

# Light emitting thin film structures based on organic luminophors embedded in porous alumina matrixes

*G.G. Gorokh, V.A. Labunov and A.G. Smirnov*  
Belarusian State University of Informatics and Radioelectronics,  
P. Brovki Str., 6, 220027 Minsk, Belarus  
Phone: +37517-2398858, e-mail: smirnov@gw.bsuir.unibel.by  
*A. V. Kukhta*

Institute of Molecular and Atomic Physics, National Academy of Sciences,  
F. Skariny Av., 65, 220600 Minsk, Belarus  
Phone: +37517-2841719, e-mail: kukhta@imaph.bas-net.by

## Abstract

*Light emitting thin film structures based on organic luminophors embedded in porous alumina matrixes are discussing. The optical properties of the luminophors in a matrix differ greatly from their properties in usual crystalline state or in a solution and they depend on the concentration of luminophors molecules of up to 10<sup>-2</sup> mol/l. Successful experiments on filling of pores with organic luminophors and the investigation of their luminescent and optical properties were carried out.*

## 1. Introduction

Recently, more and more attention has been paid to organic light emitting diode (OLED) displays because of their various advantages such as high contrast ratio, fast response time, wide viewing angle and simple device structure. Now they are emerging as the main candidate among many technologies under development for next generation of flat panel displays. Organic electroluminescent structures have been studied extensively since C.W.Tang and S.A. Van Slyke demonstrated a high performance green emission in 1987 [1]. Later intensive researches have been carried out with the focus on its potential applications in flat panel display technology. However, organic electroluminescent (EL) materials are easily degraded during operating. In addition, the thin cathodes of these devices consist of reactive metals that degrade even more rapidly than the organic EL material. OLED displays require, therefore, substrates and sealants extremely impermeable to environment influence.

Nowadays anodic oxide of aluminum (AOA) attracts more and more attention of the researchers dealing with displays and optoelectronic devices.

Anodic oxide of aluminum is a dielectric material fabricated by anodic oxidation of aluminum in liquid electrolyte in processing of an electrical current. It has high electrophysical, mechanical, thermal and unique optical properties [2]. The structure of porous AOA is described as a close-packed array of columnar hexagonal cells, containing vertical and cylindrical pores, distributed evenly throughout the oxide layer (Fig 1). AOA films, with pores diameter ranging from 500 nm to less than 5 nm, can be made easily, cheaply and reproducibly.

The opportunity of filling of AOA matrixes with organic luminophors opens prospects of novel light

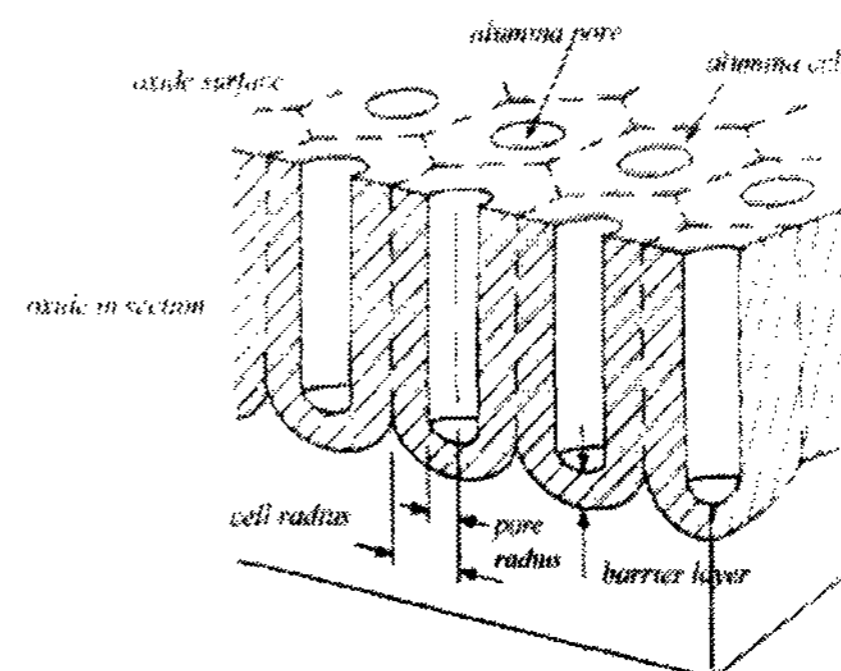


Fig.1 Schematic diagram of a porous anodic film on aluminium, showing pores in cross-section and at a plane through the oxide, each in a hexagonal cell. During anodizing, the field is distributed across the scalloped barrier layer, separating the electrolyte within the pores from the aluminium metal

emitting thin film structures fabrication. The combination of unique properties of a matrix and various properties of organic luminophors can lead to unexpected and specific effects that provide vast scientific and practical interest. But this sphere has been still poor investigated.

The preliminary experiments on filling of a AOA matrix with organic luminophors have shown that their optical properties differ greatly from a usual state [3]. The main purpose of this paper is to find the correlation between AOA modification processes and luminescent properties of a light emitting structure.

## 2. Experimental

The experimental specimens were 99.99% purity aluminum films, 2  $\mu\text{m}$  thick, E-beam evaporated on a glass substrate. Electrochemical anodizing of samples was carried out in 0.4 M aqueous solution of tartaric acid [4] with a constant current density of 6  $\text{mA}/\text{cm}^2$  at 20  $^\circ\text{C}$ . Anodic potential above 215 V was measured during anodization. The thickness of the porous AOA film reached up to 3  $\mu\text{m}$ , the average pores diameter was near 100 nm. After the anodization the samples were washed in deionized water, than they were dried on a centrifuge and in a thermostat with the temperature of 393 K during 30 minutes. To increase the AOA pore size (by widening the diameters of the pores) the specimens were etched into 2M  $\text{H}_2\text{SO}_4$  solution at 323 K during 50, 100 and 150 minutes. As a result the average diameter of the

pores after 150 minutes of etching increased up to 300 nm and the porosity of the oxide was not less than 50% (Fig.2). The morphology and structure of these films were investigated using the scanning electron microscope (JEOL JEM-100CX).

The 4-methyl-amino-N-(o-tolyl)-1,8-naphthalimide and the  $\text{Eu}^{3+}(\text{Br-BTFA})_3\text{TPPO}$  (HBr-BTFA is brominebenzoyltrifluoroacetone and TPPO is triphenylphosphinoxide) were used as organic luminophors. These materials have good electroluminescent properties [5, 6, 7]. They are known as very stable substances conserving a structure in monomolecular state. Filling of AOA matrix with an organic luminophor was made by the impregnation of a sample into the concentrated ( $\sim 10^{-3}$  mol/l) ethanol solution followed by the immediate heating in vacuum using a drying box, at temperature of 393 K for one hour to evaporate the solvent. Then the careful mechanical cleaning of oxide film surface was done. The concentration of organic molecules in pores is determined by the concentration of initial solution.

Luminescence emission spectra are recorded on SFL-1211A (Solar III) fluorometer. Absorption and reflection spectra are measured with Varian Cary 500 Scan UV-VIS-NIR absorption spectrophotometer. The relative intensity measurements are made using a usual photomultiplier and standard digital voltmeter. All measurements were made at room temperature.

## 3. Results and discussion

Fluorescent spectra of organic luminophors embedded into AOA modified matrixes during 50-, 100- and 150- minutes of chemical etching are shown in Fig. 3, 4. In all cases we observed that light intensity of both luminophors embedded into the pores are much higher than intensity of the same luminophors in a film state on a glass substrate and the own matrix luminescence. The naphthalimide spectra is usually wide with the maximum in the range of 545-550 nm whereas the  $\text{Eu}^{3+}(\text{Br-BTFA})_3\text{TPPO}$  spectra is quite sharp in the range of 615 nm. Comparing both luminescent spectra for different pore sizes we have found that, at first, after etching of AOA matrixes during 50 minutes the light intensity is decreasing slightly, but after 100 - minutes of etching these values are increasing drastically and achieved the maximum at 150 minutes. The further increasing of chemical etching considerably reduced the mechanical strength of matrixes.

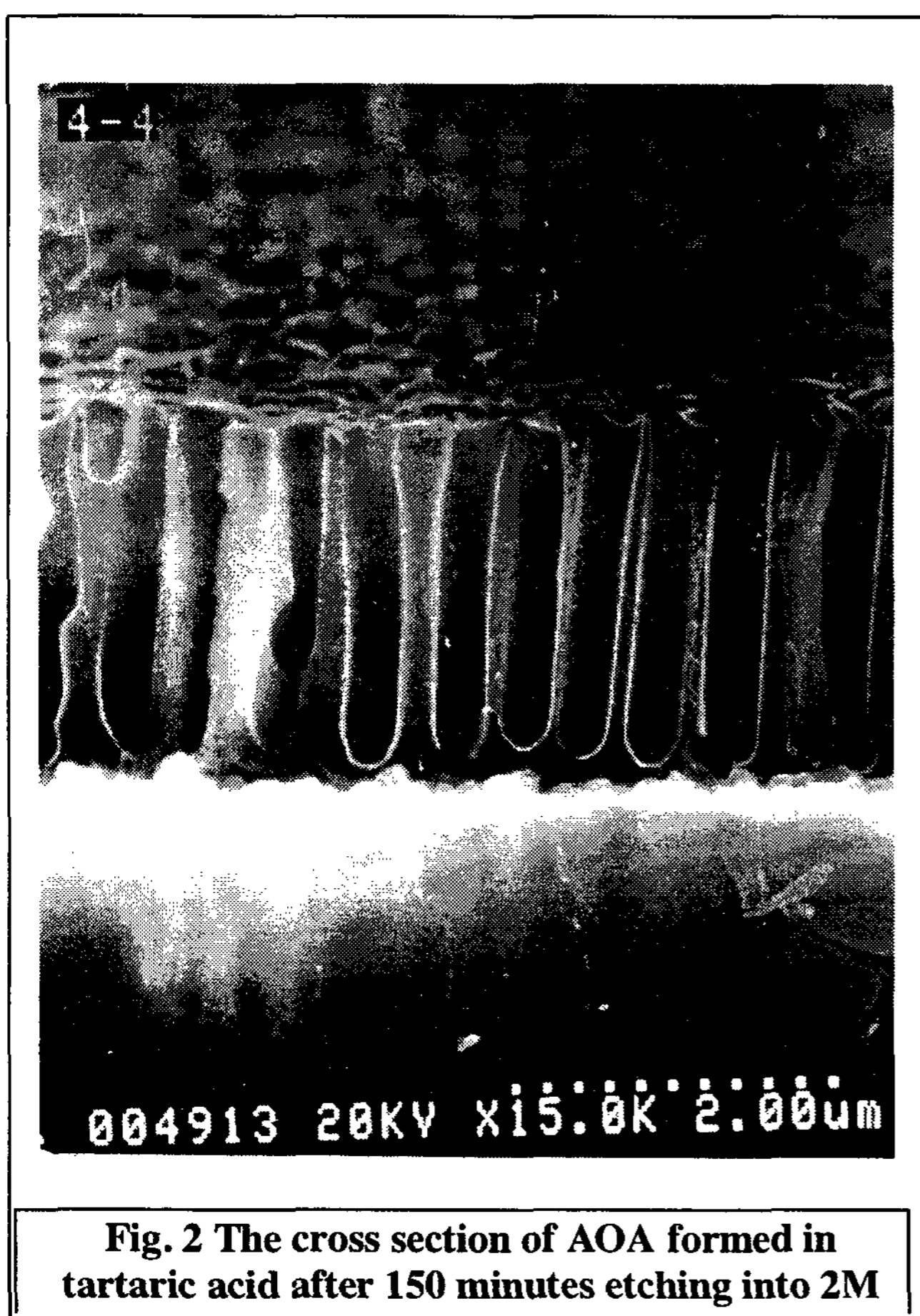


Fig. 2 The cross section of AOA formed in tartaric acid after 150 minutes etching into 2M

We can explain such a behavior that initial AOA matrix is doped with the incorporated electrolyte anions [8] which react with the luminophor molecules. The removal of this doping layer from the pore wall surface leads to deterioration of fluorescence during

initial stages of etching. When the pore volume becomes quite large the concentration of luminophor molecules is increasing considerably and, therefore, the intensity of light emission is also rising.

In our case organic molecules of luminophors

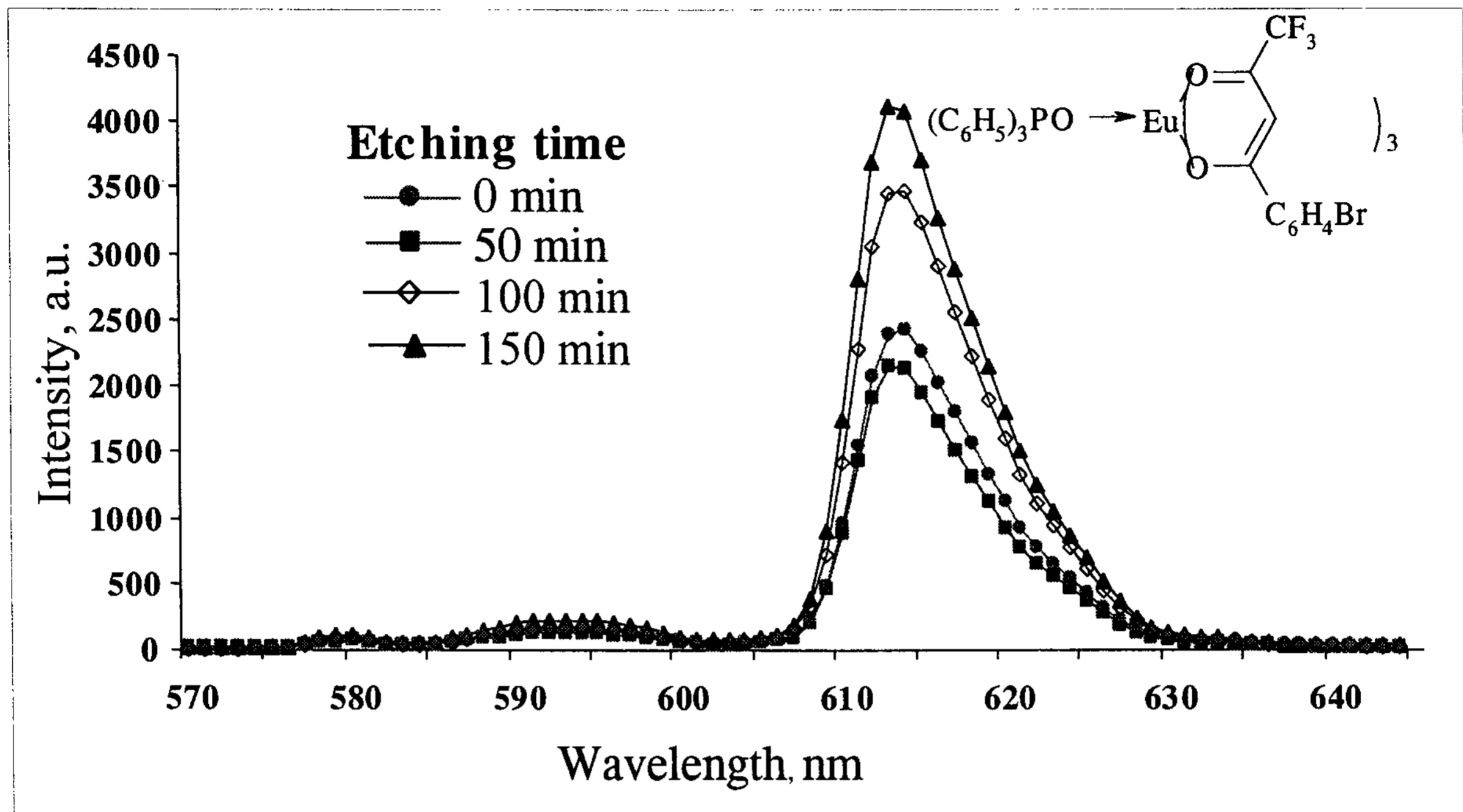


Fig.3. Photoluminescence spectra of  $Eu^{3+}(Br-BTFA)_3 \cdot TPPO$  embedded into modified AOA matrixes

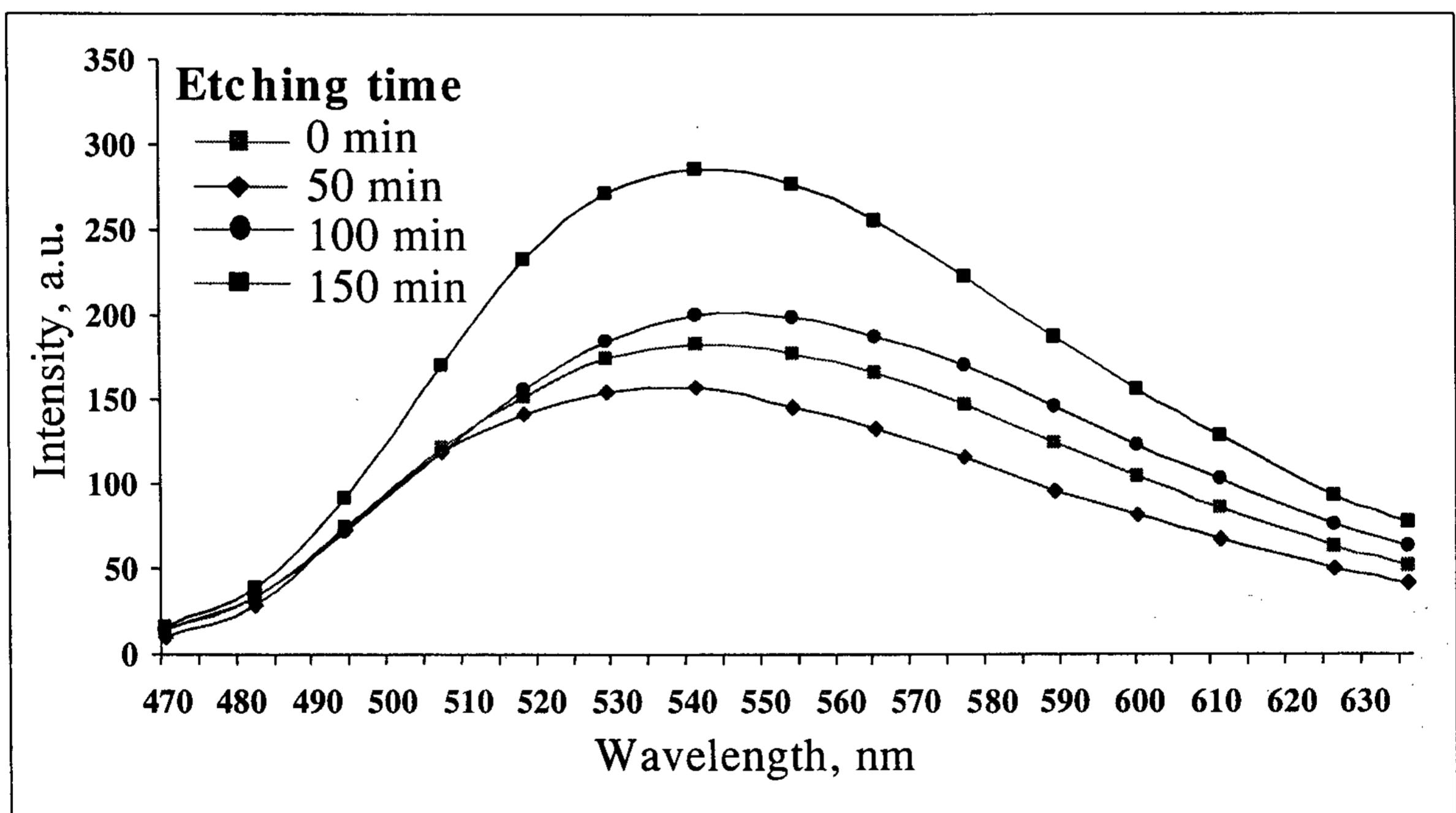


Fig.4. Photoluminescence spectra of 4-methyl-amino-N-(o-tolyl)-1,8-naphthalimide embedded into modified AOA matrixes

were physically adsorbed at walls of cylindrical pores after evaporation of solvent. Major drawback of organic luminophors in solid state is the low luminescence quantum yield due to aggregation (though in solution they luminescence intensively). However, luminophor concentration in a porous matrix can be very high, without essential luminescence quenching, because of large adsorbing surface inside the pore.

The next step of our work will be connected with the careful investigation of mechanisms of interaction of organic luminophors with an AOA matrix. It will allow studying deeply properties of a matrix, to investigate specific sorption of organic molecules on a pore wall, to carry out various sorts of updating of such matrixes that in final total will enable to receive new luminescent structures both to find out and to study new quantum - size optical and electrical effects.

#### 4. Conclusion

It has been found, that optical properties of the luminophors in a matrix differ greatly from their properties in usual crystalline state or in a solution and that its optical properties depend on the concentration of luminophors molecules of up to  $10^{-2}$  mol/l. Successful experiments on filling of AOA pores with organic luminophors and the investigation of their luminescent and optical properties were carried out.

#### 5. References

- [1].C.W.Tang and S.A. Van Slyke, *Appl.Phys.Lett.*, 51, p. 913 (1987).
- [2].G.G. Gorokh, V.F. Surganov, A.V. Surganov, in: *Abstracts of the Int. Conf. "Solid State Chemistry 2000"*, (Prague, 2000) p.169.
- [3].A.V Kukhta., G.G.Gorokh, E.E. Kolesnik, A.M . Mozalev, M.I. Taoubi, *Organic-Inorganic Electroluminescent Materials Based On Modified Porous Alumina Films; Proceedings of the 10<sup>th</sup> International Symposium Advanced Display Technologies*, 1-5 October 2001, Minsk, Belarus, C 193-197.
- [4].V.Surganov, G.Gorokh, *Anodic oxide cellular structure formation on aluminum films in tartaric acid electrolyte. - Materials Letters*, 1993, v.17, No 3/4, p.121-124.
- [5].A.V. Kukhta, E.E. Kolesnik, M.I. Taoubi, I.K. Grabchev. *J. Appl. Spectrosc.* 67 (2000) 678.
- [6].A.V. Kukhta, E.E. Kolesnik, M.I. Taoubi, D.A. Drozdova, N.R. Prokopchuk, *Synth. Met.* 119 (2001) 129.
- [7].A.V. Kukhta, E.E. Kolesnik, A.M. Mozalev, A.G. Smirnov, M.I. Taoubi, *New organic EL structures using porous alumina films*, *Proc. SID-2000*, pp. 645-647.
- [8].V. Surganov, C. Jansson, J. Nielsen, P. Morgen, G. Gorokh, A. Larsen, *Different stages of aluminium anodization studied with depth profiling techniques. - Electrochimica Acta*, 1988, v.33, No 4, p.517-519.