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Optically Reflective Polyimide Films Created by in Situ Silver Metal Formation

Adley F. Rubira,[†] James D. Rancourt, Maggie L. Caplan,[‡] Anne K. St. Clair,[§] and Larry T. Taylor*

Virginia Polytechnic Institute and State University, Department of Chemistry, Blacksburg, Virginia 24061-0212

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Polyimide precursors can be doped with organometallic complexes for the purpose of obtaining useful electrical, mechanical, etc., properties which are not characteristic of either component materials. In this regard, flexible, highly reflective silver-containing polyimide films have been prepared by incorporating (1,5-cyclooctadienehexafluoroacetylacetonato)silver(I) [Ag(COD)(HFA)] into various poly(amide acids). A variation in optical properties of the films was observed that depended upon the type of diamine–dianhydride monomer employed. Films derived from 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA) when cured in air exhibited good thermal stability and reflectivity as high as 65% regardless of the diamine used. 4,4′-Bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA) in conjunction with various diamines yielded cloudy films when cured in air. Characterization of these films and our understanding of the influence of polymer structure on surface properties is discussed.

Introduction

The aerospace, electronics, and specialty consumer markets find in polyimides a versatile candidate due to their high electrical resistivity and superior thermal and chemical stability. However, in some applications that demand, for example, high reflectivity, it is useful to have materials that possess the thermal properties of polyimides but in addition exhibit certain properties more typical of a metal. One approach to make polyimides suitable for such applications is to create polyimide composites. Incorporation of various metallic additives in polyimides using different procedures has been reported to improve (relative to the polyimide alone), mechanical,[1,2] electrical,[1-7] and optical properties.[7-9]

Silver-surfaced polyimides, because of their high solar specular reflectance and outstanding radiation resistance, are candidates for mirrored surfaces in many applications in space such as large area antennas and reflectors.[10] Traditionally silver-coated polymer has been achieved by an external process such as chemical vapor deposition, sputter technology, and lamination.[11] In these systems poor silver-polymer adhesion was noted.[12] Previously Mazur and co-workers used an interlayer deposition process to create a silver interlayer within a polyimide derived from pyromellitic dianhydride and 4,4′-oxydianiline.[9] The location of the reflective and electrically conducting layer could be adjusted by altering the experimental variables. It was not evident in this work whether large quantities of these materials could be produced.

Better adhesion between silver and polymer has been predicted to occur if a polymer were used that provided a silver site-specific interaction (i.e., thioether sulfur).[13] In this regard, polyimide films having unique optical properties as well as tightly adhering silver surfaces have been prepared by an in situ process and have been characterized. Two dianhydride-diamine combinations (some of which contained sulfur) yielded highly reflective films when their respective polyimide precursors were doped with (1,5-cyclooctadienehexafluoroacetylacetonato)silver(I) [Ag(COD)(HFA)] and subsequently thermally cured. The influence of different polyimide precursors on the distribution of silver-containing particles in the bulk and on the surface of each film has been studied as well as the chemical composition of the silver-containing particle. We report here the detailed results of this investigation.

[†] Universidade Estadual de Maringá, Departamento de Química, Av. Colombo 3690, 8702-900, Maringá-PR, Brazil.

[‡] Lockheed Engineering and Sciences Co., 144 Research Drive, Hampton, VA 23666.

[§] Materials Division, NASA-Langley Research Center, Hampton, VA 23681-0001.

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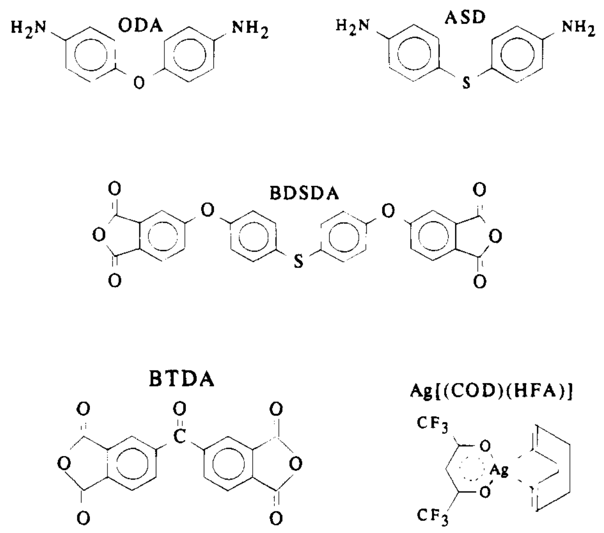

Figure 1. Monomers and additive structures.

Experimental Section

Chemicals. The following monomers (Figure 1) were used in this study: (a) 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA, Chriskev Inc., Leawood, KS) vacuum dried overnight at 110 °C; (b) 4,4′-bis(3,4-dicarboxyphenoxy)diphenyl sulfide dianhydride (BDSDA, General Electric, (Schenectady, NY), recrystallized twice from 2-butanone, and vacuum dried overnight at 120 °C, (c) 4,4′-oxydianiline (ODA), Chriskev Inc., Leawood, KS) sublimed at 185 °C and less than 1 Torr and then vacuum dried at 70 °C, overnight; (d) 4,4′-diaminodiphenyl sulfide (ASD, Chriskev Inc., Leawood, KS) vacuum dried at 80 °C overnight. *N,N*-Dimethylacetamide (DMAC) was obtained from Aldrich Chemical Co. in a Sure-Sealed bottle under N_2. The silver additive (1,5- cyclooctadienehexafluoroacetylacetonato)silver(I)[Ag(COD)(HFA)] was obtained from Aldrich Chemical Co. (Milwaukee, WS) and was used as received. The dopant was stored in the dark in a refrigerator. The additive structure is also shown in Figure 1.

Film Synthesis. Poly(amide acid) solutions were synthesized by first adding diamine (4.00 mmol) to a nitrogen-purged covered glass bottle with dry DMAC. Next, dianhydride (4.00 mmol) was added to the diamine with additional DMAC. The resulting solutions were stirred for 2 h. For the silver-modified polyimides, Ag(COD)(HFA) (2.00 mmol) was added as a solid with additional DMAC thereby resulting in a 10–20 wt % solids solution depending on the monomer combination. The silver containing poly(amide acid) solutions were then stirred for an additional 2 h at room temperature. Films were prepared by spreading the silver-containing poly(amide acid) solution onto a clean, dust-free soda glass plate, using a doctor blade (16 or 20 mil gap), followed by heating 20 min at 80 °C, then heating at 100, 200, and 300 °C each for 1 h under a dynamic (30 SCFH) atmosphere of dry breathing air (~20% O_2/ ~80% N_2). The surface of the film in contact with the soda-lime glass plate during imidization is referred to as the glass side, while that in contact with the atmosphere of the curing oven is referred to as the air side.

Measurements. Thermal analysis for the purpose of determining the glass transition temperature was performed on a Perkin Elmer Model DSC-4 differential scanning calorimeter at 10 °C/min heating rate under a nitrogen atmosphere. To determine the polymer decomposition temperature (PDT) thermogravimetric analysis was performed with a Perkin Elmer Model TGS-2 thermogravimetric system at 10 °C/min heating rate with a dynamic air or nitrogen. Elemental analyses for silver and fluorine were obtained by Galbraith Analytical Laboratories, Knoxville, TN.

X-ray photoelectron spectra (XPS) were obtained via a Perkin-Elmer Phi Model 5300 ESCA system. A magnesium anode (Kα = 1253.6 eV) operating at 400 W was used. The samples were attached to mounts by double-stick tape. The binding energies cited have been referenced to the aromatic carbon photopeak (C, 1s) of the polyimide backbone at 284.6 eV. Auger electron spectroscopy (AES) line scans were recorded with a Perkin-Elmer Phi Model 610 scanning microprobe system. Auger electron depth profiles were obtained via argon ion etching (≈50 Å/min). Scanning electron micrographs (SEM) were taken with a ISI Model SX-40 scanning electron microscope. The samples were attached to aluminum mounts using double-stick tape and coated with a thin layer of gold in order to dissipate charge. Transmission electron micrographs (TEM) were taken with a Philips Model 420 transmission electron microscope. Samples were imbedded in Polyscience ultralow-viscosity medium and cured for 8 h at 70 °C. Using a Reichert-Jung ultramicrotome with a microstar diamond knife, cross sections of the samples were obtained between 500 and 800 Å thick. These sections were placed on 200 mesh copper grids prior to analysis. Surface reflectivity measurements at 531 nm were performed on a Perkin-Elmer Lambda 5 UV-vis spectrophotometer equipped with a variable-angle reflectance accessory. Measurements were taken at 20°, 45°, and 70° angles.

Results and Discussion

In previous research from our laboratory, we have pursued the synthesis of polyimide–metal/metal oxide composites with a range of metals that includes, for example, tin,[14] cobalt,[15] iron,[16] gold,[17] platinum,[18] and copper.[19] Silver[20] has also been studied but to a more limited extent. Preliminary results have suggested that the production of highly reflective silver–polyimide films may be feasible since in many instances of our work the conversion of metal additive to the metallic state and phase separation of the nanosized particles to the film surface is realized.

In the past we have shown that with other metal systems, the chemical and physical nature of the polyimide determines in part the extent of metal reduction and surface characteristics in the thin film. For this reason, we have examined a number of diamine–dianhydride combinations with and without sulfur incorporation. The free-standing films varied considerably in physical appearance as shown in Table 1. With BTDA, the air sides of the doped, Ag(COD) (HFA), polyimide films were metallic silver and the glass sides exhibited a color varying between brown and khaki. With BDSDA, the air side was always metallic-looking but very cloudy in appearance, whereas, the glass side was dark red in color. Elemental analysis of the fully cured, doped films revealed that some of the dopant was altered during the curing process (Table 1). In other words, the found silver percentages were higher than predicted if the dopant had remained intact. For BDSDA films the silver found percentage was approximately 0.2% higher than calculated. For BTDA films the percentage was about 0.6% higher than calculated. Fluorine was considerably lower than expected if the dopant had remained intact. We believe

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Table 1. Film Information

polymer	appearance		% F		% Ag		
	air side	glass side	calcd[a]	found	calcd[a]	calcd[b]	found
BTDA-ODA/Ag(COD)(HFA)	silvery	brown	8.17	2.23	7.73	9.98	8.44
BTDA-ASD/Ag(COD)(HFA)	silvery	khaki	7.98	3.59	7.55	9.69	8.08
BDSDA-ODA/Ag(COD)(HFA)	cloudy	red	6.43	1.95	6.08	7.40	6.29
BDSDA-ASD/Ag(COD)(HFA)	cloudy	red	6.31	2.05	5.97	7.24	6.22

[a] Calculated on a 2:1 mol % ratio of polymer repeat units per mole of dopant. Assumed to be completely imidized, dry, desolvated, and additive intact. [b] Calculated on a 2:1 mol % ratio of polymer repeat units per mole of dopant. Assumed to be completely imidized, dry, desolvated, and additive converted completely to silver metal.

Table 2. Thermomechanical Properties of Flexible Silver-Modified Polyimide Films

films	T_g (°C)		PDT (°C)[a] in N_2		PDT (°C)[a] in air	
	not doped	doped	not doped	doped	not doped	doped
BTDA-ODA	270	265	628	504	609	493
BTDA-ASD	270	270	644	583	608	482
BDSDA-ODA	214	221	577	496	566	469
BDSDA-ASD	218	221	620	606	584	463

[a] Polymer decomposition temperature (PDT) which corresponds to 10% weight loss.

that a significant amount of fluorine has been lost via dopant thermal degradation, while silver has remained with the film but it has been converted to most probably silver or silver(I) oxide. This observation was not totally surprising since Ag(COD) (HFA) has a boiling point of 200 °C. Regardless of the monomer pair, all modified polyimide films were flexible and could be reproducibly prepared in terms of appearance and physical properties.

Estimates of polyimide film thermal stability were obtained by performing thermal gravimetric analysis in both dynamic air and nitrogen atmospheres, Table 2. As expected, the nondoped polyimides demonstrated slightly better thermal stability in nitrogen than in air regardless of the monomer pair. Incorporation of silver into each film (again as expected) lowered the polymer decomposition temperature (PDT). The degree to which each film PDT was lowered was greater for the air atmosphere experiments. In fact, all films showed about the same PDT in air; however, in nitrogen the ASD-derived films were approximately 90 °C more stable than other films analyzed in either nitrogen or air. The presence of silver, no doubt, serves to catalyze the oxidative degradation of the polyimide films. These results are in accordance with previous findings by Bolger,[21] who studied silver-filled die attached adhesives. Glass transition temperature (T_g via differential scanning calorimetry) for those doped polyimides containing BDSDA was lower than for doped polyimides containing BTDA by at least 50 °C. Within experimental error T_g did not appear to change when the silver additive was introduced into the respective films.

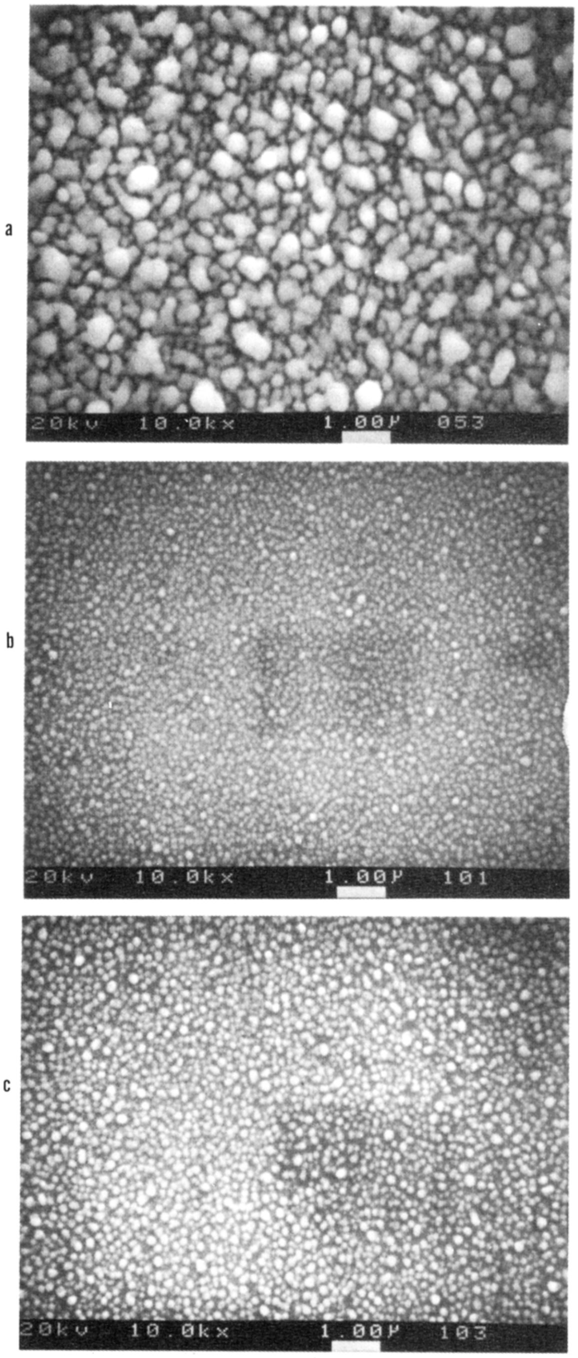

Figure 2. Scanning electron microphotographs of silver-doped (a) BDSDA/ODA, (b) BTDA/ODA, and (c) BTDA/ASD.

The most striking feature about these doped films was their metallic-looking air-side surface. As indicated previously the BTDA-derived films were exceedingly shiny. Using a variable angle reflectance accessory, percent reflectivity at 531 nm was determined (Table 3). The values obtained are relative to an optical mirror which was used as a 100% reflectivity standard. The values obtained for BTDA moieties are comparable to results obtained using laser techniques in a separate laboratory[22] and also are better than reflecting gold-

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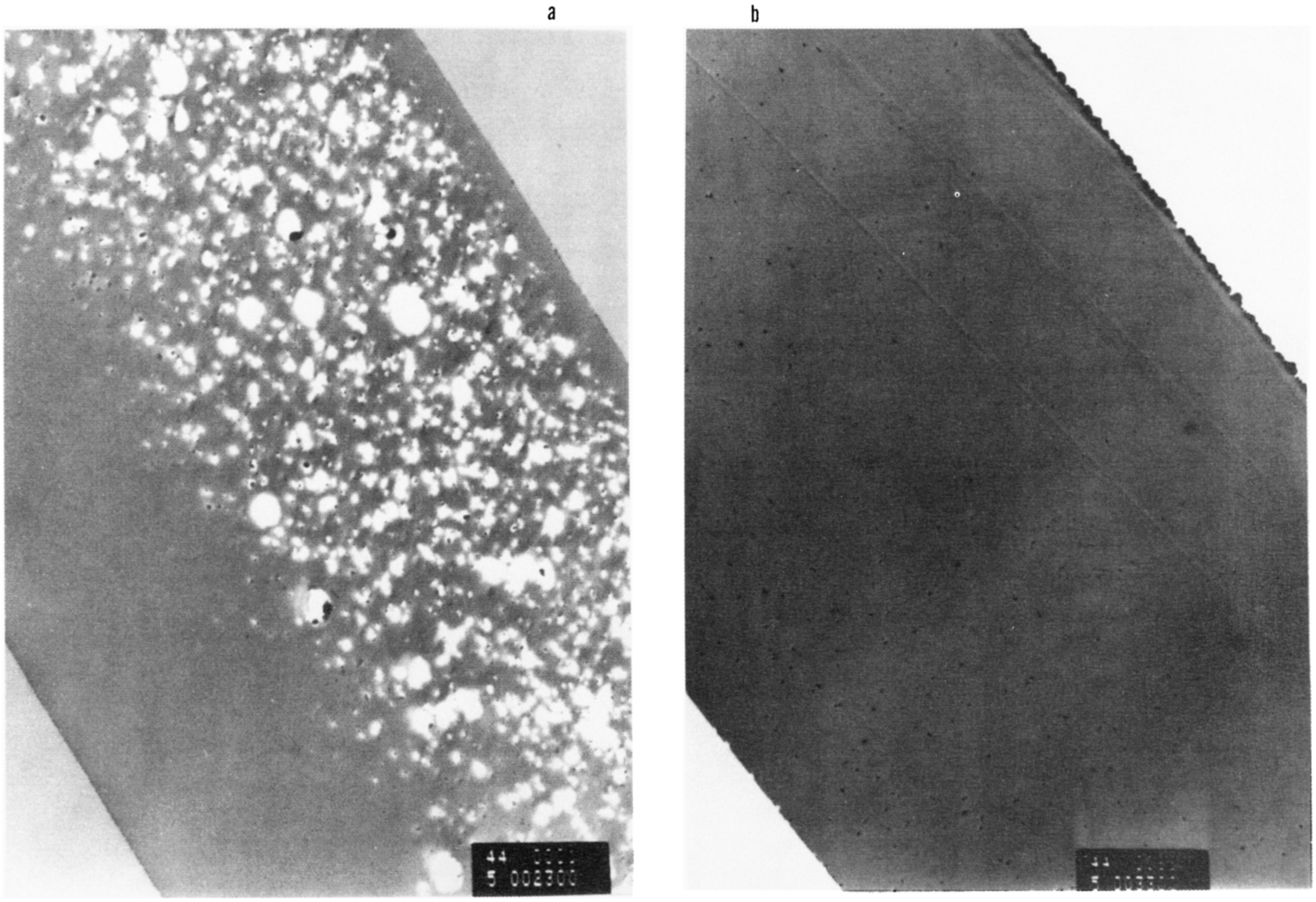


Figure 3. Transmission electron microphotographs of silver-doped (a) BTDA/ODA, magnification 4025× and (b) BDSDA/ODA, magnification 5775×.

Table 3. Percent Reflectivity for Polyimide Films Doped with Ag(COD)(HFA) at Varying Angles

film	percent reflectivity[a]		
	20°	45°	70°
BTDA-ODA	65.2 ± 0.8	56.5 ± 1.3	44.6 ± 1.4
BTDA-ASD	55.0 ± 1.2	51.3 ± 1.1	48.6 ± 0.2
BDSDA-ODA	3.9 ± 2.1	3.4 ± 2.2	8.8 ± 0.7

[a] Relative to an optical mirror which was used as 100% reflectivity standard. Wavelength at 531 nm.

doped polyimides containing BTDA.[8] Therefore, we believe that these films (BTDA/ODA, BTDA/ASD) can be used as polymeric reflector materials in the near future. As anticipated the cloudy BDSDA-derived films were poor reflectors of 531 nm radiation.

A detailed analysis of the surface density of particles and the distribution of particles in the films has been conducted in order to understand on a molecular basis the difference between reflective and nonreflective silver-containing polyimides. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been carried out. SEMs of BDSDA films show a fairly rough surface with globular-like particles (0.1–0.5 μm diameter) that appear to be bonded together (Figure 2a). The surface of BTDA-derived films are smoother with particles that are more uniform in size (~0.1 μm diameter). As Figure 2b,c shows, the particles are connected not as in the BDSDA films but rather discrete "islands" of particles are present. Cross-sectional views (TEM) of silver doped BTDA/ODA and BDSDA/ODA are shown in Figure 3. When compared with BTDA/ODA, the silver particles in BDSDA/ODA are larger and more highly concentrated on the air side surface. The holes near the glass side surface of BTDA/ODA result from the removal of particles during microtoming. The layer of particles on the air side of BTDA/ODA is approximately 70 nm thick (Figure 4a). The next 200 nm into the film is practically free of particles. Following this region we can see additional particles which appear to touch. These features are not seen in the BDSDA/ODA film (Figure 4b). Here, the surface layer is 140 nm thick, and there is apparent particle–particle interaction in the surface layer. The surfaces are rough for the BDSDA films, although there is a continuous distribution of particles of different sizes. This observation probably accounts for the lower light reflection relative to the BTDA films which have a more uniform surface of well-organized small particles. The silver-doped BDSDA-ODA film can be made much more reflective by rubbing its surface with tissue paper. For two films the percent reflectivity not polished was 4.7% and 3.1% at a measurement angle of 20°. Upon lightly polishing the surface, the percent reflectivity increased to 12.7% and 13.2%, respectively. A harder polish did not significantly change reflectivity further. Polishing caused the particles on the surface to flatten out as shown in Figure 5, thus supporting the data described above, some silver was also removed during this operation. It is interesting to note that the distribution of particles was more uniform in those polyimides which contain sulfur. Specifically, silver doped (a) BDSDA/ODA, (b) BDSDA/ASD, and (c) BTDA/ASD exhibited identical features via TEM.

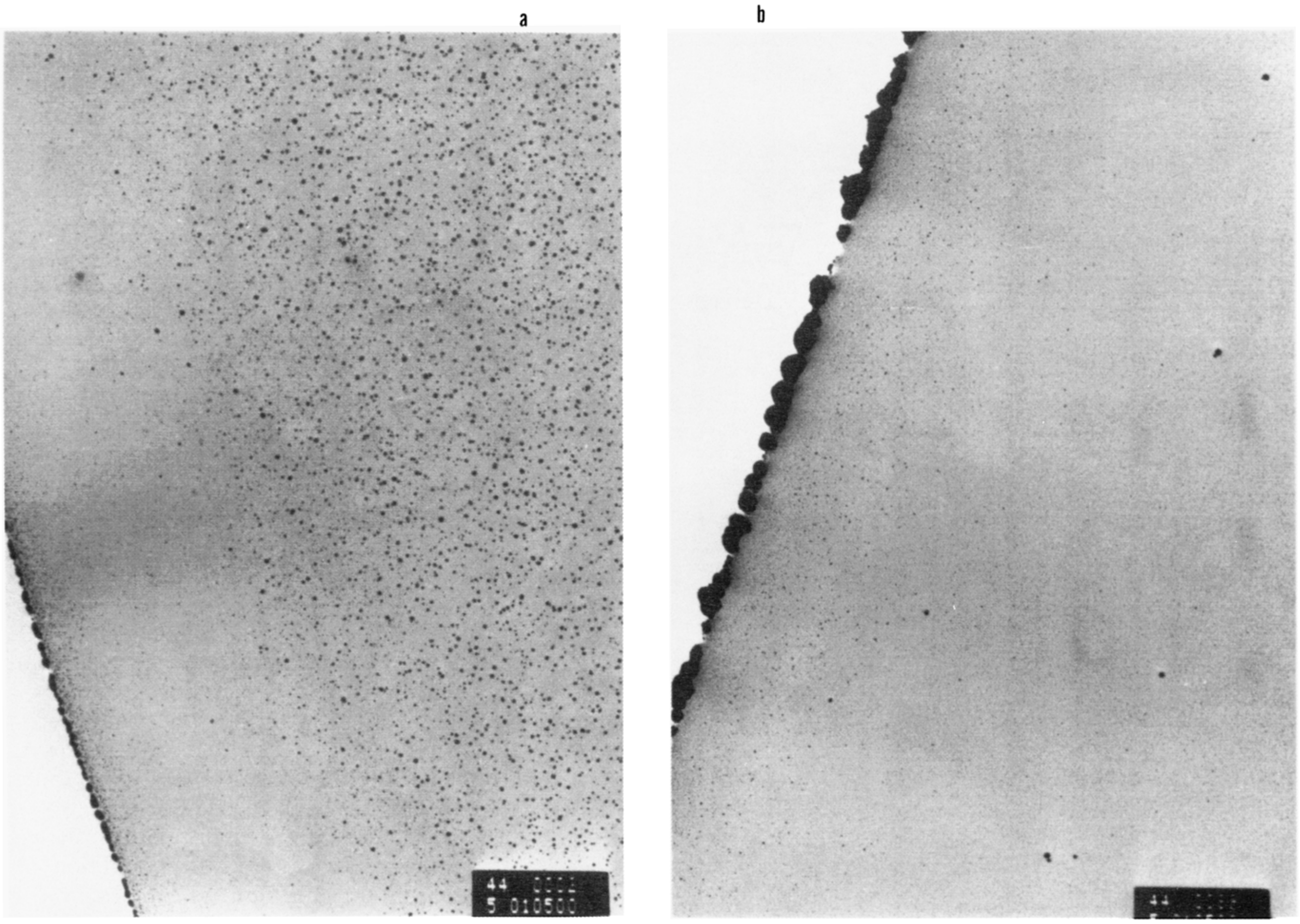


Figure 4. Transmission electron microphotographs of silver-doped (a) BTDA/ODA, magnification 18 375× and (b) BDSDA/ODA, magnification 18 375×.

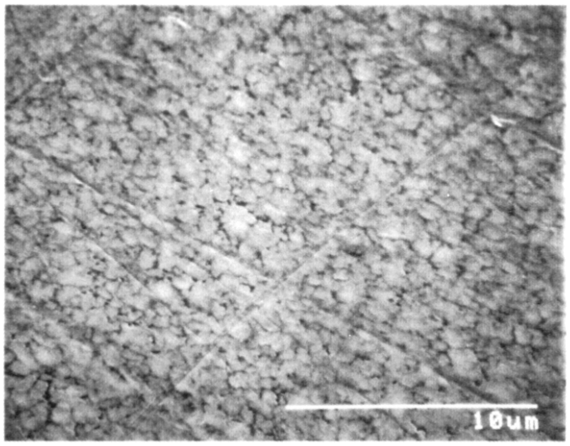


Figure 5. Scanning electron microphotograph of air side rubbed surface of silver-doped BDSDA/ODA film.

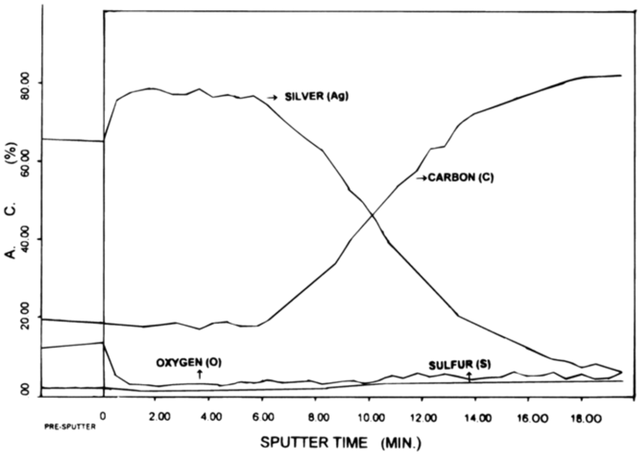


Figure 6. Auger electron spectroscopic depth profiles of air side silver-doped BDSDA/ODA films.

Silver doped polyimides were analyzed via XPS for information on surface elemental composition and chemical state. Depth profiling via Auger electron spectroscopy (AES) in conjunction with Argon ion etching was utilized to gain additional knowledge regarding the distribution of particles in the bulk of the film. Figure 6 shows in the depth profile of the air side of doped BDSDA/ODA a high concentration of silver in the surface region. This finding supports early TEM results which suggested "silver" deposits of approximately 70–150 nm thickness. Depth profiles for the other three films were similar to Figure 6.

The surface composition (elemental atomic concentration) as determined from XPS analysis of each modified film is shown in Table 4. Each film exhibits 10–50 times more silver on the air side than the glass side. Although little fluorine appears on the air side, considerable buildup of fluorine is seen on the glass side. This confirms the elemental analysis data previously discussed, which suggested that a portion of the dopant is not degraded. Surprisingly the most reflective films do not exhibit the highest concentration of air-side surface silver. It should also be noted that both surfaces also contain a significant amount of polyimide, although the C–N–O elemental compositions were not consistent

Table 4. Atomic Percents of Surface Elements for Silver-Doped Polyimide

	BTDA-ODA		BTDA-ASD		BDSDA-ODA		BDSDA-ASD	
element	air side	glass side	air side	glass side	air side	glass side	air side	glass side
C	58.6	62.2	52.4	56.4	45.5	67.1	42.4	55.5
O	13.8	13.3	13.3	11.8	18.6	12.6	14.1	18.1
N	6.4	2.7	6.0	2.4	4.1	3.0	5.6	1.6
S			2.6	1.0	3.4	1.2	2.5	4.8
F	1.1	19.9	1.5	24.5	1.2	15.8	5.0	18.4
Ag	20.1	1.9	24.2	3.9	27.2	0.3	30.4	1.7

Table 5. Relative Element Atomic Concentration of Modified Polyimide Films from XPS Analysis of the Air Side

	C	O	N	S	Ag
BTDA-ODA/AgCODHFA					
TOA = 15°	59.5	12.6	4.9		21.8
TOA = 45°	58.7	13.8	6.4		20.2
TOA = 90°	60.4	13.9	5.6		18.9
BDSDA-ODA/AgCODHFA					
TOA = 15°	39.7	23.3	3.6	6.5	25.9
TOA = 45°	45.5	18.6	4.1	3.4	27.2
TOA = 90°	41.4	21.9	4.1	6.0	25.6

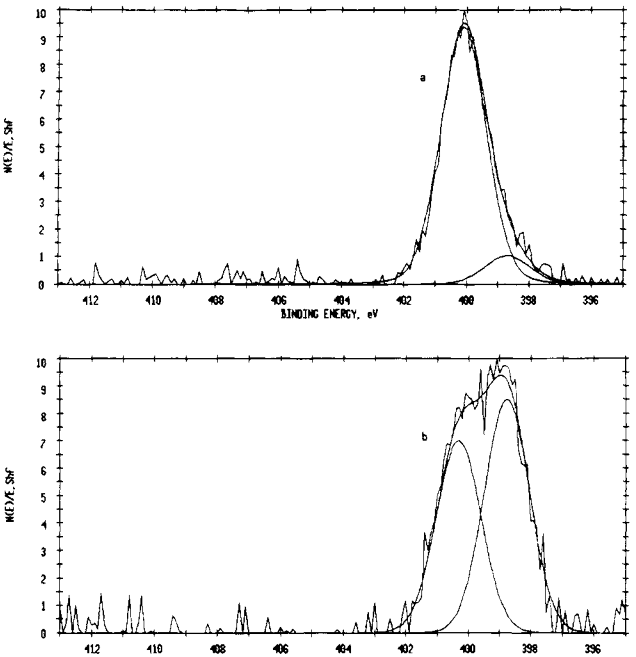
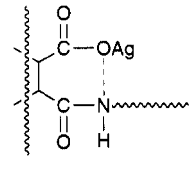


Figure 7. Nitrogen (1s) XPS photopeaks of the air side of (a) BTDA/ODA and (b) silver-doped BTDA/ODA films.

from one side of the film to the other (e.g., N is considerably greater on the air side than on the glass side).

The distribution of silver within the surface and subsurface region has been examined by variable takeoff angle (TOA) XPS for silver doped BTDA/ODA and BDSDA/ODA (Table 5). The atomic concentration of silver was reasonably constant regardless of the sampling depth for both films. Similar results were seen for the other elements sampled. This observation indicates that the polyimide and silver are intermixed.

In addition to noting the spatial elemental distribution, we were interested in the chemical state of selected elements. Evaluation of the nitrogen 1s photopeak in the doped and undoped films clearly indicates the presence of two kinds of nitrogen species. The main peak (Figure 7a) centered at 400.1 ± 0.1 eV is consistent with the imide nitrogen.[24,25] The lower binding energy peak at 398.8 ± 0.1 eV which is a minor constituent (7–10%) has previously been assigned to either an isoimide structure (23) or a linear amide group produced by decarboxylation of the original imide. The intensity of the component at 398.8 eV for the silver-doped films is remarkably higher (Figure 7b) than that observed in the undoped films (i.e., 40–60% of the total nitrogen) which may suggest appreciable silver-polymer interaction. Some researchers have previously pointed out that in silver vapor deposited[28–30] and sputter-coated films there may be strong interaction of the polyamide acid carboxyl group with silver surfaces. The formation of silver–carboxylate species in our films can be supported by the presence of a carbon 1s photopeak around 288.0 eV and an oxygen 1s photopeak at 531.2 eV (Figure 8a,b). These values match well those observed with silver benzoate, acetate,[31] behenate, and cyclohexylbutyrate.[32] The strong interaction between silver and prepolymer acid groups probably leads to incomplete imidization. The N (1s) peak at 398.8 eV (Figure 7b) could therefore be attributed to an amide nitrogen whose binding energy has shifted due interaction with Ag (structure **I**). Similar shifts have been observed for amine nitrogen chemisorbed on metal surfaces[33] and Langmuir–Blodgett polyimide films on silver surfaces.[34]



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An examination of the sulfur 2p photopeaks in the silver-doped films suggested the presence of new sulfur species not observed in the polyimide alone. Specifically new peaks are seen at 161.2, 167.9, and 168.5 eV in addition to the expected sulfur functionality at 163.3 eV.[35] The new sulfur peaks can be correlated with the

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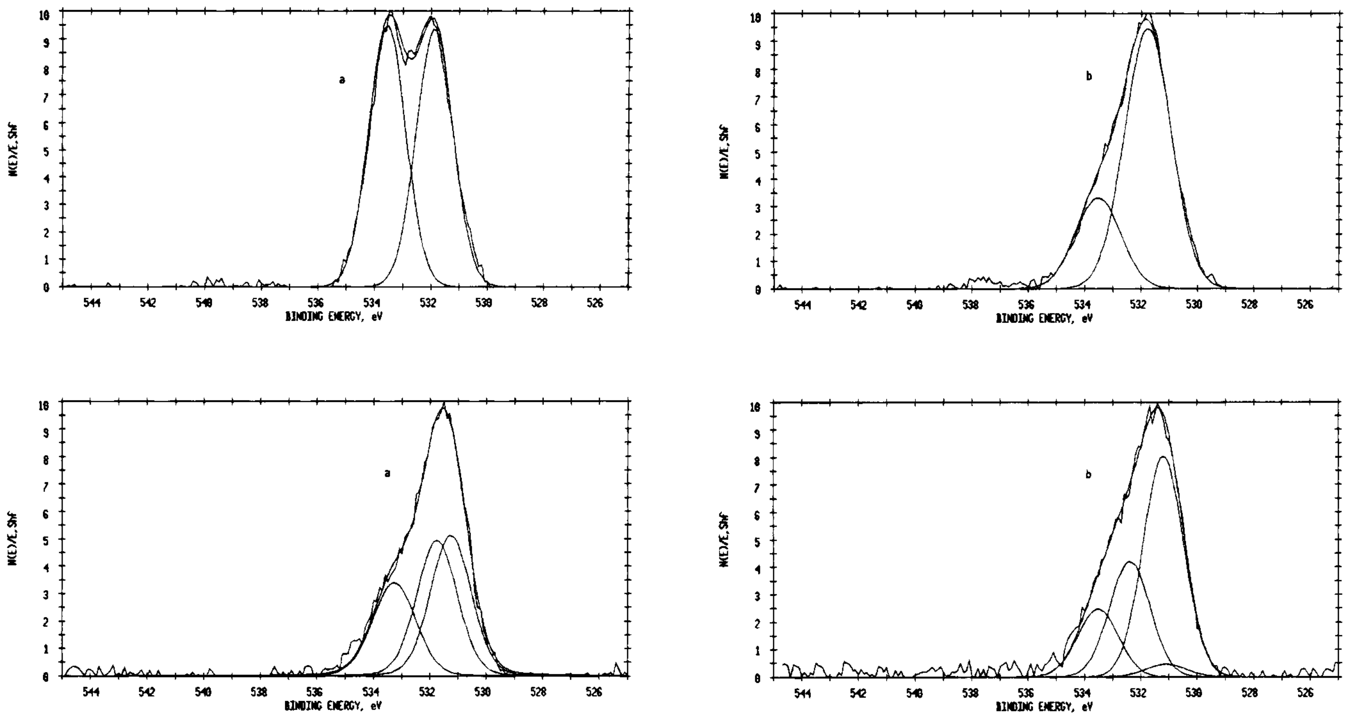

Figure 8. Oxygen (1s) XPS photopeaks of the air side of (a) BDSDA/ODA (top), silver-doped BDSDA/ODA (bottom) and (b) BTDA/ODA (top), silver-doped BTDA/ODA (bottom).

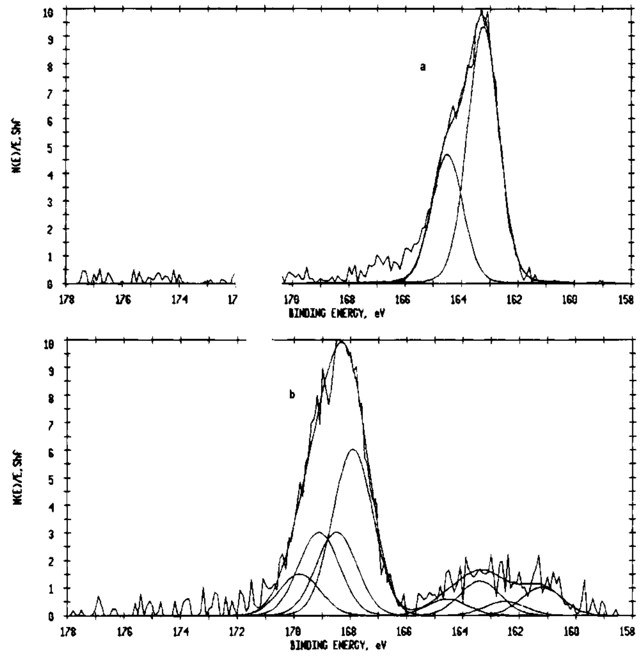

Figure 9. Sulfur 2p XPS photopeaks of the air side of (a) BDSDA/ODA and (b) silver-doped BDSDA/ODA.

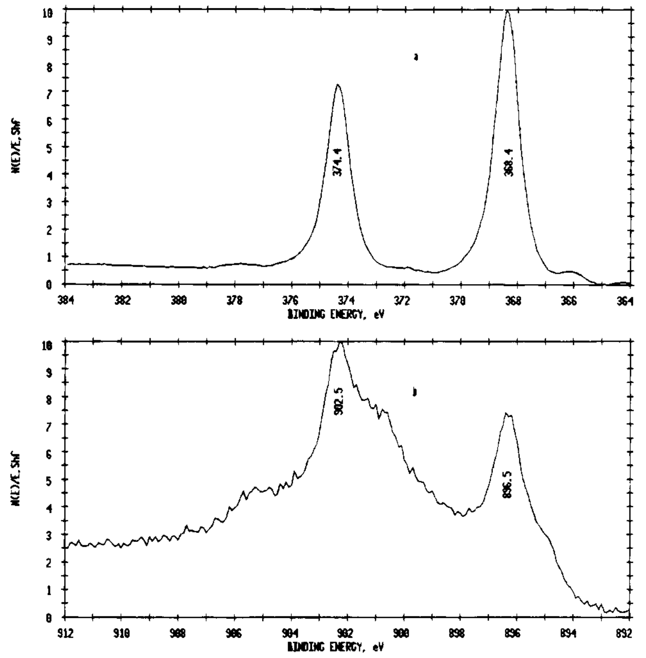

Figure 10. (a) Ag 3d XPS photopeaks and (b) Auger spectrum of the air side of doped BDSDA/ODA.

appearance of an oxygen (1s) photopeak at 531.6 eV, (Figure 9a,b). The new sulfur signals are believed to be indicative of a sulfone/sulfate moiety. As there is not sulfone/sulfate peak detected in the undoped sulfur-containing polyimide films, it is proposed that thioether oxidation is promoted by silver. While the peaks at higher binding energy can be accounted for in this way, the 161.2 peak probably arises from direct silver–polyimide sulfur interaction. Similar observations have been made by Gerenser et al.[13] with silver and poly(*p*-phenylene sulfide). We cannot rule out the possibility of Ag_2S formation either which would indicate some polyimide degradation at the film surface.

The chemical state of the silver was of interest in this study. Figure 10a shows a typical XPS spectrum (Ag 3d 5/2, 3d 3/2) for the air side of silver-doped BDSDA/ODA. The silver 3d photopeaks cannot be used alone to infer the chemical state of the silver since silver metal and silver (I) compounds have nearly identical Ag(3d 5/2, 3/2) binding energies. Schon[36] and Larson[37] have shown that the Auger shifts are frequently more significant than the XPS shifts for identification of silver chemical state. For this reason, the silver (MNN) Auger

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Table 6. Auger Parameter for Silver-Doped Polyimide Films and Related Compounds

films	Ag(3 $d_{5/2}$) B.E. (eV)	Auger peak B.E. (eV)	Ag(M_4NN) K.E. (eV)[a]	Auger parameter α (eV)[b]
BTDA/ODA	368.3	896.8	356.8	725.1
BTDA/ASD	368.2	896.4	357.2	725.4
BDSDA/ODA	368.4	896.5	357.1	725.5
BDSDA/ASD	368.6	896.8	357.0	725.6
AgHFA[c]	368.5	898.6	355.0	723.5
Ag_2O	367.9	898.5−896.5	355.1−357.1	723−725.0
Ag	367.9	895.5	358.1	726.0

[a] K.E. (eV) = (1253.6 − Auger peak B.E.). [b] α = Auger (M_4NN K.E.) + Ag (3$d_{5/2}$ B.E.). [c] AgHFA − hexafluoroacetylacetonatosilver(I).

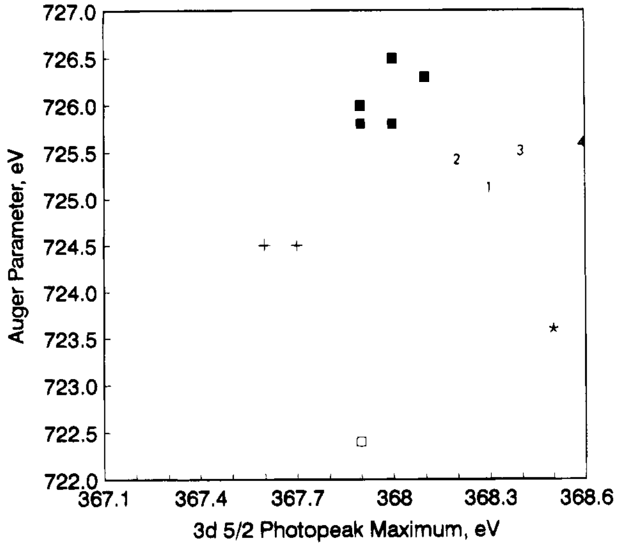

Figure 11. Auger parameter (α) versus silver 3d5/2 photopeak of silver-doped polyimide films (1-BTDA/ODA, 2-BTDA-ASD, 3-BDSDA/ODA, 4-BDSDA/ASD) and silver compounds (■, silver, *, silver TFA, +, silver(I) oxide, and □, "silver oxide").

lines were analyzed. Although they are not as intense as the photoelectron lines as shown in Figure 10b, they do have significant shifts. Previously in an attempt to estimate the chemical state of silver, workers have constructed plots of the kinetic energy of the Auger line against the binding energy of the photoelectron line which yields a two dimensional chemical state diagram.[38] An analogous plot of calculated values for selected silver compounds and silver-doped polyimides is shown in Table 6 and Figure 11. This data treatment suggests that silver in our films has not been completely converted to silver metal within the spectroscopic sampling region since the Auger parameter does not match that of silver metal (e.g., 726 eV). It nevertheless is striking that within experimental error both BTDA and BDSDA films have the same silver environment even though their reflectivities are quite different.

Conclusions

We have shown that it is possible to prepare in a one-step operation a highly reflective, very smooth, silver-surfaced (70−140 nm) polyimide film with the proper combination of monomers. Phase separation of silver was least apparent in the sulfur-containing polyimide; while, the most reflective films were those that exhibited the higher T_g. Under conventional thermal cure conditions, it appears that incomplete imidization has resulted because of significant interaction between silver ion and the acid portion of the polyimide precursor. Silver also appears to interact with thioether groups in the polymer backbone thereby causing oxidation to a "sulfone-like" moiety. Extension of this research to examine the influence of additive concentration, casting solvent, cure atmosphere and additional diamine−dianhydride combinations is in progress.

This observation is probably not very significant since reflectivity may be more controlled by polymer morphology than polymer T_g.

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