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New Reflectable Materials on the Basis of Polyimides

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Abstract

Electroconductive and reflective metallized polyimide films have been prepared by heterogeneous chemical modification of polyimide surface. By carrying out the chemical reactions *in situ* in the modified layers of polyimide surface, thereby a metal phase strongly impregnated into the polyimide surface is obtained. The steps of chemical modification have been studied on the model compound – poly(amic acid) on the basis of pyromellite dianhydride and oxydianiline, which forms insoluble sodium or potassium poly(amic-acid) salts (polyamate). Metallization of Kapton® HN & JP (from DuPont) and Upilex® S films have been carried out and the films have been characterized by XRD, XRFD, and measurements of reflectivity in the visible range and surface resistivity at elevated temperatures. It is shown that reflectivity coefficients of silvered films are 90-92% and surface resistivity is about 0.5 Ω.

Introduction

The metallized thin-filmed constructs are one of the actual problems of the space material research to develop new reflectable materials. Such devices are widely used as thermo- regulative coatings, light reflectors, collectors of solar energy, antennas and also in screen-vacuum-thermoisolation. Easiness, good plastic and elastic properties of the polymer materials as well as the possibility of unfolding the constructions in the space determine large prospects of their application.

The films on the basis of polyimides characterized by high thermoplastic and radiate stability are in the most part applied as a polymer matrix. At present time the aluminized film blends Kapton (Du Pont, USA) are used in space systems in the low-earth orbit. The aluminized coating is stable to affection of open space factors and particularly to the influence of the atomic oxygen. Due to the high reflectable characteristic in the wide spectral range the silvered polyimide films are the most perspective ones in the field of developing of satellite antennas, telescopes for transmission of information to IR-spectral range of geostationary orbits where there is no presence of atomic oxygen.

There are two principles of reflectable mirror surface formation: the secondary – precipitation of the metal on optically transparent basis layer, the primary – creation of the metal layer with the glossy surface. Because of the lack of the adhesion of silver to polyimide and the lack of optical transparency of polyimide films based on aromatic dianhydrides the formation of the secondary mirror silver surfaces on polyimides is very a difficult task. In order to increase silver adhesion to polyimide surface it is necessary to provide special technological stages of surface modification by the plasmochemical etching, ion- and electronbeam bombardment, photolytical treatment. These modification methods allow to loose a surface but the silver adhesion does not increase significantly. It is known that the polyimides based on aromatic dianhydrides are of yellow (Kapton, Du Pont, USA) and green (Upilex, Ube Corp., Japan) colors due to the formation of charge-transfer complexes. That is why the other side of the metal coating has a mirror luster of the appropriate color. Formation of the optically transparent polyimide films is the way-out of the problem. The new optically transparent polyimides based on aromatic monomers – CP-1 and CP-2 were developed in the NASA Research Centre. Silver coating inconel enables to get thin reflective films, but it should be noted that both of these materials are very expensive.

In order to reduce the price of the production of these materials, and to use them more widely not only in the space but also in the energetic, electrotechnic and microelectronic fields it is necessary to solve the problem of the primary mirror surface coating of sil-

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ver layers with the high conductivity onto the polyimide films. At present time the main metallization methods include homogenous addition of metal compounds (salts or coordination complexes) into prepolymer solution followed by film casting [2-5] or the superfluid [6] impregnation of metal compounds into polyimide films. The films modified by such way fare treated at high temperatures (during 5-7 hours at not lower than 300°). Along with thermal reducing in the coarse of film anneal there is a diffusion of metals to the film surface. But this does not lead to the preparation of stable homogenous electroconductive metal coating with high reflectable properties. Other operations on optimization of the process do not result in reflection and conductivity increase. It should be noted that these methods are not suitable for metallization of industrial homopolyimide films.

The present work is devoted to the development of polyimide silvered films, investigation of their structure and optical properties.

Experimental

Materials

Metallized polyimide films were prepared in the Laboratory of the Polymer Synthesis at the Institute of chemical sciences (ICS) by the method of chemical modification. The silver coatings on the basis layer were obtained by the silver precipitation with chemical reduction of the silver nitrate in the Li-borohydride solution and by the vacuum spraying of silver.

The polyimide film metallization technology developed at the ICS is different from the other described in literature physic – chemical approach to formation of metal phase, that allows to simplify the process substantially and make use of the polyimide films such as Kapton JP®, HN® (Du Pont, USA) Upilex R®, S® (Ube Corp., Japan), PM® (Russia). *In situ* carrying out of the chemical reactions in the modified layers make it possible to form metal phase strongly impregnated into polyimide surface. The chemical metallization was implemented in three types (I – III) with the use of different combinations of organic solvents.

Methods of analysis

X-ray-phase analysis was carried out on the difractometer DRON-3 (Russia). The average sizes of crystallites were accounted by Silyakov equation:

$$B = K\lambda/\beta \cos\theta$$

where K – constant of the equipment; λ - wavelength; β - width of peak at the semi-altitude, rad.; θ - reflection angle.

Microphotographs of the samples surfaces were taken by means of SEM Hitachi 4700 and REM S-600 at the accelerating voltage U = 10 kV and beam current 10^{-10} A. The reflection coefficients of the films were determined by means of the spectrometer SF-18 at the normal angle of light fall.

Common principles of metallized polyimide films formation

Polyimide films are obtained in two steps:

1. Interaction of the pyromellite dianhydride with oxydianiline in amide solvents with the formation of prepolymer.
2. The polyamide acid solution is poured gradually onto a glass base so that cycling of the polymer occurs with the elimination of water vapors at 300°C.

In so doing the surface morphology of the both sides of the film are different: the surface of the glass side is smooth and is marked by a high degree of luster. The airside is more dull owing to highly developed interpenetrating system of mezopores through which water and the solvent are eliminated [1].

Polyimide film metallization process is carried out in several steps by chemical modification: hydrolysis – conversion of the imide cycle into the salt of polyamide acid in the alkali solutions; chelation of the modified surface with metal cations: reduction of the silver incorporated into the polymer matrix.

In connection with that the process is carried out in the film scope the diffusion factors along with the chemical ones make their substantial contribution into the silver coating formation and complicate the process considerably. Furthermore different surface morphology of two sides of the film, that is determined by polyimide film production technology, makes also its contribution. Analyzing the complicated multifactored process of heterogeneous chemical film metallization it is necessary to divide these processes and reveal their effect on formation of the definite composite structure. Key questions that allow to estimate the correlation of *structure – property* in a whole in the suggested scheme of metallization are as follows:

1. Completeness of silver reduction under conditions of the heterogeneity of the process;
2. Extent of crystallity of metal phase;
3. Character of distribution of the metal phase through the film depth;
4. Influence of the macro – and microstructures on optical properties.

Investigation of the structure of the metallized polyimide films

X-ray diffraction analysis

We have applied X-ray diffraction analysis for investigation of silver polyimide films and the initial components – silver and polyimide film Kapton. The silver coatings were obtained on the quartz glass by the vacuum spraying and chemical precipitation when silver cations are reduced in the glass base. X-ray photographs of the initial components are shown on Fig. 1, identification of reflexes – in Table 1.

Table 1
Diffraction angles (2θ) and interface distance of the different silver coatings

Sample	1		2		3	
	2θ°	d, Å	2θ°	d, Å	2θ°	d, Å
Ag (from ref.)	38.14	2.359	44.33	2.043	64.50	1.445
Ag (spraying)	38.1		44.2		64.25	
Ag (chem.precip.)	38.0		44.1		64.25	
Ag/PI 1	38.1		44.25		64.6	
Ag/PI 2	38.1		44.4		64.8	
Ag/PI 3	38.1		44.3		64.7	

The analysis of data shows that the chemical metallization of the polyimide films allows to obtain silver coatings on the basis of polyimides of high strength. According to Silyacov equation the sizes of the silver crystalliteswere calculated (Table 2).

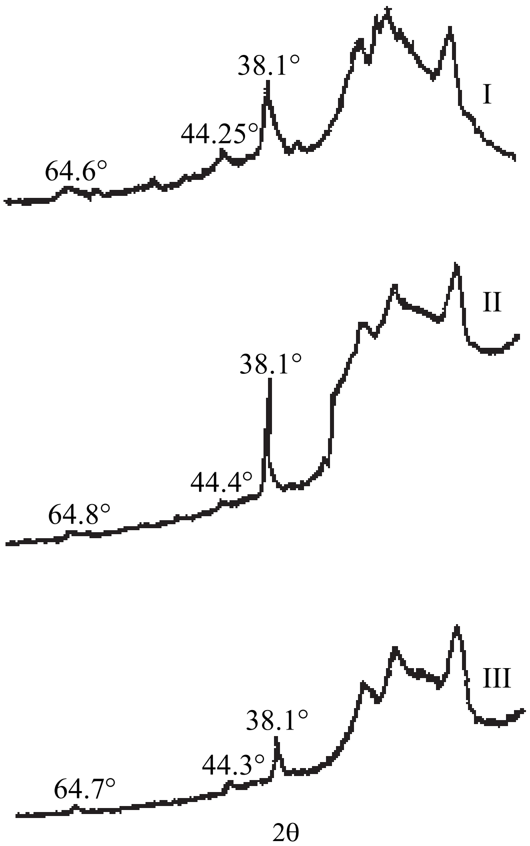

Fig. 1. X-ray small angle records of the untreated films in the dependence on modification type (I-III).

It is obvious from the data (Table 2) that the modification 2 is characterized by the least sizes of crystal lattice, *i.e.* when we used water for hydrolysis. This determined by the peculiarities of chemical and physical interaction of water and modifying organic solvent that results in appearance of the polymer matrix stress with ultimate formation of small size crystallites. The films 1 and 2 contain crystallites virtually of the same size. Besides, the comparison of silver (III) reflexes with the amorphous halo of the Kapton film let us conclude, that the thinnest silver coating is formed in the film 3, and the thickest one – in the film 1.

Considerable structural changes are observed after metallized films were annealed at 180° for 10 min. Analysis of difractogramms (Fig. 2) in Table 2 show that during an anneal there redistribution of reflex intensity has occurred and for films 1 and 2 – the

Table 2
Silver crystallites sizes in the samples of the polyimide films modified by different ways

Sample	Crystallite size, Å		
	1	2	3
Kapton/Ag:			
-before annealing	116	50.1	121
	129	49.6	134
-after annealing	204	153.8	318.9
spraying Ag	290		

new ones are appeared. The main factor is strengthening of typical reflexes for all samples that testifies the growth of crystallite degree of the silver coating. Crystallite sizes are shown in Table 2. It can be observed that for the film-1 the size of crystallites increases by 1.7 times film-2 - by three times; but for the film-3 the sizes (319 Å) are exceeding the data for the covered silver (290 Å). A sharp growth of crystallites sizes in the film-3 testifies the easiness of silver crystallites coalescence on the surface, as for the samples 1 and 2 the diffusion process limits the formation of the big sized crystallites due to the more deep modification of the surface.

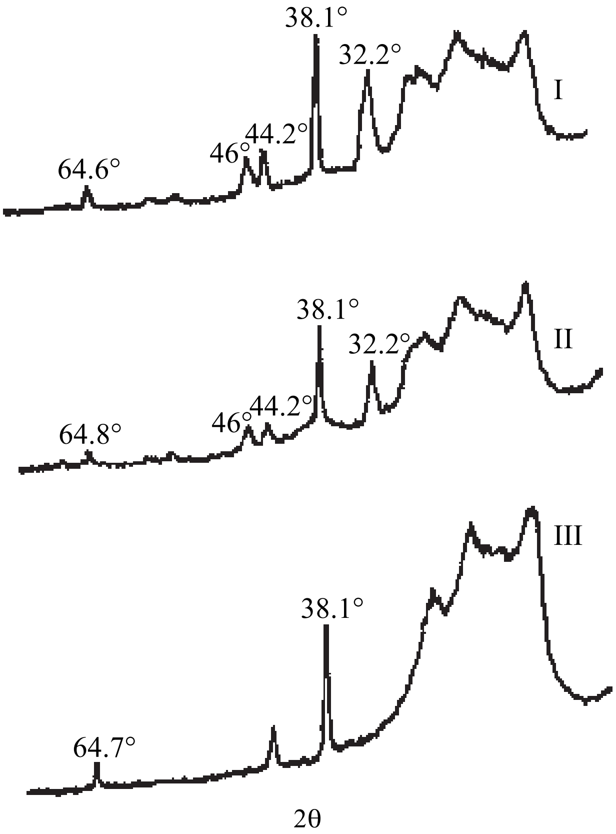

Fig. 2. X-ray small angle records of the films treated at 180°C in the dependence on modification type (I-III).

From the analysis of difractogramms it is also seen that at the angle 32 there is a reflex (110) typical for defected crystal lattice, which should not present in the perfect crystals. This fact is probably determined by the substitution of the silver atom in the elementary cell of crystal lattice for the one of the atoms of the polymer chain, *i.e.* there is a formation of some chemical bounds in course of anneal. This assumption can be prooved by the visual adhesion that is much higher for the coatings 1 and 2 in comparison with the coating 3. The reflex at 46° corresponds to the formation of the new phase – AgCl and is observed in the difractograms of the samples 1 and 2 only. This can be accounted for the use of chloride containing organic compound as the modifying agent and for the formation of silver chloride as a result.

Scanning electron microscopy

Microphotographs with high magnification of the silver surface (Fig. 3a) which was mechanically affected in artificial way (Fig. 3b) are shown in Fig.3. It is obvious that the coating is virtually complete. Under the main layer of the large grains there is a metal layer with the grains of smaller sizes.

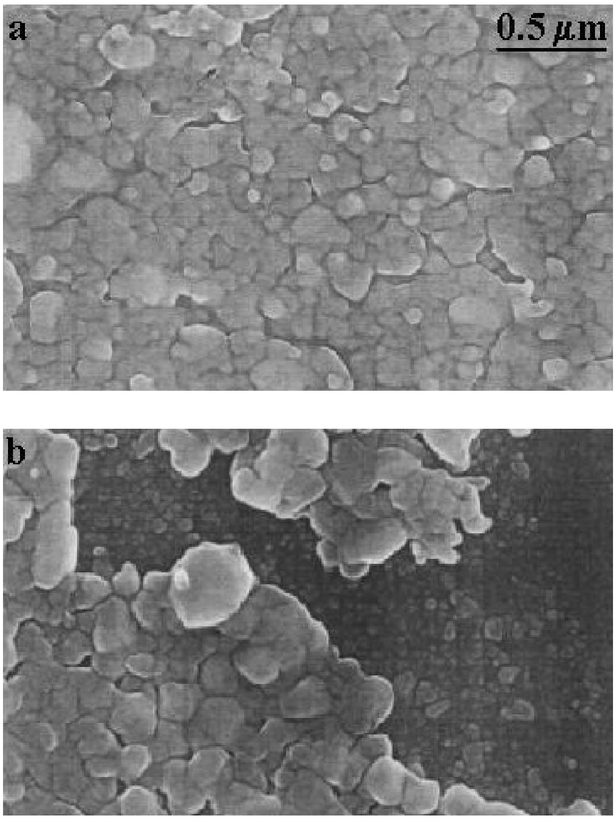

Fig. 3. Microphotos of surfaces of metallized polyimide films. Details are in the text.

A complete investigation of optical properties of metallized films was carried out in the range of 400-800 nm. The dependence of reflection coefficients of silver coatings of different sides for films 1, 2, 3 on spectrum are shown in Fig. 4. From the Figure 4 it is seen that the general regularities of reflection coefficients of silver coatings regardless of the way of their preparing are identical to the literature data

[7] according to which the minimum of the reflection and next growth can be observed at 340 nm. At 530 nm the solar radiation wherein wavelength is the most intensive and the reflection coefficients of investigated samples are of 75-90% that is much higher than those in the literature [4,5]. The analysis of curves shows that the glass side of the film 1 is the most reflectable, reflection from the airside is 5% lower. Practically, the reflectability of the both sides is the same that is confirmed by Auger – and electron microscopy data. Reflection of the film 3 is worst but its sides are virtually of the same value. The reflection coefficient of the film 2 is 10-12% lower, however these coefficients are anyway higher than the literature data. The difference in surface reflections of the film both sides indicates on different morphology of the film surfaces determined by technology of initial polyimide film casting.

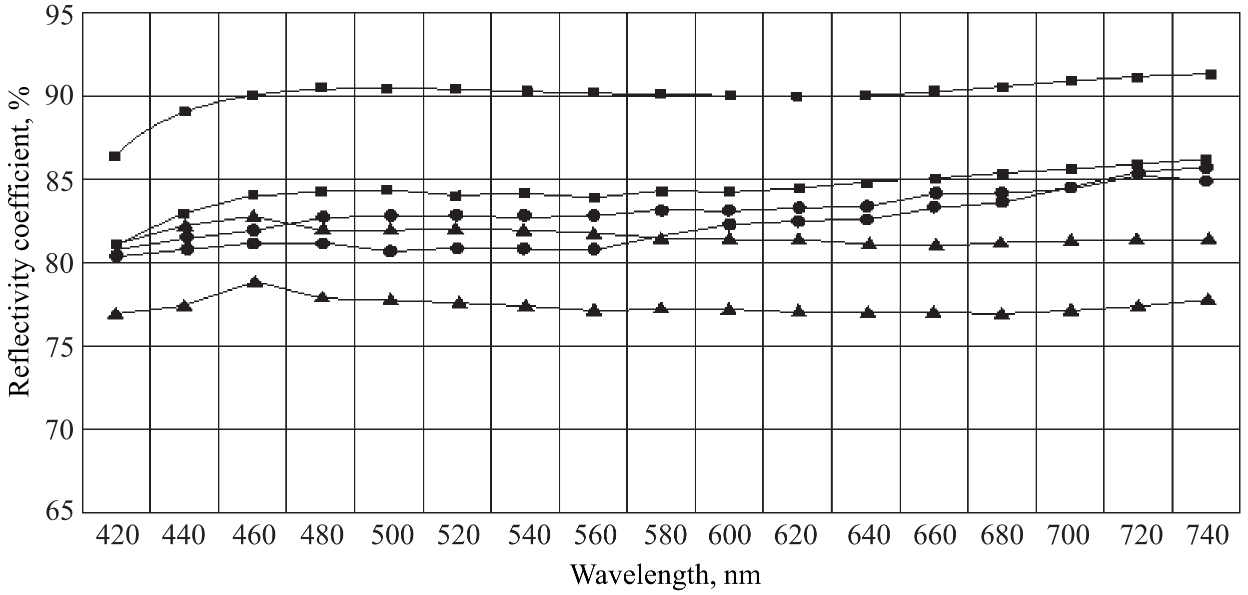

Fig. 4. Reflectivity of metallized polyimide Kapton 100 HN/Ag films prepared by different type of modification (I-III).

Optical properties

The correlation of X-ray diffraction data with optical properties of the films shows that in spite of considerably lower sizes of crystallites (50 Å) in sample 2 in comparison with samples 2 and 3 (approximately 12 Å) their reflection coefficients do not differ. It follows from this that along with the factor of crystallity of silver coating the morphology, "polishing" namely, plays also an important role. In some works [3-5] the silver layer formation is carried out by high temperature thermolysis of silver in the films. Here during thermolysis the dehydrocycling takes place with water evolving and formation of the loose surface. In this case not conductive surfaces are obtained which consist of carbon (53.8%), nitrogen (3%), oxygen (11.7%), and fluorine (24%) according to the elemental analysis data. The content of silver is 7% that indicates on the existence of silver underlayer under that upper one of polymer.

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