ISTC Project No. K-1117

Development of Technology of Electra- and Heatconductive Metallized Polyimide Constructs with High Reflectivity

Summary of Technical Report

on the work performed from January 1, 2006 to December 31, 2007

Authorized for unrestricted publication

available also at http://www.chemistry.kz

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January 2008

This work is/was supported financially by the European Union and performed under the agreement with the International Science and Technology Center (ISTC), Moscow.

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Title of the Project: Development of Technology of Electra- and Heatconductive Metallized Polyimide Constructs with High Reflectivity

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Commencement Date: January 1, 2006

Duration: 36 months

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Objectives / scope of work and technical approach / expected results

- Development of a metallization technology of industrial polyimide films.
- Development of passivation techniques by casting of polyimide thin layers on the metallized construct.
- Investigation of physical properties: electric – by a four-contact method; optical properties – by spectometrical analysis in UV-, visible and IR- regions of spectra; magnetic ones – by the definition of magnetic permeability, magnetic receptivity and magnetizing.
- Elaboration of a technology for pattern metallization of polyimide blend films.
- Investigation of physical, mechanical, and thermal properties of composites, such as surface and volume electroconductivity and their temperature dependence; the effect of resolution of metal layer thickness on the quality of surface electroconductivity; correlation between blend content and electroresistivity, mechanical properties.
- Development of electrochemical polyimide metallization technology as secondary coating.
- Study of kinetics of electrochemical metal deposition on metallized polyimide films; study of electrochemical principles of secondary metal coatings.
- Testing of diffusion characteristics of the films for different metal cations at the electrochemical metallization processes in situ and metal distribution along the film by SEM/XR analyses.
- Analyses of different electrochemical factors, such as metal type, electrolyte, voltage characteristics on coating of the primary metallized large-scale films, study of surface

passivation by means of electrochemical depositions of noble metals on the primary coating.
- Preparation of electrolyte-stable metallized polyimide films of various shapes as an element of ultra-thin condensers.
- Development of the technological documentation on new technology of electrometallized PI constructs. Simulation of cosmic effects on secondary coated films with passivated surfaces.

Obtained results

To protect the metallized films from environmental actions as well as to broaden their functional activity we deposed the secondary coating on the PI films. It was used as a modifying coating Ni, Co, Au, Rh and Pt metals. The precipitation of the secondary layers was carried out by their galvanic deposition on the surfaces of silver-modified films. The optimal conditions were chosen through singling out temperature, density of current and so on. Surface passivation by covering ultra-thin polyimide layer is the best way, however thickness of such layer should be shorter than length of fuctional waves. Thermostabilization of metal-polyimide constructs influences strongly on the formation and distribution of metal layers. Above 220°C the resistivity increases more than 2 times due to the oxidation of the top metal layers with the further deterioration of metal conductive properties. However, without annealing non-cyclized amide groups of the polymers captivate metal atoms in chelated forms. Such non-formed structure of surfacial conductive layers loses its electric properties up to 140°C, however annealed films keeps their metal-like electroconductivity within 220°C temperature regime. Annealing temperature has major effect on metal layer stabilization. Obvious redistribution of metal grains occurs during the process with concentration of metal in upper part of PI films. If before annealing delocalized metal particles of 100-1000 nm range are visible in film, annealing effect increases part of metal grains with 10-100 nm range to maximum at 175°C. Further increase of annealing temperature causes immersion of metal nanograins making more aligned size distribution.

A modification of exploited polymeric materials in order to produce some new polymeric substrate with higher performances is nowadays an alternative way to synthesize new polymeric structure. A choice of modification way is generally relies upon application field or polymer, its type and some factors of its production and processing. Some blending processes give a synergetic effects on physico-mechanical performances of polyimides allowing simultaneously processed the composites to any appropriate products. In a list of their potential users there are multilayered dielectrics and capacitors; film or fiber isolative substrates; or a flexible basis of computer microchips. Any additions of a second polymer to polyimide can change its morphology remarkably due mainly to enhance porosity of basic polymeric matrix. Analyzing the change in reflection factor with annealing temperature at λ of 530 nm one can see that films annealed at 152, 180^{o}C have the highest reflection. modification enhances as well dielectric characteristics of the final polymer composites. It is well-known that polyimides with alicyclic groups show less values of dielectric constant than those of aromatic ones. For example, a dielectric constant of polyimides consisting of 10 wt% PAA_{PM} is about 2.7-2.9; 2-3 wt% - 2.5-2.7, while these value for pure polyimides based on PAA_{BA} and PAA_{PM} are 2.2-2.6 and 3.0-3.5 relatively. Dielectric constant of fluoro-consisting BA polyimides is 1.8-2.1; and chloro-one is a bit bigger 2.2-2.4. however, other dielectric performances such as dielectric loss tangent; reduced volume resistance; or electric feasibility for both polymers and their combinative products are almost the same.

As $AgNO_3$ concentration reaches $5 \cdot 10^{-4}$ M in the chelating solution leads to homogeneous and uniform distribution of metals amid polyimide surfaces. Besides, it shows

increase of metal sorption in polymer matrix and dissolution effects at the chelation becomes diminishing. Further increase of salt concentration just leads to improvement of metal distribution and quality of metal layers. Increase of reducing agent concentration leads to decreasing of the required time exposure. At the lowest $NaBH_4$ concentration a metallization rate differs one order in comparison of other reducing solutions, as well as metal layer is not uniform. A $NaBH_4$ content $1{,}6\text{-}1{,}8 \cdot 10^{-4}$ M is minimal enough to accelerate the metallization process. Sorption of Ag ions from the solution occurs due to chemical interactions Ag cations with a surface layer of the modified film. During the process, kinetics of chelation can follow such steps:

1. Diffusion of Ag ions into the surface layer
2. Interaction of Ag cations with surfaces of the film (adsorption and adhesion)
3. Diffusion of Ag cations in solid phase of the film.

The modified layer is able to dissolve. Due to affinity of Ag to the modified polymer is high, the equilibrium on the interface of film-solution should be shifted definitely to diffusion of Ag cations into the film meanwhile the solution becomes poor of Ag ions. A mechanism of metal deposition on polyimide surface which is common for both process – primary and secondary metallization, however dissolution of surfacial poly(amic acid) higher during the first process due mainly to its direct contact with electrolyte. The substitution of K on Ag ions leads to the decrease of modified layer dissolution, so the process includes two parallel reactions: on film dissolution accompanying its chelation. The reason of weight decrease is perhaps due to lack of Ag ions in the undersurface layer, otherwise it is observed the formation of a non-soluble compound at diffusion control of the process.

Thermostabilization of metal-polyimide constructs influences strongly on the formation and distribution of metal layers. Above 220°C the resistivity increases more than 2 times due to the oxidation of the top metal layers with the further deterioration of metal conductive properties. However, without annealing non-cyclized amide groups of the polymers captivate metal atoms in chelated forms. Such non-formed structure of surfacial conductive layers loses its electric properties up to 140°C, however annealed films keeps their metal-like electroconductivity within 220°C temperature regime. The construct resembles a ultra-thin capacitor itself, including both sides of metal layers as two capacitor plates and polyimide base as dielectric. The final construct consists of three layers. The first, very thin, is the surface layer. Probably, it is the thin metal layer. Cracking of this layer leads to appearance of thin short cracks. The thickness of this layer has not been determined. The second layer is the metallized PI layer, and the concentration of the metal (Ag) decreases with the distance from the surface. The thickness of this layer is approximately 5-10 microns, however the third layer is the PI substrate.

An aging effect with a simulation of aerospace conditions and simultaneous irradiation under UV light of 290 nm is used for the control of optical and electric performances of metallized polyimide films of silver layers. The best reflective performances are maintained for metallized films passivated with polyimide protective coatings within 15 months exposure.

Keywords: polyimide, metallization, in situ impregnation, metal coatings, nanodistribution