Double-surface-silvered polyimide films prepared from BTDA/ODA and silver fluoride via direct ion exchange self-metallization technique

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Synthesis of metallized polyimide films has been an active area of research for many years. Silvered polyimide films with highly reflectivity and conductivity have found potential applications in optical devices, magnetic storage, highly active catalysis, microelectronics and aerospace industry. In-situ single-stage self-metallization process has been extensively studied for many years. Films with excellent reflectivity and conductivity have been fabricated. However, the silver precursors applied were rather expensive and the films were only produced with silver layers on the air side. The direct ion exchange self-metallization technique described here is a newly developed approach which could prepare silvered films with excellent reflectivity and conductivity on both film surfaces using simple and cheap silver salt as silver origin. It refers to develop surface metallized films from silver(I)-containing polyimide precursor films which are obtained by directly immerging the damp-dry poly(amic acid) films into an aqueous silver(I) solution to perform an ion exchange process. Since PAA is thermoplastic and dissociable, the immersion into metallic aqueous solution would result in the polycarboxylate groups through dissociation of carboxylic group in PAA molecules. In the presence of a metallic salt, the negatively charged polycarboxylate will couple to the silver cation forming the silver polyamate. Subsequent thermal treatment of the silver(I)-PAA films under tension induces silver ion reduction to give the metallized surface without resort of any discreet external reducing agent. Thermal curing also gives the imidized polyimide via cycloimidization. During the thermal cycle metal atoms and small clusters formed in the film aggregate at the surface giving metallic layers on both sides.

In the present work, double-surface-silvered polyimide films have been successfully created utilizing 3,3',4,4'-benzophenonetetracarboxylic acid dianhydride/4,4'-oxydianiline (BTDA/4,4'-ODA) based damp-dry poly(amic acid) (PAA) films as polyimide precursor and an aqueous silver fluoride (AgF) solution as silver source. Excellent surface properties have been achieved on both film surfaces with reflectivity higher than 80%/100% and electrical resistance less than $1\Omega sq^{-1}/0.3\Omega sq^{-1}$ on the upside and underside, respectively. However, superb surface performances were only obtained after heated at high temperature for enough time. The coverage of thin polymer layers on the surfaces gives very low and almost unchanged reflectivity at the early the thermal stage. Decomposition of the polyimide overlayer at high temperature endows the metallized films with exceptional properties. The relationship between surface composition, surface morphology and surface property was established. Property differences between the upside and underside of the metallized films were observed during the thermal cycle and have been detailed discussed. It is found that the occurrence of slight imidization on the upside surface renders it with worse drophilism and therefore smaller silver concentration in the near upside polymer layer which could account for the inferior surface performances relative to the underside. Finally, the thermal oxidative and catalytic effects of silver clusters did not function significantly on the polyimide matrix during the film formation process. The metallized films basically maintained the thermal and mechanical properties of the pristine polyimide.