of the surface, as evidenced by the immediate removal of the silicon species and observed changes in the C(1s), O(2p), and N(1s) emission spectra. The sodium to nitrogen ratio is 0.9 and 0.8 after 5 and 10 min of immersion, respectively, and strongly suggests that the detected surface is predominantly the disodium salt of polyamic acid (Figure 2). Further, the high-resolution C, O, and N spectra are consistent with polyamic acid formation after base hydrolysis of the Kapton surface.^{9,13–15} The formation of the disodium polyamic acid salt upon NaOH hydrolysis of PMDA-ODA



M=K, Pd, Fe

Figure 2. Chemical scheme depicting base hydrolysis and cation exchange of films of pyromellitic dianhydride-oxydianiline (PMDA-ODA) polyimide as described in this work.

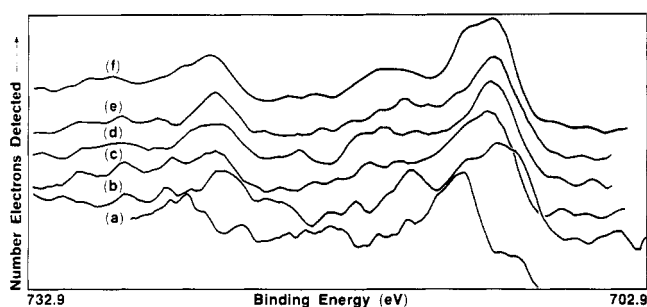


Figure 3. XPS Fe(2p_{3/2}) spectra of a Kapton film after immersion into basic ethylenediamine (10 min) followed by immersion into the iron-palladium catalyst solution (10 min) (a) as deposited, (b) after 30 seconds in situ UV irradiation, (c) after 60 s; (d) after 180 s; (e) after 210 s; (f) Kapton film after immersion into basic ethylenediamine solution (10 min), followed by immersion into K₃Fe(C₂O₄)₃ solution and UV irradiated for 210 s (5.3 J/cm²).

is analogous to that reported for hydrolysis with KOH.⁹ Surface modification of bulk polyimide films has been shown to be diffusion limited and thus immersion-time dependent.^{9,13} Also, the sodium to polyamic acid ratio is

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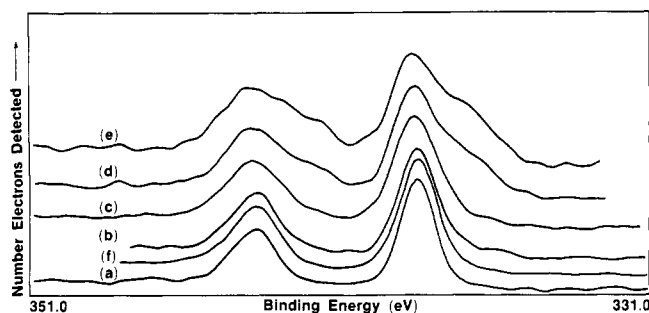


Figure 4. XPS Pd($3d_{5/2}$) spectra of a Kapton film after immersion into basic ethylenediamine solution (10 min) followed by immersion into the iron-palladium catalyst solution (10 min) (a) as deposited; (b) after 30 s in situ UV irradiation; (c) after 60 s; (d) after 180 s; (e) after 210 s; (f) Kapton film after immersion into basic ethylenediamine (10 min), followed by immersion into Pd(NH_3) $_4\text{Cl}_2$ solution and UV irradiated for 210 s (5.3 J/cm 2).

consistent with that found for treatment of polyamic acid with Na-containing base.¹⁴

Kapton films were examined after sequential immersion into the NaOH-ethylenediamine solution and the Fe-Pd catalytic solution; surface concentrations derived from the survey data are given in Table I. The high-resolution Pd($3d_{5/2}$) and Fe($2p_{3/2}$) spectra were obtained, as shown in Figures 3a and 4a, and displayed binding energies of 338.5 and 711.2 eV, respectively. These values are consistent with the reported values of Pd $^{2+}$ ¹⁶ and Fe $^{3+}$ ¹⁷ and are identical with the binding energies determined for K $_3$ Fe(C $_2$ O $_4$) $_3$ and Pd(NH_3) $_4\text{Cl}_2$ deposited onto the base-hydrolyzed Kapton separately. A second observation of the XPS data is that a 1:1 ratio of iron to palladium occurs on the surface of the Kapton film. This is quite unexpected because the potassium iron(3+) oxalate was in large excess (>10 mol equiv) to the palladium chloride concentration in solution. Although the high-resolution spectra show no binding energy shifts between the materials deposited separately and deposited a mixture (no drastic chemical state changes), the Fe-Pd-treated Kapton surface does not reflect the concentrations of the components in solution. This result was confirmed several times by using freshly prepared solutions and coating Kapton films as described earlier. The Pd/Cl and K/Fe ratios are also higher than those measured from the individual components which were deposited separately (Table I). As mentioned above, base hydrolysis of PMDA-ODA results in the formation of the disodium salt of polyamic acid. After immersion of this film into the Fe-Pd solution, ion exchange at the carboxylate groups is observed as evidenced by the complete absence of sodium signal and the incorporation of K, Fe, and Pd cations (Figure 2). Essentially, polyamic acid behaves as a cation-exchange resin with ion exchange occurring at the carboxylic acid groups.^{14,18} A facile exchange reaction of the polyamic acid sodium salt with various cations (alkali-earth and transition metals) has been previously reported.^{13,14} The ratio of iron to palladium on the modified Kapton surface may be indicative of the ion-exchange affinities for these specific

cations with the polyamic acid layer.

The rate and extent of ion exchange is dependent upon the ionic activity of the cation, which, in turn, is related to the charge and ionic strength of the cation.¹⁸ Other studies¹⁸ have shown that the ionic potential of the cation may affect the ion exchange activity. The ionic potential (IP) is defined as the charge of the ion (Z) divided by the ionic radius (r), such that $\text{IP} = Z/r$. In the current study, the nearly 1:1 ratio of the Fe to Pd and the large increase in the potassium (K) signal on the modified Kapton surface are best explained in terms of the ionic potential for the specific cations. For K $^+$, Pd $^{2+}$, and Fe $^{3+}$ present in the catalytic solution, the ionic potentials are 0.75, 2.5, and 4.7 charge/Å, respectively. Since the ion exchange activity is inversely related to IP, the activity for ion exchange is expected to be K > Pd > Fe. Therefore, the actual solution concentrations and the ionic potential of the individual cations will determine the extent of ion exchange.^{13,18}

A small exchange activity for high oxidation state metals (i.e., Al $^{3+}$ and Cr $^{3+}$) with the sodium salt of polyamic acid has been reported.¹⁴ These cations possess activity coefficients similar to that of Fe $^{3+}$,¹⁹ and the ionic potentials are 5.88, 4.76, and 4.7 charge/Å for Al $^{3+}$, Cr $^{3+}$, and Fe $^{3+}$, respectively. Thus, the relative ion-exchange activity would be given by Fe > Cr > Al. It should be further noted that the activity for Cr $^{3+}$ exchange with polyamic acid increased at higher pH.¹⁴ Thus, in this study the ionic exchange of Fe $^{3+}$ is not unreasonable and would be expected. Although the incorporation of iron is observed, it is not clear whether the entire iron oxalate complex is exchanged or if a modified iron complex (i.e., K $_2$ Fe(C $_2$ O $_4$) $_3^-$) diffuses into the modified Kapton surface to preserve charge neutrality¹⁸ (see below). Further, since XPS is a surface-sensitive technique (≈ 50 Å), the iron species could be present only at the very surface of the modified Kapton film. Since the XPS emission of the carbonyl carbons from the Kapton, the polyamic acid layer and from the K $_3$ Fe(C $_2$ O $_4$) $_3$ overlap, it is impossible to derive the stoichiometry of a specific iron species after cationic exchange. Nevertheless, the photoactivity of the oxalate system is not eliminated nor diminished (see below), and thus one would postulate that the iron is complexed by oxalate ligands in a fashion similar to the original iron oxalate complex. It is possible, although unlikely, that the iron is exchanged followed by association of free oxalate ligands to the iron center. The ionic mobility of the oxalate ligand¹⁹ is reported to be quite high, but this would require that the iron(3+) oxalate molecule be essentially decomposed in the catalytic solution.

Several comments should be made toward the ion exchange of palladium. First, the ionic potential of Pd $^{2+}$ is similar to that of other metallic cations that exchange with polyamic acid¹⁴ and cationic exchange has been reported.¹³ Second, the palladium could be bound to two adjacent carboxylate groups in the polyamic acid layer to preserve charge neutrality. Alternatively, other anionic species could serve the same purpose. Last, the ultimate reduction of Pd $^{2+}$ will lead to the active catalyst for electroless copper plating, and a mechanism for photoreduction is proposed below. The mode of copper-polyimide adhesion may relate to the ability of the polyamic acid to ion exchange and incorporate metal cations into the film. Upon photoreduction of the Pd $^{2+}$, the catalytic site for electroless copper plating is incorporated into the modified Kapton surface.

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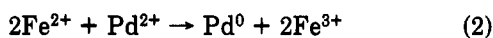
(19) Kielland, J. *J. Am. Chem. Soc.* **1937**, *59*, 1675. This paper provides activity coefficients for a variety of cations and anions that are pertinent to this study.

Thus, it is not unreasonable to assume that the presence of the carboxylate groups and their ability to ion exchange are responsible for the improved copper–Kapton adhesion (see below).

It should be noted that the exact role of the tetrasubstituted ethylenediamine is not clearly understood at this time. The binding energies of the nitrogens from the Kapton, the ethylenediamine, and Pd(NH₃)₄Cl₂ overlap. Further, the ethylenediamine consists only of C, H, N, and O, with a stoichiometry similar to that of the Kapton itself (Table I), and there is no unique “tag” to indicate how much is present on the modified Kapton surface. If any is present, ethylenediamine chelation could potentially enhance the copper to polyimide adhesion. However, a more detailed study is required to understand the role of the ethylenediamine during base hydrolysis of the Kapton surface.

After ion exchange with the catalytic solution, chlorine was found on the modified Kapton surface (Table I). The presence of Cl or other anions does not occur by ion exchange but may occur to preserve charge neutrality in the exchanged polyamic acid. Further, charge neutrality could be preserved by the oxalate ligand itself (C₂O₄²⁻) or by the presence of a modified iron oxalate anion, such as K₂Fe-(C₂O₄)₃⁻, as stated above. In any case, incorporation of either of these anionic species would explain the small surface concentration of Cl from the Fe–Pd catalytic mixture as compared to the Cl concentration for the Pd-(NH₃)₄Cl₂ solution alone. Last, the large K⁺ concentration in the hydrolyzed Kapton may be explained by both ion exchange of the free cation and its association with the iron(3+) oxalate complex. High K/Fe ratios were observed for films exposed to both the individual Fe(3+) oxalate (5.2:1) solution and to the mixed Fe–Pd solution (6.3:1).

Photochemical Considerations. The photosensitivity of potassium ferric oxalate is well documented in the literature²⁰ and as a result of its high quantum efficiency is often used as a photochemical actinometer. The quantum yield for the photoreduction of iron(3+) to iron(2+) was found to be unity or greater between 250 and 400 nm²¹ and is quite high at longer wavelengths as well.²² The photoreaction proceeds via electron transfer from an oxalate ligand orbital to a metal T_{2g} or E_g orbital,²³ thereby producing an Fe²⁺ species (eq 1). Although the exact pho-



toproducts may depend strongly upon the environment (i.e., solid, solution) during photolysis, it is generally accepted that K₂Fe(C₂O₄)₂, CO₂, and/or CO are the major photoproducts.²⁴ To confirm this, K₃Fe(C₂O₄)₃ was pressed into a KBr pellet, irradiated with UV light, and monitored by infrared (IR) spectroscopy. Upon irradiation, the immediate formation of two absorbances centered at 2345 and 663 cm⁻¹ were observed and correspond to the formation of CO₂.²⁵ The concentration of CO₂ increased

with the time of irradiation for times up to several minutes. Several other spectral changes were observed and are consistent with the reported IR absorbances of K₂Fe-(C₂O₄)₂.²⁶

In the present work, the interaction of the iron oxalate system with palladium(2+) chloride was expected to occur by a simple redox process, as shown in eqs 1 and 2, or by an electron–hole pair mechanism, as previously reported.^{10,27} In both mechanistic interpretations, however, the proximity of the iron center to the palladium species would be quite critical.

The inherent surface sensitivity of XPS allows one to readily probe the chemical state changes during the photoselective process described herein. An in situ XPS study was undertaken to understand the mechanism by which palladium metal (the active catalyst for electroless copper plating) is formed upon UV exposure of the treated Kapton film. In vacuo irradiation of the film eliminates the potential autooxidation of the primary iron(2+) photoproduct and greatly simplifies the interpretation of the mechanistic data. Thus, one can examine the photoreaction without environmental complications. Finally the high-resolution analysis of both the iron and palladium emissions enables the photoreaction to be closely monitored unambiguously.

Figures 3b–e and 4b–e show the high-resolution Fe and Pd spectra as a function of UV exposure time. It was observed that during UV irradiation, the pressure in the antechamber would increase from 10⁻⁷ Torr to the low 10⁻⁶ or high 10⁻⁶ Torr range. An immediate decrease in pressure was observed when the UV source was turned off. This observation is consistent with the formation of a gaseous photoproduct such as CO₂, as previously described.^{24–26} After a UV dose of only 756 mJ/cm² or 30 s of exposure (Figure 3b), the Fe(2p_{3/2}) peak maximum is at 710.4 eV, consistent with Fe²⁺ formation.^{26,27} Although the Fe³⁺ satellite at 721 eV is still visible, the main peak becomes narrower upon prolonged UV irradiation. The Fe(2p_{3/2}) spectra for exposures longer than 60 s (≥1.5 J/cm²) are essentially superimposable (Figures 3c–e).

The Pd(3d_{5/2}) spectrum after 30 s of UV irradiation (Figure 4b) has its peak maximum still at 338.5 eV, with only a very slight shoulder to lower BE. This shoulder shifts to still lower BE and increases in intensity with increased UV exposure. After a UV exposure dose of ≈5.3 J/cm² (210 s), 40% of the original Pd(3d_{5/2}) signal is in the low-BE shoulder.

The literature binding energy for metallic Pd is 334.9 eV.¹⁶ The low BE shoulder at low UV doses (Figure 4) is found at a binding energy >1 eV higher than that value. Binding energy shifts for Pd(3d_{5/2}) were found in Fe_{0.79}Pd_{0.21} alloy (335.9 eV).²⁸ Similarly, increasing Pd-(3d_{5/2}) binding energies with decreasing Pd content are reported,²⁹ although specific shifts were not given. Last, increasing binding energies for Pd are reported for decreasing Pd clusters size.³⁰ Therefore, at low UV doses, it appears that the reduced Pd atoms are isolated, only becoming more metallic (having mostly other Pd (0) neighbors) after continued irradiation.

The above discussions assume that the observed Pd-(3d_{5/2}) peak shifts are not due mainly to nonlinear charging

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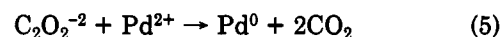
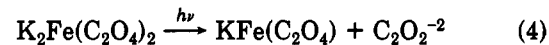
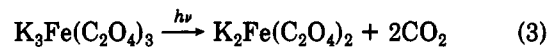
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with the insulating substrate. It has been demonstrated³¹ that XPS determination of chemical bonding effects with small metal particles on polymer substrates can be complicated by differential charging. Each high-resolution spectrum was referenced to the carbon(1s) emission so as to increase the precision of the absolute binding energies of each species. Although some experimental error is expected, the magnitude of the Pd(3d_{5/2}) binding energy shift upon irradiation is large enough to indicate that we are observing the photoreduction of Pd²⁺. Cluster size and isolation of the palladium species on the insulating substrate may account for the binding energy shift on early irradiation (<1 J/cm²). It is not possible, however, to rule out the presence of a Pd species whose formal charge is greater than zero.

Figure 3f shows the Pd(3d_{5/2}) spectrum of hydrolyzed polyimide after treatment with only Pd(NH₃)₄Cl₂ (no iron oxalate) followed by 210 s of UV radiation (dose of 5.29 J/cm²). As is clearly evident, UV photoreduction of Pd²⁺ in the absence of the Fe²⁺ species is minimal. In the presence of the iron oxalate complex, the photoreduction of palladium(2+) was slow and does not coincide with the reoxidation of Fe²⁺ back to Fe³⁺; this result indicates that the expected redox reaction (eq 2) is not operative. On the basis of our observations and the reported literature, the most likely explanation for the formation of palladium(0) is via photoconduction of electrons in the solid film or, more appropriately, molecular electron transfer from the iron(2+) oxalate to the palladium(2+) center.

Photoconductivity has been observed in a number of iron systems and is often correlated with the presence of an iron(2+) species. For example, photoconduction in iron oxide (Fe₂O₃) films³² and in iron-doped InP films³³ and the semiconducting behavior of iodine-doped organoiron complexes³⁴ (i.e., (L)Fe(CO)₃, where L is an unsaturated organic ligand) has been reported. In the iron-doped InP films, the Fe²⁺ ⁵E ⇌ ⁵T₂ electronic transitions are invoked to explain photoluminescent and conduction behavior.³³ In the iodine-doped (diene)Fe(CO)₃, Mössbauer spectroscopy indicated the formation of an iron(2+) species concurrent with the onset of the semiconducting properties. The semiconducting behavior was attributed to a low-spin Fe²⁺ complex that constructed a carrier/transport system for electrical conduction.³⁴ More specifically to the current study, the photoconductivity of ferric oxalate (solid) upon UV irradiation has been reported by several groups.^{24a,35} Further, a UV-generated photocurrent has been detected and is consistent with the formation of iron(2+) oxalate on the measuring electrode.^{35a} The photoconduction activity increased with increasing Fe²⁺ concentrations. In a separate study, the charge carriers for conduction were determined to be of electron character (n-type).^{35b} Therefore, it is postulated that reduction of Pd²⁺ to Pd⁰ occurs via molecular electron transfer from

the primary Fe²⁺ photoproduct upon continued irradiation, as shown in eqs 3–5. The XPS spectra demonstrate that



continued irradiation of the iron complex does not alter the oxidation state for times greater than 60 s; the iron remains in the 2+ state. Concurrently, it was experimentally observed that gas was evolved even at long irradiation times (>120 s). This has been confirmed by IR spectroscopy. The continued evolution of CO₂ is indicative of secondary photochemical decomposition of the primary Fe²⁺ oxalate photoproduct. The oxalate ligand, (C₂O₄)²⁻, is believed to be the source of electrons in the impending electron-transfer reaction with the Pd²⁺ center (eq 5).³⁸ Upon continued UV radiation, the primary Fe²⁺ product is decomposed, and the liberated oxalate results in reduction of Pd²⁺ to Pd⁰. For the electron/hole pair mechanism that was previously postulated,^{10,27} Pd²⁺ may be regarded as the source of holes. On the basis of the absence of Fe²⁺ oxidation, the continued production of gas(es) with prolonged irradiation and the exceedingly slow photoreduction of Pd²⁺ in the absence of the Fe³⁺ complex, an electron-transfer mechanism appears to be operative.

Process Considerations. The acute photosensitivity of the ferric oxalate system affords rapid photospeeds with low-UV doses and provides excellent image contrast upon electroless copper deposition. Uniformly plated copper patterns have been produced with UV doses ranging from as low as 200 to 800 mJ/cm². Due to the high quantum efficiency of the iron(3+) oxalate photoreduction, wavelengths varying from 250 to 400 nm may be used to produce selectively plated copper patterns. This enables commercially available UV exposure systems to be utilized to create copper circuits onto polyimide substrates. The initial copper film, or strike layer, is formed in less than 5 min of plating time in the electroless solution. The adhesive integrity of this layer is quite critical because it forms the actual interface between the copper and Kapton surfaces. It has been experimentally observed that the immersion time in the plating solution is critical. Initial plating times longer than 10 min result in adhesive failure of the "strike" layer. Base hydrolysis and/or ion exchange at the surface is time dependent^{9,13} and may be responsible for this failure. Also, the ethylenediamine molecule is exceedingly soluble in basic solutions. Thus, prolonged electroless plating at pH = 12 may interfere with the adhesive integrity of the copper-Kapton interface. It was found that the electroless plating time could be increased up to 1 h, without delamination of the copper-plated pattern, after thermally curing the substrate to 400 °C. The ability to increase the plating time enables thicker films of copper to be electrolessly plated directly in a selective manner. The polyamic acid can undergo thermal imidization except where metal carboxylates are present in the polymer backbone (i.e., K, Fe, or Pd). The presence of metal carboxylates has been shown to hinder imidiza-

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tion.¹⁴ Alternatively, the hydroxyl groups of the ethylenediamine species could undergo condensation reactions with the polyamic acid layer upon thermal activation, but this requires closer examination (good adhesion has been observed after baking to only 125 °C).

The adhesion of copper films was determined by mechanical pull-testing at 90° to the surface with a peel rate of 0.25 in./min. The metallized Kapton films produced with photoselective electroless plating were thermally imidized at 400 °C by using a typical polyimide cure cycle prior to electroplating. The copper film was then electroplated to a thickness varying between 15 and 25 μm. Measured adhesion values ranged from 70 to 110 g/mm with the average values being 80–90 g/mm. These values are quite high and indicative of the excellent adhesive strength between the plated copper film and the underlying polyimide layer. (Adhesion values of <5 g/mm are measured on copper films without base hydrolysis of the polyimide.) The ability of the polyamic acid to undergo ion exchange is believed to be instrumental in obtaining high copper–Kapton adhesion values. Similar adhesive values have been reported for polyimide–polyimide interfaces utilizing base hydrolysis.⁹ In a separate XPS surface study, the interaction of thin metallic films (i.e., copper) with polyamic acid promoted metal carboxylate formation at the surface.³⁷ At the same time, however, it is not possible to quantitate the presence of the ethylenediamine species that could substantially increase metal chelation on the modified Kapton surface. Nevertheless, the pull-test values are indicative of a high degree of adhesive integrity at the copper–Kapton interface.

The exchange of the Fe–Pd catalytic mixture and final concentration on the modified polyimide surface are critical variables to this photoselective process. These will determine the UV dose required to achieve the desired plating activity of the catalyst. The most stringent constraint, however, upon the UV exposure dose may be determined by the desired resolution of the copper-plated circuit pattern. Consistent with conventional polymer lithography, the resolution of a particular feature size is increased with increasing UV dose.² Thus, the UV exposure dose must be optimized to obtain uniform catalysis during copper plating while achieving the minimum feature size of the pattern.

The resolution of a given feature size will depend strongly upon the exposure dose and the final thickness of the electrolessly plated copper. Due to the isotropic behavior of most electroless plating solutions, the width of the feature being plated increases by a factor of twice the line thickness. For example, if a 10-μm wide line is being plated to a 2-μm thickness, then the final line width would be 14 μm. Thus far, utilizing the photoselective catalytic process to produce thin copper films (0.5-μm thickness), line widths below 10 μm are clearly resolved (Figure 5).

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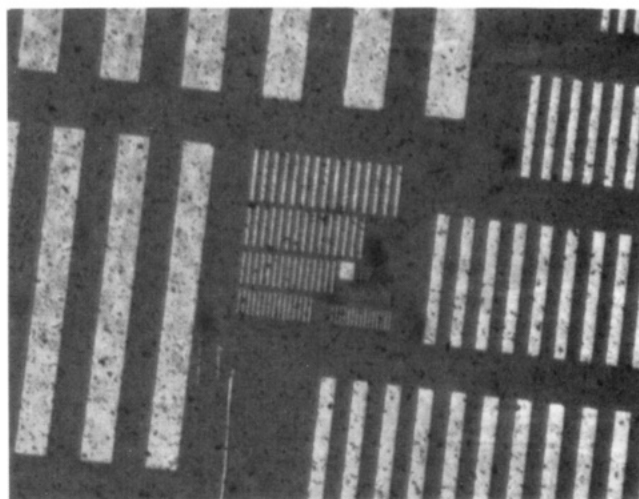


Figure 5. Section of an electrolessly plated copper pattern onto a Kapton film. The pattern was formed using a resolution target test mask and 5 min of copper plating. Optimum resolution, as evidenced by the copper-plated pattern, was a function of the total exposure dose. The minimum features resolved were 2 μm with the largest features of the inner pattern being 5 μm in width. A “clear” defect in the lithographic mask resulted in the errant copper-plated line visible in the pattern.

Conclusions

The selective formation of copper plated films onto Kapton substrates has been described. Base hydrolysis of the polymer backbone results in the formation of the disodium salt of polyamic acid. Cationic exchange occurs in the modified layer of the Kapton film upon treatment with an aqueous solution containing $K_3Fe(C_2O_4)_3$ and $Pd(NH_3)_4Cl_2$. Although the iron concentration is >10 mol equiv to the palladium concentration in solution, the observed surface ratio is 1:1. This result is best explained by the differing ionic potentials of the individual cations or their affinity for cation exchange with the hydrolyzed Kapton surface. The UV-induced reduction of iron(3+) to iron(2+) is observed to be extremely rapid, while the slower conversion of palladium(2+) to palladium metal is observed. The selective formation of palladium metal catalyst initiates electroless copper plating only in the UV-exposed areas of the treated surface. The formation of the active catalyst for electroless plating is believed to occur via electron transfer from the primary Fe^{2+} product upon secondary photolysis. The source for electrons is thought to be the oxalate ligand. The electrolessly plated copper films exhibit outstanding adhesive strength to the modified Kapton surfaces; the ability of the polyamic acid to undergo ion exchange at the carboxylate groups is believed to be primarily responsible for the high copper–Kapton adhesion values. The photoselective formation of copper-plated patterns onto polyimide substrates is readily achieved by this simplified method using limited doses of UV radiation from conventional sources. The ability to selectively deposit adherent copper films onto polyimide displays great potential for the selective metallization of microelectronic components.