Preparation of Silvered Polyimide Films with Reflective and Electrically Conductive Surfaces Using Single-Stage Self-Metallization Techniques and Factors Affecting Silver Particles Migration

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ABSTRACT: Reflective and surface conductive flexible polyimide (PI) films were prepared by the incorporation of silver(I) acetate and 1,1,1-trifluoro-2,4-pentanedione into a dimethylacetamide solution of several poly(amic acid)s which were prepared from dianhydrides and diamines. Thermal curing of the silver(I)-containing poly(amino acid)s precursor led to cycloimidization of the PI with silver(I) reduction and formation of a reflective and conductive silvered surface at about 13 wt % silver. Effects on silver particles migration and aggregation were discussed in this article. The results indicated that the PI structures with flexible chains and groups easily fabricate the silvered films, with both reflective and conductive characteristics. With the forced air condition, the evaporation rate of the solvent and water increases, which facilitates the migration of silver particles to give reflective and conductive silvered surfaces. Films were characterized by transmission electron microscopy, scanning electron microscopy, and tapping-mode atomic force microscopy. Electrical conductivity, reflectivity, and dynamic mechanical thermal analysis were performed on the metallized films. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2218–2225, 2006

Key words: polyimide; films; metal–polymer complexes

INTRODUCTION

Polyimides (PIs) constitute an important class of polymers because of their excellent thermal stability, wear resistance, outstanding electric properties, radiation resistance, inertness to solvents, good adhesion properties, long-term stability, and superior mechanical properties.[1] Silvered PI films have been an active area of interest.[2] The applications include contacts in microelectronics, highly reflective thin-film concentrators/reflectors in space environments for solar thermal propulsion, for solar dynamic power generation and for X-ray imaging telescope systems, the terrestrial concentration of solar energy to generate electric power and process heat, large-scale radio frequency antennas in space, bactericidal coatings, and flexible conductive tapes.[3]

The traditional techniques used to prepare surface silvered films can be conceptualized as external deposition, involving chemical evaporate deposition (CVD), physical evaporate deposition (PVD), and plasma-assisted CVD. Because the adhesion of silver metal to PI is notoriously poor, numerous reports have appeared in the literature that investigate to deal with the problem, for example, by chemical modification procedures.[4] In 1990s, Southward's group reported a novel inverse chemical evaporate deposition (ICVD)/or *in situ* self-metallization method.[5] The reflective and/or surface-conductive PI films had been prepared by incorporation of silver(I)-diketonate complex solution into a dimethylacetamide (DMAc) solution of the poly(amic acid)s derived from dianhydrides and diamines. ICVD method is considered as the most prospect one because it has advantages of processing simplicity and outstanding adhesion at the polymer–metal interface as compared with external deposition methods. Thermal curing of the silver(I)-containing poly(amic acid)s led to both PI and reduction of silver(I) and formed a metallized surface. Some kinds of metallized PI films were fabricated with both superb electrical conductivity and excellent reflectivity on the air-side of the films.[5]

The mechanism of silver(I) reduction and factors affecting migration and aggregation are not fully

understood.[5] Not all kinds of PI-silvered films are both highly reflective and conductive. It seems that the silver complex(I), the PI structures, the processing, etc. can strongly affect the reflectivity and conductivity of the silvered PI films. Talor and coworkers[6] suggested that free-rotational structures, such as carbonyl groups in dianhydride and diamine, help to form both highly reflective and conductive silvered PI films using supercritical fluid infusion of silver methods.[7] Among many kinds of silver(I) complexes, the *in situ* formed AgTFA from silver(I) acetate and 1,1,1-trifluoro-2,4-pentanedione (HFAH) in DMAc is the favorite one because the precursor acetate salt is readily available with high purity, is thermally and photochemically stable, and the acetate anion has moderate Bronsted basicity.[3]

In our study we chose the *in situ* AgTFA complex, the carbonyl-containing 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride (BTDA), and the carbonyl-containing 4,4′-diaminobenzophenone (DABP) in an effort to produce both reflective and conductive silvered PI films by using the ICVD method. To investigate the effects of PI structures and processing condition on the reflectivity and conductivity silvered PI films, several kinds of PI with different structure and special condition were employed. These metallized PI films, with respect to reflectivity, conductivity, thermal, mechanical, and surface properties, were characterized.

EXPERIMENTAL SECTION

Materials

BTDA was obtained from Acros and dried under vacuum for 5 h at 160°C prior to use. 4,4′-DABP was purchased from Fluka and used as-received. Pyromellitic dianhydride (PMDA), *p*-phenylene diamine (PDA), and 4,4′-oxydianiline (ODA) were obtained from Shanghai research institute of synthetic resins. Both PDA and ODA were used as-received while PMDA was dried under vacuum at 160°C for 5 h prior to use. DMAc (analytical pure) was offered by Tianjin Fu Chen Chemicals Reagent Factory and dried over 5 Å molecular sieves. Silver acetate (analytically pure, ≥ 99.0%) and TFAH (≥ 98%) were purchased from Shanghai Shiyi Chemicals Reagent Co. and Acros, respectively, and used without further purification.

Preparation of metallized PI films

BTDA/DABP poly(amic acid) solution was prepared with a 1% offset of dianhydride at 15% solids (w/w) in DMAc. The resin preparation was performed by first dissolving the diamine in DMAc in a resin ket-

tle flushed with dry nitrogen and then adding the dianhydride.[3] The resin solution was stirred for 10 h. The inherent viscosity was typically 0.7–0.9 dL g^{-1} at 35°C. PMDA/ODA, BTDA/ODA, and BTDA/PDA poly(amic acid)s solutions were prepared using similar methods.

Since silver(I) acetate is not soluble in DMAc, the soluble silver salt AgTFA was prepared from silver(I) acetate and TFAH as mentioned in Southward' review.[3,5] Addition of 15% poly(amic acid) solution to the AgTFA complex solution gave a clear homogeneous light-yellow doped resin solution. This doped poly(amic acid) solution was then cast as films onto lime glass plates using a glass stick set at 500–700 μm to give cured films of 20–40 μm thickness. After remaining in an atmosphere of slowly flowing dry air (20% relative humidity) for about 20 h, the films were thermally cured in a forced air oven and in stainless vessel respectively. Curing cycles are: room temperature $\xrightarrow{20\,\text{min}}$ 130°C/60 min $\xrightarrow{240\,\text{min}}$ 300°C/420 min $\xrightarrow{20\,\text{min}}$ 320°C/240 min. The films were removed from the glass plates by immersing in distilled water for a few minutes.

Measurements

Surface electrical resistances of all films were measured with a SDY-4 four point probe (Guanzhou, China) at room temperature. Reflectivity measurements were made with a Shimadzu 2501c UV–vis light. Spectra were acquired in the 200–800 nm spectral range at an angle of incidence of 8° with a resolution of 1 nm. Transmission electron microscopy (TEM) was carried out with a H-800 type Hitachi instrument. Scanning electron microscopy (SEM) was carried out with a Britain Cambridge MK3-250; samples were coated with ∼ 5 nm of palladium–gold alloy. Tapping-mode atomic force microscopy (AFM) images were performed using a Nanoscope IIIa (Veeco Metrology Group, CA) in tapping mode in air. Mechanical properties were determined with Instron-1185 system. Glass-transition temperatures were determined with a DMTA system of RSI (Rheometric Scientific) with a heating rate of 5°C/min.

RESULTS AND DISCUSSION

Effect of curing process on reflectivity, conductivity, and surface

The silvered PI films with 13 wt % Ag were fabricated by casting the silver(I) doped poly(amic acid) solution derived from BTDA and DABP on a glass substrate. Thermal curing cycloimidizes led the poly(amic acid) to polyimide. At the same time, silver(I) reduced to silver atoms and near-atomic silver

TABLE I
Selected Data for Silvered BTDA/DABP PI Films

Sample	Curing condition (°C/h)	Reflectivity at 531 nm (%)	Surface resistivity (Ω/sq)	Film appearances	Mechanical properties	
					Strength (MPa)	Elongation (%)
1	230/0	6	NC[a]	Dark blue	–	–
2	300/5	37	NC[a]	Green white	123.4	9.2
3	320/2	50.4	32	Silver white	125.6	8.7
4	320/4	36.3	0.8	Silver white	123.3	7.0

[a] NC, nonconductive.

clusters, which diffuse and aggregate to give reflective and conductive silvered surfaces. The air-side surface of the films exhibit metallic luster and has surface conductivity. With increasing the curing temperatures and time, the appearance of the air-side surfaces of the films exhibited different colors, from light brown, dark brown, dark blue, blue, yellow green to silver white; the conductivity increased greatly, but the reflectivity increased firstly, amounted to 50.4% at 320°C for 2 h, and then decreased. Table I presented the information maintained above. The glass-side surface always displays minimal reflectivity and no conductivity. The reflective and/or conductive surfaces were formed by silver(I) reduction and Ag clusters aggregate and migrate to the surface of the films, which can be observed by TEM. TEM micrographs (Fig. 1) showed that silver particles migrated gradually to the PI surfaces of the air-sides during thermal curing. At 230°C, the film exhibited a metallic dark blue sheen, and had only minimal particles dispersed throughout the bulk PI matrix [Fig. 1(a)]. However, the trend of silver particles migrating to the airside surface had been observed. Silver particles at the near surface area are larger than those inside the PI matrix. At 300°C/0 h, TEM showed [Fig. 1(b)] that discontinuous silver layers were formed at the PI surface, but the silvered PI film was not conductive. When cured to 320°C/2 h, air-sides of the films displayed metallic luster, and the reflectivity and conductivity reached about 50% and 32 Ω/sq respectively. TEM showed that the film had a contact surface layer of silver with a thickness of about 100–200 nm at the air-side surfaces, which are consistent with the conductive film. For films cured at 320°C/4 h, the reflectivity of the silvered PI film decreased to 36.3% and conductivity increased (surface resistivity: 0.8 Ω/sq). AFM phase images (Fig. 2) showed the morphological differences between the films cured at 320°C/2 h and 320°C/4 h. For the films cured at 320°C/2 h, AFM image showed that silver particles were partially separated by PI [Fig. 2(a)]. On the other hand, very continuous silver particles had been shown at the surface of the film cured at 320°C/4 h, which ensures the lower surface resistance. AFM 3D images showed that both of them have silver islands growth on the films sur-

face. Continuous layer was formed when the silver islands are large enough to contact each other. The reason for the higher reflectivity of the film cured at 320°C/2 h is that it has relatively smoother surface than the film cured at 320°C/4 h. With increasing the thermal treatment time, the quantities of silver particles migrating to the PI film surface increase, large silver particles are formed, and the roughness of silvered PI surfaces increases too. The rough surfaces make the reflectivity of the silvered PI films decrease. However, as the large silver particles quan-
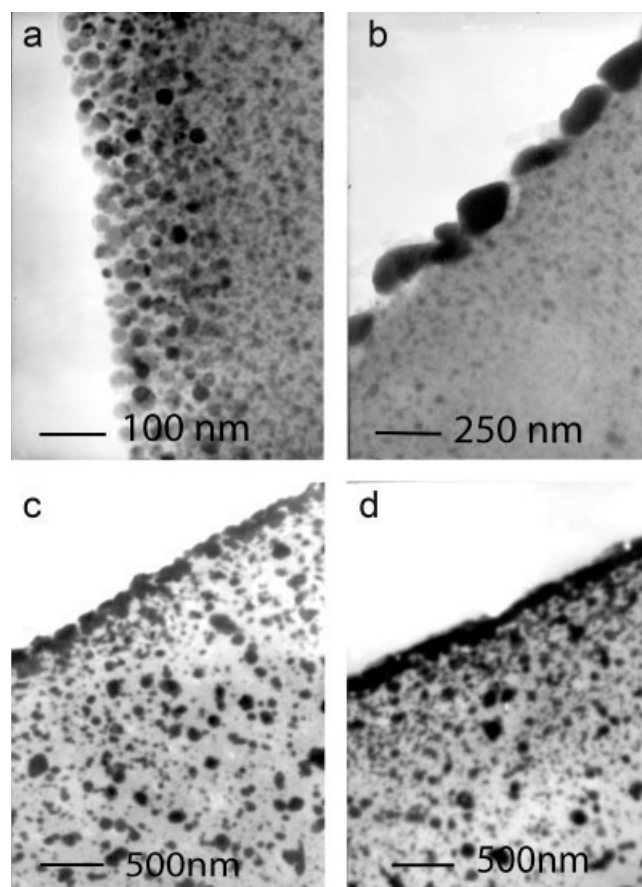

Figure 1 TEM micrographs (cross section from the metallized air-side surface down into the bulk of the film) of selected 13% AgTFA-BTDA/DABP films at different cure stages: (a) cured to 230°C for 0 h, (b) cured to 300°C for 0 h, (c) cured to 300°C for 5 h, and (d) cured to 320°C for 2 h.
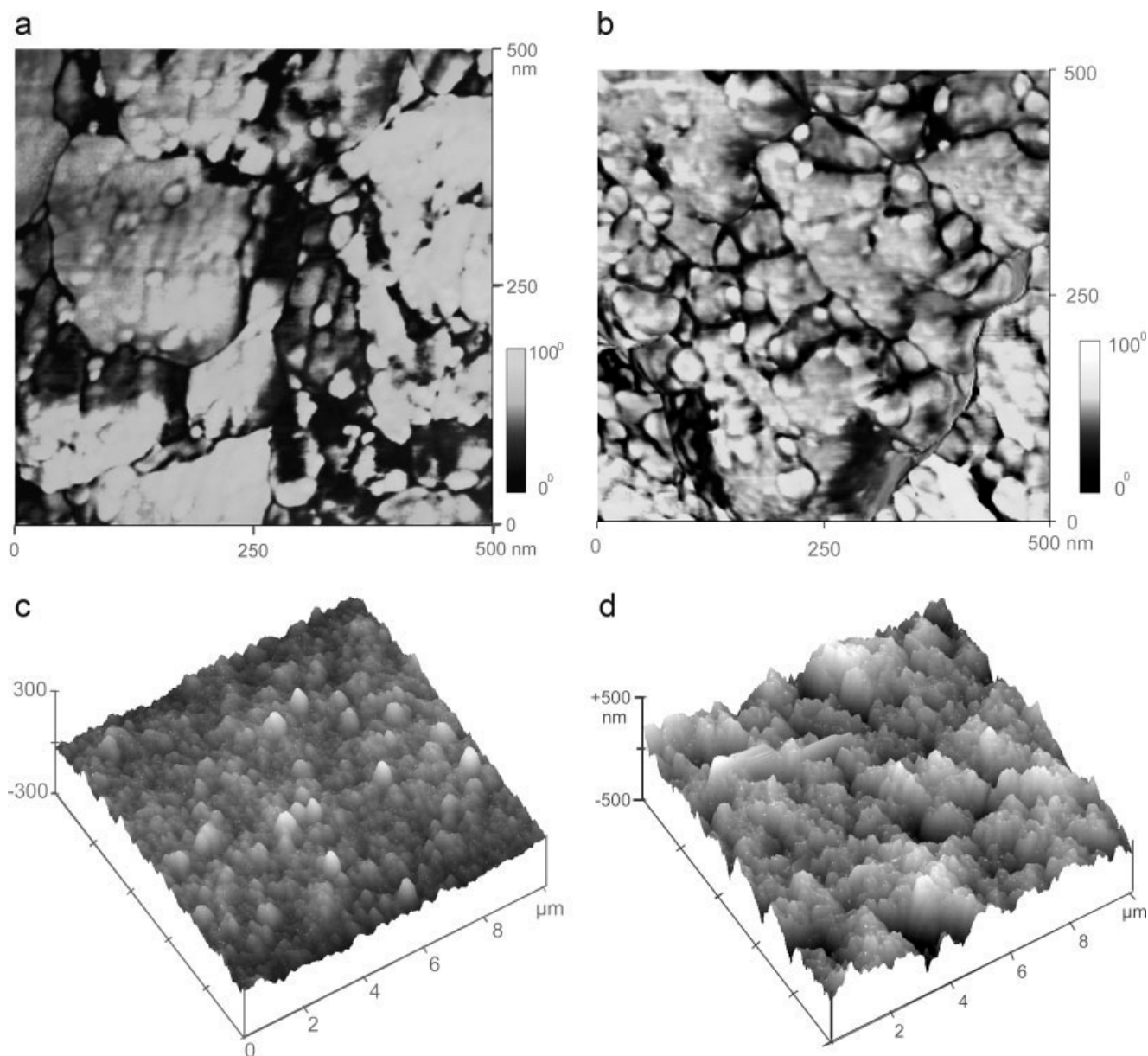
Figure 2 AFM phase images of different 13% Ag silvered PI films: (a) phase image of the films cured to 300°C for 5 h, (b) phase image of the films cured to 320°C for 2 h, (c) 3D image of the films cured to 300°C for 5 h, and (d) 3D image of the films cured to 320°C for 2 h.

tities increased at the PI surfaces, compact continuous silver layers are formed at the PI surfaces, which improve the conductivity of the PI films.

Effects of PI structures on reflectivity and conductivity of the films

To investigate the effects of PI structure on reflectivity and conductivity of the films, four kinds of PI were employed to fabricate the silvered films. The repeating units of these PIs are shown in Scheme 1. The PI films with 13 wt % Ag were made under the same curing condition. The characterizations of the films are shown in Table II. The reflectivity and conductivity of the silvered PI films depended significantly on PI structures. The BTDA/ODA and the BTDA/DABP silvered PI films all exhibited both conductivity and high reflectivity. PI structures with flexible chains and groups present the final silvered films with relatively high reflectivity and conductivity. Vibration of carbonyl and ethyl groups would prevent the silver particles from adhering with the PI matrix, which helps the silver particles migrate to the surface of the silvered PI films to produce a highly reflective and conductive surface. Similar finding has been published by Talor and coworkers.[6]
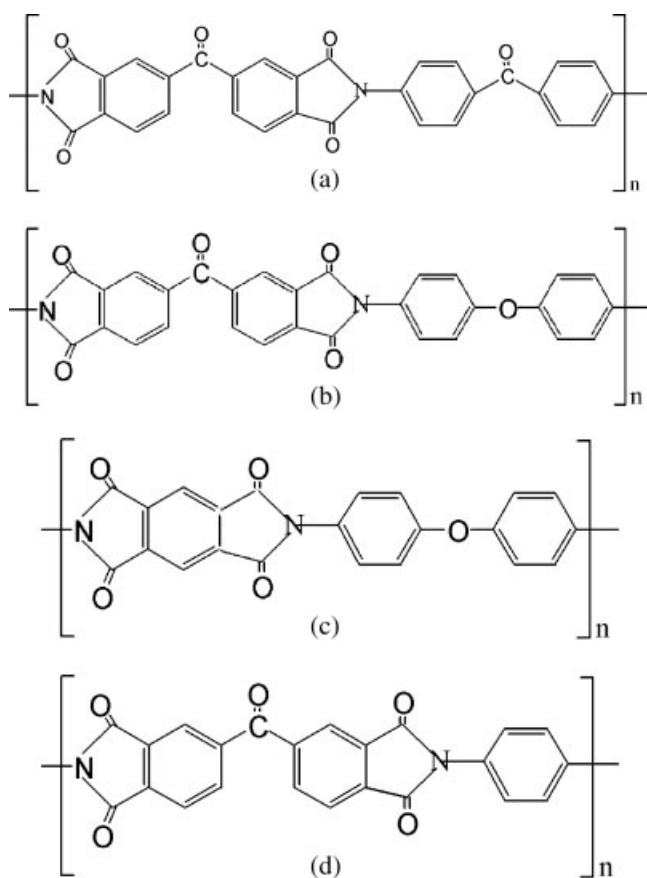
Scheme 1 Chemical structure of polyimides. (a) BTDA/DABP polyimides; (b) BTDA/ODA polyimides; (c) PMDA/ODA polyimides; and (d) BTDA/PDA polyimides.

BTDA/PDA silvered PI film showed no conductivity and useless reflectivity (6%), and presented a dark gray color. TEM (Fig. 3) showed that silver particles dispersed at the air-side films of different PIs. TEM microscopy of BTDA-ODA [Fig. 3(a)] showed that similar to the BTDA-DABP silvered films [Fig. 1(d)], these films also have a surface layer of silver that is continuous, and were ∼ 250 nm thick, consistent with the observed conductivity. However, silver layers did not form at the BTDA-PDA PI surface because of its rigid chains [Scheme 1(d)].

Mechanism of the formation of silver layer at the PI surface is probably that the silver(0) microclusters are unstable because of the high surface free-energy content and therefore they spontaneously aggregate to produce a thermodynamically stable micrometric powder.[8–10] It is a competitive process for silver atoms and near-atomic clusters to aggregate inside the PI matrix or to migrate to the PI surfaces. In most cases, the binding energy of silver particles is higher than that between silver and PI substrate; an islands growth and silver layer would form at the PI films surfaces. As PI chains move faster with the increase of curing temperature, especially when the temperature goes over the glass-transition temperature, silver(0) microclusters become very unstable in the PI matrix, and silver particles will migrate to the films surface to present the final PI film with reflective and conductive characteristics. We found that the silvered-PI exhibits reflective property only if the curing temperature is above 300°C. We suggest that for PI films with different structures different curing process should be used. The chains in BTDA/ODA PI are more flexible than those in the PMDA/ODA PI. As shown in Table II, the BTDA/ODA PI has relatively lower glass-transition temperature than that of the PMDA/ODA PI. In fact, to fabricate the silver-PI films with higher reflectivity, we always use terminal curing temperature for different PI structures, i.e., about 320°C for BTDA/DABP, about 300°C for BTDA/ODA, and about 320°C or higher for the PMDA/ODA. However, the PMDA/PDA was difficult to form both reflective and conductive silver layers because of its rigid structure; the formed silver microclusters are difficult to migrate to the PI surface.

Effects of environments and solvents on reflectivity and conductivity of the films

PI films were prepared by thermal imidization that includes depositing a poly(amic acid)s solution, drying it at room temperature, and then imidizating at temperatures from 250°C to 400°C. However, the dry poly(amic acid)s films always contain residual sol-

TABLE II
Selected Data for Different Structure of Silvered PI Films

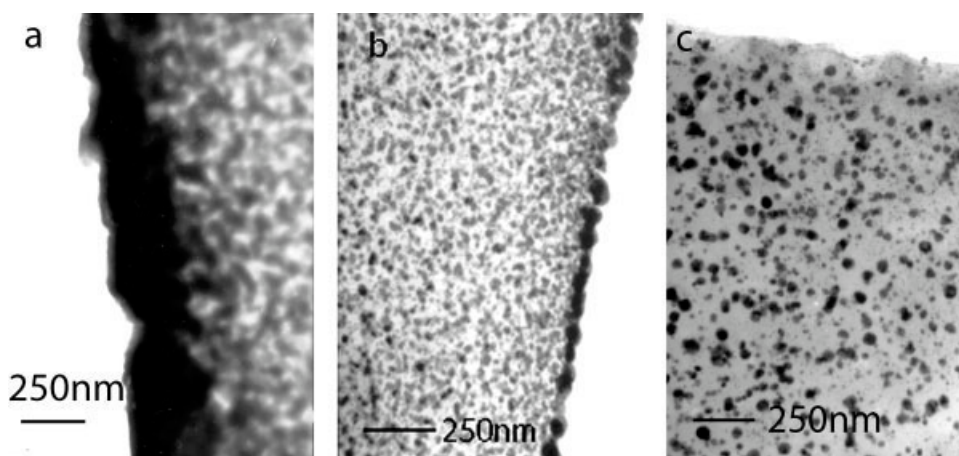| Sample	Curing condition (°C/h)	PI structure	Reflectivity at 531 nm (%)	Surface resistivity (Ω/sq)	Film appearances	T_g (°C)	Mechanical properties	
							Strength (MPa)	Elongation (%)
1	320/2	BTDA/ODA	56.3	9.8	Silver white	269	122.7	7.0
2	320/2	BTDA/DABP	50.4	32.0	Silver white	279	125.6	8.7
3	320/2	PMDA/ODA	29.5	NC[a]	Silver white	331	115.3	6.2
4	320/2	BTDA/PDA	7.0	NC[a]	Gray	–	–	–

[a] NC, nonconductive.

Figure 3 TEM micrographs of the air-side surface for 13% Ag AgTFA-different structure PIs: (a) BTDA/ODA at 320°C/2 h, (b) PMDA-ODA at 320°C/2 h, and (c) BTDA-PDA at 320°C/2 h.

vent.[11] During imidization, these residual solvent molecules evaporate together with water (the byproduct generated by imidization).

To investigate the effects of evaporation rate of solvent and water on silver particles migration, different thermal curing environments were established. We conducted the experiments by using a small stainless vessel to ensure there is no flowing air in it. The vessel has a little hole to open or close to the outside environments according to our needs. Results are shown in Table III. When the hole of the vessel was opened, the air pressure in the vessel would remain unchanged as increasing temperatures. On the other hand, when the hole was closed, it would increase as increasing temperatures because of the gas' inflation.

The evaporation rate of solvent and water may play an important role to facilitate silver particles migrating to the PI surfaces. We found that the flowing air increases evaporation rate of the solvents and waters from inside the film.

For the BTDA-DABP PI films with 13 wt % Ag, characterizations of the silvered films are shown in Table III. At the curing environment with the forced air, continuous silver layers were formed at the PI surface because the solvents and water with fast evaporation rate "push" the silver particles to the PI surfaces. The reduced near silver atoms or clusters do not have enough time to aggregate by themselves, which are easy to migrate to the PI surface. The films present with reflectivity of 50.4%. However, if forced air is not used, the silvered films had a lower reflectivity (32.1%) and are nonconductive. TEM showed that discontinuous silver layers were formed at PI film as shown in Figure 4(a). When the hole of the vessel was closed the air pressure in the vessel increased as increasing temperatures. According to the equation of ideal gas state (P1/T1 = P2/

T2),[12] as temperature is higher than 300°C, the air pressure in the vessel will be twice higher than ambient pressure. This definitely limited the evaporation rate of solvents and water in PI matrix and the silvered PI film has 12% reflectivity only. TEM showed that small amount of silver particles migrated to PI film surface [Fig. 4(b)], and most of the silver microclusters dispersed in the PI matrix. This is consistent with the observed reflectivity and conductivity.

The migration of silver particles with forced air and without forced air is different as shown in Figure 5. Without forced air, the evaporation rate of solvent or water is slow, which have little force to "push" the silver particles to the surface of PI [Fig. 5(a)]. Silver particles have enough time to agglomerate with each other to produce a thermodynamically
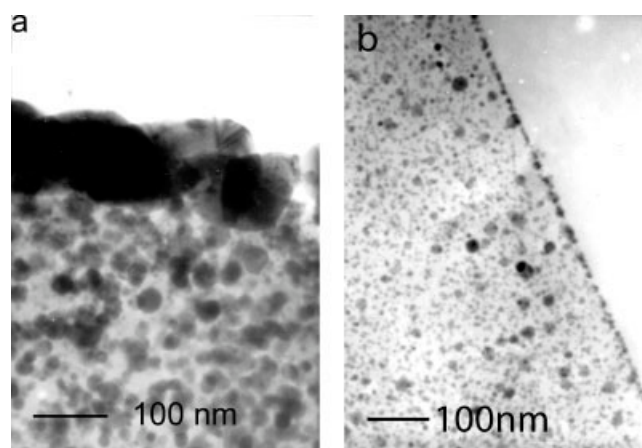

Figure 4 TEM micrographs of the air-side surface for 13% Ag BTDA-DABP PI films in calorimetric vessel: (a) 320°C/2 h with the hole open and (b) 320°C/2 h with the hole closed.

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TABLE III
Selected Data for 13% Ag BTDA-DABP/Ag Films Cured at Different Environments

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Sample	Curing environments	Reflectivity (%)	Surface resistivity (Ω/sq)	Films appearances	Mechanical properties	
					Strength (MPa)	Elongation (%)
1	In oven with forced air	50.4	32	Silver white	125.6	8.7
2	In vessel with valve open	32.1	NC[a]	Green white	126.2	6.9
3	In vessel with valve closed	12	NC[a]	Dark blue	129.6	7.9

[a] NC, nonconductive.

stable silver clusters inside the PI matrix. Because of the constraint of PI chains, larger silver clusters are very difficult to migrate to the PI surfaces.

On the other hand, with the forced air [Fig. 5(b)], the solvent and water are easily removed away by the blowing forced air, their evaporation rate increases, which had relatively stronger force to "push" the silver particles migration and to give reflective and conductive silver surfaces. It helps us to understand why silver–PI films on glass-side have small reflectivity. AFM phase image (Fig. 3) also revealed that silver particles were embedded in the PI matrix or covered by the PI, which ensured excellent adhesive properties between silver particles and PI. All the films described in Tables I–III have strongly adhered surface layers and are stable to removal of Ag by a variety of adhesive tapes as per the standard ASTM test. Soaking the composite film in water did not lead to delamination. A significant contribution may involve mechanical interlocking.

CONCLUSION

We have demonstrated that several kinds of silvered PI films can be prepared from single-phase homogeneous silver(I)-diketonate-poly(amic acid)s solutions cast on glass plates. Thermal curing had not only cycloimidized the poly(amic acid) into PI, but also reduced silver ions to silver atoms and near-atomic silver clusters, which diffused and aggregated to give reflective and conductive surfaces without the addition of reducing agents. In forced air curing environment, the metallized PI films with 13 wt % Ag can be fabricated with reflectivity, surface conductivity, and outstanding metal–polymer adhesion. Not all PI structures are effective for PI metallization. The PI structures with flexible chains and groups easily fabricate the silvered films, with both reflective and conductive characteristics. Solvents, waters, and flowing air facilitate the migration of silver particles to the PI surfaces.
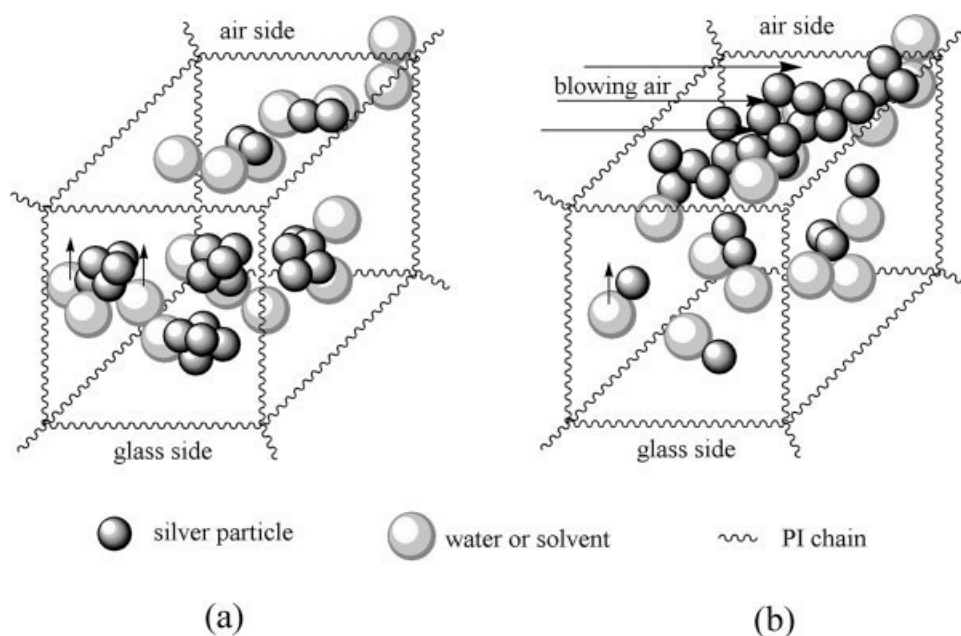

Figure 5 Models of silver particles migration process in PI matrix at different environments: (a) in without air flowing environment and (b) in air flowing environment.

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