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NETWORKS OF NANOMEMBRANES AND TUBULAR STRUCTURES OF GaN AND TiO_2 FOR MEMRISTIVE SYSTEMS AND BIOMEDICAL APPLICATIONS

134.01 – PHYSICS AND MATERIALS TECHNOLOGY

Abstract of the PhD dissertation in Physics

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The summary and the PhD dissertation can be consulted at the library of the Technical University of Moldova as well as on the ANACEC website (www.cnaa.md).

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CONCEPTUAL GUIDELINES OF RESEARCH

Actuality and importance of the topic

Gallium Nitride (GaN) is a 3rd generation semiconductor and it is considered the second most important material in the semiconductor industry after Si. It possesses remarkable optical properties, physical and chemical stability, as well as good biocompatibility. The ability to develop GaN nanostructures is of major interest for use in various fields like optoelectronics, solar energy conversion, high yield hydrogen production, high power and high frequency electronics. It has already been demonstrated that structures such as nano-pyramids, nanowires, nanotubes, or other nanometer-sized structures are much more efficient in some applications than the bulk material, primarily due to their enormous active surface area or quantum effects when the objects have dimensions of a few atomic layers [1].

Researchers from the University of North Carolina have also demonstrated that GaN is a non-toxic material that can be used for various biomedical implants, from electrodes for neuro-stimulation therapy of Alzheimer's patients to transistors for monitoring blood chemistry [2].

Titanium dioxide (TiO_2) is another intensively studied semiconductor due to its photocatalytic properties, high efficiency in solar energy conversion and the possibility of use in actual electronic devices. One dimensional nanomaterials (1D), such as nanotubes obtained by anodizing Ti foils, have demonstrated increased efficiency in solar energy conversion, due to the high light scattering effect inside the structures [3]. TiO_2 nanotubes having an enormous active surface area and a very high surface-to-volume ratio are very promising structures for air or waste water purification [4], micro- or nano-filters, coatings with self-cleaning properties, solar energy conversion by combining them with sensitizing dyes or perovskites, or biomedical applications [5].

The importance of addressed issue

The fabrication process of TiO_2 nanostructures has already been studied for several decades, using different techniques that, at the moment, are cost-effective for large scale production. Titanium dioxide nanotubes have also been studied over the years, the most effective technique proposed being electrochemical etching in different electrolytes. Depending on the electrolytes chosen, the nanotubes can be limited in dimensions such as their length, inner or outer diameter or in the ability to obtain a controllable diameter along the tubes. This is a main aspect in the study of nanotubes for photocatalytic applications, in biomedicine or as nanomotors for transport of certain molecules [6].

After the development of the first experimental memristor [7], more and more research groups tend to develop new types of such components based on different materials as well as in various configurations and to develop circuits that would ensure much faster calculation speeds and the consumption of much lower energy than the current implemented technology.

The most promising applications of memristors are non-volatile memories [8]. These components work based on the dynamics of the memristor resistance. Non-volatile memories based on memristors could store a much larger amount of information per unit area compared to current technology. Even higher efficiency can be achieved by using memristors that can store multiple logic states.

Micro- and nano-motors with autonomous propulsion in the liquid medium is an intensively studied topic at the moment, having a rather high application potential in biology and medicine, for example, for the manipulation of cells or circulating pathogenic bacteria in the bloodstream [9]. Drug delivery, hyperthermia for cancer treatment and autonomous surgery are also promising topics.

The development of ultra-lightweight semiconductor materials could gradually replace the bulk materials used, especially when they are made from materials with high chemical and high energy radiation stability. GaN based aeromaterials could be widely used for example in the aerospace industry [10].

The aim of the work

The main aim of the work consists in the development and optimization of the technological conditions for the manufacture of small-sized structures based on GaN, TiO_2 and Ga_2O_3 materials with unique properties and establishing their application directions in the field of electronics, the environment and in biomedicine.

The main objectives of the research

1. Optimization of the fabrication process of nanotubular structures based on TiO_2 and GaN and their investigation as micro- and nanoengines in aqueous solutions, controlled by means of an external light source.
2. Photocatalytic study of TiO_2 nanotubular structures for the degradation of organic compounds.
3. Development and study of memristive circuits based on ultrathin GaN membranes obtained by means of Surface Charge Lithography approach.
4. The optimization of technological conditions for manufacturing of the novel aeromaterials like aero-GaN and aero-Ga_2O_3 and the investigation of their physico-chemical characteristics through different techniques. A specific objective is the electrodynamic characterization of aeromaterials in the THz frequency range, since current and future communication systems

work or will work in THz regime, which will allow high speed data transfer. However, THz radiation can have adverse effects on human health or on other electronic equipment used in communication systems due to interferences, so it is important to find methods of protection against such radiation.

5. Study of the interaction of ZnO and GaN nanoparticles with proteins for a better understanding of the impact of their toxicity upon living cells.

Scientific research methodology

The theoretical support of the dissertation was carried out based on analysis of specialized literature accessed from the electronic libraries of the Technical University of Moldova, Joint Research Center of the European Commission from Ispra, University of Kiel, Institute of Microtechnologies from Bucharest, as well as through online access to scientific journals and open access articles.

In order to achieve the objectives of the dissertation, the following technological methods and scientific research were used:

- To obtain titanium oxide nanotubes, the electrochemical and dry plasma etching techniques were used;
- Aerogalnite and the GaN microtubes were obtained by direct growth of GaN on sacrificial ZnO template using the hydride vapor phase epitaxy (HVPE) technique;
- Surface Charge Lithography (SCL) followed by photo-electrochemical etching were used for the fabrication of ultrathin GaN membranes;
- The developed materials were characterized by the following techniques: scanning electron microscopy (SEM) for morphology study, X-Ray diffraction (XRD) and transmission electron microscopy (TEM) for structural characterization, Raman spectroscopy, photoluminescence (PL), cathodoluminescence (CL), atomic force microscopy (AFM), X-Ray dispersion spectroscopy (EDX), X-Ray photoemission spectroscopy (XPS) for the surface chemical analysis, UV-Vis spectroscopy for liquid biological samples analysis, circular dichroism (CD) for proteins secondary structure analysis, optical microscopy, electrical characterization.

The scientific novelty of the research

- Titanium dioxide nanotubular arrays have been developed with the internal diameter of the tubes gradually decreasing along the tube, an important aspect in order to use these structures as micro- or nanomotors, including the Cargo capabilities in the case of networks consisting of several nanotubes, or for increasing the degradation efficiency of organic compounds;

- Gallium nitride tubular structures with nanometer wall thickness and with a complex internal architecture were developed for the first time and their applicability as micromotors was demonstrated;
- For the first time, the memristive effect on GaN ultrathin membranes in various configurations was studied and the learning mechanisms such as habituation/dishabituation of external stimuli, an identic process to those observed in biological synapses, was demonstrated;
- In premiere, aeromaterials based on gallium nitride and gallium oxide were developed and their physico-chemical properties were investigated, identifying possibilities for their use as pressure sensors or materials for protection against high-frequency radiation (GHz and THz);
- The interaction of GaN and ZnO nanoparticles with BSA proteins was investigated by various techniques, as well as the cytotoxic effect of these complexes on living cells.

The solved scientific problem consists in the development and optimization of the technology for manufacturing tubular structures of GaN and TiO_2 by cost-effective approaches, the manufacture of aeromaterials based on GaN and Ga_2O_3, the study of the properties of the developed materials and the identification of applications in the field of medicine, environment and electronics.

Theoretical significance and applicative value of the work

- The development of micro- and nanomotors based on GaN and TiO_2 materials, that proved to be biocompatible, as well as the demonstration of Cargo and delivery capabilities of the TiO_2 nanotubes, opens the way to applications in biomedicine, namely in the controlled transport of drugs, specific proteins or even cells.
- TiO_2 anatase nanotubes, including those functionalized or doped with noble metals, with both ends opened, demonstrate increased efficiency in the degradation of organic compounds. These demonstrations allow the use of these structures widely in the cleaning of waste water or for air purification.
- The observed memristive effect on ultrathin GaN membranes is explained by the trap-controlled space charge limited current mechanism, the traps being produced in the material during the fabrication process;
- The memristive effect on a single membrane and several membranes connected in parallel demonstrates a cumulative effect identical to that observed in biological synapses. Such devices in combination with current CMOS technology would lead to increased data processing performance and would ensure a reduction in the power consumption of the devices;

- The sensitivity of the aero-GaN material upon pressure change is described according to intrinsic piezoresistive property of the material and the dynamics of the physical joints between the GaN microtetrapods according to the proposed model in the dissertation;
- The development of ultra-lightweight pressure sensors based on aero-GaN with high sensitivity and an output current in the mA range, allows the incorporation of elaborated sensors in portable equipment. Due to the stability of the material to high-frequency radiation, these sensors could also be used in aerospace applications;
- Electrodynamic, optical and chemical characterization of GaN and Ga_2O_3 aeromaterials demonstrate the possible absorption, reflection or transmission mechanisms in the material in a wide frequency range;
- The developed aero-GaN has been shown to be effective in high-frequency radiation shielding, on the other hand, aero-Ga_2O_3 possesses ultra-low reflectivity and high transparency in an ultra-wide frequency range that would allow the use of the material in various applications in electronics or IoT.

Scientific theses submitted for defense

1. The fabricated TiO_2 nanotubes with an outer diameter of 200 nm and an inner diameter varying along the tube from 120 nm to 50 nm are capable of self-propulsion through aqueous solution upon UV light irradiation with the minimum optical power density of 0.02 mW/cm^2.
2. The propulsion speed of fabricated TiO_2 micromotors is about 5.4 μm/s in the case of solution containing 5 % H_2O_2, which decreases about five times in the case of using deionized water.
3. The TiO_2 micromotors, which assume the collective effect of a cluster of nanotubes, are capable of transporting microparticles through the liquid during the photocatalytic activation by external UV light, the propulsion speed remaining unchanged, and the response time to switching on/off the light being short.
4. Thermal treatment of TiO_2 nanotubes at 450 °C, 650 °C and 850 °C leads to the modification of the crystalline structure of the material into anatase, rutile or a mixed anatase/rutile phase, resulting in a photocatalytic enhancement, the structures being able to degrade about 85 % of Methylene Blue (MB) during 25 min under UV irradiation in the case of samples annealed at 650 °C and about 50 % of MB during 25 min under irradiation with visible light in the case of samples annealed at 850 °C in air.
5. Doping TiO_2 nanotubes with Ag results in higher degradation efficiency of the organic compound Rhodamine B for 5h compared to amorphous, anatase, anatase doped with Au or Pt, or anatase samples functionalized with noble metals.

6. The configuration in parallel connection of the 15 nm thick GaN membranes possessing the memristive effect, leads to the reduction of the time required to learn the electrical stimulus by approximately 30 % in the case of using three membranes as compared to a single one.

7. Pressure sensors based on the ultra-lightweight GaN aeromaterial possess a non-linear sensitivity varying from 16.2×10^{-3} at low pressure (5 atm) to about 7.4×10^{-3} at high pressure (40 atm), due to both the piezoresistive property of the material and the dynamics of the joints between the microtetrapods with the pressure change.

8. The developed GaN aeromaterial proved to be highly effective for shielding against high frequency radiation up to 3 THz due to absorption mechanisms in the material, while the Ga_2O_3 aeromaterial is completely transparent in the X-band (8.2 – 12.4 GHz) and THz frequency range, up to 3 THz.

9. BSA protein has a very low affinity on the surface of GaN compared to ZnO nanoparticles. The given complexes of nanoparticles – protein corona - were found to be toxic at concentrations above 25 μg/ml in the case of ZnO nanoparticles and 70 μg/ml in the case of GaN nanoparticles, respectively.

Approval of the scientific results

The main results of the dissertation were presented at the following international conferences and exhibitions:

1. „The 5th International Conference on Nanotechnologies and Biomedical Engineering", November 3 - 5, 2021, Chisinau, Moldova.
2. Bristol Center for Functional Nanomaterials Annual Conference, September 17 - 18, 2020, Bristol, UK.
3. „The 4th International Conference on Nanotechnologies and Biomedical Engineering", September 18 - 21, 2019, Chisinau, Moldova.
4. „Conferința Tehnico-Științifică a Colaboratorilor, Doctoranzilor și Studenților", Technical University of Moldova, 26 – 29 March 2019, Chisinau, Moldova.
5. Training School „Nanomaterials synthesis and advanced characterization techniques at nanometer and atomic scale", June 4 - 7, 2019, Bucharest, Romania.
6. Evolutionary Computing in Optimization and Data Mining, June 24 - 27, 2019, Alexandru Ioan Cuza University of Iasi, Romania.
7. „The 3rd International Conference on Health Technology Management", 6-7 October 2016, Chisinau, Moldova.

8. „The 3rd International Conference on Nanotechnologies and Biomedical Engineering, Sept. 20 – 24 2015, Chisinau, Moldova.

9. „The 11th International Conference on Optics. Micro- to Nano-Photonics IV", 1-4 September 2015, Bucharest, Romania.

10. International Scientific Conference Light and Photonics: Science and Technology, 22th May, 2015, Alecu Russo Balti State University, Balti, Moldova.

- Silver Medal at the **EUROINVENT - 2022** exposition. Large-Sized Nanocrystalline Ultrathin β-Ga_2O_3 Membranes Fabricated by Surface Charge Lithography, Iasi, Romania, 26 – 28 May 2022.
- Gold Medal at the **EUROINVENT – 2020** exposition. Micromotors driven by UV light based on advanced hybrid GaN/ZnO nanoarchitectured microtubes, Iasi, Romania, 21 – 23 May 2020.
- Gold Medal at the **INVENT-INVEST - 2017** exposition. Cargo effect in micromotors based on networks of nanotubes, Ungheni, Moldova, February 2017.

Publications

The main results of the dissertation were published in 23 scientific papers, of which 9 articles in international journals, 2 articles in national journals and 12 articles in the proceedings of the national and international conferences, the full list of which is presented at the end of this Summary and in the Appendix 1 of the dissertation.

The volume and structure of the dissertation

The dissertation consists of Introduction part, four chapters, general conclusions and recommendations and bibliography (278 titles), being exposed on 146 pages of main text, containing 110 figures and 8 tables.

Keywords: GaN, TiO_2, Ga_2O_3, aeromaterials, micromotors, memristors, artificial synapses, pressure sensor, THz shielding, protein-corona.

DISSERTATION CONTENT

The ***first chapter*** consists of the literature review on the properties of gallium nitride and titanium dioxide materials, current growing methods, as well as a brief description of the nanostructuring methods of these materials. Some practical applications based on these nanostructured materials are also presented. The literature review on fabrication of micro- and nanomotors using various methods and materials such as organic and inorganic ones, and the investigation of physico-chemical effects related to the propulsion mechanisms through liquids, is also reported. Another compartment described in this chapter consists of a literature review in the field of memristors - types of materials that possess memristive properties, the fabrication methods of these materials and physical effects attributed to the memristive behavior. Literature review on fabrication and development of aeromaterials and their applicability in daily life is also reported.

In the ***second chapter*** the techniques used in this dissertation for the fabrication and characterization of the GaN nanomembranes, TiO_2 and GaN micro- and nanotubes as well as aeromaterials based on GaN and Ga_2O_3 are briefly described. The schematic illustration and functional description of the equipment used for nanostructures fabrication are also included such as: hydride vapor phase epitaxy, electrochemical etching, photo-electrochemical etching or surface charge lithography, as well as the equipment used for materials characterization such as scanning electron microscopy, structural and optical characterization, high frequency domain characterization with a brief description of their operating principles.

In the ***third chapter*** the characterization of GaN and TiO_2 micro- and nanotubes are thoroughly described with their applicability as micromotors. By using the techniques of electrochemical etching and dry plasma etching in Ar and SF_6, it was possible to obtain networks of TiO_2 nanotubes with both ends open (figure 1).

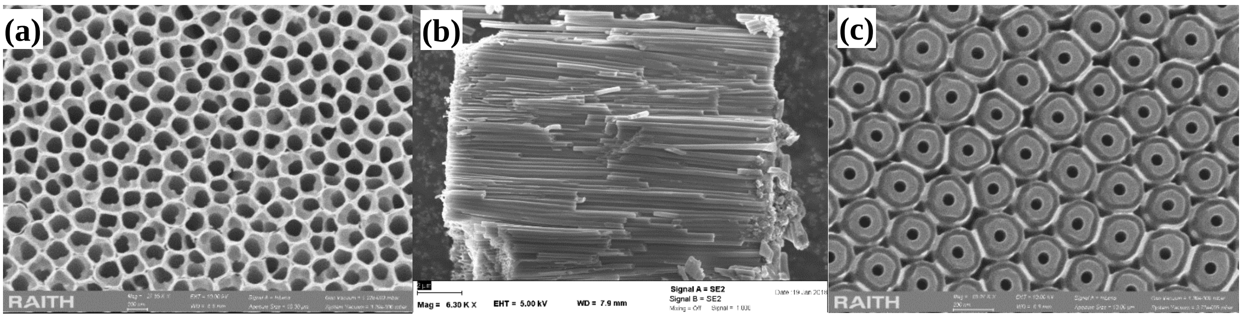

Fig. 1. SEM images of a membrane consisting of TiO_2 nanotubes: (a) top view, (b) cross-sectional view and (c) the nanotubes bottom ends after a dry plasma etching process [4]**.**

Since the as-grown TiO_2 nanotubes have an amorphous crystalline structure, they possess a very weak photocatalytic activity. For their possible use in the proposed applications, it is necessary to thermally treat the material for the purpose of crystallization. Depending on the thermal treatment conditions, the material can be transformed into anatase, rutile or a mixed anatase-rutile phase. According to the structural characterization by TEM or Raman spectroscopy techniques, shown in figure 2, the transformation process of the material into different crystalline phases was demonstrated.

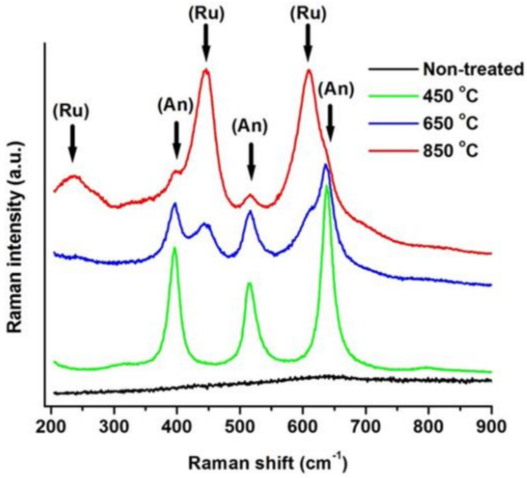

Fig. 2. Raman spectra of the TiO_2 nanotubes thermally treated at different conditions which demonstrate distinct crystalline structures [6]**.**

Individual TiO_2 nanotubes with an internal diameter gradually decreasing from 120 nm to 50 nm have been shown to be capable of self-propulsion through liquid containing a low quantity of hydrogen peroxide when irradiated with an external UV light. The schematic of the micromotors consisting of several TiO_2 nanotubes and the design of the cell in which the micromotors were investigated are presented in figure 3.

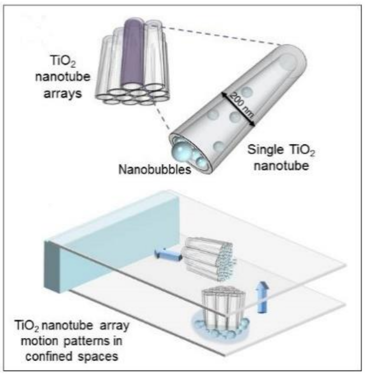

Fig. 3. Schematic illustration of a cluster of TiO_2 nanotubes with internal conical shape and the platform design used for the propulsion study of the fabricated micro- and nanomotors upon irradiation with UV light [6]**.**

The propulsion mechanism was also observed in pure water, however, the propulsion speed in this case was lower. Self-propulsion through the liquid is caused by chemical reactions occurring at the material-liquid interface through the decomposition of H_2O_2 and formation of gas bubbles upon photocatalytic activation, which, due to the geometry of the nanotubes, will tend to migrate towards the large diameter end. Thus, the release of the bubbles will create a force that will push the nanotubes through the liquid.

Another interesting effect observed consists in the possibility of microparticles transport through the liquid by the networks of nanotubes that collectively work to capture, particle delivery when the UV light is on, the propulsion speed during the particle delivery remaining unchanged, and particle release when UV light is turned off (see figure 4).

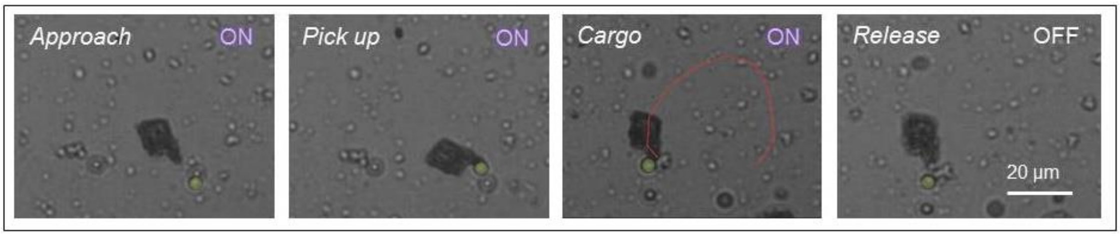

Fig. 4. Optical images of a cluster from TiO_2 nanotubes demonstrating the Cargo capability. The release of the particle takes place when the UV light is switched off [6]**.**

TiO_2 nanotubes have been shown to be effective for organic dyes degradation such as Rhodamine B or Methylene Blue under both UV or visible light irradiation. In the first experiment, the degradation efficiency of Rhodamine B was compared between the TiO_2 nanotubes with amorphous structure, anatase or anatase samples doped or functionalized with noble metals such as Au, Ag or Pt. The Ag-doped samples were shown to have an increased photocatalytic efficiency, while the other sets of samples on the contrary lead to a decrease in the degradation efficiency of Rhodamine B compared to the anatase sample (figure 5a, b).

In the degradation experiment of the organic compound MB, two types of samples were used: TiO_2 nanotubes treated at 650 °C and 850 °C. These samples have been shown to be effective for the MB degradation by using either UV or visible light. Samples treated at 850 °C, where the rutile phase predominates, possess the highest degradation rate under visible light irradiation with a decomposition of MB up to 50 % during 25 min, while samples treated at 650 °C, in which anatase phase predominates, possess the best performance by degrading around 85 % of MB under UV light irradiation during 25 min (figure 5c) [4,11,12].

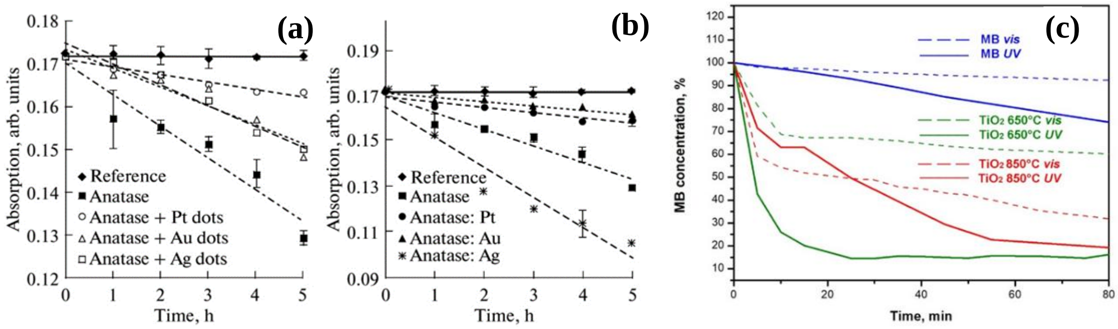

Fig. 5. Absorption time dependence upon UV light excitation of anatase TiO_2 samples: (a) doped with Au, Ag or Pt, (b) functionalized with metallic dots; (c) the degradation process of MB upon irradiation with UV or visible light [4,11]**.**

In this chapter it is also described the fabrication process and the detailed structural characterization (figure 6b, c) of GaN microtubes functionalized with Au dots on the inner walls. Due to the presence of the Au dots, during the HVPE growth of GaN and the decomposition of ZnO at high temperature and corrosive environment, the VLS growth process of $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ nanowires with gold dots termination occurs (figure 6a). The SEM image in figure 6b illustrates the morphology of microtubes and nanowires grown on the inner surface of the tubes. The TEM electron diffraction pattern of the microtubes demonstrates that microtubes are single-crystalline and have the *c*-grown direction. It has been proven that these functionalized microtubes possess photocatalytic activity upon UV light irradiation and are capable of self-propulsion in the liquid medium due to the degradation of H_2O_2. The propulsion of the microtubes through the liquid could be correlated to the difussiophoretic mechanism [13]. Larger microtubes were shown to possess a lower propulsion speed, for example a microtube with a diameter of 4.6 µm and a length of 32 µm had a propulsion speed of 1.4 µm/s, while another microtube with a dimeter of 0.9 µm and a length of 2 µm reached a propulsion speed of 5.5 µm/s (figure 6d-f). The propulsion speed difference can be primarily caused by the mass of the tubes and secondly to the difference between density of chemical species occurring due to chemical reactions after photocatalytic activation.

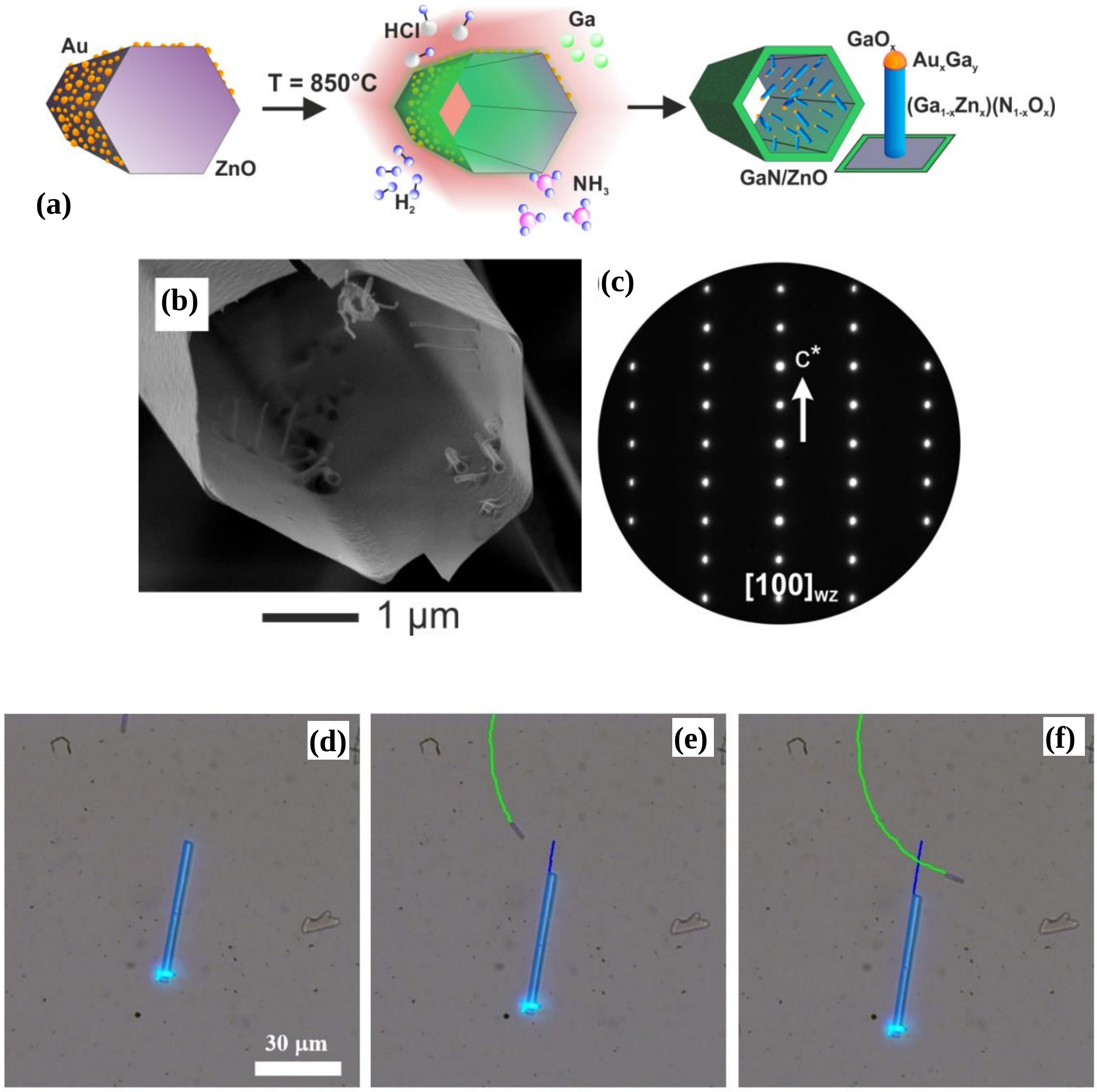

Fig. 6. (a) Schematical illustration of the grown process of GaN microtubes functionalized with Au dots; (b) SEM image demonstrating the external and internal morphology of the microtubes and (c) TEM electron diffraction pattern of the microtube. (d - f) Optical image and propulsion direction of 2 microtubes having different dimensions. The movement upon UV light irradiation at: (d) t = 0 s, (e) t = 5 s and (f) t = 10 s. The microtube with smaller dimensions has a propulsion speed 4 times higher than the smaller tube. In this experiment was used a 50 W UV lamp [13]**.**

In the **chapter 4**, the processes of fabrication of 2D GaN structures, the structural characterization (figure 7a-c), the development of memristors based on the given structures and the electrical characterization of memristors in different configurations (figure 7d, e) are described in details.

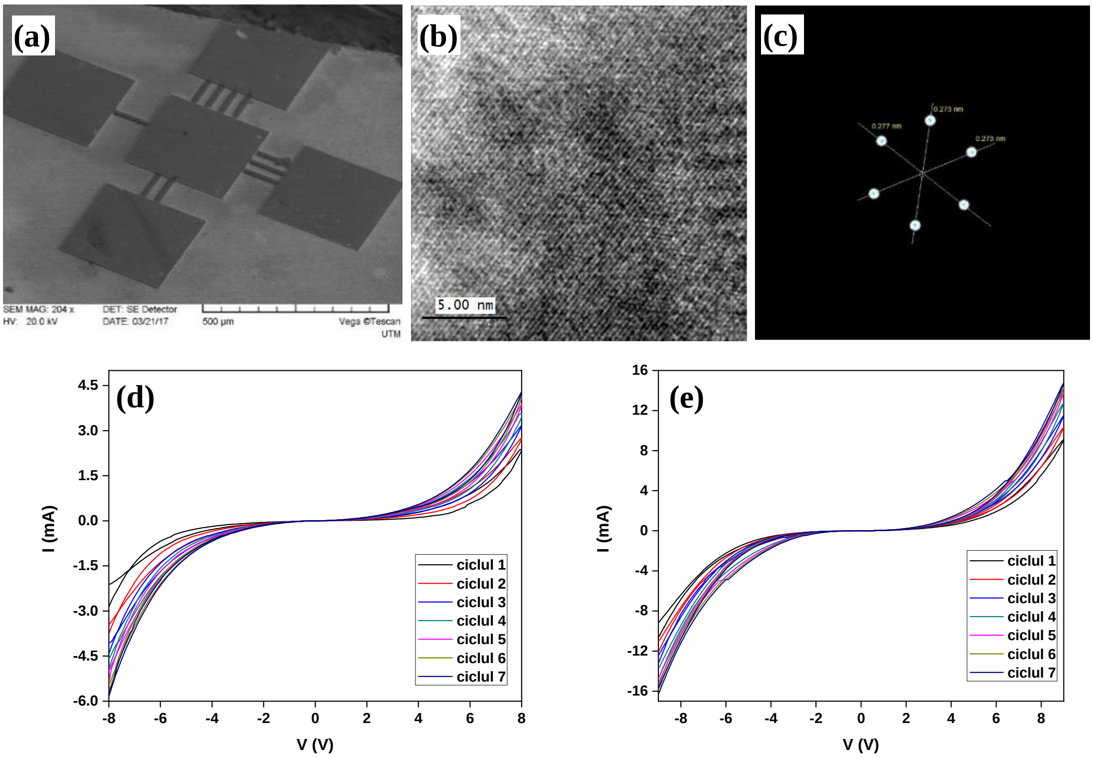

Fig. 7. (a) SEM image of the circuit with three GaN membranes in parallel connection; (b, c) HRTEM image and FFT analysis from these; (d, e) current-voltage dependencies of 1 and 3 memristors based on GaN membranes by applying consecutive voltage sweeps [14]**.**

Networks of monocrystalline ultrathin GaN membranes arranged in parallel configuration have been shown to be capable of performing simple learning mechanisms such as habituation and dishabituation and of memorizing electrical external stimulus. The habituation/dishabituation processes in material are possible due to the progressive filling of the occupied states on the surface as a result of migration of negative trapped charges under the influence of the electric field induced by traps. Increasing the number of memristors in parallel connection, the habituation process becomes faster, for example, it was demonstrated that by connecting three such memristors in parallel, the learning time decreased by about 30 % compared to a single memristor. Additionally, the asymmetry of current – time dependencies at positive or negative voltage excitation, significantly reduces when the number of membranes connected in parallel is increased, while the average time for reaching the steady state remains almost the same.

The fabrication processes of GaN and Ga_2O_3 aeromaterials are described in this chapter as well. Figure 8 illustrates the schematical process of fabrication of the mentioned aeromaterials.

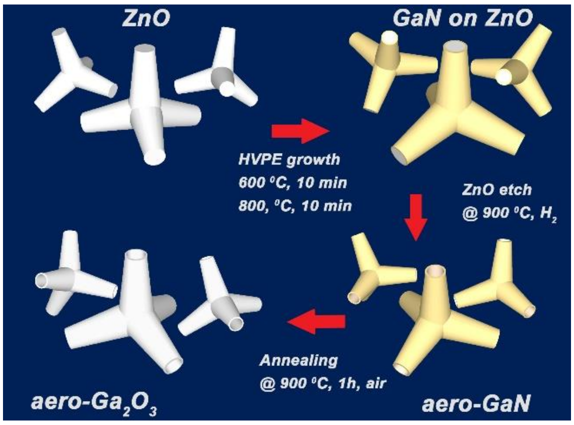

Fig. 8. Schematic representation of the technological route of aero-GaN and aero-Ga_2O_3 fabrication [15].

The fabricated aeromaterials have a porosity of about 93 % determined from relation 1:

$$\varepsilon = (1-\rho_a/\rho_t)\times 100\%, \quad (1)$$

where ρ_a represents the apparent density of the aeromaterial determined from the total mass of aero-GaN and its volume, and ρ_t represents the real density of the bulk material ($\rho_{GaN} = 6.15$ g/cm^3).

In most of the cases, an ultrathin ZnO layer was detected on the inner surface of the tubes, which can be further etched in hydrogen environment at 900 °C, the final concentration of ZnO decreasing below 1 %. This result was proved by the photoluminescence study which is shown in figure 9.

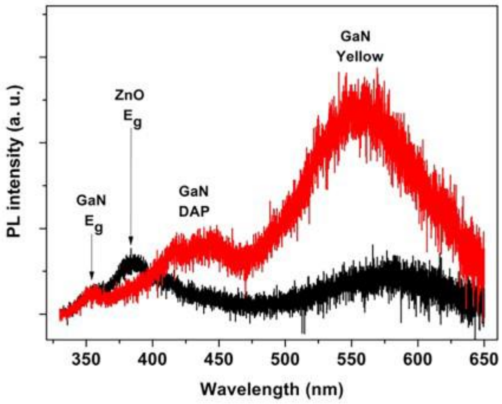

Fig. 9. Micro-PL spectra of aero-GaN before and after a post thermal treatment in hydrogen [16]**.**

It was demonstrated the applicability of ultra-lightweight GaN aeromaterial as pressure sensor able to measure pressures up to 40 atm. Figure 10 shows the SEM image reflecting the morphology of the material and the electrical response of the developed sensors as a function of pressure.

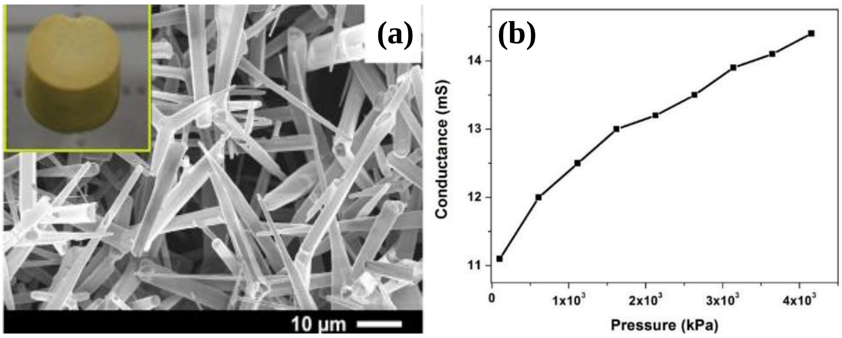

Fig. 10. (a) SEM image of the aero-GaN and (b) the electrical response of the sensor at pressures up to 40 atm [16,17]**.**

The aero-Ga_2O_3 obtained after a thermal treatment of aero-GaN proved to have a broad emission spectrum according to the results of cathodoluminescence spectroscopy (see figure 11a). After the spectrum deconvolution, the main emission peaks were found which could be assigned to donor and acceptor levels in the material.

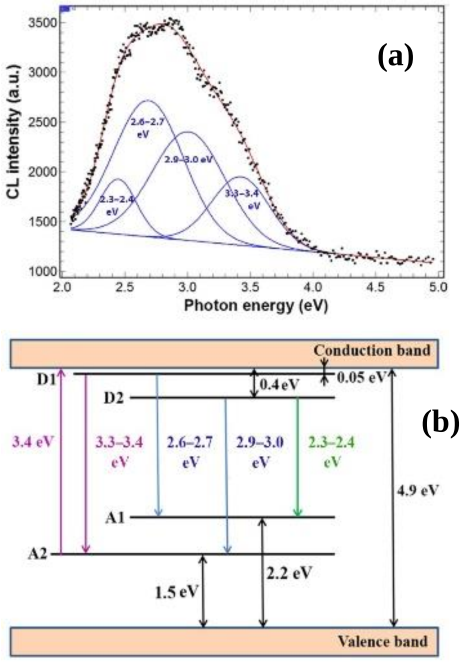

Fig. 11. (a) Aero-Ga_2O_3 CL measured spectra and its deconvolution and (b) band diagram model according to the CL spectra [15]**.**

According to the elaborated model (see figure 11b), the two blue emission bands at 2.6 – 2.7 eV, and 2.9 – 3.0 eV originate from the electronic transitions from the D1 and D2 levels to the A1 and A2 levels, respectively. The UV emission band at 3.3 – 3.4 eV can be attributed to the electron-hole recombination from the levels D1 and A2, while the green emission band at 2.3 – 2.4 eV is attributed to the electronic transition between D2 and A1 levels. Donor levels can be formed by oxygen vacancies (V_O^X) and Ga^{2+} interstitions, while acceptor levels can be assigned to Ga vacancies (V_{Ga}^X) and the Ga-O vacancy pairs [$(V_{Ga}, V_O)^X$]. The CL bands at 2.4, 2.7 and 3.0 eV were previously described as being attributed to the recombination of donor-acceptor pairs involving the same donor, while the acceptors are attributed to interstitial oxygen (O_i^0), Ga^{2-} vacancies and Ga-O vacancy pairs [$(V_{Ga}, V_O)^{1-}$], respectively [18].

The acceptors involved in the recombination process of the donor-acceptor pairs that generate the green emission band at 2.3 eV have also been assigned to either interstitial oxygen (O_i^0), octahedral Ga vacancies (V_{Ga}^{2-}), or tetrahedral Ga vacancies (V_{Ga}^{1-}), respectively [19].

The fabricated aeromaterials were electrodynamically characterized in the band-X and THz frequency range (see figure 12).

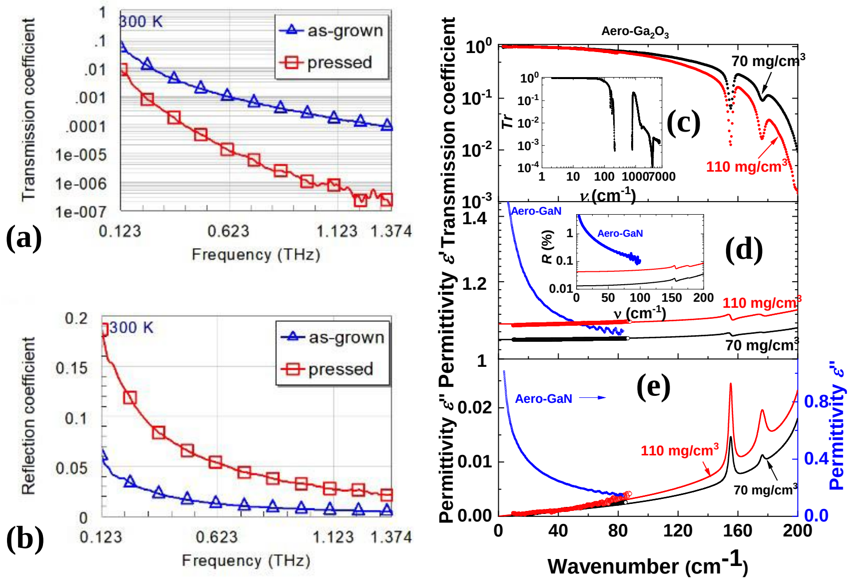

Fig. 12. The measured (a) transmission and (b) reflection coefficients and their temperature dependency of the aero-GaN samples with densities of 0.3 g/cm³ (the "as-grown" sample) and 0.35 g/cm³ ("pressed" sample) [21]**; the electrodynamic characterization in the THz region of the aero-Ga_2O_3 with densities of 70 mg/cm³ and 110 mg/cm³ as well as aero-GaN sample with density of 15 mg/cm³: the transmission coefficient T_r (c), real part ε′ (d) and imaginary part ε″ (e) of the dielectric permittivity. The curved marked with dots from figure (d) and (e) represents the THz permittivity data. The insert from figure (c): the measured spectrum of the transmission coefficient at frequencies up to 7000 cm^{-1}. The insert from figure (d): the reflectivity coefficient spectrum determined based on the measured spectra of real and imaginary parts of the dielectric permittivity using the standard Fresnel expression** [20], [22]**.**

Based on the measurements of transmission and reflection coefficients, it was demonstrated that the shielding efficiency of aero-GaN exceeds the value of 40 dB in the range 0.25 – 1.37 THz, while the aero-Ga_2O_3 has a very low reflectivity and high transparency in a wide range covering the X-band and the THz region, up to 3 THz [20].

At the end of chapter 4, the study of the interaction of GaN and ZnO nanoparticles with bovine serum albumin (BSA) was done using various modern techniques, as well as their interaction with keratinocytes HaCaT cell line in order to determine cytotoxicity of the formed complexes of NPs-protein corona.

In Table 1 the hydrodynamic size and the Zeta-Potential values of the ZnO nanoparticles in deionized water and those of the GaN nanoparticles stabilized with citrate buffer, as well as the formed complex dimensions of nanoparticles with corona of proteins incubated for 1 h are shown.

Table 1. Hydrodynamic size distribution of the NPs incubated with BSA at different ratios [23]**.**

	ZnO:BSA				GaN:BSA			
	Initial	1:5	1:1	5:1	Initial	1:5	1:1	5:1
Size, nm	123	137	136	157	182	185	183	185
Zeta-Potential, mV	26	-17	-16	-12	-50	-23	-30	-21

The conducted study demonstrates that in the case of GaN nanoparticles, a very low amount of proteins are adsorbed on the NPs surface as compared to ZnO NPs. At the same time, the mixing ratio of NP-BSA is an important factor regarding the stability of nanoparticles in solution, for example a ratio of 5:1 or higher (NPs:BSA) leads to a fast aggregation of the nanoparticles, and this can be avoided by choosing a higher concentration of proteins. The difference in the amount of proteins adsorbed on the ZnO and GaN nanoparticles is shown in figure 13 by incubating the NPs with BSA at different ratios.

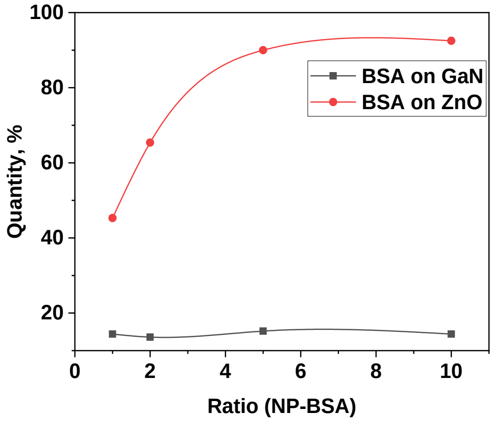

Fig. 13. Quantitative analysis of the BSA adsorbed on ZnO and GaN nanoparticles surface [23]**.**

The release of Zn^{2+} and Ga^{3+} ions from the nanoparticles incubated in the cell culture medium can induce cytotoxicity on keratinocyte cells as demonstrated in the viability tests shown in figure 14. ZnO NPs were found to be toxic at concentrations above 25 μg/ml, while GaN NPs were toxic at concentrations above 70 μg/ml.

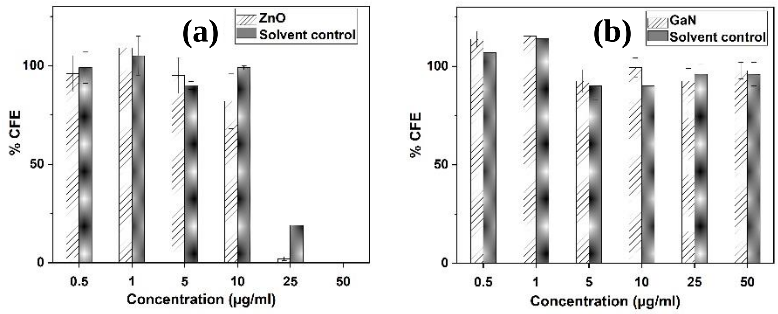

Fig. 14. Cytotoxicity study of the (a) ZnO and (b) GaN nanoparticles upon HaCaT cells [23]**.**

GENERAL CONCLUSIONS AND RECOMMENDATIONS

Based on the obtained results, the following general conclusions can be formulated:

1. The technological conditions for the fabrication of TiO_2 nanotubes with internal conical shape, whose dimeter gradually decreases from 120 nm to 50 nm were optimized, and these nanotubes were able for self-propulsion in the liquid medium consisting of low concentration of H_2O_2 (5 %) upon irradiation with external UV light. Moreover, networks of such nanotubes demonstrated to be able for capturing and transport of small particles in the liquid, the process being controllable and instant upon UV irradiation. The propulsion through the liquid is possible due to the crystalline structure of the TiO_2, which can be adjusted in the thermal treatment process. Networks of TiO_2 nanotubes with a mixed anatase-rutile phase proved the best efficiency or higher propulsion speed in the liquid containing H_2O_2 as well as in pure water, which opens the way to new practical applications in the field of biomedicine or environment [6].

2. TiO_2 nanotubes were investigated for photocatalytic degradation of Rhodamine B and MB organic dyes. TiO_2 nanotubes thermally treated at 500 °C as well as anatase samples doped with Ag showed an enhanced efficiency on Rhodamine B degradation, while doping or functionalizing the nanotubes surface with Au or Pt nanodots showed a negative effect on photocatalytic performance. On the other hand, the TiO_2 nanotubes thermally treated at 650 °C and 850 °C are effective in MB degradation under UV or visible light irradiation. Samples treated at 850 °C where the rutile phase predominates, possess the highest degradation rate under visible light, while samples treated at 650 °C where the anatase phase predominates, possess the highest degradation rate of photocatalytic degradation under UV light [4,11,12].

3. GaN/ZnO microtubular nanoarchitectures decorated with $(Ga_{1-x}Zn_x)(N_{1-x}O_x)$ nanowires having AuGa alloy dots termination were fabricated and characterized using different techniques. It was demonstrated that these microtubes can work as micromotors due to the intense photochemical reactions in aqueous solution containing H_2O_2 under irradiation with UV light. It was established that a microtube with the length of 32 µm and the diameter of 4.6 µm has a propulsion speed of 1.4 µm/s, while a tube with the length of 2 µm and diameter of 0.9 µm has a propulsion speed of 5.5 µm/s, which can be controlled instantly by turning the UV light on/off. The propulsion in the liquid of the micromotors takes place due to the difussiophoretic mechanism [13].

4. Networks of monocrystalline ultrathin GaN membranes in parallel configuration are able for simple learning mechanisms such as habituation/dishabituation and memorizing the external stimulus like electrical one. The responsible mechanism for the learning processes is the progressive filling of the surface states as a result of trapped negative charges migration under the influence of

the electric field induced by traps. Increasing the number of memristors in parallel configuration, the learning process becomes faster. Additionally, the asymmetric time response at positive or negative voltage excitation decreases significantly by increasing the number of parallel memristors, while the time for reaching the steady state remains almost the same [14,24–26].

5. A pressure sensor based on ultra-lightweight aero-GaN was fabricated and demonstrated. The nonlinear sensitivity of the sensors varies from $16.2 \cdot 10^{-3}$ at low pressure (5 atm) to $7.4 \cdot 10^{-3}$ at high pressure (40 atm). The sensitivity level and the current response in the mA range make these sensors feasible for incorporation in portable devices. Due to simple and robust structure of the sensor, it is ideal for aerospace applications [16,17].

6. Electrodynamic characteristic spectra of the aero-GaN in the THz region in the range 4 – 100 cm^{-1} and at temperatures 4 – 300 K were determined: the real and imaginary parts of the refraction index, the dielectric permittivity and the surface impedance. Based on the measured transmission and reflection coefficients, it was demonstrated that the shielding effectiveness of the aero-GaN samples exceeds the value of 40 dB in the range 0.25 – 1.37 THz. Note that 40 dB value is necessary for many industrial applications [21].

7. A new material based on ultralight porous 3D nanoarchitectures consisting of interconnected β-Ga_2O_3 microtetrapods with the walls thickness in the nanometer range and with a stoichiometric chemical composition was fabricated. This material has a very low reflectivity and high transparency in a wide range of frequencies which covers X-band and THz region, up to 3 THz [20].

8. The interaction of GaN and ZnO nanoparticles with BSA proteins was extensively studied. ZnO nanoparticles showed a high affinity for the proteins compared with GaN particles. Both types of particles showed a good stability in the cell culture medium with a small increase in the hydrodynamic size. According to the structural change analysis of the attached proteins on the NPs surface, the proteins showed a drastic modification in the secondary structure. The Zn^{2+} and Ga^{3+} ions release from the nanoparticles in the cell culture medium can induce cytotoxic effect on keratinocite cells, as it was demonstrated in the viability test of the HaCaT cells. As a conclusion, it can be stated that Ga^{3+} ions have a less toxic effect than Zn^{2+} upon HaCaT cells [23].

RECOMMENDATIONS

1. The possibility to use TiO_2 and GaN micro- and nanotubes as micro- and nanomotors could open new ways for use in biomedicine and it is recommended a more complex study on that, as for example for drug or even cells delivery systems.

2. The photocatalytic degradation of organic dyes usually leads to the formation of other molecules, whose effect could also be negative upon environment or human health, thus it is recommended a more detailed study with identification of new possible formed molecules.

3. The memristive effect on ultrathin GaN membranes could find applications in future devices such as perceptron, and one such device is under modeling process and need to be investigated in the near future.

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ADNOTARE

la teza cu titlul **“Rețele de nano-membrane și structuri tubulare din GaN și TiO_2 pentru aplicații în sisteme memristive și biomedicină”,** înaintată de competitorul Ciobanu Vladimir**,** pentru conferirea gradului de doctor în fizică, la specialitatea **134.01 “Fizica și Tehnologia Materialelor”**.

Structura tezei: Teza înaintată spre susținere a fost realizată la universitatea Tehnică a Moldovei, Centrul Național de Studiu și Testare a Materialelor (CNSTM), Chișinău, 2022, este scrisă în limba română și constă din introducere, 4 capitole, concluzii generale și recomandări și bibliografie (278 titluri), fiind expusă pe 146 pagini de text de bază (până la bibliografie), conținând 110 figuri și 8 tabele. Rezultatele obținute au fost publicate în 23 lucrări științifice, dintre care 9 articole în reviste internaționale, 2 articole în reviste naționale și 12 publicații la conferințe naționale și internaționale.

Cuvinte cheie: Nanotehnologii, GaN, TiO_2, nanotuburi, nanomembrane, nanomotoare, aeromateriale, memristor, senzori, interacțiune cu proteinele.

Domeniul de studiu: Nanotehnologii și nanomateriale noi multifuncționale.

Scopul lucrării: elaborarea condițiilor tehnologice de fabricare a structurilor de dimensiuni reduse în baza GaN, TiO_2 și Ga_2O_3 cu proprietăți unice și ilustrarea aplicativă a acestora în domeniul electronicii, mediului ambiant și în medicină.

Obiectivele cercetării: Elaborarea structurilor nanotubulare în baza oxidului de titan și a nitrurii de galiu și investigarea acestora ca micro- și nanomotoare în soluții apoase, controlate prin intermediul sursei de lumină externe. Studiul fotocatalitic al structurilor nanotubulare din TiO_2 pentru degradarea compușilor organici. Elaborarea și studiul circuitelor memristive în baza membranelor ultrasubțiri de GaN obținute prin tehnica litografiei cu sarcină de suprafață. Elaborarea condițiilor tehnologice de fabricare a aeromaterialelor precum aero-GaN și aero-Ga_2O_3 și caracterizarea fizico-chimică a acestora prin diferite tehnici. Studiul interacțiunii nanoparticulelor de oxid de zinc și nitrură de galiu cu proteinele în vederea influenței citotoxicității asupra celulelor vii.

Noutatea și originalitatea științifică: Au fost elaborate structuri nanotubulare din TiO_2 cu diametrul intern al tuburilor ce scade gradual de-a lungul tubului, un aspect principial în vederea utilizării acestor structuri în calitate de micro- sau nanomotoare, inclusiv cu proprietăți Cargo, în cazul rețelelor constituite din mai multe nanotuburi, sau pentru creșterea eficienței de degradare a compușilor organici. Au fost elaborate structuri tubulare din GaN cu grosimea pereților de dimensiuni nanometrice cu arhitectura internă complexă și a fost demonstrată aplicabilitatea acestora ca micromotoare. A fost studiat efectul memristiv pe membrane ultrasubțiri de GaN în diverse configurații și a fost demonstrat procesul de învățare a stimulilor externi sau de resetare, un proces identic observat în sinapsele biologice. Au fost elaborate aeromateriale în baza nitrurii de galiu sau al oxidului de galiu și investigate proprietățile lor fizico-chimice, fiind identificate posibilități de utilizare a acestora în calitate de senzori de presiune sau materiale pentru protecție împotriva radiației la frecvențe înalte (GHz și THz). A fost investigată interacțiunea nanoparticulelor de GaN și ZnO cu proteine BSA prin diverse tehnici, precum și efectul citotoxicității acestor complexe asupra celulelor vii.

Problema științifică principală soluționată: elaborarea tehnologiei de fabricare a structurilor tubulare din GaN și TiO_2 prin metode cost-efective, fabricarea aeromaterialelor din GaN și Ga_2O_3 și caracterizarea acestora pentru aplicații în domeniul medicinei, mediului ambiant și electronicii.

Semnificația teoretică și valoarea aplicativă a lucrării: În lucrare sunt prezentate aplicații practice în baza membranelor ultrasubțiri de GaN, micro- și nanotuburilor din GaN și TiO_2, și a aeromaterialelor noi elaborate din GaN și Ga_2O_3 precum memristori, micromotoare sau materiale de ecranare într-un diapazon larg de frecvențe. Este elaborat modelul curentului limitat de sarcinile spațiale, indus de capcanele adânci în material, ce descriu efectul memristiv în membranele de GaN. Pentru senzorii de presiune în baza aero-GaN este elaborat un model fizic ce include efectul piezorezistiv în material și dinamica legăturilor dintre microtetrapozi.

ABSTRACT

of the dissertation entitled **"Networks of nanomembranes and tubular structures of GaN and TiO_2 for memristive systems and biomedical applications"**, presented by Vladimir Ciobanu for obtaining the degree of Doctor in Physics at the specialty **134.01 Physics and Materials Technology**".

Dissertation structure: The dissertation was realized at Technical University of Moldova, Chisinau, 2022. It is written in Romanian language and consists of introduction, 4 chapters, general conclusions and recommendations and bibliography (278 references). The content of the dissertation is exposed on 146 pages of basic text, contains 110 figures and 8 tables. The obtained results were published in 23 scientific papers, including 9 articles in international journals, 2 articles in national journals and 12 publications at national and international conferences.

Keywords: Nanotechnology, GaN, TiO_2, nanotubes, nanomembranes, nanoengines, aeromaterials, memristors, sensors, interaction with proteins.

Field of study: Nanotechnologies and new multifunctional materials.

Aim of the work: Elaboration of technological conditions for fabrication of low dimensional structures based on GaN, TiO_2 and Ga_2O_3 with unique properties and applications development based on these materials in the electronics, biomedicine and environment fields.

Objectives: Elaboration of nanotube structures based on titanium dioxide and gallium nitride and their investigation as micro- and nanoengines in aqueous medium controlled by external light source. Photocatalytic study of the TiO_2 nanotubes for degradation of organic compounds. Elaboration and investigation of memristive circuits based on GaN ultrathin membranes fabricated by Surface Charge Lithography approach. Determination of technological conditions for fabrication of aeromaterials like aero-GaN and aero-Ga_2O_3 and their physico-chemical characterization using different techniques. Investigation of the interaction between ZnO and GaN nanoparticles with proteins and their cytotoxicity on the cells.

Novelty and scientific originality: TiO_2 nanotubes with gradually decrease of the internal diameter, an important parameter for their use as micro- or nanoengines including the Cargo effect in case of networks of nanotubes or for improving the efficiency of organic compound degradation were fabricated. GaN tubular structures with the thickness of the tube walls of few nanometers with complex internal architecture were fabricated and their use as microengines was demonstrated. The memristive effect on GaN ultrathin membranes in different configurations was studied and the habituation or dishabituation mechanisms of electrical stimuli was investigated, an identical process observed in biological synapses. Aeromaterials based on GaN and Ga_2O_3 were fabricated and their physico-chemical investigation was performed and identified the possibilities to use them as pressure sensors or shielding materials for high frequency radiation (GHz and THz). The interaction between GaN and ZnO nanoparticles with proteins was investigated using different techniques as well as the cytotoxicity of the formed complexes upon living cells.

The solved scientific problem: Manufacturing technology development of GaN and TiO_2 tubular structures by a cost-effective technique, GaN and Ga_2O_3 aeromaterials fabrication and their use in applications like biomedicine, environment or electronics.

Theoretical significance and practical value of the work: In this work are presented practical applications of GaN ultrathin membranes, GaN and TiO_2 micro and nanotubes, and new aeromaterials based on GaN and Ga_2O_3 materials like, memristors, microengines or shielding materials in a large frequency domain. The physical model based on trap induced space charge limited current was elaborated for describing the memristive behavior in GaN membranes. For pressure sensors based on aero-GaN a physical model was elaborated which takes into consideration both the piezoresistive property of the material and the dynamics of the microtetrapods during the pressure change.

АННОТАЦИЯ

Диссертация «**Нано-мембранные сети и трубчатые структуры из GaN и TiO_2 для применения в мемристивных системах и биомедицине**» Владимира Чобану, соискателя на степень доктора физикических наук по специальности 134.01 «Физика и технология материалов».

Структура диссертации: Диссертация, представленная на защиту, написана в Техническом Университете Молдовы, Национальный центр исследований и испытаний материалов (CNSTM), Кишинев, 2022 г., написана на румынском языке и состоит из введения, 4 глав, общих выводов, рекомендаций и библиографии (278 наименований), содержит 146 страниц основного текста (до библиографии), 110 рисунков и 8 таблиц. Полученные результаты опубликованы в 23 научных статьях, из которых 9 статей в международных журналах, 2 статьи в национальных журналах и 12 публикаций на национальных и международных конференциях.

Ключевые слова: нанотехнологии, GaN, TiO_2, нанотрубки, наномембраны, наномоторы, аэроматериалы, мемристор, сенсоры, взаимодействие белков.

Область исследования: Нанотехнологии и новые мультифункциональные наноматериалы. **Цель:** разработка технологических условий получения низкоразмерных структур на основе GaN, TiO_2 и Ga_2O_3 с уникальными свойствами и возможность их пркатического применения в области электроники, экологии и медицины.

Задачи работы: Разработка нанотрубчатых структур на основе оксида титана и нитрида галлия и изучене возможности применения полученных структур в водных растворах в качестве микро- и нано-моторов, управляемых внешним источником света. Фотокаталитическое исследование влияния нано-трубчатых структур TiO_2 на разложение органических веществ. Разработка и исследование мемристивных схем на основе ультратонких мембран из GaN, полученных методом литографии поверхностного заряда. Разработка технологических условий производства таких аэроматериалов как аэро-GaN и аэро-Ga_2O_3 и их физико-химическая характеризация различными методами. Изучение влияния наночастиц оксида цинка и нитрида галлия на цитотоксичность живых клеток при взаимодействия наночастиц с белками.

Новизна и оригинальность: разраотана технолгоия получения нанотрубок TiO_2 с постепенным уменьшением внутреннего диаметра, что является ключевым аспектом для использования этих структур в качестве микро- или наномоторов, обладающих свойством Карго в случае пакетов, состоящих из нескольких нанотрубок, а так же для увеличения эффективности разложения органических соединений. Разработаны трубчатые структуры из GaN с нанометровой толщиной стенок и сложной внутренней архитектурой, продемонстрирована возможность их примения в качестве микродвигателей. Был изучен мемристивный эффект в ультратонких мембранах GaN в различных конфигурациях, и был продемонстрирован процесс обучения или сброса под внешним воздействием, идентичный процессу наблюдаемому в биологических синапсах. На основе нитрида галлия или оксида галлия были разработаны аэроматериалы, исследованы их физико-химические свойства и определены возможности их использования в качестве датчиков давления или материалов для защиты от высокочастотного излучения (ГГц и ТГц). Взаимодействие наночастиц GaN и ZnO с белками БСА было исследовано различными методами, а также изучено влияние цитотоксичности этих комплексов на живые клетки.

Основная научная задача, решенная в диссертации, заключается в: разработке технологии изготовления трубчатых структур из GaN и TiO_2 рентабельными методами, разработка аэроматериалов GaN и Ga_2O_3 и их иследование для использования в таких областях, как медицина, защита окружающей среды или электроника.

Теоретическая значимость и прикладная ценность диссертации: в дисетрации показана возможность применения мембран GaN, микро- и нанотрубок GaN и TiO_2, а также новых аэроматериалов разработанных на основе GaN и Ga_2O_3 в качестве мемристоров, микродвигателей или экранирующих материалов работающих в широком диапазоне частот. Разработана физическая модель прохождения тока ограниченного объемными зарядами, вызванными глубокими ловушками в материале, описывающая эффект самовосстановления в мембранах GaN. Для датчиков давления на основе аэро-GaN разработана физическая модель, которая включает пьезорезистивный эффект в материале и динамику связей между микротетраподами.

CIOBANU VLADIMIR

NETWORKS OF NANOMEMBRANES AND TUBULAR STRUCTURES OF GaN AND TiO_2 FOR MEMRISTIVE SYSTEMS AND BIOMEDICAL APPLICATIONS

134.01 PHYSICS AND MATERIALS TECHNOLOGY

Abstract of the PhD dissertation in Physics

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