Chem. Mater. **2007,** *19,* 393−401

Double-Surface-Silvered Polyimide Films Prepared via a Direct Ion-Exchange Self-Metallization Process

Shengli Qi, Zhanpeng Wu, Dezhen Wu,* Wencai Wang, and Riguang Jin

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

Received August 26, 2006. Revised Manuscript Received November 13, 2006

Silver metallized polyimide films have been fabricated with excellent reflectivity and conductivity on both sides via a direct ion-exchange self-metallization technique utilizing 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride/4,4′-oxidianiline (BTDA/4,4′-ODA)-based poly(amic acid) (PAA) films as the polyimide precursor and aqueous silver nitrate ($AgNO_3$) solution as the silver origin. Silver polyamate was formed during the ion-exchange process. Heat treatment of the silver(I)-containing precursor films effects the cyclization of PAA and the simultaneous reduction of silver(I), giving silvered polyimide films. Surface reflectivity and conductivity were developed as a function of cure time and temperature and they were greatly associated with the variation of surface morphology. Property differences were exhibited on the upside and underside of the composite films. The final metallized BTDA/4,4′-ODA polyimide films maintained the essential mechanical and thermal stability of the pristine polyimide films. Films were characterized by FTIR-ATR, ICP, DSC, CA, XPS, XRD, and SEM, as well as reflectivity and conductivity measurements.

1. Introduction

Polyimides (PIs) are a class of polymers that meet many of the requirements necessary for polymers used in the aerospace and electronics applications, as they are generally characterized by excellent thermal, electronic, and mechanical properties.[1−5] Silver is the optimum metal in optics and microelectronics industries because it has an unmatched reflection coefficient (0.93) and the highest electrical conductivity in all metals ($6.3 \times 10^7 (\Omega\ m)^{-1}$).[6] Their ideal collaboration would produce optically reflective and electrically conductive polyimide−silver composite materials with undiminished thermal and mechanical properties similar to those of the host polyimide. The current widespread interest in the silver-metallized polyimide materials is driven largely by their potential applications in printed circuit board (PCB),[7] magnetic data storage,[7,8] highly active catalysis,[9,10] optical switches,[10,11] contact devices in microelectronics, highly reflective thin film reflectors and concentrators in space environments for solar thermal propulsion, large-scale radiofrequency antenna for space applications, and “adaptive” and “elastomeric” optics.[6,8,12−15]

Conventional approaches to this metallized film mainly focus on the external deposition process, including physical vapor deposition as vacuum evaporation and sputtering, chemical vapor deposition, plasma and deposition, electrodeposition, electroplating, and electrolessplating.[6,12,16,17] Metallization of polymeric films by these standard deposition techniques, however, is usually labor intensive and not always amenable for polymeric supports, because distortion or decomposition would always occur, as the films cannot bear the high temperatures employed to reductively decompose the metal precursors to native metal.[12,13] The major problem is the poorly adhered silver layer on the underlying polymer.

Boggess et al.[18] and Rosolovsky et al.[19] reported in 1997 that reflective polyimide films with silver surfaces could be prepared by supercritical fluid (SCF) impregnation with supercritical CO_2 as the carrier and subsequent thermal reduction of the incorporated silver complex within the

---

* Corresponding author. Tel: 86-6442-1693. Fax: 86-6442-1693. E-mail: wdz@mail.buct.edu.cn.

(1) Stoffel, N. C.; Hsieh, M.; Chandra, S.; Kramer, E. J. *Chem. Mater.* **1996**, *8*, 1035.

(2) Huang, X. D.; Bhangale, S. M.; Moran, P. M.; Yakovlev, N. L.; Pan, J. *Polym. Int.* **2003**, *52*, 1064.

(3) Liaw, D.-J.; Hsu, P.-N.; Chen, W.-H.; Lin, S.-L. *Macromolecules* **2002**, *35*, 4669.

(4) Acar, H. Y.; Ostrowski, C.; Mathias, L. J. In *Polyimides and Other High Temperature Polymers: Syntheis,Characterization and Applications*, 1st ed.; Mittal, K. L.; VSP: Ridderkerk, The Netherlands, 2001; Vol. 1, p 3.

(5) Lee, K.-W.; Kowalczyk, S. P.; Shaw, J. M. *Langmuir* **1991**, *7*, 2450.

(6) Southward, R. E.; Stoakley, D. M. *Prog. Org. Coat.* **2001**, *41*, 99.

(7) Akamatsu, K.; Ikeda, S.; Nawafune, H. *Langmuir* **2003**, *19*, 10366.

(8) Huang, J.-c.; Qian, X.-f.; Yin, J.; Zhu, Z.-k.; Xu, H.-j. *Mater. Chem. Phys.* **2001**, *69*, 172.

(9) Li, Y.; Lu, Q.; Qian, X.; Zhu, Z.; Yin, J. *Appl. Surf. Sci.* **2004**, *233*, 299.

(10) Andreescu, D.; Wanekaya, A. K.; Sadik, O. A.; Wang, J. *Langmuir* **2005**, *21*, 6891.

(11) Beecroft, L. L.; Ober, C. K. *Chem. Mater.* **1997**, *9*, 1302.

(12) Rifai, S.; Breen, C. A.; Solis, D. J.; Swager, T. M. *Chem. Mater.* **2006**, *18*, 21.

(13) Southward, R. E.; Thompson, D. W. *Mater. Des.* **2001**, *22*, 565.

(14) Bai, Z.; Chen, M. Y.; Tan, S. C. *Polym. Prepr.* **2002**, *43*, 1277.

(15) Southward, R. E.; Thompson, D. W. *Adv. Mater.* **1999**, *11* (12), 1043.

(16) Tian, M.; Wang, J.; Kurtz, J.; Mallouk, T. E.; Chan, M. H. W. *Nano Lett.* **2003**, *3* (7), 919.

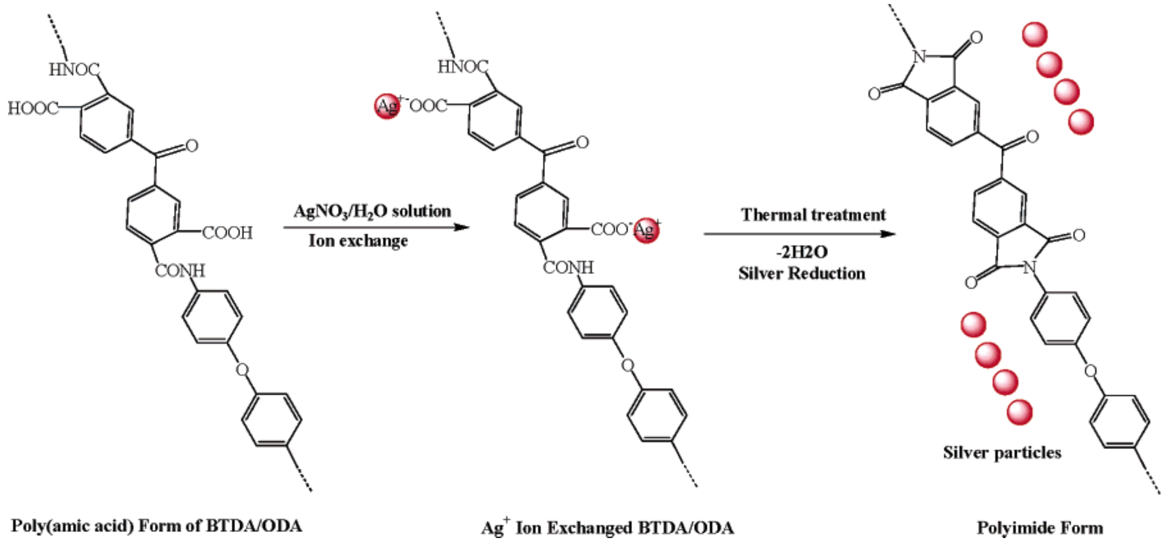
(17) Ward, L. J.; Schofield, W. C. E.; Badyal, J. P. S. *Chem. Mater.* **2003**, *15*, 1466.

(18) Boggess, R. K.; Taylor, L. T.; Stoakley, D. M.; Clari, A. K. S. *J. Appl. Polym. Sci.* **1997**, *64*, 1309.

(19) Rosolovsky, J.; Boggess, R. K.; Rubia, A. F.; Taylor, L. T.; Stoakley, D. M.; Clair, A. K. S. *J. Mater. Res.* **1997**, *12* (11), 3127.

10.1021/cm062016f CCC: $37.00

Scheme 1. Schematic Representation for the Preparation of Double-Surface-Silvered Polyimide Films via a Direct Ion-Exchange Self-Metallization Process



polyimide matrix. It is reported that the resulting films were prepared with highly reflective (max. 67.1%) silver surfaces on all sides and strong adhesion at the silver−substrate interface. However, successes was achieved only in polyimide films with a ketonic carbonyl group in either the dianhydride and/or the diamine function. It is disappointing that no electrical conductivity was observed. Meanwhile, the selectable silver additives were considerably limited and only one silver dimmer could be employed now. Furthermore, the high pressure (ca. 5000 psi) during experimental operation may be a little more dangerous. Consequently, the SCF technique was not widely investigated in this area.

Because these methods have limitations, an in situ single-stage, internal, self-metallization technique has been proposed and steadily developed by Southward,[6] Rubia and Taylor,[20,21] Warner,[22] Matsuda,[23] and Sawada[24] because of its processing simplicity and outstanding adhesion at the polymer−metal interface. It refers to develop a metallized film from a single homogeneous solution that contains both an organometallic silver complex and the desired polyimide precursor. Thermal treatment of the cast film converts the precursor into the final polyimide form with concomitant silver reduction yielding a reflective and/or conductive silvered polyimide film.

Typical representative research has been reviewed in the literature.[6,13,15] The most optimum films have been realized on the 3,3′,4,4′-benzophenonetetracarboxylic acid dianhydride/4,4′-oxidianiline (BTDA/ODA)-[25] and 3,3′,4,4′-biphenyltetracarboxylic dianhydride/4,4′-oxidianiline (BPDA/ODA)-based[26] polyimide matrices using (1,1,1-trifluoroacetylacetonato) silver(I) (AgTFA) as silver precursor, for which a maximum reflectivity greater than 97% and surface resistivity less than 0.1 Ω/sq were achieved. However, the silver precursor employed was dramatically expensive relative to simple silver salts. Meanwhile, it is unstable and requires fresh preparation. What is more, silver metallization was only realized on the air side of the film. Neither reflectivity nor conductivity was observed on the glass side. Early studies once mainly focused on simple silver(I) salts such as nitrates, carboxylates, organosulfonate, sulfate, tetrafluoborate, oxide, and trimethylphosphineiodosilver(I).[6] Only very limited success was realized; reflectivities were 18−46% on the air side for the best films, and only a few films exhibited surface conductivity. Particularly, films formed with silver nitrate were often brittle and seriously degraded without any mechanical usefulness.[27]

Here, we attempt to prepare a double-surface-silvered polyimide film using a simple silver salt, silver nitrate ($AgNO_3$), via a novel direct ion-exchange self-metallization process. The chemistry involved in the film metallization procedure reported herein closely resembles the in situ self-metallization process mentioned above, but has a distinct silver-adding protocol and a different thermal cure mode; that is, the silver(I) is added via ion exchange of damp-dry PAA films with an aqueous silver nitrate solution, and the film is then cured under tension.[28] The synthetic protocol is illustrated in Scheme 1.

A BTDA/ODA-based polyimide was chosen in our present work because outstanding surface properties have been achieved on this matrix in the in situ self-metallization process. Silver nitrate was selected because it has the best water solubility among simple silver salts and a modest cost. Characterization data suggest that double-surface-silvered polyimide films were obtained with high reflectivity and

---

(20) Rubira, A. F.; Rancourt, J. D.; Taylor, L. T. In *Metal-Containing Polymeric Materials*; Carraher, C. E., Jr., Culbertson, B. M., Pittman, C. U., Jr., Sheats, J. E., Zeldin, M., Eds.; Springer: New York, 1996; p 357.

(21) Rubira, A. F.; Rancourt, J. D.; Taylor, L. T.; Stoakley, D. M.; Clair, A. K. S. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35* (4), 621.

(22) 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* (7), 1847.

(23) Matsuda, S.- i.; Ando, S. *Polym. Adv. Technol.* **2003**, *14*, 458.

(24) Sawada, T.; Ando, S. *Chem. Mater.* **1998**, *10*, 3368.

(25) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Clair, A. K. S. *Chem. Mater.* **1999**, *11*, 501.

(26) Southward, R. E.; Thompson, D. W. *Chem. Mater.* **2004**, *16*, 1277.

(27) Southward, R. E.; Thompson, D. S.; Thompson, D. W.; Caplan, M. L.; Clair, A. K. S. *Chem. Mater.* **1995**, *7*, 2171.

(28) Qi, S.-L.; Wu, D.-Z.; Bai, Z.-W.; Wu, Z. P.; Yang, W.-T.; Jin, R.-G. *Macromol. Rapid Commun.* **2006**, *27*, 372.

conductivity on both sides and that the essential mechanical and thermal properties of the parent films were retained. The uniqueness of this approach lies in the direct use of damp-dry PAA films to perform an ion-exchange reaction and the realization of reflective and conductive silver layers on both film surfaces.

2. Experimental Section

2.1. Materials. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Acros Organics and used without further purification. 4,4′-Oxidianiline (4,4′-ODA) was obtained from the Shanghai Research Institute of Synthetic Resins and recrystallized in ethyl acetate prior to use. Dimethylacetamide (DMAC) (analytically pure, ≤0.1% water) was purchased from Tianjin Fu Chen Chemicals Reagent Factory and used after distillation. Silver nitrate ($AgNO_3$) (analytically pure, ≥99.8% content) was produced by Beijing Chemical Works and used as received.

2.2. Preparation of the Silver-Metallized BTDA/ODA Polyimide Films. The synthesis of poly(amic acid) precursor was performed by first dissolving the 4,4′-ODA diamine in DMAC and then adding the BTDA dianhydride gradually. After being stirred at ambient temperature for 2 h, a yellow viscous resin solution was prepared with a 1% (mol/mol) offset of dianhydride at 20 wt % solid content in DMAC. The inherent viscosity was 1.62−1.81 dL g^{-1} at 35 °C. Films were then cast from the homogeneous precursor solution. However, ion exchange with aqueous $AgNO_3$ solution could not be carried out on these solvent-rich films, as white precipitate would occur when they were immersed into the water solution. It is necessary that damp-dry PAA films should be first produced by simply keeping the wet films in an atmosphere of slowly flowing dry air or a vacuum oven to evaporate most of the solvent. The damp-dry films were then peeled from the glass substrate and immerged into an aqueous silver nitrate solution to perform the ion exchange. In the present study, 40−45 μm thick damp-dry films with DMAC content in the range of 35−38% were utilized for ion exchange in a 0.4 M aqueous $AgNO_3$ solution. Absence of light is necessary during ion exchange, because silver nitrate aqueous solution is sensitive to photolysis. Following ion exchange, the PAA−silver(I) films were rinsed with distilled water and then thermally cured under tension in a forced-air oven.

The cure cycles employed are heating over 1 h to 135 °C and holding for 1 h, heating to 300 °C over 2 h, and remaining constant at 300 °C. Thermal curing induced cycloimidization of the PAA precursor to the polyimide form and silver reduction of silver(I) to native silver, giving metallized surfaces as illustrated in Scheme 1. Surface properties on the upside and underside were investigated. For clarity, the surface of the damp-dry PAA film in contact with the glass substrate is referred to as the underside, whereas that exposed to the atmosphere is referred to as the upside.

2.3. Film Characterization. The incorporation of silver ions within the PAA films was quantified by a Seiko Instruments SPS 8000 inductively coupled plasma (ICP) atomic emission spectrometer. The measurements were performed after the ion-exchanged PAA films were dissolved in a 5 wt % nitric acid solution. The silver content was calculated using the solvent-containing damp-dry PAA as the base.

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the films were collected using the Nicolet Nexus670 IR spectrometer. Contact-angle measurements were performed on both sides of the films using an OCA contact-angle system (Data Physics Instruments GmbH) with an input power of 55 W.

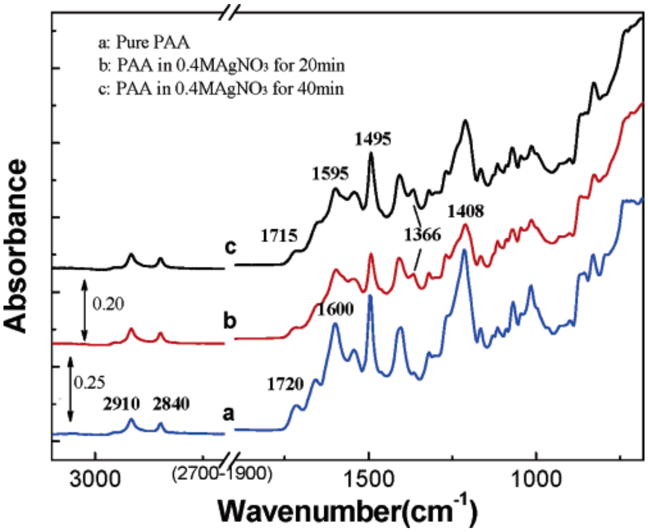


Figure 1. FTIR-ATR spectra for the pure PAA film and silver(I)-containing PAA films with different ion-exchange times. (The measurements were performed on the underside of the film).

Reflectivity spectra (relative to a $BaSO_4$ mirror set at 100% reflectivity) were scanned on a Shimazu 2501PC UV/VIS spectrophotometer with an incidence angle of 8° in the 200−800 nm wavelength range. The values at 531 nm were selected to represent the film's reflectance in the visible light region. Surface electrical resistivities were measured with a RTS-8 four-point probe meter produced by Guangzhou Semiconductor Material Academe in China.

Samples used for surface morphology observations were coated with ca. 5 nm platinum prior to measurements. The surface images were then recorded on a Hitachi S-4300 field emission scanning electron microscope (FE-SEM) operating at 15 kV.

X-ray diffraction was performed on the underside of the silvered films using an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan). The diffractograms were recorded in the 20−90° region with a scanning rate of 0.18° per second. X-ray photoelectron spectra (XPS) were collected using an Escalab 250 spectrometer (Thermo Electron Corporation) in the fixed analyzer transmission mode. The instrument is equipped with a monochromatic Al Kα X-ray source. The pressure in the analysis chamber was maintained at 2×10^{-10} mbar or lower during each measurement.

Differential scanning calorimetry (DSC) spectra were collected using a Netzsch[4] differential scanning calorimeter with a flow rate of 20 mL min^{-1} at 5 K min^{-1}. Thermal gravimetric analysis (TGA) was performed with a Netzsch[4] TG 209 system heating at 10 K min^{-1}. Mechanical properties were evaluated using an Instron-1185 system.

3. Results and Discussion

3.1. Consideration of the Ion-Exchange Process. The possible and ideal chemistry for the formation of polyimide−silver composite films have been shown in Scheme 1. It is supposed that a silver−polycarboxylate salt (silver polyamate) would be formed in situ when the damp-dry PAA films were immersed into the silver(I) aqueous solution to perform an ion-exchange process. Because PAA is thermoplastic and dissociable, the subsequent immersion into metallic aqueous solution would probably result in the polycarboxylate groups through dissociation. Consequently, in the presence of a metallic salt, the negatively charged polycarboxylate will couple to the silver cation, forming the silver polyamate.

ATR-FTIR measurements were performed on the PAA films before and after ion exchange, as shown in Figure 1. The spectra in the range of 1900−1200 cm^{-1} provide the most useful information. Absorbance bands at 1720, 1660, 1600, 1543, 1495, and 1408 cm^{-1} were displayed for the pure BTDA/ODA PAA (Figure 1a). The band at 1720 cm^{-1} is related to the carbonyl stretching vibrational mode of carboxylic acid. The peaks at 1660 and 1543 cm^{-1} are attributed to the amide I band (carbonyl stretching) and amide II band (coupling of C−N stretch and N−H deformation), respectively. The bands at 1600 and 1495 cm^{-1} are corresponding to the phenyl groups of BTDA and ODA, respectively.[5,29] Following ion exchange, as displayed in spectra b and c of Figure 1, the spectra exhibit several significant differences. The first and most important changes are the appearance of a new absorbance peak at 1366 cm^{-1} and the broadening of the band near 1600 cm^{-1}, which represent the characteristic absorption of the carboxylate symmetric and asymmetric stretching, respectively, indicating the formation of silver polyamate.[30,31]

However, these spectra changes are not so striking, and thus contact-angle measurements were conducted on the PAA films before and after ion exchange to provide further evidence for the formation of silver polyamate. Prior to ion exchange, the upside and underside of the film had water contact angles of 68 and 50°, respectively. However, they increased to 78 and 72° following ion exchange in a 0.4 M aqueous $AgNO_3$ solution for 40 min, suggesting the formation of more hydrophobic film surfaces. This is consistent with the production of silver−poly(amic acid) salt, which does not have good solubility in water, as many silver salts do.

ICP measurements indicate that silver ions incorporated within the PAA films were only 4.04 and 4.32 wt % after ion exchange in a 0.4 M aqueous $AgNO_3$ solution for 20 and 40 min, respectively. This suggests that the ion-exchange reaction occurred only partially along the polymer chains, which is considerably necessary for retaining the basic structural and physical properties of the pristine films. Unfortunately, PAA is hydrolyzable in aqueous solution because of the hydrophilic amide groups in the repeating unit. However, under the present experimental conditions, hydrolysis of the PAA matrix could not play a significant role because the overall ATR-FTIR spectra before and after ion exchange were only slightly altered and no macroscopical variations could be observed on the ion-exchanged film. The excellent mechanical properties after curing (shown later) also confirmed this expectation. However, it would be better to shorten the ion-exchange time to avoid shrinkage of the precursor polymers. In the present work, ion-exchange times no longer than 40 min were used to synthesize the silvered polyimide films.

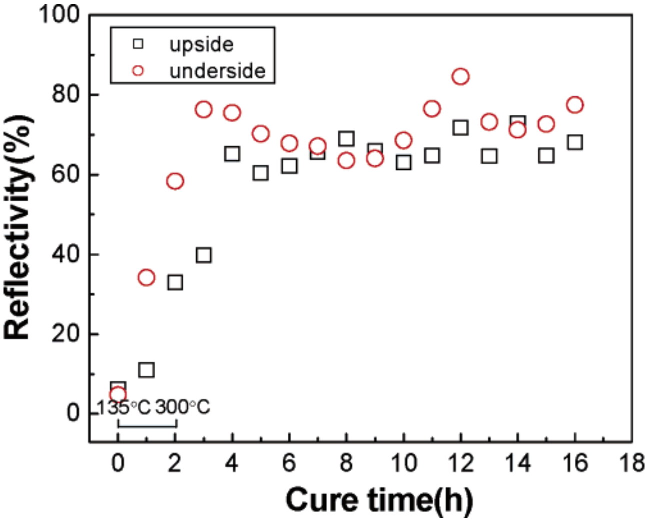


Figure 2. Plots of reflectivity vs cure time/temperature for both surfaces of the hybrid films ion-exchanged in a 0.4 M aqueous $AgNO_3$ solution for 40 min. (Time zero is at 135 °C for 1 h).

Table 1. Surface Resistivity for the 40 min Ion-Exchanged Composite Films Cured at 300 °C for Different Times

sample no. in Figure 2	cure time at 300 °C (h)	surface resistance (Ω/sq)	
		upside	underside
7	4	>1 × 10^6	>1 × 10^6
8	5	18	15
9	6	3.8	2.7
10	7	4.3	1.5
12	8	6.2	2.1
13	9	4.1	1.3
14	10	5.0	2.5
15	11	2.4	3.1
16	12	1.7	1.3
17	13	2.5	1.1

3.2. Formation of Double-Surface-Silvered Polyimide Films. Silvered polyimide films have been prepared upon heat treatment of the ion-exchanged precursor films. Thermal curing leads to cycloimidization of PAA and induces simultaneous reduction of silver ions to native metal atoms, giving a silvered polyimide film as illustrated in Scheme 1. Because the PAA films have been peeled from their glass substrate prior to ion exchange, a uniform tension must be applied to fix them during heat treatment. Otherwise, curl, shrinkage, and deformation would occur because of the thermoplastic characteristics of the uncured PAA. The employment of tension is also necessary to obtain good mechanical properties.

Surface reflectance characterization results of the metallized films are shown in Figure 2. Apparently, both film surfaces have been well-metallized after being cured at 300 °C for several hours. Optimum reflective films were achieved at 300 °C for 9 h with ca. 84% reflectivity on the upside and ca. 71% on the underside. Table 1 presents the surface resistance data for the samples in Figure 2. It is also exciting to note that surface electrical conductivity has been realized on both film surfaces at 300 °C for 5 h with values on the order of ca.15 Ω/sq. Further heat treatment at 300 °C yields more conductive film surfaces with surface resistivity less than ca. 2 Ω/sq. Films obtained at 300 °C for 9 h achieved resistances of 4.1 and 1.3 Ω/sq on the two sides. Thus, it is assumed that double-surface-silvered polyimide films with excellent reflective and conductive performances have been prepared.

Fabrication of silver-metallized polyimide films using simple silver salts, especially silver nitrate, has already been

---

(29) Pramoda, K. P.; Liu, S.; Chung, T.-S. *Macromol. Mater. Eng.* **2002**, *287*, 931.

(30) Okumura, H.; Takahagi, T.; Nagai, N.; Shingubara, S. *J. Polym. Sci., Part B: Polym. Phys.* **2003**, *41*, 2071.

(31) Thomas, R. R.; Buchwalter, S. L.; Buchwalter, L. P.; Chao, T. H. *Macromolecules* **1992**, *25*, 4559.

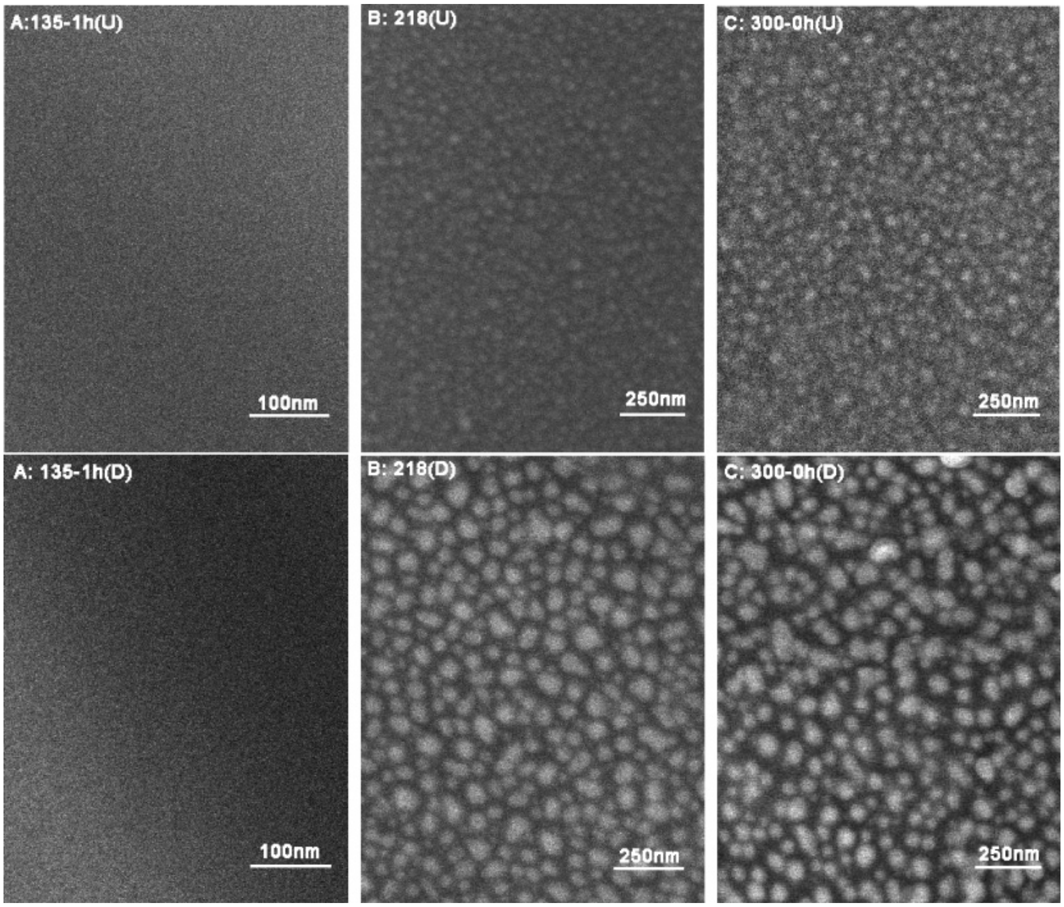


Figure 3. FE-SEM images of silvered polyimide films with an ion-exchange time of 40 min in a 0.4 M aqueous $AgNO_3$ solution and thermally treated to (A) 135 °C for 1 h, (B) 218 °C, and (C) 300 °C for 0 h. (U, upside of film; D, underside of film).

attempted by Southward et al.[27] utilizing the in situ single-stage self-metallization technique. However, a reflectivity of only 20% was observed on the air side, and no conductivity was achieved. The films prepared were often brittle and could not be removed from the casting plates without disintegrating, which was suggested to arise from the destructive effect of the nitrate radical. However, silvered polyimide films with excellent surface and mechanical properties (shown later) have been prepared in our work using the same polyimide matrix and same silver precursor.

The great success in the direct ion-exchange self-metallization process is suggested to originate from the different silver(I) adding protocol and subsequently different chemical state of silver(I) in PAA films relative to the in situ process, in which the silver nitrate was physically blended with only the precursor. Because of the absence of aqueous solvent, the silver(I) could only exist as silver nitrate complex and coordination with carboxylic acid groups could seldom occur. This makes the silver(I) reduction rather difficult, as observed for the pure crystalline silver nitrate. Meanwhile, the nitrate radicals would exist during the whole cyclization process and degrade the precursor film, gradually giving brittle films with very poor reflectivity. However, in the present method, silver ions were loaded as silver polyamate through the ion-exchange reaction. The formation of COO^-Ag^+ groups makes the reduction of silver ions much easier than that of silver nitrate, because the coordination sites at silver (I) involve the donor groups from the macromolecules. For instance, Andreescu et al.[10] has prepared PAA−silver nanoparticle membranes by thermally treating the formed silver polyamate at 105 °C. Furthermore, the adverse effect of the nitrate radical was considered to be weak because of its small content. Thus, reflective and conductive films with good mechanical properties were produced. Although the properties may not be comparable to that of the Southward's BTDA/ODA[25] (or BPDA/ODA[26])−AgTFA films, the achievement of double-surface silver metallization is advantageous.

3.3. Surface Properties and Surface Morphology of the Silvered Films. Figure 2 shows the development of reflectivity as a function of cure time/temperature for the 40 min ion-exchanged films. As thermal curing proceeds, the plots show a rapid increase in reflectivity before 300 °C. When heated at 300 °C for ca. 2 h, both surfaces provisionally reach their maxima in reflectivity. Further curing does not improve the reflectivity and inversely gives a slight decrease. Then, after heating at 300 °C for 6 h, the reflectivity goes up again and the film reached its optimum reflectivity of 71%/84% at 300 °C for 9 h. SEM measurements were performed on these films to determine the variation of surface morphology and to identify the relationship between surface properties and surface topography.

Figure 3 shows the SEM micrographs for the upside and underside surfaces of the PAA−silver(I) films cured before 300 °C. After being heated at 135 °C for 1 h (time zero in Figure 2), the silver-doped films exhibit the identical totally transparent yellow appearance of the BTDA/ODA PAA

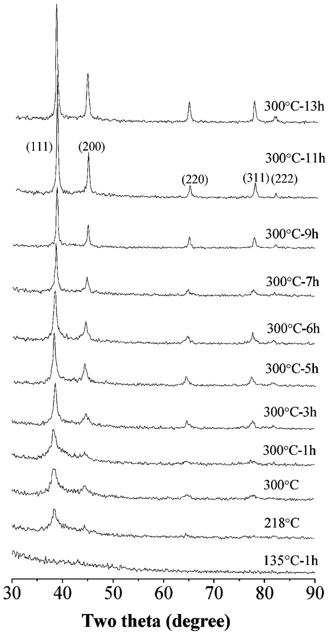


Figure 4. X-ray diffraction patterns as a function of cure time/temperature in silver 111, 200, 220, 311, and 222 regions for the 40 min ion-exchanged composite films.

films. SEM images in Figure 3A display two rather plain surfaces without any silver particles, which was consistent with the very low reflectivity. X-ray diffraction pattern in Figure 4 for the 135 °C, 1 h films also exhibits no reflections expected for the face-centered cubic (FCC) silver metal. However, reflective silver surfaces were soon formed after the temperature was raised to 218 °C or higher, as can be seen from images B and C of Figure 3. Many silver particles were present on the surface of the composite films, and there was an increasing silver coverage on the polymer surfaces with treatment time, which could reasonably explain the rapid increase in reflectivity.

Further curing the films at 300 °C results in a further increase in the number of silver particles on the film surface, as can be observed from the SEM images in Figure 5. Silver metallic luster for the composite films becomes significant after heating to 300 °C for 2 h. This indicates the formation of well-defined silver layers, which could account for the provisional maximum reflectivity. However, the slight decrease in reflectivity from 300 °C for 2 h to 300 °C for 6 h was very strange, as the agglomeration occurred significantly at this stage; well-established silver layers have been formed after 300 °C for 3 h as shown in images B and C of Figure 5. It is suggested that the formation of rough surfaces due to silver aggregation during this period could be responsible for the decrease in reflectivity.[21,32]

After 300 °C for 9 h, completely different surface topographies have been formed on the metallized films, as seen from the SEM images in Figure 6. Continuous netlike surface patterns were formed on both film surfaces, and excellent surface electrical conductivities were achieved on

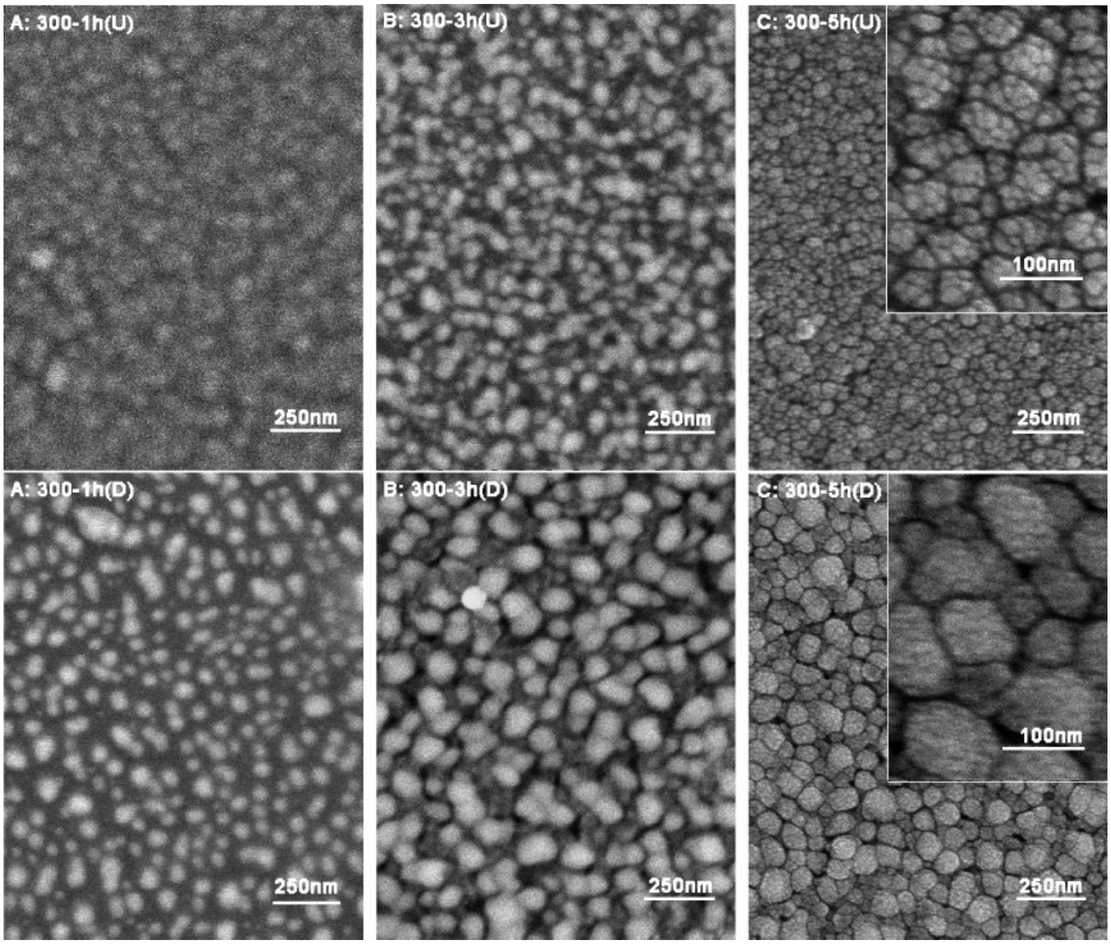


Figure 5. FE-SEM micrographs recorded for the two sides of the composite films with an ion-exchange time of 40 min in a 0.4 M aqueous $AgNO_3$ solution and thermally treated at 300 °C for (A) 1, (B) 3, and (C) 5 h. (U, upside of film; D, underside of film).

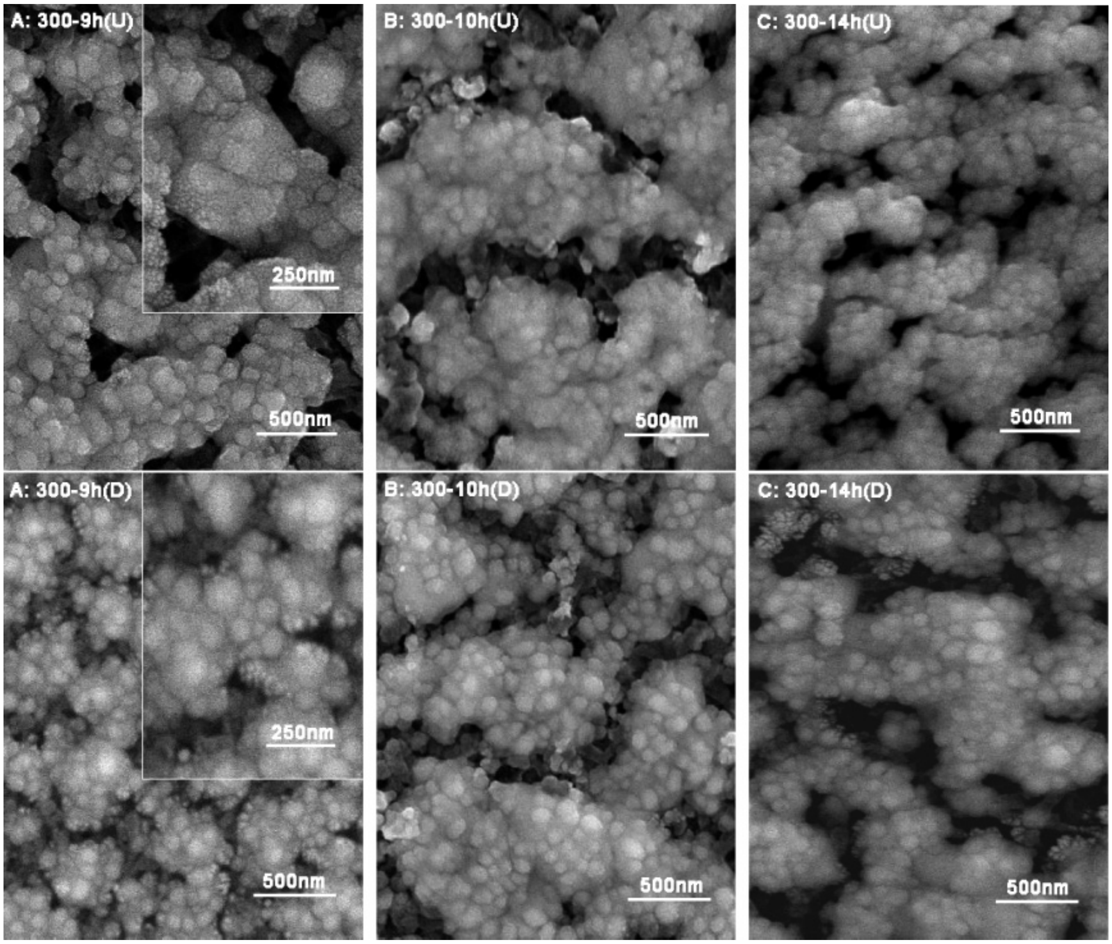


Figure 6. FE-SEM micrographs for the two surfaces of the composite films with an ion-exchange time of 40 min in a 0.4 M aqueous $AgNO_3$ solution and cured at the final stage of thermal curing cycle (at 300 °C): (A) 9, (B) 10, and (C) 14 h. (U, underside of film; D, upside of film).

Table 2. XPS Surface Composition for the Underside Surfaces of the BTDA/ODA−$AgNO_3$ Films Cured at 300 °C

thermal history of sample	relative at %		
	C(1s)	O(1s)	Ag(3d)
300 °C for 1 h	70.65	18.86	10.49
300 °C for 6 h	51.66	16.64	31.7
300 °C for 9 h	46.93	23.48	29.59
300 °C for 14 h	43.94	22.05	34.01

all the films as listed in Table 1. However, an obvious faint whitish “haze” was present on the surfaces of these finally cured films. Actually, it has appeared since the sample was treated at 300 °C for 7 h. This whitish substance was suggested to arise from the degradation of the polyimide matrix on the surface induced by the thermal catalytic and oxidative effects of silver particles. XPS data shown in Table 2 show a very low carbon concentration and a high silver concentration at this period, confirming the occurrence of this polymer decomposition. We suggest that the surface polyimide decomposition and the subsequent formation of continuous silver layers could act as a good interpretation of the further increase in film conductivity and reflectivity after heating at 300 °C for 7 h as shown in Figure 2.

3.4. Silver Aggregation. The XRD diffractograms exhibit very distinct peaks characteristic of the crystalline state for FCC silver metal from 218 °C. The average silver crystallite size before 300 °C estimated by the Scherrer equation using the full width at half-maximum (fwhm) of the strongest characteristic reflection (111) was no more than 15 nm. However, SEM images in Figure 3 show the distribution of much bigger silver particles with sizes of 30−40 and 50−65 nm on the upside and underside, respectively. This suggests distinct silver agglomeration has occurred at such an early stage of thermal cycle. Films exhibit the appearance of yellow after being treated at 135 °C for 1 h, blue at 218 °C, and grass green at 300 °C, which also confirmed the silver aggregation. The great morphology changes resulting from silver aggregation led to the dramatic increase in reflectivity before 300 °C.

Significant silver aggregations proceed continuously, as can be seen from the enlarging surface silver particles shown in Figure 5. After being heated to 300 °C for 5 h, silver particles on the film surface have achieved an average size as large as ca. 100 nm. However, these much bigger silver particles are still composed of many smaller silver nanoparticles, as can be clearly observed from the amplified images in Figure 5C. XRD patterns in Figure 4 from 300 °C for 3 h to 300 °C for 7 h show that the FWHM of the (111) reflection only slightly narrowed at this interval, indicating a very slow and limited growth of silver crystallite at such a high temperature for such a long time.

On the basis of these observations, we suppose that the formation of basic silver crystallites had already been

---

(32) Qi, S.-L.; Wu, D.-Z.; Wu, Z.-P.; Wang, W.-C.; Jin, R.-G. *Polymer* **2006**, *47*, 3150.

accomplished at the early stage of the thermal cycle (at most before 300 °C for 1 h). Further thermal treatment could perfect the crystallite but not improve the crystallite size significantly, as shown in the XRD patterns in Figure 4. The dominant behavior upon further thermal treatment at 300 °C is silver agglomeration, which is suggested to be requisite for preparing a highly reflective and conductive silver surface. That is, prior to treatment at 300 °C for 5 h (Figure 5B), silver particles are separated from each other, giving nonconductive surfaces. It is the aggregation that makes the separated silver particles stack together as shown in Figure 5C and consequently endows the film with resistances of 18 and 15 Ω/sq on the upside and underside, respectively.

Silver aggregation at the final stage occurred to such an enormous extent that silver agglomerations on the surface have already been presented in a lumpish fashion, as observed in Figure 6A−C. However, as above, these lumpish aggregations still consist of many small silver nanoparticles but with a slightly larger size. This is consistent with the obvious sharpening in XRD reflections and the appearance of five perfect peaks in Figure 4 for films cured to 300 °C for 9 h and longer, indicating a continuous growth and further perfection of the silver crystallite. DSC analysis (not shown) in air detected a strong exothermal peak near 340 °C, which is most likely attributed to the silver aggregation. It is supposed that the heat generated here would inversely accelerate the silver aggregation and more importantly, in the presence of oxygen, induce the silver-catalyzed polymer degradation to give conductive and highly reflective surfaces.[25] The optimum films were only obtained until this stage. Different from the conductive films at 300 °C for 5 h (Figure 5C), netlike silver patterns have been formed on all the films now, as in Figure 6. Thus, excellent conductivity was achieved that was due to this positive effect of silver aggregations.

3.5. Property Differences between the Two Sides. As mentioned above, double-surface-silvered polyimide films have been successfully achieved in the BTDA/ODA−aqueous $AgNO_3$ system. However, it is noteworthy to realize that properties of the two surfaces are not identical to each other during the whole thermal cycle, as can be observed from the reflectivity in Figure 2, surface resistance in Table 1, and SEM images in Figures 3, 5, and 6. It seems that the underside surfaces are always superior to the upside, especially regarding the reflectivity at the early thermal stage (Figure 2); the underside was also metallized earlier, as shown in Figure 3. These differences still exist even when the well-established silver layers have been formed, as found on the optimum film heated at 300 °C for 9 h. The UV−vis reflective spectra for this film, shown in Figure 7, suggest that the underside reflectivity is constantly higher (ca. 13% difference) than the upside in the whole visible light region.

The more compact morphologies on the underside observed in the SEM images might account for these differences. However, the occurrence of these differences is unexpected. Contact-angle measurements on the PAA films suggest that the contact angles are 68 and 50°, respectively, before ion exchange. The better wettability of the underside surface is supposed to be due to more solvent remaining in the near surface layer during the solvent evaporation process as it adheres to the glass. The contact angles increased to 78 and 72°, respectively, after ion exchange in a 0.4 M aqueous $AgNO_3$ solution for 40 min, corresponding to the formation of silver polyamate. XPS analysis indicates that the concentration of silver ions loaded on the upside was only 2.16%, which is much lower than that on the underside, with a silver atomic concentration of 4.4%. Coincidentally, the 22° increased contact angle of the underside is twice that of 10° increased upside contact angles, which might also imply a higher silver concentration on the underside. It is more likely that the better hydrophilism of the underside makes the approach and diffusion of silver ions to the carboxyl group relatively easier, allowing the loading of more silver ions into the underside surface. Consequently, the different silver(I) content in the precursor films results in great property differences on the two sides of the metallized films.

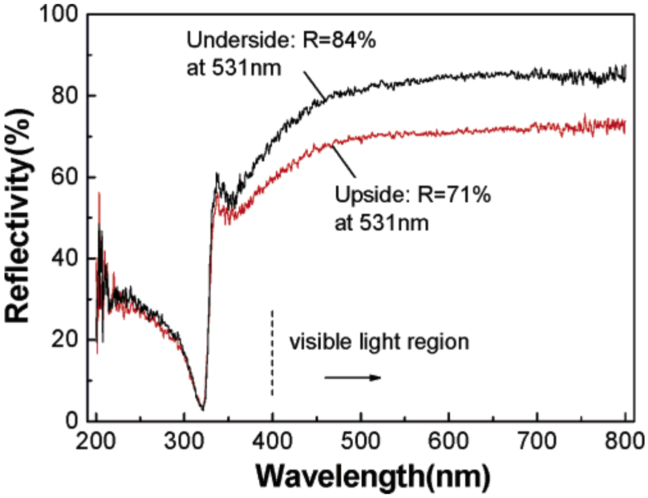


Figure 7. UV−Vis spectra of the upside and underside surfaces as a function of light wavelength in the 200−800 nm region recorded for the metallized polyimide films ion-exchanged in a 0.4 M aqueous $AgNO_3$ solution for 40 min and thermally treated to 300 °C for 9 h.

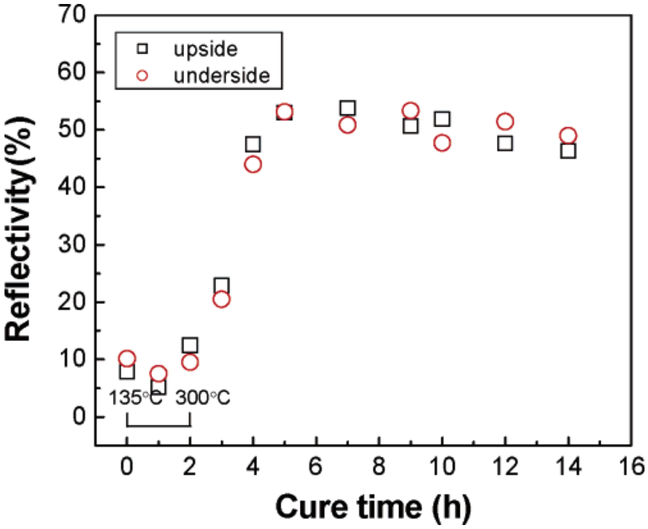


Figure 8. Development of reflectivity on both the upside and underside surfaces as a function of cure time/temperature for the polyimide−silver composite films with an ion-exchange time of 20 min in a 0.4 M aqueous $AgNO_3$ solution. (Time zero is at 135 °C for 1 h).

3.6. Factors Influencing the Film Metallization. Polyimide silver composite films with an ion-exchange time of

Table 3. Thermal and Mechanical Properties of the Polyimide−Silver Composite Films

film samples	ion-exchange time (min)	tensile strength (MPa)	modulus (MPa)	percent elongation	temp. at which 10% weight loss reached in N_2 (°C)	temp. at which 10% weight loss reached in air (°C)
pristine PI at 300 °C, 6 h	0	121.3	2250.3	19.4	565	569
PI−silver at 300 °C, 5 h	20	124.7	2531.4	14.6	569	432
PI−silver at 300 °C, 9 h	40	108.3	2632.8	12.9	575	443

20 min have also been fabricated. Figure 8 displays the reflectivity for the films cured to different time/temperature. Although the films were double-surface metallized, the reflectivity on both film surfaces was rather disappointing, with values no greater than 56%. In addition, conductivity was never achieved, even when thermal treating the films at 300 °C for 12 h. This is unexpected, because ICP measurements suggest that the silver content in the 20 min ion-exchanged PAA film was 4.01 wt %, which does not differ significantly from the 4.32 wt % in the 40 min ion-exchanged film.

Possible reasons would be focused on the acceleration effect of water molecules on the silver reduction process, as found in the UV-light-induced reduction of silver ions on an alkaline-modified polyimide layer.[7] It is reasonable that hydrolysis occurred more substantially in the 40 min ion-exchanged films, and therefore more water molecules will be absorbed. Upon cycloimidization, most of these water molecules would be dehydrated from the poly(amic acid) repeating units. Their acceleration effect will promote the silver reduction and consequently give metallized films with much more desirable properties.

3.7. Thermal and Mechanical Properties. Silver particles have a significant catalytic and oxidative decomposition effect on the polyimide matrix at a high temperature. The incorporation of silver into the polyimide has diminished its high-temperature thermal stability, as displayed in Table 3. Whereas in a nitrogen atmosphere, the 10% weight-loss temperature of the hybrid films is almost the same as that of the pristine polyimide, in air, there is a significant reduction in stability, with the temperature of 10% weight loss being ca. 130 °C lower than the parent film. Nevertheless, the stability of the silvered films could also meet many requirements. However, the tensile strength and modulus in Table 3 for the metallized films are grossly identical to that of the pure polyimide. This suggests that the basic polymer structure is not damaged dramatically by ion exchange in aqueous silver solution and the formation of silver clusters in the bulk. The essential structural and mechanical properties of the polyimide matrix have been retained.

4. Conclusions

This work demonstrates that double-surface-silvered polyimide films could be fabricated by thermal treating the silver(I)-containing PAA films with silver ions loaded through an ion-exchange reaction of the damp-dry precursor films with an aqueous silver solution. Utilizing BTDA/ODA-based polyimide as matrix and aqueous silver nitrate solution as silver precursor, we have prepared the silvered polyimide films with an optimum reflectivity of 71%/84% and surface resistance of 4.1/1.3 Ω/sq on the upside/underside, respectively. The formation of silver polyamate during ion exchange was confirmed. Property differences were observed on the two sides of the metallized films. The higher solvent content on the underside endows it with better wettability and subsequently more silver content, resulting in silvered surfaces with more excellent performances. Silver aggregation was found to be very important for the formation of highly reflective and conductive surfaces. Finally, characterization results suggest that the metallized films basically maintained the thermal and mechanical properties of the pristine polyimide.

Acknowledgment. We acknowledge the financial support of the National Natural Science Foundation of China (NSFC, Project 50573007) and the program for New Century Excellent Talents in University (NCET-040118).

CM062016F