23.4 Fabrication Process of Lanthanide-Doped Xerogel/Porous Anodic Alumina Structures for an Image Formation

A. Smirnov**, I. Molchan, N. Gaponenko, V. Labunov**

Belarusian State University of Informatics and Radioelectronics, 220027 Minsk, Republic of Belarus

Abstract

We report on the developed fabrication method of lanthanide-doped xerogel/porous anodic alumina structures for an image formation via the aluminum anodization, the sol-gel synthesis, and the photolithography process. The structures of europium- or terbium-doped xerogel/porous anodic alumina are also considered in view of application in electroluminescent devices.

1. Introduction

Mesoporous materials with the pores of the submicron to micron range are been investigated as a wide application area. Utilizing a unique self-organized matrix of porous anodic alumina (PAA) is considered to be very promising for application in flat display technologies, micro- and optoelectronics, magnetic recording, formation of nanotubes etc. PAA is synthesized by anodizing of aluminum mainly in inorganic acid solutions and has reproducible regular morphology determined by anodizing conditions. Recently, we proposed to employ mesoporous materials as a template for the fabrication of the luminescent films obtained by sol-gel method. Such kind of films could be prepared from a coatable colloidal solution, which is a dispersion of colloidal particles of the diameters of 1 to 100 nm in a liquid.

The embedment of optically active trivalent lanthanide ions into periodically arranged matrix of PAA via sol-gel process gives an opportunity to fabricate luminescent materials that have high photoluminescence (PL) intensities [1]. Among other mesoporous matrices including porous silicon or artificial opals, PAA is the most prospective one for embedment of optically active species by sol-gel method due to its reproducible morphology and relatively low cost of synthesis, and a row of interesting optical properties.

The paper summarizes our recent results on synthesis and investigation of luminescent properties from europium- and terbium-doped xerogel solids confined in mesopores of anodic alumina films. The method for fabrication of photoluminescent images based on anodization, photolithography, and sol-gel processes is proposed. The structures lanthanide-doped xerogel/PAA is also considered in view of application in electroluminescent (EL) devices.

2. Photoluminescent images

The PL from the structures Eu- or Tb-doped xerogel film/PAA is visible by a naked eye at the temperature range from 300 to 10 K. Any UV source is suitable to excite lanthanides in the structures considered, such as xenon or deuterium lamp, or laser source. Moreover, it should be noted that these structures possess high thermal and chemical stability and do not degrade their luminescent properties for a long time. In this connection, we have developed two methods for fabrication of luminescent images utilizing anodising, photolithography, and sol-gel processes (Fig. 1).

At the initial step of the first method (Fig 1 a) [2], the silicon substrate with sputtered aluminum film (1) is coated with photoresist (2). The standard photolithography procedure is applied to transfer the required image from mask to aluminum layer (3). Further, the aluminum is anodized into the opened windows (4) followed by the deposition of luminescent xerogel film into anodized areas (5), after that the photoresist is removed (6). Exposition to a proper excitation light allows emission from xerogel-filled areas, and accordingly observation of the luminescent images (7). The second method (Fig 2. b) differs from the described above that the photolithography is applied to the surface of porous anodic alumina. The samples of photoluminescent images, fabricated through the process above using Tb- and Eu-doped xerogels, are shown in the Fig. 1 c, d.

The possible applications of developed structures may include fabrication of identification markers, watermarks etc. with high stability in rugged environments.

3. Electroluminescent Structures

EL devices are currently the focus of substantial research effort due to their potential application in flat panel display industry. The most of the papers in this area are directed to synthesis of organic EL materials, and high luminous efficiencies at low operational voltages have been demonstrated [3]. However, organic compounds generally have a number of disadvantages, including poor thermal and mechanical stability. In addition, while electrical transport in organic materials has improved, the room temperature mobility is fundamentally limited by the weak van der Waals interactions between organic molecules (as opposed to the stronger covalent and ionic forces found extended inorganic systems) [4]. Therefore, the stability and electrical transport characteristics of organic materials contribute to reduced device lifetime. The most widespread inorganic sulfide-based phosphors such as ZnS:Mn, SrS:Cu etc. in contrast have inappropriate voltage-current characteristic with the threshold voltage as a rule above 150 V below which little light is emitted [5]. Further, such materials have wide emission bands, and their synthesis involves expensive vacuum processes.

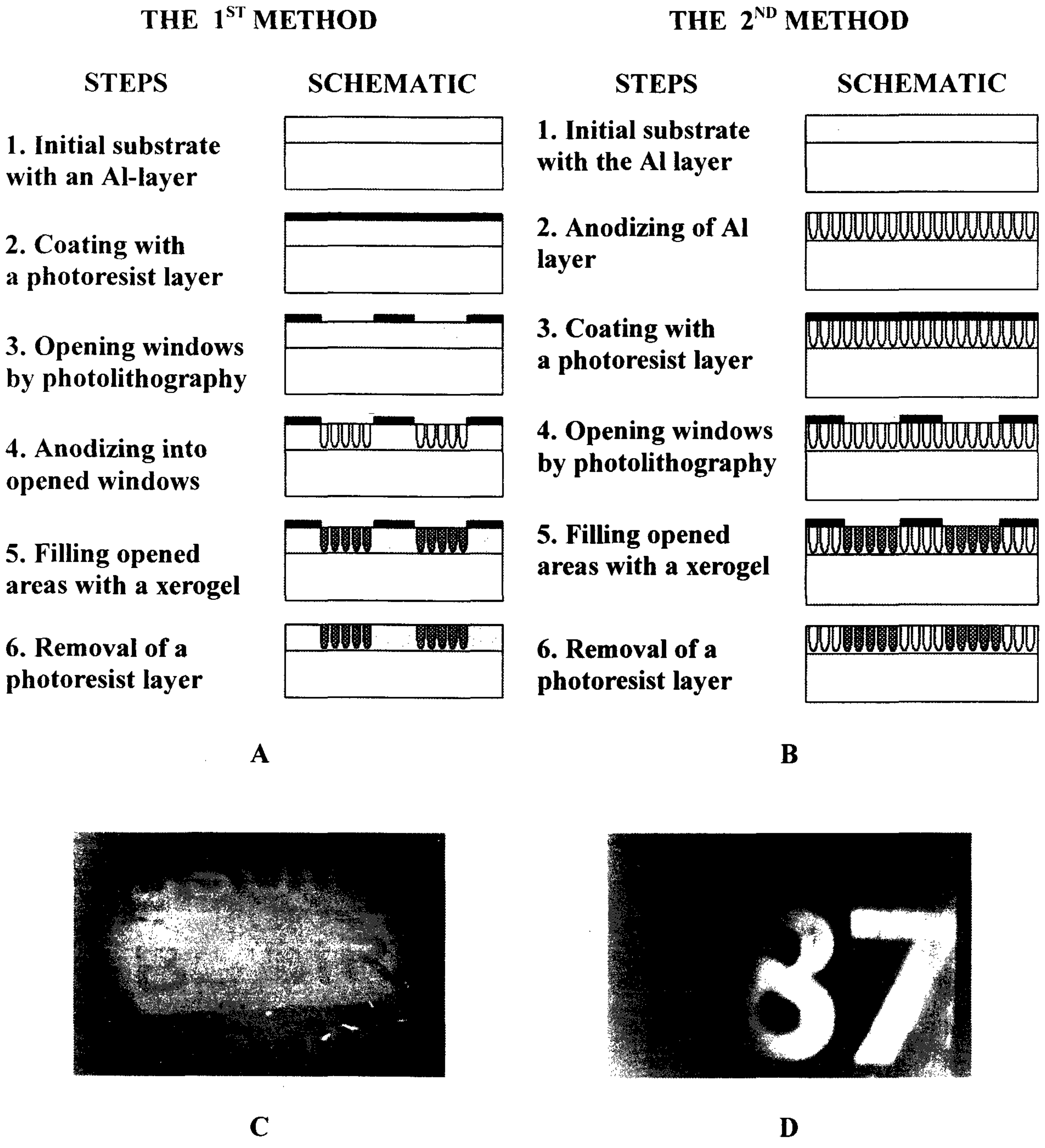


Fig. 1. The schemes for fabrication of photoluminescent images (a, b) and related photographs of the fabricated structures with Eu- (c) and Tb-doped (d) xerogel films

In this connection, it is of interest the use of oxide-based phosphor materials that may be synthesized via simpler vet methods such as chemical deposition, sol-gel synthesis, and offer excellent chemical and thermal stability. By embedding the trivalent lanthanide ions into such materials during synthesis process, the emission in all visible spectral range is achieved. Furthermore, the lanthanide ions have narrow and fixed spectral bands and theoretical upper limit of quantum efficiency is about 100 % that is unachievable for other type materials.

The developed EL structure represents PAA filled with Eu- or Tb-doped In_2O_3 or SnO_2 xerogel films with the ITO electrode formed onto glass surface that is mechanically pressed onto top surface of PAA (Fig. 2 a), the silicon substrate serves as the second electrode.

The standard EL device (Fig. 2 b) employs a transparent substrate, typically glass, coated with a transparent conducting layer, which serves as the bottom electrode. The bottom insulator, phosphor, and top insulator layers reside between the bottom transparent conductor and a top opaque conducting layer. This layer serves both as an electrical contact and as a reflector to direct light generated in the phosphor layer out through the glass substrate. The purpose of insulating layers are limiting the current flowing through the phosphor, and prevention the breakdown between two electrodes due to possible non-uniformities of thin phosphor layer. The second design of EL device is so-called inverted structure.

The inverted structure is similar to the standard structure and contains the same insulator-phosphor-insulator sandwich, but the inverted structure is built on an opaque substrate, and a transparent top contact is employed. The inverted structure makes it possible to use higher processing temperatures than the standard structure, since a substrate with a melting point higher than that of glass can be used. Another variation of the EL device structure is the single insulator structure. In this structure, the top insulator is not deposited in order to simplify processing.

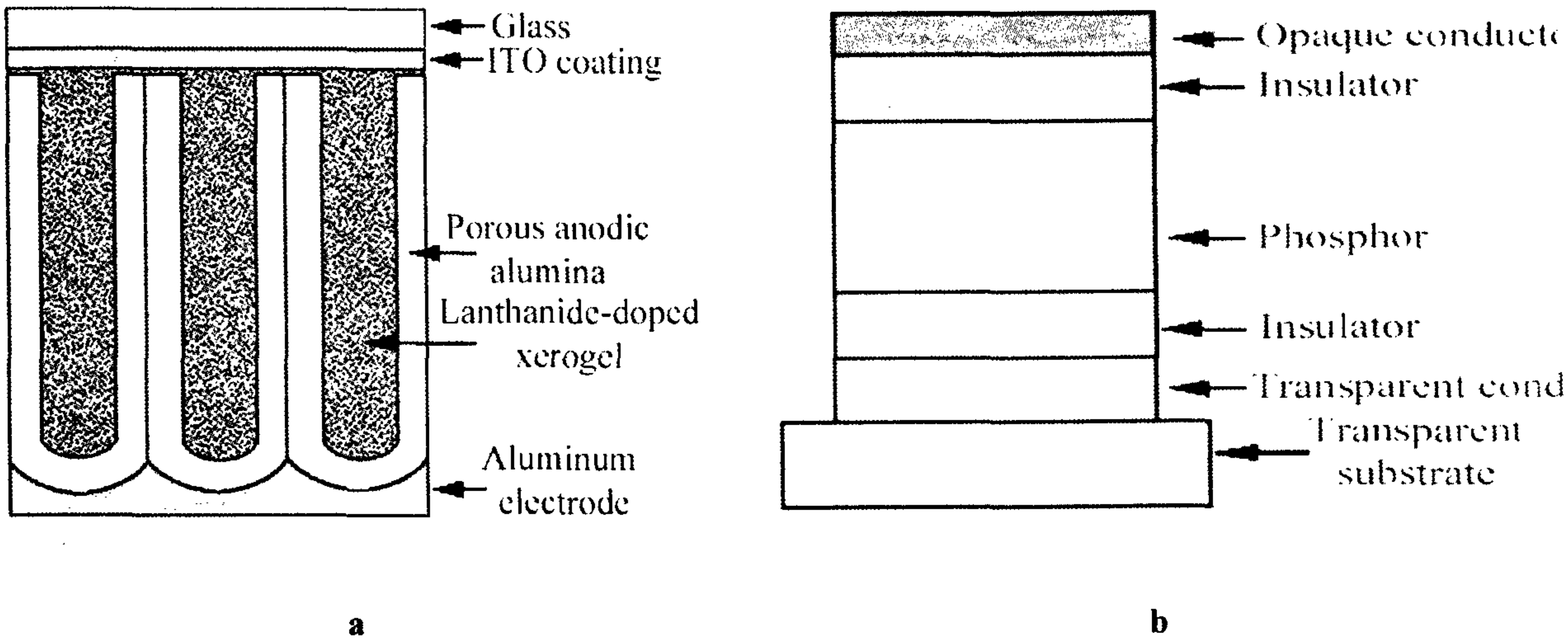


Fig 2. Schematic views of EL cells: a – based on PAA- lanthanide-doped xerogels; b – standard type

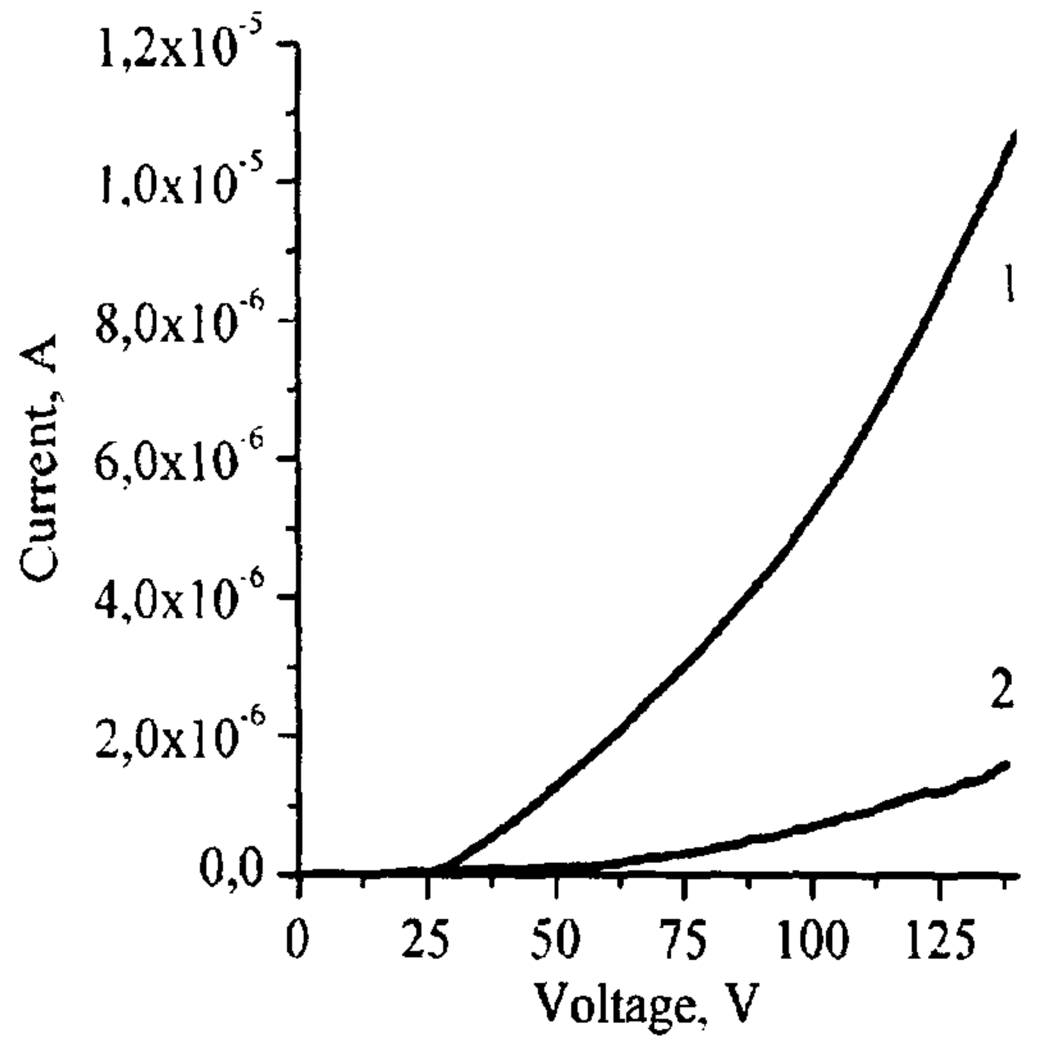
From the considered above, the following advantages are achieved utilizing PAA as a template of EL cell:

- simpler fabrication process, the cell structure is formed during anodization process: insulator layer is the barrier layer of PAA, the template for phosphor is the porous layer, the one of the electrode is the non-anodized aluminum or silicon substrate;
- non-uniformity of phosphor layer does not degrade the performance of device, porous layer prevents the breakdown between two electrodes, therewith by choosing its thickness the high breakdown voltage may be achieved;
- both PAA and xerogel films allows application of high-temperature processing.

3. Experimental results

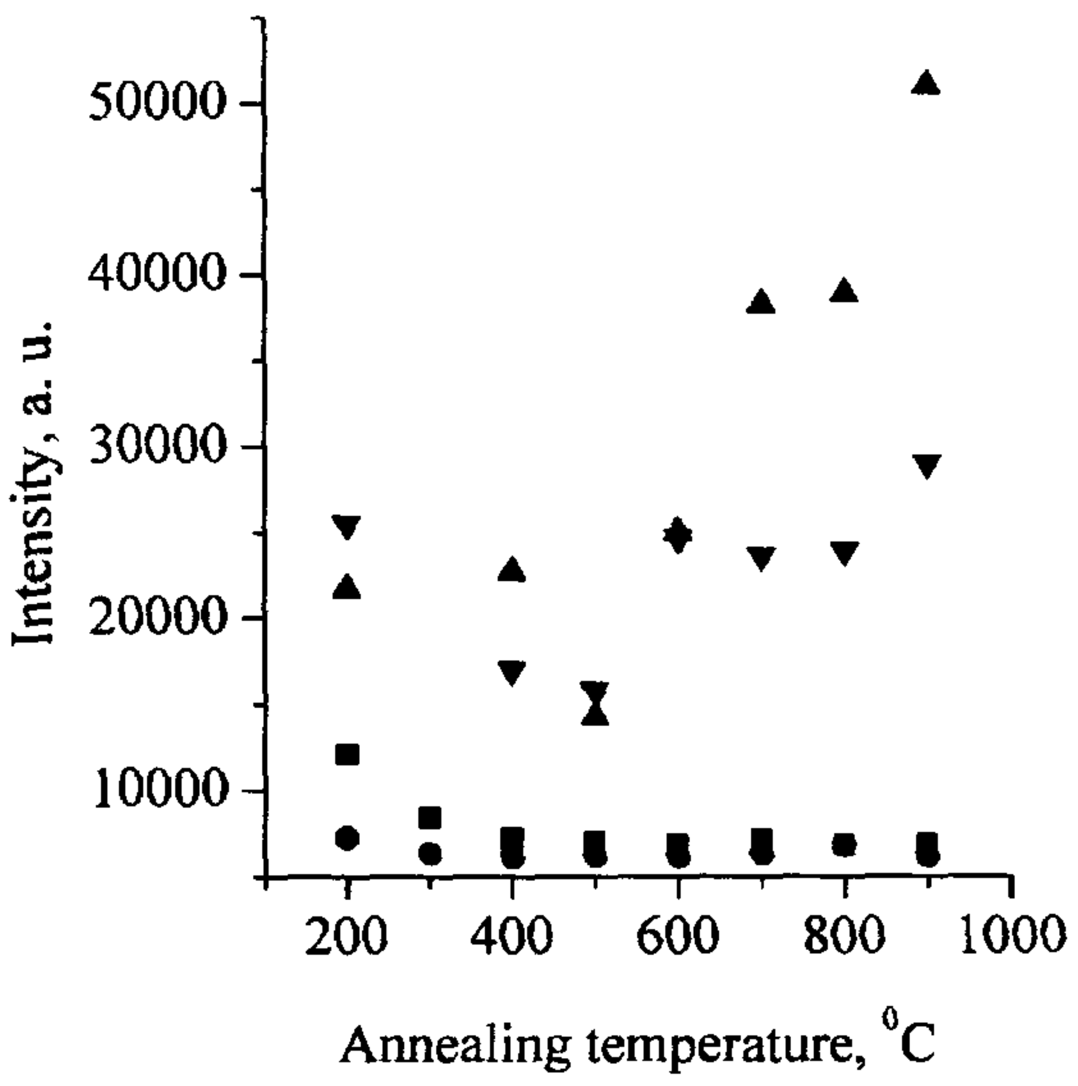
In the Fig. 3. the voltage-current characteristics (VCC) of the EL structures are presented, it is seen that In_2O_3 xerogel based structures operate at lower voltages than that of SnO_2. The visible emission in red (Eu-doped xerogels) and green (Tb) regions appears at the voltages above 40 and 90 V for In_2O_3 and SnO_2 xerogels accordingly when the positive potential is connected to ITO electrode. From the shape of VCC it could be concluded that the EL mechanism involves double injection (holes from ITO layer and electrons from bottom electrode) and recombination of carriers in the phosphor with transferring the energy to lanthanide ions resulting in emission of photons. Both the samples with PAA thickness of 5 and 15 μm demonstrated visually about equal intensity of emission.

To investigate the temperature stability of the structures, the PL measurements were carried out in relation to Eu-doped xerogels formed on PAA and monocrystalline Si substrates and annealed in the range 200...900°C (Fig. 4). It was difficult to perform correctly the analogous EL measurements, because the mechanical ITO contact did not provide the necessary accuracy of measurements. It is seen from the figure that PAA changes the PL behavior with annealing temperature in comparison to flat substrate; the minimum in intensity is appeared near 500°C. As a whole, the PL intensity changes weakly for In_2O_3 xerogel with the processing temperature, whereas as for SnO_2 xerogels the higher temperatures are more appropriate that could be connected with crystallization processes at high temperatures.



a

Fig. 3. Voltage-current characteristics of EL structure fabricated on PAA of 15 micron thick: xerogel Eu_2O_3-In_2O_3 (curve 1), Eu_2O_3-SnO_2 (curve 2). Sample dimensions are 5×5 mm^2.



b

Figure 4. PL intensity of $^5D_0 \rightarrow {}^7F_2$ spectral band (612 nm) from Eu_2O_3 in In_2O_3 xerogel fabricated on mono-Si (•), SnO_2 on mono-Si (□), In_2O_3 on PAA of 5 μm thick (▲), and SnO_2 on PAA (▼).

5. Conclusions

The method for fabrication of photoluminescent images based on aluminum anodization, sol-gel synthesis and photolithography is proposed.

The EL structures based on lanthanide-doped inorganic xerogel and PAA were studied for the first time. In spite of high operating voltages, the structures are of great interest due to absence of organic compounds and possibility to manipulate the design and performance of the device by tailoring PAA morphology.

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6. References

[1]. N. V. Gaponenko, J. Appl. Spectroscopy, 69 (2002), 1.

[2.] N. V. Gaponenko, I. S. Molchan, G. E. Thompson, V. Lambertini, P. Repetto, J. SID 11 (2003), 27.

[3]. X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, K. Leo, Appl. Phys. Lett. 78 (2001), 410.

[4]. D. B. Mitzi, K. Chondroudis, C. R. Kagan, IBM J. Res. & Dev. 45 (2001), 29.

[5]. D. Li, B. L. Clark, D. A. Keszler, Chem. Mater. 12 (2000), 268.