

# Synthesis and Characterization of Self-Metallizing Gold-Doped Polyimide Films

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## SYNOPSIS

State-of-the-art methods for producing reflective polymer films for space applications involve multiple steps, and the integrity of the metal-polymer interface is less than optimal. A more efficient process was developed that consists of doping polyamic acid resins with gold additives and curing them to form self-metallizing polyimide films. Several moderately reflective, flexible metallic gold films were produced that have good thermal stability and mechanical properties, a strong metal-polymer interface, and in some cases, electrical conductivity. It was found that the polymer system, gold additive, gold concentration, and heat treatment all affect the reflectivity, flexibility, and conductivity of the resulting polyimide films by affecting the degree of metallization of the film surface. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

It is desirable that metallized films used on large space reflectors, antennae, and solar concentrators be highly reflective, thermally stable, flexible, electrically conductive in some cases, and have good adhesion of the metallic surface to the base polymer. The methods currently employed to produce metallized films, such as sputter coating, are multiple-step processes. Furthermore, the metal layer is usually not chemically bonded to the base polymer, therefore giving less than optimal adhesion.<sup>1</sup> This work addresses the development of a single-step process for the production of flexible, conductive, and reflective polyimide (PI) films having improved adhesion of the surface metallic layer.

Metal additives have been incorporated into PI systems in past research to produce films having properties such as reflectivity, electrical conductivity, or improved high temperature adhesive properties.<sup>2-9</sup> Hydrogen tetrachloroaurate(III) trihydrate (auric acid) has been added to PI systems by other researchers, and the resulting films were flexible, nonconductive, and occasionally had a metallic gold luster on one or both film surfaces, but were not highly metallized.<sup>10</sup> This work expands on these efforts and examines a

variety of concentrations of two gold additives in three PI systems to develop an improved self-metallizing PI film. The goal was to produce films suitable for use in space more efficiently than current methods and with a highly metallized surface that adhered well to the base polymer. In addition to having a reflective metal surface, it was desired that the films have the flexibility, mechanical strength, thermal stability, and electrical conductivity required for space applications.

Gold dopants were added to the polyamic acid resins before casting them into films and curing them. The cured gold/PI films were evaluated qualitatively for reflectivity, flexibility, and adhesion of the metallic layer. Conductivity measurements and thermal properties were obtained for all films. Mechanical testing, X-ray photoelectron spectroscopy (XPS), and reflectivity measurements were performed on the most promising films. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were used to image the metallic layer and evaluate the metal-polymer interface.

## EXPERIMENTAL

### Materials

The 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride (6FDA) and 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) were obtained

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commercially and vacuum dried for 24 h at 80°C, melting points 239 and 219°C, respectively. The 4,4'-oxydianiline (ODA) was obtained commercially and used as received (melting point, 187°C). The 2,2-bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) was obtained as a specialty chemical from the Ethyl Corporation and recrystallized (melting point, 158°C). Hydrogen tetrachloroaurate(III) trihydrate (auric acid) was obtained from Aldrich Chemical Co. and Sigma Chemical Co. Triethylphosphinegold(I) succinimide was synthesized at Radford University, Radford, VA, by Dr. Robert Boggess using a method analogous to that used by Sadler et al. to prepare triethylphosphinegold(I) phthalimide.<sup>11</sup>

### Preparation of PI Films

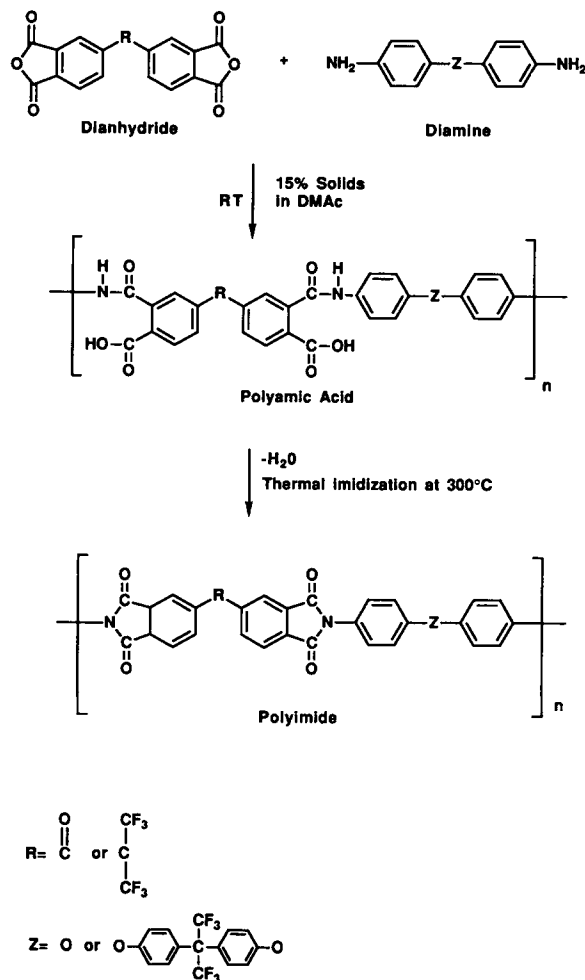
The reaction route for the preparation of polyamic acids and PI films is shown in Figure 1. The polymer systems utilized in this study were 6FDA/ODA, BTDA/ODA, and BTDA/4-BDAF. The polyamic acid resins were prepared from equimolar amounts of diamine and dianhydride as solutions containing 12–15% solids (w/w) in *N,N*-dimethylacetamide (DMAc). The reaction consisted of first dissolving the diamine in DMAc in a flask flushed with dry nitrogen, and then adding the dianhydride and stirring at room temperature for a minimum of 5 h.

Gold additives were incorporated into polyamic acid resins and stirred until completely dissolved. All additives were soluble in the polymer solutions, having been screened from a variety of candidate additives for this property. The concentration of gold in all of the doped films was between 12 and 25% by weight.

Undoped and gold-containing polyamic acid resins were cast as films onto soda lime glass plates using a scalpel set to obtain cured film thicknesses of  $2.54 \times 10^{-3}$  cm. Films were imidized by heating in a forced air oven for 1 h each at 100, 200, and 300°C and were removed from the glass plates by soaking them in water. Films to be tested for reflectivity were cast to completely cover  $2 \times 2$  in. glass plates, cured as above, and left on the plates for testing. Postcures were performed on selected films while they were still on the glass plates and consisted of heating them at 300°C for up to 30 h.

### Characterization

Monomer melting points (onset) were determined by differential thermal analysis (DTA) at a heating rate of 20°C/min on a DuPont Model 910 DTA. Inherent viscosities of the polyamic acid resins were



**Figure 1** Reaction route for the preparation of polyimide films.

obtained at a concentration of 0.5% (w/w) in DMAc at 35°C. Differential scanning calorimetry (DSC) was performed on a Seiko DSC 210 at a heating rate of 20°C/min. Thermogravimetric analyses (TGAs) were obtained on the films in flowing air (15 cc/min) at a heating rate of 2.5°C/min using a Seiko TG/DTA 200.

Surface resistivities were measured with an Alessi four-point probe. For those films having resistivities in the range of or  $> 10^4 \Omega$ , measurements were made using a Hewlett-Packard 8510 Automated Network Analyzer. TEM was performed at the Virginia Institute of Marine Science (Gloucester Point, VA) on a Zeiss CEM-902 transmission electron microscope using 30,000 $\times$  magnification. Film samples were embedded in epoxy and cross sections obtained using an ultramicrotome. SEM was conducted with a Hitachi S-510 scanning electron microscope using magnification of 10,000 $\times$ . Reflectivity was measured at a 20° angle and a wavelength of 531 nm on a

Perkin–Elmer Lambda 5 UV/VIS spectrophotometer with a specular reflectance accessory. XPS of cured film surfaces was obtained from the Department of Chemistry, VPI & SU (Blacksburg, VA). Mechanical testing was performed at room temperature on a Sintech Model 2000/2 table-top load frame.

Three techniques were used to investigate metal layer formation in the gold-doped PI films. The Fisher Johns Melting Point Apparatus permitted continuous observation of a drop of doped resin during heat treatment from room temperature to 300°C. Although it was not possible to dwell at a given temperature, this method allowed observation of changes in the appearance of the film at different temperatures. A second technique, using the Mettler FP 82 hot stage in conjunction with a Nikon polarizing light microscope, allowed for dwell times and greater magnification during the heating process, but was limited to observation during the time that the film remained translucent. A third method involved casting films of doped resin and curing them incompletely. The films were removed at several different points during the cure and examined by SEM to determine the degree of metallization by noting the presence and continuity of a metal layer.

Two types of simple qualitative techniques, the tape test and the scratch test, are routinely used for measuring adhesion in metal-coated plastics.<sup>1</sup> In this study, a modified version of the scratch test was used to test the integrity of the metal–polymer interface.

## RESULTS AND DISCUSSION

### Hydrogen Tetrachloroaurate(III) Trihydrate Doped Films

Screenings of auric acid doped resins of different gold concentrations with a Fisher Johns melting point apparatus indicated that a concentration in excess of approximately 10 wt % was required in most resin systems to produce a metallic gold surfaced film. A much higher concentration, approximately 20%, was shown to be required for conductivity. Because both conductivity and reflectivity were desirable, a 20% gold concentration was initially employed in this work.

Auric acid has been added to PIs in the work of Madeleine et al. producing a nonconductive metallic gold surface layer on the side of the film exposed to glass during cure (glass side).<sup>10</sup> A nonconductive metallic gold surface with a “reflective gold luster” has been produced in some auric acid doped PI films on the side of the film exposed to air during cure

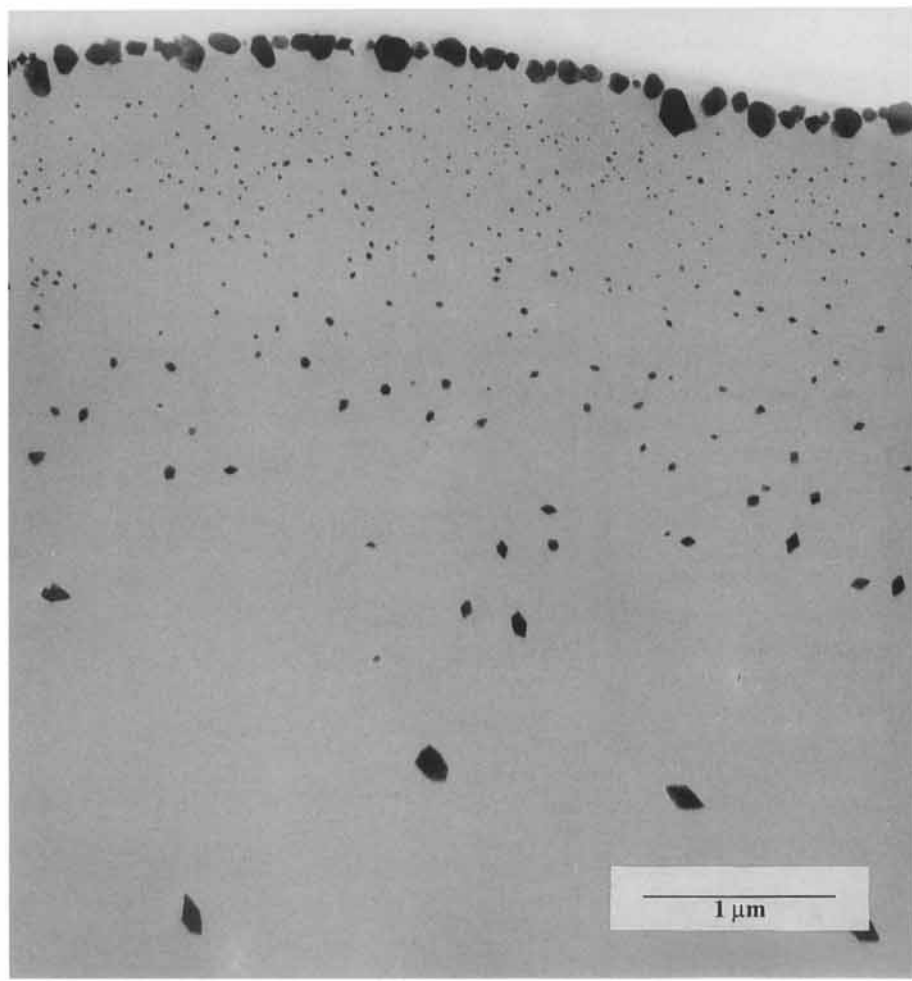
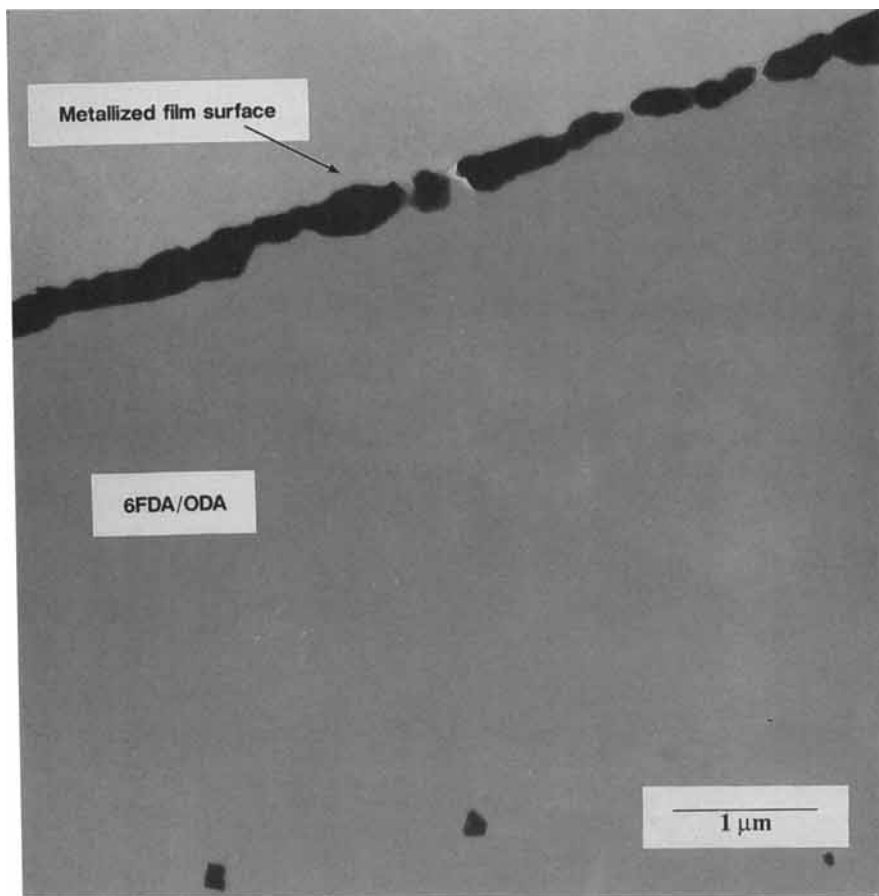
(air side).<sup>12</sup> The surface layer, however, was neither well-developed nor highly reflective.

Polyamic acid resins of this study exhibited inherent viscosities between 0.9 and 1.6 dL/g. Table I lists the thermal properties, appearances, flexibility, and conductivity of undoped and auric acid containing PI films that were made from these polyamic acid resins. Glass-transition temperatures ( $T_g$ 's) of doped 6FDA/ODA and BTDA/4-BDAF films were the same or lower than the undoped controls. Doped BTDA/ODA films had higher  $T_g$ 's than the control. Dynamic TGA data showed that the doped films had exceptional thermal stability. Metallized air-side surfaces, one of them brown and the other two gold, were produced in the polymer systems doped with 20% gold. The 21% gold 6FDA/ODA film was very pale metallic gold, conductive, and brittle. The 20% concentration of gold in BTDA/ODA produced a brittle, conductive film with a warmer gold color. The third resin system doped with auric acid, BTDA/4-BDAF, produced a 20% gold film that was metallic light brown, brittle, and had conductive edges. Although these films were metallic gold, they had hazy or matte finishes that were not highly reflective.

In an effort to achieve a metallized but more flexible and reflective film, the concentration of gold in these PI systems was reduced. Reducing the gold concentration to 16% in 6FDA/ODA and BTDA/ODA did not substantially reduce the brittleness, and it substantially reduced the conductivity, reflectivity, and apparent metallization in these two polymer systems. TEM showed that as the concentration of gold decreased, the thickness and continuity of the gold surface layer also decreased. The 21% gold [Fig. 2(a)] and 16% gold [Fig. 2(b)] 6FDA/ODA films were representative of this phenomenon. These micrographs also showed that the metal layer was embedded in the base polymer, explaining its excellent resistance to removal by abrasion. SEM illustrated the greater continuity of the gold layer in the 21% gold film [Fig. 3(a)] compared to the 16% gold film [Fig. 3(b)]. Other researchers have also found that an “island type” metal layer such as that in the 16% gold film is less conductive than a continuous layer of metal.<sup>13</sup> A 17% gold BTDA/4-BDAF film had a highly reflective gold surface and was conductive and fingernail creasable. This film was chosen for further tests because it combined all of the desired properties.

### Triethylphosphinegold(I) Succinimide Doped Films

Triethylphosphinegold(I) succinimide was added to the same three polymer resin systems, but at a

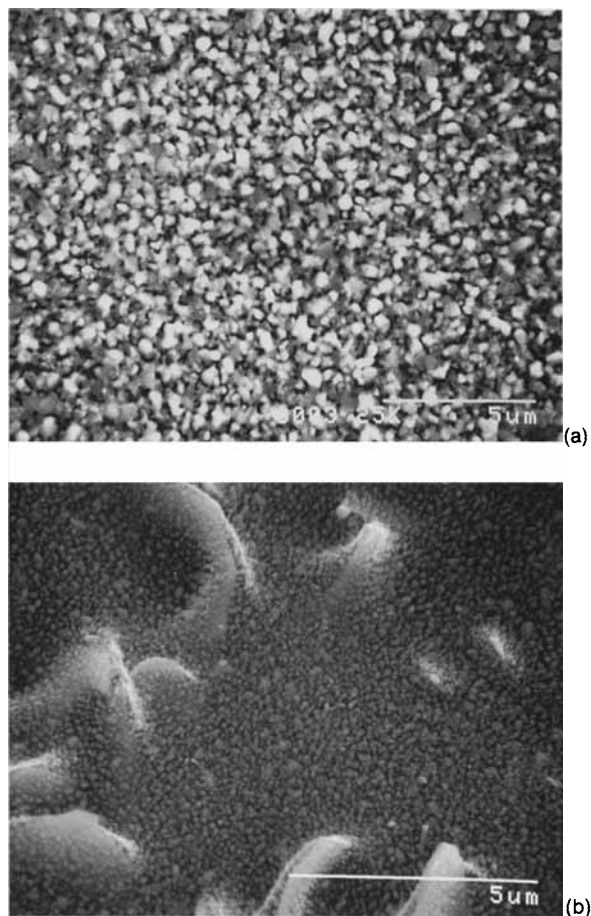


slightly higher concentration (Table II). The  $T_g$  of the doped 6FDA/ODA film was lower than the undoped control;  $T_g$ 's of the doped BTDA/ODA and BTDA/4-BDAF films were somewhat higher. The thermal stability of the succinimide-doped films was lower than undoped controls and also lower than the less heavily doped auric acid modified films. The 24% gold 6FDA/ODA film was metallic dark brown, fingernail creasable, and nonconductive. The BTDA/ODA and BTDA/4-BDAF films doped with 25% gold were also metallic pinkish gold, flexible, and nonconductive. TEMs showed metal distributed throughout the films as uniformly small particles, and well-defined metal layers were not present. The 25% gold BTDA/4-BDAF film was representative of this phenomenon (Fig. 4). The BTDA/ODA and BTDA/4-BDAF films doped with the succinimide additive were reflective enough to merit further study. Although conductivity is desirable, it was not considered to be a critical property in this investigation. For applications in space, an electrical resistivity of less than  $10^9 \Omega$  has been found useful for draining static charges on space components.<sup>14</sup>

### Reflectivity and Conductivity

Four films were selected for reflectivity measurement and were given postcures of up to 30 h at 300°C (Table III).

When the most promising film from those in Table I, 17% gold BTDA/4-BDAF, was cast onto a 2 × 2 in. glass plate and cured, the film stress cracked and reflectivity could not be measured. This apparent reduction in flexibility has been observed before when metal-doped resins are cast to completely cover the small glass plates used for reflectivity measurements. Thus a 13% gold reflectivity film sample was prepared that had cracked edges and did not appear as reflective as the higher concentration film. Its reflectivity was 35%. In an effort to obtain a more flexible specimen, a 12% gold film was prepared. The surface was a bit rough and the film was not as reflective, measuring only 12%. Because of the lower gold concentrations, the reflectivities of the 12 and 13% auric acid containing films were significantly lower than the 17% gold film. The BTDA/4-BDAF and BTDA/ODA films doped with gold succinimide had reflectivities of 18 and 13%, respectively. After postcure, the reflectivity of the 12% gold BTDA/4-BDAF film doped with auric acid doubled, and the 13% gold BTDA/4-BDAF film im-



**Figure 3** Scanning electron micrographs of the surfaces of 6FDA/ODA films doped with (a) 21% and (b) 16% auric acid.

proved from 35 to 41%. The reflectivity of the 25% gold BTDA/4-BDAF succinimide-doped film also improved significantly after postcure; the reflectivity of the 25% gold BTDA/ODA succinimide-doped film rose only slightly.

In addition to increasing reflectivity, postcuring increased conductivity. The resistivity of the standardly cured 13% gold BTDA/4-BDAF film derived from auric acid was  $1 \times 10^4 \Omega$ , and that of the film postcured 21 h was  $8 \times 10^3 \Omega$ , as measured by network analyzer. The 25% gold BTDA/4-BDAF film containing succinimide was  $4 \times 10^4 \Omega$  before postcure, but after a 30-h postcure, parts of it were  $1 \Omega$ . Although the air-side metal layer was enriched by postcure, all of the postcured films remained fingernail creasable.

In previous studies with copper-doped PIs, postcuring films at temperatures as high as 350°C was

**Figure 2** Transmission electron micrographs of the surfaces of 6FDA/ODA films doped with (a) 21% and (b) 16% auric acid.

**Table I Auric Acid-Doped Polyimide Films**

Polymer	Percent Gold	$T_g$ by DSC	10% Wt Loss by TGA	Appearance	Flexible	Resistivity ( $\Omega$ )
6FDA/ODA	0	299	507	Clear pale yellow	Yes	$> 10^4$
	16	289	503	Flat metallic gold	No	$> 10^4$
	21	269	507	Reflective metallic gold	No	0.1
BTDA/ODA	0	275	524	Clear yellow	Yes	$> 10^4$
	16	281	501	Reflective metallic brown	No	$> 10^4$
	20	314	516	Reflective metallic gold	No	0.1
BTDA/4-BDAF	0	247	510	Clear yellow	Yes	$> 10^4$
	17	249	490	Reflective metallic gold	Yes	0.4
	20	236	506	Flat metallic brown	Yes	Edges 2180

noted to increase the degree of metallization.<sup>4</sup> The increased metallization of the gold-doped films in this work was due to an increase in the number of gold particles on the air-side surface. At least two mechanisms are believed to be involved. Film thickness measurements indicated that some polymer degradation had occurred during the postcure, which causes a buildup of metal on the surface. In addition, other studies of PI-metal interfaces have shown that annealing film at 300°C enhanced the diffusion of deposited gold into the polyimide.<sup>15</sup> Likewise, in this research the postcure caused further migration of gold particles to the air side enhancing the metallic layer. By enriching the air-side gold particle layer, postcuring improved properties such as conductivity and reflectivity that are proportional to the degree of metallization. The postcuring process did not decrease the flexibility of the films.

Conductivity was related to the thickness and continuity of the metal layer in gold-doped PI films. Figure 2(a) is a typical TEM of a highly metallic gold film having a nearly continuous metal layer as thick as 0.35  $\mu\text{m}$ . A particle-free zone (depletion zone) was always present just beneath the metal layer. Films having these characteristics were brittle. The TEM in Figure 2(b) depicts the surface of a typical nonconductive film, where particles did not form a continuous layer. Instead, they were present as "islands" surrounded by polymer having a higher electrical resistivity. There were no depletion zones in nonconductive films doped with auric acid. As a rule, the nonconductive less metallic-looking films were more flexible than conductive metallic films. Although SEM and TEM work confirmed that a metallized surface was required for reflectivity, the exact surface characteristics for optimizing this property were not established.

The TEM of the 17% gold BTDA/4-BDAF film doped with auric acid (Fig. 5) illustrates the unique

features that allowed for conductivity, reflectivity, and flexibility to coexist in this film. The gold layer was no more than approximately 0.25- $\mu\text{m}$  thick, significantly thinner than in other conductive films. This was the only conductive auric acid doped film that lacked a depletion zone. The thinner metal layer and the homogeneous dispersion of gold particles throughout the film may have contributed to the film's greater flexibility.

#### PI-Metal Interface

In this work, the adhesion of the gold particle layer to the base polymer was assessed qualitatively by mechanically abrading the surface of the film with a paper wiper or finger and then noting any damage. In this version of the scratch test, none of the films showed damage. The TEMs illustrated that the gold particles of the metal layer were embedded in the polymer. Figure 6 shows a TEM of the air-side surface of a PI film with a poorly adhered metal layer, in which the metal particles lay on top of, not in the base polymer. The dopant was a different gold additive from those used herein, and the gold surface could be removed easily by rubbing it.

A variety of studies of the metal-PI interface have shown that metal-polymer adhesion as measured by peel strength is significantly better when the polyamic acid resin is cast onto a metal and then cured thermally, than if the cured polyimide has metal applied to it, for example, by vacuum deposition.<sup>16</sup> The reason for the superiority of the polyamic acid derived interface is that a chemical bond forms between the polymer and the metal during the imidization process.<sup>17</sup> It is believed that the well-adhered gold layers on films in this study were bonded to the polymer in the same way, because in these self-metallizing films the layer formed during the imidization process.

**Table II Succinimide-Doped Polyimide Films**

Polymer	Percent Gold	$T_g$ by DSC	10% Wt Loss by TGA	Appearance	Flexible	Resistivity ( $\Omega$ )
6FDA/ODA	0	299	507	Clear pale yellow	Yes	$> 10^4$
	24	289	486	Reflective metallic brown	Yes	$> 10^4$
BTDA/ODA	0	275	524	Clear yellow	Yes	$> 10^4$
	25	281	473	Reflective metallic gold	Yes	$> 10^4$
BTDA/4-BDAF	0	247	510	Clear yellow	Yes	$> 10^4$
	25	251	470	Reflective metallic gold	Yes	$> 10^4$

### Isothermal and Mechanical Properties

In other studies, several different metals have been examined in a comparison of the interface integrity of metal-on-polyimide to polyimide-on-metal. It has been found that heat treatment results in a variety of chemical changes in the polyamic acid/metal interfaces, depending on the metal being used. Interactions range from little or none, to polymer degradation occurring simultaneously with imidization, to total destruction of the polymer.<sup>18</sup> Although Cu and Ag have been found to form carboxylates with polyamic acids that lead to an inhibition of imidization, Au is less reactive, forming very few complexes or carboxylates and showing no inhibition of imidization or degradation of the polymer.<sup>19,20</sup> The gold-doped films in this study had thermal and mechanical properties consistent with these results.

As shown previously in Table I, when the thermal stability of all of these films was measured by dynamic TGA, the 10% weight loss temperatures were usually only slightly less than those of undoped control films, with the succinimide-doped films being less thermally stable than those having auric acid. Isothermal TGAs were performed on controls and the four postcured films in air at 300°C (Fig. 7). Only the succinimide-doped films showed substantial weight loss at 300°C in air. When the same films were run isothermally in nitrogen at 300°C, the 25% gold succinimide-doped BTDA/4-BDAF was the only film that showed more than 1% weight loss, and it lost 11%. Films that showed greater than 10% weight loss in air or nitrogen were run in the same atmosphere at 150°C, at which temperature there was no appreciable weight loss for any of the films. A temperature of 150°C is probably the maximum expected use temperature for space applications, and a nitrogen atmosphere most closely approximates that environment.

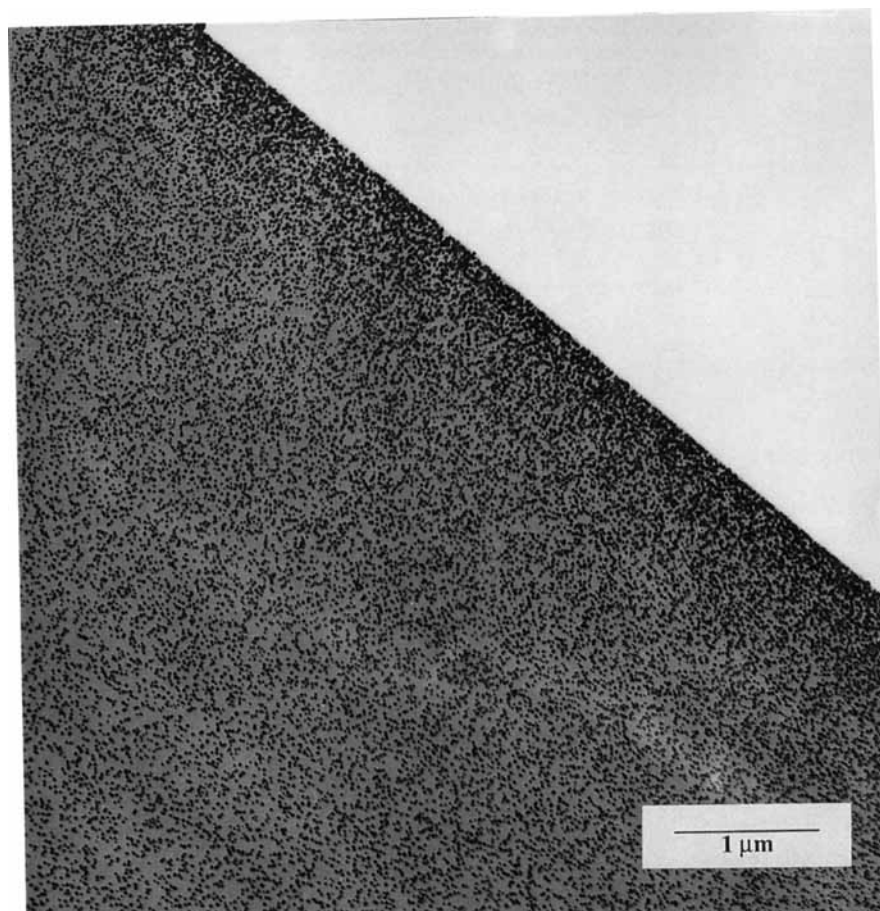
Tensile properties of several of the standardly cured gold films and their undoped controls, and one postcured film are shown in Table IV. The ad-

dition of metal did alter the mechanical properties of the films, but not in a uniform way. The results were dependent on the resin system. For BTDA/4-BDAF, the tensile strength was lower for the doped films than the control film. The modulus, however, increased or remained the same for auric acid doped films and decreased for succinimide-doped films. The postcured auric acid modified film had properties similar to the control. The succinimide-doped BTDA/ODA film, which had the metal distributed evenly throughout the film as small particles and no metal layer on the surface, had a higher modulus and tensile strength than the control.

### Formation of Gold Layer in Auric Acid Doped Films

Studies on the nucleation and growth of gold particles using auric acid in a variety of colloidal systems have shown that these two processes are separate. Nucleation is the process whereby a discrete particle of a new phase forms in a homogeneous or single-phase system. Because gold nuclei are only  $10^{-3}$   $\mu\text{m}$ , it is difficult to observe nucleation directly.<sup>21</sup> The appearance and frequency of small particles (approximately 1  $\mu\text{m}$ ) have been used to signal nucleation in PI films doped with auric acid.<sup>10</sup> Growth, defined as a process in which additional material deposits on the particle causing it to increase in size, is readily observed using various microscopic techniques. Reduction of the gold is believed to occur at some time during the growth phase in colloidal systems.<sup>22</sup> At some point during heat treatment, gold particles migrate to one or both film surfaces. All three processes, nucleation, growth, and migration, are required to achieve a metallic film surface.

Melting point apparatus studies with a variety of auric acid doped resins showed that during heating, the resin changed colors several times before the surfaces, developed a graininess at approximately 145°C. Metallic gold color was first



**Figure 4** Transmission electron micrograph of the surface of the 25% gold succinimide-doped BTDA/4-BDAF film.

noted between 155 and 165°C. Studies by other researchers have shown that metallization occurred in auric acid doped PI between 160 and 200°C.<sup>23</sup> Although the metallization began at approximately 155°C in this work, the gold color intensified over the next 100°C.

With the hot stage, it was possible to program dwell times into the thermal treatment. A gold-

doped 6FDA/ODA film treated at 100°C in air produced a clear brown film having many small indigo-colored specks. A higher magnification revealed that many of these particles had geometric shapes. Correlation with previous TEM and SEM results indicated that these were gold particles; therefore, nucleation had apparently begun by 100°C. Colloidal gold was found in other PIs doped with auric acid

**Table III** Surface Properties of Gold-Doped Polyimide Films

Polyimide	Dopant	Calculated % Gold	Postcure (h at 300°C)	% Reflectivity at 20°, 531 nm	% Gold on Surface by XPS	Resistivity (Ω)
BTDA/4-BDAF	Auric acid	12	None	12	8	Not measured
			21	24	8	Not measured
		13	None	35	6	$1 \times 10^4 \Omega$
	Succinimide		21	41	16	$8 \times 10^3 \Omega$
		25	None	18	< 1	$4 \times 10^4 \Omega$
			30	45	14	As low as 1 Ω
BTDA/ODA	Succinimide	25	None	13	2	$3 \times 10^4 \Omega$
			30	15	5	Not measured





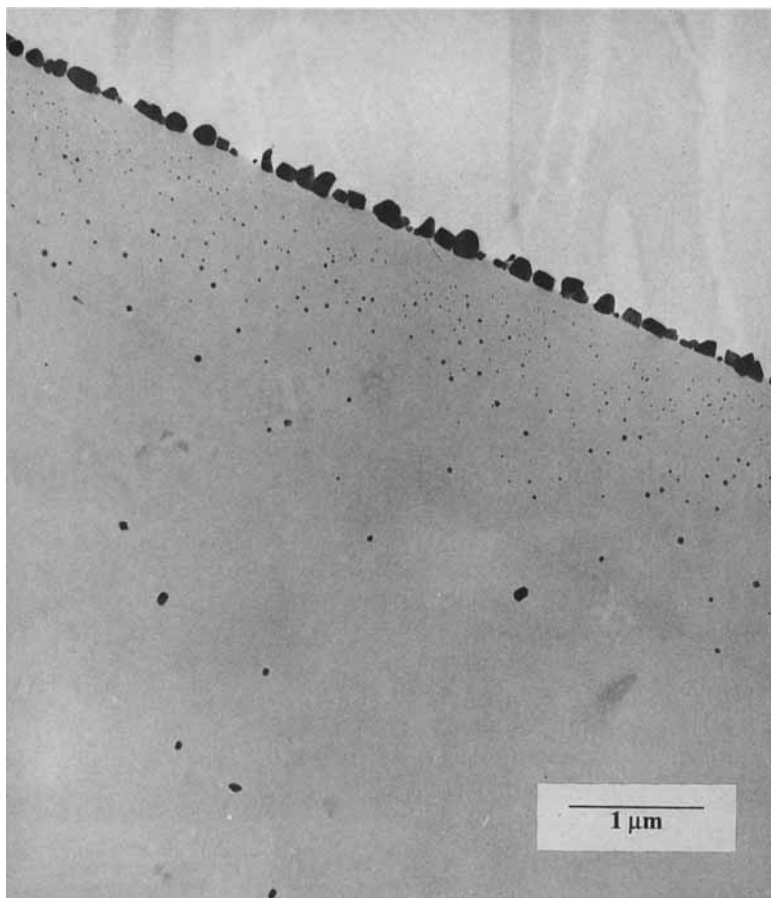
**Figure 5** Transmission electron micrograph of the surface of the 17% gold auric acid doped BTDA/4-BDAF film.

at 100°C, and it was postulated that it may have formed at room temperature.<sup>10</sup> When the film was further heated in the hot stage, the color darkened and the number and size of the particles increased until the film became opaque at approximately 200°C. Growth apparently occurred before and during particle migration to the surface. When the metal layer was formed, the film became opaque, preventing further observation by this method.

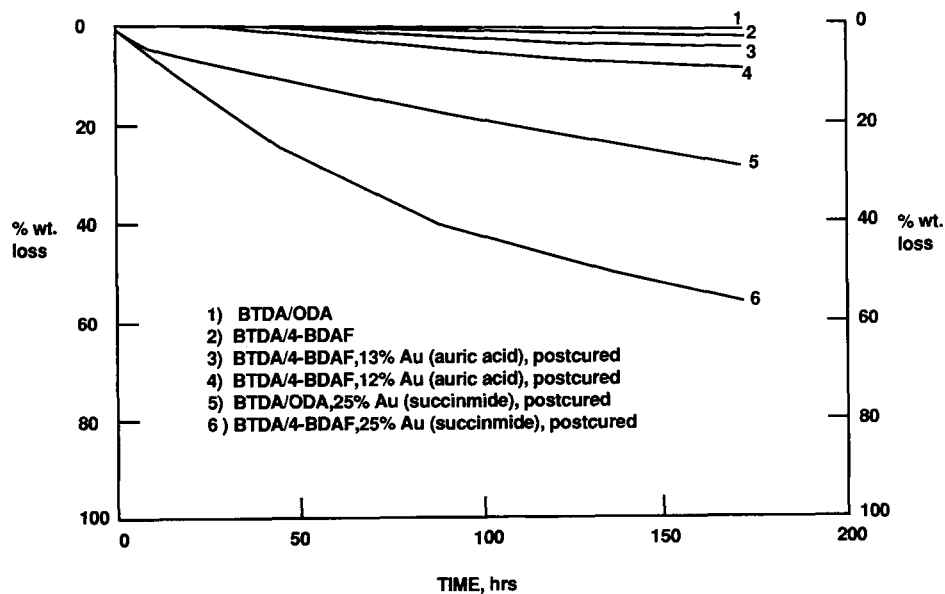
Partial cure studies with auric acid doped 6FDA/ODA demonstrated that after 1 h at 100°C there was no metal layer on the air-side surface, based on SEM using magnification as high as 30,000×. When the film was heated to 200°C, a well-developed particle layer was noted. The layer was therefore well-formed when the film reached 200°C. Another film heated 1 h each at 100 and 150°C, showed discrete metal particles on the air side by SEM, although they were comparatively small and did not form a continuous layer. Therefore, it would appear that sometime between 150 and 200°C, as suggested by melting point and hot-stage studies, a continuous

metallic layer formed. From SEM investigations of partially cured films, it appeared that the metal layer was developing by a combination of particle growth and continued particle migration to the surface, based on the increased size of individual particles and the improved continuity in the metal layer.

A number of mechanisms have been suggested for gold migration to the air side of the polymer film during cure. XPS analysis of gold in auric acid doped PI films has shown that the reduction of gold takes places simultaneously with migration, indicating that phase separation may result from the incompatibility of the gold and polymer phases.<sup>10</sup> It was also noted, however, that the preponderance of gold on the air side suggested that the evolution of volatiles played a role in the migration of the metal. Water of imidization in polyamic acid derived films and solvent loss and dopant/PI decomposition products in both polyamic acid derived and soluble PI films have all been suggested as possible transport vectors. The timing of the metallization process at between 155 and 200°C noted in this work may in-



**Figure 6** Transmission electron micrograph of the surface of a gold-doped polyimide film having a metallic surface that is not abrasion resistant.



**Figure 7** Isothermal TGAs of undoped and gold-doped polyimide films in air at 300°C.

**Table IV** Tensile Properties of Gold-Doped Polyimide Films

Polyimide	Dopant	% Gold	Postcure	Modulus (ksi)	Tensile Strength (ksi)
BTDA/4-BDAF	None	0	None	338	15.8
	Auric acid	12	None	359	15.1
		13	None	387	13.6
			21 hr	338	15.2
	Succinimide	25	None	307	14.7
BTDA/ODA	None	0	None	405	17.7
	Succinimide	25	None	485	20.1

dicates that the evolution of solvent has a role in the buildup of metal on the air side of the film, because the boiling point of DMAc is 165–167°C. Numerous studies of polyamic acid resins cured on metals (Cu, Ag, Pd, Pt, Au) have yielded the conclusion that solvent plays a key role in the migration of metal particles into the polymer matrix from the interface.<sup>23,24,25</sup>

## CONCLUSIONS

Auric acid and gold succinimide dopants were added to BTDA/ODA, 6FDA/ODA, and BTDA/4-BDAF polyamic acid resins that were cast and cured as films. Several moderately reflective, flexible metallic gold PI films were produced. Results indicated that the PI system, additive, metal concentration, and heat treatment affected the reflectivity, flexibility, and conductivity by affecting the degree of surface metallization. Postcuring the films at 300°C increased reflectivity and conductivity without sacrificing flexibility. The metallic surfaces of all of the films were abrasion resistant.

The properties of flexibility, reflectivity, and conductivity all related to the metal surface layer, but in different ways. The specific requirements for reflectivity were not discovered, although it was clear that a substantial amount of metal must be present on the surface for the film to be reflective. A higher gold concentration and more continuous metal layer was required for low resistivity (1 Ω) than was needed for moderate reflectivity (20–40%). Conductivity required a nearly continuous metal layer close to 0.35-μm thick in most polymer systems. Highly conductive films were usually much less flexible than nonconductive films. The increased thickness and continuity of the metal layer and the adjacent depletion zone in conductive films were believed to cause the observed brittleness. It was difficult to make a film having all of the desired properties—flexibility, reflectivity, and conductivity.

The succinimide additive in BTDA/ODA and BTDA/4-BDAF polyamic acid resins produced films that were fairly reflective, flexible, and conducting. One succinimide-containing film, 25% gold in BTDA/4-BDAF, was 45% reflective, flexible, and conductive after a 30-h postcure. Mechanical properties were excellent. The thermal stability, however, was significantly lower than the auric acid containing films.

The 17% auric acid doped BTDA/4-BDAF had all three desired properties in moderation. Although the film's reflectivity could not be measured, this film appeared to be the most reflective of the study. This and the 13% auric acid doped film that was postcured were found to have resistivities in a usable range. Thermal and mechanical properties were excellent.

Although further work is needed to optimize this technique, there is no doubt that self-metallizing PI films, made in a simple one-step process, hold great promise for space applications.

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