# Control of Reflectivity and Surface Conductivity in Metallized Polyimide Films Prepared via in Situ Silver(I) Reduction

Robin E. Southward,[†] David W. Thompson,*[,†] and Anne K. St. Clair[‡]

*Department of Chemistry and Department of Applied Science, College of William and Mary, Williamsburg, Virginia 23185, and the Materials Division, National Aeronautics and Space Administration, Langley Research Center, Hampton, Virginia 23681*

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Optically reflective and surface-conductive polyimide films have been prepared by the incorporation of silver(I) acetate and trifluoroacetylacetone into a dimethylacetamide solution of the poly(amic acid) formed from 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride (BTDA) and 4,4′-oxydianiline (4,4′-ODA). Thermal curing of the silver(I)-containing poly(amic acid) leads to imidization with concomitant silver(I) reduction, yielding a reflective and conductive silver surface if the silver(0) concentration is greater than ca. 12% by weight and the film is cured to a final temperature of 340 °C. The metallized BTDA/4,4′-ODA films retain the essential mechanical properties of undoped films and have good thermal stability particularly in nitrogen atmospheres. The bulk of the polymer is not electrically conducting. Films were characterized by X-ray, DSC, TGA, XPS, TEM, SEM, and AFM.

## Introduction

The formation of metallic silver films on inorganic and organic polymeric substrates is of substantial interest. Applications include (a) contacts in microelectronics,[1] (b) highly reflective thin-film concentrators/reflectors in space environments for solar thermal propulsion,[2] for solar dynamic power generation,[3] and for $\gamma$-ray imaging telescope systems,[4] (c) the terrestrial concentration of solar energy to generate electric power and process heat,[5] (d) large-scale radio frequency antennas in space,[6] (e) bactericidal coatings,[7] and (f) surface-conductive flexible polymeric tapes.[8] For large-scale metallized surfaces and for space applications of metallized substrates, polymeric supports offer substantial advantages with regard to weight, flexibility, and fragility. Thin-film polymeric reflectors, concentrators, or antennas for space applications have the ability to be packaged into relatively small volumes and subsequently unfurled to form large structures. It is the synthesis of thin silvered surfaces on polymeric substrates which is the subject of this report.

One important route to metallized films is chemical vapor deposition, CVD, which externally deposits metal on a substrate surface by thermal decomposition of an appropriate molecular precursor coupled with reduction of a positive valent metal ion to the native state.[9] In the case of silver, however, there is a distinct lack of stable, volatile silver complexes which serve as CVD precursors. Although recent progress has been reported by Puddephatt et al.[10] and by Girolami et al.[11] in the synthesis of appropriate silver complexes for CVD and in understanding why earlier silver complexes have not been as volatile as anticipated from copper(I) analogues, yet the preparation of large films via silver CVD deposition remains a difficult and costly technical problem. Additionally, the adhesion of passive non-oxophilic metals such as silver which are condensed onto polymeric surfaces has been poor.[12−14] In this paper we wish to report on a procedure that might be viewed as the inverse of CVD, that is, an internal rather than external thermal decomposition/reduction of a polymer-soluble metal complex yielding native metal atoms or clusters that migrate from the bulk of the polymer to give surface-metallized films exhibiting excellent adhesion. In CVD a silver(I) complex such as (triethylphosphine)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)silver-

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[†] College of William and Mary.

[‡] NASA−Langley Research Center.

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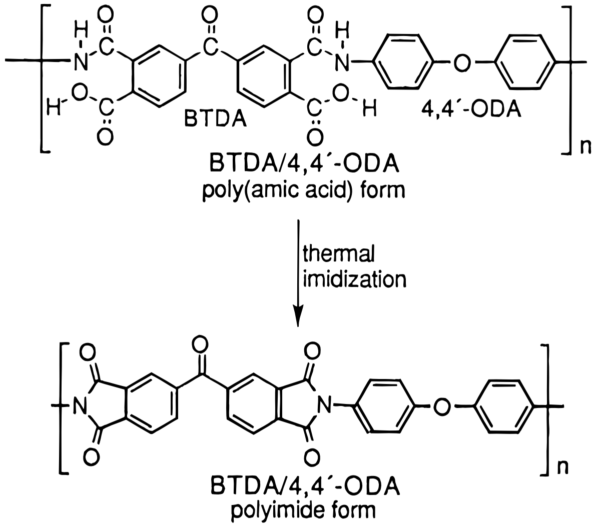
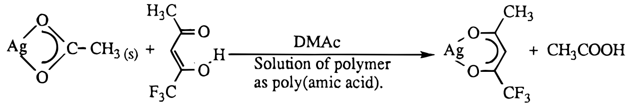
**Scheme 1**



**Scheme 2**



(I)[10a] or bis(trimethylphosphine)(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)silver(I)[11b] is vaporized and passed with hydrogen over a heated substrate surface. The silver(I) precursor is thermally decomposed with concomitant reduction of silver(I) to metallic silver. In the system reported in this work a silver(I) complex, very similar in nature to the CVD complexes mentioned above, is dissolved in a polymer solution. From this polymer−metal ion solution a film is cast and then heated to effect thermal reduction of silver(I) in the complex to silver metal and imidization of the film. Migration or phase separation of the silver(0) atoms/clusters occurs to give a thin film of silver (ca. 100 nm) at the polymer surface.

We have chosen to study the construction of silvered surfaces on polyimide films derived from BTDA and 4,4′-ODA (Scheme 1) since polyimides have unusual thermal-oxidative and chemical stability.[15−17] This stability is essential for the composite film to survive thermal curing in an oxygen atmosphere where silver(0) is known to function as an oxidation catalyst toward carbon framework molecules.[18] Also, BTDA/4,4′-ODA has given excellent silver films in previous work involving similar in situ formation of silvered films.[19,20] Our experimental protocol (Scheme 2) involves doping a dimethylacetamide (DMAc) solution of the poly(amic acid) form of BTDA/4,4′-ODA with silver(I) acetate, which is insoluble in DMAc, and with trifluoroacetylacetone, TFAH. The mildly acidic $\beta$-diketone is deprotonated by the acetate anion leading to the in situ formation of the soluble (1,1,1-trifluoro-2,4-pentanedionato)silver(I) complex, AgTFA.[21] After casting the silver(I)-containing polymer solution into a film, thermal treatment both imidizes the poly(amic acid) and effects reduction of silver(I) to metallic silver, part of which migrates to give a metallized surface. The silver(I) species must be soluble in the polymer solution and the subsequent solventless polymer matrix to give uniform metallic surfaces. Thus, trifluoroacetylacetone serves to solubilize silver(I) via complex formation and to promote reduction of silver(I) in such a manner as to control the reflectivity and conductivity of the final films.

In recent work we have shown that in DMAc silver(I) acetate and silver(I) fluoride can be dissolved and the silver(I) ion complexed in situ by 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, HFAH. With BDTA/4,4′-ODA, these additives led to highly reflecting silver films which did not exhibit surface or volume conductivity.[19] The use of the isolable and soluble complex [(HFA)-(COD)Ag], COD = 1,5-cyclooctadiene, also gave films which were reflective but not conductive.[20] The synthesis and isolation of the AgTFA complex were reported in 1981 by Wenzel and Siever.[21] However, this complex has proven extremely difficult to prepare in a reproducible manner and is unstable to light and air. With selected samples of isolable AgTFA, prepared by the method of Wenzel and Siever, we have been able to prepare films of high quality that are surface conductive and reflective,[22] although the reflectivity is less than that obtained with the silver(I)−HFAH systems.[19,20] Thus, a more convenient and reproducible route to the reflective/conductive AgTFA-doped films is highly desirable. In this paper we report such a route which is based on the in situ formation of a photolytically stable AgTFA polymer-solvated complex and present characterization data for the resultant silvered films with respect to conductivity, reflectivity, composition, morphology, and thermal properties. A preliminary account of a portion of this work has appeared.[23]

## Experimental Section

**Materials.** 4,4′-ODA and "Ultrapure" BTDA were obtained from Wakayama Seika Kogyo Co., Ltd. (via Kennedy and Klim, Inc.) and Allco (Galena, KA), respectively. The 4,4′-ODA was used as received. BTDA was dried under vacuum at 160 °C for 5 h prior

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to use. The melting points of the monomers as determined by DTA were 218 and 188 °C, respectively. TFAH was purchased from Lancaster and was redistilled under nitrogen before use. Silver(I) acetate (99.999%) and DMAc (HPLC grade <0.03% water) were purchased from Aldrich and used without further purification.

The BTDA/4,4′-ODA poly(amic acid) solution employed in this study was prepared with a 1% offset of dianhydride at 12% solids (w/w) in DMAc. The resin preparation was performed by first dissolving the diamine[15] in DMAc in a resin kettle flushed with dry nitrogen and then adding the dianhydride. The resin was stirred for a minimum of 5 h. The inherent viscosity was 1.7 dL/g at 35 °C.

**Preparation of BTDA/4,4′-ODA Metallized Films.** Silver(I) acetate is not soluble in DMAc, and the further addition of the poly(amic acid) form of BTDA/4,4′-ODA does not coordinate sufficiently with silver(I) of the acetate salt to bring it into solution. However, if 1.5−2 equiv of TFAH are dissolved in DMAc followed by the addition of silver(I) 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. DMAc containing the TFAH (1 g) was used to dissolve silver(I) acetate (see Table 1 for silver and TFAH stoichiometries) for every 5 g of 12% BTDA/4,4′-ODA poly(amic acid) solution. The 12% poly(amic acid) solution was then added by weight to give the desired silver-to-polymer ratio. The light yellow silver(I)-doped resins were stirred for 30 min before casting films. The doped films were not light sensitive for at least 24 h. Thus, special precautions were not taken to protect the films from light.

A series of films with varying concentrations of silver(I) acetate and HFAH was made as reported in Table 1. Undoped and doped poly(amic acid) solutions were cast as films onto soda lime glass plates using a doctor blade set at 500−650 $\mu$m to obtain cured films 20−25 $\mu$m in thickness. After remaining in an atmosphere of dry slowly flowing air (10% relative humidity) for 2−18 h, the films were thermally cured in a forced air oven. Cure cycles are listed in Table 1. The films were removed from the glass plates by lifting the edges with a razor blade and soaking in deionized water at the ambient temperature. Reflectivity samples were affixed onto 5 × 5 cm glass plates.

**Characterization Techniques.** Monomer melting points were determined by DTA at a heating rate of 20 °C/min on a DuPont Thermal Analyzer 2000. Inherent viscosities of the poly(amic acid) resin were obtained at a concentration of 0.5% (w/w) in DMAc at 35 °C. TGAs were obtained on the cured films in both flowing air and nitrogen (50 mL/min) at a heating rate of 2.5 °C/min using a Seiko TG/DTA 200 or TG/DTA 220. 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 70−125 °C. The CTE samples were desiccated for 24 h before analysis. Surface resistivities of all films were measured with an Alessi four-point probe. TEM was done at the Virginia Institute of Marine Science on a Zeiss CEM-920 transmission electron microscope. Scanning SEMs were obtained on a Hitachi S-510. 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 5 or 9 UV/vis spectrophotometer equipped with a variable-angle specular reflectance accessory using a wavelength of 531 nm. 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 done in the contact mode with a Digital Instrument NanoScope III Multimode Scanning Probe Microscope. Elemental analyses were done by Galbraith.

## Results and Discussion

**Film Preparation and Synthetic Considerations.** Thermal imidization and curing of BTDA/4,4′-ODA poly(amic acid) solutions in DMAc containing soluble silver(I) as the AgTFA complex leads to polyimide films with uniformly metallized surfaces when viewed on the macroscopic level. As presented in Table 1 these films have only modest specular reflectivity (29−52% at 20°) relative to the HFAH analogues reported earlier by us which gave specular reflectivities for similar silver concentrations in the range 75−82% at 20°.[19] Surface conductivity is a function of silver concentration and the thermal cure cycle; only at higher silver concentrations and higher final cure tempertures do the films become conductive. This is to be contrasted with the AgHFA analogues for which surface conductivity was never observed under conditions similar to the TFA systems reported herein. All AgTFA metallized films are flexible and can be creased tightly without breaking. The bulk of the surface silver is strongly adhered to the polymer as observed in the analogous AgHFA systems.[19]

To obtain even modest levels of reflectivity and conductivity upon thermal treatment, it is necessary that the silver(I) remain soluble in the poly(amic acid)−DMAc solution and in the solvent depleted poly(amic acid) film that results during the cure cycle. The silver(I) species must remain in a mononuclear or very minimal polynuclear state throughout the polymer matrix until reduction of silver(I) occurs. Precipitation of a silver(I) compound before the onset of reduction to silver(0) tends to give micron-sized metallic silver particles of irregular shape which yield neither reflective nor conductive surfaces. Crystal structures of [(HFA)(PMe$_3$)Ag][10a,11] and [(HFA)(PMe$_3$)$_2$Ag][11] show that these complexes in the solid state are mononuclear with trigonal planar and distorted tetrahedral structures, respectively; crystal structures for [(HFA)(COD)Ag][24] and [(HFA)(Me$_2$PCH$_2$PMe$_2$)Ag],[10b] on the other hand, show that the molecular units are dinuclear in silver(I). It seems reasonable to expect that the AgTFA complex in a coordinating solvent, albeit weakly, like DMAc should be mononuclear as the phosphine−HFA analogues are. This mononuclearity facilitates the formation of single silver(0) atoms upon reduction which is optimal for migration of metallic silver to the polymer surface to form an acceptably smooth and uniform

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**Table 1. Reflectivity, Thermal, and Surface Resistivity Data for Silver(I) Acetate/Trifluoroacetylacetone BTDA/4,4′-ODA Films**

| percent silver (calc)[a] | thermal cure treatments | polymer repeat unit to silver ratio | TFAH to Ag(I)ratio | percent reflectivity of silvered films (as a function of angle) | | | $T_g$, °C (DSC) and [CTE[h]ppm/K] | 10% wt loss °C (air) | 10% wt loss °C ($N_2$) | surface resistivity[d] (Ω/sq) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | 20° | 45° | 70° | | | | |
| control | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−300−1h/2h−50−end | na | na | | na | | 271 [42.8] | 524 | 540 | nonconductive |
| 7.8 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 2.61 | 3.14 | 49 (41)[f] | 41 (34)[f] | 35 (28)[f] | 280 | 367 | 562 | nonconductive |
| 10.6 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.87 | 1.99 | 47 | 41 | 35 | 276 [33.1] | 345 | 556 | nonconductive |
| 12.3 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.58 | 2.01 | 34 | 34 | 38 | 272 | 347 | 525 | 1.3 |
| 12.4 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.57 | 1.49 | 29 | 30 | 38 | c | g | 558 | 15 |
| 12.5 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.56 | 1.07 | 38 | 36 | 40 | c | 327 | 567 | 4.3 |
| 13.3 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.44 | 1.57 | 46 | 44 | 45 | *c* [27.7] | 300 | 527 | 10 |
| 13.5 | precured 18 h in film box. 10m−100−1h/15m−200−1h/1h−340−1h/2h−50−end | 1.42 | 1.98 | 28 (84)[e] | 28 (84)[e] | 35 (79)[e] | 263[b] | 352 | 551 | 0.8 |
| 12.0 | precured 2 h in film box. 10m−100−1h/30m−150−1h/30m−200−1h/30m−300−1h/2h−50−end | 1.62 | 1.04 | 34 | 24 | 9 | 273 [35.5] | 357 | 543 | nonconductive |
| 12.0 | the 12.0% film above was sintered with the cycle: 10m−100−10m/15m−200−1h/1h−340−1h/2h−50−end | 1.62 | 1.04 | 37 (52) | 39 (59) | 42 (g) | *c* [35.3] | 331 | 554 | 0.4 |
| 13.0 | precured 2 h in film box. 10m−100−1h/30m−150−1h/30m−200−1h/30m−300−1h/2h−50−end | 1.49 | 1.70 | 31 | 23 | 9 | 272 | 361 | 536 | nonconductive |
| 13.0 | the 13.0% film above was sintered with the cycle: 10m−100−10m/15m−200−1h/1h−340−1h/2h−50−end | 1.49 | 1.70 | 40 | 47 | 46 | c | 289 | 455 | 0.7 |

[a] Calculated for the silver acetate−TFAH dopant system decomposing completely to silver metal. [b] Weak transition. [c] Not observable. [d] Four-point probe. The glass side of all films was not conductive. [e] The reflectivity increases to 84, 84, and 79% at 20, 45, and 70°, respectively, when the surface is rubbed lightly with a Leblanc Model 3292 soft metal polishing cloth. [f] The reflectivity decreases to 41, 34, and 28% at 20, 45, and 70°, respectively, when the surface is rubbed lightly with a Leblanc polishing cloth as for entry *e*. [g] Polished reflectivities; could not be measured at 70° due to small sample size. [h] The CTE films were cured and analyzed as described in the Experimental Section; the films were cooled from their maximum cure temperature to 50 °C over a 2 h period.

metallic layer. Faupel and Foitzik[25] have demonstrated in physical vapor deposition studies that only single atoms or small clusters of silver(0) can diffuse within a polyimide matrix and that this diffusion is facile only above the glass transition temperature. $T_g$ for imidized BTDA/4,4′-ODA is near 275 °C; however, the effective $T_g$ of the mixed poly(amic acid)/polyimide/solvent-impregnated system is much less than 275 °C, and thus, silver(0) migration during most of the thermal cycle should not be inhibited by a rigid glassy state.

We chose silver(I) acetate 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, and the acetate anion has moderate Bronsted basicity. Silver(I) fluoride and silver(I) oxide have been used in previous work to prepare in situ AgHFA complexes,[10,19b] but these precursors are more difficult to maintain in high purity than silver acetate due to combinations of light, thermal, and moisture sensitivity. Solubilization of silver(I) acetate is accomplished readily as illustrated in the reaction shown in Scheme 2 above where TFAH undergoes proton transfer to the acetate ion producing the $\beta$-diketonate complex and acetic acid. Both products are soluble in the BTDA/4,4′-ODA−DMAc poly(amic acid) solution. While a 1:1 ratio of TFAH to silver(I) acetate is sufficient to bring silver(I) into solution in the poly(amic acid)−DMAc solution, we found that TFAH/Ag(I) ratios in the 1.5−2.0 to 1 range gave doped solutions which were slightly less viscous and easier to manipulate. Overall, the metallized film properties do not appear to be sensitive to the Ag(I)−TFAH ratio over the range of 1:1 to 1:3, respectively. When silver(I) acetate, which is only sparingly soluble in DMAc, is added without TFAH ligand to a DMAc solution of BTDA/4,4′-ODA, immediate gelation of the polymer occurs, presumably via coordination of polyamide carboxylate groups to silver(I). Since gelation does not occur in the presence of TFAH, this is solid evidence for formation of the AgTFA complex. Silver(I) as the TFA complex undergoes thermally promoted reduction to give metallized polymer surfaces while acetic acid is volatized from the polymer. Complexation of silver(I) is important to film metallization as the use of silver nitrate alone, which is soluble in DMAc, leads only to films which have low reflectivity, are not conductive, and have unacceptable mechanical porperties.[28]

**Reflectivity and Conductivity Patterns.** In our previous work with silver(I) acetate−HFAH−BTDA/4,4′-ODA systems none of the metallized surfaces was conducting even though excellent reflectivity was obtained; even when metallized films were postcured at 340 °C, conductivity could not be induced.[19] The same was true for metallized films prepared with the isolable [(HFA)(COD)Ag] complex.[20] The TFA ligand differs only slightly from the HFA ligand by replacement of fluorines in one methyl group with hydrogens. This renders the TFA anion slightly more basic (p$K_a$ = 6.3)[29] than the HFA anion (p$K_a$ = 4.35).[30] Thus, there seemed to be little reason to expect that the Ag(I)−TFA system should give metallized films which differed significantly from those prepared with the HFA analogue. However, reference to Table 1 shows that the use of TFAH gives metallized films which are very different from their HFAH congeners in both reflectivity and conductivity. None of the TFAH films cured to a maximum of 300 °C exhibited surface conductivity at silver concentrations up to 13.5%. (Films at 12.0% and 13.0%, which were cured to 300 °C, are displayed in Table 1, and their properties are representative of films which were prepared with lower concentrations of silver and cured to a maximum of 300 °C.) All films cured only to 300 °C had a metallic green luster and showed reflectivities at 20° in the 30−35% range. The appearance of these TFAH films and their reflectivities are strikingly different from the closely related HFAH systems, which are very reflective and exhibit the luster of brightly polished silver and commercial silvered glass mirrors. No TFAH films were conductive when cured only to a final temperature of 300 °C consistent with observations for the HFA films.

However, when the TFAH films of this report were subjected to postcure or sintering conditions, which involved a final temperature of 340 °C for 1 h (see Table 1), films which had greater than ca. 12% silver-developed conductive surfaces. They also exhibited an increase in specular reflectivity, which now did not diminish as a function of increasing angle of incidence. Films with silver concentrations less than ca. 11% did not become conductive when sintered at 340 °C. This is very different behaviour than observed with the HFAH analogues which were always nonconductive under identical thermal conditions.

The visual appearance of the 12.0% and13.0% TFA films of Table 1 before and after sintering is very different. Cured only to 300 °C the films have a metallic green sheen, but after postcuring at 340 °C the films adopt a silver-colored metallic luster which is somewhat dull as seen in their reflectivities which were in the 40−50% range. However, as shown for the conductive 13.5% film of Table 1, only very light polishing with a Leblanc "soft metal polishing cloth" increases reflectivity values above 80% while maintaining conductivity.

The X-ray diffraction patterns presented in Figure 1 for the 12.0% pair of films of Table 1 reflect the obvious visual difference seen in 300/340 °C film pairs. For the films cured to 300 °C only, one observes the four intense reflections (111, 200, 220, 311) of face-centered cubic crystalline silver. However, these reflections are broad and are consistent with the particle size of silver clusters being in the nanometer range as suggested by the Scherrer equation. After sintering at 340 °C the reflections become quite sharp. The X-ray patterns suggest differing degrees of aggregation of silver. The TEMs (Figure 2) of the 12.0% pair of films show distinct differences. The film cured to 300 °C, which exhibits a metallic green sheen, has only a minimal concentration of metallic silver at the air-side surface and a collage of silver particles dispersed throughout the bulk of the

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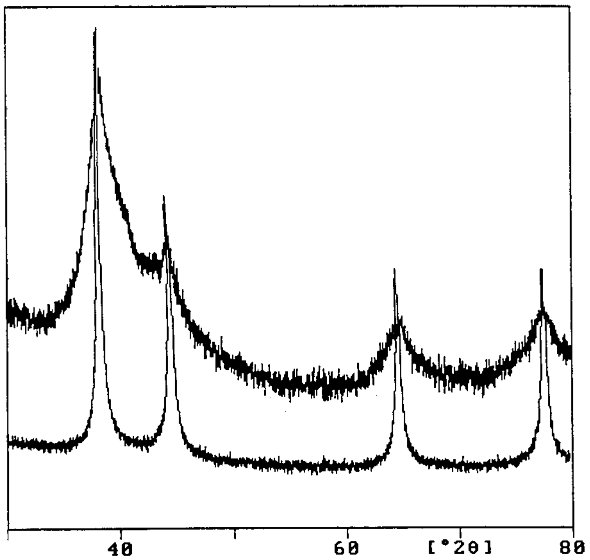
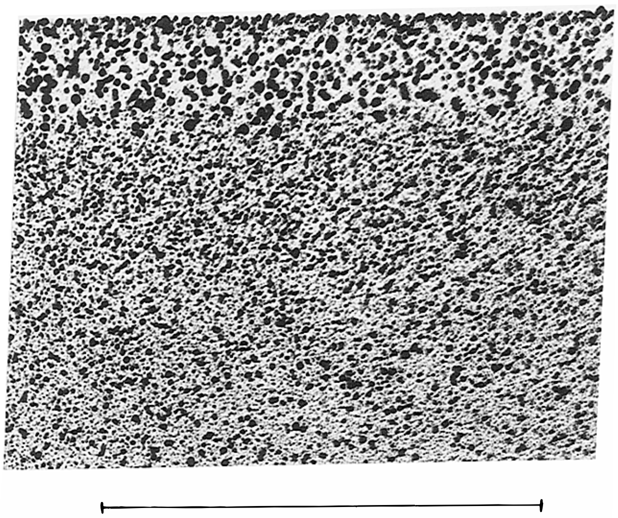
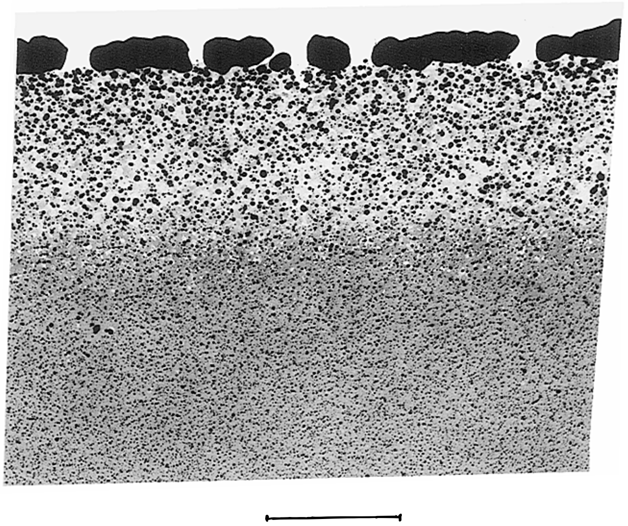


**Figure 1.** X-ray diffraction patterns of BTDA/4,4′-ODA silver(I) acetate/trifluoroacetylacetone films (12.0% Ag): (A, upper curve) film cured to 300 °C; (B, lower curve) the film in A sintered at 340 °C for 1 h.

polymer matrix. The TEM for the 340 °C postcured film shows a well-defined surface layer of silver with a thickness on the order of 200 nm. The size of the silver particles in the postcured film on average are larger than those in the film cured only to 300 °C which is consistent with the narrower X-ray reflections of this film. The SEM displayed in Figure 3 of the 300 °C 12.0% film shows a much smoother and less detailed surface structure than that for the 340 °C sintered film. At 300 °C the film exhibits what appears to be isolated silver islands emerging from the surface of the polymer. The islands are not in contact, and therefore the film is not conductive. Upon sintering at 340 °C the SEM shows a substantial increase in silver at the film surface, and the surface morphology is such that there are conductive metallic pathways extending over the polymer. The lacework open morphology of the surface may account for the decreased specular reflectivity (increased diffuse reflectance) of this film (37%) relative to an HFAH analogue (82%) which has a very regular array of silver islands at the surface.[19] Finally, the AFMs of the 12.0% pair of films and the 13.3% film of Table 1, along with the AFM for a 9.9% silver BTDA/4,4′-ODA film which is 79% reflective at 20° prepared with silver(I) acetate−HFAH, are shown in Figure 4. The surface of the 12.0% film cured to 300 °C is relatively smooth with an intimation of metallic silver islands breaking through the film surface; this micrograph is reasonably similar to that of the undoped parent polymer film, suggesting that there is still much polymer at the film surface, which is consistent with TEM data. However, on postcuring to 340 °C the surface becomes much more irregular and appears to be more or less continuous as is suggested by its becoming conductive. Both of these force micrographs are distinctly different from that of a 9.9% silver BTDA/4,4′-ODA film[19] prepared with HFAH and silver(I) acetate where one sees a rather regular topology of pillowed islands of silver; we presume that it is this more ordered array of silver particles which is essential for high specular reflectance.



Cured to 300 °C



Sintered at 340 °C

**Figure 2.** TEM micrographs of BTDA/4,4′-ODA silver(I) acetate/trifluoroacetylacetone films with 12.0% silver(0) cured at 300 °C in air and subsequently sintered at 340 °C in air for 1 h (the bar is 1 $\mu$m).

It does not appear that the lack of surface conductivity in films cured to 340 °C with less than 12% silver is due to not having reached the percolation threshold. TEMs for BTDA/4,4′-ODA−AgHFA films, which are not conductive, show that there is ample silver at or near the film surface, and the TEM of 10.6% of this work (Figure 6) suggests sufficient silver for surface conductivity. It appears in our silver work,[19] and in the analogous [(HFA)(COD)Ag]−BTDA/4,4′-ODA work[20] that the lack of surface conductivity is attributable to thin sections of polymer film which insulate silver aggregates and cover the film surface. Such a surface overlayer is suggested by two observations: (1) the XPS spectra Table 2 show a high atom percentage of carbon, oxygen, and nitrogen at the film surface for the 12.0% film cured only to 300 °C in roughly the ratios expected for pure BTDA/4,4′-ODA and (2) our nonconductive silvered films show virtually no tendency to tarnish under ambient conditions for periods of more than 1 year. There are also a limited number of references to the formation of

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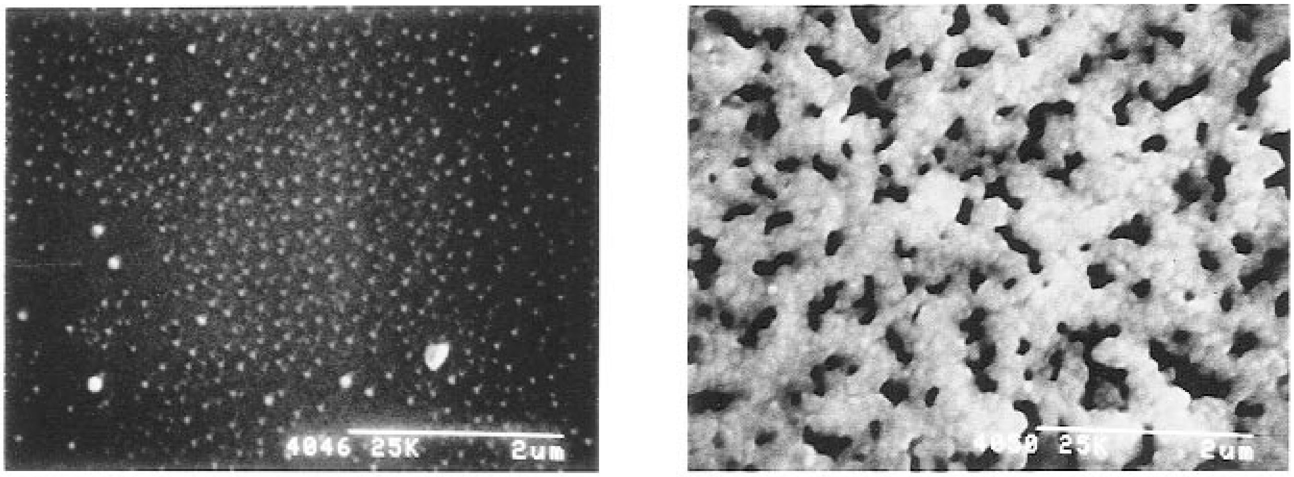

**silver(I) acetate/trifluoroacetylacetone**

non-conductive
**(300 °C)**

**silver(I) acetate/trifluoroacetylacetone**

conductive
**(340 °C)**

**Figure 3.** SEM micrographs of a BTDA/4,4′-ODA silver(I) acetate/trifluoroacetylacetone film with 12.0% silver(0) cured at 300 °C in air, and the same film subsequently sintered at 340 °C in air for 1 h (the bar is 2 $\mu$m).

**Table 2. X-ray Photoelectron Spectral Surface Composition Data for the Silver Acetate/Trifluoroacetylacetone BTDA/4,4′-ODA Film at 12.0% (Relative Atomic Percent)**

| thermal cycle (°C)[a] | $Ag^0$ (calc) | film surface | silver | fluorine | carbon | oxygen | nitrogen | surface resistivity (Ω/sq) |
|---|---|---|---|---|---|---|---|---|
| 100, 150, 200, 300 | 12.0 | air | 7.35 | 0.12 | 76.9 | 12.3 | 3.31 | nonconductive |
| 100, 150, 200, 300 sintered for 1 h at 340 | 12.0 | air | 23.1 | 0 | 50.4 | 24.8 | 1.70 | 0.5 |

[a] All thermal cycles were done in air.

an overlayer in polyimide films with gold,[32] copper,[33] and cobalt oxide[34] surfaces prepared via self-metallization procedures. We are currently looking in more detail at the possibility of polymer overlayers on these in situ silver metallized films.

As mentioned earlier, TFAH and HFAH have similar structures and properties. Thus, we were surprised to see that they lead to very different metallized films with BTDA/4,4′ODA. Clearly, it is not a simple silver(I) cation undergoing reduction via reaction with a segment of the polymer or solvent. If this were the case, the two ligand systems as well as silver nitrate all should give similar films; in fact, all three systems give very different films and differing silver particle morphologies.[19,28] There must be a role for the ligand. The TGA curves of Figure 7 do suggest that the TFA ligand does have a pronounced effect on the thermal stability of the $\beta$-diketonate complex relative to HFA. The TGA for the solid AgTFA complex (our best preparation using the procedure of Wenzel and Siever[21]) shows that the onset of silver(I) reduction occurs near 125 °C. The analogous solid HFA complex has not been isolated per se but has been prepared as the 1,5-cyclooctadiene complex, [(HFA)(COD)Ag],[35] which has been reported to give reflective but not conductive films[20] similar to the films prepared from silver(I) acetate/HFAH.[19] In the TGA curve for [(HFA)(COD)Ag] we first see loss of COD, which is complete at ca. 160 °C, and then we see the onset of silver(I) reduction. Thus, reduction of the silver(I) with the HFA ligand requires greater thermal energy than that for the TFA ligand; if the electron for silver(I) reduction comes from the ligand, this trend is consistent with the greater inductive withdrawing character of the hexafluoro ligand relative to the trifluoro ligand, i.e., it is more difficult to abstract an electron from HFA than TFA. It is not clear to us how the difference in reduction tendency of the two complexes should manifest itself in the final metallized polymer.

**Metallized Film Composition Data.** Elemental analysis data for selected films of Table 1 are presented in Table 3. The calculated values in Table 3 were determined by assuming that all organic components (TFA and acetic acid) of the silver(I) dopant system were volatilized in some form from the film and that only metallic silver and framework BTDA/4,4′-ODA remained. This assumption is supported by previous studies with silver(I)−HFA complexes which were mentioned above.[19,20] The elemental percentages found for the film prepared at 12.0% silver and cured to 300 °C corresponded reasonably well to the calculated values, i.e., 12.8% versus 12.0%. The silver found is somewhat high (12.8 versus 12.0), and the carbon found is lower then expected (60.8 versus 62.9). This is consistent with a small loss of polymer due to air oxidation which is catalyzed by metallic silver since the films were cured in a forced air oven. One also sees a small but significant amount of fluorine (0.54%) in the polymer which may result from partial reaction of a TFA fragment with the polymer chain. In our analogous HFAH−silver(I) systems reported previously,[19] a simi-

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**Table 3. Elemental Analyses for Silver Acetate/Trifluoroacetylacetone-Doped BTDA/4,4′-ODA Films**

| | calculated (wt %) | | | | | found (wt %) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| thermal treatment[a] | Ag | F | C | H | N | Ag | F | C | H | N |
| 100, 200, 300 | control[b] | 0 | 71.6 | 2.90 | 5.76 | 0 | 0.065 | 70.4 | 3.05 | 5.58 |
| 100, 200, 340 | 10.6 | 0 | 64.0 | 2.58 | 5.11 | 13.6 | 0.053 | 61.2 | 2.16 | 5.03 |
| 100, 200, 340 | 13.3 | 0 | 62.0 | 2.51 | 4.96 | 21.2 | <0.03 | 56.0 | 1.86 | 4.68 |
| 100, 150. 200, 300 | 12.0 | 0 | 62.9 | 2.54 | 5.03 | 12.8 | 0.54 | 60.8 | 2.09 | 4.92 |
| 100, 150, 200, 300 sintered for 1 h at 340 | 12.0 | 0 | 62.9 | 2.54 | 5.03 | 22.5 | 0.52 | 53.9 | 1.75 | 4.49 |

[a] All thermal cycles were done in air. [b] Control is offset 1% by weight in dianhydride.

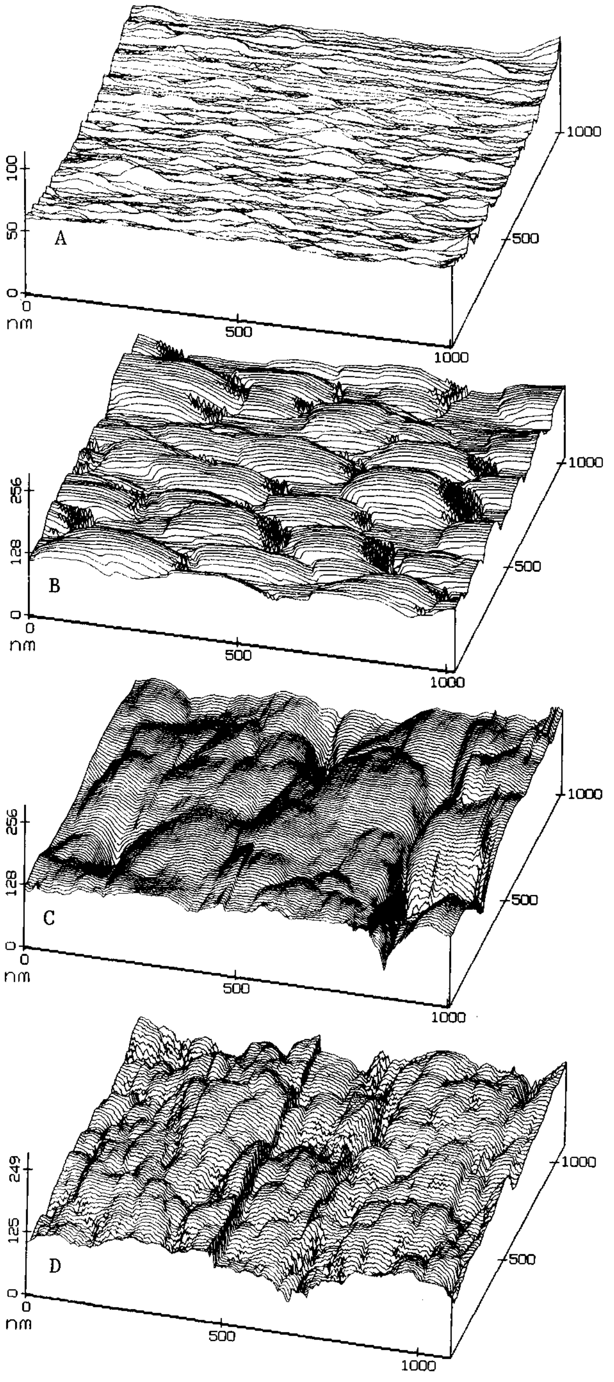

**Figure 4.** Atomic force micrographs of a 12% silver(I) acetate/trifluoroacetylacetone BTDA/4,4′-ODA film cured to 300 °C in air and sintered at 340 °C in air (A and C); a 9.9% silver(I) acetate/hexafluoroacetylacetone BTDA/4,4′-ODA film cured to 300 °C in air (B); and a 13.3% silver(I) acetate/trifluoroacetylacetone BTDA/4,4′-ODA film cured to 340 °C in air (D). Micrographs: A (top of page); D (bottom of page).

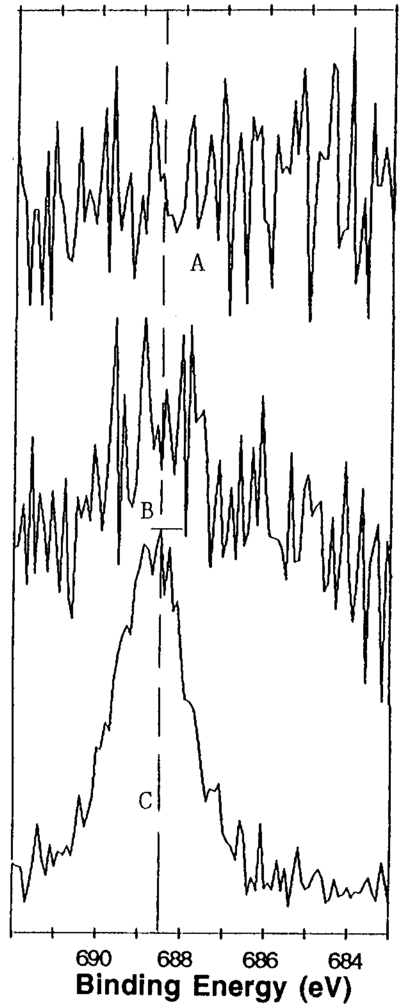

**Figure 5.** F(1s) XPS spectra for a 12.0% silver-BTDA/4,4′-ODA film prepared from silver(I) acetate/trifluoroacetylacetone and cured to 300 °C (B) followed by sintering at 340 °C (A) and for a 9.9% BTDA/4,4′-ODA film prepared from silver(I) acetate/hexafluoroacetylacetone and cured to 300 °C in air (C).

larly doped and cured BDTA/4,4′-ODA solution (prepared to have 12.8% silver) was found to have 2.5% fluorine. The X-ray photoelectron spectra Figure 5 of the air side of the 12.0% metallized film shows a weak F 1s peak at 688.4 eV which is consistent with that expected for a $CF_3$ group. Inorganic fluoride, such as in silver(I) fluoride, is observed in the 684−685 eV range. In the (HFA)Ag−BDTA/4,4′-ODA systems XPS data clearly showed that the fluorine in the metallized film was bound in $CF_3$ groups and was not ionic fluoride as expected in silver(I) fluoride.[19a] We presume similar chemistry is taking place in the analogous TFAH system but to a lesser extent, consistent with a smaller concentration of fluorine in the TFA ligand. When the 12.0% silver film which was initially cured to 300 °C was subsequently sintered at 340 °C for 1 h, there was a dramatic change in overall composition. As Figure 5 shows, the weak fluorine peak at 688.4 eV has vanished,

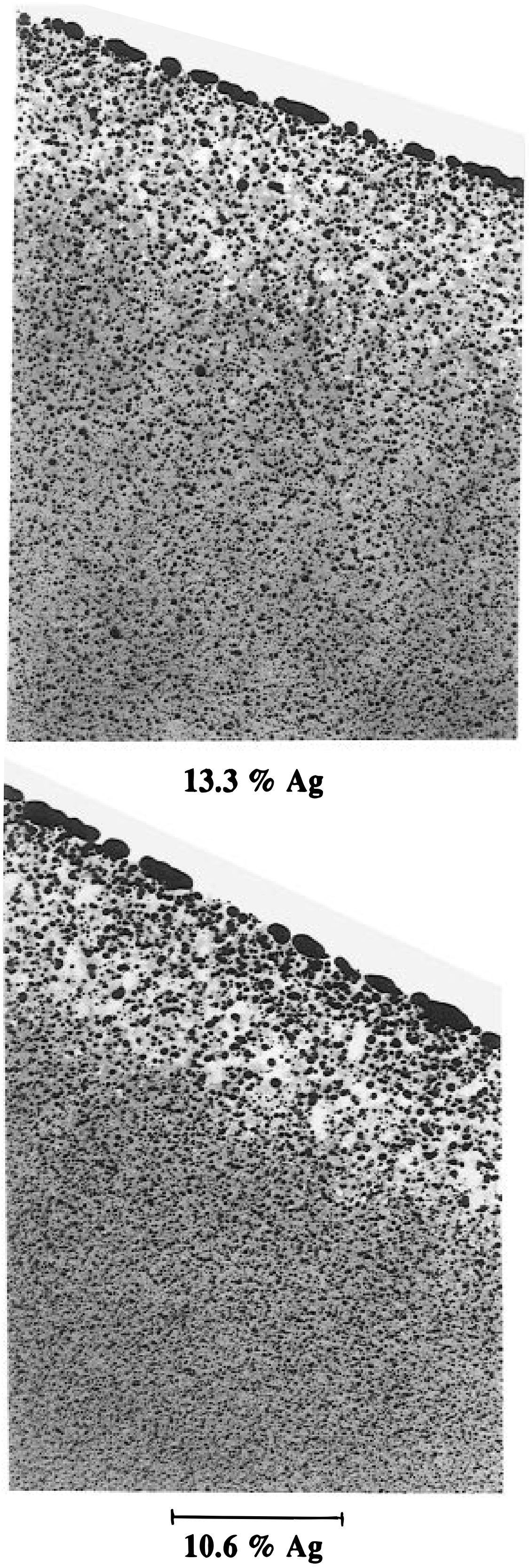

**Figure 6.** TEM micrographs of the air side of BTDA/4,4′-ODA silver(I) acetate/trifluoroacetylacetone films (see Table 1) with 10.6% and 13.3% silver(0) cured to 340 °C in air. The bar is 1 $\mu$m for both films.

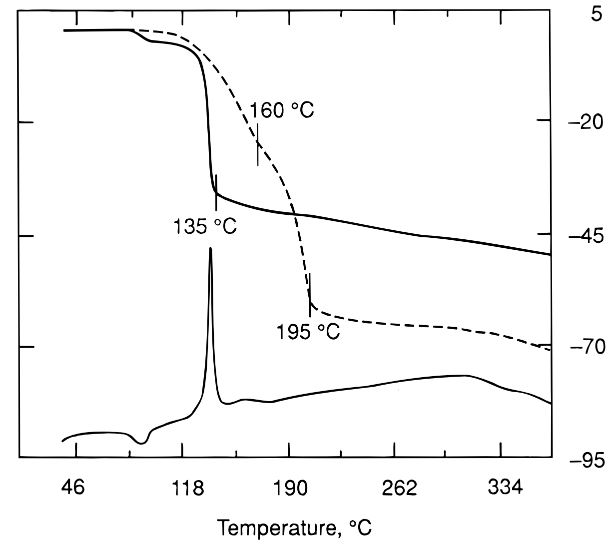

**Figure 7.** Thermogravimetric curves for the solid complexes (trifluoroacetylacetonato)silver(I) (solid line) and (1,5-cyclooctadiene)(hexafluoroacetylacetonato)silver(I) (dashed line). Ordinate is percent weight loss.

presumably due to oxidative degradation of polymer, and silver at the surface increases. The atomic percentages of carbon and nitrogen are distinctly lowered while the relative amount of silver increases from 12.8% to 22.5%, and the relative concentration of oxygen increases. It appears that at 340 °C the surface of the polyimide undergoes extensive oxidative degradation. Since undoped BDTA/4,4′-ODA films are completely stable in air at 340 °C, the oxidative degradation must be catalyzed by silver metal, which is a well documented phenomenon in organic chemistry.[26,27]

The analytical data show that not only does the thermal cure cycle in air play a role in the degradation of the polymer, but the concentration of silver in the polymer is important. We found that no films sent through the cure cycle of Table 1 having a maximum temperature of 300 °C became surface conductive, and only films having greater than ca. 12% silver became conductive when cured to a maximum temperature of 340 °C. For example, curing films prepared to have 10.6 and 13.3% silver to the 340 °C maximum as described in Table 1 led to metallized films with very different conductivities, composition, and angle dependence of the specular reflectivity. At silver concentrations less than ca. 12%, as illustrated with the 10.6% sample of Table 1, curing the doped films to 340 °C does not give conductive films, and one sees only a modest amount of oxidative polymer degradation. At silver concentrations greater than ca. 12%, as illustrated with the 13.3% film of Table 1, curing the doped films to 340 °C does give conductive films, and one sees extensive oxidative polymer degradation; the reflectivity no longer decreases with increasing angle of incidence. One might think that the difference in surface conductivity for the 10.6 and 13.3% films should be reflected in the microscopy. The TEMs for these two latter films are shown in and are very similar and do not reveal their difference in conductivity; the SEMs and AFMs are similarly uninformative. It appears that significant oxidation degradation of polymer is essential to develop surface conductivity and that silver must be in sufficient concentration in the resin to at least partially break through the surface to begin the catalytic degradation process which ultimately exposes greater quantities of silver metal as the polymer undergoes surface degradation. If the silver concentration is too low, the polymer blankets the silver particles which keeps them from dissociatively activating molecular oxygen[34] and attacking the polymer framework. Elemental analysis data shows that the silver in the 10.6% film has given rise to some degradation as the percent carbon is 2.8% lower than expected and silver is elevated by 3.0%. With the same cure conditions as for the 10.6% film, the 13.3% film, which is conductive, shows a percent carbon which is 12.1% low and a percent silver which is 10.5% high. It appears that in the range between 10.6% and 12.3% the silver(I)-doped polymers give metallized films which move from nonconductive to surface conductive.

**Thermal Data for Metallized Films and Silver Complexes.** The presence of metallic silver aggregates in the BTDA/4,4′-ODA matrix adversely affects the thermal stability of the metallized film . As seen from the data in Table 1 the temperature for 10% weight loss in air as determined by TGA is roughly in the range 300−350 °C. This still allows a reasonably wide thermal use range for these metallized films, particularly for space applications. The weight loss in air is clearly due to silver catalyzed dioxygen degradation since 10% weight loss in a nitrogen atmosphere is essentially the same as that for the parent polymer. The conductive films where silver is concentrated at the surface are degraded more rapidly than the nonconductive films as would be expected since the conducting films have continuously exposed silver clusters to activate molecular oxygen. For analogous AgHFA films of earlier work,[20] which could not be made conductive under the conditions studied herein for the TFA films and, therefore, most reasonably have a more substantial surface polymer layer protecting the silver particles, the 10% weight loss temperatures are all higher (361−376 °C) for films ranging in silver from 2.5 to 17.9%.

The linear coefficients of thermal expansion (CTE) for the 10.6, 13.3, and 12.0 % AgTFA films of Table 1 are 33.1, 27.7, 35.5, and 35.3 ppm/°C, respectively. These are much lower than the CTE for the parent polymer at 42.8 ppm/°C and than those observed in the analogous AgHFA films at 42.7, 43.6, and 42.8 ppm/°C for 5.0, 7.4, and 9.9% silver,[19a] respectively. 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, and the CTE of metallic silver is 19 ppm/°C. It is also possible that there is metallic promoted cross-linking of the polymer which is giving a lowered CTE, although we do not see any large increase in $T_g$ values as might be expected for cross-linked films.[36] Nonetheless, the CTE values for the AgTFA metallized films which are conductive are significantly lower than the parent polymer and nonconductive AgHFA films.

**Conclusions.** The use of the (trifluoroacetylacetonato)silver(I) complex, prepared in situ from silver(I) acetate and trifluoroacetylacetone, with proper control of concentration and cure temperatures gives flexible silver surface metallized films which are conductive and exhibit modest reflectivity. The reflectivity of the conductive films can be increased to >80% with only very light polishing which removes a very minimal superficial layer of metal particles. The surface layer of silver is strongly adhered to the polymer, presumably held in place by an interlocking mechanism arising from the substantial fraction of polymer that remains at the metallized surface as determined by XPS. It is now clear that the morphology and properties of in situ self-metallized silver films are a subtle phenomenon which is strongly dependent on the nature of the silver(I) species which is dispersed in the initial polymer solution from which films are cast. Thus, it is possible to obtain metallized films where both surface conductivity and reflectivity can be controlled. Further optimization of both conductivity and reflectivity in polyimide and other polymers will be described in subsequent publications.

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