ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 142 (2001) 67–72

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photochemical formation of the electroluminescent image in polymer–silica gel nanoparticle composites

A.V. Vannikov*, A.D. Grishina, M.G. Tedoradze,
V.A. Kolesnikov, M.A. Brusentseva

Frumkin Institute of Electrochemistry, RAS, Leninsky Prospect 31, Moscow 117071, Russia

Received 9 May 2001; accepted 12 May 2001

Abstract

The paper is devoted to the investigation of the light-sensitive polymer layers providing the photochemical formation of the electroluminescent image. The process is based on a photochemical dissolution of aluminium film in a polymer layer with formation of the emitting light Al–organic complexes. The electroluminescence intensity increases with the increase of the exposure dose. Silica gel adding into composition results in 80–100-fold increase of the intensity. The unexposed areas of the layers do not emit the light.

Keywords: Polymer light-sensitive layer; Photochemical dissolution of aluminium; Aluminium–organic complexes; Electroluminescence

1. Introduction

Earlier, we have published a process for the photochemical dissolution of metallic films evaporated onto a support by acid and coloured products that are produced under exposing in a light-sensitive polymer layer cast on top of the metallic film [1,2]. There were elaborated polymer layers in which a photochemical dissolution of aluminium results in a formation of the electroluminescent (EL) image [3,4]. This article studies the influence of the silica gel nanoparticles added into the polymer composites on EL.

Recently, it has been demonstrated that mixing insulating oxide nanoparticles (SiO_2, TiO_2 and another) into electroluminescent polymers results in the enhanced radiance in polymer light-emitting diodes by more than an order of magnitude [5,6]. It was given a guess that the nanoparticles modify the device structure resulting in the enlargement of the interface between electrodes and composite materials to enable more effective injection and transport as well as inhibiting the formation of current filaments and shorts through the polymer thin layer. It was also suggested the formation of the capillary and capillary forces that amplify the current density and EL. The EL increase at incorporation of the SiO_2 nanoparticles inside an electroluminescent polymer layer has been account with the decrease of the effective thickness of the polymer layers [7]. Insertion of 1 nm SiO_2 film between the ITO (indium tin oxide) anode and polymer layer results in a 0.5–0.7 eV reduction of the hole injection barrier and in the sequel in a enhancement in EL brightness [8].

We now report a photochemical formation of the EL image in the layers which contain *m*-cresol-formaldehyde novolac resin (NR) and tetrabromomethane (CBr_4) producing an acid under illumination and also different precursors for the formation of the metallo-organic complexes. Fig. 1 shows the molecular structures of the NR and precursors such as aurintricarboxylic acid, triammonium salt (Aluminon), Malachite Green dye (MG^+) and pyrocatecholsulfone phthalein (Pyrocatechol Violet, PV). It is known that these precursors form the aluminium–organic complexes of ratio 1:1 [9].

As it was shown in previous publications, for example in [2], the following processes ensure the Al film dissolution into light-sensitive polymer layer.

1. The photochemical production of acid (photoacid). In the polymer compositions considered in this article the fragments of the NR polymer chains as the donor and the CBr_4 as the acceptors form a donor–acceptor complexes $NR^{\bullet}CBr_4$ having optical absorption in region 300–400 nm. The photoexcitation of the complex involves electron transfer from NR to CBr_4 with the

---

* Corresponding author. Tel.: +7-95-9523-122; fax: +7-95-9520-846.
E-mail address: van@elchem.ac.ru (A.V. Vannikov).

1010-6030/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S1010-6030(01)00473-7

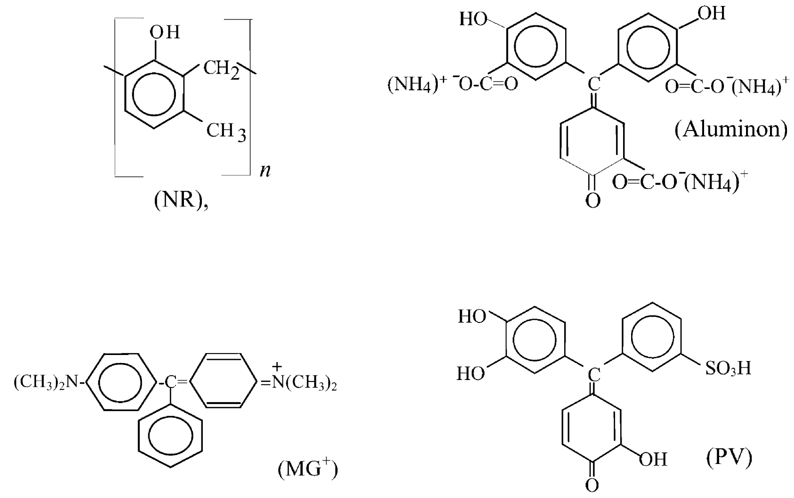
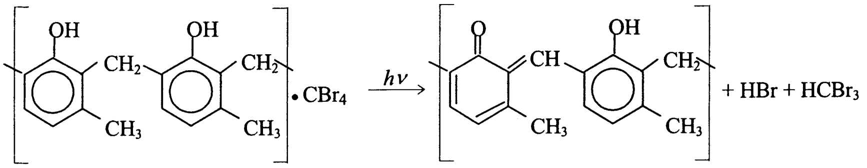


Fig. 1. Molecular structures of the NR and precursors for aluminium–organic complex formation such as Aluminon, Malachite Green (MG^+) and Pyrocatechol Violet (PV).

formation of the hydrobromic acid in the reaction [10] as follows:

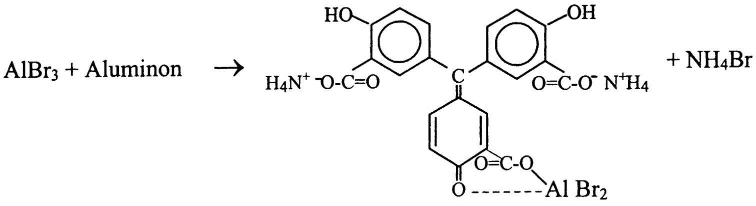


(1)

2. The oxidation of Al^0 in the interface zone:

$$Al^0 + 3HBr \rightarrow AlBr_3 + 1.5\,H_2 \qquad (2)$$

3. The formation of the metallo-organic complex with the precursor [2], for example, is as follows:



(3)

The shown structure of the complex is given in monograph [9].

2. Experimental

The polymer layers consisting of CBr_4 ($1.8\,mol\,dm^{-3}$) and different concentrations of the precursor were cast from ethanol–acetone (2:1) solution onto a glass substrate coated with conducting film SnO_2 using a spin-coating technique. The polymer compositions containing silica gel nanoparticles were formed as follows. At first the precursor and silica gel were added into the ethanol–acetone solution and kept for 24 h. For this time the optical density of the solution above silica gel considerably decreased for Aluminon and MG^+ but did not change in case of PV indicating that only the first two precursors were adsorbed by silica gel. After that the NR and CBr_4 were added into the solution. Then the composition was intensively mixed and cast onto the SnO_2 film.

The sandwich structures consisting of glass substrate/ SnO_2/light-sensitive polymer layer were exposed from the polymer layer side by band 365 nm of a mercury lamp to different exposure doses. Aluminium film was deposited by vacuum vapour deposition onto the surface of the exposed polymer layer. The residual CBr_4 was evaporated under vacuum and a polymer layer lost the light-sensitivity. As known from the work on the Al etching [2] the Al film on the exposed surface warps but remains on support when the polymer layer contains only the photoacid-forming components without the precursor. Only the polymer layers additionally containing the precursor dissolve Al film.

The Al film was partially dissolved into the irradiated areas of the polymer layer at keeping at room temperature. The remaining part was used as an Al cathode. The thickness of the photochemically modified polymer layer, 120–150 nm, was crude estimated from the optical absorption at 320 nm. The cathode area was 0.1 cm^2. In detached experiments, these diodes were covered with a thin film of the evaporated low molecular poly(vinyl alcohol) (PVA) in order to prevent the influence of molecular O_2 [11].

3. Results and discussion

3.1. *The dark conductivity of the polymer compositions*

The dissolution of the Al film increased the dark conductivity of the exposed areas of the polymer layer. To characterise the conductivity the dark xerographic discharge curves for the model sandwich structures glass plate/SnO_2/Al film/polymer layer of thickness about 300 nm were measured. In these experiments the ions produced by a positive corona discharge were deposited on the polymer layer surface for 10 s. The generated surface potential was near to the potential of saturation. The conductivity σ ($s\,cm^{-1}$) is related to the time of the surface potential discharge by half after corona switching off $\tau_{1/2}$ (s) by the formula

$$\sigma = (8.85 \times 10^{-14} \varepsilon \ln 2)/\tau_{1/2} \tag{4}$$

where ε is the dielectric constant. The discharge process for the unexposed layer consisting only of NR characterises by $\tau_{1/2} = 4800$ s [9]. The time $\tau_{1/2}$ was measured equal to 1380 s for the unexposed Aluminon containing polymer composition without silica gel. The $\tau_{1/2}$ decrease and hence, the σ increase (Eq. (4)) indicate that Aluminon provides the charge transport through the doped polymer layers. The values $\tau_{1/2} = 3100$ and 600 s were measured for the composition additionally containing silica gel 30 wt.% before and after an exposure to the dose 5.6 $J\,cm^{-2}$, respectively. The considerable increase of the time $\tau_{1/2}$ at incorporation of silica gel marks that adsorption of Aluminon on silica gel decreases the concentration of the transporting centres in the space between nanoparticles, and hence, decreases the charge carrier mobility. The reduction of $\tau_{1/2}$ from 3100 to 600 s, and hence, more then five-fold increase of conductivity (formula 4) for the exposed layers was caused by the dissolution of the Al film into the polymer layer according to the reactions (1–3) with the formation of the new transport centres. Thus, Aluminon and aluminium–Aluminon complexes function as the charge transporting centres.

3.2. *The EL diodes having a structure glass plate/SnO_2 film as the anode/polymer composite/Al film as the cathode*

To provide the optimal composition, the dependence of the EL intensity on the Aluminon and silica gel concentration was measured after keeping the diodes at room temperature for 24 h. The EL intensity and the current had have well-marked maximal and minimal values, respectively, for the NR containing Aluminon 0.7 $mol\,dm^{-3}$ and 30 wt.% of silica gel concentration. All data given below were measured for the polymer composites containing these optimal concentrations of Aluminon and silica gel. Fig. 2 compares the EL spectra measured at bias voltage of $V = 13$ V for a polymer composite with and without silica gel. The shown spectra were measured after 24 h and 20 days aging of the samples. As seen in Fig. 2, silica gel added into the polymer composite increased EL intensity from 5 (spectrum 1) to 400 relative units (spectrum 3) and displaces the maximum from 480 to 505 nm. The additional dissolution of the Al cathode provides the shown in Fig. 2 gradual increase of the EL intensity for the initial several days (spectra 2 and 4). The EL intensity did not change after 20 days of the diode aging. The further increase of the EL intensity up to 900 relative units after the vacuum deposition of the upper PVA film onto diode surface (spectrum 5) can be connected with the known decrease of the molecular oxygen content [11], which acts as electron trap.

The emission represented in Fig. 2 by spectrum 5 (EL intensity = 900 relative units at 508 nm and width of the spectrum on half-height is about 250 nm) was measured to correspond to brightness 10 $cd\,m^{-2}$ at current density 0.035 $A\,cm^{-2}$, and hence, to the efficiency about 0.03 $cd\,A^{-1}$.

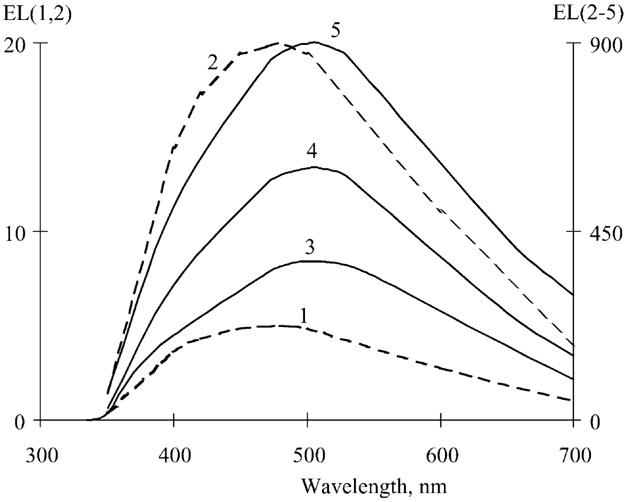


Fig. 2. The EL spectra of the diodes SnO_2/polymer layer/Al at bias voltage 13 V for layer from NR containing Aluminon 0.7 $mol\,dm^{-3}$(1, 2, left ordinate) and additional silica gel 30 wt.% (3–5, right ordinate). The aging time: 24 h (1, 3) and 20–70 days before (2, 4) and after coating by PVA (5). Exposure dose is 5.6 $J\,cm^{-2}$.

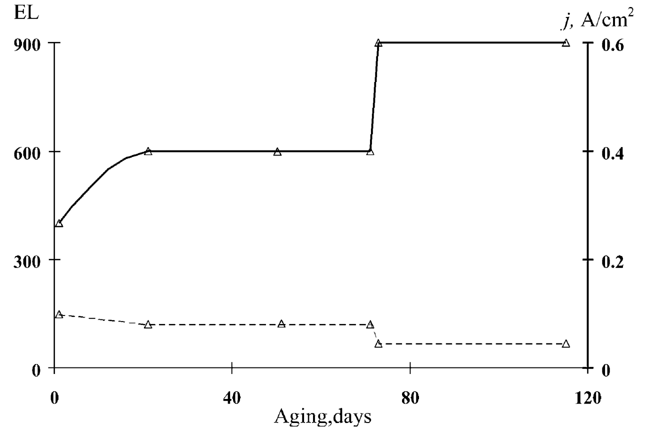


Fig. 3. The EL intensity (solid line) and the current density (dashed line) vs. time of the diode aging. The exposure dose equals 5.6 J cm^{-2}.

The dependence of both the EL intensity and the current density on the aging time of the diode after exposing to dose 5.6 J cm^{-2} are given in Fig. 3. As seen, the EL intensity increase is accompanied by the current density decrease. This effect can be connected with a transformation of a part of the hole transport centres into the electron transporting Al–Aluminon complexes. At the low concentration of these complexes, the excess holes cross the layer and are non-radiatively discharged on cathode. The transformation of the excess hole transporting centres into the electron ones increases the probability of the electron–hole meeting in the volume of the layer leading to the radiative recombination.

The photoluminescence (PL) excitation and emission spectra of the Aluminon containing NR layer cast on a quartz plate were measured. NR PL did not appear in the absence of the additions. The PL excitation spectrum of Aluminon for the emission wavelength 425 nm has a peak at 300 nm and shoulder in the region shorter 280 nm. The photoemission spectra with peaks at 397 and 425 nm correspond to the excitation wavelengths 250 and 300 nm. Their intensities is related as ∼1:0.1. The peak of the PL spectrum measured after the whole photochemical dissolution of the Al film in the polymer layer in the sandwich structure consisting of quartz plate/light-sensitive polymer layer/Al-film is displaced to 460 nm at an excitation by the wavelength 300 nm. This spectrum can belong to the aluminium–Aluminon complex PL. The EL spectrum (Fig. 2) is considerably broader than the PL one and comprises the region PL of the Aluminon alone (a short-wave part of the spectrum) and the aluminium–Aluminon complexes (a long-wave part of the spectrum). Hence, the Aluminon and Al–Aluminon complexes being the electron transporting centres as it was mentioned above are also centres of the radiative electron–hole recombination. The shown in Fig. 2 red shift of the EL spectra in the silica gel containing layers can be ascribed to the change of the complex ligand structure when adsorbing on silica gel.

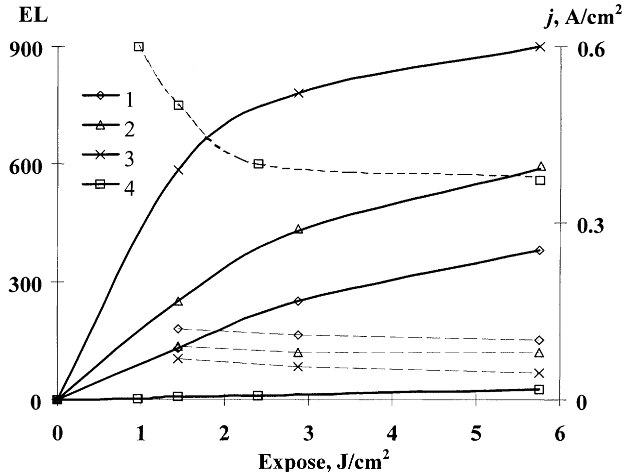


Fig. 4. The dependences of both the EL intensity (solid lines) and the current density (dotted lines) on exposure dose for the polymer layers with (1–3) and without (4) silica gel. The time of the diode aging after exposure: 24 h (1); 20–70 days (2, 4). PVA film coats the top of the diode (3) (EL and j are marked by the same points).

Fig. 4 shows the dependence of both the EL intensity and the current density on the exposure dose for the polymer layers with and without silica gel. As seen, the EL increases and current density decreases as a result of the silica gel addition and also with the increasing exposure dose. The unexposed areas of the layers do not emit the light.

The EL time response was measured by using the single 40 μs voltage pulses. Both the transient current and the EL intensity are shown in Fig. 5. As seen, the EL begins rising without the time delay evidencing the high mobility of the initial charge but it achieves half maximal value after about 3 μs delay. This time may be attributed to the transit time T_{tr} before the encounter of the charges residing in the centres of the moving packets which have the trap-limited mobility, μ. The mobility can be present by formula $\mu = (L_{\mathrm{tr}})^2/T_{\mathrm{tr}}V$ where L_{tr} is the transit distance for the charges and $V = 13\,\mathrm{V}$ is applied voltage. For our case, $L/2 < L_{\mathrm{tr}} < L$ and $L = 150\,\mathrm{nm}$ is a thickness of the layer. The crude estimate gives value $\mu \approx 1.5 \times 10^{-6}\,\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$.

Both the EL intensity and current density versus bias voltage are given in Fig. 6. The EL appears at about 6 V and reaches the EL intensity about 1250 relative units at bias voltage 16 V.

The EL spectra were measured for diodes containing layers doped by MG^+ 0.007 mol dm^{-3}. The EL intensity of the diode increases about 100 times (from 7 to 700 relative units) when using the silica gel nanoparticles addition and the PVA film cover. To understand a key function of the silica gel, the non acid-forming the poly(methyl methacrylate) (PMMA) matrix instead of NR was used. The composition consisting of PMMA, $\mathrm{CBr_4}$ and MG^+ photochemically dissolved the Al film in the silica gel presence and did not dissolve in its absence. This effect can be ascribed to the transformation of the MG^+ cation groups into neutral ones

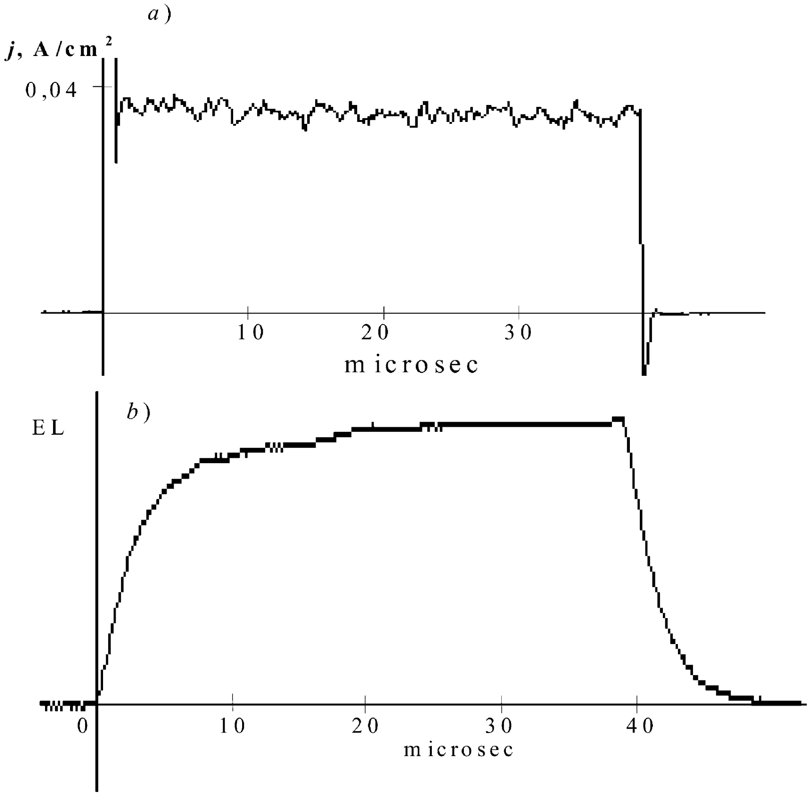


Fig. 5. The time response of current density (a) and EL intensity (b) upon application of a 40 μs rectangular pulse of voltage 13 V. The exposing dose 5.6 J cm^{-2}; the aging time about 110 days. The diode is covered by PVA film.

at a formation of the adsorption bonds between MG$^+$ and silica gel. Neutral dye is a donor and participates in the acid forming photochemical reaction similar to reaction (1).

Thus, the relative low EL intensity in the silica gel absence for the Aluminon and MG$^+$ containing layers can be connected with trapping of mobile electrons on cationic nitrogen containing groups and hence, with the decrease of the probability of the radiative electron–hole recombination. A transformation of the nitrogen cationic groups into neutral ones as a result of the interaction with silica gel leads to the decrease of the these trap concentration and to the increase of the probability of the radiative electron–hole recombination.

Fig. 7 shows the EL spectra (relative units) for polymer layer containing the Pyrocatechol Violet as the precursor that does not contain cationic nitrogen groups (see Fig. 1).

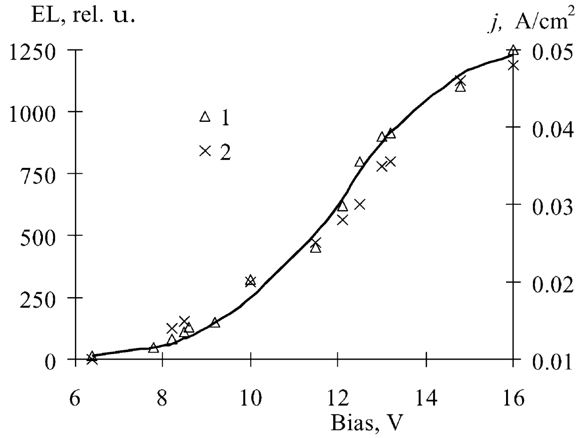


Fig. 6. The dependences a EL intensity (1) and a current density (2) on bias voltage.

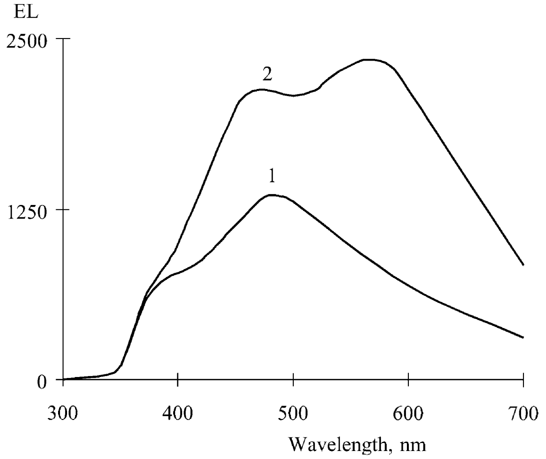


Fig. 7. EL spectra (relative units) of the diodes consisting of SnO_2 as the anode/PV containing polymer layer exposed to dose 5.6 J cm^{-2}/Al as the cathode measured at bias voltage 13 V after the aging of the diode for 20 days before (1) and after coating by PVA (2). PV 0.26 mol dm^{-3}.

As mentioned above, the silica gel slightly adsorbs the PV dye. Silica gel added into this composition leads to the slight decrease of the EL intensity unlike the nitrogen containing dyes. The EL intensities in Fig. 7 are higher than for doped by Aluminon the silica gel containing layers. This correlation confirms the guesses that (1) just cationic nitrogen groups are responsible for relatively low EL intensity being the traps for mobile electrons and (2) the cationic groups transform into neutral ones when adsorbing on the silica gel. As seen in Fig. 7, the PVA coaver leads almost to two-fold increase of the EL intensity owing to appearance of the long-wave part of the spectra which belongs to the Al–PV complex emission. This effect can be connected with the decrease of the molecular oxygen that traps the mobile electrons.

The all above presented results allow to suggest the next processes. (Below P is the precursor that is Aluminon, MG^+ and PV.) The cathodic process $(Al–P) + e^- \rightarrow (Al–P)^{\bullet -}$; followed by the electron transport which is a multiple successive electron hopping from the radical–anion to the neighbour neutral complex $(Al–P)^{\bullet -} + (Al–P) \rightarrow (Al–P) + (Al–P)^{\bullet -}$ and so on. A molecular O_2 traps the electrons in the process

$$(Al–P)^{\bullet -} + O_2 \rightarrow (Al–P) + O_2{}^{\bullet -} \quad (5)$$

The precursors are the transporting centres for holes. The anodic formation radical–cation $P + h \rightarrow (P)^{\bullet +}$ followed by the hole transport $P^{\bullet +} + P \rightarrow P + P^{\bullet +}$ and so on and by a formation of the excitons P^* and $(Al–P)^*$ as a result of the recombination processes $P^{\bullet +} + (Al–P)^{\bullet -} \rightarrow P^* + (Al–P)$ and $P + (Al–P)^*$. Then it follows the light emission $(P)^* \rightarrow P + h\nu$ and $(Al–P)^* \rightarrow (Al–P) + h\nu$. The electron capture in the process (5) decreases the probability of the radiative electron–hole recombination.

4. Conclusion

New light-sensitive polymer compositions based on photochemical dissolution of Al-films with production of the Al–dye complexes are elaborated. These complexes are responsible for electron transport and electroluminescence of the exposed areas of the layers. The EL intensity increases with the increase of the exposure dose of the illumination and electroluminescence absents on unexposed areas the same layer. Silica gel adding into composition increases in 80–100 times the EL intensity for dyes containing cationic nitrogen groups. The Al–dye complexes act as both the transport centres and the light-emitting chromophores. The relative low EL intensity for the Aluminon and MG^+ containing layers in the silica gel absence can be connected with trapping of mobile electrons by cationic nitrogen containing groups, and hence, with a decrease the probability of the electron–hole recombination. The formation of the adsorption bonds with silica gel causes a transformation of the Aluminon and MG^+ cationic groups into the neutral ones. This effect leads to the decrease of the concentration of the deep electron traps and the increase of the EL intensity.

The increase of the EL intensity after deposition of the PVA film can be connected with the well known decrease of the molecular oxygen content as molecules O_2 are also the electron traps.

Acknowledgements

The research described in this publication was supported by Grant no. 872-98 from International Science and Technological Center and by Project no. 99-03-32111 from Russian Foundation for Basic Research.

References

[1] A.V. Vannikov, A.D. Grishina, M.G. Tedoradze, Mendeleev Commun. (1992) 62.

[2] A.D. Grishina, M.G. Tedoradze, A.V. Vannikov, J. Photochem. Photobiol. A: Chem. 92 (1995) 223.

[3] A.D. Grishina, M.G. Tedoradze, V.A. Kolesnikov, M.A. Brusentseva, A.V. Vannikov, High Energy Chem. 33 (1999) 396.

[4] A.D. Grishina, M.G. Tedoradze, V.A. Kolesnikov, E.I. Maltsev, M.A. Brusentseva, A.I. Kostenko, A.F. Popov, A.V. Vannikov, High Energy Chem. 34 (2000) 309.

[5] S.A. Carter, J.C. Scott, P.J. Brock, Appl. Phys. Lett. 71 (1997) 1145.

[6] L. Bozano, S.E. Tuttle, S.A. Carter, P.J. Brock, Appl. Phys. Lett. 73 (1998) 3911.

[7] P.W.M. Blom, H.F.M. Schoo, M. Matters, Appl. Phys. Lett. 73 (1998) 3914.

[8] X.M. Ding, L.M. Hung, L.F. Cheng, Z.B. Deng, X.Y. Hou, C.S. Lee, S.T. Lee, Appl. Phys. Lett. 76 (2000) 2704.

[9] V.N. Tikhonov, Analytic Chemistry of Aluminium, Science, Moscow, 1971, 266 pp. (in Russian).

[10] A.D. Grishina, M.G. Tedoradze, O.V. Kurii, V.A. Kolesnikov, A.V. Vannikov, Sci. Appl. Photo. 39 (4) (1998) 321.

[11] A.D. Grishina, A.V. Vannikov, J. Sci. Appl. Photo-cinematogr. 31, (4) (1986) 276 (in Russian).