# Inverse Chemical Vapor Deposition: A Novel Single Stage Synthesis of Highly Reflective and Conductive Silvered Polymeric Films

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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 into a dimethylacetamide solution of the poly(amic acid) formed from 3,3′,4,4′-benzophenone tetracarboxylic acid 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 a reflective and conductive silver surface approaching that of the native metal. The metalized films retain the essential mechanical and thermal properties of the parent film. Films were characterized by X-ray diffraction, transmission and scanning electron microscopy, tapping mode atomic force microscopy, X-ray photoelectron spectroscopy, and conductivity, reflectivity, thermal, and mechanical measurements.

## Introduction

There is currently intense activity in the synthesis of hybrid materials where an inorganic phase subsists as nanometer-size particles uniformly dispersed throughout an organic macromolecular matrix. Synthetic areas include biomimetic mineralization in polymers,[1] silica, silicate, and other oxometal−polymeric hybrid materials[2−5] and stabilization of metal clusters by polymeric matrixes.[6] Within the latter area, nanometer-sized metal clusters (e.g., platinum, palladium, and gold) constrained in polymeric matrixes have distinctive linear and nonlinear optical properties,[7,8] enhanced catalytic activity,[9] and quantum size-restricted electronic and magnetic properties owing to incompletely developed band structures.[10] We here disclose a novel dimension to the paradigm of metal cluster−polymeric hybrid materials which results in the synthesis of silver-metalized polymeric films exhibiting specular reflectivity and electrical conductivity essentially that of the native metal.

The synthesis of metal clusters both in aqueous and organic media frequently involves the use of colloid-stabilizing polymers such as poly(vinyl alcohol), polyvinyl pyrollidinone, poly(amide imide)s, and other macromolecules.[11] We have invoked this concept with the goal of synthesizing silver-metalized polymeric films exhibiting high specular reflectivity and conductivity. Our initial approach[12,13] involved thermally (150−225 °C) induced reduction of positive valent silver complexes in polymeric films resulting in matrix-stabilized metal clusters. Upon heating the composite films to 300−340 °C, colloid stabilization is compromised, and metal clusters undergo aggregation, yielding composite materials which are either modestly reflective or surface conductive, but not both. We wanted to achieved simultaneously both the reflectivity and conductivity of polished silver. However, efforts prior to this report have not been completely successful; our most reflective films ($R = 80\%$)[13] were not conductive, and our conductive films (0.5 Ω/sq for a 70 nm silver layer)[12] had poor reflectivity.

We now report a silver(I)−polymer system coupled with thermal conditions which yields silvered films with both exceptional reflectivity and surface conductivity. There are numerous applications for such metalized films, including the fabrication of lightweight optical mirrors and sunshields for the NASA Next Generation Space Telescope;[14−16] large-scale inflatable radio fre-

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(1) (a) Calvert, P.; Rieke, P. *Chem. Mater.* **1996**, *8*, 1715 and references therein. (b) Mann, S.; Burkett, S. L.; Davis, S. A.; Fowler, C. E.; Mendelson, N. H.; Sims, S. D.; Walsh, D.; Whilton, N. T. *Chem. Mater.* **1997**, *9*, 2300.

(2) Mascia, L. *Trends Polym. Sci.* **1995**, *3*, 61.

(3) Novak, B. M. *Adv. Mater.* **1993**, *5*, 422.

(4) Schubert, U.; Husing, N.; Lorenz, A. *Chem. Mater.* **1995**, *7*, 2010.

(5) Sanchez, C.; Ribot, F. *New. J. Chem.* **1994**, *18*, 1007.

(6) *Clusters and Colloids: From Theory to Applications*; G. Schmid, Ed.; VCH: Weinheim, 1994.

(7) Creighton, J. A.; Eadon, D. G. *J. Chem. Soc., Faraday Trans.* **1991**, *87*, 3881.

(8) Gehr, R. J.; Boyd, R. W. *Chem. Mater.* **1996**, *8*, 1807 and references therein.

(9) Lewis, L. N. *Chem. Rev.* **1993**, *93*, 2693.

(10) Halperin, W. P. *Rev. Mod. Phys.* **1986**, *58*, 533 and references therein.

(11) Troger, L.; Hunnefeld, H.; Nunes, S.; Oehring, M.; Fritsch, D. *J. Phys. Chem. B* **1997**, *101*, 1279 and references therein.

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

(13) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; St. Clair, A. K. *Chem. Mater.* **1997**, *9*, 1691.

(14) Horner, G.; Stoakley, D.; St. Clair, A. K. *Bull. Am. Astron. Soc.* **1996**, *189*, 60.06.

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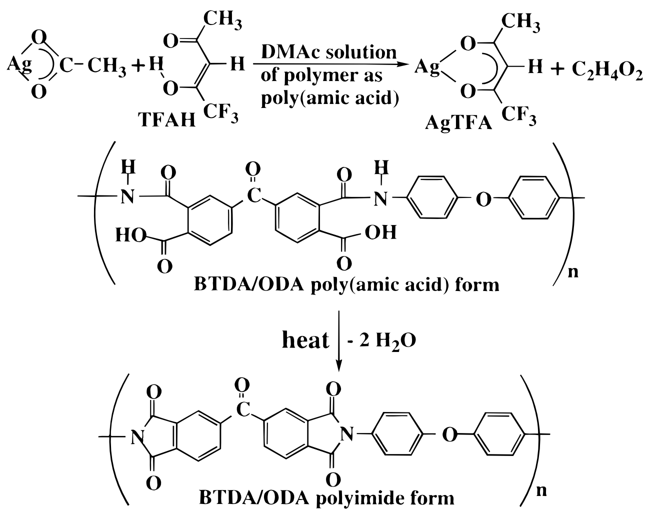
**Scheme 1**



quency antennas for the management of electromagnetic signals in space,[17] silver-coated tubing to deter catheter-induced urethritis,[18] the construction of adaptive and elastomeric optical devices,[19,20] the terrestrial concentration of solar energy to process heat and generate electric power,[21] and flexible conductive patterned surfaces and tapes.[22] Polymeric supports offer substantial advantages in weight, flexibility, and packaging options relative to traditional substrates such as glass, ceramics, and metals.

Specifically, the research described herein focuses on the deposition of metallic silver on polymeric films by a single stage, internal, self-metalization process. Efforts center on silver, since its specular reflectance above 350 nm is unexcelled, and its hemispherical reflectance is greater than 97% weighted over 250−2500 nm, the range of the solar spectrum.[21a] We chose aromatic poly(amic acid)−polyimide polymers because of their outstanding chemical and thermal stability, which is essential for our thermally induced surface metalization process since silver catalyzes air oxidation of organic structures.[23] Our synthetic protocol is illustrated in Scheme 1. Silver(I) acetate (AgA) and 1,1,1-trifluoro-2,4-pentanedione (TFAH) are allowed to react in dimethylacetamide (DMAc) to give in solution the (1,1,1-trifluoro-2,4-pentanedionato)silver(I) complex, AgTFA. A DMAc solution of the poly(amic acid) form of BTDA/ODA is added to the DMAc solution of AgTFA. A film is then cast. Thermal curing of the silver(I)−poly(amic acid) film effects reduction of silver(I) coupled with cycloimidization of the amic acid. As the polymer imidizes, silver(0) atoms and clusters aggregate at the surface to give a conductive and reflective film. Characterization of these films with respect to reflectivity, resistivity, thermal, mechanical, and surface properties will be detailed.

It is natural to ask what the impetus for our commitment to this internal metalization process is since there are well-established methods to fabricate thin metal films. The answer is processing simplicity and *unfailing adhesion* at the polymer−metal interface. Established methods used to prepare metalized films require the external deposition of the metallic phase onto a substrate surface. Techniques include physical vapor deposition, chemical vapor deposition (CVD), electrodeposition, and electroless chemical deposition. Metalization of polymeric films by these methods involves several stages.[24] First, the base film is prepared. Second, the surface of the polymer is modified via plasma, ion beam, chemical, etc. manipulation to enhance adhesion. Third, the metal is deposited onto the film surface. While external deposition works well for reactive metals such as aluminum, with passive metals such as silver and gold, adhesion is generally unacceptable.[25−27] Furthermore, most external methods are not convenient for preparing films with large areas as would be required for inflatable antenna and sunshield fabrication. (Electroless silver deposition via spraying can be used to prepare films of large area; however, we found that the silver layer adheres poorly to polyimides.) Finally, CVD is not useful with polymers since they seldom can be heated without distortion or degradation to the temperatures needed to reduce a positive valent metal from a volatile precursor. The film metalization protocol reported herein can be conceptualized as inverse chemical vapor deposition**.** Our process is an internal rather than an external thermal reduction of a metal complex precursor yielding metal atoms and near-atomic metal clusters which aggregate to give reflective and conductive metallic surfaces with uncompromised adhesion at the metal−polymer interface.

## Results and Discussion

**Reflectivity, Conductivity, and Surface Properties.** Silvered BTDA/ODA films with distinctive optical and electrical properties have been fabricated by the pathway outlined in Scheme 1. Table 1 displays characterization data for three representative films cured at 300 °C for 7 h. The second entry is a silvered film (120 × 200 mm) cast from the same silver-doped resin that was used to prepare small glass slides (27 × 46 mm) coated with metalized polymer for the reflectivity versus temperature/time plot of Figure 1. Entries 3 and 4 are for films prepared from the same resin solution. The films differ only in that one was cast directly onto a glass plate, whereas the other silver-doped film was

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(15) Angel, R., Martin, B.; Miller, S.; Sandler, D. Burns, D.; Tenerelli, D.*Bull. Am. Astron. Soc.* 1996, *189*, 60.07.

(16) Triolo, J. J.; Heaney, J. B. Hass, G. *SPIE* 1977, *21*, 46.

(17) Freeland, R. E.; Bilyou, G. *43rd Congress of the International Astronautical Federation, IAF-92-0301*, Washington, D.C., 1992.

(18) (a) Liedberg, H.; Lundeberg, T. *Urol. Res.* **1989**, *17*, 359. (b) Lundeberg, T. *Lancet* **1986**, November 1, 1031.

(19) Hubin, N.; Noethe, L. *Science* **1993**, *262*, 1390.

(20) Wilbur, J. L.; Jackman, R. J.; Whitesides, G. M.; Cheung, E. L.; Lee, L. K.; Prentiss, M. G. *Chem. Mater.* **1996**, *8*, 1380.

(21) (a) Jorgensen, G.; Schissel, P. *Metallized Plastics*; Mittal, K. L., Susko, J. R., Eds.; Plenum: New York, 1989; Vol. 1, pp 79−92. (b) Neidlinger, H. H.; Schissel, P. *Soc. Photo-Optical Instrum. Eng. Proc.* **1987**, *823*, 181. (c) Schissel, P.; Goggin, R. M.; Shintion, Y. D. *Soc. Photo-Optical Instrum. Eng. Proc.* **1987**, *823*, 190. (d) Neidlinger, H. H.; Schissel, P. *International Symposium on Plymers for Advanced Technologies*; M. Lewin, Ed., VCH: Weinheim, 1988; pp 34−51.

(22) Yan, L.; Zhao, X.-M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1998**, *120*, 6179 and references therein.

(23) Hucknall, D. J. Academic Press: London, 1974.

(24) *The Chemistry of Metal CVD*; Kodas, T. T., Hampden-Smith, M. J., Eds.; VCH: Weinheim, 1994.

(25) Burger, R. W.; Gerenser, L. J. *Metallized Plastics*; Mittal, K. L., Ed.; Plenum: New York, 1992; Vol. 3, pp 179−193.

(26) Mittal, K. L. *J. Vac. Sci. Technol.* **1976**, *13*, 19.

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

**Table 1. Reflectivity, Thermal, and Resistivity Data for (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)−BTDA/ODA Films Cured to 300 °C for 7 h and Cast on a Glass Plate (Films 1−3) and on a Parent Polyimide Base (Film 4)**

| film no. | % silver (calcd)[a] | reflectivity of silvered films[b] (as a function of angle) 20° | 30° | 45° | 55° | 70° | $T_g$, °C (DSC) | CTE (ppm/K) | surface resistivity[c] (polished film) (Ω/sq) | tensile strength (Ksi) | modulus (Ksi) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0 | not applicable | | | | | 275 | 42.8 | $7 \times 10^{15}$ (air)<br>$2 \times 10^{17}$ (glass) | 19.7 | 450 |
| 2 | 13.0 | 98 | 97 | 97 | 95 | 91 | 276 | 34.3 | <0.1 | 19.7 | 474 |
| 3 | 12.8 | 98 | 98 | 98 | 99 | 92 | 270 | 33.0 | <0.1 | 20.2 | 468 |
| 4 | 12.8 | 95 | 95 | 94 | 92 | 91 | 273 | 32.8 | <0.1 | 19.3 | 445 |

[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.

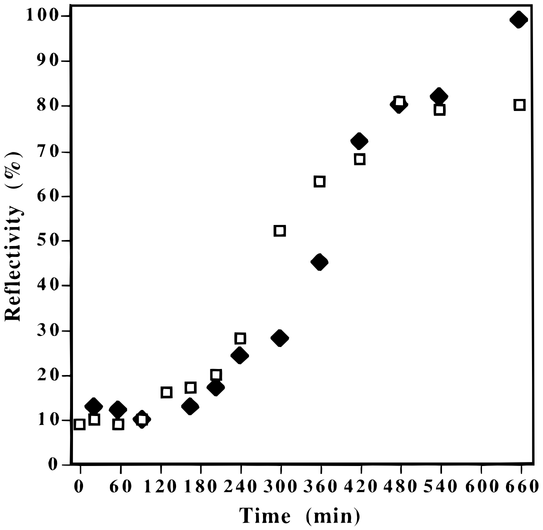

**Figure 1.** Reflectivity as a function of the thermal cure cycle for AgTFA−BTDA/ODA films with silver concentrations of 10.7% (□) and 13.0% (◆). Time zero is at 135 °C after 1 h; the temperature rises from 135 to 300 °C over 240 min and then remains constant at 300 °C. See Experimental Section for cure details.

cast more thinly onto an undoped BTDA/ODA polyimide film (affixed to a glass plate) previously cured to 300 °C. Casting the silver-doped resin onto a parent base conserves silver and ensures that the mechanical and thermal properties of these "film-on-film" composites closely resemble those of the pure polyimide. Adhesion between surface silver and polyimide and adhesion between parent polyimide and silver-doped BTDA/ODA layer is outstanding. Boiling films in water does not give any delamination of silver from polyimide or parent polyimide from doped polyimide. Also, no adhesive tapes removed any silver from the surface as per the ASTM adhesion testing protocol. Since these composite films are cured above the glass transition temperature, $T_g$, thermal welding occurs, giving strong adhesion.[28] Composite films were cast to give a doped to undoped layer thickness ratio of 1:6. Previous work[12,13] shows that there is no diffusion of silver into the undoped BTDA/ODA base. The specular reflectivity values for the films of Table 1 are greater than 90% at 531 nm, the approximate solar maximum. There is little angle dependence, consistent with a reflective surface that is dominated by silver metal.[29] The films have sheet resistivities consistent with a metallic silver surface.

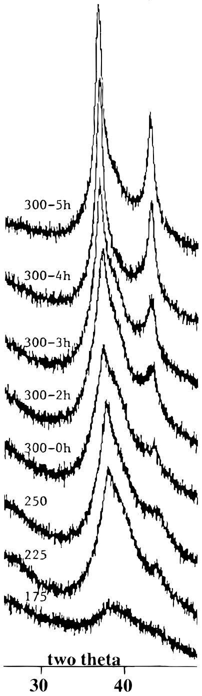

**Figure 2.** X-ray diffraction patterns in the silver 111 and 200 region for selected 10.7% AgTFA−BTDA/ODA of Figure 1. Samples were withdrawn from the oven at the temperatures which are at the left of each curve.

We followed the evolution of the silvered surface by casting a AgTFA−BTDA/ODA solution onto a series of glass slides (27 × 46 mm) and measuring the reflectivity of individual films as they were withdrawn at selected temperatures over the cure cycle. Figure 1 shows a plot of reflectivity as a function of cure time and temperature for 10.7 and 13.0% silver resins. After heating at 135 °C for 1 h, the silver(I)-doped films have the yellow appearance of undoped BTDA/ODA films. X-ray diffraction shows no reflections for face-centered cubic silver. Surface luster becomes apparent near 275 °C; however, X-ray reflections for silver are seen as early as 175 °C, as shown in Figure 2. Peaks are broadened between 175 and 300 °C, which suggests that silver formed in the earlier stages of the cure is dominated by nanometer-sized crystallites (<ca. 5 nm) which exhibit Scherrer broadening.[30] As the cure progresses, silver clusters grow larger with a corresponding sharpening of the diffraction peaks. The TEMs of Figure 3, for 10.7% film samples withdrawn at 275 °C, 300 °C, and after 7 h at 300 °C, show this particle growth with time**.** The

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(28) (a) Brown, H. R.; Yang, A. C. M.; Russell, T. P.; Volksen, W.; Kramer, E. J. *Polymer* **1988**, *29*, 1807.

(29) Drummer, L. F.; Haas, G. Physics of Thin Films, Vol. 2; Haas, G., Thun, R. E., Eds.; Academic Press: New York, 1964; pp 305−361.

(30) Klug, H. P; Alexander, L. E. *X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials*, 2nd ed.; John Wiley and Sons: New York, 1974.

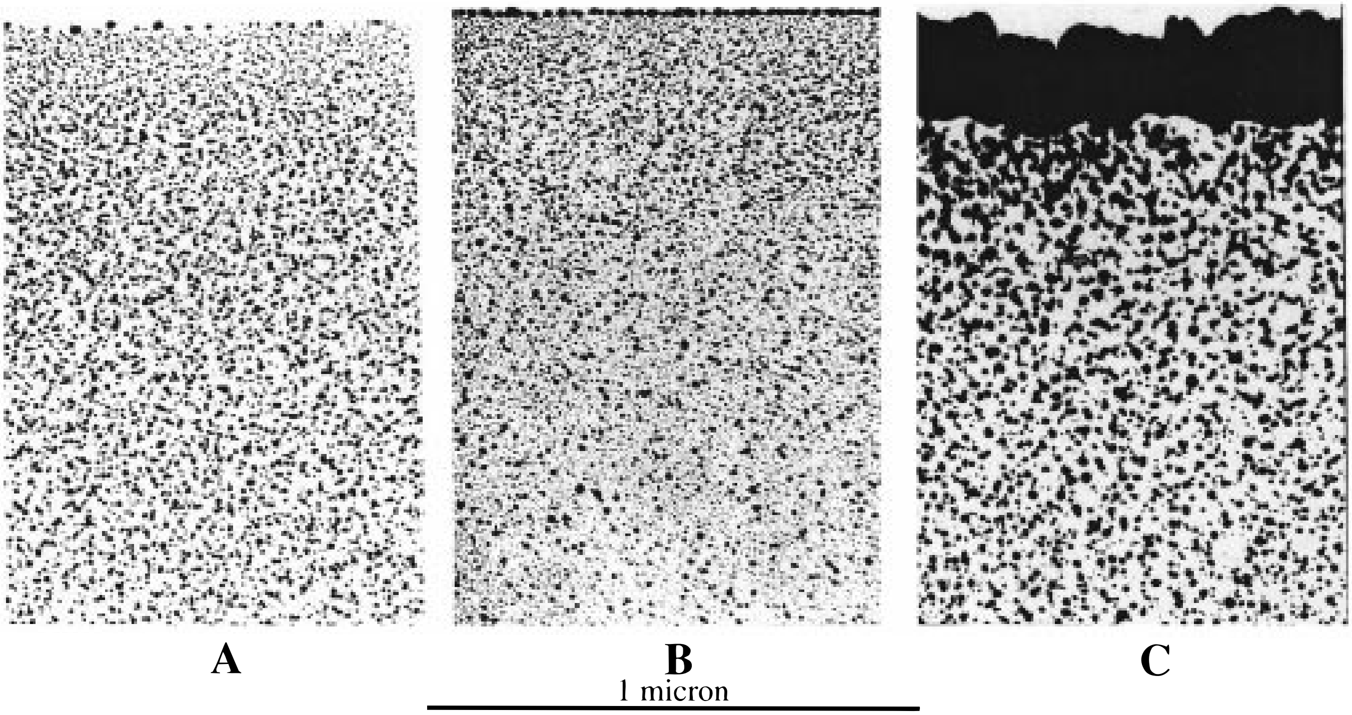

**Figure 3.** Transmission electron micrographs (cross sections from the metalized air-side surface down into the bulk of the film) of selected 10.7% AgTFA−BTDA/ODA films of Figure 1 at different cure stages: (A) cured to 275 °C for 0 h; (B) cured to 300 °C for 0 h; (C) cured to 300 °C for 5 h. Films A and B are not conductive; film C has a sheet resistance of 5−15 Ω/sq.

reflectivity curves for the 10.7 and 13.0% films are similar for most of the thermal cycle. The reflectivity for the 10.7% sample levels near 80% after 4 h at 300 °C; however, for the 13.0% sample the reflectivity after 7 h at 300 °C approaches 100% of the reflectivity of the Perkin-Elmer optical mirror used as a standard, i.e., the film surface has a reflectivity which is essentially that of polished silver. The 10.7% films do not become electrically conductive until cured for 5 h at 300 °C; the 13% films become conductive after curing for 3 h at 300 °C. Films with less than ca. 10% silver do not become conductive under any of the conditions examined. After numerous trials, an optimal silver concentration of ca. 13% was found for fabricating films with both high reflectivity and conductivity.

In our previous work with BTDA/ODA−silver(I) acetate-1,1,1,5,5,5-hexafluoro-2,4-pentanedione (HFAH), the metalized surfaces showed excellent reflectivity ($R$ = 80%) but were never conductive, even when heated to 340 °C.[13] The TFA ligand of this current paper differs only slightly from the HFA ligand by replacement of fluorines with hydrogens in one methyl group. We did not expect the AgA−TFAH system to give films which differed significantly from AgA−HFAH. However, the TFAH films are strikingly different. Clearly, ligand effects play a dominant role in metalization. This conclusion is further supported by our observations that silver(I) nitrate and silver(I) tetrafluoroborate, which have noncoordinating anions, give degraded and brittle films under similar conditions. Thus, one cannot simply take any silver(I) compound with a poly(amic acid) and obtain metalized polyimide films of high quality.

TEM and SEM micrographs (Figures 3C and 4B) of a conductive 10.7% film of Figure 1 cured to 300 °C for 5 h display the depth and morphology of the silver surface**.** The cross sectional (from the air-side reflective surface) TEM shows a surface layer of silver which is continuous and ca. 190 nm thick, consistent with the observed conductivity. The SEM reveals that the air-side surface has an irregular but distinctive topography which would sustain conductivity. The networked, porous, spongelike texture of the surface is due to a combination of sintering and oxidative surface polymer degradation. It is instructive to compare this SEM with that for the closely related 10.7% AgHFA−BTDA/ODA film (Figure 4A), where the two systems differ only by one trifluoromethyl group**.** The surface micrograph of the nonconductive AgHFA sample displays a very different morphology. There are discrete isolated metal particles with diameters in the 100−200 nm range. The particles are separated from one another by intervening surface polymer. This is clear from the X-ray photoelectron spectra (XPS) which show C, N, and O ratios close to those of the parent polymer.[13] The tapping mode atomic force micrographs of Figure 5, for a conductive 12.8% film with $R$ = 96% prepared in the identical manner as entry 3 of Table 1, show an islandlike topography on both the micron scale (Figure 5A) and on the nanometer scale (Figure 5B). The films are smooth with respect to the reflectivity concerns with image raw means of 17 and 3.4 nm for parts A and B of Figure 5, respectively. The difference between the AgTFA and AgHFA systems is striking and demonstrates that subtle changes in ligand structure have pronounced effects on film properties.

XPS data for three of the fourteen films (10.7% silver) used to generate the reflectivity curve of Figure 1 are displayed in Table 2. For the film cured to 275 °C, which is minimally reflective and has little silver at the surface, XPS data for the reflective surface show only 2.8% Ag and a C, N, O ratio which is close to that of the parent polyimide. For the film cured to 300 °C for 0

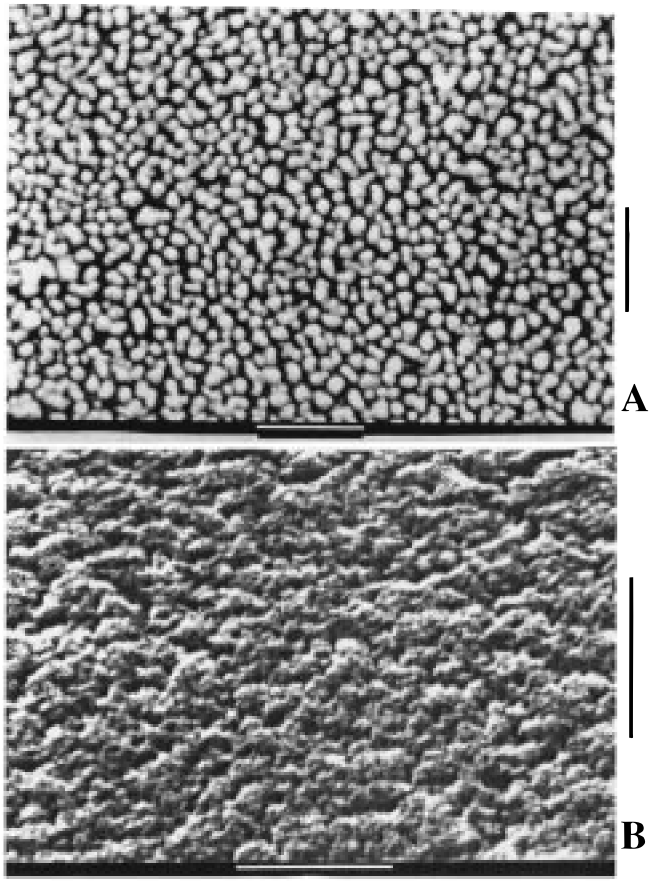

**Figure 4.** Scannning electron micrographs: (A) air-side-metalized surface of a 10.7% Ag film prepared with Ag(HFA)-(COD)−BTDA/ODA; the film was cured to 300 °C for 2 h ($R$ = 71%; not conductive); (B) air-side-metalized surface of a conductive (6 Ω/sq) 10.7% Ag film prepared with AgTFA−BTDA/ODA; the film was cured to 300 °C for 5 h ($R$ = 81%). Scale bars are 1 $\mu$m.

h, the measured reflectivity is 28%, with an increase in surface Ag to 4.0%; the C, N, O ratio remains near that of the parent. However, on curing at 300 °C for 5 h the air-side silver concentration jumps to 27% with a measured reflectivity of 80%. Still, there is substantial carbon at the surface, although ion milling experiments show that further into the surface silver is ca. 98%. We suggest that the carbon-containing material is partially degraded surface BTDA/ODA polymer. This is supported by the large atom percent of oxygen, which we presume is from partial oxidation of polyimide. Thus, part of the mechanism to develop a highly reflective and conductive surface involves oxidative degradation of polymer. This is further supported by the fact that curing a AgTFA−BTDA/ODA film in nitrogen does not give a highly reflective surface. The glass side of the film cured to 300 °C for 5 h has much less silver and an organic composition closer to that of the parent polymer.

Table 3 displays bulk analytical data for two of the fourteen 13% silver films of Figure 1. The first sample of Table 3 was withdrawn after 3 h at 300 °C and was 72% reflective but not conductive. Data for this sample show approximately the correct amount of silver and polyimide expected for a system without polymer decomposition. However, the thermal-oxidative effects of a longer cure time become evident for the second sample of Table 3 withdrawn after 7 h at 300 °C. This sample is highly reflective (100%) and conductive, and the bulk elemental analysis shows an increase in the silver concentration to ca. 19% with a corresponding diminution of C, H, and N concentrations. Diffusion of oxygen into the interior of the film must be minimal since bulk properties resemble those of the parent.

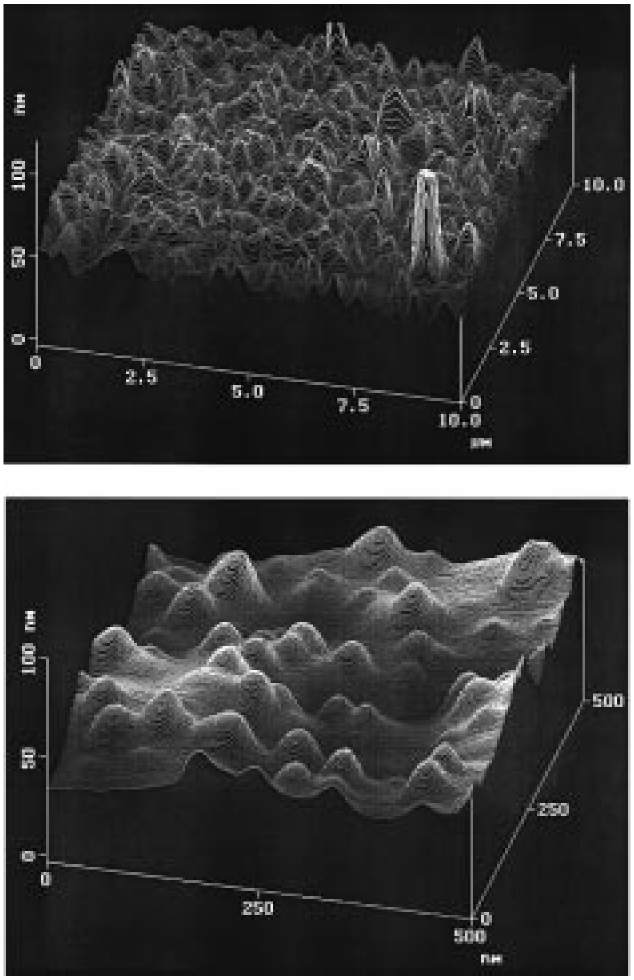

**Figure 5.** Tapping mode atomic force micrographs at different magnifications of the air-side-silvered surface of the 12.8% film of Table 1 cast on a parent BTDA/ODA base ($R$ = 96%; sheet resistivity < 0.1 Ω/sq).

**Thermal and Mechanical Properties.** Selected thermal and mechanical properties are presented in Table 1. The glass transition temperatures of the metalized films do not vary from that of undoped BTDA/ODA by more than a few degrees. This suggests that the bulk polymer structure is not compromised by the reduction of silver(I) and the formation of silver(0). However, the formation of metal clusters in the bulk of the polymer as well as on the surface diminishes the high-temperature thermal-oxidative stability of the hybrid film. Although in a nitrogen atmosphere the temperature at which there is 10% weight loss is not vastly different from that of the undoped polymer, in air there is a reduction in stability with 10% weight loss temperature that are ca. 150−200 °C lower than the control. Nonetheless, the thermal stability of the mirrored films in air is more than adequate for most purposes.

The linear coefficients of thermal expansion (CTE) for the three films of Table 1 are 33−34 ppm/K. These are significantly lower than for the parent polymer at 43 ppm/K and than for the analogous AgHFA films at 43,

**Table 2. X-ray Photoelectron Spectroscopic Surface Composition for Selected (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)-BTDA/ODA (10.7% Ag) Films of Figure 1**

| wt % silver | thermal history[a] | reflectivity (%) at 20° | resistivity[b] (Ω/sq) | film surface | relative atomic percent | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Ag | F | C | O | N |
| parent | 300 for 1 h | na | na | air | 0 | 0 | 78 | 16 | 5.4 |
| 10.7 | 275 for 0 h | 20 | NC | air | 2.8 | 0.0 | 78 | 15 | 4.4 |
| 10.7 | 300 for 0 h | 28 | NC | air | 4.0 | 0.47 | 78 | 13 | 4.5 |
| 10.7 | 300 for 5 h | 79 | PC | air | 27 | 0.33 | 45 | 26 | 1.6 |
| | | | | glass | 3.7 | 4.5 | 69 | 19 | 3.1 |

[a] All cure cycles involved heating from 22 to 135 °C over 20 min and holding for 1 h followed by heating over 240 min to 300 °C and holding at 300 °C for varying times. Samples were removed at various times in the cure. [b] na = not applicable. PC = partially conductive with some but not all portions of the film registering conductivity; NC = not conductive.

**Table 3. Elemental Analyses for Two 13.0% (1,1,1-Trifluoro-2,4-pentanedionato)silver(I)−BTDA/ODA Films Cured together for Different Lengths of Time**

| thermal treatment (resistivity) | calcd (wt %)[a] | | | | found (wt %) | | | |
|---|---|---|---|---|---|---|---|---|
| | Ag | C | H | N | Ag | C | H | N |
| cured to 300 for 3 h (not cond.) | 13.0 | 62.3 | 2.5 | 5.0 | 14.2 | 61.2 | 2.65 | 5.3 |
| cured to 300 for 7 h (<0.1 Ω/sq) | 13.0 | 62.3 | 2.5 | 5.0 | 18.8 | 58.2 | 2.5 | 5.1 |

[a] Calculated for the silver(I) acetate−1,1,1-trifluoro-2,4-pentanedione dopant decomposing completely to silver metal and volatile components which are lost from the film.

44, and 43 ppm/K for 5.0. 7.4, and 9.9% silver, respectively.[12] Thus, in the conductive AgTFA films we may be seeing a hybrid value for the CTE reflecting the fact the surface silver aggregates are in contact with one another. The CTE of metallic silver is 19 ppm/K. Again, the variation in CTE values between the AgTFA and AgHFA systems demonstrates the pronounced differences that can arise due to subtle ligand effects.

For metalized films of Table 1, the tensile strengths are, within experimental error, those of the parent. The modulus for the two films cast on a glass plate are elevated ca. 5% while the value for the silvered film cast on a BTDA/ODA base is virtually the same as for the undoped polyimide. TEM does not indicate any porous nature of the silvered-doped films, consistent with similar mechnical properties between doped films and the parent. All of the films are flexible and can be tightly creased without rupture.

**Synthetic Aspects of Film Preparation.** The AgTFA complex is introduced to the poly(amic acid) resin via an in situ synthesis. While the preparation of solid AgTFA has been reported in the literature,[31] it is unstable and difficult to prepare reproducibly. Thus, we chose to synthesize AgTFA in poly(amic acid) solutions via the in situ reaction of AgA and TFAH, both of which can be obtained in pure and stable form. Combining AgA, TFAH, and BTDA/ODA in DMAc under ambient conditions leads to formation of a homogeneous solution of the AgTFA complex. The basicity of the acetate anion and the large formation constants associated with metal−$\beta$-diketonate complexes led to proton transfer from TFAH to the acetate anion, giving AgTFA and acetic acid. Even though AgTFA is not isolated, we can be assured that this complex is formed. First, AgA by itself is not soluble in DMAc. Second, when the poly(amic acid) is added to AgA alone, immediate polymer gelation occurs. The pathway for gelation is deprotonation of the aromatic carboxyl groups of the poly(amic acid) via transfer to the more basic acetate ions of AgA. Carboxylate groups of the polymer then coordinate to Ag(I) ions to form the extended gel network. It is well-known that silver carboxylate complexes are dimeric, involving the coordination of two carboxylate groups.[32] If TFAH is added to AgA before the addition of the poly(amic acid), no gelation occurs, and the insoluble AgA dissolves. Third, evidence for AgTFA complex formation is supported by observing the HFAH−AgA system. Using HFAH rather than TFAH with AgA in BTDA/ODA gives a similarly clear homogeneously doped resin solution. Again, we assume that the AgHFA complex is formed. When films of the in situ AgHFA−BTDA/ODA system are thermally cured, silver-metalized surfaces with 80% reflectivity are produced. Now, the AgHFA complex can be isolated in pure form as the ($\eta^4$-1,5-cyclooctadiene) adduct [(COD)(HFA)Ag]. When this solid complex is dissolved in DMAc with BTDA/ODA and a film is thermally cured, metalized films are produced with identical properties to those films prepared via the in situ AgA−HFAH route.[33] We take this as strong evidence that AgHFA is formed in both systems. We chose AgA as the precursor to formation of the in situ AgTFA complex because the acetate salt is readily available in high purity, is thermally and photochemically stable, and is not hygroscopic. We found that TFAH/Ag(I) ratios of 1.35:1 rather than 1:1 gave doped solutions which were somewhat less viscous and more easily processed.

To obtain even modest levels of reflectivity and conductivity, it is necessary that the silver(I) complex remain soluble in the initial poly(amic acid)−DMAc solution and in the solvent-depleted poly(amic acid) film that results during the cure cycle. The silver(I) precursor must not precipitate in the polymeric matrix at any time during the cure cycle or only micron-sized silver particles of irregular shape will result, which give poorly reflecting surfaces. It is important to have only single atoms or small clusters formed in the curing polymer, since Faupel and Foitzik[34] have demonstrated in physical vapor deposition studies that diffusion is facile only with particles of near atomic sizes and above the glass transition temperature ($T_g$) of the polymer. For imidized BTDA/ODA the $T_g$ is 275 °C; however, the effective $T_g$ of the mixed poly(amic acid)/polyimide system with

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(31) Wenzel, T. J.; Sievers, R. E. *Anal. Chem.* **1981**, *53*, 393.

(32) (a) Coggin, P.; McPhail, A. T. *J. Chem. Soc., Chem. Commun.* **1972**, 91. (b) Blakeslee, A. E.; Hoard, J. L. *J. Am. Chem. Soc.* **1965**, *78*, 3029.

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

(34) (a) Faupel, F. *Proceedings of the International Conference on Polymer−Solid Interfaces, Namur, Belgium, Sept. 1991*; IOP Publishing: Ltd., 1992; p. 171. (b) Foitzik, A.; Faupel, F. *Mater. Res. Soc. Symp. Proc.* **1991**, *203*, 59.

residual solvent is much less.[35] Thus, silver migration during the thermal cycle should not be inhibited by a rigid glassy state.

## Conclusions

We have synthesized silvered BTDA/ODA polyimide films from single phase silver(I) acetate−1,1,1-trifluoro-2,4-pentanedione−BTDA/ODA solutions cast and cured on glass plates. Depending on concentration and thermal conditions, metalized 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 the thermal stability of the film in air to ca. 325 °C, the metalized polymers still have a wide thermal use range. We have also shown that BTDA/ODA films cast on a parent BTDA/ODA polyimide base yield highly reflective and conductive composite films. This "film-on-film" approach minimizes the silver required for the formation of a reflective surface and ensures composite polymer properties which are those of the parent polyimide.

## Experimental Section

**Materials.** 4,4′-ODA and "Ultrapure" BTDA were obtained from Wakayama and Allco (Galena, KA). The ODA was used as received. BTDA was dried under vacuum at 160 °C for 5 h prior to use. TFAH was purchased from Lancaster and was redistilled under nitrogen before use. Silver(I) acetate (99.999) and DMAc (HPLC grade) were purchased from Aldrich and used as received. The BTDA/ODA poly(amic acid) solution was prepared with a 1% offset of dianhydride at 15% solids (w/w) in DMAc. The resin was stirred for of 5 h. The inherent viscosity was 1.7−1.8 dL/g at 35 °C.

**Preparation of BTDA/4,4′-ODA Metallized Films.** 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. However, if ca. 1.35 equiv of TFAH is dissolved in DMAc followed by the addition of the acetate, dissolution occurs readily with formation of the AgTFA complex. Thus, silver-containing resin solutions were prepared by first dissolving silver(I) acetate in a small volume of DMAc containing TFAH. The 15% poly(amic acid) solution was then added by weight to give the desired silver-to-polymer ratio. 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 cured films 20−25 mm thick. 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 7 h.

**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. Linear CTEs were obtained with a Seiko TMA 100 station at a heating rate of 2 °C/min and are reported as the average value over the temperature range of 70−125 °C. Surface resistivities of all films were measured with an Alessi four-point probe. TEMs were recorded on a Zeiss CEM-920 instrument. SEMs were obtained on a Hitachi S-510. 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 9 UV/VIS spectrophotometer equipped with a variable angle specular reflectance accessory using a wavelength of 531 nm, the solar maximum. X-ray data were obtained with a Philips 3600 diffractometer. X-ray photoelectron spectra were obtained with a Perkin-Elmer Phi Model 5300 ESCA. Atomic force micrographs were collected in the contact mode with a Digital Instrument NanoScope III multimode scanning probe microscope. Elemental analyses were done by Galbraith.

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(35) Kim, S. I.; Pyo, S. M.; Ree, M. *Macromolecules* **1997**, *30*, 7890.