Electric and Optical Properties of Polyimide Surface Films Modified by Metals

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Abstract

Electric and optical properties of polymer films, which were prepared on the basis of polyimides and metallized by binary aggregates Ag with Ni and Co, have been investigated. The metallized polyimide films with additional coating from Ni, Au and Rh have been studied too. It has been found that the temperature dependence of the specific surface resistance in the metallized films at the temperature from 25 up to 160°C was in the well agreement with linear law. The specific surface resistance at 20°C and temperature coefficient showed low values and was 0.16-2.24 Ω and 0.69×10^{-4}-19.18×10^{-4} K^{-1} respectively. The film reflection coefficient in visible spectrum field at wavelength of 530 nm was 75% and essentially enlarged with wavelength increasing.

Introduction

One of the actual problems of the space material science technology is the preparation of new high reflecting film coatings and polymer metallized films with a big surface conductivity which are very perspective for this purpose. Such films are also perspective for application in microelectronics as a subtract in the production of semiconductor films with amorphous, micro- and nanocrystall structure. It was known that silver coatings have high reflectance and conductivity. At the same time the formation of initial mirror surfaces from silver with good conductivity on the polyimide films is very complicated because of poor silver adhesion to polyimide surface [1]. Special polyimide surface preparation by plasma-chemical etching, ionic or electron bombardment and also photolytic methods does not increase adhesion. The using of metal compounds, such as salts or coordination complexes, directly in solution at the preparation procedure of polyimide films, with consequent silver reduction by thermal diffusion, does not form homogeneous and strong conducting metal coating with high reflectance [2-4].

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In recent publications [5-8] the possibility of effective chemical modification of the polymer polyimide film surface by metals has been shown. Film metallization was carried out by specially developed technology with the use of heterogeneous chemical reaction (*in situ*) in a near-surface polyimide layer. Silver and its binary composites with nickel and cobalt [7,8] were used as metal parts. Metallization of both surfaces of a polyimide film has been achieved by developed technology. The metallized surface polymer layers had high hardness and good adhesion [7,8], however electric and the optical properties of such films were not studied enough [9,10]. Besides there was a problem of secondary metallic coating influence on the previously metallized polyimides in terms of their conduction and reflectivity.

This paper is discussing the investigation results of electric and optical properties of dielectric polymer films modified metals.

Experimental

Two groups of the metallized polyimide Kapton films were objects of the investigation. Polyimide Kapton 100 HN and Kapton 200 HN films, metal-

lized by binary composite of silver with nickel (Ag/Ni) and cobalt (Ag/Co) [7,8] represented the first group. Synthesized films were annealed at 150°C within 10 minutes for structure and properties stabilization. The second group consisted of Kapton 100 HN polyimide films (Ag/Ni) with additional Ni, Au and Rh coatings by special know-how technology provided at the Center of physico-chemical analysis of al-Farabi Kazakh National University.

The electric properties were investigated on samples with planar structure by direct current. Silver was utilized as electrode material. The electric field strength had low parameters and was 20 mV/cm that eliminated sample heating by electro-caloric effect. The temperature dependence of surface resistance ($\rho_s(t)$) was measured in the temperature range from 25 up to 160°C. The spectral parameters of reflection factors (R) were measured in the wavelength interval from 400 up to 750 nm for samples 2.2 cm^2 square. The measurement was conducted on facial and reverse film sides. The errors in determination of $\rho_s(t)$ and R were $\Delta\rho_s = \pm 0.05$ Ω and $\Delta R = \pm 1\%$.

Results

Kapton films metallized by Ag/Ni & Ag/Co

The typical temperature dependence of specific surface resistance $\rho_s(t)$ of the front face of Kapton 100 HN (Ag/Ni, Co) and Kapton 200 HN (Ag/Ni) films has been shown in Fig. 1. It is evident to see for all films with temperature increasing there was a little increasing of $\rho_s(t)$ according to the linear way. It is well known, that such variation $\rho_s(t)$ of films with temperature was characteristic for the majority of pure metals in special temperature range [11-13]. Carrying out the analogy of resistivity dependence from temperature for pure metals it is possible to represent dependence $\rho_s(t)$ of synthesized films by proportion:

$$\rho_s(t) = \rho_{s_0}(1 + \alpha_s t) \qquad (1)$$

where: $\rho(t)$ – specific surface resistance at temperature t, ρ_{s_0} – specific surface resistance at 0°C, α_s – temperature coefficient of specific surface resistance.

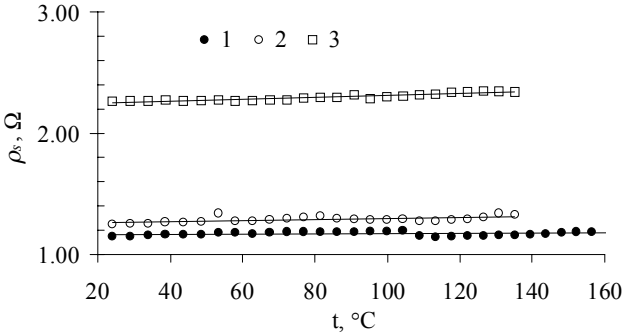

Fig. 1. The temperature dependence of specific surface resistance (ρ_s) for metal films deposited on Kapton 100 HN (curves 1, 3) and Kapton 200 HN (curves 2): 1, 2 – Ag/Ni, 3 – Ag/Co.

The analysis of the metallized films $\rho_s(t)$ dependence demonstrates, which can be well explained by the equations (1):

$$\begin{aligned} &\text{1- Kapton 100 HN Ag/Ni: } \rho_s(t) = 1.16\times(1 + 0.69\times10^{-4}t) \\ &\text{2- Kapton 200 HN Ag/Ni: } \rho_s(t) = 1.25\times(1 + 3.20\times10^{-4}t) \\ &\text{3- Kapton 100 HN Ag/Co: } \rho_s(t) = 2.23\times(1 + 3.59\times10^{-4}t) \end{aligned} \qquad (2)$$

Note, that the specific surface resistance of films in a transverse direction $\rho_\perp$ (which is between facial and reverse side of the metallized coating) exceeded 10^{16} Ω×cm, and it is characteristic for the Kapton non-metallized films. This fact testifies that polyimide matrix saved dielectric properties after metallization procedure of both surfaces of Kapton films.

The spectral dependence of reflection coefficient $R(\lambda)$ in visible spectrum part for front face of films is shown in a Fig. 2. Figure shows high film reflectivity. The film coefficients of reflection have close to values and essentially increase with wavelength eHNancing. Such kind of dependence R from λ, as well as $\rho_s(t)$, is characteristic for pure metals [13]. Magnitude R of investigated films was noticeably higher compared with data available in the references [14,15].

The values of film specific surface resistance at 20°C, temperature coefficient of specific surface resistance and reflection coefficient in the range of 530 nm, which is maximum in a spectrum of solar radiating, are summarized in Table 1.

From data shown in the Table 1 followed that investigated films with practically identical reflection coefficients essentially was differed by values of ρ_s and α_s. It was noted that film parameters ρ_s are a

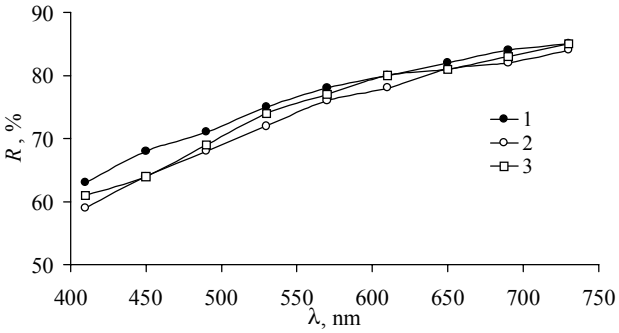

Fig. 2. The spectral dependence of reflection coefficient (R) for metal films deposited on Kapton 100 HN (curves 1, 3) and Kapton 200 HN (curves 2): 1, 2 – Ag/Ni, 3 – Ag/Co.

little bit higher, and α_s is much lower in comparison with the same characteristics for pure silver (α_{Ag} at 20°C was 36×10^{-4} °C^{-1}).

Films 1 (Kapton 100 HN Ag/Ni) had optimal data of high conduction and reflectivity.

It is important that ρ_s, α_s and R, definite for revert surfaces of the metallized films essentially did not differ from values for the front face.

Table 1

Specific surface resistance (ρ_s), temperature coefficient of surface resistance (α_s) and reflection coefficient (R) for films deposited on Kapton 100 HN (1, 3) and Kapton 200 HN (2). 1, 2 – Ag/Ni, 3 – Ag/Co

Kapton 100 HN Ag/Ni	1	2	3
ρ_s, Ω at 20°C	2.15	0.16	1.29
α_s, 10^{-4} °C^{-1} at 20°C	5.57	19.18	11.63
R, % at λ = 530 nm	71	74	64

Kapton films 100 HN Ag/Ni coated by Ni, Au and Rh

Metallized films of Kapton 100 HN Ag/Ni were coated with defensive plating from Ni, Au and Rh for stabilizing electric and optical properties.

Typical temperature dependence of a specific surface resistance $\rho_s(t)$ of film front face with protecting coatings is shown in Fig. 3. It is evidently that for all films with temperature increasing there was the minor growth of $\rho_s(t)$ by the linear way:

$$\begin{aligned} &1 - \text{Kapton 100 HN (Ag/Ni)Ni: } \rho_s(t) = 2.13\times(1 + 5.63\times10^{-4}t) \\ &2 - \text{Kapton 100 HN (Ag/Ni)Au: } \rho_s(t) = 0.15\times(1 + 20.00\times10^{-4}t) \\ &3 - \text{Kapton 100 HN (Ag/Ni)Rh: } \rho_s(t) = 1.26\times(1 + 11.90\times10^{-4}t) \end{aligned} \quad (3)$$

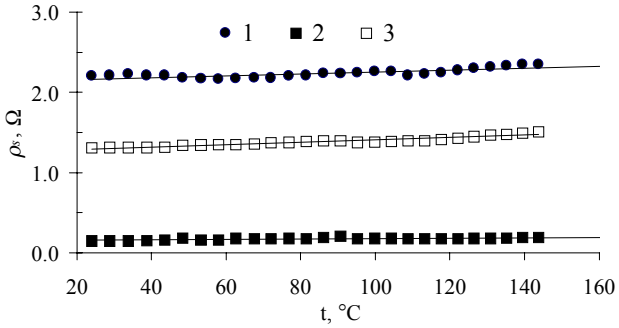

Fig. 3. Temperature dependence of specific surface resistance (ρ_s) for coated metal films deposited on Kapton 100 HN Ag/Ni: 1 – Ni, 2- Au, 3 – Rh.

Specific surface resistance of films in a transverse direction $\rho_\perp$ after protecting coatings deposition, did not change being 10^{16} Ω×cm.

The spectral dependence of reflection coefficients $R(\lambda)$ of the front face of Kapton 100 HN films (Ag/Ni) with protecting coatings is shown in Fig. 4. From the figure you can see that $R(\lambda)$ of films in the range of 400 nm had similar values and increased with wave length λ growing. The most essential reflectivity increasing was in the long wavelength spectrum range for Kapton films 100 HN Ag/Ni with gold protecting coating.

The values of film specific surface resistance at 20°C, temperature coefficient of specific surface resistance and reflection coefficient in the range of 530 nm are shown in Table 2.

Table 2 shows that the protecting coatings can change parameters of Kapton films100 HN Ag/Ni.

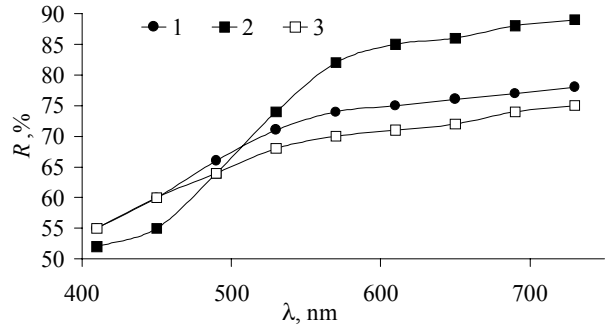

Fig. 4. The spectral dependence of reflection coefficient (R) for coated metal films deposited on Kapton 100 HN Ag/Ni: 1 – Ni, 2 – Au, 3 – Rh.

The protecting coating from Au practically does not change reflection coefficient R of initial films at λ = 530 nm, but considerably reduces ρ_s in ~ 7 times and essentially increases α_s in ~ 28 times. The protecting coatings from Ni and Rh increase ρ_s. At the same time essential increasing of α_s and noticeable reducing of R on 4 ÷ 9% were identified. Kapton film 100 HN Ag/Ni with a protecting coating from Au had optimal characteristics.

Table 2

Specific surface resistance (ρ_s), temperature coefficient of surface resistance (α_s) and reflection coefficient (R) for coated metal films deposited on Kapton 100 HN Ag/Ni. 1 – Ni, 2 – Au, 3 – Rh, 4 – Rh

Kapton 100 HN Ag/Ni	1	2	3
ρ_s, Ω at 20°C	2.15	0.16	1.29
α_s, 10^{-4} °C^{-1} at 20°C	5.57	19.18	11.63
R, % at λ = 530 nm	71	74	64

It has been reported that application of protecting coatings in Kapton films 100 HN Ag/Ni preparation noticeablly stabilized their electric and optical properties during time exposure.

Discussion

Let's consider electric and optical behavior of Kapton films metallized by Ag/Ni and Ag/Co. Evidently the differences in ρ_s and α_s parameters of these films and the similar values of their reflection coefficients R can be explained by features of their microstructure, which are connected with technological conditions of their preparation and composition of binary aggregates on the silver base. Structure express analysis of films by X-ray diffraction method ($\lambda_{K_\alpha Cu}$ = 1.5418 Å) shows, that all metallized film surfaces had polycrystalline structure. The film grain size was from 44 up to 66 Å. Film 1 (Kapton 100 HN Ag/Ni) has minimum grain size. The electric resistance of films will be determined by dissipation of charge carriers inside a grain and on the grain boundary (including pores), if we do not take into account influence of adsorbed impurity atoms by film surface. Increasing of ρ_s by the linear way with growth of temperature has been identified in all investigated films, that testifies phonon mechanism of charge carriers dissipation in the investigated temperature range. Such dissipation mechanism is characteristic for pure metals [12,16]. On the other hand, much low parameter values α_s compared with similar characteristic for pure metal Ag, testify about the defining contribution of grain boundaries to electric resistance value. It seems that the boundary grain state essentially depended on features of preparation methods of Kapton film metallized surfaces and on conditions of consequent heat-treatment. Changing boundary grain states it is possible to control electric parameters of the metallized films.

The high values of film reflection coefficient in the visible spectrum part testify about high quality of the metallized coatings. To all appearance, practically identical values of film reflection coefficients are caused by similar grain size of the metallized surfaces of films and because their size is much less than wave length of a visible band.

So, these are necessary additional investigations to find out the reasons of electric and optical parameter variations of Kapton films 100 HN Ag/Ni under influencing of protecting coatings from Ni, Au and Rh

Finally, it has been reported that the metallized dielectric polymer films on the basis of polyimides have high-conductivity properties and high reflection coefficients. The obtained results open out new application perspectives for dielectric polyimide films modified by metals in microelectronics for semiconductor devices.

Conclusions

The metallized dielectric polyimide Kapton films were obtained by a method of surface chemical modification with the use of heterogeneous chemical reaction (*in situ*) in a near-surface polyimide layer and have been characterized by good conductive properties and high reflection coefficients in the visible spectrum part. Kapton films 100 HN Ag/Ni had optimal parameters, namely high conduction and reflectivity.

The differences in electrical parameters of Kapton films and the similar values of their reflection coefficients R can be explained by features of their microstructure, which are connected with technological conditions of their preparation and composition of binary aggregates on the silver base and conditions of consequent heat treatment.

The application of protecting coatings in Kapton films 100 HN Ag/Ni stabilized their electric and optical properties. The protecting coating from Au practically did not inflect reflection coefficient R of the

initial Kapton films 100 HN Ag/Ni at λ = 530 nm, but considerably increased R in the long wavelength part of visible spectrum band and essentially decreased specific surface resistance.

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