

Synthesis of New Metallized Polyimide Films with High Optical and Physical Performances

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Abstracts

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, 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 isophthaloylchloride and methylenedianthranilic acid which forms insoluble sodium or potassium poly(amic acid) salts (polyamate). Metallization of Kapton[®] HN & JP (from DuPont) and Upilex S[®] (from Ube) films has been carried out and the films have been characterized by X-ray diffraction (XRD), X-ray fine diffraction (XRFD), 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 /sq.

Introduction

One of main directions of search for new materials with specific physical properties is metallization of polymer films. Creation of such materials is a difficult task because of low adhesion of metals to polymer surfaces. Such classical methods as vacuum evaporation and electrolytic deposition require special steps for physical or chemical modification of surfaces.

Polyimides (PIs) are widely used for special technological applications because of their high thermal, radiation and chemical resistance, excellent dielectric characteristics and ability to form strong flexible films [1,2]. To fulfill requirements for different technological applications such as low electrical resistivity and high reflectivity, which are more typical for metals, creation of stable metal-polyimide composites is a necessity.

Thermostable PI films doped with different metals have the potential for use as thin film mirrors/

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reflectors for use in space, microelectronics, electrochemistry, as well as ferromagnetic materials for magnetic recording, etc. The problem of preparation of strong flexible films with stable electroconductivity can be solved by modification of polyimide (PI) films, particularly by chemical metallization.

The objective of creating reflective, electroconductive metallized PI films is achieved by different methods: homogeneous or heterogeneous. The homogeneous approach [3-6] is to dissolve additives (metal salts and organometallic complexes) into a poly(amic acid) solution (in an amide solvent). The resulting films of prepolymer upon thermolysis (100-300°C) undergo both cycloimidization and metallization. The metallization process includes thermal reduction of metal cations, aggregation of metal clusters with their simultaneous transport, diffusion in the bulk near-surface layer and final appearance of the metal (silver) on the surface of polyimide film. The ease with which Ag(I) cation is reduced ($E = 0.80$ V) raises a synthetic question: Does any Ag(I) compound that is soluble in dimethylacetamide

(DMAc) and in the solvent of free poly(amic acid)-polyimide yield essentially the same metallized surface with respect to reflectivity and conductivity [7]. The answer is no; there is clearly a ligand effect on the polymer constrained reduction of Ag(I) and subsequent migration to give metallic surfaces. Preparation of metallized films through Ag(I) acetate and trifluoro acetylacetonate resulted in electroconductive films ($0.5 \Omega/\text{sq}$) for a 70 nm silver layer but had poor reflectivity [8]; metallization through Ag(I) acetate 1,1,1,5,5,5-hexafluoro-2,4 pentadione resulted in reflective ($R = 80\%$) but never conductive films even when heated at 340°C [9]. Replacement of fluorines by hydrogen in one methyl group [10] led to formation of different films: electroconductive ($< 0.1 \Omega/\text{sq}$) and reflective (100%) films. The ligand effect plays a dominant role in this type of metallization.

Another approach includes the heterogeneous modification of the films by supercritical fluid infusion of (1,5-cyclooctadiene-1,1,1,5,5,5-hexafluoro) acetylacetonate of silver(I) into fully cured polyimide film followed by annealing at 300°C [11]. It was shown that preliminary chemical modification of a polyimide film (on the basis of pyromellitic dianhydride and oxydianiline PMDA-ODA) surface by alkali solution resulted in production of a reflective surface which allowed one to conclude that a coordination site on the polymer backbone was necessary to produce a reflective surface.

It was found [12-15] by introducing organic or inorganic compounds of low molecular weight, into the stretched polymer films, allowed them to fix oriented ordered structures. The elongation of films [(polypropylene, poly(ethylterephthalate), poly(vinyl chloride)], in the presence of active compounds results in fixed porous structure of films. Loading of the modified polymer films by metal cations followed by their chemical reduction (by sodium borohydride) is one of the efficient ways of preparing metal filled polymer composite films. The size of metal particles (from 4-7 nm up to 132 nm) is controlled by the nature of the polymer matrix as well as by conditions of metal reduction. It is known that interaction of metal salts with reducing agent – sodium borohydride (NaBH_4) aqueous solution-leads mainly to formation of black precipitate, most likely as thin dispersed metal phase with particle size 1-2 nm [16]. Heterogeneous chemical reduction of a metal in the bulk of a polymer matrix can result in electroconductive or reflective films and this is what makes this type of metallization very promising.

A combination of these two approaches is presented in reference [17]. Modified films obtained by homogeneous doping of poly(amide imide)s solution in amide solvent by transition metal salts were reduced in an aqueous solution of sodium borohydride. Thus metallized poly(amide imide) films exhibited low resistivity, around $1-10 \Omega/\text{sq}$ and surface morphology was not uniform.

In this work we present formation of a metal phase by carrying out *in situ* chemical reactions in modified polyimide films, as well as results of investigation of their structure and physical properties.

Experimental

Materials

Isophthaloylchloride was prepared according to reference [18] with M.p. 43°C . Neutralization equivalent was determined by saponification followed by potentiometric titration of alkali excess by acid solution and was found to be 101.2 (calculated 101.5).

Methylenedianthranilic acid was prepared from o-aminobenzoic acid and formaldehyde according to reference [18]. Neutralization equivalent determined by reverse titration was found to be 143.5 (calculated – 143.5).

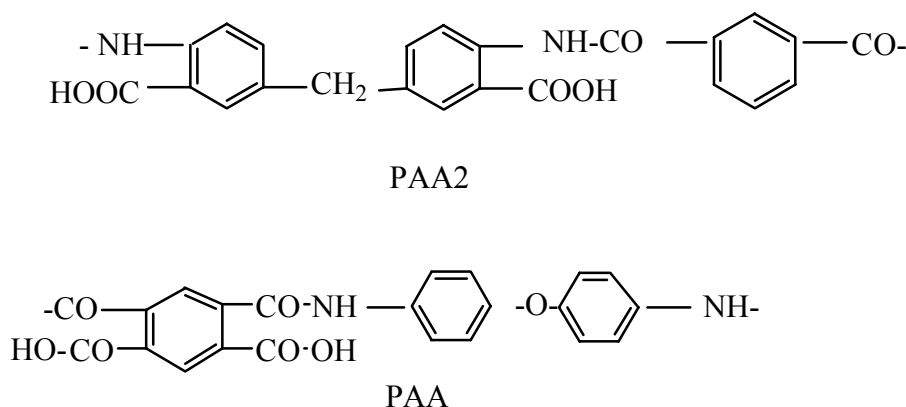
Metal salts AgNO_3 , AgAc , CuAc_2 , CuCl_2 , $\text{Cu}(\text{NO}_3)_2$, CoAc_2 , CoCl_2 , $\text{Co}(\text{NO}_3)_2$, NiAc_2 , NiCl_2 , $\text{Ni}(\text{NO}_3)_2$ and reducing agent NaBH_4 were used as received from Aldrich.

Polyimide films Kapton® HN & JP (from DuPont de Nemours) and Upilex S® (from Ube) were used after washing with water detergent solution and thermally treated at 200°C for 1 hour.

Synthesis of poly(amic acid) based on isophthaloylchloride and methylenedianthranilic acid (PAA-2) was prepared by the reaction of equimolar amounts of methylenedianthranilic acid and isophthaloylchloride in N-methyl-2-pyrrolidone in an inert atmosphere for 2 hours. Films were cast from PAA2 – see Scheme 1 below, solution and dried at room temperature under vacuum. Neutralization equivalent was determined to be 208.1 (calculated 208.1).

Modification of polyimide films

Hydrolysis of polyimide films was carried out in aqueous, alcohol and alcohol-aqueous solutions of KOH or NaOH. Chelation was carried out by immersion of hydrolyzed films into an aqueous solu-



Poly(amic acid) structures: PAA2 from methylenedianthranilic acid and isophthaloylchloride; PAA from PMDA and ODA

Scheme 1

tion of metal salt. Reduction of the chelated films was carried out in an aqueous solution of NaBH_4 .

Measurements

Metal (M) content was determined as follows: M/PAA2 film was burned at $500\text{--}600^\circ\text{C}$ and the residue was dissolved in HCl solution. The resulting solution of metal was photocolometrically analyzed to determine the amount of metal. Content of potassium during KOH treatment of PAA2 film was determined by the reverse titration method.

IR spectra were recorded on Jasco 810 spectrometer.

Surface electrical resistivity was measured by the two probe technique with electrodes in contact with the metalized surface of PI film.

Reflectivity spectra were recorded on IR-65V spectrometer. *Scanning electronic microscopy (SEM)* and *X-ray fine diffraction (XRFD)* analysis were carried out on a "SEM-Cambridge S.360 Instruments" microscope. *X-ray diffractometry* was recorded with a diffractometer "Zeifert analysis".

Results and Discussion

Heterogeneous chelation of PAA2 films

Surface modification of PI films is widely used to enhance incorporation of metal atoms into the films [19,20]. One of the main chemical modification routes is hydrolysis of polyimide followed by exchange of K^+ ions by Pd^{2+} cations. This step of metallization process is the most important because it determines the quality and adhesion properties of fi-

nal metal coating. It is well known that sodium or potassium polyamate dissolves in alkali solutions and final hydrolysis represents itself as an equilibrium process of polyimide \rightarrow polyamate chemical conversion and "washing away" of modified layer. Moreover, PI surface is characterized by well developed system of mesoporous structure formed during the second step of PI formation (transformation of poly(amic acid) film into polyimide with elimination of water and solvent). The diameter of the porous channels is achieved to be 15-20 nm which increases during hydrolysis in 3M KOH aqueous solution up to 20-80 nm [21], and the thickness of the modified layer becomes 1-2 μm depending on the temperature of hydrolysis [22, 23]. Evaluation of surface properties of both sides of Kapton type polyimide reference film [24] by contact angle measurements and reflection spectroscopy has shown that the degree of imidization of polyimide films for glass side surface was not as high as that for the air side surface at the same temperature treatment.

In order to exclude the effect of surface morphology and polyimide: poly(amic acid) ratio of different films sides during hydrolysis process, we have taken more hydrolytically stable PAA2 film which can be considered as a model compound of poly(amic acid) (PMDA/ODA). Insolubility of PAA2 polyamate salts allows to achieve practically 100% conversion of PAA/K^+ into $\text{PAA2}/\text{M}^{n+}$ and to investigate further steps of metallization.

In Figure 1 are presented IR-spectra of PAA2 film (curve 1) and hydrolysed PAA2 film in 1% KOH aqueous solution (curve 2). We see that hydrolysis of PAA2 film gives the same characteristic bands in infrared as of polyamate structure of PI based on

PMDA and ODA as described in the literature [22]; formation of carboxylate structure: displacement of 1408 cm^{-1} (carbonyl) band to 1420 cm^{-1} (carboxylate), bands of amide I ($\nu = 1680\text{ cm}^{-1}$, 1670 cm^{-1}) which shifts to 1660 cm^{-1} , 1650 cm^{-1} and band of amide II ($\nu = 1590\text{ cm}^{-1}$) which shifts to 1575 cm^{-1} . The results of the investigation of duration of alkali treatment of PAA2 film on potassium content is presented in Fig. 2. It is seen that hydrolysis of PAA2 film proceeds for 30 minutes and achieves practically 100% conversion.

Exchange of K^+ ions with the transition metals takes place following the hydrolysis in aqueous metal salt solution. The spectra of chelated PAA2 films (curves 3 and 4, Fig. 1) are practically the same as for PAA2/ K^+ except a shift of NH vibration bands ($\nu = 3330\text{ cm}^{-1}$ to 3290 cm^{-1}) which points towards the formation of ion-coordination complexes between the NH group of PAA2 potassium salt and the metal cation.

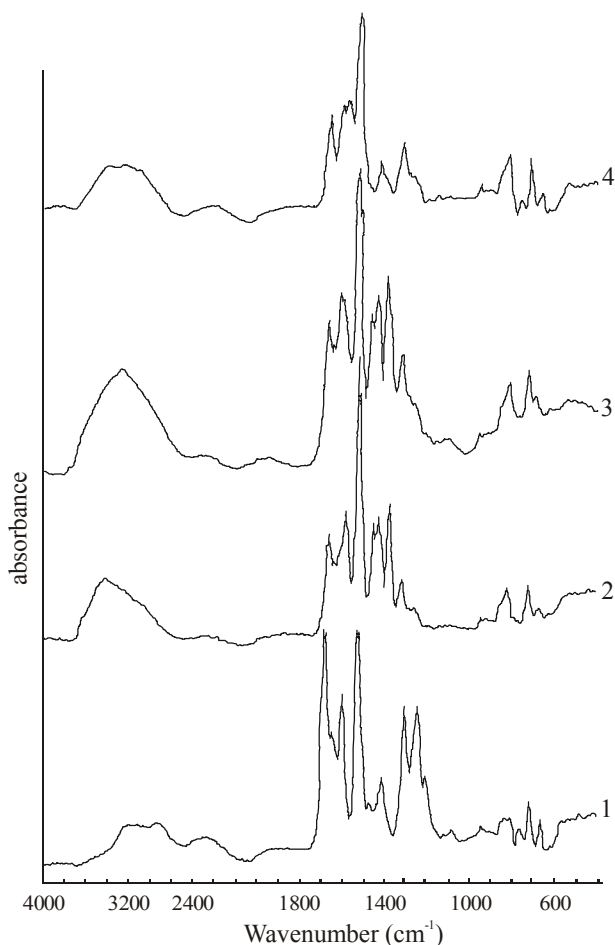


Fig. 1. IR spectra of: 1 – PAA2 film; 2 – hydrolysed PAA2 film; 3 – PAA2 film chelated by Cu^{2+} ; 4 – PAA2 film chelated by Ag^+ .

Determination of copper content in the film in the process of ion exchange shows that exchange of K^+ by Cu^{2+} cations proceeds nearly with 100% conversion (Fig. 2). This process suggests that there is no need to convert polyamide structure into poly(amic-acid) one by additional step of acidic treatment followed by metal loading [20].

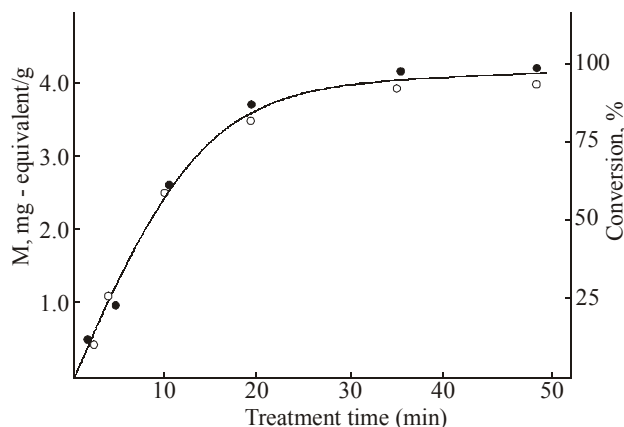


Fig. 2. Content M (mg-equivalent/g) of potassium (\bullet) and copper (\circ) in PAA2 film as a function of treatment duration. Conversion: degree of conversion of PAA2 carboxyl groups into potassium (\bullet) and copper (\circ) carboxylates.

Because of low degree of dissociation of COOH groups, ion exchange through carboxylate is more efficient and can also be applied for modification of polyimide based on PMDA and ODA. Such a way of modification allows to avoid the acidification step [20].

The data in Table 1 show that potassium forms carboxylate structure with PAA2 in the ratio 2:1 (K^+ :PAA2). Bivalent cations of copper and cobalt form carboxylates with a ratio near 1:1. In spite of monovalence of silver cation, carboxylate structure lies between 1:1 and 1:2 which is probably due to heterogeneity of the process. The tensile strength of chelated PAA2 films increases which shows that metal loading does not result in embrittlement of the films.

Heterogeneous reduction of chelated films

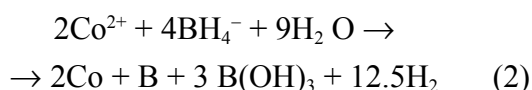
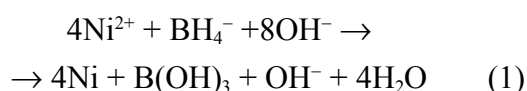
Thus PAA2 films chelated by cations of transition metals (Ag^+ , Cu^{2+} , Ni^{2+} , Co^{2+}) were subjected to reduction by NaBH_4 in aqueous or alcohol-aqueous solutions. NaBH_4 is a strong reducing agent with reduction potential $E = 1.24\text{ V}$ [16]. On immersion of chelated films into alcohol-aqueous solutions of NaBH_4 , reduction of the incorporated metal cations

Table 1
Characteristics of PAA2 films chelated with transition metal cations

Ion M ⁿ⁺	Colour	Metal content, %		Nitrogen content, %		σ*, MPa
		found	calculated	found	calculated	
K	colorless	15.64	15.87	5.34	5.68	90
Cu	green	11.90	13.29	5.26	5.86	115
Co	pink	11.30	12.44	5.43	5.91	110
Ag	colorless	25.20	34.22	5.12	4.44	120

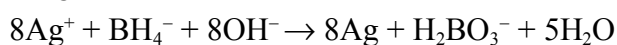
* tensile strength

takes place in 7-10 s and leads to formation of films with metallic lustre. (It should be noted that reactions proceeding during reduction of chelated films are complicated due to heterogeneous nature of the process). We suggest that reduction of cations in the bulk of PI film proceeds according to the following reactions:



The reactions of soluble nickel [25] and cobalt [16] salts in a basic medium in the presence of different ligands leads to formation of not spongy precipitates, but compact metal coatings with high lustre. Such ligands contain amine and amide groups and are called lustre forming agents. Their function is to adsorb on the surface of growing metal grains and limit their size. Probably the monomer unit of polyamate network of modified layer plays the role of lustre forming agent. An important observation was that all precipitates obtained under conditions of reduction of metals in the aqueous solution were characterized by significant incorporation of metal boride. Later it will be shown that cobalt or nickel coatings obtained by heterogeneous reduction in the bulk of polyimide modified layer do not contain boron.

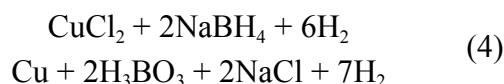
The reaction of sodium borohydride with silver results in the formation of pure metal, independent of the acidity of the reduction medium and presence of ligands [26,27].



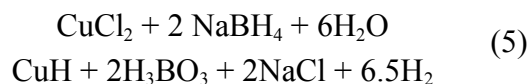
Reduction of Cu²⁺/PAA2 films is complicated and indefinite. The process of Cu²⁺ → Cu⁰ in solutions goes via different intermediate products and depends

on media conditions as well as reagents ratio. Moreover, reduction of the films is complicated by the heterogeneous nature of the process, *i.e.* it is limited by diffusion of the BH₄⁻ ions into the film. Previously [28] it was stated that interaction of NaBH₄ with CuCl₂ resulted in different products depending on the ratio (α = CuCl₂:NaBH₄) of the reagents and pH of the solution:

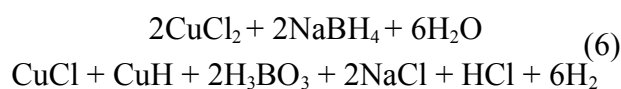
- at α = 0.1-0.25; pH 9-9.5 the reaction proceeds as:



- at α = 0.25-0.5; pH 7-9:



- at α = 1; pH 5:



According to reaction (4) metallic copper can be formed in the film under conditions of large excess of BH₄⁻ ions (α = 0.1 to 0.25). This is not acceptable in conditions of heterogeneous process because the reaction proceeds at large excess of Cu²⁺ ions in the bulk of chelated modified layer and is limited by diffusion of BH₄⁻ ions into the film. The black film formed corresponds to CuH/PAA2 film according to reaction (5). This is confirmed by chemical conversions of CuH/PAA2 film which are similar to the conversions of CuH: gas liberation (H₂) is observed in the immersion of the CuH/PAA2 film into NaOH solution; in ammonia solution the film takes on its initial slightly blue color (Cu²⁺/PAA2); CuH represents itself as a strong reducing agent. During immersion of CuH/PAA2 black film into a solution of AgNO₃ the intense process of H₂ liberation and formation of metallized silver surface with mirror reflection takes place.

Metallized polyimide films

Polyimide films (Kapton and Upilex) were metallized by similar methodology: hydrolysis, chelation and reduction. All films were covered with metallic lustre surface, strongly impregnated into polyimide surface with excellent adhesion. (All tests on delamination by using an adhesive tape showed that adhesion was good).

An SEM micrograph of the surface of metallized (Ag) polyimide Kapton 100HN film is shown in Fig. 3. Surface (dark background) is characterized by a uniform coating consisting of grains with 0.3–0.5 μm in size covered by light spots (silver particles) of size 0.4–0.7 μm , some of them achieve size of 1.2–4 μm . XRFD has shown that black background is silver layer (Fig. 4a) and light spots are silver particles (Fig. 4b). According to XRFD analysis it is seen that the intensity of silver peaks (silver particles, Fig. 4a) is 316 counts while for background silver layer (Fig. 4b) it corresponds to 900 counts. According to these data we estimate the thickness of silver layer as 2.2–2.5 μm . The SEM micrograph of silvered Upilex 25S film (Fig. 5) shows that silver coating is thinner (intensity – 33 counts, Fig. 5a) and uniform (grain size is around 0.3–0.4 μm) and the largest silver particle size is 0.5 μm . (Such metallized surface structure is a result of morphology of original films, which is characterized by more uniform compact surface of Upilex film as compared to Kapton).

We believe that during immersion of chelated film into NaBH_4 (pH 10) solution, silver cations due to their high mobility diffuse back to the surface along these channels and are reduced in the near-surface

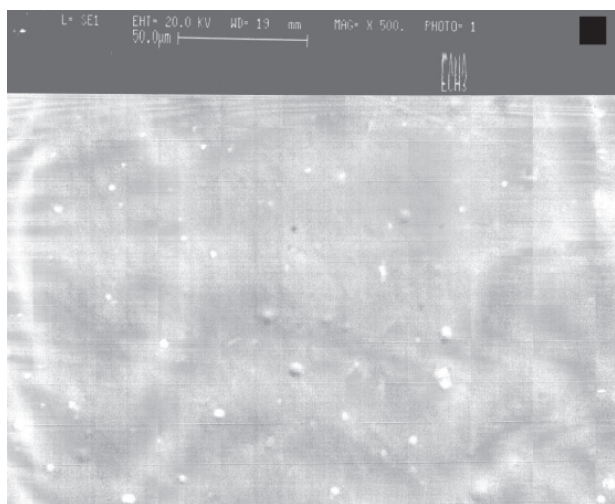


Fig. 3. SEM micrograph of Ag/Kapton 100 HN film.

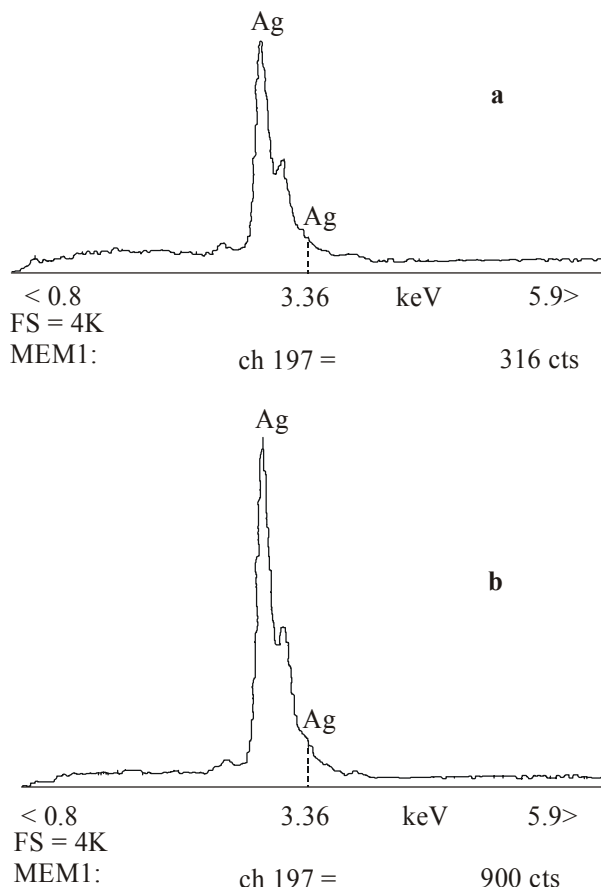


Fig. 4. XRFD patterns of Ag/Kapton 100HN film: a – light spot on the surface of the film; b – background of the film (dark surface).

layer. So silver particles on the surface of the film are the result of surface morphology of polyimide films. X-ray diffractogram of silvered Kapton 100 HN film (Fig. 6(1)) shows 111 ($\theta = 19.105^\circ$, $d = 2.3535 \text{ \AA}$) and 200 reflections ($\theta = 22.240^\circ$, $d = 2.0352 \text{ \AA}$) face centered cubic silver. We believe that silver coating formed by chemical reduction at room temperature and dried at 130°C is characterized by a definite crystal structure. Previously [29] the study of annealing of PMDA-ODA poly(amic acid) doped with silver acetate has shown unclear 111 peaks and the absence of other peaks were due to two reasons: very thin dispersed form of silver and distortion of crystal lattice. As the cure progresses, silver crystallites grow larger with a corresponding sharpening of the diffraction peaks (Fig. 6) and appearing of new peaks. We can conclude that *in situ* chemical metallization of polyimide surface results in the formation of silver phase with crystal structure. Increase of temperature leads to reverse diffusion of reduced silver to the surface, and growth and perfection of crystal lattice.

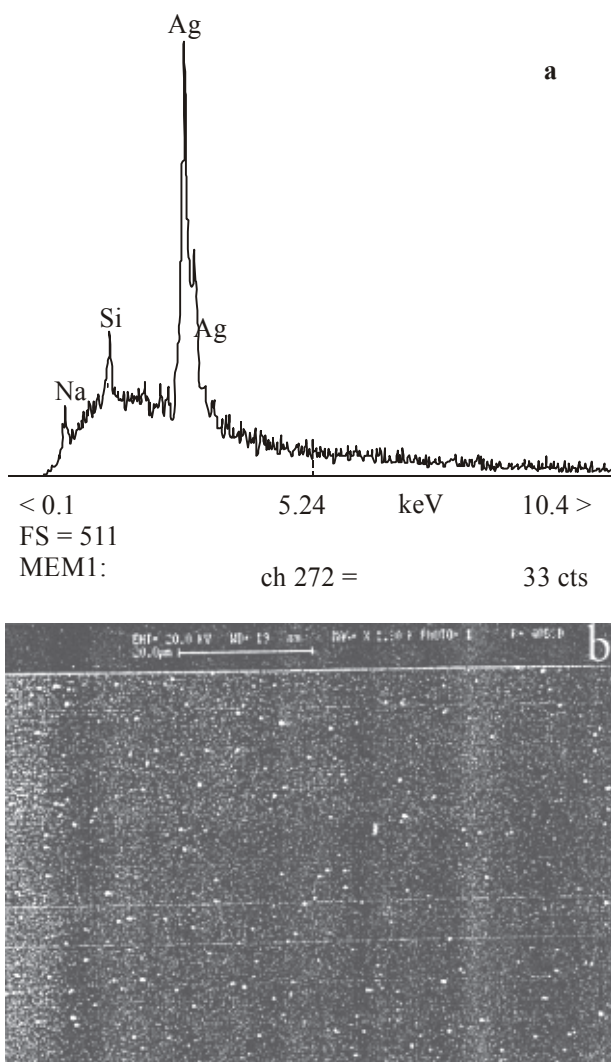


Fig. 5. SEM micrograph of Ag/Upilex 25S film (bottom); XRF analysis (top) of Ag/Upilex 25S film (background).

According to this methodology nickel and cobalt coated Kapton 100HN composite specimens were also prepared. The structure of these coatings is characterized by larger size of background metal grains (0.8-1.2 μm) and particles 4 μm (Figs. 7, 8). X-ray diffractometry has shown that nickel and cobalt metal phases are amorphous (independent of curing). This fact gives reasons to believe that because of significantly lower mobility of Ni^{2+} and Co^{2+} cations compared to Ag^+ , they do not move back to the near-surface layer of the film and are reduced in the bulk of modified layer. By electrochemical deposition of nickel and cobalt, the layers with lustre can be obtained only in the presence of lustre forming agents [16]. It is suggested that monomer units of modified polyimide matrix play the role of lustre forming agent and form metal grains with a size between 800-1200 nm.

The highly diffusive silver coatings obtained by

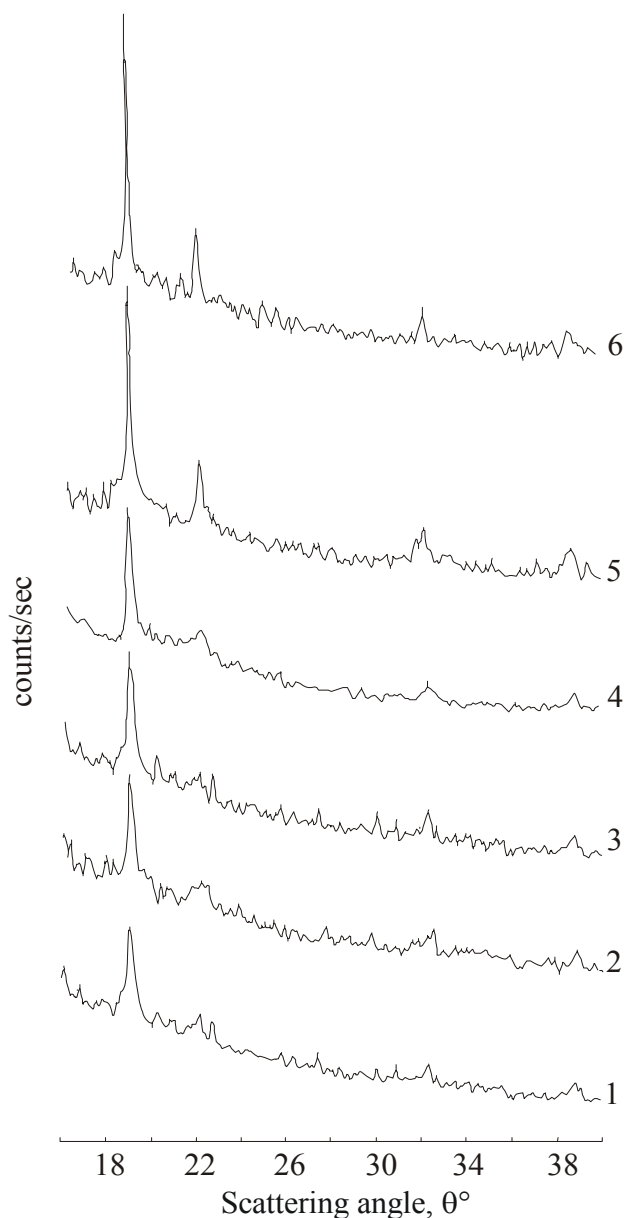


Fig. 6. X-ray diffractograms of Ag/Kapton 100 HN film cured at different temperatures: 1 – 130°C; 2 – 150°C; 3 – 180°C; 4 – 200°C; 5 – 225°C; 6 – 250°C.

this technique are not stable at temperatures higher than 250°C. As curing progresses at temperatures higher than 250°C, some whitish haze begins to appear. As this takes place, reflectivity decreases. Light polishing of the surface restores the original optical properties. We assume that this is due to the appearance of silver on the surface of the film and gradual degradation of surface structure followed by conversion of silver into a powder form. The same process was described during curing of silvered polyimide films based on BPDA-ODA [7], however this process takes place at 300°C because of the difference in the microstructure of these films.

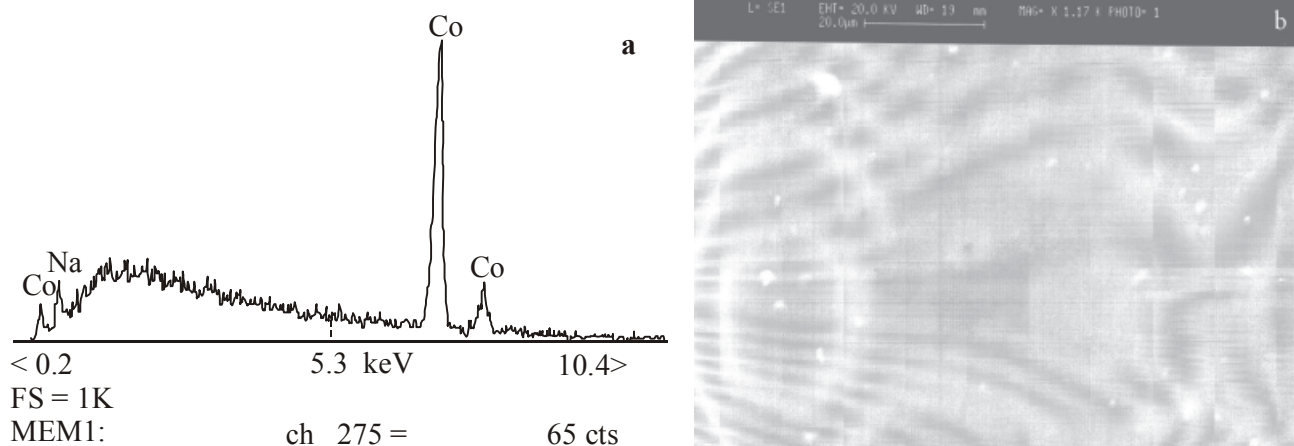


Fig. 7. XRFD analysis – (a); SEM micrograph of Co/Kapton 100 HN film – (b).

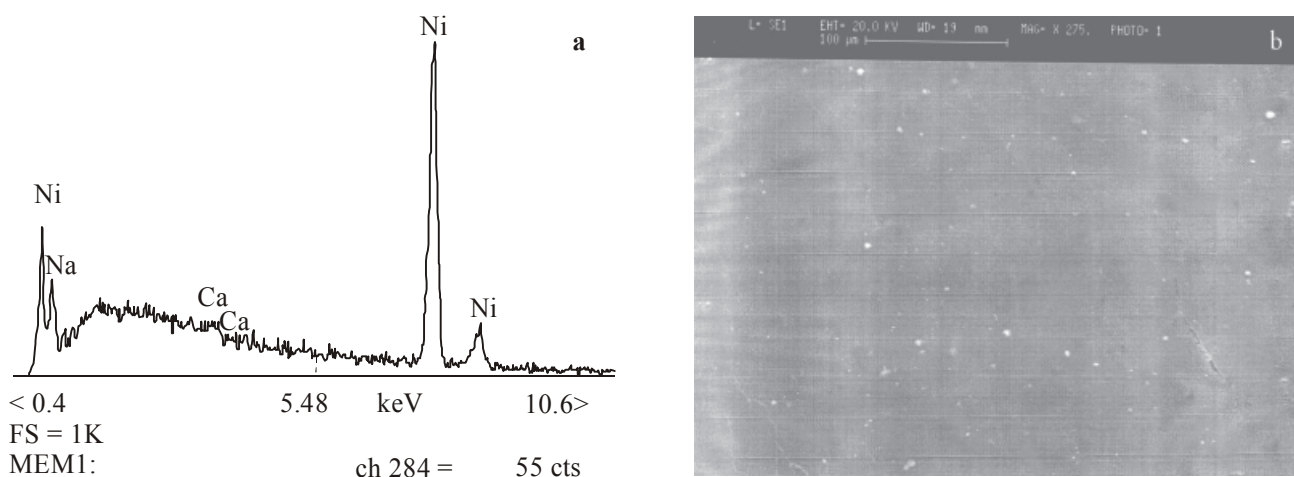


Fig. 8. XRFD analysis – (a); SEM micrograph of Ni/Kapton 100HN film – (b).

To stabilize diffusion of silver at temperatures higher than 250°C and to prevent its appearance on the surface of coating we obtained Ag-Ni and Ag-Co composite coatings on polyimide Kapton HN and Upilex 25S films. Curing up to 300°C showed good stability of silver coating.

Physical properties of metallized Kapton films

Thus formed silvered polyimide films have good electrical conductivity. In Figure 9, the temperature dependence of surface resistivity for Ag/Kapton 100 HN and Ag-Ni/Kapton 100 HN films cured at 200°C is presented. It is found that the relationship is linear.

However, different sides of metallized films are characterized by some differences in surface resistivity, which is due to difference in their surface morphology. If we compare the air sides of the films it is seen that silver coating stabilized by nickel is the most conductive, probably because of more deeper incorporation of silver-nickel layer. Glass sides of both films has practically the same resistivity. In the measured temperature range, the surface resistivity practically does not change for all four surfaces. Temperature dependence of surface resistivity $\rho_s(t) = \rho_{0s}(1 + \alpha_s t)$ (where ρ_{0s} and α_s are at 20°C; ρ_s – surface resistivity, α_s – thermal coefficient of resistivity) follows the equations:

- 1: $\rho_s(t) = 0.85 \times (1 + 9.3 \times 10^{-4} t)$ – glass side of Ag-Ni/Kapton 100 HN
- 1*: $\rho_s(t) = 0.48 \times (1 + 1.5 \times 10^{-4} t)$ – air side
- 2: $\rho_s(t) = 0.87 \times (1 + 8.1 \times 10^{-4} t)$ – glass side of Ag/Kapton 100 HN
- 2*: $\rho_s(t) = 1.22 \times (1 - 0.8 \times 10^{-4} t)$ – air side

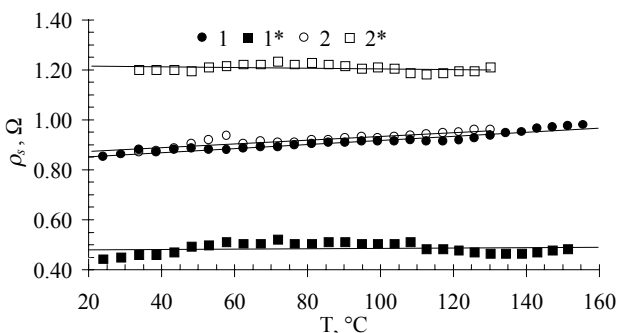


Fig. 9. Temperature dependence of surface resistivity (ρ_s) of different sides of metallized Kapton 100 HN films: 1 – glass side; 1* – air side of Ag-Ni coating; 2 – glass side; 2* – air side of Ag coating.

It is obvious that temperature coefficients are lower than for pure silver for which $\alpha = 0.0036$ [30, 31]. Possible explanation of such behavior may be the incorporation of silver layer into the polymer matrix. Surface resistivity of Ni/PI and Co/PI films measured at room temperature lies in the range 10 – 100 Ω/sq .

Figure 10 shows reflectivity spectra of glass sides of four metallized Kapton 100 HN polyimide films measured in relation to silver reference mirror. Visually the air side for thick Kapton films (500, 300, 200 HN) has slightly lower reflectivity. Reflectivity for both sides of Kapton 100, 75, 50 and 30 HN is practically the same. Reflectivity of the films at $\lambda = 531$ nm (wavelength of the most intensive solar irradiation) is 91% for Ag/PI film, 81% for Ag-Ni/PI, 47% for Ni/PI film and 41% for Co/PI film.

Conclusions

It can be concluded that heterogeneous chemical modification of polyimide films consist of consequent steps of hydrolysis in alkali solutions, chelation by metal cations in metal salts solutions and the follow-

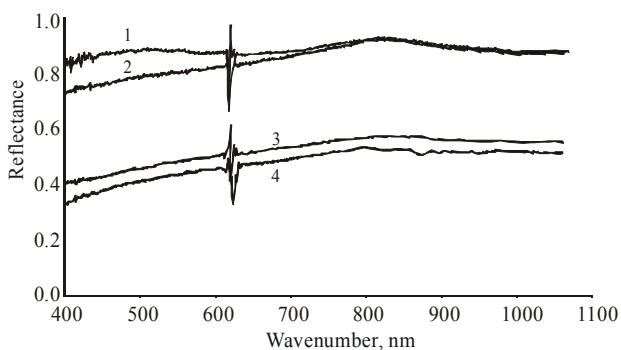


Fig. 10. Reflectivity spectra of Kapton 100HN films metallized by: 1 – Ag; 2 – Ag-Ni; 3 – Ni; 4 – Co.

ing reduction in aqueous solutions of sodium borohydride allows to form metal phase, strongly impregnated into the near-surface layer of polyimide film. Silver forms crystal structure whereas cobalt and nickel coatings are amorphous. In general, the metallized surface produced by this method represents itself in the background layer of grain structure covered by metal particles of larger size. It is suggested that the grain structure is due to the original morphology of the PI surface characterized by developed mesoporous system.

The preparation of metallized polyimide films by *in situ* chemical modification provides their high electroconductivity and reflectivity.

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