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 substrate 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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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 $\Delta \rho_s = \pm 0.05 \Omega$ 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:

$$\rho_s(t) = \rho_{s0}(1 + \alpha_s t)$$  \hspace{1cm} (1)

where: $\rho_s(t)$ – specific surface resistance at temperature $t$, $\rho_{s0}$ – specific surface resistance at 0°C, $\alpha_s$ – temperature coefficient of specific surface resistance.

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

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 $10^{16} \Omega \times \text{cm}$, 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 enhancing. Such kind of dependence $R$ from $\lambda$, 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 $\rho_s$ and $\alpha_s$. It was noted that film parameters $\rho_s$ are a
little bit higher, and $\alpha_s$ is much lower in comparison with the same characteristics for pure silver ($\alpha_{Ag}$ at 20°C was $3.6 \times 10^{-4}$ °C⁻¹).

Films 1 (Kapton 100 HN Ag/Ni) had optimal data of high conduction and reflectivity. It is important that $\rho_s$, $\alpha_s$ and $R$, definite for revert surfaces of the metallized films essentially did not differ from values for the front face.

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 protective 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:

1 - Kapton 100 HN (Ag/Ni)Ni: $\rho(t) = 2.13 \times (1 + 5.63 \times 10^{-4}t)$
2 - Kapton 100 HN (Ag/Ni)Au: $\rho(t) = 0.15 \times (1 + 20.00 \times 10^{-4}t)$
3 - Kapton 100 HN (Ag/Ni)Rh: $\rho(t) = 1.26 \times (1 + 11.90 \times 10^{-4}t)$

Fig. 3. Temperature dependence of specific surface resistance ($\rho_s$) 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 $\lambda$ 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.

| Material        | $\rho_s$, Ω at 20°C | $\alpha_s$, 10⁻⁴ °C⁻¹ at 20°C | $R$, % at $\lambda = 530$ nm |
|-----------------|---------------------|------------------------------|-----------------------------|
| Kapton 100 HN Ag/Ni | 2.15                | 5.57                         | 71                          |
| Kapton 200 HN Ag/Ni | 0.16                | 19.18                        | 74                          |
| Kapton 200 HN Ag/Co | 1.29                | 11.63                        | 64                          |

**Table 1**

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

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 $\lambda = 530$ nm, but considerably reduces $\rho$ in ~ 7 times and essentially increases $\alpha$, in ~ 28 times. The protecting coatings from Ni and Rh increase $\rho$. At the same time essential increasing of $\alpha$ and noticeable reducing of $R$ on $4 \div 9\%$ were identified. Kapton film 100 HN Ag/Ni with a protecting coating from Au had optimal characteristics.

### Table 2

| Kapton 100 HN Ag/Ni | 1   | 2   | 3   |
|---------------------|-----|-----|-----|
| $\rho_s$, $\Omega$ at 20°C | 2.15 | 0.16 | 1.29 |
| $\alpha_s$, $10^4$°C$^{-1}$ at 20°C | 5.57 | 19.18 | 11.63 |
| $R$, % at $\lambda = 530$ nm | 71   | 74   | 64   |

It has been reported that application of protecting coatings in Kapton films 100 HN Ag/Ni preparation noticeably 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 $\rho$ and $\alpha$ 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 ($\lambda_{K,Co} = 1.5418$ 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 $\rho$ 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 $\alpha$ 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 inffect reflection coefficient $R$ of the...
initial Kapton films 100 HN Ag/Ni at $\lambda = 530$ nm, but considerably increased R in the long wavelength part of visible spectrum band and essentially decreased specific surface resistance.

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References

1. Sacher E., Kovalchuk S.P., J.-J. Pireaux (ed.), Metallization of polymers. 2001, p.533.
2. Shakauskas M., Vyashkyalis A. Chimicheskaya metallizatsiya plastmass. Leningrad, Chimia, 1985, p. 114.
3. Lee R.W., Viehbeck A. in Polyimides. Fundamental and applications. Grosh M.K., Mittal K.L. (ed.), NY, Plenum press, 1996, p. 912.
4. Matienzo L.J., Unertl W.N. in Polyimides. Fundamental and applications. Ghosh M.K., Mittal K.L. (ed.) NY, Plenum press, 1996, p. 912.
5. Kudaikulova S., Zainullina A., Boiko G., Zhubanov B., Abadie M.J.M. Sci. Israel - Technol Adv., 2(3-4):1 (2000).
6. Kudaikulova S., Zainullina A., Boiko G., Zhubanov B., Vygodskii Ya., Abadie M.J.M. Sci. Israel - Technol Adv., 2(3-4):10 (2000).
7. Syzdykova A., Kudaikulova S., Boiko G., Zhubanov B., Figovsky O., Sidorov V., Abadie M.J. M. Proc. STEPI V, 5-th Eur. Techn. Symp. Polyimides and High Performance Functional Polymers (Chemistry, Physics & Properties), 3-5 May 1999, Montpellier, France. M.J.M. Abadie (ed.), 2001, p. 200.
8. Kudaikulova S. Izvestia NAS RK, Ser. Phys., 2002.
9. Abadie M.J.M., Prikhodko O., Kudaikulova S., Boiko G., Zhubanov B., Voytekunas V. Proc. 2-nd Int. Symp. Polyimides and other high temperature polymers: synthesis, characterization and applications, 2001, Newark, USA.
10. Prikhodko O., Kudaikulova S., Zhubanov B., Voytekunas V., Abadie M.J.M. Proc. STEPI VI Eur. Techn. Symp. Polyimides and High Performance Polymers, Montpellier, France, 14-16 May 2002.
11. Koshkin N.I., Shirkevich M.G. Handbook on elementary Physics, Moscow, Nauka, 1988, p. 256.
12. Tables of Physical Constants. Reference Book ed. by Academician Kikoin I.K., Moscow, Atomizdat, 1976, p. 1006.
13. Masterov Yu.A., Saksonov Yu.V. Serebro, splavi i bimetalli na ego osnove. Moscow, Metallurgiya, 1979. p. 296.
14. Southward R.E., Thompson D.W., Clair A.K. St. Chem. Mater. 9:1691 (1997).
15. Southward R.E., Boggs C.M., Thompson D.W., Clair A.K. St. Chem. Mater. 10:1408 (1998).
16. Blakemore J.S., Solid State Physics, Moscow, p. 608.

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