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Metal−Polyimide Nanocomposite Films: Single-Stage Synthesis of Silvered Polyimide Films Prepared from Silver(I) Complexes and BPDA/4,4′-ODA

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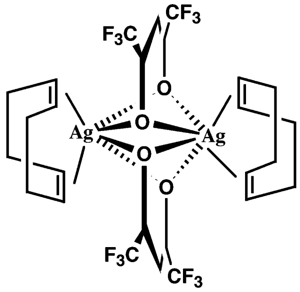
Highly reflective and surface conductive flexible polyimide films have been prepared by the incorporation of silver(I) acetate and 1,1,1-trifluoro-2,4-pentanedione or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione into a dimethylacetamide solution of the poly(amic acid) formed from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and 4,4′-oxydianiline. Thermal curing of the silver(I)-containing poly(amic acid) leads to cycloimidization of the polyimide precursor with concomitant silver(I) reduction yielding reflective and conductive silvered surfaces with properties approaching those of the native metal. The metallized films usually exhibit mechanical and thermal properties close to that of the parent polyimide. Films were characterized by X-ray diffraction, transmission and scanning electron microscopy, and X-ray photoelectron spectroscopy.

Introduction

Endrey[1] disclosed in a 1963 patent that films of silver(I) carboxylate complexes dissolved in amide solutions of poly(amic acid)s gave metallized surfaces which were electrically conductive when cured in air to the polyimide at 300 °C followed by heating in nitrogen for several hours at 275 °C. A large excess of pyridine was necessary to prevent gelation. No mention of the reflectivity of the films was made, and no mechanical or thermal data were presented. No publications by Endrey or others at DuPont elaborating this initial work have appeared.

Similar reduction of silver(I) in poly(amic acid) films was further demonstrated in the 1980s using simple silver(I) salts such as nitrates, carboxylates, trifluoromethane sulfonate, and sulfate by Taylor and others[2−5] and Auerbach.[6] Only very limited success was realized in achieving reflective and conductive metallized surfaces; reflectivities were 18−46% for the best films, and only a few films exhibited surface conductivity after varied “post-cure” thermal treatments. Films formed with silver nitrate were often brittle and degraded.

From 1994 to 1998 Taylor and co-workers[7−10] published noteworthy poly(amic acid)/polyimide metallization work using a more elaborate silver(I) precursor, namely, the (1,1,1,5,5,5-hexafluoroacetylacetonato)(1,5-cyclooctadiene)silver(I), AgHFA(COD) complex,



which has a dimeric oxygen-bridged solid-state structure with unusual bridging β-diketonate ligands.[11] The complex is soluble in DMAc and in solvent-depleted poly(amic acid) matrixes. Thermal curing of poly(amic acid)−silver(I) films to 300 °C (usually in air) (ca. 3−19 wt % silver) gave metallized films which had air-side reflectivities of 4−65%. Nearly all films were not

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surface-conductive. The specular reflectance was highest (65%) with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride/4,4′-oxydianiline, BTDA/ODA, films. Several conclusions can be drawn from AgHFA(COD) of Taylor and co-workers. First, it is possible to develop a uniform near-surface layer of silver particles which exhibit significant reflectivity in a polymer film by thermal reduction of the dissolved silver(I) complex. Second, films that were found to be highly reflective were not conductive, whereas the films which exhibited little or no metallic reflectivity were at times conductive. Taylor and co-workers also disclosed in a patent that (1,1,1-trifluoro-2,4-pentanedionato)silver(I), AgTFA, in BTDA/ODA gives surface-conductive films, although no reflectivity observations were reported; however, it proved difficult to reproducibly prepare solid AgTFA[12] and the reported films.[13]

One drawback to the use of Ag(HFA)(COD) and AgTFA is their instability and stench. The first complex “loses olefin slowly when exposed to air over long periods of time” and “should be stored in a tightly closed container and kept in a refrigerator” according to Partenheimer and Johnson[14] who reported its synthesis. Also, Ag(HFA)(COD), alone and in curing films, has a stench associated with the readily liberated 1,5-cyclooctadiene ligand. AgTFA is difficult to prepare and store as a pure solid.[13,15] Within the same time frame of the Taylor et al. efforts we reported[16−19] details of synthetic modifications for the fabrication of silver-metallized films. The two β-diketonate complexes, AgHFA and AgTFA, were freshly prepared in situ (without isolation as solids) without additional stabilizing ligands such as COD and dissolved in a solution of BTDA/ODA poly(amic acid). Films were cast and cured to 300 °C. Surface-silvered polyimide films as high quality were produced with strikingly different additive-dependent properties. The AgHFA films were highly reflective but not conductive with isolated near-surface silver nanoparticles, and the AgTFA films are both highly reflective and conductive with a continuous surface silver layer. The glass transition temperatures, T_g, for the metallized films is close to that for the parent polymer as are the moduli and tensile strengths, which indicates that there is minimal damage to the essential polyimide structure when silver(I) in either of these complexes undergoes reduction to metal upon heating.

We now report extension of our in situ single-stage polyimide metallization approach to the synthesis and characterization of specularly reflective and electrically conductive surface silvered nanocomposite polyimide films fabricated from dimethylacetamide solutions of the poly(amic acid) formed from 3,3′,4,4′-biphenyltetracarboxylic dianhydride and 4,4’-oxydianiline, BPDA/ODA, containing AgTFA or AgHFA.

Experimental Section

Materials. 4,4′-ODA and “Ultrapure” BTDA were obtained from Wakayama and Allco (Galena, KA). Oxydiphthalic anhydride (ODPA) was purchased from Occidental. The 4,4’-ODA was used as received. BTDA and BPPA were dried under vacuum at 160 °C for 5 h prior to use. 1,1,1-Trifluoro-2,4-pentanedione, TFAH, was purchased from Lancaster and was redistilled under nitrogen before use. Silver(I) acetate (99.999), DMAc (HPLC grade), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, HFAH, 1,1,1-trifluoro-2,4-pentanedione, TTFAH, and pyridine were purchased from Aldrich and used as received. The BPDA/ODA poly(amic acid) solutions were prepared with a 0.5 mol % excess of dianhydride at 15% solids (w/w) in DMAc. The resins were stirred for 5 h. The inherent viscosities were 1.2 dL/g at 35° C.

Preparation of BPDA/ODA Metallized Films. The following procedure was used to prepare films containing silver(I) β-diketonate complexes where the β-diketones were 1,1,1-trifluoro-2,4-pentanedione, TFAH, and 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, HFAH. 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 dissolving or 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. Doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 500−650 mm to obtain 20−25-mm-thick cured films. Films used for the percent reflectivity versus time/temperature measurements were cast on petrographic slides 27 × 46 mm. After remaining in 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 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.

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. 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. SEMs were obtained on a Amray 1810; samples were coated with ca. 5 nm of palladium/gold alloy. Reflectivity measurements were made (relative to a Perkin-Elmer polished aluminum mirror with a reflectivity coefficient of 0.92 at 531 nm) 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 via a Perkin-Elmer Phi Model 5400 ESCA system. A magnesium anode (Kα = 1253.6 eV) operating at 400 W was used. Binding energies were assigned relative to an assumed aromatic carbon signal (C, 1s) of 284.6 eV.

Elemental analyses were done by Galbraith Analytical Laboratories.

Results and Discussion

Metallized Film Synthesis. The synthetic protocol for the single-stage internal metallization of BPDA/ODA is outlined in Figure 1. AgTFA and AgHFA were freshly synthesized without isolation of the solid complexes for each film preparation. Silver(I) acetate (AgOAc) and 1,1,1-trifluoro-2,4-pentanedione (TFAH) or 1,1,1,5,5,5-hexafluoro-2,4-pentandione (HFAH) were allowed to

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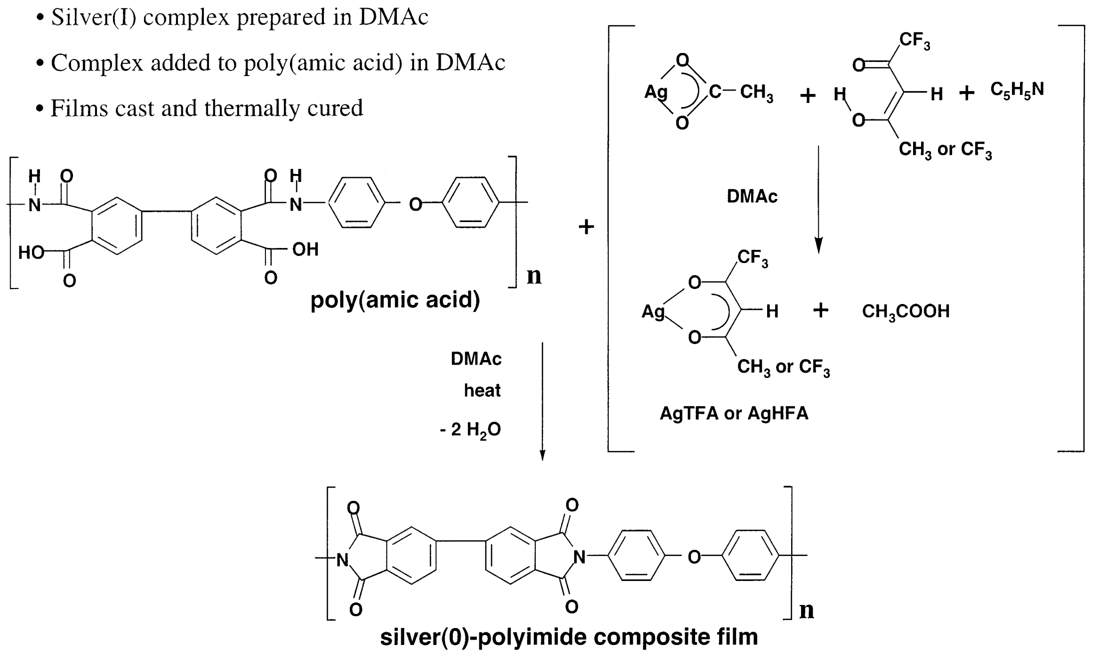

Figure 1. Single-stage synthetic scheme for metallized BPDA/ODA polyimide films with silver(I) acetate−trifluoroacetylacetone−pyridine in dimethylacetamide.

Table 1. Reflectivity Data for (1,1,1-Trifluoro-2,4- pentanedionato)silver(I)−Pyridine−BPDA/ODA Films Cured to 300 °C for Varying Times and Cast on a Glass Plate

percent silver (calculated)[a]	time/temperature cure conditions for the measured film	resistivity (Ω/square)[c]	percent reflectivity of silvered films[b] (as a function of angle)				
			20°	30°	45°	55°	70°
13.0% Ag from AgTFA and pyridine	300 °C for 4 h	<0.1	101	101	99	98	89
13.0% Ag from AgTFA without pyridine	300 °C for 5 h	<0.1	101	101	98	96	90
8.0% Ag from AgTFA and pyridine	300 °C for 4 h	NC	69	not measured			
13.0% Ag from AgHFA without pyridine	300 °C for 0 h	NC	74	72	65	56	45

[a] Calculated for the AgTFA system decomposing to silver metal and volatile components which are lost from the film. [b] Reflectivity data are relative to a Perkin-Elmer polished aluminum optical mirror set at 100%. [c] Four-point probe. NC is not conductive.

react in dimethylacetamide (DMAc) to give a solution of the (β-diketonato)silver(I) complex, AgTFA or AgHFA, respectively, via proton transfer from the β-diketone to the acetate anion of AgOAc. For the preparation of the AgTFA complex the addition of pyridine aids in proton transfer and gives a less viscous final resin solution. The silver(I) complex solutions were added to the poly(amic acid) solution. Stirring gave homogeneous light yellow solutions.

Even though AgTFA and AgHFA were not isolated, it is certain that these complexes were formed for the following reasons. First, AgOAc by itself is not soluble in DMAc. With addition of the β-diketones the AgOAc undergoes dissolution (i.e., reaction). Second, when the AgOAc alone is added to the poly(amic acid) solution, immediate gelation occurs. If TFAH or HFAA are added to AgOAc before the addition of the poly(amic acid), no gelation occurs. Third, evidence for AgHFA complex formation is supported by observing that the in situ HFAH−AgOAc reactants in the closely related BTDA/ODA poly(amic acid) gives a similarly clear homogeneously doped resin solution. When films of the in situ AgHFA−BTDA/ODA system are thermally cured, silver metallized surfaces are produced with 80% reflectivity. Now, the AgHFA complex prepared from HFAH and AgOAc can be isolated in a pure crystalline form as the (η^4-1,5-cyclooctadiene) adduct, [Ag(HFA)(COD)]. When this solid COD complex is dissolved in DMAc with BTDA/ODA, thermal curing gives metallized films with properties identical to those films prepared via the in situ AgOAc−HFAH route.[7,16] This is reliable evidence that AgHFA and AgTFA complexes are formed with the in situ approach utilized in our work.

It is important to have single atoms or small clusters of silver initially formed in the curing polymer since Faupel et al.[20] and Kovacs and Vincett[21] have demonstrated in physical vapor deposition studies that particle diffusion in the polymer is facile only with atomic or nanometer-sized particles and above the glass transition temperature (T_g) of the polymer. For imidized BPDA/ODA T_g is 273 °C; however, the effective T_g of the mixed poly(amic acid)/polyimide system with residual solvent is much less.[22] Thus, silver particle migration during the thermal cycle should not be inhibited by a rigid glassy state.

Reflectivity and Conductivity. Table 1 displays reflectivity (531 nm) and resistivity data for four silvered films cured at 300 °C from 0 to 5 h. Films with 13% silver prepared from silver(I) acetate (AgOAc) and 1,1,1-trifluoro-2,4-pentanedione both with and without pyridine have low surface resistivities and high specular

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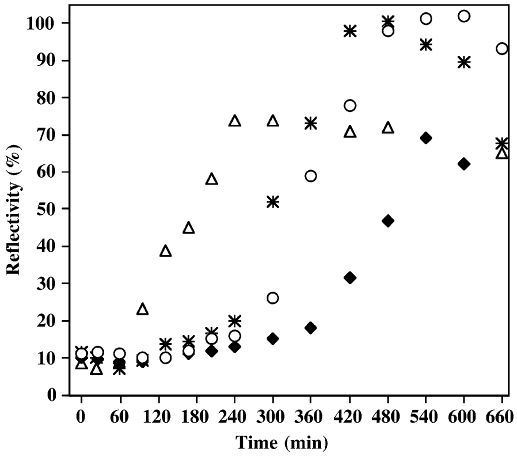

Figure 2. Reflectivity as a function of the thermal cure cycle for (1,1,1-trifluoro-2,4-pentanedionato)silver(I)−pyridine−BPDA/ODA and (1,1,1,5,5,5-trifluoro-2,4-pentanedionato)silver(I)−BPDA/ODA films: (○) 13% Ag from AgTFA−BPDA/ODA without pyridine; (∗) 13% Ag from AgTFA−BPDA/ODA with pyridine; (◆) 8% Ag from AgTFA−BPDA/ODA without pyridine; (△) 13% Ag from AgHFA−BPDA/ODA without pyridine. Time zero is at 135 °C after 1 h; the temperature rises from 135 to 300 °C over 240 min and then remains constant at 300 °C. See Experimental Section for cure details.

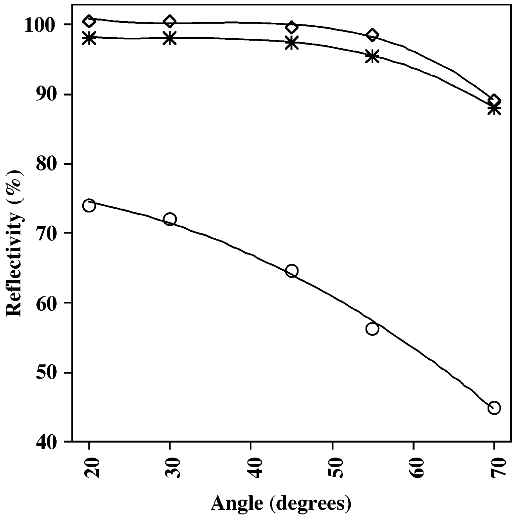

Figure 3. Angle dependence of reflectivity for BPDA/ODA films with 13% silver. (◇) AgTFA with pyridine films cured at 300 °C for 4 h; (∗) AgTFA without pyridine cured at 300 °C for 4 h; and (○) AgHFA cured to 300 °C for 0 h.

reflectivity approaching that of pure polished silver (Figure 2). As we have observed in earlier work with BTDA/ODA,[17] the addition of pyridine to the reaction mixture does not have a pronounced effect on properties of the final metallized films. There is also little angle dependence of the reflectivity (Figure 3), as is the case for a pure silver mirror.[23] For 8% silver AgTFA films the maximum reflectivity is much less, 69%, and there is a pronounced decrease in reflectivity with increasing angle of incidence. No surface conductivity was seen for 8% films. SEM micrographs for 8% films show that there are isolated nanometer-sized silver particles at the surface which are close enough for reflection of visible light but do not provide a continuous pathway necessary for conduction. When AgHFA is used at 13% silver, the reflectivity reaches a maximum of 74% without a conductive surface being formed. There is also a substantial decrease in reflectivity with increasing angle of incidence, which is consistent with a noncontinuous metallized surface which has significant surface BPDA/ODA polyimide that absorbs strongly at 531 nm.

The development of specular reflectivity as a function of cure time and temperature was followed by casting silver(I)-doped poly(amic acid) solutions onto a series of glass slides (27 mm × 46 mm) and measuring the reflectivity of individual films as they were withdrawn from the oven at selected time/temperatures during the cure protocol. Figure 2 shows plots of reflectivity versus cure time/temperatures for the four systems of Table 1. After heating at 135 °C for 1 h (the zero of time for the four plots), the silver(I)-doped films have the identical totally transparent amber appearance of undoped BPDA/ODA films, and X-ray diffraction (XRD) shows no reflections expected for face-centered cubic silver metal. Surface luster for the three AgTFA systems only becomes significant after heating to 300 °C for 1 h; however, XRD diffraction peaks for silver are seen (Figure 4) as early as 200 °C for the 13% AgTFA−BPDA/ODA−pyridine series of Figure 2. The X-ray peaks are broadened for samples in the 200−300 °C-2 h range, which suggests that silver(0) formed in the early stages of the cure is dominated by small nanometer-sized crystallites that exhibit the Scherrer effect.

The AgHFA−poly(amic acid) system metallizes much earlier than the corresponding AgTFA system. Replacement of the remaining CH_3 group in the TFA ligand by a second CF_3 group to form the HFA ligand renders the HFA ligand more electron-withdrawing. Thus, a AgHFA molecule should accept an electron from an external reducing reagent more readily than AgTFA; this is supported by polarographic studies of Patterson and Holm.[24] There is also a more pronounced angle dependence of the reflectivity for the AgHFA system (Figure 3). We suggest that this is due to a significant amount of polyimide at the surface, which strongly absorbs in the visible region. Indeed, it is not possible for silver particles to actually emerge through the polymer and reside on the surface since the surface energy of the polymer is much lower than that of silver metal.[20,21] This being true, how then do the AgTFA films become truly surface-metallized exhibiting metallic surface conductivity? Elemental analysis data discussed below provide an answer.

Figure 5 shows TEMs of the air-side surface for four 13% silver AgTFA−pyridine−BPDA/ODA films heated to increasing temperatures and times. The specular reflectivities for these same films are displayed in Figure 2. For the 275 and 300 °C-0 h films for which the reflectivities are low at 17 and 19%, there is a uniform distribution of silver nanoparticles from the surface down to a depth of at least 2 μm into the bulk. There is no obvious buildup of surface silver evident from the micrographs. In the 2-h time frame from 300 °C-0 h to 300 °C-2 h the reflectivity increases significantly from 19 to 73% and the micrographs show the

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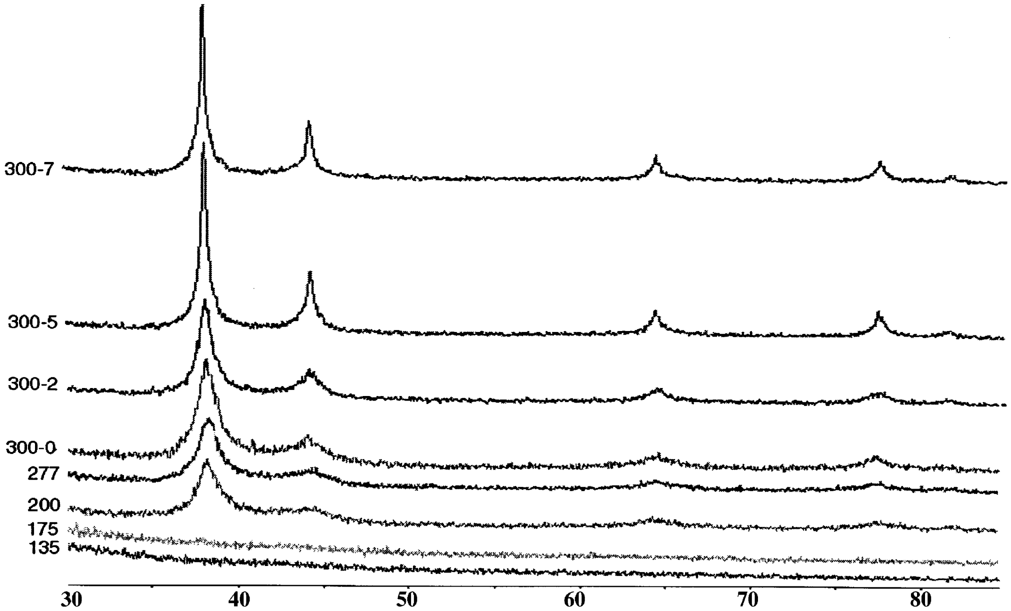

Figure 4. X-ray diffraction patterns for silver 111, 200, 220, and 311 planes for selected 13% (1,1,1-trifluoro-2,4-pentanedionato)-silver(I)−pyridine−BPDA/ODA films. (The temperature at which the film was removed from the cure cycle is shown at the left.)

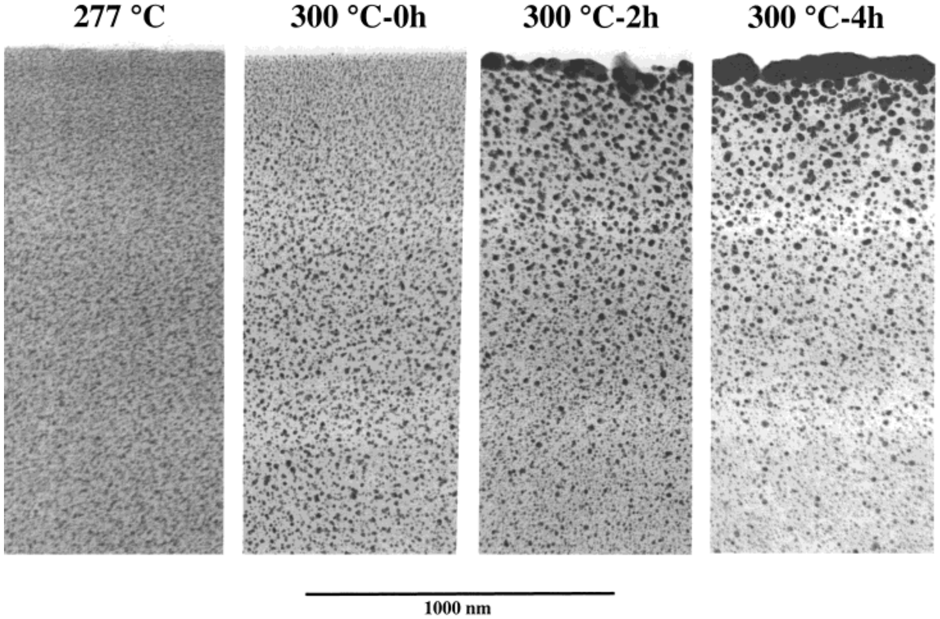

Figure 5. Transmission electron micrographs of the air-side surface for 13% silver (1,1,1-trifluoro-2,4-pentanedionato)silver-(I)−pyridine−BPDA/ODA films at four temperature/times in the cure cycle.

formation of a thin surface layer of silver, although the film is not yet surface-conductive. The silver particle size is seen to increase from the air-side surface down to a depth of ca. 400 nm. When the reflectivity reaches a maximum at 300 °C-4 h, the micrograph shows a well-defined surface layer of silver which is nominally 80 nm in thickness. The surface now exhibits metallic conductivity. The near surface particle size has also increased slightly. SEM data in Figure 6 show the surface structure for the four 13% silver AgTFA−pyridine BPDA/ODA films of Figure 2 cured to 275 °C, 300 °C-1 h, 300 °C-3 h, and 300 °C-4 h. For the first two films there are only very small silver aggregates which do not appear to be in contact with one another, and hence the films are not conductive. After heating at 300 °C for 3 h, one sees the appearance of large (ca. 50−150 nm) particles which do form an interconnected network as is confirmed by the observed surface conductivity. Finally, at 300 °C-4 h there are very large irregularly shaped particles which are in contact to form a continuous network, and this film exhibits high surface conductivity. The SEM mircographs suggest that the surface is not composed of a single solid silver phase as might be inferred from the TEM data. The 100-nm thickness of the TEM films only gives the illusion of a solid silver layer.

Figure 7 shows TEMs for the casting plate glass side, middle (bulk), and air side of the AgTFA−pyridine film cured to 300 °C for 0 h. The glass side of the film was never observed to exhibit significant metallic reflectivity. As can be seen in Figure 7, there are small isolated silver particles at the glass−polyimide interface with most particles in the 15−25-nm range. In the bulk of the films there are particles of silver which are similar

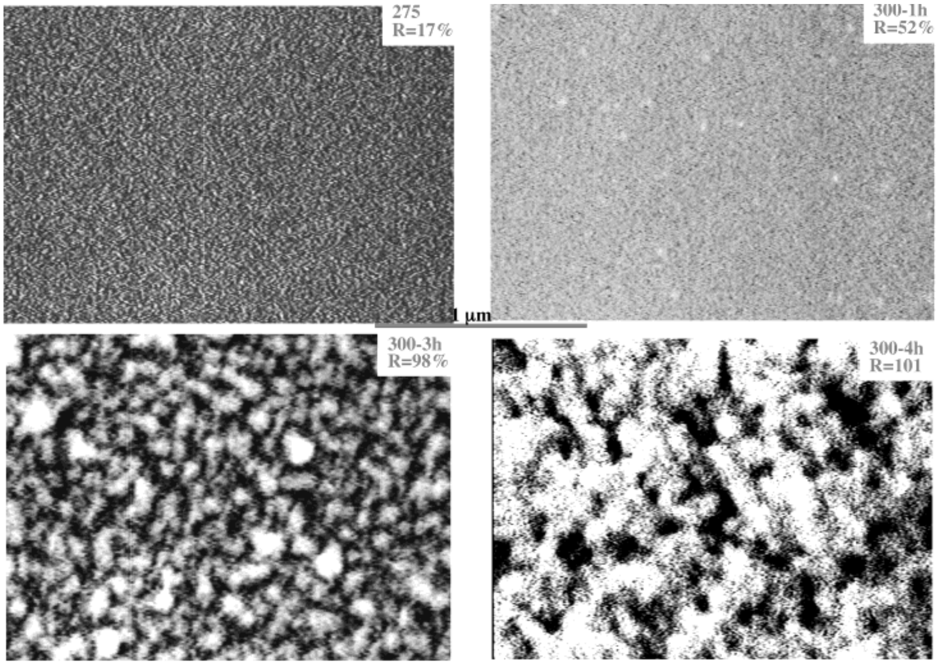

Figure 6. Scanning electron micrographs (air-side surface) of (1,1,1-trifluoro-2,4-pentanedionato)silver(I)−pyridine−BPDA/ODA 13% Ag films at varying cure temperature/times which are detailed in the upper right corner of each micrograph.

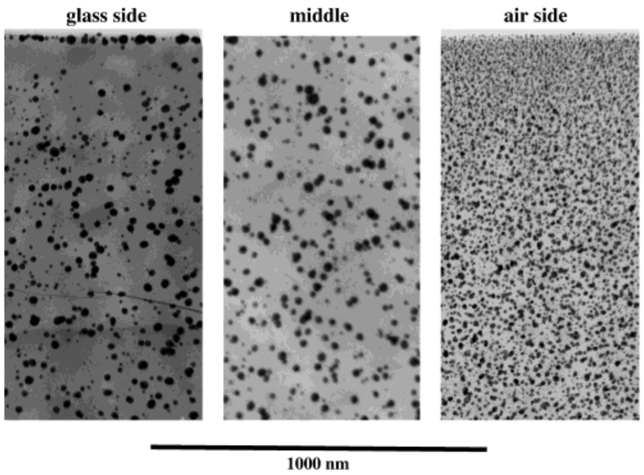

Figure 7. Transmission electron micrographs showing silver particle distribution for the glass side, bulk middle section, and air side (left to right, respectively) of the (1,1,1-trifluoro-2,4-pentanedionato)silver(I)−pyridine−BPDA/ODA film cured to 300 °C and immediately withdrawn from the oven (the 300 °C-0 h film).

Table 2. Elemental Analyses for (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)−Pyridine−BPDA/ODA Films

temperature/time cure conditions	calculated (wt %)				found (wt %)			
	Ag	C	H	N	Ag	C	H	N
cured to 275 °C for 0 h	13.0	63.8	2.68	5.31	12.8	63.9	2.90	5.36
cured to 300 °C for 1 h					12.4	63.2	2.68	5.28
cured to 300 °C for 2 h					14.8	62.8	2.78	5.37
cured to 300 °C for 4 h					18.3	61.4	2.65	5.08

in size to those near the glass−polymer interface. However, for the air side of the film the particle size is much smaller. The majority of particles in the first 200 nm from the surface are in the 2−5-nm range; thereafter, the particle size increases but is still smaller on average than the particle size seen in the bulk and at the glass-side surface. We suggest that it is this small particle size near the air-side surface which effectively catalyzes the oxidative degradation of polyimide as elemental analytical data support. The near-surface particle size in AgHFA films is always much larger at 50−100 nm and these films never are observed to have a conductive surface. Thus, we suggest that the only way in which one can develop a metallic surface is to oxidatively degrade surface polyimide in such a manner that small silver particles come into contact with one another to form much larger particles which eventually form a continuous network. Indeed, we have shown that curing in a nitrogen atmosphere does not yield surface-conductive films.[17]

Bulk and Surface Elemental Analytical Data and the Mechanism of Metallized Surface Formation. Table 2 displays total elemental (via-a-vis surface) analytical data for four of the fourteen 13% AgTFA−pyridine silver films of Figure 2. The samples withdrawn from the thermal cure cycle at 275 and 300 °C-1 h, with reflectivities of 17 and 52%, respectively, have C, H, N, and Ag composition values that are reasonably close to that expected for polyimide and silver with the ligand in some form being lost from the system, that is, there is no significant loss of polyimide due to oxidative degradation to volatile products. However, thermal-oxidative effects of a longer cure time at 300 °C become evident for two samples withdrawn at 300 °C after 2 and 4 h with reflectivities of 73 and 101%, respectively. Both theses samples are conductive with bulk elemental analyses showing an increase in the silver concentration to 14.8 and 18.3% with a corresponding diminution of C, H, and N concentrations. Since pure undoped polyimides including BPDA/ODA are completely stable indefinitely at 300 °C in air with 10% weight loss temperatures of >500 °C, there must be a silver-catalyzed oxidative degradation of polyimide to volatile products such as CO, CO_2, H_2O, etc. in the silvered films after prolonged heating in air. Silver is well-known for the catalytic oxidation of organic frameworks.[25] Diffusion of oxygen into the interior of the film must be

Table 3. X-ray Photoelectron Spectroscopic Air-Side Surface Composition for Selected (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)−(No Pyridine)−BPDA/ODA Films[a]

wt % silver	time/temperature cure history	reflectivity (%) at 20°	resistivity (Ω/square)	Ag	F	C	O	N
parent PI with no Ag	NA	NA	NA	0.0.0	0.0	80.0	14.3	5.71
parent PI with 13% Ag with no ligand left	NA	NA	NA	1.78	0.0	78.6	14.0	5.61
13% BPDA/ODA	300 °C for 0 h (not etched)	20	NC	6.70	0.0	86.6	3.16	3.58
13% BPDA/ODA	300 °C for 0 h etched (etched Ar+ for 8 min)	73	NC	7.98	0.0	86.4	1.53	4.14
13% BPDA/ODA	300 °C for 2 h (not etched)	73	NC	32.3	0.0	53.6	12.2	1.98
13% BPDA/ODA	300 °C for 4 h (not etched)	101	>0.1	52.12	0.0	27.5	17.3	3.08

[a] Relative atomic percent. (The films of Figure 2. NA means not applicable; NC is not conductive.)

Table 4. Thermal, Mechanical, and Resistivity Data for (1,1,1-Trifluoro-2,4- pentanedionato)silver(I) BPDA/ODA Films[a]

percent silver (calc)[a]	T_g, °C (DSC)	10% wt loss °C (air)	10% wt loss °C (N_2)	surface resistivity (Ω/square)	tensile strength (Ksi)	elongation at break (%)	modulus (Ksi)
control	273	543	543	NC	19.6	9	419
13.0	283	347	538	<0.01	17.9	5	462
8.0	263	376	563	NC	19.6	7	448

[a] The 13% film was made with pyridine; the 8% film was made without pyridine. (Cure cycle: 0.33 h to 135 °C for 1 h; 4 h to 300 °C; 300 °C for 4 h for the control and 13% samples and 300 °C for 1 h for the 8.0% sample. NC is not conductive.)

minimal since bulk properties resemble those of the parent as seen from the data in Table 4.

XPS spectra (Table 3) were determined on the air side, that is, the reflective side, of films cured to 300 °C for 0, 2, and 4 h over which range the specular reflectivity was rapidly evolving from 20 to 101%. For the 300 °C-0 h film with a reflectivity of 20% we see that the silver concentration is beginning to build at the surface, and the surface has an atom percentage of 6.7, the theoretical surface concentration of Ag being 1.8. What is most interesting for this film is that there is a significant increase in the carbon concentration with a corresponding decrease in the oxygen concentration. The C:O ratio in the parent polyimide film is 5.6:1; this is increased to 27:1 for the 300 °C-0 h film. At 300 °C for 2 and 4 h, conditions at which the films become highly reflective and ultimately conductive, the C:O ratio decreases to 4.4:1 and 1.6:1, that is, there is a marked increase in oxygen at the surface. Why this marked initial increase in the C:O ratio relative to pure polyimide for the 300 °C-0 h film? Since we know that the films by 300 °C-4 h become both reflective and electrically conductive, there must ultimately be silver metal at the air-side surface of the film. How do metallic silver particles get to the surface? They cannot spontaneously move to the surface since silver has a much greater surface area than the polyimide. Faupel and co-workers[20] have amply demonstrated that silver and gold metal atoms and clusters always embed themselves into a polyimide and other polymers upon deposition. Kovacs and Vincett[21] have also demonstrated this effect for selenium and other metallic elements vapor-deposited onto polymers above T_g. However, these latter work have shown additionally that larger metal clusters will form a regular array of very near surface nanoparticles. So while metal particles generated within a mobile (above T_g) polymer film cannot end up on the true surface of the film, they may well form a significant concentration and array of metal particles only nanometers from the surface. In our metallized polymer system it seems clear from the elemental analysis data (Table 2) that the mechanism for forming the silver surface is a metal-promoted oxidative degradation of the BPDA/ODA polymer to volatile products, which then exposes the silver at the surface. Thus, we now tentatively suggest that the increase in the C:O ratio to 27:1 for the 300 °C-0 h film to be due to the partial oxidation of the polymer to an elemental form carbon (amorphous or graphitic) which is subsequently to be oxidized to and lost as carbon monoxide and/or carbon dioxide.

Table 5. Film Thickness as a Function of Cure Cycle Temperature/Time and Reflectivity for Selected (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)−Pyridine−BPDA/ODA Films of Figure 2

cure temperature/time	film thickness (μm)	% reflectance (specular)
275 °C	36	17
300 °C for 0 h	30	20
300 °C for 1 h	24	52
300 °C for 2 h	23	73
300 °C for 3 h	23	98
300 °C for 4 h	22	101

Table 5 displays the total composite film thickness as measured by TEM for films from 275 °C to 300 °C-4 h. One sees that there is a marked decrease in film thickness at approximately the same time that the reflectivity is rapidly increasing. This is also consistent with a silver-catalyzed degradation of polyimide at the reflective surface.

Thermal and Mechanical Data. Thermal data (Table 4) for the 8% AgTFA and 13% AgTFA−pyridine silvered films shows that metallization of the polyimide leads to modest changes in T_g, the significance of which is not clear since T_g is elevated for the 13% film but diminished for the 8% film. In previous metallization work with BTDA/ODA we did not see changes in T_g.[18,19] 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 that for the parent polymer; however, the metallized films in a nitrogen atmosphere have essentially the same stability as the parent film in air or nitrogen. Clearly, silver metal promotes polymer degradation as expected.[25] The tensile

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(25) Hucknall, D. J. *Selective Oxidation of Hydrocarbons*; Academic Press: London, 1974.

strength of the films is similar to that of the parent polyimide, although the 13% film is of lower strength. The tensile modulus is elevated by ca. 7%; the elevation of polyimide moduli upon doping with inorganic substrates is a commonly observed phenomenon. All films are flexible and can be tightly creased without fracture as observed for the parent film.

Conclusion

We have synthesized silvered BPDA/ODA polyimide films from single-phase silver(I) acetate-1,1,1-trifluoro-2,4-pentanedione or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione-BTDA/ODA solutions cast and cured on glass plates. Depending on concentration and thermal conditions, metallized films can be fabricated with excellent specular reflectivity, surface conductivity, outstanding metal–polymer adhesion, and intact mechanical characteristics. 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. While there is not a single solid layer of silver metal on the surface for the films which are observed to have excellent conductivity, these surface-metallized films may well be useful as precursors for vapor-deposited silver films so that much improved adhesion between the polymer and deposited metal layer can be achieved.

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