Single-Stage Synthesis and Characterization of Reflective and Conductive Silver−Polyimide Films Prepared from Silver(I) Complexes with ODPA/4,4′-ODA

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ABSTRACT Reflective and surface conductive polyimide films were prepared by the incorporation of silver(I) acetate and trifluoroacetylacetone into a dimethylacetamide solution of the poly(amic acid) formed 3,3′,4,4′-oxidiphthalic dianhydride (ODPA) and 4,4′-oxidianiline (4,4′-ODA). Thermal curing of (trifluoroacetylacetonato)silver(I)−poly(amic acid) films led to cycloimidization with concomitant silver(I) reduction, which yielded a reflective and conductive silver surface at selected silver concentrations if the film was cured to a final temperature of 300 °C for several hours. The metallized ODPA/4,4′-ODA films retain the essential mechanical properties of an undoped film and have good thermal stability, particularly under a nitrogen atmosphere. The bulk of the composite film was not electrically conductive. The use of (hexafluoroacetylacetonato)silver(I) and silver(I) tetrafluoroborate as sources of silver(I) with ODPA/4,4′-ODA yielded modestly reflective films that never developed conductivity. The silvered films prepared with (trifluoroacetylacetonato)silver(I) can be patterned using mask-etch techniques. Comparisons are made among four similar silver−polyimide systems, with the polyimides being ODPA/4,4′-ODA, BTDA/4,4′-ODA, BPDA/4,4′-ODA, and 6FDA/4-BDAF.

KEYWORDS: silver • polyimide • reflectivity • conductivity.

INTRODUCTION

Physical vapor deposition is the dominant method for producing metallized polyimide films, except where passive metals, such as silver, palladium, and gold, are involved. For passive metals the direct adhesion to polyimide films is not acceptable (1−7). Thus, interest has focused in recent years on developing synthetic methods, other than vapor deposition, to form passive metal thin films that are strongly adhered to a base polyimide. Selected alternative methods invoke electroless reduction of metal ions to metal and have focused on silver for surface-metallized films, since silver is modest in cost, highly electrically conductive, and of exceptional specular reflectivity. Attention herein will be confined to silvered polyimide films. Applications for silvered polyimide films are numerous, including (1) electrical circuit fabrication on flexible dielectric platforms via pattern-mask-etch techniques, (2) antennas formed on and embedded in dielectric materials, (3) electromagnetic shielding, (4) mirrors/reflectors on flexible and processable dielectric bases, and other uses as recently detailed (8).

One approach (8−17), which is used in this study, to preparing silvered polyimide films has been to add a soluble silver(I) complex or salt to a poly(amic acid) precursor in a polar aprotic solvent such as *N*,*N*-dimethylacetamide (Figure 1). A film is then cast. After solvent removal, the doped films are heated to ca. 300 °C, which effects both reduction of the silver(I) ion to native silver and cycloimidization of the poly(amic acid) to polyimide. The adhesion of silver at the polyimide surface is excellent, via a polymer−metal particle interlocking mechanism as previously described (10, 18, 19). Silver atoms and small clusters aggregate to give a surface layer of metal particles with thicknesses from 50 to 200 nm, depending on the silver(I) complex used. Films with excellent specular reflectivity and/or high electrical conductivity have been prepared. Silver nanoparticles are found uniformly distributed in the bulk of the film as well. The characteristics of the surface with regard to reflectivity and conductivity vary with structure of the silver(I) anion/ligand. Importantly, the mechanical and thermal properties of the polymer composite films are not compromised by the presence of the metallic phase, except for stability in air at high temperatures.

Continuing the interest in metallized polyimides, we here report studies on the synthesis of silvered polyimide films, using the approach in Figure 1, where the polyimide is derived from 4,4′-oxidiphthalic anhydride (ODPA) and 4,4′-oxidianiline (4,4′-ODA) monomers with the silver(I) compounds being (hexafluoroacetylacetonato)silver(I), (trifluoroacetylacetonato)silver(I), and silver(I) tetrafluoroborate. The ODPA/4,4′-ODA silvered films were characterized with

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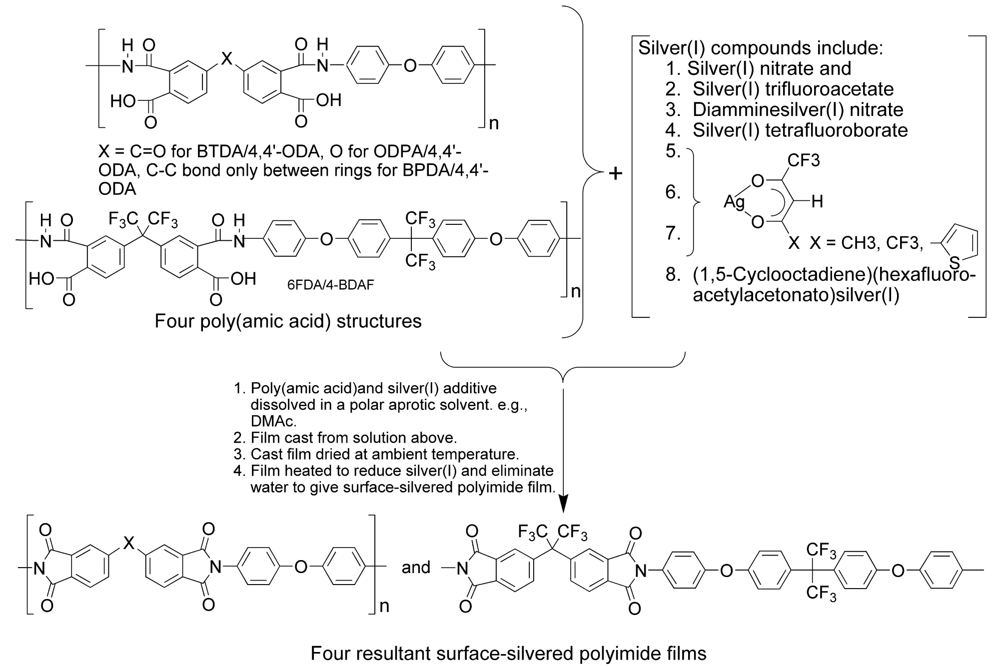

FIGURE 1. Schematic for thermally promoted metal ion reduction of silver(I)-doped poly(amic acid) films as a route to surface-metallized polyimide films. (Representative polyimides and silver(I) additives are shown.)

respect to conductivity, reflectivity, thermal, and mechanical properties. Metallized film properties were examined by scanning and transmission electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, and elemental analysis. Results are compared with those of other silver polyimide metallization work using the related polyimides BTDA/4,4′-ODA, BPDA/4,4′-ODA, and 6FDA/4-BDAF, (8−10, 20, 21) in an attempt to understand those factors which allow control of the formation of silvered films. (See Figure 1 for polyimide structures.)

EXPERIMENTAL SECTION

Materials. 4,4′-Oxydiphthalic anhydride (ODPA, 99+%) and 4,4′-oxidianiline (4,4′-ODA, 99.8%) were purchased from Chriskev Co. (Leawood, KS) and used without further purification, except that ODPA was dried under vacuum at 150 °C. Silver(I) acetate (99.99%), DMAc (99.8%, anhydrous), hexafluoroacetylacetone (HFAH), trifluoroacetylacetone (TFAH, 98%), and pyridine (99+%) were purchased from Aldrich and used as received. The ODPA/4,4′-ODA poly(amic acid) solution was prepared under dry nitrogen with a 1% offset of dianhydride at 15% solids (w/w) in DMAc. The inherent viscosity was measured at 1.4 dL/g at 35 °C.

Preparation of ODPA/4,4′-ODA Metallized Films. The following procedure was used to prepare films containing silver(I) β-diketonate complexes, where the β-diketones were trifluororoacetylacetone (TFAH) and hexafluoroacetylacetone (HFAH). (Details are elaborated in earlier silver−polyimide work (9, 10, 20).) Silver(I) acetate is not soluble in DMAc. Subsequent addition of the poly(amic acid) does not coordinate or solvate silver(I) of the acetate salt to bring it into solution; rather, silver(I) acetate alone gels the poly(amic acid). Thus, silver-containing poly(amic acid) solutions were prepared by first slurrying silver(I) acetate in a small volume of DMAc containing the diketone: 1.35 equiv of TFAH or 1.1 equiv of HFAH. Addition of 15% poly(amic acid) solution to the silver(I)−diketonate complex solution gave a clear homogeneous doped resin. (Addition of an equimolar amount to pyridine, relative to AgOAc, to the solution for AgTFA synthesis facilitates the reaction of AgOAc and gives metallized films similar to those made without pyridine.) Doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 500−650 microns to obtain cured films of 25−35 μm thickness. Films used for the percent reflectivity versus temperature/time measurements were cast on 27 × 46 mm petrographic slides. After they were placed under an atmosphere of slowly flowing dry air (10% 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 closed. The doped films are perfectly clear when taken from the films box; that is, the silver(I) component remains soluble in the solvent-depleted polymer matrix. The cure cycle involved heating over 20 min to 135 °C and holding for 1 h, heating to 300 °C over 4 h, and holding at 300 °C for varying times. Films are readily removed from the casting plate by scoring the edge with a razor blade while immersing the plate in deionized water.

Patterning of Silvered Films. A 13% AgTFA−ODPA/4,4′-ODA film heated at 300 °C for 5 h was patterned using a red Sanford permanent marking pen, the ink serving as a mask to prevent etching. The unprotected silver was etched from the film using Transene Company, Inc. (Danvers, MA), Silver Etchant type TFS. Finally, the ink was removed by rinsing with 95% ethanol, and the metallized pattern was uncovered (see Figure 1 SI in the Supporting Information for a visual display of the patterning protocol).

Characterization. Glass transition temperatures were determined on films in sealed pans with a Seiko DSC 210 system with a heating rate of 20 °C/min. Thermogravimetric analysis (TGA) was done on the cured films under both flowing air and nitrogen (50 mL/min) at a heating rate of 2.5 °C/min using a Seiko TG/DTA 220. Linear coefficients of expansion were determined over a 70−125 °C range with a Seiko TMA100 system. Surface resistivities of all films were measured with an Alessi four-point probe. The probe was checked with 100 Ω/square ITO on poly(ethylene terphthalate). TEMs were done on a Zeiss CEM-920 instrument. Scanning electron micrographs (SEMs) were obtained on Amray 1810 and Hitachi S-4700 instruments; nonconductive samples were coated with ca. 5 nm of palladium/gold alloy. Reflectivity measurements were made

Table 1. Reflectivity Data for AgTFA−ODPA/4,4′-ODA Films[a]

calcd amt of silver (%)[b]	TFAH:silver (mol)	polymer repeat unit: silver (mol)	time at final 300 °C temp (h)	reflectivity of silvered films[c] (as a function of angle) (%)					surface resistivity[d] (Ω/sq)
				20°	30°	45°	55°	70°	
control	NA[e]	NA	1			NA			NC
13	1.35	1.86:1	1	23	21	16	11	8	NC
			2	64	62	56	50	43	NC
			3	74	72	69	65	63	0.2
			5	64	63	60	57	58	0.1
			7	66	65	62	59	58	0.05
			7[c]	[99]	[98]	[96]	[92]	[88]	0.05
8	1.35	2.5:1	4	54	49	43	36	24	NC
			5	60	57	51	45	40	NC
			6	69	67	60	55	52	0.3
			7	52	51	48	45	46	0.3
			7[c]	[65]	[65]	[61]	[57]	[53]	0.2

[a] Cure cycle: 0.33 h to 135 °C for 1 h; 4 h to 300 °C; 300 °C for varied times. [b] Calculated for the AgTFA dopant system decomposing completely to silver metal with volatile byproducts being lost from the film. [c] The wavelength is 531 nm. Reflectivity data are relative to those of a Perkin-Elmer polished aluminum optical mirror set to 100%. Values in brackets are for polished films. [d] Four-point probe. NC = not conductive. [e] NA = not applicable.

(relative to a Perkin-Elmer polished aluminum mirror with a reflectivity coefficient of 0.92 at 531 nm, which is approximately the solar maximum) with a Perkin-Elmer Lambda 35 and/or Lambda 9 UV/vis spectrophotometer equipped with a variable-angle specular reflectance attachment. X-ray data were obtained with a Philips 3600 diffractometer. X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 5300 ESCA instrument; samples were internally referenced to the lowest energy C1s peak set at 285 eV. Elemental analyses were done by Galbraith Analytical Laboratories.

RESULTS AND DISCUSSION

Metallized Film Synthesis. Films were prepared as outlined in the Introduction and Figure 1, where the silver(I) additives were (trifluoroacetylacetonato)silver(I) (AgTFA) and (hexafluoroacetylacetonato)silver(I) (AgHFA), both prepared in situ, and silver(I) tetrafluoroborate ($AgBF_4$). With all silver(I) additives the cured composite ODPA/4,4′-ODA films had an air-side silvered surface with properties that depended on the silver(I) ligand/anion: HFA^-, TFA^-, and BF_4^-. The glass side of the films did not develop a well-defined or useful metallic surface. Final free-standing metallized films were easily handled without tearing; all could be tightly creased without fracturing.

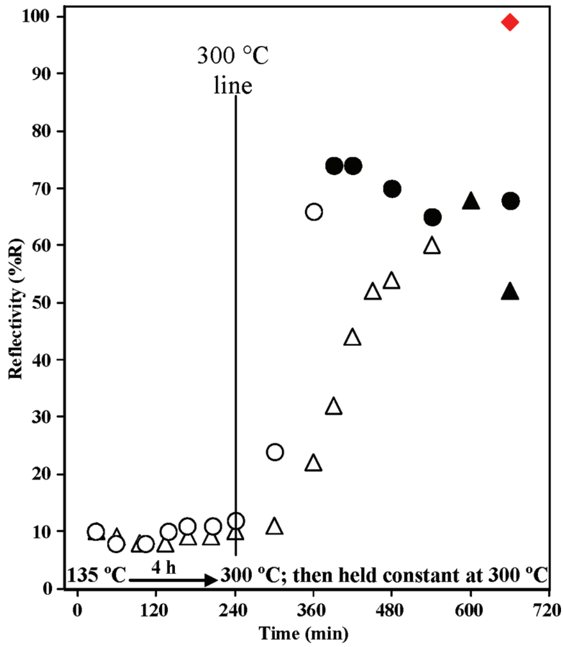

FIGURE 2. Reflectivity versus thermal cure cycle for AgTFA−ODPA/4,4′-ODA metallized films at 8% (△) and 13% silver (○). The solid symbols (▲ and ●) represent conditions at which the silvered film is electrically conductive; the single diamond-shaped point (◆) is the 13% film after 660 min at 300 °C that was polished. Heating protocol: the cast film was heated over 20 min from room temperature to 135 °C and held for 1 h; the temperature then rose from 135 to 300 °C over 240 min; thereafter the temperature remained constant.

Specular Reflectivity and Electrical Conductivity. The development of reflectivity and conductivity was followed by casting silver(I)-doped poly(amic acid) solutions onto a series of glass slides and measuring the properties of individual films after they were withdrawn from the oven at selected temperatures/times. Table 1 and Figure 2 display reflectivity and resistivity data for series of 8% and 13% silvered films prepared with AgTFA. (The 13% silver concentration was chosen to conform to previous work, (18, 21) where 13% silver was approximately the minimal amount that gave well-developed surface conductive films after being held at 300 °C; the 8% value was also chosen to conform to earlier studies of polyimide metallization (10, 20, 22, 23).) Focusing on the 13% films, one sees that they do not begin to develop reflectivity until after being at 300 °C for 1 h. The reflectivity is modest at 23%, albeit with conductivity. Thereafter, the reflectivity increases rapidly reaching a maximum of 74% at 300 °C for 3 h with concomitant metallic conductivity. Further heating at 300 °C leads to a modest decrease in reflectivity, although conductivity increases. Considering the sheet resistivity and the thickness (ca. 200 nm by TEM, vide infra) of the surface

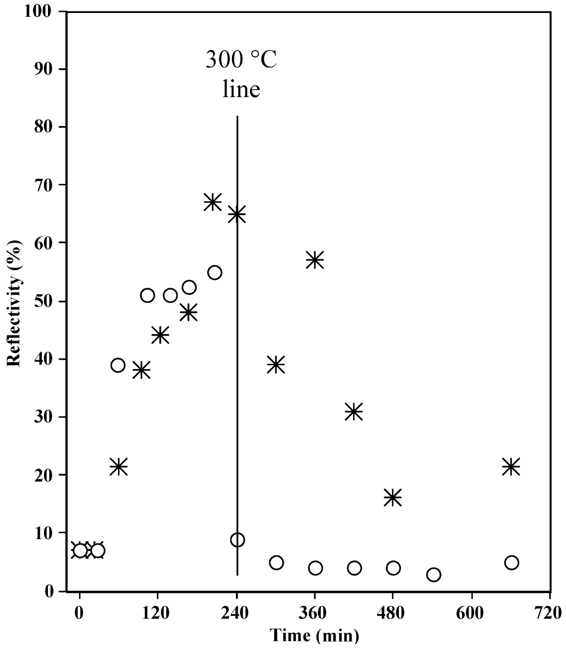

FIGURE 3. Reflectivity versus thermal cure cycle for AgHFA–ODPA/4,4′-ODA metallized films at 8% (*) and 13% (○) silver. None of the films was electrically conductive. The thermal cure cycle is the same as in Figure 2.

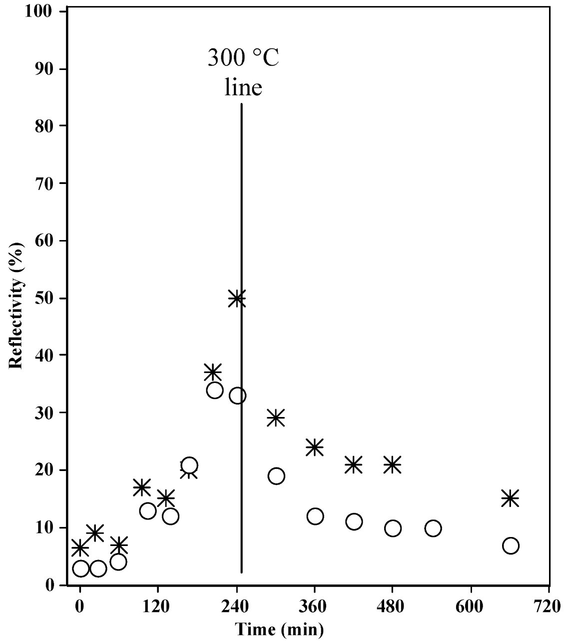

FIGURE 4. Reflectivity versus thermal cure cycle for $AgBF_4$–ODPA/4,4′-ODA metallized films at 8% (*) and 13% (○) silver. None of the films was electrically conductive. The thermal cure cycle is the same as in Figure 2.

silver layer for the film heated to 300 °C for 7 h, the bulk resistivity of the silver surface is $1.0 \times 10^{-6}\ \Omega$ cm (24), which is near that of pure silver at $1.6 \times 10^{-6}\ \Omega$ cm. Interestingly, if the 13% film cured at 300 °C for 7 h is polished gently (25), the reflectivity improves to 99%. The adhesion of silver to polyimide is unfailing, such that polishing does not dislodge any metal particles. The 8% AgTFA silvered films reach a maximum reflectivity (69%) later in the cure cycle than the 13% analogue. Both the maximum reflectivity and the first observation of conductivity occur only after 6 h at 300 °C. (TEM for the 8% AgTFA film heated at 7 h for 300 °C is shown in Figure 2 SI in the Supporting Information. The bulk resistivity is ca. $1.5 \times 10^{-6}\ \Omega$ cm.)

Figures 3 and 4 display reflectivity data for ODPA/4,4′-ODA films doped with AgHFA and $AgBF_4$. While both sets of films develop a silver surface, the reflectivities are lower than that for the corresponding AgTFA–ODPA/4,4′-ODA films of Figure 2. Interestingly, none of the AgHFA and $AgBF_4$ films ever exhibited conductivity, even after heating at 300 °C for 7 h. Polishing did not render the films reflective or conductive, which is consistent with silver particles being just beneath the polyimide–air interface; that is, there is an overlayer of polyimide, first observed by Taylor et al. (26) and later by us (8) and rationalized by Kovacs and Vincett (27, 28), such that the apparent metallic surface is fully encapsulated, as discussed more thoroughly later. The AgHFA films developed a silver surface much earlier than the corresponding AgTFA films; however, films showed an irregular, coarse, microbubbled/blistered surface upon reaching 300 °C. These roughened surfaces caused the specular reflectance to fall dramatically (Figure 3). This is different behavior relative to that of the corresponding BTDA/4,4′-ODA and BPDA/4,4′-ODA films studied earlier, which maintain a smooth surface with high reflectivity at 300 °C over several hours (9, 10). The reflectivity of the $AgBF_4$ is modest but is less than that for the corresponding BTDA/4,4′-ODA films reported previously (29). The $AgBF_4$ films were not characterized beyond reflectivity (Figure 4) and conductivity due to minimal potential usefulness.

Bulk and Surface Elemental Analytical Data and the Mechanism for Metallized Surface Formation. The AgTFA–ODPA/4,4′-ODA films are exceptional among the three silvered-ODPA/4,4′-ODA film sets prepared with AgTFA, AgHFA, and $AgBF_4$. The 13% AgTFA films, in particular, have the best reflectivity, especially when polished (25), and they are the only film types that developed conductivity. The uniqueness of the AgTFA films is due to the fact that they develop a metallized surface by a selective silver-catalyzed oxidative degradation of surface polyimide with concomitant growth of a metallic surface as silver nanoparticles aggregate upon being freed from the ablating polyimide matrix. This mechanism also explains the unfailing adhesion of surface silver, some of which is anchored to silver particles still significantly locked in the bulk of the polyimide. Unequivocal evidence for this polyimide oxidative degradation growth mechanism follows.

Table 2 displays total (bulk plus surface) elemental analysis data for four 13% AgTFA–ODPA/4,4′-ODA films of Figure 2, the films being at 276 °C and at 300 °C for 1, 3, and 7 h. The films withdrawn at 276 and 300 °C after 1 h with reflectivities of 11 and 23%, respectively, have C, H, N, and Ag mass percents that are close (±0.7%) to those expected for polyimide and silver metal, with the ligand having been lost/volatilized from the composite system in some form, e.g., as intact TFAH or thermally degraded products therefrom. Thus, there is minimal loss of polyimide from oxidative (O_2 in air) degradation to volatile products such as CO, CO_2, H_2O, etc., which is consistent with a “10% weight loss”

Table 2. Elemental Analysis (Mass Percent) of Selected 13% AgTFA-Doped ODPA/4,4′-ODA Films[a]

thermal cure of sample	silver	fluorine	carbon	hydrogen	nitrogen
calcd[b]	13.0	0	61.7	2.59	5.14
found for 276 °C, 0 h	12.6	0.10	61.3	2.97	5.25
found for 300 °C, 1 h	13.7	0.10	60.7	2.91	5.28
found for 300 °C, 3 h	16.2	0.11	59.2	2.83	5.10
found for 300 °C, 7 h	23.4	0.10	51.7	2.54	4.50

[a] Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Films are the same as those of the reflectivity plot in Figure 2. [b] The ODPA-4,4′-ODA resin was prepared as 1 mol % dianhydride in excess of the diamine.

temperature of ca. 530 °C determined by thermal gravimetric analysis (Table 3) for the pure polyimide in air. However, thermal-oxidative effects for lengthier cure times at 300 °C become pronounced. For samples at 300 °C after 3 and 7 h, reflectivities increase to 74 and 66% (99% polished (25)), respectively, and both these films are conductive. Analysis showed a marked increase in silver to 16.2% (300 °C, 3 h) and 23.4% (300 °C, 7 h) with a diminution in carbon. Since neat polyimides, including ODPA/4,4′-ODA, are stable at 300 °C in air, there must be a silver-catalyzed oxidative degradation of polyimide to volatile products in the composite silvered films after extended heating in air at 300 °C. Indeed, silver is well-known for the catalytic oxidation of organic frameworks (30). Diffusion of oxygen into the interior of the film is slow over the time scale of the heating, since film properties of the 8% and 13% AgTFA—ODPA/4,4′-ODA composite films resemble those of the parent polyimide, as seen from the glass transition temperature (T_g), coefficient of thermal expansion (CTE), and mechanical data in Table 3.

X-ray photoelectron (XPS) spectral data presented in Table 4 also support the oxidative degradation pathway to reflective and conductive AgTFA films. Data were taken on the air side of the 13% AgTFA—ODPA/4,4′-ODA films cured at 276 °C and at 300 °C for 1, 3, and 7 h with specular reflectivities of 11, 23, 74, and 68%, respectively, with the last two films being conductive. For the film at 276 °C the silver concentration was 1.76 atom %, which is that expected for the silver(I) additive being homogeneously dispersed throughout the composite film: i.e., no silver enrichment at the surface and no polyimide degradation. Indeed, the TEMs of Figure 5 for the 276 °C and 300 °C, 1 h films show clearly no enrichment of surface silver. With increased time at 300 °C (3 and 7 h), surface silver builds, as seen in Figures 5 (TEM) and 6 (SEM). The increase in silver concentration from 2.49 atom % at 300 °C for 1 h to 21.3 atom % at 300 °C for 3 h is striking and correlates with the jump in reflectivity to 74% (Figure 3) and the marked decrease in resistivity (0.2 Ω/sq; Table 1).

Let us consider further the formation of a surface silver layer. We know with certainty from experiment and theory that metal atoms and clusters cannot spontaneously move out of the polymer matrix onto the surface. Faupel and coworkers (31) and Kovacs and Vincett (27, 28) have elegantly demonstrated experimentally and theoretically that the stable state of a metal—polymer system is for the metal particle to be fully embedded in the polymer. That is, when the surface free energy of the metal (γ_M) is greater than the interfacial free energy (γ_{MP}) plus the surface free energy of the polymer (γ_P), i.e., $\gamma_M > \gamma_{MP} + \gamma_P$, a metal particle must embed in the polymer. For inorganic particles this relationship is general. Exceptions to embedding occur only because of kinetic considerations such as the polymer being in the glassy state, i.e., below T_g, and/or the metal particle size being large. Thus, the only pathway to a silvered polyimide surface beginning with a silver(I)-doped poly(amic acid) is to have the thermally curing hybrid film undergo loss of surface polyimide to bare the metal at the air-side surface, which, from analytical data, is clearly the case for the AgTFA films.

The question now remains as to why AgHFA and $AgBF_4$ in ODPA/4,4′-ODA do not generate silver surfaces by oxidative ablation of polyimide. Consistent with previous efforts (9, 29, 32), both of these systems undergo silver(I) reduction at much lower temperatures than for the AgTFA system (9, 29). This is seen in the earlier development of reflectivity for AgHFA and $AgBF_4$ films of Figures 3 and 4 compared with AgTFA films. Significant reflectivity is observed at ca. 175 °C for the 13% AgHFA films and at ca. 200 °C for the 13% $AgBF_4$ films; for the 13% AgTFA system reflectivity does not begin to emerge until much later in the thermal cycle: specifically, only after being at 300 °C for 1 h. A temperature for the onset of reduction for 13% AgTFA and AgHFA films can be approximated from the X-ray patterns shown in Figure 7. For the AgHFA films reduction of silver(I) first appears at ca. 135 °C, whereas for the AgTFA films, reduction first appears at the much higher temperature of ca. 175 °C. That the X-ray diffraction peaks for the AgHFA films become rather narrow, beginning at ca. 150 °C, and remain narrow through the 300 °C range is strong evidence that the aggregation of silver atoms/clusters occurs rapidly, just after the beginning of silver(I) reduction, relative to the AgTFA films, where obvious Scherrer broadening is seen up to ca. 300 °C for 0 h. Ree et al. (33) have shown in a thermally curing poly(amic acid)—polyimide system derived from pyromellitic dianhydride and 3,4′-oxidianiline, PMDA/3,4′-ODA, a classic polyimide similar to ODPA/4,4′-ODA of this work, that imidization begins at ca. 125 °C. At 175 °C imidization is ca. 75% complete and is ca. 98% complete by 200 °C. (See Figure 3 SI in the Supporting Information for temperature studies of imidization extent.) Thus, in the AgTFA—ODPA/4,4′-ODA system, relative to the AgHFA and $AgBF_4$ systems, atom/cluster mobility is much more restricted because of the greater rigidity of the polymeric system with a high fraction of polyimide relative to poly(amic acid); consequently, the silver particle size on reaching 300 °C is smaller. The particle sizes at the surface of a 13% AgHFA film cured to 300 °C for 0 h are ca. 100 nm, as seen in the SEM of Figure 8. Now, the point is that with AgTFA as the additive, when 300 °C is reached in the thermal cycle, the silver particle sizes are predominately ≤10 nm. These

Table 3. Thermal, Mechanical, and Resistivity Data for AgTFA−ODPA/4,4′-ODA Films[a]

calcd amt of silver (%)[b]	T_g(DSC) (°C)	CTE (ppm/K)	10% wt loss (°C)[c] air	10% wt loss (°C)[c] N_2	surface resistivity (Ω/sq)[d]	tensile strength (Ksi)	elongation at break (%)	modulus (Ksi)
control	264	32.6	528	540	NC	18.8	12	306
13	263	28.4	337	550	0.1	17.3	10	330
8	266	32.8	357	548	NC	17.3	17	328

[a] Cure cycle: 0.33 h to 135 °C for 1 h; 4 h to 300 °C; 300 °C for 5 h. [b] Calculated for the silver(I) acetate−trifluoroacetylacetone dopant system decomposing completely to silver metal and volatile components which are presumed to be lost from the film. [c] Determined by TGA. [d] Four-point probe. NC = not conductive.

Table 4. X-ray Photoelectron Spectroscopic Composition Data for the Air Side, i.e., Metallized, Surface of Selected AgTFA−ODPA/4,4′-ODA Films of Figure *2* and Table *2*

amt of silver (wt %)[a]	thermal history[b]	reflectivity at 20 °C (%)	resistivity (Ω/sq)[c]	composition (rel atom %) silver	fluorine	carbon	oxygen	nitrogen
ODPA/ODA (calc with 13% Ag)	NA	NA	NC	1.79	0	76.4	16.4	5.46
13	276 °C, 0 h	11	NC	1.76	0.34	77.3	15.9	4.65
13	300 °C, 1 h	23	NC	2.49	0.00	76.3	17.7	3.53
13	300 °C, 3 h	74	0.2	21.2	0.12	49.2	28.7	0.83
13	300 °C, 7 h	68[d]	0.05	23.7	0.10	34.8	40.0	1.39

[a] Calculated for the AgTFA complex decomposing completely to silver metal and volatile components which are lost from the film. [b] All sample cure cycles began with heating from room temperature to 135 °C over 20 min and holding at this temperature for 1 h followed by heating over 240 min to 300 °C and holding at 300 °C for varying amounts of time. [c] Four-point probe. NC = not conductive. [d] This is a 7 h sample different from that cited in Table 1.

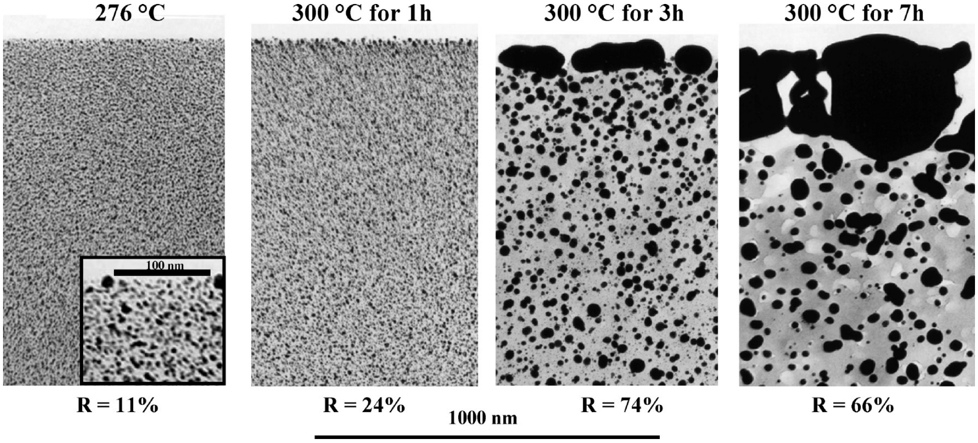

FIGURE 5. Transmission electron micrographs for selected 13% AgTFA−ODPA/4,4′-ODA films of Figure 2 cured to 276 °C and to 300 °C for 0 h, 300 °C for 3 h, and 300 °C for 7 h.

small particle sizes, with high effective surface areas, are expected to be more effective in catalyzing polyimide degradation, which allows a silver layer to build. The much larger particles of the AgHFA and $AgBF_4$ systems, covered by a thin overlayer of polymer as observed (26, 31, 34, 35) and as required thermodynamically, are not effective in degrading polyimide.

Comparisons among AgTFA−Polyimide Systems. To date we have studied thoroughly four AgTFA−polyimide couples at 13% silver, the polyimides being ODPA/4,4′-ODA (this paper), BTDA/4,4′-ODA (10), BPDA/4,4′-ODA (9), and 6FDA/4-BDAF (8, 11, 34), with the goal of controlling the surface reflectivity and conductivity. How do these four systems compare? What similarities and differences are expected and are observed?

BTDA/4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA are typical of oft referred to “classic polyimides” and are similar in structure, varying only in the connecting link, C═O, O, or direct C−C bond, between the two aromatic rings in the dianhydride unit (Figure 1). They exhibit very similar thermal, chemical, and mechanical properties. For example, T_g values for all are ca. 270 °C, 10% weight loss temperatures in air are ca. 530 °C, the CTEs are similar, fractional free volumes vary little, permeability coefficients for small molecules such as O_2, N_2, H_2, are CH_4 are very close, all are insoluble in the final imide form, and so on (36−39). These pronounced similarities suggest that the fabrication and resultant properties of the BTDA/4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA metallized films, formed from silver(I)-doped poly(amic acid)s, might well be comparable. Indeed, we suggest that this is the case when looking at the most important properties of this study: that is, reflectivity and conductivity. Figure 9, which displays

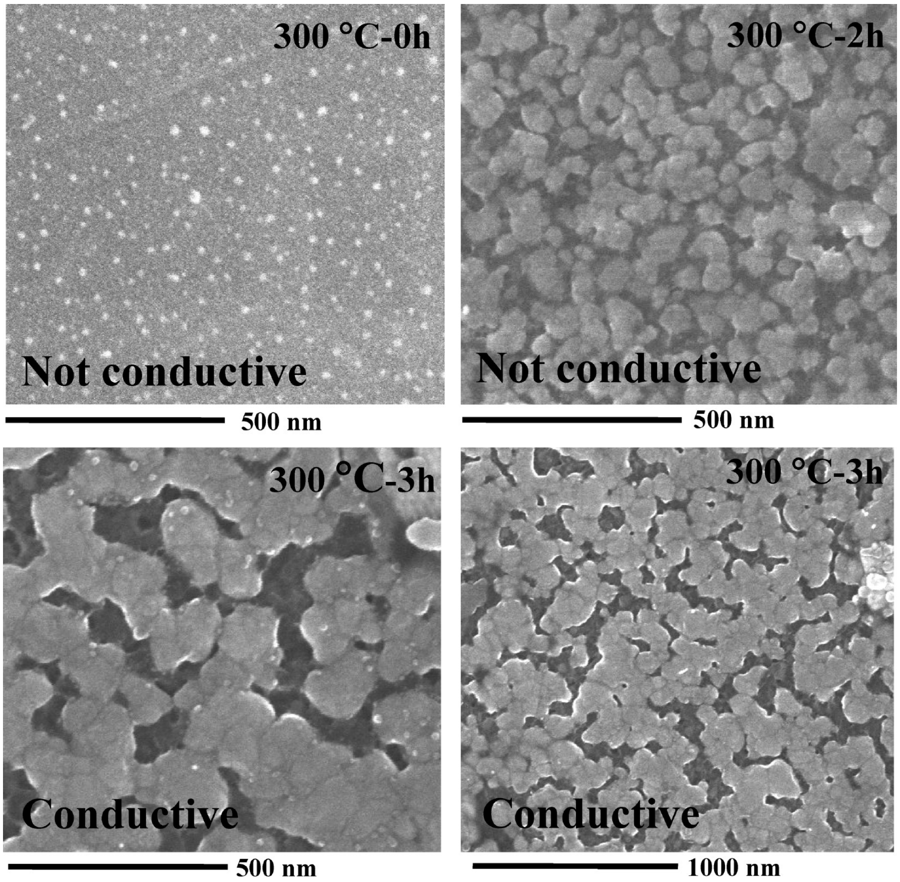

FIGURE 6. Scanning electron micrographs for selected 13% AgTFA−ODPA/4,4′-ODA films of Figure 2 cured to 300 °C for 0 h, 300 °C for 2 h, and 300 °C for 3 h. The photo at the bottom right is a lower magnification of the bottom left film, showing more of the silver network structure.

reflectivity versus cure temperature/time with the first observation of conductivity marked by a circle (○), confirms a strong similarity of metallization behavior for the AgTFA-BTDA/4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA couples. While there are differences, they are modest. All films exhibit significant reflectivity, particularly if one allows for a final soft polishing (25), and all exhibit metallic conductivity. All metallized films retain the essential mechanical properties of the parent polyimide, and there is little effect on T_g. The films have comparable thermal cure cycle profiles with regard to the development of reflectivity and conductivity, particularly allowing for difficulties in the exact reproducibility of heterogeneous solid-state reactions compared with homogeneous solution reactions (40). The X-ray diffraction peaks for silver as a function of heating are similar with regard to the temperature at which one first sees metallic silver and with regard to peak widths (Scherrer broadening) related to the size of nanoparticles. While we have observed pronounced silver(I) ligand/anion effects on polyimide metallization (29), there are not dramatic differences among the three classic polyimides that we have investigated when the silver(I) additive is held constant.

The question then arises as to what one might expect from a polyimide that is radically different from the three classic polyimides above, and what insight might the metallization of a very different polyimide shed on the metallization pathway. Toward this end we chose to study, and have reported the results thereof (34), the nonclassical fluorinated polyimide 6FDA/4-BDAF with both the dianhydride and diamine having bulky, nonpolarizable hexafluoroisopropylidene units (Figure 1), with 13% AgTFA. As summarized by Stern (39), 6FDA/4-BDAF is strikingly different from classical polyimides. The substitution of $-C(CF_3)_2$ groups has pronounced effects on polyimide behavior relative to classical polyimides such as PMDA/4,4′-ODA, BTDA, BPDA, ODPA, etc. In particular, chain stiffness is increased, chain packing is inhibited, and interchain interactions via charge transfer complexation are reduced due to the nonpolarizable CF_3 groups and bulky $-C(CF_3)_2$ units. These effects give 6FDA/4-BDAF a much higher fractional free volume, much enhanced permeability coefficients for small molecules, higher coefficients of thermal expansion, lower dielectric constants, soluble imide forms of the polymer, etc., even though T_g values and mechanical properties are similar to those of BTDA/4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA. With higher fractional free volume and enhanced permeability coefficients for 6FDA/4-BDAF, the formation of silver atoms in a thermally curing 6FDA/4-BDAF film might well yield larger silver nanoparticles with a corresponding diminution of silver-catalyzed thermal ablation of polyimide at the surface due to decreased effective silver surface area. Indeed, this early and larger silver particle size is what is seen at the air-side surface of heated silver(I)−6FDA/4-BDAF films (Figure 9 and Figures 4 SI and 5 SI in the Supporting Information).

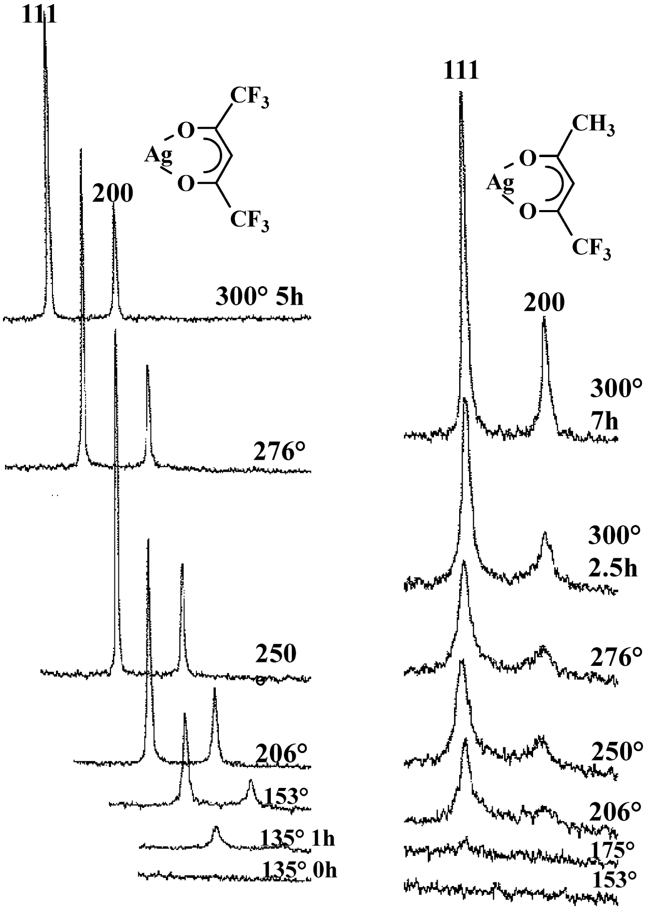

FIGURE 7. X-ray diffraction patterns in the *hkl* = 111, 200 region with *d* spacings of 2.37 and 2.04 Å, respectively, as a function of cure time/temperature (Celsius) for 13% silver–ODPA/4,4′-ODA films: (left) AgHFA–ODPA/4,4′-ODA films; (right) AgTFA–ODPA/4,4′-ODA films. Films are those of Figures 2 and 3.

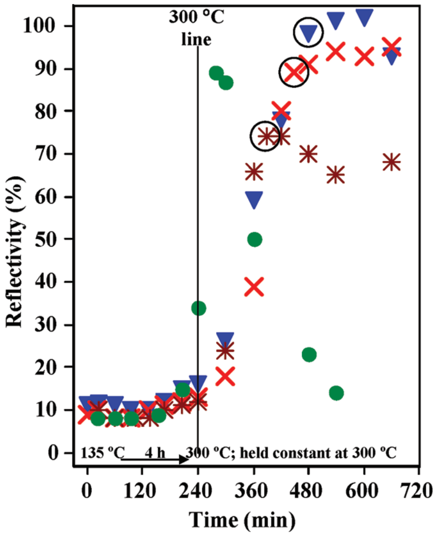

FIGURE 9. Comparison of reflectivity and conductivity for four metallized polyimides prepared at 13% silver with AgTFA and the poly(amic acid) precursor. The polyimides are: (×) BTDA/ 4,4′-ODA, (▼) BPDA/4,4′-ODA, (*) ODPA/4,4′-ODA, and (●) 6FDA/4-BDAF. The three circles surrounding one point for each system represent the first observation of metallic conductivity in a film series; the 6FDA/4-BDAF film never developed a metallic conductive surface.

In reference to the reflectivity data (Figure 9) for the 13% AgTFA–6FDA/4-BDAF system, when 6FDA/4-BDAF is the matrix for silver(I) reduction and subsequent surface metallization, we see dramatically different behavior relative to the three classic analogues. Most striking is that the fluorinated polyimide never develops a conductive surface. It does develop high reflectivity (89%) at 300 °C and 0.67 h, which is ca. 1–2 h sooner than for the BTDA, BPDA, and ODPA congeners, consistent with enhanced migration facility of silver atoms/clusters, at least near the film air-side surface. TEM and SEM micrographs (Figure 4 SI in the Supporting Information) show that, for the 6FDA/4-BDAF system, particles ca. 100 nm in diameter have formed at the surface, being at 300 °C for ca. 1 h. These are much greater in size than those seen for the three classic polyimides under similar conditions. As mentioned, large silver nanoparticles are not effective in catalyzing the degradation of surface polyimide to build the silver layer. As the time at 300 °C increases, the surface silver particles of the AgTFA–6FDA/4-BDAF film undergo further aggregation and increase in size but never grow into a continuous, conductive layer as SEM micrographs show (Figure 4 SI in the Supporting Information). That migration of silver atoms/clusters is more rapid in 6FDA/4-BDAF polyimides is also seen from the fact that 2% silver–6FDA/4-BDAF films prepared with AgHFA develop an 80% specularly reflective silvered surface (8); with the classic polyimides BTDA/4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA, use of 2% silver never gave a reflective film. (Figure 5 SI

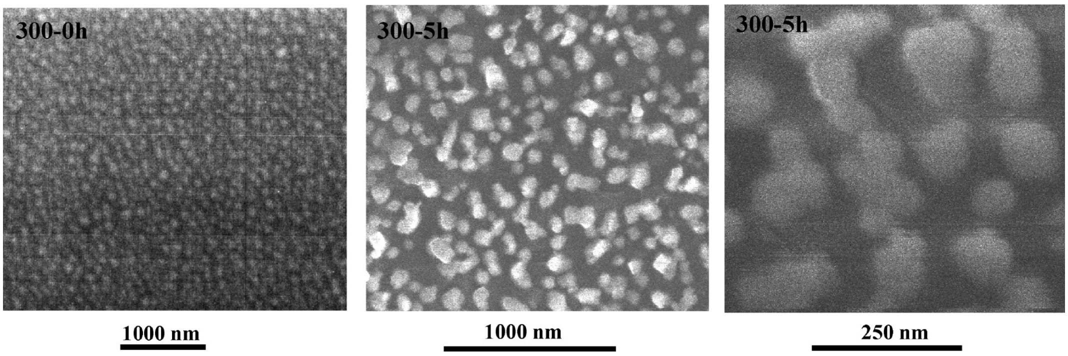

FIGURE 8. Scanning electron micrographs of the 13% AgHFA–ODPA/4,4′-ODA film cured to 300 °C for 0 h (left) and cured to 300 °C for 5 h (middle and right; different magnifications of the same film). Films are the same as in Figure 3, showing reflectivities of 9% and 3%, respectively. The films are visually metallized but microblistered in most of the area, which minimizes reflectivity. The SEMs were taken on a smooth portion of each film.

in the Supporting Information shows via TEM the well-defined surface silver layer for a 2% 6FDA/4-BDAF film.)

Thermal and Mechanical Data. Thermal data for the 8 and 13% AgTFA films (Table 3) show that metallization of the polyimide at either silver concentration does not significantly alter T_g. The tensile strength is only slightly lowered, and the modulus is slightly elevated. Overall, the presence of the thin silver surface coupled with an array of silver nanoparticles in the bulk does not adversely influence T_g and basic mechanical properties. This is not unexpected, since there is only weak interaction between passive metals and polyimides (1). In previous metallization work (8−10) with BPDA/4,4′-ODA and BTDA/4,4′-ODA we also saw only modest changes in selected thermal and mechanical properties. The one thermal property of the metallized films that is degraded is the temperature at which 10% weight loss in air is observed. This weight loss in air for silvered films occurs ca. 175 °C lower than for the parent polymer; however, the metallized films under a nitrogen atmosphere have essentially the same stability as the parent film in air or nitrogen. The CTE for the 8% silver film is not different from that of the parent polyimide and for the 13% film is only modestly lower. Again, this is consistent with weak metal−polyimide interfacial forces and also with the fact that the surface silver film is thin and not completely continuous, as seen in the SEMs of Figure 6.

CONCLUSION

Silvered ODPA/4,4′-ODA polyimide films have been synthesized from single-phase silver(I) acetate−trifluoroacetylacetone, silver(I) acetate−hexafluoroacetylacetone, or $AgBF_4$−poly(amic acid) solutions cast on glass plates and heated to 300 °C. Only the AgTFA−ODPA/4,4′-ODA films develop both high specular reflectivity and conductivity. The development of the metallized surface requires a very selective oxidative ablation of surface polyimide to expose the silver surface. Films prepared with AgHFA and $AgBF_4$ develop modest reflectivity but remain nonconductive. The metallized films exhibit outstanding metal−polymer adhesion at the surface and mechanical characteristics very near those of the parent polyimide, the latter indicating minimal interaction between silver nanoparticles and polyimide. While the formation of metallic silver lowers thermal film stability in air to ca. 350 °C, the metallized polymers still have a wide thermal use range. The surface metallized films derived from AgTFA are readily patterned using an organic soluble masking agent, etching away unmasked surface silver, and finally, washing off the mask.

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Supporting Information Available: Figures giving additional TEM micrographs for the air-side surfaces for the 8% silver AgTFA−ODPA/4,4′-ODA film cured to 300 °C for 7 h, for four 13% silver AgTFA−polyimide (4,4′-ODA, BPDA/4,4′-ODA, and ODPA/4,4′-ODA, 6FDA/4-BDAF) films, and for a 2% silver AgHFA−6FDA/4-BDAF film, additional SEM micrographs of the air-side silvered surface for a 13% silver AgTFA−6FDA/4-BDAF film, a graph summarizing the extent of poly(amic acid) imidization as a function of temperature, and a description of patterning with photographs of a patterned film. This material is available free of charge via the Internet at http://pubs.acs.org.

REFERENCES AND NOTES

(1) Matienzo, L. J.; Unertl, W. N. In *Polyimides:Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; MarcelDekker: New York, 1996; pp 629−696.

(2) Sener, U.; Entenberg, A.; Kahn, B.; Egitto, F. D.; Matienzo, L. J.; Debies, T.; Takacs, G. A. *Polyimides Other High Temp. Polym.* **2005**, *3*, 535–552.

(3) Zhang, J.; Sullivan, M. B.; Zheng, J. W.; Loh, K. P.; Wu, P. *Chem. Mater.* **2006**, *18*, 5312–5316.

(4) Zaporojtchenko, V.; Strunskus, T.; Behnke, K.; v. Bechtolsheim, C.; Thran, A.; Faupel, F. *Microelectron. Eng.* **2000**, *50*, 465–471.

(5) Yang, C.-Y.; Chen, J. S.; Hsu, S. L. C. *J. Vac. Sci. Tech., A* **2005**, *23*, 862–868.

(6) Rozovkis, G.; Vinkevicius, J.; Jaciauskiene, J. *J. Adhes. Sci. Technol.* **1996**, *10*, 399.

(7) Murdey, R.; Stuckless, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 3995–3998.

(8) Davis, L. M.; Thompson, D. S.; Thompson, D. W.; Southward, R. E. *Polyimides Other High Temp. Polym.* **2007**, *4*, 261–286.

(9) Southward, R. E.; Thompson, D. W. *Chem. Mater.* **2004**, *16*, 1277–1284.

(10) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1999**, *11*, 501–507.

(11) Warner, J. D.; Pevzner, M.; Dean, C. J.; Kranbuehl, D. E.; Scott, J. L.; Broadwater, S. T.; Thompson, D. W.; Southward, R. E. *J. Mater. Chem.* **2003**, *13*, 1847–1852.

(12) Qi, S.-L.; Wu, D.-Z.; Wu, Z.-P.; Wang, W.-C.; Jin, R.-G. *Polymer* **2006**, *47*, 3150–3156.

(13) Qi, S.; Wu, Z.; Wu, D.; Wang, W.; Jin, R. *Langmuir* **2007**, *23*, 4878–4885.

(14) Qi, S.; Wu, Z.; Wu, D.; Wang, W.; Jin, R. *Chem. Mater.* **2007**, *19*, 393–401.

(15) Qi, S.; Wu, Z.; Wu, D.; Jin, R. *J. Phys. Chem. B* **2008**, *112*, 5575–5584.

(16) Li, Y.; Lu, Q.; Qian, X.; Zhu, Z.; Yin, J. *Appl. Surf. Sci.* **2004**, *233*, 299–306.

(17) Sawada, T.; Ando, S. *Chem. Mater.* **1998**, *10*, 3368–3378.

(18) Southward, R. E.; Thompson, D. W. *Adv. Mater.* **1999**, *11*, 1043–1047.

(19) Southward, R. E.; Stoakley, D. M. *Prog. Org. Coatings* **2001**, *41*, 99–119.

(20) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; St. Clair, A. K. *Chem. Mater.* **1995**, *7*, 2171–2180.

(21) Southward, R. E.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 501–509.

(22) Rubira, A. F.; Rancourt, J. D.; Caplan, M. L.; St. Clair, A. K.; Taylor, L. T. *Chem. Mater.* **1994**, *6*, 2351.

(23) Rubira, A. F.; Rancourt, J. D.; Taylor, L. T.; Stoakley, D. M.; St. Clair, A. K. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 621–636.

(24) The bulkresistivity is given by theproduct of the sheet resistivity in Ω/square times the silverlayer thickness. The accepted resisitivity of pure silver is 1.6×10^{-6} Ω cm.

(25) SunshineSunshine Polishing Cloth (www.SunshinePolishingCloth.com). Silver is a soft metal (2.5−3mohs) and is therefore polished and manipulated easily.

(26) Rancourt, J. D.; Porta, G. M.; Taylor, L. T. *Int. SAMPE Tech. Conf.* **1987**, *19*, 564–575.

(27) Kovacs, G. J.; Vincett, P. S. *J. Colloid Interface Sci.* **1982**, *90*, 335–351.

(28) Kovacs, G. J.; Vincett, P. S. *Can. J. Chem.* **1985**, *63*, 196–203.

(29) Southward, R. E.; Thompson, D. W. *Metallized Plastics* **2001**, *7*, 171–188.

(30) Hucknall, D. J. *SelectiveOxidationof Hydrocarbons*; Academic Press: London, 1974.

(31) Faupel, F.; Willecke, R.; Thran, A. *Mater. Sci. Eng., R: Reports* **1998**, *R22*, 1–55.

(32) Southward, R. E.; Thompson, D. W. *Mater. Des.* **2001**, *22*, 565–576.

(33) Shin, T.; Ree, M. *Macromol. Chem. Phys.* **2002**, *203*, 791–800.

(34) Davis, L. M.; Thompson, D. S.; Dean, C. J.; Pevzner, M.; Scott, J. L.; Broadwater, S. T.; Thompson, D. W.; Southward, R. E. *J. Appl. Polym. Sci.* **2007**, *103*, 2409–2418.

(35) Deshmukh, R. D.; Composto, R. J. *Chem. Mater.* **2007**, *19*, 745–754.

(36) Mittal, K. L., Ed. *Metallized Plastics:Fundamentals and Applied Aspects*; Brill Academic: Boston, 2001; Vol. 7.

(37) Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561–694.

(38) Li, Y.; Wang, X.; Ding, M.; Xu, J. *J. Appl. Polym. Sci.* **1996**, *61*, 741–748.

(39) Stern, S. A. *J. Membr. Sci.* **1994**, *94*, 1–65.

(40) Ribeiro, F. H.; Schach Von Wittenau, A. E.; Bartholomew, C. H.; Somorjai, G. A. *Catal. Rev.* **1997**, *39*, 49–76.

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