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Reflective and conductive surface silvered polyimide films prepared via in-situ technique using copolyimide as matrix

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Abstract

Reflective and/or conductive surface silvered polyimide films have been prepared by using random and block copolyimide derived from pyromellitic dianhydride (PMDA), 4,4′-oxydiphthalic anhydride (ODPA) and 4,4′-oxydianiline (4,4′-ODA) as matrix and (trifluoroacetylacetonato) silver(I) (AgTFA) freshly synthesized from silver acetate and trifluoroacetylacetone as silver precursor. Influence of copolyimide structure on film metallization process and development of film reflectivity and conductivity during the thermal curing cycle were investigated. The metallized films were characterized by DMTA, X-ray diffraction, XPS, TEM, SEM.

Keywords: Polyimide; Copolyimide; Silver

1. Introduction

Surface metallization of polyimide films has been extensively investigated due to the combination of the superb thermal, mechanical and chemical properties of the polyimide matrix [1–3] and the excellent optical and/or electrical properties of the metal employed [4]. Silver is the metal of interest since it has a low reduction potential which favors silver (I) reduction and because of its unexcelled reflection coefficient (0.93) and the highest electrical conductivity in all metals ($6.3\times10^7\ \Omega\ \mathrm{m}^{-1}$) [5]. Such silvered polyimide films with highly surface reflectivity and/or conductivity have found great space and microelectronic applications such as highly reflective thin film reflectors and concentrators in space environments for solar dynamic propulsion, contacts in microelectronics and patterned conductive surfaces on a flexible dielectric base, etc. [4–11].

Established approaches have been developed to construct such metallized films through external deposition of the metal phase onto the substrate surface by thermal decomposition of a metal complex precursor, such as physical vapor deposition, chemical vapor deposition and electrodeposition [5,9,12]. However, metallization of polymeric films by these standard deposition techniques are very complex since it usually involves several different stages and the surface of the substrate always need to be modified via various processes to enhance the metal–substrate adhesion [13]. Additionally, such deposition methods are not suitable for polymers since distortion or decomposition would always occur as the films can not stand the high temperatures required to reductively decompose the metal precursors to native metal. But the most prominent problem is the notoriously poor adhesion at the polymer–metal interface attributed to the separated construction of the two phases [7,14].

In this paper we focused on the in-situ single-stage self-metallization technique, which was recently proposed by Southward [5] and Taylor [11,15] and has been greatly developed due to its processing simplicity and outstanding adhesion at the polyimide–silver interface. It refers to the incorporation of the silver(I) precursor into solution of poly(amic acid)s formed from a variety of dianhydrides and diamines to obtain a homogeneous silver(I)-containing poly(amic acid)s solution. Then thermal curing of the cast films from such solution leads to cycloimidization of the poly(amic acid) to polyimide with concomitant silver(I) reduction and surface aggregation of the silver particles yielding a reflective and/or conductive silver surface. During the thermal curing cycle, polyimide cycloimidization and in-situ silver reduction were accomplished in a single step giving the desired polyimide/silver composite films, which is necessary to avoid distortion and thermolysis of the matrix during metallization process.

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Various aromatic polyimide matrixes with different molecular structure and many positive valence silver compounds have been attempted in this self-metallization technique. All of these films were prepared with good adhesion at the polymer–metal interface due to the mechanical interlocking mechanism. Also, the excellent mechanical and thermal properties of the parent film were retained. However, not all silver(I) precursors are effective surface metallization agents and not all poly(amic acid)s metallize with equal facility [5]. Efforts on various systems have rarely achieved completely successful. Most reflective films were not conductive, and most conductive films had poor reflectivity [16,17]. Properties of silvered polyimide films have prominent dependence on the molecule structure of the polymer matrix. Pronounced metallization differences can be given in polymeric matrixes with even rather subtle changes in the structure of the macromolecule as seen in AgTFA-3,3′, 4,4′,-benzophenonetetracarboxylic dianhydride (BTDA)/ODA and AgTFA-ODPA/ODA systems [14]. ODPA/ODA differs from BTDA/ODA only by replacing the carbonyl group of BTDA/ODA with an ether linkage. However, only modest reflective films were prepared for the ODPA/ODA based system, while for the BTDA/ODA based films more than 90% reflective films were fabricated with a surface electrical resistivity less than 0.1 Ω/sq. Research works are too limited to suggest the detailed structure influences on the metallization process [16,18].

Up to now, only homopolyimides derived from single diamine and single dianhydride were employed in the research. Herein, we report our insitu single-stage polyimide metallization investigations on the preparation of surface silvered polyimide films by choosing copolyimides with different sequence structures derived from PMDA, ODPA and ODA as matrix and (trifluoroacetylacetonato) silver(I) as silver precursor.

PMDA/ODA was chosen because of its rigid rod-like structure which would facile surface polyimide degradation to obtain a conductive film [5,7], while ODPA/ODA was the polyimide species of interest due to its much more flexible chain structure which seems to conduce to the silver migration to form a reflective surface [11,18] and its better thermal stability which is necessary to endow the metallized copolyimide films with properties of initial polyimide.

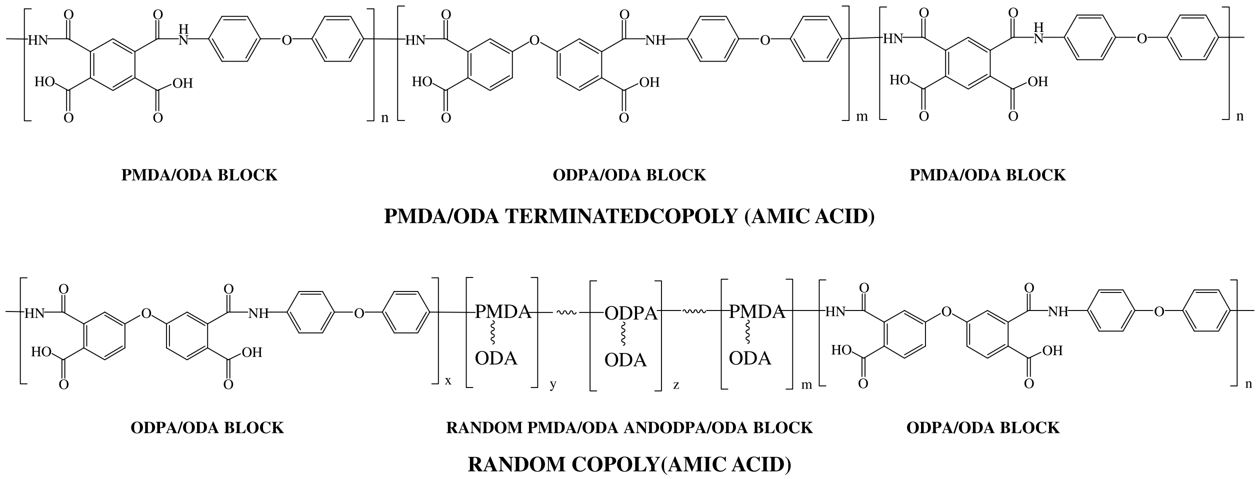
2. Experimental section

2.1. Materials

PMDA, ODPA and 4,4′-ODA were purchased from Shanghai research institute of synthetic resins. PMDA and ODPA were dried under vacuum at 160 °C for 5 h and ODA was recrystallized in ethyl acetate prior to use. Dimethylacetamide (DMAC) was provided by Tianjing Insulating Materials Factory and was redistilled before use. Silver(I) acetate (analytic pure, ≥99.0%) was produced by Shanghai Shiyi Chemicals Reagent Company and trifluoroacetylacetone (TFAH, ≥98%, for laboratory use only) was purchased from ACROS ORGANICS, both of them were used without further purification.

2.2. Synthetic of metallized PMDA/ODPA-ODA copolyimide films with different sequence structures

The following procedures were used to prepare (PMDA/ODPA–ODA)-based metallized films with different sequence structures. Resin synthesis was performed by first dissolving the diamine in DMAC and then adding the dianhydries. Block copoly(amic acid) was fabricated by two-step polymerization approach [19]. That is, the diamine was dissolved in solvent followed by the addition of unequivalent dianhydride to form a diamine-terminated prepolymer. When the reaction was completed, another dianhydride was added to the above mixture to complete the unbalanced stoichiometry yielding the desired block copolyimide precursor. PMDA/ODA-terminated copoly(amic acid) resins were synthesized by the incorporation of ODPA and PMDA orderly. The random analogs could be easily attained by addition of the mixed dianhydrides into the diamine in one-step polymerization [20]. The ideal scheme of synthesizing polyimide with different sequence structures was illustrated in Scheme 1. PMDA/ODA



Scheme 1. Ideal structures of copolyimides with different copolymerization sequences derived from PMDA, ODPA and ODA.

and ODPA/ODA homopolyimides have also been synthesized. Different sequential PMDA/ODPA–ODA poly(amic acid) solutions and that of the homopolyimides were prepared with a 1% offset of dianhydride at 13% solids (w/w) in DMAC. The inherent viscosity was among 1.73–2.28 dL/g at 35 °C.

The AgTFA complex was freshly produced by dissolving silver(I) acetate in a small volume of DMAC containing TFAH with three times mole equivalent to the silver acetate. The 13% copoly(amic acid) solution was then added by weight to give the desired silver-to-polyimide ratio. Wet films with thickness at 35–40 μm were cast from the doped resin solutions. Large portions of solvent were removed by holding the films in the ambient environment for 18–20 h, then thermal curing was performed in a forced air oven to give silver metallized copolyimide films. For all samples the cure cycle was 1 h to 135 °C; at 135 °C for 1; 4 h from 135 to 300 °C and hold constant.

2.3. Film characterization

Reflectivity measurements were performed (relative to a $BaSO_4$ mirror set at 100% reflectivity) with a SHIMADZU UV-2501 C UV/VIS spectrophotometer using a wavelength of 531 nm. Surface resistivities were measured with SDY-4 four point probe made by GuangZhou Semiconductor Material Academe. Glass transition temperatures were determined with a DMTA system of RSI (Rheometric Scientific, Inc.) with a heating rate of 5 °C/min. X-ray diffraction data were obtained using an X-ray diffractometer (D/Max2500VB2+/PC, Rigaku, Japan). Transmission electron micrographs were recorded on a HITACHI H-800TEM instrument. Scanning electron microscopes were obtained on an SEM-4500 (JEOL Ltd Tokyo, Japan) after samples were coated with ca. 5 nm of gold. X-ray photoelectron spectra were obtained using an ESCALAB 250 spectrometer (Thermo Electron Corporation) in the fixed analyzer transmission mode.

3. Results and discussion

3.1. Structural considerations of synthesized copolyimides

PMDA/ODPA–ODA copoly(amic acid)s with different molecule sequence as illustrated in Scheme 1 have been synthesized by two-step or one-step polymerization. DMTA analysis was performed on the films cast from these poly(amic acid)s to verify the exact molecular structure. Fig. 1 shows the DMTA spectrum of the different sequential polyimides derived from PMDA, ODPA and ODA.

Only one glass transition peak is detected at the final cycloimidization stage as can be observed in Fig. 1(A) and (D) for homopolyimides of PMDA/ODA and ODPA/ODA. Fig. 1(B) is related to the copolyimide obtained using two-step polymerization by orderly adding ODPA and PMDA with equivalent molal quantity. Two glass transition peaks at ca. 350 and 300 °C are observed which basically corresponds to the single peak of PMDA/ODA (at ca. 380 °C) and ODPA/ODA (at ca. 260 °C), respectively. This demonstrates that the block copolyimide was obtained with each blocked chain length long enough to maintain its individual properties. Internal approach of the two peaks in copolyimide is mainly attributed to the superb compatibility between PMDA/ODA and ODPA/ODA polyimides. The copoly(amic acid) prepared by the incorporation of PMDA and ODPA dianhydrides mixtures into the DMAC solution of ODA shows only one obvious glass transition peak (at ca. 280 °C) between that of the pure PMDA/ODA and ODPA/ODA homopolyimide which suggests a random copolyimide was formed. A small peak at ca. 220 °C is probably due to the formation of some longer ODPA/ODA segments.

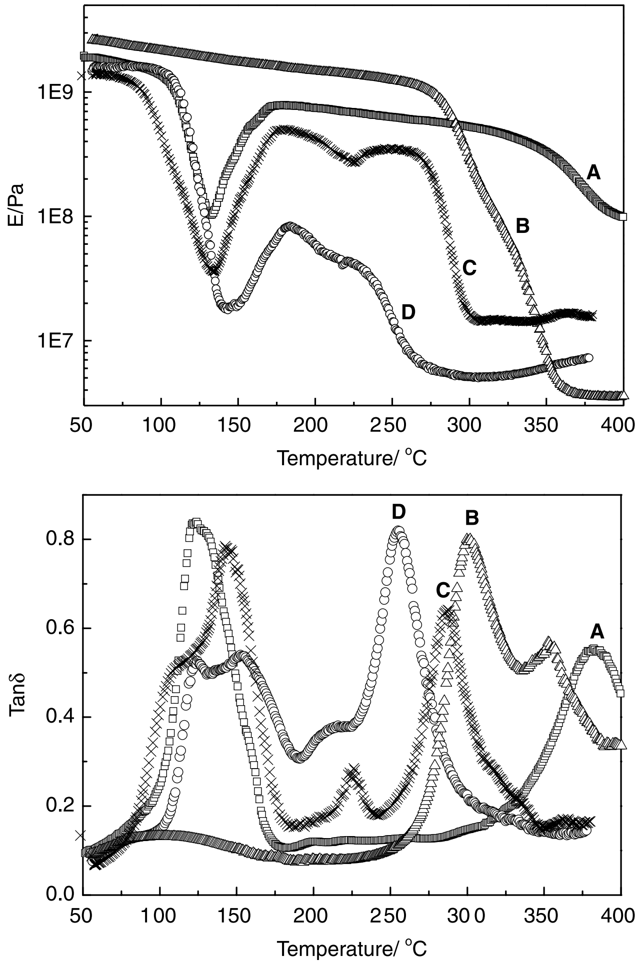


Fig. 1. DMTA analysis of the copoly(amic acid)s derived from PMDA, ODPA and ODA via two-step or one-step polymerization. (A): PMDA/ODPA, one step polymerization; (B): PMDA/ODPA-ODA, two step polymerization; (C): PMDA/ODPA-ODA, one step polymerization; (D): ODPA/ODA, one step polymerization. (For B and C, PMDA and ODPA are equal molar mass. Film B was measured after it was cured at 300 °C for 2 h).

3.2. Reflectivity, conductivity and surface morphology

3.2.1. Silvered block copolyimide films

Silvered homopolyimide and block copolyimide films have been prepared by thermal curing of the films cast from silver(I)-doped copoly(amic acid). Conductive films with surface resistivity less than 7 Ω/sq have been fabricated for

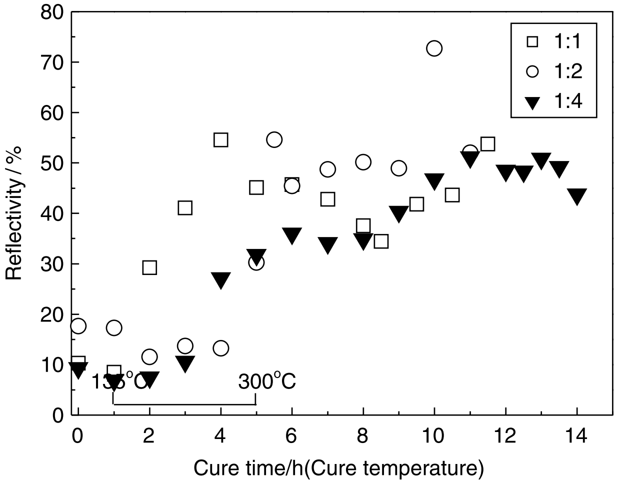


Fig. 2. Development of reflectivity as a function of cure time/temperature for the 10% silver doped copolyimide films derived from PMDA, ODPA and ODA with varying PMDA/ODPA molar ratio (time zero is at 135 °C for 0 h).

the 10% silvered PMDA/ODA based homopolymide films, but with a poor reflectivity no more than 30% (relative to $BaSO_4$ plate set at 100%). While for the corresponding metallized ODPA/ODA films, our investigations show that only reflecting films were obtained with a maximum reflectivity of 28% and no conductivity was achieved.

Fig. 2 displays the variation of reflectivity during the thermal curing cycle for the 10% silver doped copolyimide films with PMDA/ODPA molar ratio at 1:1, 1:2 and 1:4, respectively. The corresponding surface conductivity data for these three films cured at different thermal stage are shown in Table 1.

All these three films have reached a maximum reflectivity over 55% as can be seen in Fig. 2, but at different cure stage. Though only modest reflectivity was achieved, conductivity data in Table 1 suggest that the composite films were fabricated with surface resistivity at ca. 50–10 Ω/sq. That is, both reflective and highly conductive films have been prepared with this block copolyimide matrix, for which can be regarded as a good combination of the two metallized homopolyimide films.

Elaborative observation of the curves in Fig. 2 could approximately divide the step-wise reflectivity variation process into four distinct stages. That is, before ca. 300 °C, a constant region at the early stage of the thermal curing cycle followed by a sharp climb in reflectivity could be clearly observed, to which we referred as the first constant region and the first rising region. Then, as the films were kept at 300 °C, another constant region in which reflectivity holds constant or slightly decreases, and finally a re-increase in reflectivity were visualized. They are named as the second constant region and the second rising region. Such step-wise increase in reflectivity was especially evident in the 1:4 PMDA/ODPA copolyimide films, on which great characterizations have been made in order to clarify the mechanism relating to such variation of reflectivity. SEMs in Fig. 3 show the surface morphology variation during the thermal curing cycle. The silver aggregation process was also traced by X-ray diffractometer as displayed in Fig. 4.

Face centered cubic silver crystallites at smaller sizes have been shaped at early stage of the thermal curing cycle (<180 °C) as suggested by the broad X-ray diffraction peaks in Fig. 4. Fig. 3(A) and (B) for films at this stage also show the observation of spherical silver aggregates though in an unclear image probably due to the existence of polyimide matrix on top surface [5,14]. However, these small silver particles were only scattered on the surface and separated from each other. Furthermore, the amount is far from enough to cover the whole area and, therefore, only give a poor reflectivity. No obvious variations of surface morphology were detected at this early stage as seen in Fig. 3(A) and (B), which could act as a good interpretation of the appearance of the first constant region of reflectivity in Fig. 2.

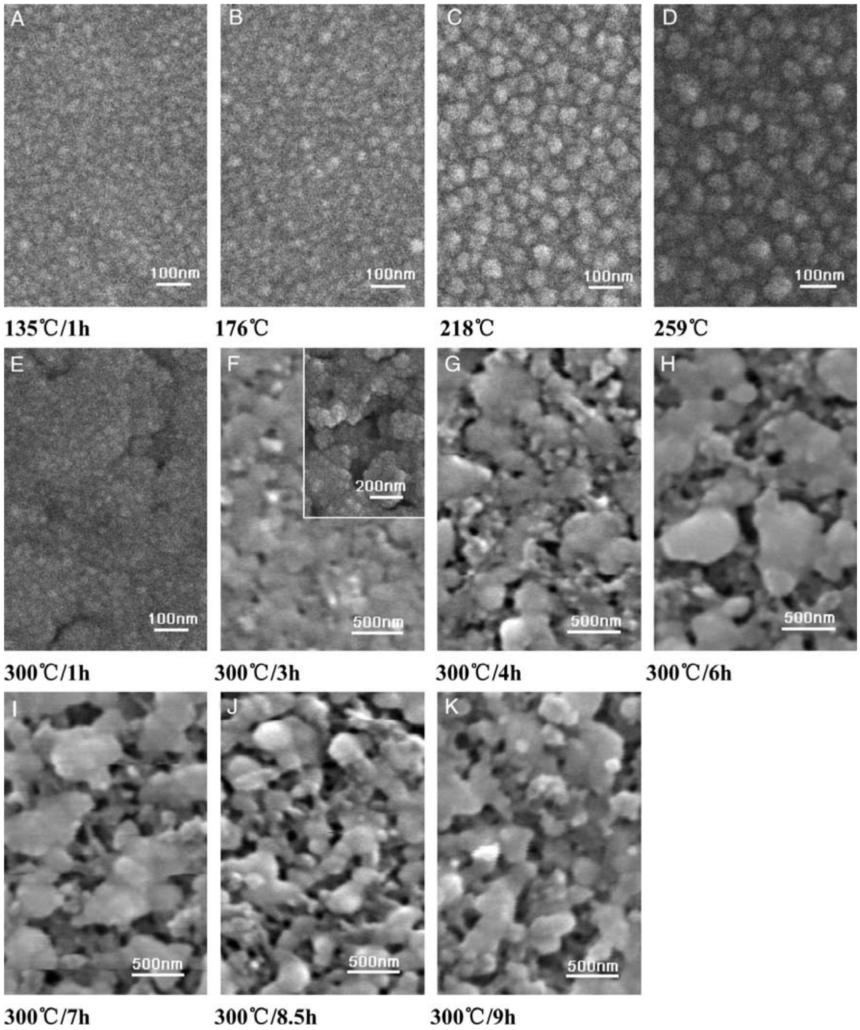
For the film cured to 218 °C, SEM in Fig. 3(C) shows a surface with more and much bigger spherical silver particles uniformly distributing on it, which is consistent with the beginning of the sharp reflectivity increase. The continuous sharpening XRD peaks suggest a rapid size increase of the silver crystallite when the film was further heated to 300 °C for 1 h. More importantly, great morphology changes have been resulted as can be seen in Fig. 3(C)–(E). Especially, a rather different morphology is achieved at 300 °C for 1 h, on which great many separated silver particles are combined together to give lumpish agglomerations. Metallic silver luster was exhibited then and we suppose a packed surface silver layer has been formed. Consequently, the great morphology variation and silver layer formation leads to the first sharp rise in reflectivity.

Further, silver aggregation is continued as can be seen from the continuingly sharpened X-ray peaks in Fig. 4 until 300 °C for 4 h after which the XRD patterns coincided with each other and no further aggregation occurred again. Characterization data in Table 1 shows conductive film with surface resisitivity at 90 Ω/sq was obtained at 300 °C for 2 h which demonstrates that continuous silver surface has already been formed. However,

Table 1
Surface resistivity data for the PMDA/ODPA–ODA–AgAc/TFAH block copolyimide metallized films with 10% silver content cured at 300 °C

Time (h)	0	1	2	3	4	5	6	7	8	9
PMDA/ODPA = 1:1	NC[a]	NC	NC	NC	NC	NC	5[b]	–[c]	–	–
PMDA/ODPA = 1:2	NC	500	50	30	30	30	5	–	–	–
PMDA/ODPA = 1:4	NC	NC	90	50	50	50	40	15	20	10

[a] NC means not conductive, that is, the surface resistivity is beyond the measuring range of the SDY-4 four point probe instrument, 2000 Ω/sq.
[b] The unit of surface resistivity is Ω/sq.
[c] Not analyzed.



135℃/1h 176℃ 218℃ 259℃
300℃/1h 300℃/3h 300℃/4h 300℃/6h
300℃/7h 300℃/8.5h 300℃/9h

Fig. 3. Scanning electron micrographs for the 10% silvered block copolyimide films with PMDA/ODPA molar ratio at 1:4 and withdrawn from the oven at different thermal stage.

SEMs of Fig. 3(F) and (G) at this stage exhibit rather rough topography with many irregular silver clouds, which might be responsible for the slight reflective decrease during this period in Fig. 2 due to their diffuse reflection [11,14]. Nevertheless, a second constant region of reflectivity is kept which may be due to the already well-defined surface silver layer.

Reflectivity for the 1:4 copolyimide films underwent the second rising region from 300 °C for 4 h and reached another higher value. Surface conductivity also began to increase simultaneously with surface resistivity decreased from 50 to 10 Ω/sq in several hours. Meanwhile, a faint whiteish ‘haze’ was observed on the film surface, which undoubtedly arouse from the degradation of polyimide surface catalyzed in part by Ag metal [21,22]. However, no prominent morphology change has taken place except that the surface silver agglomerations became increasingly clear as can be seen in Fig. 3 (H)–(K). XPS data in Fig. 5 for the films cured to 300 °C for 4, 7 and 8.5 h also show an increasing silver content on film surface which suggest the gradual exposure of surface silver layer. We suppose it is the silver exposure behavior resulting from the gradual degradation of the polymer covering on the silver surface that leads to the improvement of both reflectivity and conductivity at this final cure stage.

Step-wise variation in reflectivity remains the same for other two films with PMDA/ODA molar ratio at 1:1 and 1:2,

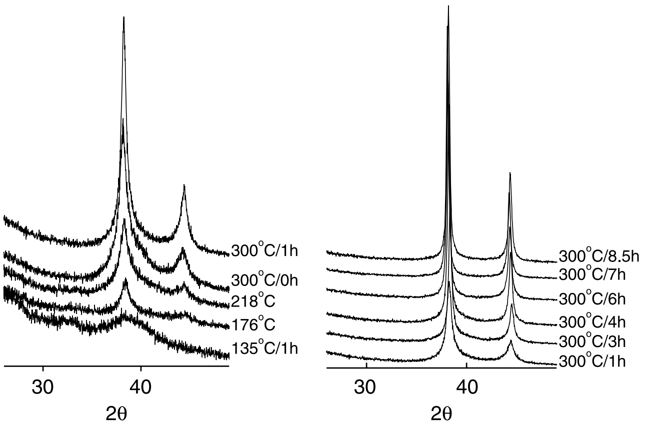


Fig. 4. X-ray diffraction patterns for the 1:4 block PMDA/ODPA–ODA copolyimide films with 10% silver content and cured at different stage of the thermal curing cycle.

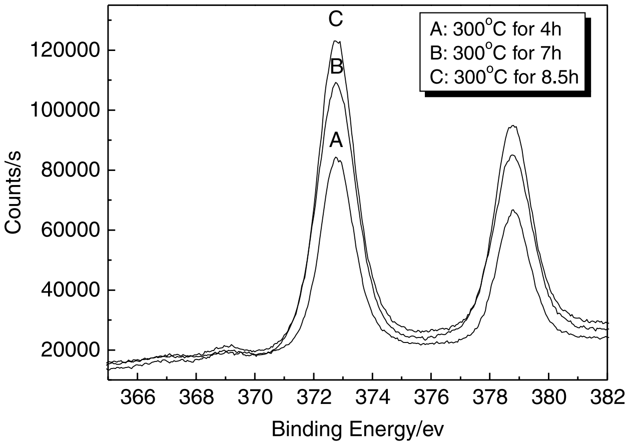


Fig. 5. Silver 3d XPS spectra for the 10% silver doped block copolyimide films with PMDA/ODPA molar ratio at 1:4 and cured to 300 °C for 4, 7 and 8.5 h, respectively.

however, the first sharp increase region was observably delayed with decreasing PMDA/ODA molar ratio, that is, the 1:1 film exhibits an increase in reflectivity first. Unfortunately, data at this point are insufficient to give a reasonable interpretation.

3.2.2. Silvered random copolyimide films

Fig. 6 shows the development of reflectivity as a function of cure time and temperature for the 10% silver doped random PMDA/ODPA–ODA copolyimide films with PMDA/ODPA molar ratio at 1:1. The reflectivity variation process exactly resembles its block counterparts discussed above. However, this random copolyimide/silver films have been prepared with a maximum reflectivity of only 40% and conductivity was not achieved even cured to 300 °C for 10 h.

TEM micrograph in Fig. 7 shows that a continuous though not well-defined silver layer has been formed when the film was cured to 300 °C for 8 h. However, the silver agglomerates on the film surface are obviously separated from each other as can be seen from Fig. 8. And conductivity was not achieved.

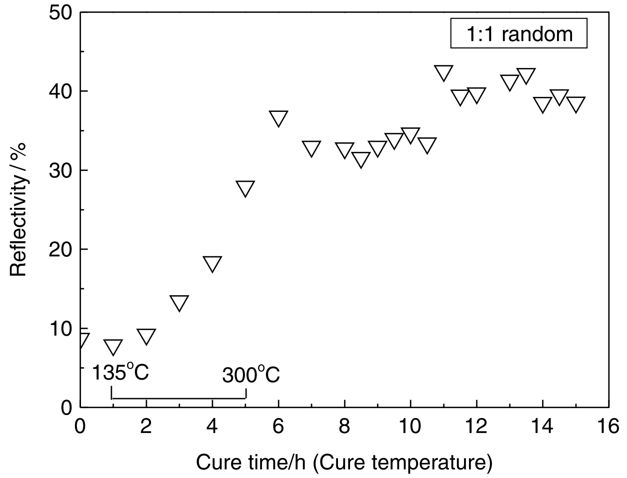


Fig. 6. Reflectivity as a function of cure time and temperature for the 10% silver doped random copolyimide synthesized from PMDA, ODPA and ODA with equivalent dianhydrides.

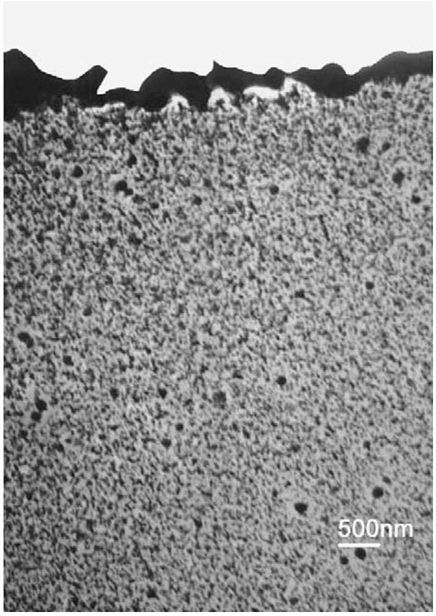


Fig. 7. Transmission electron micrograph for the 10% silver doped random PMDA/ODPA–ODA based copolyimide films cured at 300 °C for 8 h.

Such prominent differences of reflectivity and conductivity between the block and random films reflect the great influences of polymer chain structure or copolymerization sequences on film metallization. We suppose that the synergistic effect existing in the block copolyimide would significantly contribute to such differences. Both PMDA/ODA block chain and ODPA/ODA block chain in the copolyimide can exhibit their individual functions as in their bulk homopolyimides, that is, the relatively easy degradation of PMDA/ODA to give

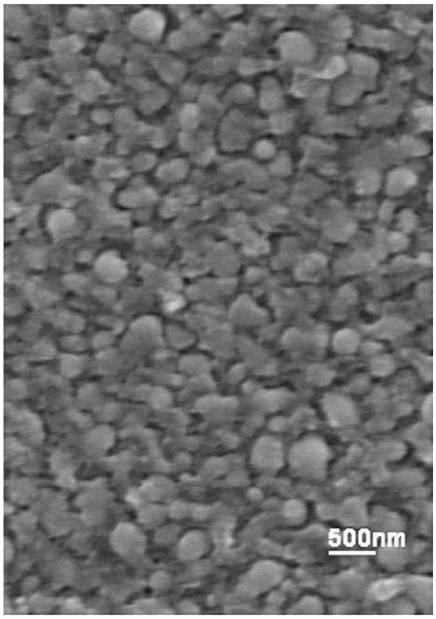


Fig. 8. Scanning electron micrograph for the 10% silver doped random PMDA/ODPA–ODA based copolyimide films cured at 300 °C for 8 h.

a conductive film and the flexibility of ODPA/ODA which could facile particle migration to form a reflective silver layer. However, this synergistic effect was completely destroyed by the random distribution of PMDA/ODA and ODPA/ODA segments along the copolyimide chains. Consequently, only lower reflective and non-conductive copolyimide/silver films were fabricated on this random matrix.

4. Conclusions

Reflective and/or conductive surface silvered copolyimide films have been produced by using block and random copolyimides derived from PMDA, ODPA and ODA as matrix and (1,1,1-trifluoroacetylacetonato) silver(I) as silver precursor. Both reflective and conductive films were obtained on the block matrix with a maximum reflectivity over 55% and surface resistivity $<10\ \Omega$/sq. However, only 40% reflectivity was observed for the silvered random copolyimide films and no conductivity was achieved. Polymer chain structures have prominent effect on the silver metallization process. And the step-wise variation of reflectivity during the thermal curing cycle has been fully clarified.

Acknowledgements

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