

Reflective and Electrically Conductive Palladium Surface-Metallized Polyimide Nanocomposite Membranes

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ABSTRACT: A previous article (Southward and Thompson, *Chem Mater* 2004, 16, 2091) focused on the characterization of surface metallized palladium-BTDA/4,4'-ODA (3,3',4,4'-benzophenone tetracarboxylic dianhydride-4,4'-oxydianiline) hybrid membranes formed by *in situ* reduction of Pd²⁺ to Pd⁰ during thermal imidization of the poly(amic acid) via the protocol of St. Clair et al. (*J Am Chem Soc* 1980, 102, 876). The present work extended the Pd-polyimide metallization synthesis to the BPDA/4,4'-ODA (3,3',4,4'-biphenyltetracarboxylic dianhydride-4,4'-ODA) polymer. The effects of the Pd²⁺ ligand on the reductive metallization of BTDA/4,4'-ODA were also examined for the PdCl₂(SMe₂)₂, PdBr₂(SMe₂)₂, and Pd(CF₃COO)₂ complexes. The hybrid films were characterized by specular and diffuse reflectivity and by conductivity measurement. Maximum specular reflectivity was in the

range of 35%–55%, and conductivity was in the range of 1–10 Ω/square. Scanning electron microscopy and transmission electron microscopy revealed that the initial Pd metal particles formed within the films were in the 3–8 nm range in size. These particles increased in size with irregular shapes at the surface as the metallic exterior emerged. A fraction of the nanometer-sized Pd particles remained uniformly distributed throughout the bulk of the film. The mechanism for the formation of a metallic surface required selective oxidative degradation of the polyimide at the polyimide–air interface. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2708–2716, 2006

Key words: polyimides; nanocomposites; conducting polymers

INTRODUCTION

Recently, we elaborated work initiated in 1980 by St. Clair et al.¹ on a novel single-stage synthesis of surface-metallized palladium–polyimide films that also had nanometer-sized palladium particles distributed throughout the bulk. Specifically, the four-coordinate palladium(II) complex, trans-[Cl₂(SMe₂)₂Pd],^{2–4} was dissolved in the poly(amic acid) form of BTDA/4,4'-ODA in dimethylacetamide (see Fig. 1, with X = C=O). The palladium concentration was relatively low at 5 wt % (0.6 vol %) in the product hybrid membrane. Thermal treatment in air (i.e., an oxygen-containing atmosphere) of the doped films to 300°C for approximately 1 h gave imidized films with a metallic palladium layer at the air-side surface. The films exhibited surface electrical conductivity in the metallic range and modest to excellent specular reflectivity coupled with excellent metal–polymer interfacial adhesion. The interior of the film contained isolated quasispherical palladium nanoparticles. Electrical conductivity was confined to the air-side surface of the film; neither the glass side nor the bulk of the film was conductive.

Palladium-metallized films have several potential applications. First, there is interest in the use of partially embedded palladium seed layers on polyimide surfaces to anchor a second metal to the film surface for circuitry applications, particularly metals such as copper and silver that do not adhere well to polyimides.^{5–9} Second, there is research directed toward flexible and patterned conductive and reflective hybrid films; palladium is highly conductive and has excellent reflectivity at longer electromagnetic radiation wavelengths. For example, Seita et al.¹⁰ photochemically developed palladium circuit patterns on surface-modified polyimide films. Finally, there is ongoing interest in palladium-filled polymeric membranes^{11–16} and palladium-doped carbon molecular sieve membranes (produced by palladium-catalyzed degradation of polymer to carbon) for hydrogen separation¹⁷ and catalytic hydrogenation reactions.¹⁸

The work reported in this article extended this palladium–polyimide metallization synthesis to the BPDA/4,4'-ODA (3,3',4,4'-biphenyltetracarboxylic dianhydride-4,4'-ODA) polymer (Fig. 1, with X = a C–C bond only between the two aromatic rings). In addition, the effects of the palladium(II)-ion (Pd²⁺) ligand on metallization of BTDA/4,4'-ODA were examined using the complexes PdCl₂(SMe₂)₂, PdBr₂(SMe₂)₂, and Pd(CF₃COO)₂. The metallized polyimides were prepared by first preparing the Pd²⁺ complexes in a dimethylacetamide solution of the poly(amic acid)

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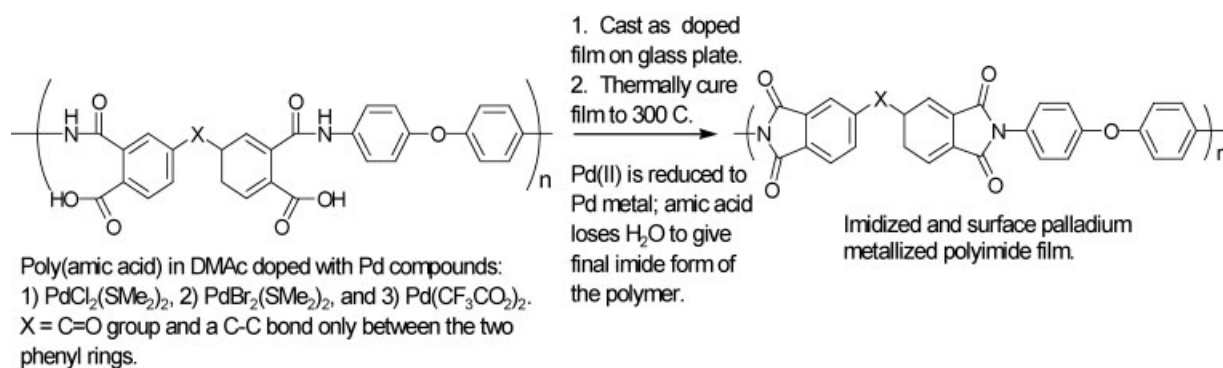


Figure 1 Synthetic scheme for the preparation of palladium-metallized polyimide films.

form of polyimide. Second, Pd-doped films cast on glass plates were thermally cured to 300°C in air in order to reduce Pd²⁺ to the native metal, followed by membrane surface metallization. The metallized films were characterized by scanning and transmission electron microscopy, conductivity, measurements, and reflectivity measurements.

EXPERIMENTAL

Materials

The 4,4'-ODA, BTDA, and BPDA were obtained from Wakayama via Chriskev Chemical Company (Leawood, KS). The 4,4'-ODA was used as received. BTDA and BPDA were dried under vacuum at 150°C for 10 h prior to use; this was crucial for obtaining quality resin solutions. The chloride, bromide, and acetate salts of palladium(II), dimethylsulfide, trifluoroacetic acid, and dimethylacetamide (anhydrous) were purchased from Sigma-Aldrich (Milwaukee, Wisconsin) and used as received. The poly(amic acid) solutions were prepared with a 0.5% excess offset of dianhydride at 15% solids (w/w) in DMAc. The resins were stirred for more than 5 h before use and were newly made for each metallized film preparation. Inherent viscosity was in the range of 0.9–1.5 dL/g at 35°C. We have previously shown that resin viscosity does not affect *in situ* metallization of silvered polyimide films.^{19–21} PdCl₂(SMe₂)₂ was prepared by a method described in the literature,³ except that the complex was used as prepared in solution without isolation, as described below.

Preparation of BTDA/4,4'-ODA- and BPDA/4,4'-ODA-palladium-metallized films

Procedure to prepare metallized films with PdX₂(SMe₂)₂ complexes (where X = Cl or Br) synthesized without isolation in the solid state

PdX₂ (0.127 g of PdCl₂ or 0.191 g of PdBr₂), for the BTDA/4,4'-ODA films, or PdCl₂ (0.110 g), for the

BPDA/4,4'-ODA films, followed by SMe₂ (0.178 g) was added to 1.0 g of DMAc (molar ratio of Pd : SMe₂ = 1 : 4). After 5 min a clear red solution of the *in situ* PdX₂(SMe₂)₂ complex formed. This solution was added via syringe to 10.0 g of a freshly prepared 15% solids poly(amic acid) solution in DMAc. The resulting Pd(II)-poly(amic acid) solution was stirred for 2 h to ensure homogeneity. Doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 600 μm to obtain about 25-μm-thick films after thermal curing. Films used for the reflectivity versus time/temperature measurements were cast on 27 × 46 mm petrographic slides. After remaining in an atmosphere of slowly flowing dry air (150 scfh and 4% relative humidity) for 18 h, the films were thermally cured in a forced-air oven with the intake vent of a GS Blue M oven (Series 146 with Pro-350 controller) closed and the exit vent opened slightly, to only 15% of maximum. The cure cycle involved heating to 135°C over 20 min, maintaining that 135°C temperature for 1 h, heating to 300°C over 4 h, and finally maintaining that 300°C temperature for varying times. Films could be readily removed from the casting plate by immersing in deionized water.

Procedure to prepare composite films with palladium(II) trifluoroacetate formed *in situ* from palladium(II) acetate and trifluoroacetic acid

Pd(OAc)₂ (0.161 g) and trifluoroacetic acid (0.252 g) were added to 1.0 g of DMAc and stirred to give a clear red solution. This solution was added with stirring as in the first procedure, described above, to 10.00 g of the 15% solids poly(amic acid) solution. The doped poly(amic acid) solution was treated as before to prepare metallized films.

Characterization

The surface resistivity of all films was measured using the four-point probe technique, with calibration routinely checked with 100 Ω/square indium tin oxide

on poly(ethylene terephthalate). Transmission electron microscopy (TEM) was performed on a Zeiss CEM-920 instrument. Samples were sliced at 100 nm. Scanning electron micrographs (SEMs) were obtained on a Hitachi S-4700 instrument on samples coated with about 5 nm of palladium/gold alloy when not conductive. Measurement of specular reflectivity was performed (relative to a Perkin–Elmer polished aluminum mirror with a reflectivity coefficient of 0.92 at 531 nm; palladium has a reflectivity of ca. 60% vs. Al at 531 nm) with a Perkin–Elmer Lambda 35 UV–vis spectrophotometer equipped with a variable-angle specular reflectance accessory using a wavelength of 531 nm, which is near the solar maximum. Diffuse reflectance measurements were performed with a Perkin–Elmer Lambda 19 equipped with a 150-mm integrating sphere made by Labsphere and standardized with Spectralon. Palladium metal analyses were done gravimetrically by heating the polyimide–metal hybrid films to 650°C in air in a platinum crucible for 30 min. The polymer was lost, leaving only Pd metal. The theoretical percentage of Pd in this study was always calculated relative to polyimide and Pd alone. The ligands of the Pd complex were assumed to be lost.

RESULTS AND DISCUSSION

BPDA/4,4'-ODA-PdCl₂(SMe₂)₂-metallized films

Fabrication

These films were synthesized by preparing a DMAc solution of the PdCl₂(SMe₂)₂ complex from direct reaction of palladium(II) chloride and dimethyl sulfide at the ambient temperature. The complex solution was then added to a DMAc solution of the poly(amic acid) of BPDA/4,4'-ODA, as illustrated in Figure 1. The poly(amic acid) resin, an intense yellow in color, was newly prepared for each set of films. The final Pd²⁺-doped poly(amic acid) solutions were clear and dark red in color. Film samples were prepared at two concentrations, 5.2 and 2.7 wt % (the calculation based only on the masses of Pd metal and the final imidized form of the polymer; the ligands were assumed to be lost from the system¹). Because of the high density of Pd (12 g/cm³), the volume percents were very low, 0.66 and 0.33, respectively. Taylor et al. previously had prepared and used PdCl₂(SMe₂)₂ as an isolated crystalline solid with BTDA/4,4'-ODA.¹ We found subsequently that this Pd complex could be prepared and used more expeditiously, that is, without isolation as a solid, by simply dissolving PdCl₂ in an SMe₂–DMAc solution; complex formation essentially occurred immediately.²² This approach allowed a wide range of additional dihalobis(dialkyl sulfide)palladium(II) complexes to be used with PdCl₂ for polymer doping with minimal effort. In our previous

study, we showed that metallized films prepared with isolated PdCl₂(SMe₂)₂ in DMAc were indistinguishable from those prepared in DMAc without isolation.²² All films were thermally treated to a final temperature of 300°C for 2 h or less and were tough and flexible without fracturing under vigorous hand manipulation and tight creasing. The adhesion of Pd to the polyimide was excellent, which was attributable to the partial embedment (mechanical interlocking) of Pd nanoparticles in the surface of the polymer. Films heated beyond 2 h at 300°C begin to degrade with respect to both optical and mechanical properties. We have established that the degradation is Pd-catalyzed air oxidation of the polyimide structure.²² After heating for 3 h or more at 300°C, freestanding films could no longer be removed from the glass plate.

Reflectivity and conductivity

Figure 2 displays the total, specular, and diffuse reflectivity data as a function of time/temperature for [PdCl₂ + 4 SMe₂]-BPDA/4,4'-ODA films at 5.2% Pd. The specular and diffuse reflectivity remained in the dielectric range through a temperature of 275°C of the prescribed thermal cycle. Thereafter and near 300°C the specular reflectivity increased steadily, reaching a maximum after 1.5 h at 300°C. With an increasing residence time at 300°C, the specular reflectivity then

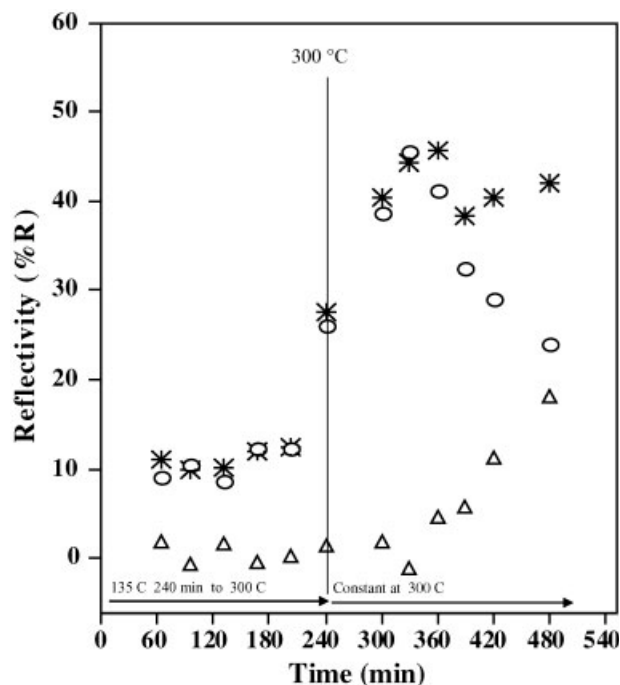


Figure 2 Total (*), specular (O), and diffuse (Δ) reflectivities for 5.2% Pd films formed with BPDA/4,4'-ODA and nonisolated PdCl₂(SMe₂)₂ from PdCl₂ + 4 SMe₂. [For Figs. 2 and 3 the cure was: 20 min to 135°C; hold for 60 min (time zero on the plots); 135°C–300°C over 240 min; hold at 300°C.]

TABLE I
Surface Resistivity of 5.2% Pd [PdCl₂(SMe₂)₂]-BPDA/4,4'-ODA Films Shown in Figure 2

Temperature ^a	Sheet resistivity ^b (Ω /square)
25°C–300°C	Not conductive
300°C for 1 h	9
300°C for 2 h	4
300°C for 3 h	2
300°C for 4 h	3

^a Thermal program: 20 min to 135°C, hold for 1 h, 240 min to 300°C, hold at 300°C.

^b Measured by the four-point probe technique.

diminished while the diffuse component increased to maintain an approximately constant value of total reflectivity. The increase in diffuse reflectivity must have been a result of the greater surface roughness that developed with time as the polyimide was degraded to volatile products, leaving a thick (ca. micron-sized) Pd multiparticle layer. After 4 h at 300°C the residual degraded film remaining on the plate was approximately 70%, rather than 5.2%, palladium metal. Although specular reflectivity decreased with time after 1.5 h at 300°C, surface conductivity remained high, as can be seen in Table I. After being

at 300°C for more than 3 h, intact films could no longer be detached from the plate, that is, oxidative degradation of the polymer structure was critical.

The development of significant reflectivity and conductivity with temperature/time, that is, the development of a thin Pd layer that resided at the film–air interface without a polymer overlayer, crucially depended on the selective degradation of surface-only polyimide to volatile products. This had to be so because the surface free energy of metals is always greater than the sum of the interfacial free energy and the polymer surface free energy, $\gamma_M > \gamma_{MP} + \gamma_P$. Thus, a metal particle placed on the surface of a polymer must thermodynamically embed completely into the macromolecular phase; this has been thoroughly demonstrated by Kovacs and Vincett,^{23–25} Faupel et al.,²⁶ and Zaporozhchenko et al.²⁷ We recently showed that as reflectivity began to increase near 300°C, the percentage of Pd in the film increased and that at the point of maximum reflectivity the Pd concentration had increased from 5.2% to about 8%.²² This degradation appeared to proceed selectively from the air-side surface inward as the mechanical properties of the metallized film at maximum reflectivity were still near those of the parent polyimide. Curing in nitrogen or argon atmospheres does not give a metallized surface.²⁸ Thus, to form a Pd surface, it is essential to

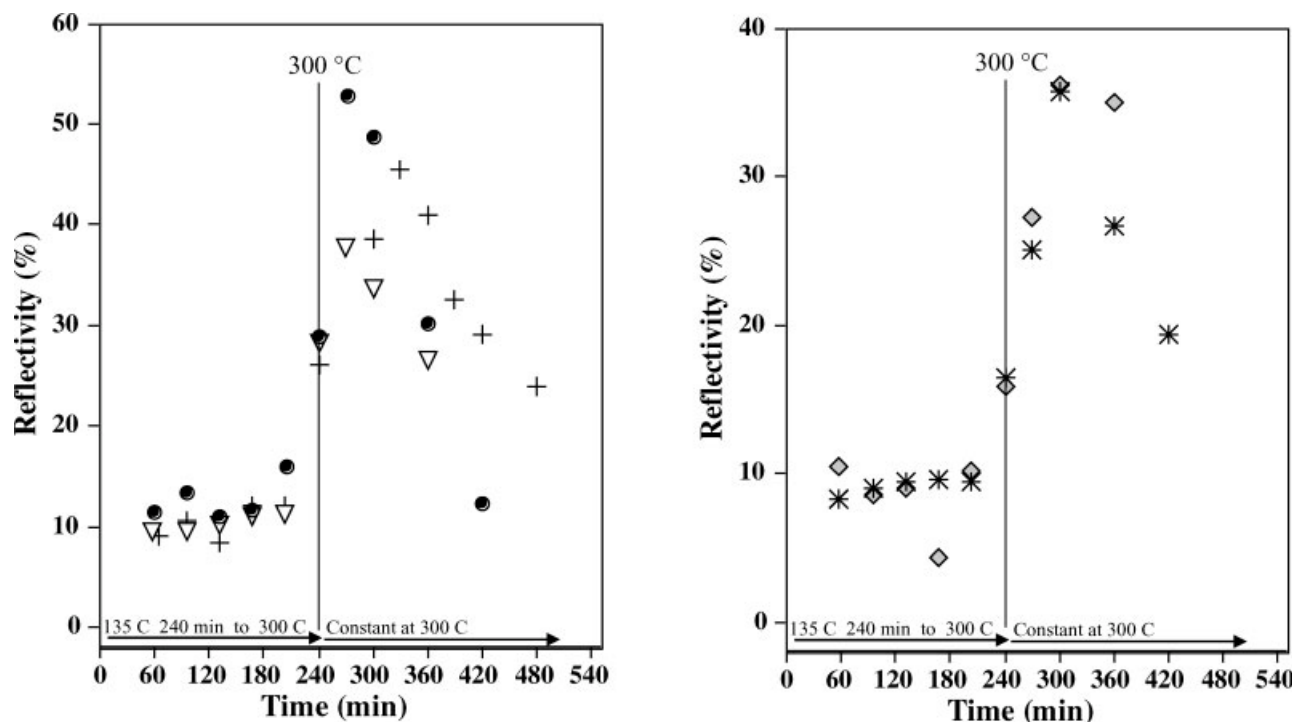


Figure 3 (Left) Specular reflectivity as a function of time/temperature for three BPDA/4,4'-ODA films (●, ▽, +) at 5.2% Pd prepared independently on different days. The three resin solutions were prepared with the same reagents using the PdCl₂ + 4 SMe₂ + DMAc *in situ* solution added to 15% poly(amic acid) in DMAc. (Right) Same as on left except two samples prepared at 2.7% Pd.

have surface and near-surface polyimide oxidatively degraded to volatile products. That is, the formation of the metallized surface involves solid-state, heterogeneous surface degradation/ablation reactions. The difficulties of controlling heterogeneous surface reactions, relative to homogeneous solution reactions, may account for the observations (Fig. 3, left) that from run to run, samples of 5.2% Pd cured in a Blue M Series 146 forced-air oven showed variation in the maximum specular reflectivity and moderately different temperatures at which the maximum reflectivity was observed. Maximum reflectivity at 531 nm of three independent samples was 38%, 45%, and 53%, respectively, with time/temperature values in the range of 0.5–1.5 h at 300°C. (The reflectivity of Pd versus Al at 531 nm is only ca. 60%; it is much better at long wavelengths.) Films produced at 2.7% Pd (Fig. 3, right) appeared to have better reproducibility from run to run but lower maximum reflectivity. The conductivity values were much less variable and did not relate to the observed differences in reflectivity.

Figure 4 demonstrates the importance of air (oxygen) flow through the oven to the development of the metallized surface. If the air intake of the Blue M (Series 146) forced-air oven was opened beyond about 50% of maximum with the exhaust vent opened at 15% of maximum, the films in this richer oxygen atmosphere developed no significant specular reflectivity, and the polyimide was extensively degraded earlier, beginning when a temperature of 300°C was first reached. The maximum specular reflectivity was obtained at minimal oxygen with the exhaust vent at 15% of maximum and the air vent securely closed; this limited the flow of air through the oven to that due to leakage.

Electron microscopy—nature and formation of metallized surface

Figure 5 shows SEM scans of five $[\text{PdCl}_2 + 4(\text{SM}e_2)]\text{-BPDA}/4,4'\text{-ODA}$ films at 5.2% Pd from 275°C to 300°C for 2 h (the same films, designated by solid circles, are on the left-hand side of Fig. 3). As can be seen on the left-hand side of Figure 3, significant reflectivity (29%) developed by 300°C at 0 h; however, the film was not electrically conductive. The first conductive film appeared about 30 min later (300°C/0.5 h), with the reflectivity increasing to 53%. Thereafter, as with other Pd–polyimide film systems, specular reflectivity decreased. At 275°C the SEM of the surface showed it consisted of isolated Pd particles approximately 3–8 nm in size (see inset, Fig. 5). When a temperature of 300°C was first reached, an islandlike patchwork array of Pd aggregates forming was observed; the metallic arrays did not contact one another. These “patches” contributed to a developing specular reflectivity of 29% at 300°C.

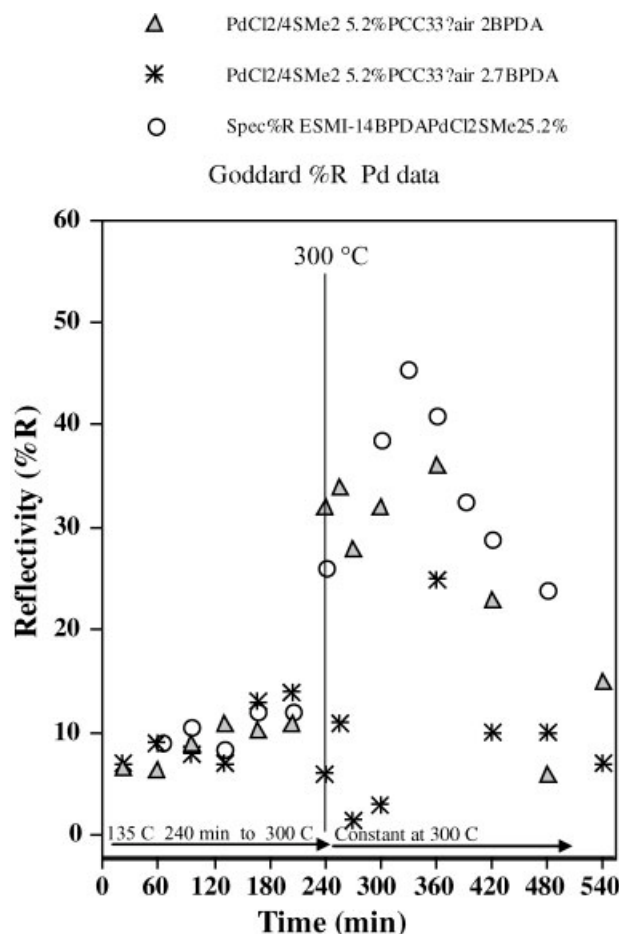


Figure 4 Effect of air (oxygen) intake on the specular reflectivity of 5.2% Pd BPDA/4,4'-ODA films prepared as in Figure 3. (○) Air intake vent closed; (△) air intake opened 40% of maximum; (*) air intake opened 55% of maximum.

The patchwork arrays grew in size from 300°C at 0 h to 300°C at 1 h. A clearly developed network of Pd eventually formed, as can be seen in the micrographs of the 300°C/1 h and 300°C/2 h films. We have shown that the development of conductivity correlated with slow oxidative degradation of the polyimide.²² The surface of the 300°C/2 h film was more uneven than that of the 300°C/1 h film, which may account for the decrease in specular reflectivity to 30% coupled with an increase in the diffuse component.

Figure 6 shows the TEM of the air-side surface of the $[\text{PdCl}_2 + 4\text{SM}e_2]$ with BPDA/ODA shown in Figure 2 heated to 300°C for 1.5 h with a reflectivity of 46%. Visible was a layer of Pd metal approximately 50–70 nm thick with some irregularities. The surface was consistent with that seen in the SEM micrographs. Much smaller particles, on the order of 5–10 nm in diameter, were visible in the bulk, also consistent with the SEM data.

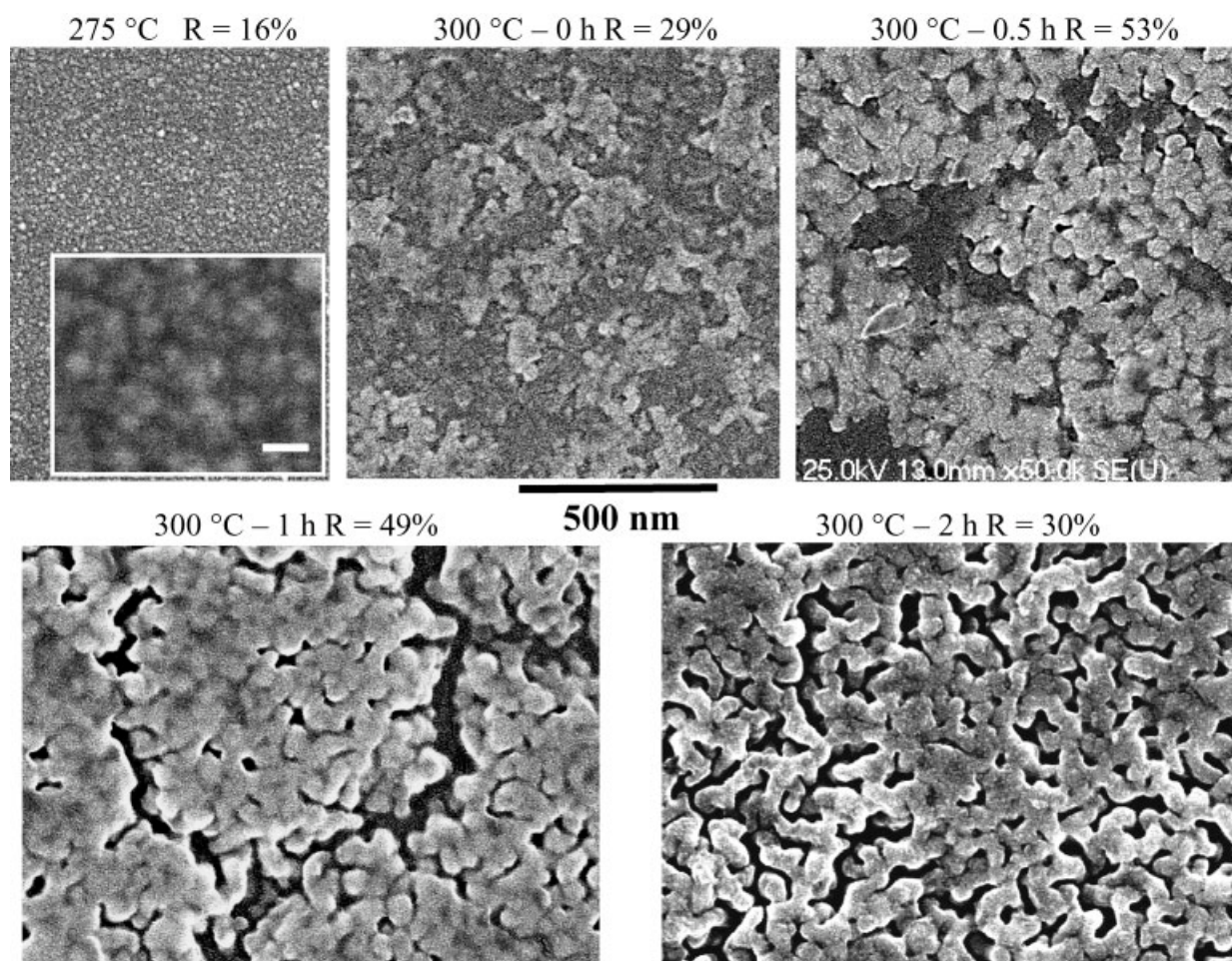


Figure 5 SEM micrographs of a series of $\text{PdCl}_2(\text{SMe}_2)_2$ -BPDA/4,4'-ODA films (5.2% Pd) withdrawn from the cure cycle at the indicated temperatures: 275°C, 300°C after 0 h, 300°C after 0.5 h, 300°C after 1 h, and 300°C after 2 h, with reflectivity = 16%, 29%, 53%, 49%, and 30%, respectively. The thermal cycle was: 20 min to 135°C, 135°C–300°C over 4 h, hold at 300°C. The scale bar (500 nm) applies to all figures. The inset on the 275°C micrograph is at a magnification of 500K; the scale bar is 10 nm (these are the same films as in Fig. 3 identified with filled circles).

Comparisons among Pd complexes and polyimide structures

$\text{PdCl}_2(\text{SMe}_2)_2$, $\text{PdBr}_2(\text{SMe}_2)_2$, and $\text{Pd}(\text{CF}_3\text{COO})_2$ complexes in BTDA/4,4'-ODA

Figure 7 shows that $\text{PdCl}_2(\text{SMe}_2)_2$ and $\text{Pd}(\text{CF}_3\text{COO})_2$ in BTDA/4,4'-ODA produced films that had modest to excellent maximum specular reflectivity, 35% and 53%, respectively, which emerged sharply near 300°C. The trifluoroacetate film reached maximum specular reflectivity some 30 min sooner than did the $\text{PdCl}_2(\text{SMe}_2)_2$ film. After achieving the maximum reflectivity, the specular reflectivity quickly degraded for the $\text{PdCl}_2(\text{SMe}_2)_2$ system and dramatically degraded for the $\text{Pd}(\text{CF}_3\text{COO})_2$ system; however, the films remained highly conductive. Both film types exhibited surface resistivity of approximately 10 Ω /square at maximum reflectivity. Surprisingly, the dibromo analog of $\text{PdCl}_2(\text{SMe}_2)_2$ -BTDA/4,4'-

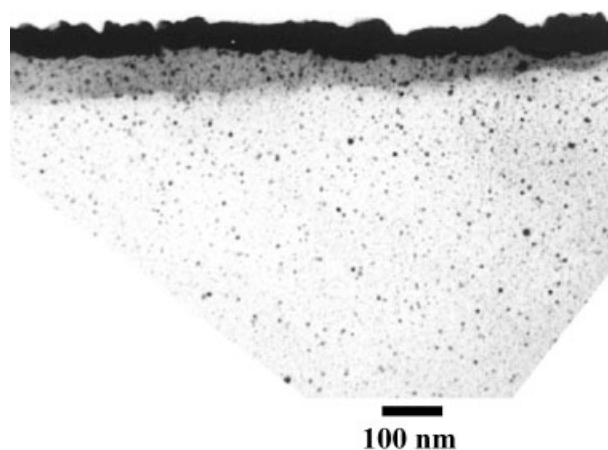


Figure 6 TEM of the air-side surface of the 5.2% Pd film, taken from the oven at 300°C after 1.5 h prepared from *in situ* $\text{PdCl}_2 + 4 \text{ SMe}_2$ with BPDA/4,4'-ODA in DMAc (same film as in Fig. 4 with %R = 46).

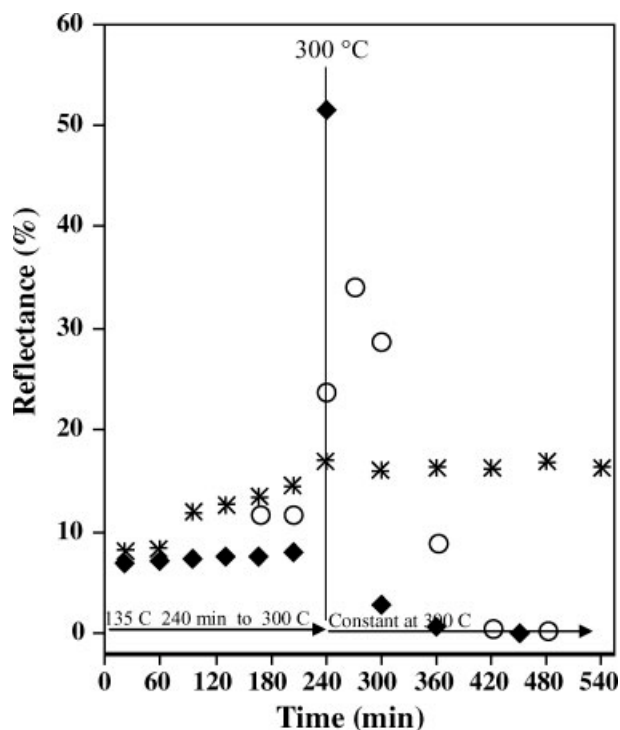


Figure 7 Specular reflectivity as a function of cure time/temperature for BTDA/4,4'-ODA films at 5.2% Pd from differing palladium(II) complexes: (○) $\text{PdCl}_2(\text{SMe}_2)_2$, (*) $\text{PdBr}_2 + 4 \text{SMe}_2$, and (◆) $\text{Pd}(\text{OAc})_2 + 2 \text{CF}_3\text{COOH}$ in DMAc.

ODA system never became significantly reflective or conductive. The SEM micrographs of dichloro and dibromo samples taken from the oven at 300°C after 2 h, shown in Figure 8, were strikingly different. The particle size in the dibromo sample remained very small, in the 2–7 nm range, whereas the particles in the dichloro sample²² grew from approximately 5 nm to much larger sizes. We do not know any rea-

son for such a difference between these congeners, but it is in line with our observations of pronounced ligand effects on the development of both the reflectivity and conductivity of analogous silver metallization systems.²⁰

Polyimide comparisons

In an article on single-stage metallization of traditional polyimides with a silver complex [η^4 -1,5-cyclooctadiene)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)silver(I)], Rosolovsky et al.²⁹ stated: "A strong correlation between the presence of [a] ketonic group [e.g., the carbonyl group in BTDA] in the polyimide structure and the formation of mirror surfaces was detected." However, we did not observe any evidence of this "ketonic" effect in the metallization of BTDA/4,4'-ODA³⁰ and BPDA/4,4'-ODA³¹ with (1,1,1-trifluoro-2,4-pentanedionato)silver(I); these two polyimides produced highly reflective and conductive films that were essentially identical. Figure 9 shows the data for the development of specular reflectivity as a function of cure time/temperature for the two polyimide film systems, BPDA/4,4'-ODA and BTDA/4,4'-ODA doped with $\text{PdCl}_2(\text{SMe}_2)_2$ at 5.2% Pd. From these and the two additional sets of reflectivity data for BPDA/4,4'-ODA shown on the left-hand side of Figure 3, we did not see evidence of any significant difference between the two polyimides in the propensity to metallize. The two sets of Pd films showed similar surface conductivity, with the BPDA/4,4'-ODA set observed to be slightly more conductive. Thus, it remains unclear what the detailed role of this polyimide is in the formation of palladium-metallized surfaces. We have preliminarily observed that the use of the fluorinated polyimide 6FDA/4-BDAF yielded

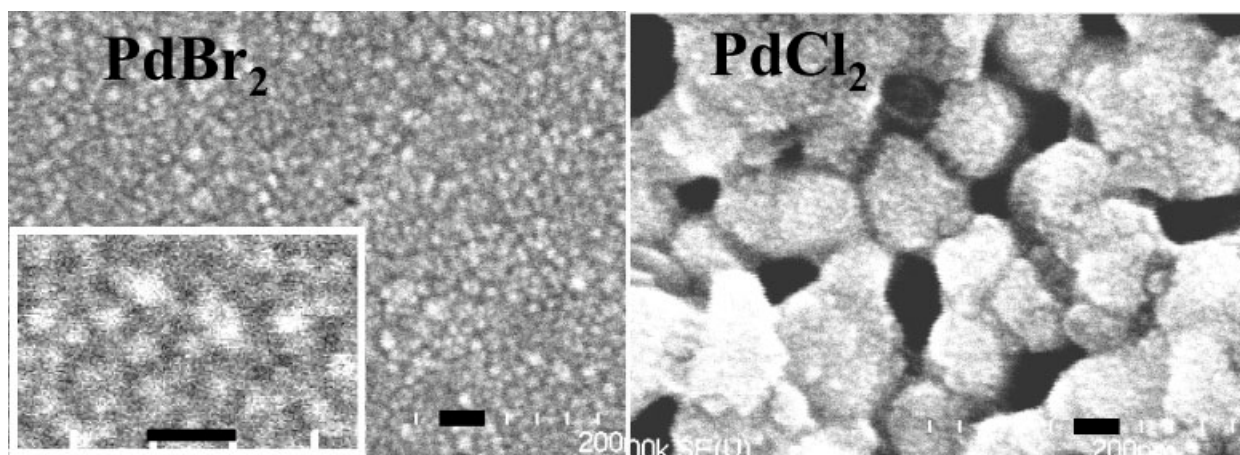


Figure 8 SEMs of BTDA/4,4'-ODA films shown in Figure 2 at 5.2% Pd prepared from PdBr_2 and PdCl_2 as described in Figure 7. Both films were cured as described in Figure 2 and withdrawn from the oven after being at 300°C for 2 h. All three scale bars are 20 nm.

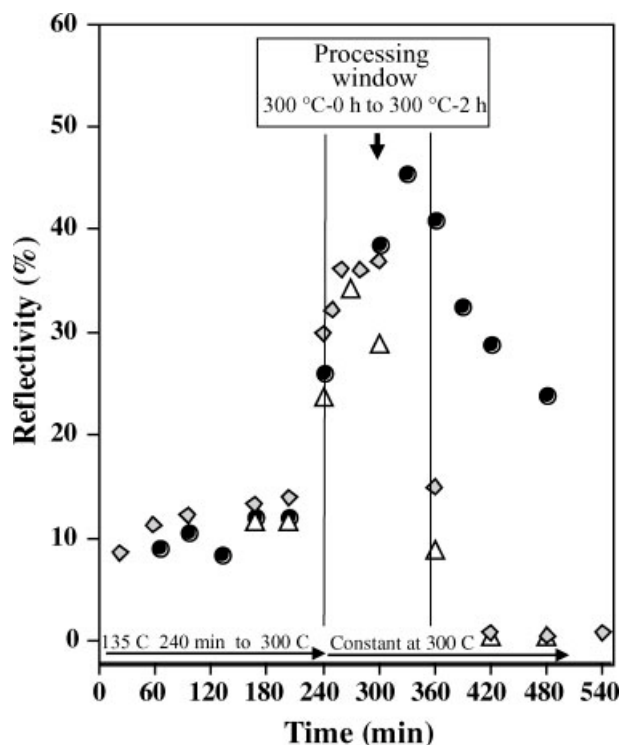


Figure 9 Polyimide comparisons—development of specular reflectivity as a function of cure time/temperature for two polyimide films, BPDA/4,4'-ODA and BTDA/4,4'-ODA doped with PdCl₂(SMe₂)₂ at 5.2% Pd (solvent: DMAc): (●) PdCl₂(SMe₂)₂ prepared without isolation in BPDA/4,4'-ODA; (◇) isolated PdCl₂(SMe₂)₂ in; BTDA/4,4'-ODA; (△) PdCl₂(SMe₂)₂ prepared without isolation in solution in BTDA/4,4'-ODA.

films with low reflectivity and conductivity that lacked structural integrity.³²

CONCLUSIONS

Palladium–polyimide metallization has been successfully extended in the present study to the BPDA/4,4'-ODA polymer. Maximum specular reflectivity for the BPDA/4,4'-ODA films was in the 35%–55% range after curing at 300°C for 0–2 h; electrical conductivity was in the range of 1–10 Ω/square. After achieving maximum reflectivity all BPDA/4,4'-ODA film surfaces degraded on further heating at 300°C until freestanding films could not be removed from the casting plates, which occurred after approximately 3 h. The mechanism for the formation of a metallic surface requires selective oxidative degradation of the polyimide at the air-side interface, which concomitantly concentrated and enlarged the size of metal nanoparticles at the surface.

The effects of the divalent palladium (Pd²⁺) ligand on metallization of the initially studied BTDA/4,4'-ODA were also examined for the PdCl₂(SMe₂)₂, PdBr₂(SMe₂)₂, and Pd(CF₃COO)₂ complexes. Although

PdCl₂(SMe₂)₂ and Pd(CF₃COO)₂ produced similar BTDA/4,4'-ODA films that were both reflective and conductive, unexpectedly, the closely related complex PdBr₂(SMe₂)₂ never produced reflective or conductive films. The reason for this is unknown. Comparing the reflectivity and conductivity data coupled with microscopy observations made it clear that surface-metallized films from the two polyimides, BPDA/4,4'-ODA and BTDA/4,4'-ODA, were essentially identical. Although it has been suggested that carbonyl functionality in the dianhydride unit of the polyimide is important for producing high-quality surface-metallized films with the use of silver(I) additives, this does not hold for the palladium films synthesized in the present study.

SEM and TEM micrographs revealed that the initial (ca. 275°C) Pd metal particles formed in the films were in the 3–8 nm range in size and were quasispherical in shape but increased in size and shape irregularity on the surface as a metallic phase emerged. A fraction of the nanometer-sized Pd particles remained uniformly distributed throughout the bulk of the film. Beginning near 300°C the nanometer-sized Pd particles catalyzed oxidative degradation of polyimide on and near the surface to volatile products and grew into larger particles via sintering to form a network. Formation of a metallized surface by oxidative ablation of the polyimide to expose and then allow metal cluster sintering was expected because the high surface free energy of the metal particles relative to the organic polymeric materials (ca. 10 : 1) thermodynamically precluded a metal surface developing via metal cluster migration from the bulk to the surface.^{23–27} The film surface did not have a continuous layer of metal in the manner that occurs with physical vapor deposition; that is, the surface had nanoporous voids of random shapes. Finally, a relatively narrow processing window existed in the thermal cure protocol within which to generate film that was optimum for specular reflectivity, conductivity, and mechanical integrity.

Recently, Gaddy et al.³³ reported an extraordinary observation of a photochemical-thermal protocol for Pd(II)–poly(amic acid)/polyimide films that led to double-metallic Pd layers with a layer separation of approximately 400 nm. Thus, further interesting materials from the Pd(II)–polyimide system may yet be uncovered.

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