Thin-film fractal nanostructures formed by electrical breakdown

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Abstract. This is a study of the fractal micro- and nanostructures formation caused by the electrical breakdown of the indium-tin oxide (ITO) covered with various organic coatings. The samples were created by covering a glass substrate with a 1 to 10um-thick layer of indium-tin oxide. Some of the samples were then coated with organic layers of polycarbonate, poly(methyl methacrylate) and others. In order to create high local electrical field densities a special setup based on a eutectic GaIn liquid needle was created: it allowed for the contact area of 60um in diameter and application of the step voltage swept from 20 to 300 volts. The setup also contained a spectrometer for measuring the spectra of the breakdown optical effects. The results showed that the destruction of ITO led to the formation of the spiral fractal nanostructures, parameters of which depended on the thickness of the layer and the presence of the organic cover. In case of the latter, polymer coating was shown to visualize and zoom the topography of the nanostructures which might be used as a method of “polymer photography” for such fractal formations. The analysis of the spectra showed their dependence on the parameters of the structures which proves the possibility of conducting optical diagnostics of the created structures.

1. Introduction
Formation of the fractal micro- and nanostructures is one of the relevant objectives of the state-of-the-art material science. It is mostly due to the fact that fractal nanostructures offer highly-developed surface and exert unique adsorption and catalytic properties, which may be advantageous in designing new types of optoelectronic devices, next generation gas sensors, fractal p-n junctions for photovoltaics and even structures for biomedical application. The product ion methods are supposed to ultimately form a brand new technique of the not-too-distant future – fractal nanolithography. The application example of this technique could be a method of local formation of the fractal nanostructures via hydrophilic modification by means of atomic-force microscopy and self-assembly of colloidal nanoparticles during evolution of the sol [1,2]. The gist of the method comprises the initial tracing of the areas of high hydrophilicity and the interaction between the substrate and the sol-gel nanoparticles along with the subsequent formation of the fractal nanostructures in those local areas in the “bottom-up” process [3,4]. This paper studies the formation of the fractal micro- and nanostructures by means of the electrical breakdown. The investigation of the breakdown process occurring in conventional conducting film materials is of big technical interest for optoelectronic applications, especially for the flexible electronics.

2. Samples and setup
The typical cross-section of the organic light-emitting structure is shown in the Figure 1(a). Generally, such structures are fabricated on the transparent glass or quartz substrates. Thus, the emission from the
structure’s active layers can pass through the substrate, which also imposes restrictions on the transparency of the layers between the substrate and the active medium. For the visible band light-emitting devices one of the most popular materials of the active layer is a small-molecule compound Alq3 (Tris-(8-hydroxyquinoline)aluminium); the hole-transporting layer is generally TPD (N,N’-diphenyl-bis(4-methylphenyl)-biphenyl-4,4’diamine) – a wide-bandgap organic material, also transparent in the visible range of the spectrum. Nevertheless, the behaviour and the quality of the structure is mostly influenced by the cathode layer. In organic light-emitting structures the most commonly used cathode materials are oxide compositions of indium-tin (ITO), tin oxides doped with fluoride (FTO) and some other materials like ZnO, etc. This paper studies the processes occurring in the transparent cathode layer under high current densities, offers a method of analysis and describes the correlation between such processes and properties of the layer. What is more, the details of the fractal nanostructures formation are described and the method of polymer-based visualisation is offered.

For the purposes of the study of the breakdown processes occurring in the transparent electrode layers and fractal nanostructures formation several structures were created, as shown in the Figure 1(b).

![Figure 1](image1.png)

**Figure 1.** Typical structure of the organic light-emitting diode (a) and the structures created for the study (b).

The samples were created by covering a glass substrate (0.5-3 mm thick) with a 1-10 um layer of indium-tin oxide (ITO). Some of the samples were then coated with various organic layers. Apart from the abovementioned ones, polycarbonate (PC) and poly(methyl methacrylate) (PMMA) were used. Organic layers were ether spin-coated or formed by means of vacuum thermal evaporation under 10^-6 torr. In order to create high local electrical field densities a special setup based on a eutectic GaIn liquid needle was created. It allowed for the contact area of 60um in diameter. Electrode was formed by extracting the needle out of the Ga/In eutectic drop. The setup provided the application of the step voltage swept from 20 to 300 volts. ITO layer acted as the second electrode in the setup. The current-limiting resistor could be varied from 1 to 20 kOhm. 100 Ohm resistor was connected serially to the sample in order to measure the current flowing through the structure. Voltage on this resistor was also measured by a digital oscilloscope. The visual control system allowed for the digital camera footage with a resolution of approximately 5 um. The setup also included the spectrometer which provided spectral measurements of the breakdown emission with a high wavelength and timing resolution. Additionally, there was a magnetic field application capability. Fractal micro- and nanostructures created during the experiments were examined by means of high-resolution optical and atomic-force microscopy and metallographic analysis.

![Figure 2](image2.png)

**Figure 2.** Fractal nanostructure without (a) and with magnetic field applied (b).
3. Results
The study showed that ITO disruption was localized in the current channels (tracks) with their shape depending on the ITO layer thickness. Tracks in the thin ITO films (100-300 nm) were almost linear and 200-400 um long. As for the thicker films (more than 300 nm), tracks were shaped as a multiloop spiral with a diameter of approximately 1 mm. Figure 2 represents the view of the 500-nm thick ITO layer after a local breakdown. As shown, the breakdown track is spiral with multiple branches, mostly oriented outwards. Thus, extensive fractal nanostructures are present on the surface of the ITO after a breakdown. The shape of the structure depends on the properties of the oxide layer, its resistance and crystal structure in particular. The shape is generally symmetrical and formed as an extending spiral, as shown in the Figure 2(a). In presence of the magnetic field the structure is oriented along with its H-vector and is elongated, as shown in the Figure 2(b).

Figure 3 represents more detailed pictures of fractal microstructures formed by the breakdown of the oxide layers. Results were obtained by the method of metallographic analysis. Spiral branched structure is clearly arranged.

![Figure 3](image)

**Figure 3.** Images obtained by means of metallographic analysis.

In order to obtain even more detailed information about structures the samples were examined by means of atomic-force microscopy (AFM). As seen from the Figure 4, track width was about 2-5 um with a depth of 500 nm. It is important to notice the bulges on the edges of the channel about 300 nm high.

![Figure 4](image)

**Figure 4.** AFM pictures of the breakdown tracks.

The explanation of the observed results of optical and atomic-force microscopy might be as follows. In case of the breakdown of the indium-tin oxide layers placed on the glass substrate a dynamic system emerges coming amid formation of the filament path on the surface which defines the shape of the fractal microstructure. Such shape would depend on the timing and current parameters of the breakdown. Having said this, the breakdown-generated heat consumption processes actually come to the fore, therefore increasing the influence of the thermal conductivity of the film. Thermal emission causes the formation of the additional surface – the filament path – and the development of the fractal nanostructure.

Thus, the discontinuity of the oxide material takes place, followed by its partial evaporation (sublimation) and amorphisation of the circumjacent to the filament area of the layer. This leads to the formation of the “bulge – channel – bulge” structure – the shift of the material to the edges of the structure caused by the thermal shock. Depending on the crystal structure of the layer, spiral or radial tracks are obtained.
Figures 5 to 7 represent results of the optical spectroscopy. Figure 5 contains the spectrum of the breakdown emission of the ITO layer 3 µm thick and with resistance of 100 Ohm per square. A linear spectrum with a dominant peak at 583 nm is obtained, secondary peaks of which depend on the properties of the oxide layer. In this case a spiral structure is created, as shown in the Figure 2(a). In case of the breakdown of the 20 Ohm per square structure, peaks at 410 and 450 nm exert higher intensity, as shown in the Figure 6, and the radial fractal structure is formed. Thus, oxide layers can be characterised by the optical spectroscopy methods.

![Figure 5](image5.png)

**Figure 5.** Spectrum of the breakdown emission (ITO, 100 Ohm/square). Inset: oscilloscope pattern of the breakdown process.

![Figure 6](image6.png)

**Figure 6.** Spectrum of the breakdown emission (ITO, 20 Ohm/square).

Time-domain spectral analysis of the fractal nanostructures breakdown formation in the ITO layers allows for acquiring data on relevant luminescent processes. Figure 7 shows the development of the spectrum with time step of 4 milliseconds. Apart from the primary line, a considerable number of secondary peaks is present, each of which corresponds with some radiative transition during the processes of thermal shock, material sublimation and fractal nanostructure formation.
Disruption of the ITO layer is best visualisable when studying the samples coated with polymer layer (e.g., poly(methyl methacrylate), PMMA) which increases the contrast of the image obtained. Besides, an electrical contact between ITO and the Ga/In needle emerges only after the breakdown and disruption of the polymer coating itself. As soon as the PMMA was disrupted at approximately 100 volts, this voltage was applied directly to ITO which enables much higher current density flowing through the thin (around 10 um) channel in the ITO, heating processes inside which lead to the destruction and evaporation of the polymer in the track and, eventually, disruption of the ITO in the vicinity of the channel.

Therefore, coating transparent oxide layers with polymers allows for visualisation of the breakdown processes in the structure. The “polymer photography” method may be used to estimate the quality of the oxide layer. Figure 9 contains several AFM images of the ITO based structures. Top left image is a typical radial fractal structure of the disrupted ITO. Top right and bottom left images represent the filaments paths in the structures coated with PC and PMMA respectively. Due to the lower activation energy of the sublimation processes, polymers’ evaporation is much more intense, which leads to the
considerable extension of the track. The cross section of the track is shown on the bottom right image. It is easy to notice the bulges at the edges of the channels, which are due to the shift of the polymer material as a consequence of the thermal shock.

4. Conclusion
The results of the study showed that the electrical destruction of ITO led to the formation of the spiral and fractal nanostructures, parameters of which depended on the thickness of the layer and the presence of the organic cover. In case of the latter, polymer coating was shown to visualize and zoom the topography of the nanostructures which might be used as a method of “polymer photography” for such fractal formations. The analysis of the spectra showed their dependence on the parameters of the structures which proves the possibility of conducting optical diagnostics of the created structures.

5. References

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