

Latent Synthesis of Electrically Conductive Surface-Silvered Polyimide Films

Luke M. Davis,^{*,†} Christopher J. Abelt,[†] Joseph L. Scott,[‡] Evguenia Orlova,[‡] and David W. Thompson^{*,†}

Departments of Chemistry and Biology, The College of William and Mary, Williamsburg, Virginia 23187

ABSTRACT A facile ambient temperature route to the fabrication of surface silver-metallized polyimide films is described. Silver(I) trifluoromethanesulfonate or silver(I) nitrate and a polyimide, derived from 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and an equimolar amount of 4,4'-oxydianiline and 3,5-diaminobenzoic acid, were dissolved together in dimethylacetamide. Silver(I)-doped films were prepared at thicknesses of 25–40 μm and depleted of solvent by evaporation at ambient temperature and low humidity. The silver(I)-ion-containing films were then treated with aqueous solutions of the reducing agents hydrazine hydrate and hydroxylamine, which brought forth surface-silvered films exhibiting conductivity on the order of bulk polycrystalline silver accompanied by modest-to-high specular reflectivity.

KEYWORDS: silver • polyimide • nanoparticles • hydrazine • hybrid material

INTRODUCTION

The formation of thin metal films on a dielectric polyimide base and the chemistry and physics of the resultant metal–polyimide interfacial region continue as active areas of research (1–12). The persistent technique for producing metal surfaces on polymers is physical vapor deposition. While vapor deposition with active metals such as aluminum and chromium is effective and convenient for fabricating metallized polyimide composite structures with good metal–polymer adhesion, deposition of more passive metals such as silver, gold, and copper is problematic because of adhesive failure at the metal–organic interface (7). Herein we disclose an innovative metal–polyimide fabrication route, leading to silvered polyimide films that possess unflinching adhesion of metal to polymer, metal-like electrical conductivity, and, at times, high specular reflectivity.

Recently, in the polyimide domain, attention has focused on the use of fluorinated polyimides as materials for electrical and electro-optical devices (13–20), often having metallic phases coupled with the polyimide (1, 2, 21–29). Fluorine-containing polyimides possess several enhanced properties relative to traditional polyimides (e.g., Kapton, Upilex R and S, and Ultem), including fully imidized as well as amic acid forms that are soluble in organic solvents, lower dielectric constants, lower moisture absorption, and such marked transparency in the visible region of the electromagnetic spectrum that fluorinated polyimides are often referred to as “colorless” polyimides (30). Fluorinated polyimides retain the excellent thermo-oxidative and chemical stability of traditional polyimides. Unfortunately, the adhesion of vapor

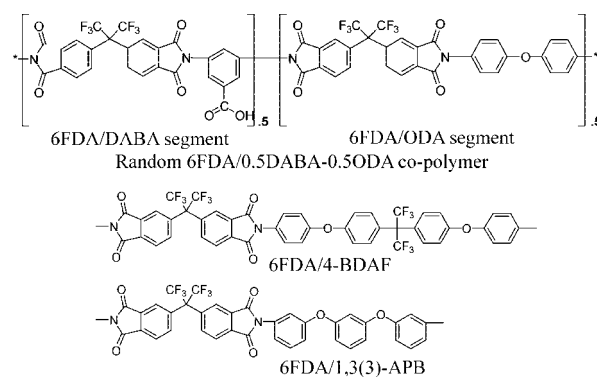


FIGURE 1. Selected polymer structures.

deposited or electrolessly deposited passive metals to fluorinated polyimides, even more so than with traditional polyimides, remains a serious problem (3, 4, 6, 7, 11, 12, 31, 32).

As an alternative approach to vapor deposition of passive metals onto fluorinated polyimides, we reported previously a single-stage, thermally promoted chemical reduction route to the surface-silvered fluorinated polyimides 6FDA/4-BDAF and 6FDA/1,3(3)-APB (1, 2). (See Figure 1 for structures.) The protocol involves (1) dissolving a silver(I) complex with a polyimide precursor in a polar aprotic solvent such as dimethylacetamide (DMAc), (2) casting a film of the silver(I)-doped polymer solution on a glass plate, and (3) heating the solvent-depleted film in air to temperatures in the range of 250–300 °C. During thermal treatment of the metal-ion-doped film, silver(I) is reduced to the native metal, some of which selectively aggregates at the air side of the curing silver–polymer film. Disappointingly, all of the visually metallized films, even those having high reflectivities, were not electrically conductive. This absence of electrical conductivity is due to the fact that the surface contains well-formed nanoparticles of silver that are not in contact,

* To whom correspondence should be addressed. E-mail: dwthom@wm.edu.
Received for review August 27, 2008 and accepted October 27, 2008

[†] Department of Chemistry.

[‡] Department of Biology.

DOI: 10.1021/am800023b

© 2009 American Chemical Society

essential for electrical conductivity, but are sufficiently close to give significant reflectivity.

With the inadequacy of our thermal approach for producing conductive metallized films on fully imidized polymers, we sought a new methodology taking place at ambient temperatures to give conductive metal surfaces with strong adhesion. It is such a fabrication route that we now describe. The work presented herein has the potential for the straightforward fabrication of (1) metallic electrical circuits on dielectric platforms by ink-jet and etching procedures, (2) metallic antennae on and embedded in dielectric materials, (3) metallic coatings for electromagnetic shielding, and (4) anti-infective coatings. Strikingly, the path described herein does not require elevated temperature, elevated pressure, vacuum, strong acid, strong base, any other harsh environment, or sophisticated equipment. Furthermore, the resultant surface matches or exceeds that produced by any other means in combined criteria of electrical conductivity and adhesion. As such, this work represents a new dimension in the surface metallization of select polyimides.

RESULTS AND DISCUSSION

Context for the Synthesis of Surface-metallized 6FDA/0.5 DABA–0.5 ODA Polyimide Films. In our previously reported (1, 2) thermally promoted, high-temperature silver(I) reduction route to the synthesis of surface-metallized fluorinated polyimide films, 6FDA/4-BDAF and 6FDA/1,3(3)-APB (Figure 1), a silver(I) complex was dissolved either with poly(amic acid) or with the soluble polyimide form of poly(amic acid), in an aprotic polar solvent, e.g., DMAc. A cast film of either the silver(I)-doped poly(amic acid) or the silver(I)-doped, cycloimidized, parent polyimide, depleted of solvent, was then heated to 275–300 °C, which brought forth a lustrous and reflective, *but never conductive*, silver surface on a fully imidized parent form of the polymer. (In the situation of a silver(I)-doped poly(amic acid) film, thermal treatment both reduces silver(I) to metal and cycloimidizes the amidecarboxylic acid groups to the imide structure.) The completely imidized structure is the only polymer form with applied usefulness primarily because of hydrolytic instability of poly(amic acid) films. A natural question that arises for a soluble, fully imidized, and ultimately useful form of a polyimide is whether such polyimides, when doped with silver(I) and depleted of solvent, might be more expeditiously metallized to give an electrically conductive metallic surface. Specifically, could a silvered surface not be realized with relative ease and rapidity by treating the doped films with an aqueous solution (water being a nonsolvent for the polyimide) of a chemical reducing agent such as hydrazine hydrate, hydroxylamine, or sodium borohydride at ambient temperatures? The answer to this question is in the negative based on our preliminary work (33) with 6FDA/4-BDAF and 6FDA/1,3(3)-APB. For example, treatment of silver(I)-doped 6FDA/4-BDAF and 6FDA/1,3(3)-APB fully imidized films with the reducing agents just mentioned, even at concentrations of silver(I) as high as 10 wt %, results only in darkening of the silver(I)-doped films without any metallic conductivity or reflectivity. We attribute

these negative results to a lack of rapid silver(I) ion mobility in the amorphous, glassy, hydrophobic 6FDA/4-BDAF and 6FDA/1,3(3)-APB films, which then leads to the random formation of some silver(0) particles within the bulk of the polyimide rather than at the surface as the reducing species diffuses into the polyimide structure.

What might be done to improve silver(I) ion mobility so as to achieve surface metallization? With this question in mind, we thought that the inclusion of pendant, hydrophilic carboxylic acid groups along the polyimide chain would enhance the absorption of water in the polymer film, leading to modest polyimide swelling and thereby allowing for more facile silver ion migration (34, 35). This pendant carboxylic acid idea was supported by our observations (22) that the silver(I)-doped poly(amic acid) films of 6FDA/4-BDAF and 6FDA/1,3(3)-APB, each with two pendant carboxylic acid groups per repeat unit, underwent chemical reduction using dilute hydrazine hydrate in water at room temperature to give highly conductive and reflective silvered surfaces. Unfortunately, poly(amic acid) films have not found useful applications because of hydrolytic instability. Thus, only the fully imidized polyimide form is important to pursue with regard to low-temperature surface metallization. The efficacy of pendant carboxylic groups is further supported by the work of Abadie et al. (45–47) and Akamatsu et al. (48, 49). They first employed a concentrated strong base, e.g., 5 M aqueous potassium hydroxide, to hydrolyze the surface of fully imidized Kapton (PMDA/ODA) films to the potassium salt of the poly(amidecarboxylic acid) form of the polymer. Silver(I) ions from aqueous silver nitrate were then exchanged for potassium ions. A surface metallic silver layer was finally produced by chemical reduction, typically with aqueous sodium borohydride.

Furthermore, our working hypothesis focuses on the use of the fully imidized form of polyimide that was formed by *chemical* imidization rather than by thermal imidization, most particularly cycloimidization in a pyridine–acetic anhydride solution. While IR data do not show any differences between thermally and chemically imidized polyimides (36); nonetheless, ion mobility is critically dependent on the polyimide chemical and thermal history (37). This is illustrated in the observations of Manring (38) and Mazur et al. (35), where they found that ion mobility, specifically silver(I), nitrate, sodium, and borohydride ions, is extremely hindered in Kapton prepared by thermal imidization at 350 °C but facile in chemically imidized (pyridine–acetic anhydride) PMDA/ODA. They also reported that “thermally imidized PMDA/ODA swells very little” in polar solvents such as dimethylformamide and acetonitrile, while chemically imidized PMDA/ODA films “swelled by as much as 100% in [dimethylformamide] and 36% in acetonitrile.” Such swelling by polar solvents enhances ion mobility.

6FDA/0.5 DABA–0.5 ODA Polyimide. Because silver(I) dissolved in 6FDA/4-BDAF and 6FDA/1,3(3)-APB fully imidized films, containing no pendant carboxylic acid groups, did undergo at least partial reduction (indicated by only a darkening of the bulk film, a common sign of the

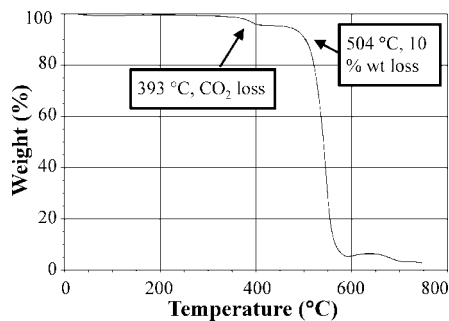


FIGURE 2. TGA of the 6FDA/0.5 ODA–0.5 DABA copolymer of this study showing 10% weight loss at temperatures above 500 °C. (Note the loss of ca. 3.5 wt % near 400 °C arising from decarboxylation of pendant carboxylic acid groups.)

solution-phase formation of disperse silver(0) nanoparticles), we thought enhancement of the silver(I) ion mobility might generate a fully metallized surface at the polyimide–aqueous reducing agent interface. To achieve such an enhancement, we chose to prepare the polyimide copolymer of the 6FDA dianhydride (1 mol) with equimolar amounts of 3,5-diaminobenzoic acid (DABA; 0.5 mol) and 4,4'-oxydianiline (ODA; 0.5 mol), which introduces a pendant carboxylic acid group via the DABA diamine component (Figure 1). The polyimides formed from 6FDA and DABA only, as well as several copolyimides of 6FDA with DABA and a second diamine, have been synthesized and characterized independently of the work reported herein and have characteristics typical of polyimide films, i.e., excellent thermal-oxidative stability, high glass transition temperatures, and excellent film-forming properties (39–43). For this work, we chose to incorporate ODA as a second diamine to maintain the mechanical properties of the copolymer near those of 6FDA/ODA, which is a recognized high-performance polyimide with excellent mechanical properties (44). The 6FDA/0.5 DABA–0.5 ODA poly(amic acid) random copolymer of this work was synthesized by a combination of 6FDA dianhydride with an equimolar quantity of the two diamines in DMAc. This poly(amic acid) was then chemically imidized in a solution of pyridine and acetic anhydride. After imidization, the solid polymer was precipitated by the addition of the pyridine–acetic anhydride solution of the polyimide to water. A cream-colored solid polyimide resulted. The glass transition temperature was measured at 326 °C by differential scanning calorimetry (DSC), intermediate to that of 6FDA/ODA at 275 °C and 6FDA/DABA at 346 °C. The thermogravimetric analysis (TGA) profile (Figure 2) of the copolyimide is completely typical of that observed for polyimides with 10% weight loss at >500 °C, with a heating rate of 10 °C/min. Cast films of the copolyimide can be tightly creased without fracture as is typical for common polyimides such as various Kaptons. These data leave no question that a polyimide of standard properties has been synthesized.

Synthesis of Surface-Metallized Films with the 6FDA/0.5 DABA–0.5 ODA Polyimide. The 6FDA/0.5 DABA–0.5 ODA fully imidized copolymer and silver(I) triflate, the latter prepared in situ from silver(I) oxide and triflic acid, were first dissolved in DMAc. After stirring for 5 min to ensure homogeneity, a latent silver ion film was cast on a glass

Table 1. Metallization of 6FDA/0.5 DABA–0.5 ODA Films (22 °C) with 4.0 wt % Silver(I) as the CF_3SO_3^- Salt^a

| aqueous reducing solution | | ammonia (aqueous) | metallization time (min) | reflectivity ^b (%) | resistivity ^c (ohm/sq) |
|-------------------------------|-------|-------------------|--------------------------|-------------------------------|-----------------------------------|
| agent | vol % | | | | |
| N ₂ H ₄ | 1.0 | none | 9.1 | 71 | 0.3 |
| N ₂ H ₄ | 0.5 | none | 13.5 | 70 | 1.6 |
| N ₂ H ₄ | 0.1 | none | 17.0 | 75 | 0.5 |
| NH ₂ OH | 1.0 | none | 6.7 | 88 | 3.9 |
| NH ₂ OH | 0.5 | none | 8.3 | 84 | 5.9 |
| NH ₂ OH | 0.1 | none | 9.5 | 88 | 2.7 |
| NH ₂ OH | 1.0 | 0.1 M | 2.3 | 73 | 4.9 |
| NH ₂ OH | 0.5 | 0.1 M | 2.8 | 72 | 5.7 |
| NH ₂ OH | 0.1 | 0.1 M | 2.5 | 61 | 5.4 |

^a Ag(CF₃SO₃) was prepared without isolation from equivalent amounts of Ag₂O and CF₃SO₃H in DMAc. The percent silver is calculated on polymer and silver only; the anion is not included.

^b Specular reflectivity relative to a Perkin-Elmer aluminum mirror with an absolute reflectivity of 0.92. ^c Surface resistivity measured via the four-point probe technique.

Table 2. Metallization of 6FDA/0.5 DABA–0.5 ODA Films (22 °C) with 8.0 wt % Silver(I) as the CF_3SO_3^- Salt^a

| aqueous reducing solution | | ammonia (aqueous) | metallization time (min) | reflectivity ^b (%) | resistivity ^c (ohm/sq) |
|-----------------------------------|-------|-------------------|--------------------------|-------------------------------|-----------------------------------|
| agent | vol % | | | | |
| NH ₂ OH | 1.0 | none | 1.6 | 44 | 0.1 |
| N ₂ H ₄ | 1.0 | none | 3.3 | 13 | 1.8 |
| CH ₃ NHNH ₂ | 1.0 | none | 15.5 | 23 | <i>d</i> |
| NH ₂ OH | 1.0 | 0.1 M | 1.1 | 49 | <0.1 |
| N ₂ H ₄ | 1.0 | 0.1 M | 2.1 | 37 | <0.1 |
| CH ₃ NHNH ₂ | 1.0 | 0.1 M | 8.6 | 6.5 | <i>d</i> |

^a Ag(CF₃SO₃) was prepared without isolation from equivalent amounts of Ag₂O and CF₃SO₃H in DMAc. The percent silver is calculated on polymer and silver only; the anion is not included.

^b Specular reflectivity relative to a Perkin-Elmer aluminum mirror with an absolute reflectivity of 0.92. ^c Surface resistivity measured via the four-point probe technique. ^d Resistivity is high, outside of the reliable four-point probe range. Two-point resistances are in the kilohm region.

plate and placed in a film box with dry air flowing through the box to evaporate DMAc. After 15 h, 96% of the solvent was lost. Subsequently, between 0.1 and 1.0 vol % of aqueous hydrazine or aqueous hydroxylamine was placed on the top of the film. Within several minutes, the silver(I)-doped films became opaque with the gradual formation of a brilliant silver mirror, which exhibits electrical conductivity in the metallic range. Equally striking is the fact that all of the silvered films prepared in this study exhibited unailing metal-to-polyimide adhesion. No silver can be dislodged by any adhesion tape tests (per ASTM D3359-08) or by rubbing of the surface with a soft polishing cloth. The results of several latent metallization experiments are summarized in Tables 1–3.

Surface Resistivity and Specular Reflectivity of Metallized Ag(CF₃SO₃)–6FDA/0.5 DABA–0.5 ODA Films. Tables 1 and 2 summarize resistivity data for the metallization of silver(I) trifluoromethanesulfonate–6FDA/0.5 DABA–0.5 ODA films using aqueous solutions of hydra-

Table 3. Metallization of 6FDA/0.5 DABA–0.5 ODA Films at 8.0 wt % Silver(I) as the NO₃⁻ Salt^a

| aqueous reducing solution | | ammonia (aqueous) | metallization time (min) | reflectivity ^b (%) | resistivity ^c (ohm/sq) |
|-----------------------------------|-------|-------------------|--------------------------|-------------------------------|-----------------------------------|
| agent | vol % | | | | |
| NH ₂ OH | 1.0 | none | 1.7 | 63 | 3.7 |
| N ₂ H ₄ | 1.0 | none | 7.5 | 63 | 2.7 |
| CH ₃ NHNH ₂ | 1.0 | none | 10.1 | 12 | <i>d</i> |
| NH ₂ OH | 1.0 | 0.1 M | 0.7 | 25 | 4.9 |
| N ₂ H ₄ | 1.0 | 0.1 M | 1.5 | 65 | 2.0 |
| CH ₃ NHNH ₂ | 1.0 | 0.1 M | 5.9 | 45 | 7.4 |

^a The percent silver is calculated on polymer and silver only; the anion is not included. ^b Specular reflectivity relative to a Perkin-Elmer aluminum mirror with an absolute reflectivity of 0.92. ^c Surface resistivity measured via the four-point probe technique. ^d No measurable conductivity.

zine hydrate and hydroxylamine. The silver concentration in the cast films (excluding solvent) was 4.0 wt % (Table 1) and 8.0 wt % (Table 2) corresponding to 0.55 and 1.1 vol % based on densities of 10.5 g/cm³ for silver and 1.45 g/cm³ (estimated) for the polyimide. The concentrations of the reducing agents ranged from 0.1 to 1.0 vol %. We chose hydrazine and hydroxylamine as reducing agents rather than the more common sodium borohydride because of the minimal byproducts of the reduction, which are dinitrogen, water, and hydronium ions.

Of note for the 4.0 and 8.0 wt % silver films are the following: (1) hydroxylamine develops a metallized surface more rapidly than hydrazine hydrate, (2) reflectivities are greatest with hydroxylamine, and (3) treatment of the films with dilute aqueous ammonia for 5 min before application of the reducing agent significantly increases the rate of formation of a metallized surface but without enhancement of either reflectivity or conductivity. Methylhydrazine is not as effective as either hydrazine or hydroxylamine. Reflectivity values are significantly higher for the 4 wt % films, which may be due to a slower and more ordered formation of the silvered surface. This was not studied in detail because the primary concern was with high conductivity.

Table 3 presents data using 8.0 wt % silver(I) nitrate rather than the trifluoromethanesulfonate salt. The differences between the polyimide films derived from the nitrate and the trifluoromethanesulfonate salts are modest, with the surface resistivities being somewhat higher for the nitrate films. Again, reflectivities are modest. We have not emphasized using the nitrate salt because it has been observed that subsequent heating of polyimides containing nitrate anions leads to substantial polymer degradation due presumably to the oxidizing character of this anion.

Figure 3 shows scanning electron micrographs (SEMs) for 4 wt % silver(I)–6FDA/0.5 DABA–0.5 ODA films reduced with 1.0% hydrazine hydrate or 1.0% hydroxylamine. The surface silver is a predominately continuous layer with something like typical grain boundary morphology, although there are some random gaps mostly on the order of tens of nanometers. While the micrographs of Figure 3 appear to show that the hydroxylamine films have a slightly denser packing of silver relative to the hydrazine hydrate films, the

latter films have a modestly lower surface resistivity. This may be due to a much larger particle size in the hydrazine hydrate films with fewer grain boundaries and a lessened probability of polyimide intervening between silver particles and grains. It appears that there is a much greater array of nanometer-sized quasi-spherical particles in the hydroxylamine-reduced film with voids having been filled by additional silver reduction. That the metal particles on the two films of Figure 3 are in virtually complete space-filling contact is supported by the fact that annealing such films up to ca. 275 °C leads to minimal lowering of the resistivity. This is consistent with the formation of a silver layer composed of polycrystalline bulk silver rather than quasi-spherical submicron particles with a substantial intervening polymer.

Figure 4 displays transmission electron micrographs (TEMs) for an 8 wt % silver film prepared with AgOTf–6FDA/0.5 DABA–0.5 ODA and reduced with 1.0 vol % hydroxylamine (Table 2). The development of the film leads to a surface silver layer with a thickness of ca. 400 nm, which is ca. 60% of that expected if all of the silver ion had migrated to the surface. Indeed, it is clear that silver nanoparticles are found in the bulk of the polyimide as well as at the surface. Work is in progress to increase the amount of surface silver by using sterically large reductants that cannot diffuse easily into the bulk of the polymer. There do not appear to be any significant quantities of silver(I) ions left in the film after reduction. After a silvered surface is produced by reduction as for the films in the tables, subsequent treatment of the reverse side of the film does not give a second, reverse-side silver layer or even any darkening of the reverse side of the film. While the inclusion of ions might have been of concern for electrical applications, we have previously shown in many publications that nanometer-sized silver particles in the bulk of polyimide films do not adversely affect mechanical properties (1, 2, 21, 22). Additionally, silver nanoparticles not in direct contact do not alter the electrical properties of polyimide films (1, 2).

Proposed Mechanism for the Formation of the Silver Surface.

Related to surface silver formation in this work are studies by Akamatsu et al. (48, 49). These authors present data for the formation of a silver surface on aqueous KOH-hydrolyzed Kapton (PMDA/ODA), opening surface and near-surface imide rings to the amidecarboxylic acid structure. The surface of a 50 μm Kapton film was hydrolyzed to the amic acid with 5 M KOH to a depth of ca. 3.3 μm. The potassium ions of the metal carboxylate salt entities of the hydrolyzed film were exchanged with silver ion using excess aqueous silver nitrate. The film was dried. Exposed as a dry substrate to UV radiation, the silver-ion-containing film did not develop a metallic silver surface. However, when water was placed on the top of the film, exposure to UV light then brought forth the formation of a surface silver layer with a bulk resistivity of 1 ohm cm. The thickness of the silver layer was ca. 80 nm. Clearly, the presence of water on the silver(I)-doped surface plays a powerful role in developing the metallic layer. On the basis

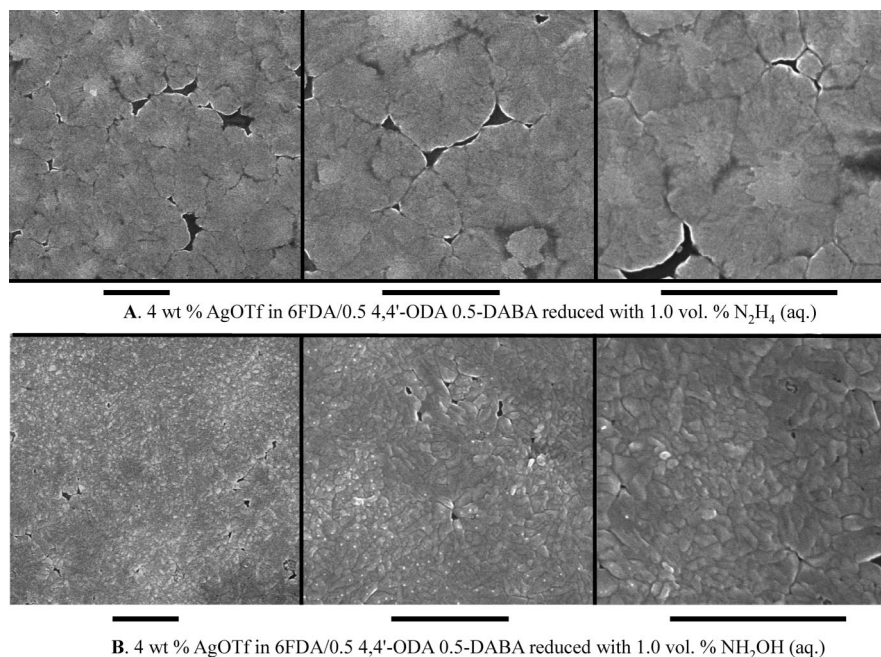


FIGURE 3. SEMs of two silvered-6FDA/0.5 ODA–0.5 DABA films prepared with hydrazine hydrate (A) and hydroxylamine (B) at 4.0 wt % silver. Scale bars are all 1000 nm.

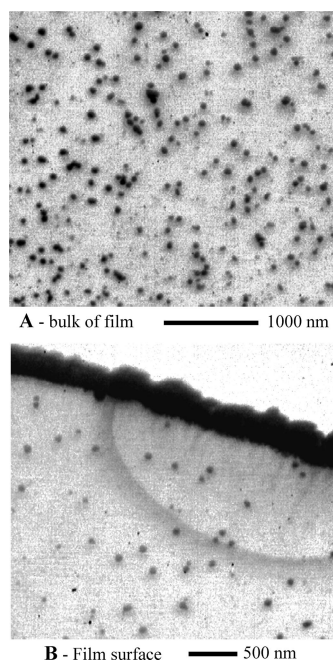


FIGURE 4. TEMs of an 8 wt % silver film prepared from 6FDA/ODA–DABA–AgOTf and reduced with 1.0 vol % hydroxylamine. Surface silver layer B is ca. 400 nm; a surface layer composed of all of the silver in the film would have been ca. 690 nm. Part A is the interior, i.e., bulk of the film.

of the calculated I/I_0 ratio for the irradiation frequency at a depth of 1000 nm of only 0.037 and the surface water requirement described above, Akamatsu et al. (49) stated, “The reduction of silver ions therefore occurs predominantly near the surface of the [KOH] modified layer at an early stage of irradiation.” That is, silver atoms and clusters do not form in the bulk of the poly(amic acid) and subsequently migrate to the surface.

In another set of studies, this time reducing similarly prepared silver(I)-doped hydrolyzed Kapton films with so-

dium borohydride, Akamatsu et al. (48) suggest a similar mechanism for chemical reduction. It was shown using glow-discharge optical emission spectroscopy that the initial silver(I)-doped poly(amide carboxylate) layer of the Kapton film had a “homogeneous” (48) distribution of silver(I) ions. After soaking of the film for 5 min in aqueous sodium borohydride, the silver “finally localized only at the top surface” (48) of the film, comprising a metallic surface. As in the photoreduced version, this was attributed to carboxylate anion-mediated migration of silver ions to the surface where chemical reduction takes place. A few silver nanoparticles were observed in the bulk of the film, ascribed to partial borohydride anion migration into the film.

On the basis of our own observations and the related studies presented above, we suggest that in the films described herein silver(I) ions migrate from the bulk of the film in significant quantity to the film surface, where they are reduced upon contact with aqueous reducing agent to form a reflective and conductive metallic surface. The TEMs of Figure 4 confirm that a considerable portion of the silver originally distributed uniformly as ions in the film does migrate to the surface during the reduction protocol. On the basis of a film surface area of ca. 225 cm², the silver present at the surface of the 8 wt % silver film in the TEM represents ca. 60% of the total silver present in the polymer. In light of this result, two possible mechanisms suggest themselves. In each case, there is no question that the reducing agent diffuses into the film because silver nanoparticles are observed in the bulk of the film. The only mechanistic question is whether the silver migrates to the surface as silver(0) atoms and clusters after reduction or as aquated silver(I) ions prior to reduction. The extensive work of Kovacs and Vincett (50, 51) and Faupel and co-workers (10) for metal vapor deposition on polymer films excludes the possibility of

silver(0) atoms and clusters migrating to the top of a film, particularly so when the metal-containing films are below the glass transition temperature. We thus conclude that the primary mechanism for silver transport to the surface is as silver(I) ions prior to reduction to silver metal, driven by the concentration gradient.

Finally, we suggest that the nearly twofold acceleration of reduction of silver(I) resulting from ca. 5 min of pretreatment with aqueous ammonia arises from two interactions. We suggest first that the carboxylic acid groups of the DABA moiety are neutralized by the basic ammonia, and ammonium carboxylate couples are formed. This gives a modest ionic structure to the polyimide film, which should enhance water absorption into the polymer structure and thus facilitate silver(I) ion mobility. Additionally, because ammonia with silver(I) forms the diamminesilver(I) complex cation, $K_f \approx 10^8$, this complex ion may migrate more rapidly than the aquated silver(I) ion because of the fact that the strongly ammine-bound silver(I) cation cannot interact as well with donor/ligand functionalities of the polymer as the weakly aquated silver(I) ion. TGA profiles of undoped 6FDA/0.5 DABA–0.5 ODA polyimide films before and after treatment with ammonia indicate that the ammonia-treated films absorb approximately 5 times more water in a 5-min soak in deionized water than do the untreated films (ca. 5% water absorption in the treated film compared to ca. 1% water absorption in the untreated film). This strongly supports the former hypothesis. The latter hypothesis remains at present merely speculation; however, silver(I)'s generally strong preference for complexation as the diammine complex cation lends some credence to this supposition.

EXPERIMENTAL SECTION

Materials. The following chemicals were purchased from Sigma-Aldrich (Milwaukee, WI) and were used without further purification: trifluoromethanesulfonic acid (98%), hydrazine monohydrate (98%), hydroxylamine (50% aqueous solution), methylhydrazine (98%), silver(I) oxide (99%), 3,5-diaminobenzoic acid (DABA; 98%), dimethylacetamide (DMAc; 99.8%, anhydrous), and pyridine ($\geq 99\%$). Acetic anhydride (ACS certified) was obtained from Fisher (Pittsburgh, PA). 2,2-Bis[3,4-dicarboxyphenyl]hexafluoropropane dianhydride (6FDA) was obtained from Hoechst Celanese (Frankfurt, Germany) and vacuum dried for 5 h at 160 °C prior to use. 2,2-Bis[4-(4-aminophenoxy)phenyl]hexafluoropropane (4-BDAF) and 4,4'-oxydianiline (ODA) were obtained from Wakayama Seika Kogyo Co., Ltd., via Chriskev Co., Inc. (Leawood, KS), and used without further treatment.

Recrystallization of DABA. DABA is soluble in hot water. However, at temperatures greater than ca. 50 °C, the diamine solution becomes black, and the resulting diamine after reprecipitation is a disconcerting green-gray in color; at times only a dark oil results. Heating the water only to 35 °C did not cause intense darkening of the solution. The diamine has limited solubility at this temperature, but the recrystallized product was an off-white color rather than greenish-gray. As an example, 10 g of DABA was added to 900 mL of deionized water. The slurry was stirred on a hot plate at 35 °C for 10 min. Not all of the crude DABA dissolved. The mixture was filtered while hot, and the filtrate was kept at 0 °C for 15 h. The recrystallized DABA was filtered and washed with 800 mL of cold water. A cream-colored solid (ca. 4 g) was isolated. The solid was dried under vacuum at 100 °C for 15 h.

Preparation of the Polyimide Form of the Copolymer Formed from 6FDA with an Equimolar Mixture of DABA and ODA. 1. Synthesis of Poly(amic acid). The polymer was formed using a 250-mL resin kettle, the top of which was equipped with a nitrogen gas inlet, a stirring rod housing with the stirring rod attached to an overhead stirrer, and a stopper. To remove water from the glassware, the kettle was heated several minutes with a heat gun with dry nitrogen gas flowing through the system. Under a slow flow of nitrogen gas, DABA (3.016 g, 198.2 mmol) and ODA (3.972 g, 198.4 mmol) were added as solids directly to the kettle. DMAc (60 mL) was then added, and the mixture of diamines was dissolved by stirring. 6FDA (17.603 g, 396.3 mmol) was then added as a solid directly to the resin kettle under a slowly flowing nitrogen stream. An additional 40 mL of DMAc was added. The final reaction mixture was then stirred at room temperature for 15 h. The flask became warm to the touch after ca. 3 min, indicating that the dianhydride–diamine reaction was proceeding.

2. Synthesis of the Polyimide Form by Chemical Imidization. The poly(amic acid) copolymer prepared above was slowly poured into a magnetically stirred solution of 150 mL of acetic anhydride and 150 mL of pyridine. This solution was heated to ca. 60 °C and stirred for 3 h. The solution was then allowed to cool to the ambient temperature. The polyimide solution was added over ca. 30 min from a dropping funnel into 500 mL of deionized water contained in a rapidly stirring blender. Periodically, cubes of ice were added to keep the temperature near ambient. The water-precipitated polyimide was vacuum-filtered and washed with 500 mL of deionized water. The final polyimide was dried at 100 °C in air and then in a vacuum oven at 150 °C for 10 h to ensure the removal of residual water, acetic acid, and pyridine. Isolated yield: 95%.

Synthesis of 6FDA/0.5 DABA–0.5 ODA Silvered Films. A 6FDA/0.5 DABA–0.5 ODA film containing 8.0 wt % silver (considering only silver metal and polyimide) is described here as illustrative of all metallized film syntheses. Silver(I) oxide (0.172 g, 0.742 mmol) was added to a 12-mL glass jar, followed by 2.0 g of DMAc, trifluoromethanesulfonic acid (0.222 g, 1.48 mmol), and finally another 2.0 g of DMAc, respectively. The reaction mixture was stirred for 15 min to form in situ the silver(I) trifluoromethanesulfonate salt (AgOTf). To this silver(I) salt solution was added 2.00 g of the fully imidized form of the 6FDA/0.5 ODA–0.5 DABA copolymer, followed by 4.0 g of additional DMAc. The resulting 20 wt % solids solution was stirred for 1 h. The silver-doped solution was cast onto a glass plate at a thickness of 0.45 mm using a doctor blade. The film was then placed in a film box for 15 h with dry air flowing through the box to evaporate DMAc. After 10.5 h in the film box, 95.9% of DMAc evaporated; after 23 h, 96.4% evaporated. The top, air side of the tack-free film was then treated in some areas with 1.0 vol % hydroxylamine and in separate areas with 1.0 vol % hydrazine monohydrate. The reducing agent solution was left on top of the film until the film became visually opaque. This qualitative assessment was standardized by describing as opaque any film through which a thick (ca. 2 mm), dark-colored line drawn on a white background could not be seen. After reaching opacity, all metallized films were rinsed thoroughly with water to remove trifluoromethanesulfonic acid, excess ions, and unreacted reductant. After the film was metallized in the manner just described, subsequent treatment of the glass side of the film did not produce a metallized or even darkened surface, verifying that most silver(I) ions have migrated to the air-side surface, with the remainder of the silver(I) ions being reduced beneath the surface within the bulk of the polyimide.

Characterization. Sheet resistivity measurements for metallized films were taken with a Lucas Signatone SYS-301 four-point probe. TEM images were acquired on a Zeiss CEM-920 instrument; samples were embedded in epoxy and cut at 100 nm. SEM images were obtained on a Hitachi S-4700 field

emission instrument. TGA was performed using a TA Instruments Q500 instrument. Reflectivity measurements were made (with respect to a Perkin-Elmer polished aluminum mirror AQ14 with a reflectivity coefficient of 0.92 at 531 nm) with a Perkin-Elmer Lambda 35 UV-vis spectrophotometer at 531 nm equipped with a variable-angle specular reflectance attachment. DSC was performed with a TA Instruments 2920 modulated DSC.

CONCLUSION

A straightforward and cogent method has been developed to fabricate silver surface-metallized 6FDA/0.5 DABA-0.5 ODA polyimide films with surface resistivities on the order of bulk polycrystalline silver. Of crucial importance, the silver film is unfailingly adhered to the base polyimide, something that cannot be achieved with physical vapor deposition of native silver onto high-performance polymers. Furthermore, no harsh conditions (e.g., high temperature, strong acid or base, and high pressure) are required to complete this process.

Acknowledgment. The authors express their gratitude to the Jeffress Memorial Trust and the Virginia Space Grant Consortium for partial support of this work.

REFERENCES AND NOTES

- Davis, L. M.; Thompson, D. S.; Dean, C. J.; Pevzner, M.; Scott, J. L.; Broadwater, S. T.; Thompson, D. W.; Southward, R. E. *J. Appl. Polym. Sci.* **2007**, *103*, 2409–2418.
- Davis, L. M.; Thompson, D. S.; Thompson, D. W.; Southward, R. E. *Polyimides Other High Temp. Polym.* **2007**, *4*, 261–286.
- Romand, M.; Charbonnier, M. *Polyimides Other High Temp. Polym.* **2007**, *4*, 287–343.
- Zhang, J.; Sullivan, M. B.; Zheng, J. W.; Loh, K. P.; Wu, P. *Chem. Mater.* **2006**, *18*, 5312–5316.
- Kuribayashi, M.; Narita, Y.; Shibata, M. *J. Appl. Polym. Sci.* **2006**, *99*, 1627–1632.
- Yang, C.-Y.; Chen, J. S.; Hsu, S. L. *C. J. Vac. Sci. Technol., A* **2005**, *23*, 862–868.
- Murday, R.; Stuckless, J. T. *J. Am. Chem. Soc.* **2003**, *125*, 3995–3998.
- Mittal, K. L., Ed. *Metallized Plastics: Fundamentals and Applied Aspects*; Brill Academic Publishers: Boston, 2001; Vol. 7.
- Mittal, K. L.; Ghosh, M. K., Eds. *Polyimides: Fundamentals and Applied Aspects*; Marcel Dekker: New York, 1996.
- Faupel, F.; Willecke, R.; Thran, A. *Mater. Sci. Eng. Rep.* **1998**, *R22*, 1–55.
- Matienzo, L. J.; Unertl, W. N. In *Polyimides: Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; pp 629–696.
- Zaporojtchenko, V.; Strunskus, T.; Behnke, K.; v. Bechtolsheim, C.; Thran, A.; Faupel, F. *Microelectron. Eng.* **2000**, *50*, 465–471.
- Sasaki, S.; Nishi, S. In *Polyimides: Fundamentals and Applications*; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996; pp 71–120.
- Miyadera, N.; Kuroda, T.; Takahashi, T.; Yamamoto, R.; Yamaguchi, M.; Yagi, S.; Koibuchi, S. *Mol. Cryst. Liq. Cryst.* **2003**, *406*, 233–243.
- Matsuura, T.; Ando, S.; Sasaki, S. *Fluoropolymers* **1999**, *2*, 305–350.
- Matsuura, T.; Ando, S.; Sasaki, S.; Yamamoto, F. *Macromolecules* **1994**, *27*, 6665–6670.
- Ando, S.; Matsuura, T.; Sasaki, S. *Polym. J.* **1997**, *29*, 69–76.
- Ando, S. F. *J. Photopolym. Sci. Technol.* **2004**, *17*, 219–232.
- Carturan, S.; Quaranta, A.; Bonafini, M.; Vomiero, A.; Maggioni, G.; Mattei, G.; de Julian Fernandez, C.; Bersani, M.; Mazzoldi, P.; Della Mea, G. F. *Eur. Phys. J., D* **2007**, *42*, 243–251.
- Cosutchi, A. I.; Hulubei, C.; Ioan, S. *J. Optoelectron. Adv. Mater.* **2007**, *9*, 975–980.
- Southward, R. E.; Pevzner, M.; Thompson, D. W. *Mater. Res. Soc. Symp. Proc.* **2003**, *775*, 193–198.
- Warner, J. D.; Pevzner, M.; Dean, C. J.; Kranbuehl, D. E.; Scott, J. L.; Broadwater, S. T.; Thompson, D. W.; Southward, R. E. *J. Mater. Chem.* **2003**, *13*, 1847–1852. Synthesis of hexafluoroisopropylidene-containing polyimide–silver nanocomposite films evolving specularly reflective metal surfaces.
- Matsuda, S.; Ando, S.; Sawada, T. *Electron. Lett.* **2001**, *37*, 706–707.
- Matsuda, S.-i.; Ando, S. *Polym. Adv. Technol.* **2003**, *14*, 458–470.
- Sawada, T.; Ando, S. *Chem. Mater.* **1998**, *10*, 3368–3378.
- Sawada, T.; Ando, S.; Sasaki, S. *Appl. Phys. Lett.* **1999**, *74*, 938–940.
- Koizumi, S.; Matsuda, S.; Ando, S. *J. Photopolym. Sci. Technol.* **2002**, *15*, 231–236.
- Matsuda, S.-i.; Yasuda, Y.; Ando, S. *Adv. Mater.* **2005**, *17*, 2221–2224.
- Quaranta, A.; Carturan, S.; Bonafini, M.; Maggioni, G.; Tonezzer, M.; Mattei, G.; de Julian Fernandez, C.; Della Mea, G.; Mazzoldi, P. *Sens. Actuators, B* **2006**, *B118*, 418–424.
- Clair, A. K. S.; Clair, T. L. S.; Slemp, W. S.; Ezzell, K. S. *NASA Tech. Mem.* **87650**, **1985**.
- Sener, U.; Entenberg, A.; Kahn, B.; Egitto, F. D.; Matienzo, L. J.; Debies, T.; Takacs, G. A. *Polyimides Other High Temp. Polym.* **2005**, *3*, 535–552.
- Rozovkis, G.; Vinkevicius, J.; Jaciauskiene, J. *J. Adhes. Sci. Technol.* **1996**, *10*, 399.
- Unpublished observations.
- Owen, J. R. *Electrochem. Sci. Technol. Polym.* **1987**, *1*, 45–46.
- Mazur, S.; Lugg, P. S.; Yarnitzky, C. *J. Electrochem. Soc.* **1987**, *134*, 346–353.
- Mazur, S.; Reich, S. *J. Phys. Chem.* **1986**, *90*, 1365–1372.
- Stone, C. D. A Study of the Morphology of PMDA-ODA Polyimide Films. Ph.D. Thesis, North Carolina State University, Raleigh, NC, 1992.
- Manring, L. E. Patterned metal interlayer in polymer matrix. U.S. Patent 4,774,157, 1988.
- Hsu, T.-C.; Chen, C.-F.; Wu, S.-S. Second order nonlinear optical polyimides having benzobisthiazole-based pendant groups, and preparation of the same. Pat. Appl. 2007001154, 2007.
- Kim, K.-J.; Park, S.-H.; So, W.-W.; Ahn, D.-J.; Moon, S.-J. *J. Membr. Sci.* **2003**, *211*, 41–49.
- Kim, J. H.; Koros, W. J.; Paul, D. R. *Polymer* **2006**, *47*, 3094–3103.
- Song, N.; Wang, Z. Y. *Macromolecules* **2003**, *36*, 5885–5890.
- Xiao, S.; Huang, R. Y. M.; Feng, X. *Polymer* **2007**, *48*, 5355–5368.
- Sroog, C. E. *Prog. Polym. Sci.* **1991**, *16*, 561–694.
- Prikhodko, O.; Kudaikulova, S.; Abadie, M. J. M. *Eurasian Chem.—Technol. J.* **2004**, *6*, 31–35.
- Kudaikulova, S.; Prikhodko, O.; Boiko, G.; Zhubanov, B.; Voyteknas, V. Y.; Abadie, M. J. M. *Polyimides Other High Temp. Polym.* **2003**, *2*, 389–406.
- Kudaikulova, S.; Boiko, G.; Zhubanov, B.; Prikhodko, O.; Voyteknas, V. Y.; Abadie, M. J. M. *Eurasian Chem.—Technol. J.* **2004**, *6*, 57–66.
- Ikeda, S.; Akamatsu, K.; Nawafune, H. *Trans. Mater. Res. Soc. Jpn.* **2003**, *28*, 1267–1270.
- Akamatsu, K.; Ikeda, S.; Nawafune, H. *Langmuir* **2003**, *19*, 10366–10371.
- Kovacs, G. J.; Vincett, P. S. *Can. J. Chem.* **1985**, *63*, 196–203.
- Kovacs, G. J.; Vincett, P. S. *J. Colloid Interface Sci.* **1982**, *90*, 335–351.

AM800023B