Fabrication of Surface-Silvered Polyimide Films via Direct Ion Exchange Self-Metallization Technique

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1 Introduction

Surface-silvered polyimide film, which combines the excellent thermal and mechanical properties of the polyimide matrix and the unmatched optical and electrical properties of the surface silver layer as well as its many other outstanding performances such as flexibility, light weight, and ease of processing, has been found widely attractive in aerospace and microelectronic industry.[1, 2]

Several approaches have been developed to construct such metallized films including external deposition,[3-5] supercritical fluid infusion [6, 7] and in-situ single stage self-metallization[4]. However, to achieve surface metallization, expensive silver complexes must be employed in these strategies. And the films were usually prepared with only one silvered surface. Recently, a direct ion exchange self-metallization technique has been developed in our work and double-surface-silvered polyimide films with high reflectivity and conductivity has been fabricated with this method.[8-11] It works by performing an ion-exchange reaction of damp-dry poly(amic acid) film in aqueous silver solution to load the silver ions into the polyimide precursor. Subsequent thermal treatment under tension converts poly(amic acid) into the final polyimide matrix with concomitant silver reduction and aggregation yielding silver layers on polymer surface. The uniqueness of this method lies in the direct use of damp-dry poly(amic acid) film to perform ion exchange and the achievement of double-surface-silver metallization using simple silver compound such as silver nitrate, silver fluoride as the silver origin. In the present work, we report our efforts on the formation of surface silver layers on three different polyimides including PMDA/ODA, ODPA/ODA and BTDA/ODA via this direct ion exchange self-metallization process using three different silver salts including silver nitrate, silver fluoride and silver ammonia complex cation as the silver precursor.

2 Experimental

2.1 Materials

3,3',4,4'-Benzophenonetetracarboxylic dianhydride (BTDA) was purchased from Acros Organics and used without further purification. Pyromellitic dianhydride (PMDA), 4,4'-oxydiphtahlic anhydride (ODPA) and 4,4'-Oxydianiline (4,4'-ODA) were obtained from Shanghai Research Institute of Synthetic Resins. Dimethylacetamide (DMAc) (analytical pure, $\leq 0.1\%$ water) was purchased from Tianjin Fu Chen Chemicals Reagent Factory. Silver nitrate ($AgNO_3$) (analytic pure, $\geq 99.8\%$ content) was produced by Beijing Chemical Works. Silver fluoride (AgF) (analytic pure, $\geq 98\%$ content) was obtained from Zhejiang Dongyang Galt Fine Chemical Co., Ltd. Ammonia solution (analytic pure, 25-28 wt %) were purchased from Tianjin No.3 Chemical Reagent Factory. Silver-ammonia complex cations ($[Ag(NH_3)_2]^+$) were easily prepared by adding dilute ammonia solution dropwise into the aqueous $AgNO_3$ solution until a transparent solution was obtained.

2.2 Synthesis of the double-surface-metallized polyimide films

The following procedure was used to prepare the surface-silvered polyimide films via the direct ion exchange process. The poly(amic acid) resin solutions were synthesized by first dissolving the diamine in
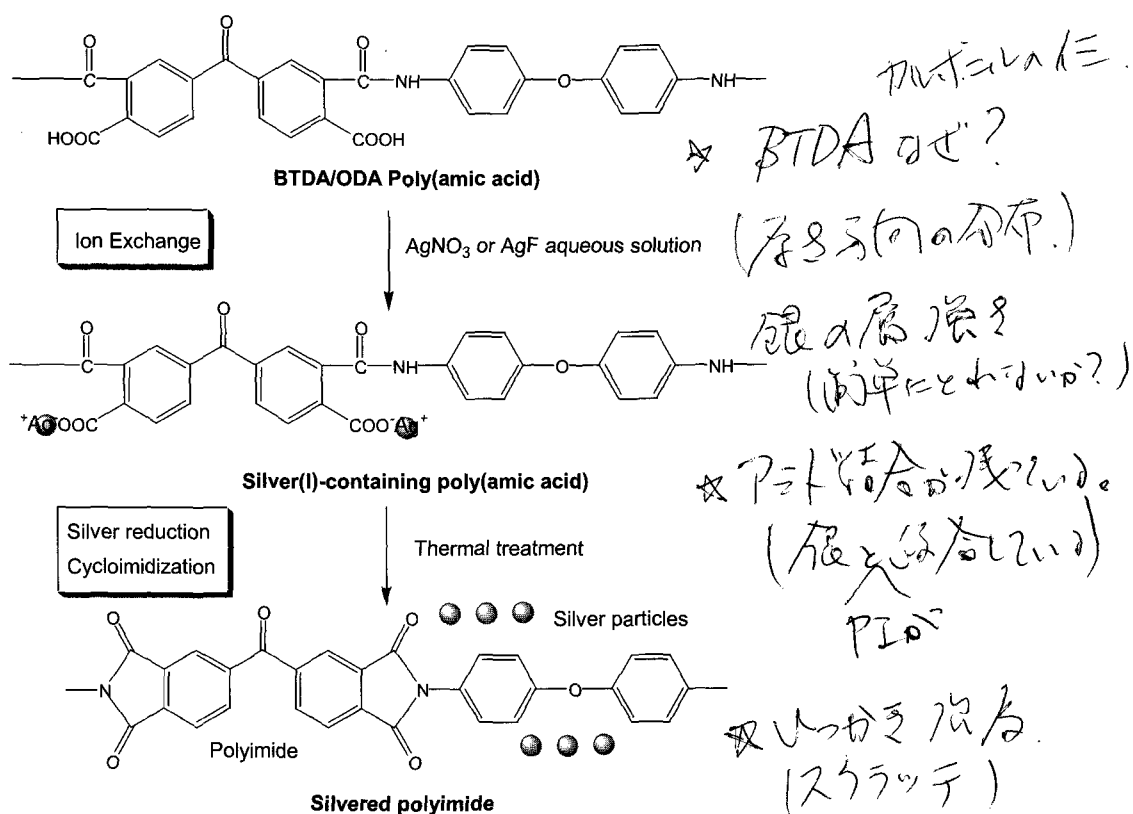
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dimethylacetamide (DMAc) and then adding the dianhydride (1 mol% offset) gradually. The solid contents were set at 20 wt%, 12 wt% and 10 wt% for the BTDA/ODA, ODPA/ODA and PMDA/ODA precursor resins. The inherent viscosity of the poly(amic acid) resin was 1.62-1.81 dl g^{-1}, 1.5-1.7 dl g^{-1}, 2.6-3.4 dl g^{-1}, respectively.

Damp-dry poly(amic acid) films were prepared by spreading the synthesized homogeneous precursor resin solution onto a clean glass plated followed by solvent evaporation in an atmosphere of slowly flowing dry air or a vacuum oven. These films were then peeled from the glass substrate and treated in the aqueous silver solution to load silver ions into the matrix through ion exchange. After being rinsed thoroughly with deionized water, the silver(I)-doped films were thermally treated under tension to cycloimidize the poly(amic acid) and to reduce the silver(I) producing the metallized polyimide films, as depicted in Scheme 1. The thermal cycles are heating over 1h to 135°C and holding for 1h, heating to 300°C over 2h, and remaining constant at 300°C. For clarity, the surface of the damp-dry PAA film in contact with the glass substrate is referred to as the upside, while that exposed to the atmosphere is referred to as the underside.

BTDA/ODA Poly(amic acid)

Ion Exchange

AgNO$_3$ or AgF aqueous solution

Silver(I)-containing poly(amic acid)

Silver reduction
Cycloimidization

Thermal treatment

Silver particles

Polyimide

Silvered polyimide

Scheme 1. Illustrative protocol for the synthesis of the silver metallized BTDA/ODA based polyimide film via direct ion exchange self metallization process.

2.3 Film characterization

Surface reflectivity (relative to a BaSO$_4$ mirror set at 100% reflectivity) was measured on a Shimazu 2501PC UV/VIS spectrophotometer with an incidence angle of 8° at a wavelength of 531 nm. Surface electrical resistivities were determined with a RTS-8 four point probes meter. Scanning electron micrographs were recorded on a HITACHI S-4300 system operating at 15 kV. The Samples were coated with ca. 5nm platinum prior to measurements. Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectra of the films were collected using the Nicolet Nexus670 IR spectrometer. Thermal gravimetric analysis (TGA) was performed with a Netzsch TG 209 system heating at 10 K min^{-1}. Mechanical properties were evaluated using an instron-1185 system.

3 Results and Discussion

3.1 Surface reflectivity, surface conductivity and surface morphology of the metallized films

The ideal chemistry involved in the film preparation process is depicted in scheme 1. After ion exchange in aqueous silver solution, thermal treatment of the silver(I)-containing poly(amic acid) film would convert the precursor into its final polyimide form with simultaneous silver reduction and aggregation yielding the silver metallized polyimide films. In the present work, three different polyimides including PMDA/ODA, ODPA/ODA and BTDA/ODA have been selected as the polymer matrix. And three different silver salts including silver nitrate, silver fluoride and silver ammonia complex cation were employed as the silver precursor. Table 1 gives the surface reflectivity and conductivity data for the optimum surface-metallized polyimide films prepared from some selected polyimide-silver salt system.

Table 1. Surface reflectivity and conductivity of the optimum surface-silvered polyimide films prepared on different polyimide matrices using different silver precursors.

Polyimide matrix	Ion exchange history	Thermal history	Reflectivity (%)		Conductivity (Ω sq^{-1})	
			upside	underside	upside	underside
PMDA/ODA	in 0.2M AgNO$_3$ for 40min	300℃-4h	65.7	69.4	0.4	0.5
ODPA/ODA	in 0.2M AgNO$_3$ for 40min	300℃-7h	43.9	52.7	>10^6	>10^6
ODPA/ODA	in 0.1M AgF for 40min	300℃-7h	51.4	71.8	>10^6	>10^6
BTDA/ODA	in 0.4M AgNO$_3$ for 40min	300℃-9h	71.7	84.5	4.1	1.3
BTDA/ODA	in 0.1M AgF for 40min	300℃-3h	78.6	102.4	0.3	0.5
BTDA/ODA	in 0.01M [Ag(NH$_3$)$_2$]$^+$ for 5min	300℃-4.5h	81.8	93.1	0.6	0.6

As can be seen from Table 1, double-surface-silver-metallized film has been prepared on the PMDA/ODA-based polyimide matrix with maximum reflectivity of 65.7% / 69.4% and surface resistivity of 0.4 / 0.5 Ω sq^{-1} on the upside / underside, respectively, when silver nitrate was utilized as the silver precursor. However, for the ODPA/ODA-based polyimide film, only modestly reflective surface silver layers were achieved and electrical conductivity has never been obtained when silver nitrate and silver fluoride were used. Films prepared using BTDA/ODA-based polyimide as the matrix achieved very high surface reflectivity and conductivity. The optimum one was the film prepared from the BTDA/ODA-silver fluoride system, with maximum reflectivity over 80% / 100% and surface resistivity of 0.6 / 0.2 Ω sq^{-1} on the upside and underside, respectively. Silver ammonia complex cation has the highest efficiency for polyimide silver metallization, which is suggested to be due to its alkaline characteristic. Films with maximum reflectivity of 81.8% / 93.1% and surface resistance of 0.6 / 0.6 Ω sq^{-1} on the upside/underside have been fabricated by employing very dilute silver ion solution (0.01 M) and very short ion exchange time (5 min). The results shown here indicate that both polyimide and silver structures have significant influence on the surface properties of the final metallized films.
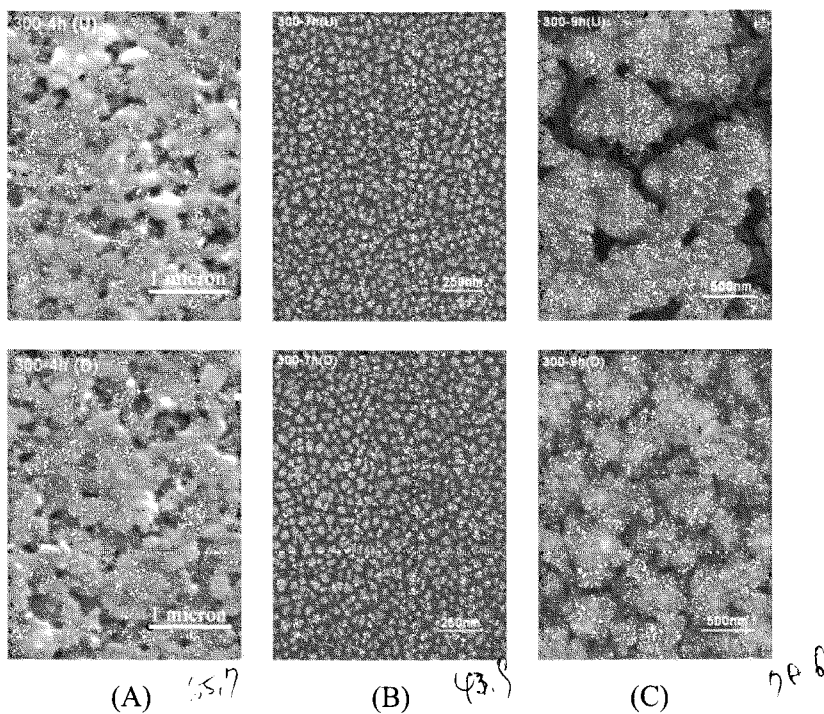
Figure 1. Scanning electron micrographs of the silvered polyimide films derived from (A) PMDA/ODA-AgNO₃, (B) ODPA/ODA-AgNO₃, (C) BTDA/ODA- AgNO₃, (E). (U: upside of the composite film; D: underside of the composite film.)

The surface morphologies of the three selected polyimide/silver hybrid films prepared using silver nitrate as the silver origin are shown in Figure 1. As displayed, well-established silver layers have been formed on both the upside and underside of the metallized films. However, the surface topographies of the silvered films are rather different from each other. SEM micrographs exhibit continuous net-like silver surfaces for the films derived from PMDA/ODA (Figure 1A) and BTDA/ODA (Figure 1C) based polyimide, which are consistent with their excellent electrical conductivity. While for the ODPA/ODA based polyimide, the films (Figure 1B) were metallized with only island-like silver aggregates separated from one another on the surfaces, which account for the non-conductivity. The ODPA/ODA polyimide differs from the BTDA/ODA only by replacing the carbonyl groups of BTDA with an ether linkage. However, they produce metallized films with completely different surface morphologies and surface properties. This implies that the polyimide structure has very significant influence on the film metallization process. Here, the nucleophilic and reactive carbonyl groups in the BTDA, which are considered to be more favorable to silver reduction,[12] are suggested to be responsible for the superior surface properties and morphologies of the BTDA/ODA based films.

3.2 Investigation of the ion exchange process

Poly(amic acid)s have significantly higher cation-complexing properties than their imide forms, because of the presence of many active carboxylic acid groups in the macromolecules. [13]In our recent publications[9-11], we have demonstrated that silver ions can be successfully loaded into the poly(amic acid) films by ion exchange in aqueous silver(I) solution through the coordination of the negatively charged polycarboxylate groups with the positive silver ions to form a silver polycarboxylate salt, silver polyamate, in the precursor film.

However, an unexpected phenomenon that should be noted is that after ion-exchanged in silver ion solution, the poly(amic acid) films can not be dissolved in its initial good solvent such as dimethylacetamide (DMAc), dimethylformamide (DMF) or N-methyl-2-ketopyrrolidine (NMP). However,

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for the bare PAA film and its analogues after in distilled water, re-dissolution could be easily achieved in few minutes in these solvent. And we suggest that it is the loaded metal ions that induce the crosslinking of the macromolecules resulting in the indissoluble silver-containing precursor films.

Structural variations of poly(amic acid) molecules during the ion exchange process have always been the primary concern. Due to the existence of massive amide groups, poly(amic acid) molecules are substantially hydrolysable in aqueous solution, particularly when free reactive metal ions are involved. It is very probable that hydrolysis would break polymer chains and some of the polymer parts would be dissolved in the solution. To quantitatively evaluate the damaging effect, a method has been set up (not shown here) and the mass changes of poly(amic acid) after ion exchange have been measured, as shown in Figure 2. Figure 2-a suggests that, after in distilled water, only ca. 1 wt % PAA macromolecules or its parts are lost into the solution. This indicates that the hydrolysis effect of water on PAA molecules is rather limited and what mainly occurred in pure distilled water should be the dissociation of carboxylic acid groups. However, great mass losses have been observed for the PAA films after ion exchange in silver ion solutions, as shown in Figure 2-b with ca. 14 wt% lost in 0.4 M silver nitrate solution and Figure 2-c with ca. 16 wt% lost in 0.1 M silver fluoride solution. This suggests that silver ions have strong accelerated effects on the hydrolysis of PAA molecules.
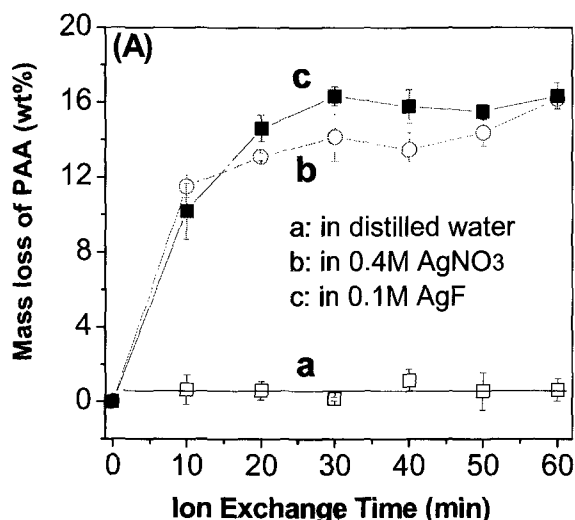

Figure 2. Mass losses as a function of treatment time for the poly(amic acid) films in (a) distilled water, (b) 0.4 M aqueous silver nitrate solution and (c) 0.1M silver fluoride solution.

3.3 Structural, thermal and mechanical properties

Although silver ions strongly accelerate the hydrolysis of poly(amic acid) and a large amount of poly(amic acid) parts have been dissolved in solution, FTIR spectra in Figure 3 suggests that the silver-doped PAA films after thermal treatment maintained the essential structural and physical features of the parent film since the overall spectra before and after hybridization didn't exhibit any distinct alteration except the absorbance intensity. And characterization data also indicate that the final metallized film maintains the basic mechanical properties of the polyimide matrix. However, due to the catalytic and oxidative effects of the silver particles[14, 15], thermal stability of the polyimide-silver hybrid films in air were ca. 130~160 ℃ degraded. While the 10 wt%-loss temperatures were still higher than 400℃ and the hybrid films are also more than adequate for many high-temperature applications.
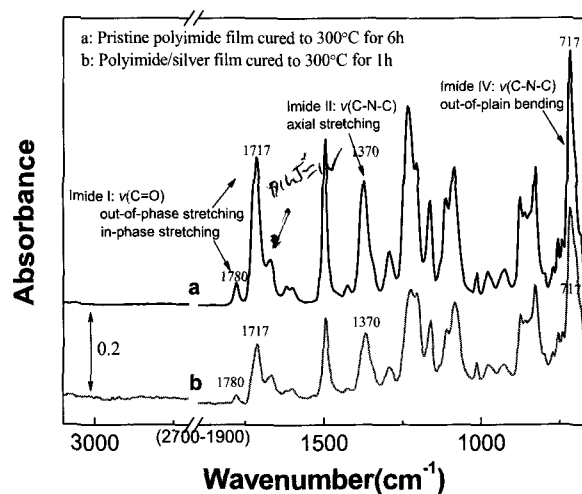
Figure 3. FTIR-ATR spectra of (a) the pure PAA film cured at 300℃ for 6h and (b) the PAA film ion-exchanged in 0.4 M aqueous silver nitrate solution for 40 min and cured at 300℃ for 1h.

4 Conclusions

The work presented here indicates that double-surface-silvered polyimide films with high reflectivity and conductivity have been fabricated via the direct ion exchange self-metallization technique by employing simple silver compounds including silver nitrate, silver fluoride and silver ammonia complex cation as the silver precursor. Our studies with PMDA/ODA, ODPA/ODA and BTDA/ODA as the polyimide matrix suggest that both polyimide structure and silver species have very significant influence on the film metallization process and the surface properties of the final hybrid films. With maximum reflectivity over 80% / 100% and surface resistivity of 0.6 / 0.2 Ω sq^{-1} on the upside and underside, respectively, the surface-silvered polyimide films derived form the BTDA/ODA-AgF system exhibit the optimum surface performance among all the hybrid films. And with an ion exchange time of only 5 min in a very dilute silver solution (0.01M), the achievement of metallized films with maximum reflectivity of 81.8% / 93.1% and surface resistance of 0.6 / 0.6 Ω sq^{-1} on the upside/underside indicates that silver ammonia complex cation is the most efficient silver precursor for polyimide surface metallization. Silver ions have very strong accelerating effect on the hydrolysis of poly(amic acid) chains and a large amount of poly(amic acid) has been dissolved into the aqueous silver solution during the ion exchange process. However, the final metallized films maintain the major mechanical and thermal properties of the pristine polyimide.

Acknowledgement

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