This book is devoted to issues related to fabrication and comparative characterization of porous III-V and II-VI semiconductor compounds fabricated by electrochemical etching. To extend the area of applications it was proposed to combine electrochemical etching and pulsed electrochemical deposition approaches for micro-nanodevice manufacturing. The versatility of morphologies and the application of porous semiconductor compounds are discussed in details in this book.

Among key points can be mentioned: Electrochemistry as cost-effective approach for porosification of semiconductor compounds in a controlled fashion; Types of pores in semiconductor compounds; Self-ordering of pores in semiconductor compounds; Multilayer porous structures with modulation of the degree of porosity; Uniform deposition of self-assembled monolayer of metal dots via pulsed electroplating according to the proposed "hopping electrodeposition"; Applications of self-organized arrays of pores including those functionalized by metal.

The significant aspects of many technological processes, characterization and device design are collected in this monograph, making it a timely and valuable practical guide not only for specialists in materials science and engineering, nanoscience and nanotechnologies, electrochemistry of semiconductors, but also for students and PhD students.

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EDUARD MONAICO

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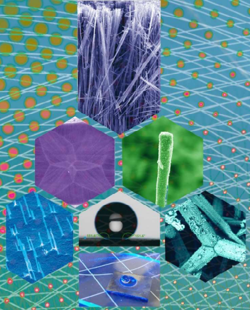

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TECHNICAL UNIVERSITY OF MOLDOVA

National Center for Materials Study and Testing

Eduard MONAICO

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Reviewers:

Prof. Dr. **Vladimir FOMIN**	*Institute for Integrative Nanoscience, Leibniz Institute for Solid State and Materials Research (IFW Dresden), Dresden, Germany*
Prof. Dr. **Mircea DRAGOMAN**	*National Institute for Research and Development in Microtechnologies (IMT Bucharest), Bucharest, Romania*

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CHAPTER THREE

Preface and Acknowledgements

This book is the result of 20 years of my research activity at National Center for Materials Study and Testing within Technical University of Moldova in the field of porous semiconductors obtaining with controlled morphology with impact upon their properties. The book is based on a substantial number of papers and other publications that the author, together with supervisor and other researchers have published since about 2002. It also includes of course the comparison with the results from many other groups.

This book is devoted to issues related to fabrication and comparative characterization of porous III-V and II-VI semiconductor compounds fabricated by electrochemical etching. Nowadays, anodization of semiconductor compounds represents a cost-effective top-down approach in nanofabrication. To extend the area of applications it was proposed to combine electrochemical etching and pulsed electrochemical deposition approaches for micro-nanodevice manufacturing. The versatility of morphologies and the application of porous semiconductor compounds will be discussed in details in this book.

Among key points can be mentioned: Electrochemistry as cost-effective approach for porosification of semiconductor compounds in a controlled fashion; Types of pores in semiconductor compounds; Self-ordering of pores in semiconductor compounds; Multilayer porous structures with modulation of the degree of porosity; Uniform deposition of self-assembled monolayer of metal dots via pulsed electroplating according to the proposed “hopping electrodeposition”; Applications of self-organized arrays of pores including those functionalized by metal.

Many of the results given come from a cooperation with Prof. Kornelius Nielsch during the research fellowship offered to the author by the Alexander von Humboldt Foundation (Bonn, Germany) at University of Hamburg, Germany (2012-2014) and at Institute for Metallic Materials (IMW), Leibniz Institute of Solid State and Materials Research (IFW Dresden), Dresden, Germany (March-May 2018). The fellowships financially supported by the Alexander von Humboldt Foundation, as well as equipment donation gave me the opportunity to gain valuable experience and to become visible at the national and European levels.

The work includes the research carried out within projects conducted by author as manager of projects: individual CRDF / MRDA (2009); young researchers (2009-2010 and 2011-2012); state program (2016-2017); STCU (2017-2019), institutional project (2016-2020), bilateral Belarus-Moldova (2019-2020), state program project (2020-2023) #20.80009.5007.20, postdoctoral grant #21.00208.5007.15/PD (2021-2022) and as executant in many national and international projects (INTAS, CRDF, SCOPES, STCU, FP7, H2020).

The author would like to thank to researchers contributed to the field of porous III-V semiconductors, in particular to my supervisor Prof. Ion Tighineanu from Academy of Sciences of Moldova, Prof. Veaceslav Ursachi from Academy of Sciences of Moldova, Prof. Helmut Föll from Kiel University (Germany), Dr. Sergiu Langa (Germany) as well as to co-authors of joined papers: Prof. Kornelius Nielsch (Germany), Prof. Marius Enăchescu (Romania), Prof. Sergei Gaponenko (Belarus), Dr. Vladimir Sergentu, Dr. Tudor Braniște, Dr. Victor Zalamai, Dr. Gleb Colibaba, Vladimir Ciobanu, Vadim Morari, etc. The author is also thankful to European Commission under the H2020 grant #810652 'NanoMedTwin' for financial support of Open Access publication of the research articles.

The opportunity to share the obtained results and experience with the students and master students at Technical University of Moldova was given to the author by Prof. Victor Șontea convincing me to be involved in teaching with two courses: "Nano-Micro-Electronic Devices" (licentiate level) and "Nanoelectronic Devices" (master level).

The book is designated for students, Ph.D. students and specialists in material science and engineering, nanoscience and nanotechnologies, electrochemistry of semiconductors, new materials for photonics, nano- and microelectronics, micro- and optoelectronics.

List of Abbreviations

AAO – anodic aluminum oxide
AFM – atomic force microscopy
ALD – atomic layer deposition
CA – contact angle
CE – counter electrode
CL – cathodoluminescence
CLO or curro – current-line oriented
CO or crysto – crystallographically oriented
CPE – constant phase element
CV cyclic voltammetry
CVT – chemical vapor transport
DBRs – distributed Bragg reflectors
DL – double layer
Donor–acceptor pair (DAP)
EC electrochemical
EDAX (EDX) – energy dispersive X-ray analysis
EECs – electrical equivalent circuits
EIS – electrochemical impedance spectroscopy
FIB – Focused Ion Beam
FR – photoresist
FWHM – full width at half maximum
HVPE – Hydride Vapor Phase Epitaxy
ip – in-plane
IR – infrared
I-V curve – current - voltage curve
KPFM – Kelvin Probe Force Microscopy

LDPCD – long-duration-photoconductivity decay
LOPC – LO-phonon-plasmon-coupled
MOCVD – Metal Organic Chemical Vapor Deposition
MPS – multilayer porous structures
NIMs – negative index materials
NTs – nanotubes
NWs – nanowires
OCP – open circuit potential
oop – out-of-plane
PCM – point contact microscopy
PDMS – polydimethylsiloxane
PEC – photoelectrochemical
PFP – pore formation potential
PL – photoluminescence
PPC – persistent photoconductivity
PSi – porous silicon
RE – reference electrode
RR – remanence ratio
RS – Raman spectra
SAED – selected area electron diffraction
SCR – space charge region
SEM – scanning electron microscopy
TEM – transmission electron microscopy
UV – ultraviolet
VSM – vibrating sample magnetometer
WE – working electrode
WZ – wurtzite
XRD – X-ray diffraction
ZB – zincblende
ZPL – zero-phonon-line

“Imagination is more important than knowledge. Knowledge is limited. Imagination encircles the world.”

– Albert Einstein

Introduction

Starting with the rapid development of nanotechnology in the 1990s, a variety of porous materials has been reported. The wide class of porous materials includes both organic and inorganic materials such as porous metals, porous semiconductor and dielectrics, porous ceramics, polymer foams, metal-organic frameworks etc. [1–3]. Porous solids often serve as structural bodies in nature, including in wood, bones and other biological objects. Depending on their nature, porous materials are prepared by specific technologies involving a lot of fundamental concepts, and they find specific fields of applications determined by their properties.

Among semiconductor materials, considerable interest has been triggered by the discovery of luminescent porous Si three decades ago [4]. The efficiency of porous silicon LED's has risen by 5 orders of magnitude over the years and currently is approaching commercial viability for some integrated display applications [5]. With the time, it was shown at the laboratory research level that porous Si is suitable for many applications, including optic and optoelectronic applications (light emitting devices, optical waveguides, photonic crystals, optical resonators, distributed Bragg reflectors and diffraction gratings), electronic applications (gas sensing, gettering, lithium-ion batteries, and solar cells antireflection coatings), microfluidics, medical applications etc. [6–10].

Recently, it was proposed to produce size-controlled nanocrystalline (nc-Si) dot colloids by exposing porous silicon (PSi) in solvents to pulse laser, which results in fragmentation of the PSi layer with a considerably higher yield than the conventional techniques [11]. This was shown to pave the way for emerging functions of nanostructured PSi related to strong visible photoluminescence of about 40% in quantum efficiency in the red band, efficient quasi-ballistic hot electron emission from an nc-Si diode due to multiple-tunneling transport mode through nc-Si dot chain, and enhanced to a practical level thermo-acoustic conversion due to an extremely low thermal conductivity and volumetric heat capacity of nc-Si layer. Applications of the quasi-ballistic electron source in flat panel display, multibeam parallel lithography, high-sensitivity image sensor and reductive deposition of thin films have been demonstrated.

Meanwhile, the transition of the porous silicon from academic studies to industry is in progress. Prototype devices on large area wafers taking advantages of the isolating properties of PSi, including power AC switches, radio-frequency (RF) devices and energy micro-sources, have been demonstrated through collaboration between GREMAN and ST Microlectronics [12]. Nevertheless, wide implementation of PSi in the field of electronic component manufacturing still needs significant investment, development, optimization and validation of reliable equipment and processes in terms of throughput. BOSCH GmbH uses PSi in high-volume industrial production of micro-electro-mechanical (MEMS) devices, particularly in manufacturing of monolithically integrated pressure sensors [13]. SOLEXEL in collaboration with SCREEN is particularly active in the field of photovoltaic cells manufacturing with the design and the development of high throughput production equipment [12].

On the other hand, developing of technological methods for the preparation of porous alumina templates, including the ones with periodically ordered pore arrangement, triggered off extensive activities in research for template synthesis of various nanoscale materials, it being an elegant, inexpensive, and technologically simple approach [14].

Nowadays, there are several well studied self-ordered porous materials finding applications in many fields, e.g.: (i) porous anodic aluminum oxide (AAO) [15]; (ii) TiO_2 nanotubes [16]; and (iii) self-ordered porous III-V semiconductor compounds [17–21].

Porous anodic aluminum oxide attracted a huge interest due to the pioneer works of Martin [22] and Masuda and Fukuda [23]. Self-organized nanoporous structures with hexagonal ordered distribution of pores were obtained on a highly pure Al surface via electrochemical anodization in acidic medium [24,25]. AAO templates have many advantages over the polycarbonate membranes like high pore density, thermal stability, cost effectiveness and versatility. Pore diameter, length, inter-pore spacing, and pore ordering can be easily tailored by tuning the anodizing parameters such as voltage, time, electrolytes, pH value, and temperature [25].

Both of these materials are prepared by electrochemical etching of Si wafers in the case of porous Si, and Al wafers in the case of porous alumina templates. Electrochemistry offers an accessible and cost-effective approach for preparation of porous template with tailored architecture on the submicrometer scale. However, Si is a material with indirect energy band gap corresponding to the infrared spectral range, which strongly restricts the area of applications for porous Si. On the other hand, porous alumina templates exhibit high resistivity and therefore they often play a passive role in nanofabrication processes, since they are used mostly for the templated synthesis of nanowire arrays, which are prospective for several applications [26]. The templated growth of nanowires via electroplating is provided usually by the metal contact deposited on the back side of the high-resistivity membranes. To produce electroplating of metal nanodots and nanotubes into alumina templates, additional technological steps are required, e.g. chemical modification of the inner surface of the pores prior to electrodeposition, which leads to the incorporation of spurious phases in the nanotube walls [27].

In comparison with porous alumina, TiO_2-based nanomaterial has attracted a lot of attention in research and is considered a semiconductor nanoarchitecture with potential for a variety of applications due to its unique structural, optical and electronic properties, non-toxicity, corrosion resistance, etc. Compared to porous alumina, the templates from titanium dioxide have a number of advantages such as accessibility, biocompatibility, high photocatalytic characteristics, photostability etc. TiO_2 nanotubes (NTs) can be fabricated via facile hydrothermal method, solvothermal method, template-mediated techniques and electrochemical anodic oxidation, the last one representing a cost-effective approach. The fabrication of TiO_2 nanotubes was first demonstrated back in 1984 and nowadays, 4 generations of such nanostructures are known. First and second generations used aqueous solutions containing HF acid or fluorine salts and allowed fabrication of nanotubes with length up to 5 μm. However, in the latest generations, organic solutions containing fluoride salts are used which allows the fabrication of NTs up to 1000 μm long [28,29]. Despite the fact that TiO_2 is considered a semiconductor material, its electrical conductivity is relatively low.

In connection with this, semiconductor porous structures with controlled conductivity are of major interest. Porous materials from III-V and II-VI groups are perfect candidates able to fill this gap. An essential contribution to the controlled nanostructuring of III-V semiconductor compounds was made by the groups of H. Föll, I. Tiginyanu, and P. Schmuki. The systematization of technological parameters, morphologies, pore geometries etc. allowed one to elucidate the regularities of self-ordering during the pore growth [17,19,30]. Besides the optimum electrochemical parameters (electrolyte nature and its concentration, applied anodization potential, temperature, etc.), an important factor leading to self-ordering proved to be the presence of the crystallographically oriented pores. It is worth to mention that self-ordering in porous materials is introduced without any lithographic means.

Lithographic masks are used solely to control the direction of pore growth in the restricted space under the fotorezist leading to spectacular porous architectures [31]. Moreover, using holes in the photoresist mask leads to the formation of non-connected pore networks in a semiconductor wafer for microfluidic applications.

Producing of nanodots, nanotubes, as well as 2D metallo-semiconductor interpenetrating networks are promising for various nanoelectronic, optoelectronic, plasmonic, and nanophotonic applications. Metal nanodots are obtained routinely in solutions, but positioning them on a chip remains a significant challenging. Conventional controlled patterning approaches like electron beam lithography [32], stencil lithography [33,34], and extreme ultraviolet interference are very expensive. In spite of the fact that low-cost alternatives such as nanoimprint [35] and nanosphere techniques [36] exist, they are limited because they imply complicated resists, lift-off processes, and cannot be accurately controlled as to their positioning, size, and shape. The high conductivity of the semiconductor nanotemplate skeleton provides conditions for uniform electrochemical deposition of metal species on the inner surface of pores, resulting in the formation of arrays of metal nanotubes embedded in semiconductor matrix.

The optoelectronic applications of metallic nanotubes are based on the extended dielectric/metal interface that can sustain the propagation of electromagnetic waves coupled to collective oscillations of the conduction electrons in the metal, the so called surface plasmon polaritons, allowing the manipulation and transmission of light on the nanoscale [37,38]. 2D metallo-semiconductor networks may find potential applications in photonic integrated devices and circuits [37].

Since semiconductor compounds provide more space for tailored nanofabrication in terms of compositions, bandgaps, mechanisms of the pore growth and new properties with large potential for applications, their porosification was widely explored during the last two decades.

This monography will focus on different aspects of pore growing, including self-organized pore formation, which results in production of ordered arrangements of pores, on properties of the produced semiconductor compound porous materials and nanocomposites on their basis, on various actual applications and future prospects.

"The science of today is the technology of tomorrow."

– Edward Teller

Chapter One

1. ELECTROCHEMICAL DISSOLUTION MECHANISMS: COMPARATIVE ANALYSIS OF III-V (InP, GaAs, GaP, GaN) AND II-VI SEMICONDUCTOR COMPOUNDS (CdSe, ZnSe, $Zn_XCd_{1-X}S$, ZnO)

1.1 Dissolution mechanisms and types of pores: crystallographically oriented, current line oriented, and fractal pores.

Over the last decades, it was demonstrated that electrochemistry is one of the most accessible and cost-effective approaches for tailoring the architecture of semiconductor materials at the nanoscale level by introducing porosity. One of the key problems with electrochemical (EC) methods of introducing porosity in semiconductor materials is the appropriate choice of the electrolyte composition. This problem is solved individually for each material. Due to the narrow band gap of InAs it is relatively difficult to reach nanostructuring in this compound via electrochemical etching techniques. Nevertheless, the formation of InAs micro- and nano-pencils was reported [39]. However, the obtained structures are inhomogeneous. More recently, it was shown that the morphology of the porous InAs layers can be controlled by the composition of the electrolyte and the applied electrochemical parameters [40]. It is difficult to control the mechanism of pore growth in InAs, since in narrow bandgap semiconductors uniform electrochemical etching proves to occur simultaneously with the pore growth, thus resulting in the limitation of the achieved depth of the produced porous layer.

Usually, three types of pores can be generated in semiconductor compounds: current-line oriented (**CLO or *curro pores***), crystallographically oriented (**CO or *crysto pores***), and fractal pores. The characteristics of the pores (shape, velocity of growth, etc.) depend on the specific anodization conditions [41]. It was established that CO pores grow at current densities lower than a certain threshold value, whereas CLO pores grow at current densities higher than the threshold value. The threshold values depend strongly on the free carrier density in semiconductor crystal, electrolyte concentration, and temperature. The main feature of the CO pores is that they grow along definite crystallographic directions. In case of sphalerite crystal structures, they grow along <111>B crystallographic directions, independent of the initial surface orientation, the angle between pores being approximately of 109° (Figure 1.1a,b). They tend to have a triangular cross-section and the pore walls and tips show a pronounced crystallographic anisotropy as well [42]. A very important property of the crysto pores is their ability to intersect each other, thus opening a new way for semiconductor 3D structuring (Figure 1.1c). Crysto pores are inherent to Si, GaP, InP and GaAs, however no crysto pores have been observed up to now in II-VI semiconductor compounds such as ZnSe and CdSe. On the other hand, curro pores are inherent to Si, GaP, InP and ZnSe (Figure 1.1d and Figure 1.1e), however no curro pores have been observed so far in GaAs. No intersection of curro pores was demonstrated experimentally up to now.

Fractal pores are the third type of pores observed in Si, III-V and II-VI semiconductor compounds. A fractal is normally defined as an object that can be divided into parts and each of these parts will be similar to the original object. The structures presented in Figure 1.1f,g are not perfect fractals, but the pores are called fractal due to their fractal-like way of growth, i.e. each point of a pore in such a structure can be a source for one or more similar pores growing in totally different directions. The existence of fractal pores not only opens new insides regarding the mechanism of pore formation in semiconductors, but is also interesting for optical applications, for example nonlinear optical effects.

In the case of InP, at the beginning of the anodization process multiple branching of a primary pore in the nucleation layer results in a whole set of secondary pores oriented along crystallographic directions <111>B. The end points of the set of pores originating from the same root nucleus form a linear domain and serve as

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A P P E N D I X B

The list of published papers by the author discussed in this monograph

The list of publication is divided in two parts: the published articles after (**Part I**) and before (**Part II**) the defense of PhD thesis in 2009 entitled "Morphology and optical properties of porous structures on the basis of II-VI semiconductor compounds".

- **Part I**

1.	**Self-organized porous semiconductor compounds. Chapter book.** Ion Tiginyanu**, Eduard Monaico.** ***Encyclopedia of Condensed Matter Physics,*** ECMP 2nd Edition, Elsevier, 2023**.** In press.
	Abstract: This chapter provides a review of self-organization of pores in semiconductor compounds when subjected to electrochemical etching. The influence of key factors upon self-organization is elucidated under anodization of semiconductor compounds at high applied potentials or current densities implying growth of current line-oriented pores. A comparative analysis of the morphologies of pores in III-V and II-VI compounds is performed. It is shown that the direction of pore propagation can be efficiently controlled using photolithographic masks deposited prior the anodization. Besides, the formation of quasi-ordered nanotubular structures of titania via anodization of titanium foils is reviewed. The possibility for the deposition of self-organized size-saturated monolayer of metal nanodots using pulsed electroplating on porous semiconductor templates is highlighted. The prospects of application of described porous structures in light-driven micro-engines as well as in photocatalytic, photonic, electronic and ferromagnetic device structures are discussed.
2.	Monaico, E.I.; **Monaico, E.V**.; Ursaki, V.V.; Tiginyanu, I.M. Controlled Electroplating of Noble Metals on III-V Semiconductor Nanotemplates Fabricated by Anodic Etching of Bulk Substrates. *Coatings* **2022**, *12*, 1521, doi:10.3390/coatings12101521.
	Abstract: Porous templates are widely used for the preparation of various metallic nanostructures. Semiconductor templates have the advantages of

	controlled electrical conductivity. Site-selective deposition of noble metal formations such as Pt and Au nanodots and nanotubes is demonstrated in this paper for porous InP templates prepared by anodization of InP wafers. Metal deposition is performed by pulsed electroplating. The produced hybrid nanomaterials are characterized by scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX). It is shown that uniform deposition of the metal along the pore length can be realized with optimized pulse parameters. The obtained results are discussed in terms of optimum conditions for the effective electrolyte refreshing and avoiding its depletion in pores during the electroplating process. It is demonstrated that the proposed technology can also be applied for the preparation of metal nanostructures on porous oxide templates, when it is combined with thermal treatment for the oxidation of the porous semiconductor skeleton.
3.	Călin Constantin Moise, Geanina Valentina Mihai, Liana Anicăi, **Eduard V. Monaico**, Veaceslav V. Ursaki, Marius Enăchescu and Ion M. Tiginyanu. Electrochemical deposition of ferromagnetic Ni nanoparticles in InP nanotemplates fabricated by anodic etching using environmentally-friendly electrolyte. *Nanomaterials* **2022**, *12*, 3787, doi:10.3390/nano12213787.
	Abstract: Porous InP templates possessing the thickness up to 100 μm and uniformly-distributed porosity have been prepared by anodic etching of InP substrates exhibiting different electrical conductivities, involving an environmentally-friendly electrolyte. Ni nanoparticles were successfully deposited by pulsed electroplating into prefabricated InP templates without additional deposition of passivating films. The parameters of electrodeposition including the pulse amplitude, pulse width and interval between pulses have been optimized to reach a uniform metal deposition covering the inner surface of nanopores. The electrochemical dissolution of n-InP single crystals was investigated by measuring the current-voltage dependences, while the Ni decorated n-InP templates have been characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The proposed technology is expected to be of interest for sensing and photocatalytic applications, as well as for the exploration of their plasmonic and magnetic properties.
4.	**Monaico, E.V**.; Morari, V.; Kutuzau, M.; Ursaki, V.V.; Nielsch, K.; Tiginyanu, I.M. Magnetic Properties of GaAs/NiFe Coaxial Core-Shell Structures. *Materials* **2022**, *15*, 6262, doi:10.3390/ma15186262.
	Abstract: Uniform nanogranular NiFe layers with Ni contents of 65%, 80%, and 100% have been electroplated in the potentiostatic deposition mode on

	both planar substrates and arrays of nanowires prepared by the anodization of GaAs substrates. The fabricated planar and coaxial core-shell ferromagnetic structures have been investigated by means of scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). To determine the perspectives for applications, a comparative analysis of magnetic properties, in terms of the saturation and remanence moment, the squareness ratio, and the coercivity, was performed for structures with different Ni contents.
5.	**Monaico, E.V**.; Morari, V.; Ursaki, V.V.; Nielsch, K.; Tiginyanu, I.M. Core–Shell GaAs-Fe Nanowire Arrays: Fabrication Using Electrochemical Etching and Deposition and Study of Their Magnetic Properties. *Nanomaterials* **2022**, *12*, 1506, doi:10.3390/nano12091506.
	Abstract: The preparation of GaAs nanowire templates with the cost-effective electrochemical etching of (001) and (111)B GaAs substrates in a 1 M HNO_3 electrolyte is reported. The electrochemical etching resulted in the obtaining of GaAs nanowires with both perpendicular and parallel orientations with respect to the wafer surface. Core–shell GaAs-Fe nanowire arrays have been prepared by galvanostatic Fe deposition into these templates. The fabricated arrays have been investigated by means of scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). The magnetic properties of the polycrystalline Fe nanotubes constituting the shells of the cylindrical structures, such as the saturation and remanence moment, squareness ratio, and coercivity, were analyzed in relation to previously reported data on ferromagnetic nanowires and nanotubes.
6.	Ursaki, V.V.; Lehmann, S.; Zalamai, V.V.; Morari, V.; Nielsch, K.; Tiginyanu, I.M.; **Monaico, E.V**. Core–Shell Structures Prepared by Atomic Layer Deposition on GaAs Nanowires. *Crystals* **2022**, *12*, 1145, doi:10.3390/cryst12081145.
	Abstract: GaAs nanowire arrays have been prepared by anodization of GaAs substrates. The nanowires produced on (111)B GaAs substrates were found to be oriented predominantly perpendicular to the substrate surface. The prepared nanowire arrays have been coated with thin ZnO or TiO2 layers by means of thermal atomic layer deposition (ALD), thus coaxial core–shell hybrid structures are being fabricated. The hybrid structures have been characterized by scanning electron microscopy (SEM) for the morphology investigations, by Energy Dispersive X-ray (EDX) and X-ray diffraction

	(XRD) analysis for the composition and crystal structure assessment, and by photoluminescence (PL) spectroscopy for obtaining an insight on emission polarization related to different recombination channels in the prepared core–shell structures.
7.	**Monaico, E.V**.; Morari, V.; Kutuzau, M.; Ursaki, V.V.; Nielsch, K.; Tiginyanu, I.M. Ferromagnetic Core-Shell Coaxial Nanostructures on Gallium Arsenide Substrates. *Rom J Phys* **2022**, *67*, published on-line: https://rjp.nipne.ro/accpaps/23773438A554DFDDC177E6DC5EC0288760 A92556.pdf.
	Abstract: Fe and NiFe coatings have been electrochemically deposited on GaAs nanowires arrays prepared by electrochemical etching of (001) and (111)B GaAs substrates in a 1M HNO3 electrolyte. It was found that deposition in galvanostatic mode is preferable for Fe coatings, while it is not suitable for NiFe alloys. Potentiostatic deposition was applied for Ni0.65Fe0.35 coatings. The fabricated ferromagnetic coaxial core-shell structures have been investigated by means of scanning electron microscopy (SEM) and vibrating sample magnetometry (VSM). A comparative analysis of magnetic properties of the produced structures in terms of saturation and remanence moment, squareness ratio, and coercivity, was performed between planar and coaxial structures, between Fe and NiFe coatings, as well as between different orientations of the magnetic field with respect to the nanowires axis.
8.	**Monaico, E.V**. Engineering of Semiconductor Compounds via Electrochemical Technologies for Nano-Microelectronic Applications. *J. Eng. Sci.* **2022**, *29*, 8–16, doi:10.52326/jes.utm.2022.29(1).01.
	Abstract: The paper is focused on electrochemical approaches for nanostructuring of semiconductor compounds with further applications in nano – microelectronic devices. A cost-effective technology for nanowires and nanotubes obtaining by pulsed electrochemical deposition is presented. Functionalization of elaborated nanostructures with gold or platinum via electroplating improves the properties of the nanostructures. An optimization of the varicap design to increase the capacitance is proposed and discussed as well as the optimization of pulsed electrochemical deposition of several hundred micrometer long Pt nanotubes is performed. Herein, the elaboration of contacts to GaAs nanowires via different approaches for photoelectrical investigations is reported.
9.	**Monaico, E.V**.; Busuioc, S.; Tiginyanu, I.M. Controlling the Degree of Hydrophilicity/Hydrophobicity of Semiconductor Surfaces via

	Porosification and Metal Deposition. In Proceedings of the 5th International Conference on Nanotechnologies and Biomedical Engineering; Tiginyanu, I., Sontea, V., Railean, S., Eds.; Springer International Publishing: Cham, 2022; pp. 62–69.
	Abstract: In this paper we present a systematic study of bulk GaAs wafers and gold-decorated GaAs surfaces exhibiting hydrophilic and hydrophobic behaviors. The wetting properties can be switched to superhydrophilicity and superhydrophilicity by simple electrochemical etching providing engineered porous morphologies. The results open interesting technological perspectives for the exploitation of GaAs surfaces.
10.	Zalamai, V.V.; Colibaba, G.V.; Monaico, E.I.; **Monaico, E.V**. Enhanced Emission Properties of Anodized Polar ZnO Crystals. *Surf. Eng. Appl. Electrochem.* **2021**, *57*, 117–123, doi:10.3103/S1068375521010166.
	Abstract: Polar ZnO single crystals were microstructured in a controlled fashion by electrochemical etching. Surfaces with pyramids and inversed pyramids on oxygen and zinc faces, respectively, were received. Photoluminescence spectra of bulk and anodized ZnO samples were investigated at room and low temperatures. Cathodoluminescence images were also recorded from areas with different structures. A significant enhancement of light emission of the prepared microstructures was achieved after anodization. This allows to use such microstructures in light emitting devices and solar cells.
11.	Monaico, E.I.; **Monaico, E.V**.; Ursaki, V.V.; Tiginyanu, I.M. Evolution of Pore Growth in GaAs in Transitory Anodization Regime from One Applied Voltage to Another. *Surf. Eng. Appl. Electrochem.* **2021**, *57*, 165–172, doi:10.3103/S106837552102006X.
	Abstract: The paper reports the results of investigation of the pore growth during anodic etching of (111)-oriented wafers of Si-doped n-GaAs in an environmentally friendly NaCl based electrolyte, with switching the applied voltage from a high voltage to lower one and vice-versa. Switching of the applied voltage in the process of anodization was found to cause the formation of layered porous structures with different degrees of porosity. Crystallographically oriented pores shaped as triangular prisms were produced in a stationary regime of anodization, while a more complex morphology of pores was observed at the interface between the two layers with different degrees of porosity, including pores composed of three circular ones. Based on the results of the morphology study using scanning electron

	microscopy, a possible mechanism of the formation of such kind of pores in the dynamic transitory regime of anodizing is discussed.
12.	**Monaico, E**.; Tiginyanu, I.; Ursaki, V. Porous Semiconductor Compounds. *Semicond. Sci. Technol.* **2020**, *35*, 103001, doi:10.1088/1361-6641/ab9477.
	Abstract: In this **review paper**, we present a comparative analysis of the electrochemical dissolution of III–V (InP, GaAs, GaN), II–VI (ZnSe, CdSe) and SiC semiconductor compounds. The resulting morphologies are discussed, including those of porous layers and networks of low-dimensional structures such as nanowires, nanobelts, and nanomembranes. Self-organized phenomena in anodic etching are disclosed, leading to the formation of controlled porous patterns and quasi-ordered distribution of pores. Results of templated electrochemical deposition of metal nanowires, nanotubes and nanodots are summarized. Porosification of some compounds is shown to improve luminescence characteristics as well as to enhance photoconductivity, second harmonic generation and Terahertz emission. Possible applications of porous semiconductor compounds in various areas are discussed.
13.	Monaico, E.I.; **Monaico, E.V**.; Ursaki, V.V.; Honnali, S.; Postolache, V.; Leistner, K.; Nielsch, K.; Tiginyanu, I.M. Electrochemical Nanostructuring of (111) Oriented GaAs Crystals: From Porous Structures to Nanowires. *Beilstein J. Nanotechnol.* **2020**, *11*, 966–975, doi:10.3762/bjnano.11.81.
	Abstract: A comparative study of the anodization processes occurring at the GaAs(111)A and GaAs(111)B surfaces exposed to electrochemical etching in neutral NaCl and acidic HNO_3 aqueous electrolytes is performed in galvanostatic and potentiostatic anodization modes. Anodization in NaCl electrolytes was found to result in the formation of porous structures with porosity controlled either by current under the galvanostatic anodization, or by the potential under the potentiostatic anodization. Possibilities to produce multilayer porous structures are demonstrated. At the same time, one-step anodization in a HNO_3 electrolyte is shown to lead to the formation of GaAs triangular shape nanowires with high aspect ratio (400 nm in diameter and 100 μm in length). The new data are compared to those previously obtained through anodizing GaAs(100) wafers in alkaline KOH electrolyte. An IR photodetector based on the GaAs nanowires is demonstrated.
14.	**Monaico, E.V.;** Monaico, E.I.; Ursaki, V.V.; Tiginyanu, I.M. Free-Standing Large-Area Nanoperforated Gold Membranes Fabricated by Hopping Electrodeposition. *ECS J. Solid State Sci. Technol.* **2020**, *9*, 064010, doi:10.1149/2162-8777/aba6a2.

	Abstract: A room-temperature two-step cost-effective electrochemical technology is proposed for the preparation of free-standing Au nanomembranes. A thin Au film with the thickness less than 100 nm was deposited by pulsed electroplating on a GaAs substrate in the first step, while electrochemical etching was applied in the second technological step to introduce porosity into the GaAs substrate underneath the Au film. It has been shown that detachment of the film from the substrate occurs at optimized parameters of anodic etching. Scanning electron microscopy imaging of the deposited Au film revealed its nanoparticulate structure generated via the mechanism of hopping electrodeposition, i.e. the film proved to consist of a monolayer of Au nanoparticles with the mean diameter around 20–30 nm. It was found that nanoholes with the diameter controlled by the duration of negative voltage pulses can be introduced into the Au film during electroplating. The purity of the detached Au nanomembranes was demonstrated by the energy dispersive X-ray analysis. The flexibility, nanoparticulate structure along with possibilities to transfer the prepared nanomembranes to various substrates make them promising for new optical, plasmonic and electronic applications.
15.	Monaico, E.I.; Trifan, C.; **Monaico, E.V.;** Tiginyanu, I. Elaboration of the Platform for Flexoelectric Investigation of GaN Microtubes. *J. Eng. Sci.* **2020**, *XXVII (4)*, 45–54, doi:10.5281/zenodo.4288263.
	Abstract: In this paper, the design and elaboration of a cost-effective technological process for the fabrication of the platform for the study of flexoelectric properties of GaN microtubes with the diameter of 2 - 5 µm and the thickness of the microtube walls of 50 nm is proposed. The impact of the design as well as the electrochemical etching parameters (applied voltage, duration of anodization) on the obtained channel dimensions is investigated. The proposed technological route implies electrochemical etching of n-InP semiconductor crystal in an environmentally friendly electrolyte at high etch rate. The technological process was optimized experimentally. It was proposed to introduce a perpendicular channel in which the microtube will be placed to reach a higher stability on the platform during the measurements.
16.	**Monaico, E.**; Ursachi, V.; Tighineanu, I. Frontierele Electrochimiei și Aplicații în Nanotehnologii. *Fiz. Şi Tehnol. Mod.* **2020**, *18*, 8–18.
	Abstract: The paper describes the application of electrochemical processes in nanotechnologies to obtain different nanoscale objects with morphology

	according to design and controlled positioning. It was explained the mechanism of "jumping electrodeposition", which allows the deposition of a monolayer of Au points. The electrochemical methods addressed in this paper can be used for estimating the conductivity of semiconductor nanostructures. It is demonstrated that the combination of electrochemical nanostructuring of semiconductor substrates and the electrochemical deposition of metals is an effective tool for manufacturing new hybrid metal-semiconductor nanoarchitectures for various electronic and photonic applications.
17.	**Monaico, E.;** Moise, C.; Mihai, G.; Ursaki, V.V.; Leistner, K.; Tiginyanu, I.M.; Enachescu, M.; Nielsch, K. Towards Uniform Electrochemical Porosification of Bulk HVPE-Grown GaN. *J. Electrochem. Soc.* **2019**, *166*, H3159, doi:10.1149/2.0251905jes.
	Abstract: In this paper, we report on results of a systematic study of porous morphologies obtained using anodization of HVPE-grown crystalline GaN wafers in HNO_3, HCl, and NaCl solutions. The anodization-induced nanostructuring is found to proceed in different ways on N- and Ga-faces of polar GaN substrates. Complex pyramidal structures are disclosed and shown to be composed of regions with the degree of porosity modulated along the pyramid surface. Depending on the electrolyte and applied anodization voltage, formation of arrays of pores or nanowires has been evidenced near the N-face of the wafer. By adjusting the anodization voltage, we demonstrate that both current-line oriented pores and crystallographic pores are generated. In contrast to this, porosification of the Ga-face proceeds from some imperfections on the surface and develops in depth up to 50 μm, producing porous matrices with pores oriented perpendicularly to the wafer surface, the thickness of the pore walls being controlled by the applied voltage. The observed peculiarities are explained by different values of the electrical conductivity of the material near the two wafer surfaces.
18.	**Monaico, Ed**.; Monaico, E.I.; Ursaki, V.V.; Tiginyanu, I.M.; Nielsch, K. Electrochemical Deposition by Design of Metal Nanostructures. *Surf. Eng. Appl. Electrochem.* **2019**, *55*, 367–372, doi:10.3103/S1068375519040070.
	Abstract: We report on the application of specially-designed masks for the purpose of electrochemical etching of InP single crystals which enables one to change in a controlled fashion the direction of propagation of pores, including those propagating in directions parallel to the top surface of substrates. The fabricated templates have been used to electrochemically deposit metallic nanostructures along predefined directions and to develop

	two-dimensional arrays of metallic nanotubes or nanowires embedded in semiconductor matrices.
19.	Wolff, N.; Jordt, P.; Braniste, T.; Popa, V.; **Monaico, E**.; Ursaki, V.; Petraru, A.; Adelung, R.; Murphy, B.M.; Kienle, L.; Tiginyanu, I. Modulation of Electrical Conductivity and Lattice Distortions in Bulk HVPE-Grown GaN. *ECS J. Solid State Sci. Technol.* **2019**, *8*, Q141, doi:10.1149/2.0041908jss.
	Abstract: The nature of self-organized three-dimensional structured architectures with spatially modulated electrical conductivity emerging in the process of hydride vapor phase epitaxial growth of single crystalline n-GaN wafers is revealed by photoelectrochemical etching. The amplitude of the carrier concentration modulation throughout the sample is derived from photoluminescence analysis and the localized heterogeneous piezoelectric response is demonstrated. The formation of such architectures is rationalized based on the generation of V-shaped pits and their subsequent overgrowth in variable direction. Detailed structure analysis with respect to X-ray diffraction and transmission electron microscopy gives striking evidence for inelastic strain to manifest in distortions of the $P6_3mc$ wurtzite-type structure. The deviation from hexagonal symmetry by angular distortions of the β angle between the basal plane and c-axis is found to be of around 1°. It is concluded that the lattice distortions are generated by the misfit strains originating during crystal growth, which are slightly relaxed upon photoelectrochemical etching.
20.	Gaponenko, S.V.; **Monaico, E**.; Sergentu, V.V.; Prislopski, S.Y.; Tiginyanu, I.M. Possible Coherent Backscattering of Lightwaves from a Strongly Absorbing Nanoporous Medium. *J. Opt.* **2018**, *20*, 075606, doi:10.1088/2040-8986/aac841.
	Abstract: We report on anomalous light retroreflection from strongly absorbing nanoporous semiconductor materials, GaAs and InP, with strongly polarized retroreflected light with linear polarization coinciding with that of incident beams. The high polarization of retroreflected waves suggests coherent backscattering as the underlying physical mechanism. This phenomenon resulting from multiple scattering is supposed to be possible in an absorbing medium owing to longitudinal electromagnetic waves generated at interfaces. Strong absorption for transverse waves has negligible effect on longitudinal ones and therefore does not prevent their multiple scattering but ensures a high refraction index promoting strong scattering. This hypothesis is supported by a theoretical model and calculations.

21.	Prislopski, S.Y.; Gaponenko, S.V.; **Monaico, E**.; Sergentu, V.V.; Tiginyanu, I.M. Polarized Retroreflection from Nanoporous III–V Semiconductors. *Semiconductors* **2018**, *52*, 2068–2069.
	Abstract: Retroreflected light with strong linear polarization coinciding with that of the incident beams is detected from strongly absorbing nanoporous III–V semiconductors. Because of high polarization of retroreflected waves we assume that coherent backscattering is the underlying physical mechanism of this phenomenon.
22.	**Monaico, E.V**.; Tiginyanu, I.M.; Ursaki, V.V.; Nielsch, K.; Balan, D.; Prodana, M.; Enachescu, M. Gold Electroplating as a Tool for Assessing the Conductivity of InP Nanostructures Fabricated by Anodic Etching of Crystalline Substrates. *J. Electrochem. Soc.* **2017**, *164*, D179, doi:10.1149/2.1071704jes.
	Abstract: Electroplating is shown to represent a simple and effective tool for assessing the conductivity of InP nanostructures fabricated by electrochemical etching of InP wafers. A mixture of nanowalls, nanowires and nanobelts was fabricated by anodic etching of crystalline bulk *n*-InP with free electron concentration of 1.3×10^{18} cm^{-3} under applied voltage of 13 V. We found that electroplating of Au occurs differently on these three nanostructures under identical electroplating conditions. A monolayer of densely packed Au nanodots with the diameter of around 20 nm is deposited on nanowires, while the density of Au nanodots deposited on nanowalls proves to be much smaller. At the same time no electroplating occurs on nanobelts. The evidenced distinctive features of electroplating processing are determined by different electrical conductivities of InP nanostructures. The produced materials are characterized by scanning electron microscopy (SEM), high-resolution scanning transmission electron microscopy (HR-STEM), electron nano-diffraction, selected area electron diffraction (SAED), and energy dispersive X-ray analysis (EDAX).
23.	Braniste, T.; Ciers, J.; **Monaico, Ed**.; Martin, D.; Carlin, J.-F.; Ursaki, V.V.; Sergentu, V.V.; Tiginyanu, I.M.; Grandjean, N. Multilayer Porous Structures of HVPE and MOCVD Grown GaN for Photonic Applications. *Superlattices Microstruct.* **2017**, *102*, 221–234, doi:10.1016/j.spmi.2016.12.041.
	Abstract: In this paper we report on a comparative study of electrochemical processes for the preparation of multilayer porous structures in hydride vapor phase epitaxy (HVPE) and metal organic chemical vapor phase deposition (MOCVD) grown GaN. It was found that in HVPE-grown GaN, multilayer porous structures are obtained due to self-organization processes leading to

	a fine modulation of doping during the crystal growth. However, these processes are not totally under control. Multilayer porous structures with a controlled design have been produced by optimizing the technological process of electrochemical etching in MOCVD-grown samples, consisting of five pairs of thin layers with alternating-doping profiles. The samples have been characterized by SEM imaging, photoluminescence spectroscopy, and micro-reflectivity measurements, accompanied by transfer matrix analysis and simulations by a method developed for the calculation of optical reflection spectra. We demonstrate the applicability of the produced structures for the design of Bragg reflectors.
24.	Braniste, T.; **Monaico, E**.; Martin, D.; Carlin, J.-F.; Popa, V.; Ursaki, V.V.; Grandjean, N.; Tiginyanu, I.M. Multilayer Porous Structures on GaN for the Fabrication of Bragg Reflectors. In Proceedings of the Nanotechnology VIII; SPIE, May 30 2017; Vol. 10248, pp. 83–89.
	Abstract: We report on the development of electrochemical etching technology for the production of multilayer porous structures (MPS) allowing one to fabricate Bragg reflectors on the basis of GaN bulk substrates grown by Hydride Vapor Phase Epitaxy (HVPE). The formation of MPS during anodization is caused by the spatial modulation of the electrical conductivity throughout the surface and the volume of the HVPE-grown GaN substrate, which occurs according to a previously proposed model involving generation of pits and their overgrowth. We found that the topology of the porous sheets constituting the MPS is different in the vicinity of N-face and Ga-face of the bulk wafer, it being of conical shape near the N-face and of hemispherical shape near the Ga-face. The composition of electrolytes, their concentration as well as the anodization potential applied during electrochemical etching are among technological parameters optimized for designing MPS suitable for Bragg reflector applications. It is shown also that regions with various porosities can be produced in depth of the sample by changing the anodization potential during the electrochemical etching.
25.	Sergentu, V.V.; Ursaki, V.; **Monaico, Ed**.; Tiginyanu, I.M.; Prislopski, S.Ya.; Gaponenko, S.V. Dark Modes Backscattering as Possible Rationale for Anomalous Retroreflection from Strongly Absorbing Porous Nanostructures. In *Physics, Chemistry and Application of Nanostructures*; 2017; pp. 30–33 ISBN 978-981-322-452-0.

	Abstract: The previously discovered anomalous retroreflection in a strongly absorbing nanostructured medium is explained by using “dark” and “bright” modes. The consideration provides rationale not only for the retroreflection itself but explains correlations with absorption and differences for s- and p-polarized radiation retroreflection.
26.	**Monaico, E**. Fabricarea Nanostructurilor Poroase Pe Bază de Design. *Fiz. Şi Tehnol. Mod.* **2017**, *59*, 24–33.
	Abstract: In the work it is reported the application of a special design of masks for the purpose of electrochemical etching of InP single crystals, which enables a controlled changing the direction of propagation of pores, including those propagating in directions parallel to the top surface of substrates. The fabricated templates have been used to electrochemically deposit metallic nanostructures along predefined directions and to develop two-dimensional arrays of metallic nanotubes or nanowires embedded in a semiconductor matrix.
27.	Monaico, E.; Brincoveanu, O.; Mesterca, R.; URSAKI, V.; Prodana, M.; Enachescu, M.; Tiginyanu, I. Pulsed Electroplating of Metal Nanoparticles Form DODUCO Electrolytes. In Proceedings of the 9th International Conference on Microelectronics and Computer Science; Chisinau, Republic of Moldova, October 19-21, 2017; pp. 16–20.
	Abstract: The mechanisms of Au deposition on InP porous substrates during a pulsed electroplating process are investigated by means of Topography imaging and Current Mapping measurements. The obtained results confirm the formation of Schottky barriers at the interface of the semiconductor substrate with Au nanoparticles with diameters around 20 nm, and corroborate the hypothesis that the mechanism of Au nanoparticles self-assembling into monolayers is governed by the formation of such Schottky barriers. The analysis of current-voltage curves suggest also the deposition of a dielectric film over the larger Au particles produced with long duration pulsed electroplating from DODUCO solutions.
28.	Anicai, L.; Golgovici, F.; Monaico, E.; URSAKI, V.; Prodana, M.; Enachescu, M.; Tiginyanu, I. Influence of Metal Deposition on Electrochemical Impedance Spectra of Porous GaP and GaN Semiconductors. In Proceedings of the 9th International Conference on Microelectronics and Computer Science; Chisinau, Republic of Moldova, October 19-21, 2017; pp. 60–64.
	Abstract: A comparative analysis of electrochemical impedance spectroscopy (EIS) characterization is performed in porous GaN and GaP

	templates with and without metal nanostructured layers deposited by pulsed electroplating. The porous semiconductor templates are produced by electrochemical etching of bulk substrates. The EIS data are interpreted in terms of electrical equivalent circuits (EECs) deduced by fitting the experimental data from Nyquist plots. It is found that the EIS data of porous electrodes without electroplating are best fitted with EECs with both the charge transfer and mass transfer components of the Faradaic impedance, while electroplating reduces the importance of the mass transport component, i. e. of the Warburg impedance, associated with diffusion, in favor of the charge transport phenomena.
29.	Sergentu, V.V.; Prislopski, S.Y.; **Monaico, E.V**.; Ursaki, V.V.; Gaponenko, S.V.; Tiginyanu, I.M. Anomalous Retroreflection from Nanoporous Materials as Backscattering by \`dark' and \`bright' Modes. *J. Opt.* **2016**, *18*, 125008, doi:10.1088/2040-8978/18/12/125008.
	Abstract: In this paper the mechanisms of previously experimentally observed anomalous retroreflection in a strongly absorbing nanostructured medium are explained by using 'dark' and 'bright' modes. The observed regularities are analyzed for both s-polarized and p-polarized incident radiation with respect to the contribution from 'dark' and 'bright' modes and the influence of the absorption on the scattering indicatrix. The theoretical consideration provides explanation not only for the retroreflection itself but explains also correlations with absorption and differences for retroreflection efficiency for s- and p-polarized radiation. The possibilities of using 'dark modes' for processing and transmission of energy are discussed.
30.	Tiginyanu, I.; Stevens-Kalceff, M.A.; Sarua, A.; Braniste, T.; **Monaico, E.**; Popa, V.; Andrade, H.D.; Thomas, J.O.; Raevschi, S.; Schulte, K.; Adelung, R. Self-Organized Three-Dimensional Nanostructured Architectures in Bulk GaN Generated by Spatial Modulation of Doping. *ECS J. Solid State Sci. Technol.* **2016**, *5*, P218, doi:10.1149/2.0091605jss.
	Abstract: Self-organized 3D nanostructured architectures including quasi-ordered concentric hexagonal structures generated during the growth of single crystalline *n*-GaN substrates by hydride vapor phase epitaxy (HVPE) are reported. The study of as-grown samples by using Kelvin Probe Force Microscopy shows that the formation of self-organized architectures can be attributed to fine modulation of doping related to the spatial distribution of impurities. The specific features of nanostructured architectures involved have been brought to light by using electrochemical and

	photoelectrochemical etching techniques which are highly sensitive to local doping. The analysis of the results shows that the formation of self-organized spatial architectures in the process of HVPE is caused by the generation of V-pits and their subsequent overgrowth accompanied by the growth in variable direction. It is demonstrated for the first time that the electrical and luminescence properties of HVPE-grown GaN are spatially modulated throughout, including islands between overgrown V-pit regions. The dependence of doping upon growth direction is confirmed by the micro-cathodoluminescence characterization of HVPE-grown pencil-like microcrystals exposing various crystallographic planes along the tip. These results are indicative of new possibilities for defect engineering in gallium nitride and for three-dimensional spatial nanostructuring of this important electronic material by controlling the growth direction.
31.	Tiginyanu, I.; Ursaki, V.; **Monaico, E**. Template Assisted Formation of Metal Nanotubes. In *Nanostructures and Thin Films for Multifunctional Applications: Technology, Properties and Devices*; Tiginyanu, I., Topala, P., Ursaki, V., Eds.; NanoScience and Technology; Springer International Publishing: Cham, 2016; pp. 473–506 ISBN 978-3-319-30198-3.
	Abstract: This chapter provides a review of methods for the production of metal nanotubes and their applications. The importance of nanotemplated growth of nanowires and nanotubes for nanofabrication, and the advantages of nanotubes over nanowires are revealed. Technological approaches for producing various templates, as well as advantages and drawbacks of specific templates, such as ion-track membranes, porous alumina templates, and porous semiconductor templates for nanofabrication are discussed, especially with respect to their suitability for the production of metal nanotubes. Technological methods applied for deposition of metal nanotubes with a focus on electrodepostion and electroless deposition are overviewed for each type of porous templates, and their mechanisms and peculiarities are evidenced. The prospects of application of nanomaterials based on porous nanotemplates in electronics, energy sector, optics, photonics, computers and communications, magnetism and biomedical sciences are explored.
32.	Colibaba, G.V.; **Monaico, E.V.**; Goncearenco, E.P.; Inculet, I.; Tiginyanu, I.M. Features of Nanotemplates Manufacturing on the II-VI Compound Substrates. In Proceedings of the 3rd International Conference on Nanotechnologies and Biomedical Engineering; Springer, Singapore, 2016; pp. 188–191.

	Abstract: Application of ZnSe, ZnS, ZnSSe, CdS, ZnCdS and ZnO single crystal substrates for the preparation of nanoporous matrices by electrochemical etching using various electrolytes is analyzed. We demonstrate prospects of using ZnSe and ZnCdS compounds for the fabrication of nanopore arrays with pore diameter down to 30 nm, as well as of ZnO substrates for the preparation of nanohills or nanopits arrays. The limitations for producing similar structures on the basis of ZnS and ZnSSe substrates are evidenced.
33.	Tiginyanu, I.; **Monaico, E**.; Nielsch, K. Self-Assembled Monolayer of Au Nanodots Deposited on Porous Semiconductor Structures. *ECS Electrochem. Lett.* **2015**, *4*, D8, doi:10.1149/2.0041504eel.
	Abstract: We demonstrate the possibility to cover the surface of GaP and InP porous structures by a self-assembled monolayer of electrochemically deposited nanoscale Au nanodots. After nucleation, each dot was found to increase in sizes up to a critical transverse dimension, the process of pulsed electrodeposition of gold being continuously supported by the formation of new nanodots. The density of deposited Au dots is shown to be dependent upon the number and width of the applied voltage pulses. The deposition of "size-saturated" dots continues until the entire surface exposed to the electrolyte is covered by a monolayer of self-assembled Au nanodots.
34.	Tiginyanu, I.; **Monaico, E**.; Sergentu, V.; Tiron, A.; Ursaki, V. Metallized Porous GaP Templates for Electronic and Photonic Applications. *ECS J. Solid State Sci. Technol.* **2015**, *4*, P57, doi:10.1149/2.0011503jss
	Abstract: We report on fabrication of two-dimensional metallo-semiconductor networks by using pulsed electroplating of Pt inside electrochemically-prepared porous GaP layers with parallel pores possessing diameters in the micrometer and sub-micrometer ranges. The electrochemical parameters were optimized for a uniform metal deposition on the inner surface of porous template. A variable capacitance device fabricated on Pt/GaP Schottky diodes forming at the interface of Pt/GaP interpenetrating networks showed a much higher capacitance density variation as compared to standard devices. The results of calculations demonstrate also good focusing properties of flat photonic lenses assembled from metallized porous GaP slabs, especially at long wavelengths including the far infrared spectral range.
35.	**Monaico, E**.; Postolache, V.; Borodin, E.; Ursaki, V.V.; Lupan, O.; Adelung, R.; Nielsch, K.; Tiginyanu, I.M. Control of Persistent

	Photoconductivity in Nanostructured InP through Morphology Design. *Semicond. Sci. Technol.* **2015**, *30*, 035014, doi:10.1088/0268-1242/30/3/035014.
	Abstract: In this paper, we show that long-duration-photoconductivity decay (LDPCD) and persistent photoconductivity (PPC) in porous InP structures fabricated by anodic etching of bulk substrates can be controlled through the modification of the sample morphology. Particularly, the PPC inherent at low temperatures to porous InP layers with the thickness of skeleton walls comparable with pore diameters is quenched in structures consisting of ultrathin walls produced at high anodization voltages. The relaxation of photoconductivity in bulk InP substrates, porous layers, and utrathin membranes is investigated as a function of temperature and excitation power density. The obtained results suggest that PPC in porous InP layers is due to porosity induced potential barriers which hinder the recombination of photoexcited carriers, while the photoconductivity relaxation processes in ultrathin membranes are governed by surface states.
36.	**Monaico, E**.; Tiginyanu, I.; Volciuc, O.; Mehrtens, T.; Rosenauer, A.; Gutowski, J.; Nielsch, K. Formation of InP Nanomembranes and Nanowires under Fast Anodic Etching of Bulk Substrates. *Electrochem. Commun.* **2014**, *47*, 29–32, doi:10.1016/j.elecom.2014.07.015.
	Abstract: We demonstrate that fast anodic etching of bulk crystalline substrates of *n*-InP via photolithographically defined windows leads to the formation of nanomembranes and nanowires being promising for device applications. It is shown that, under potentiostatic etching conditions, the morphology of etched samples strongly depends on the applied voltage. We found that anodization at 5–7 V results in the formation of highly porous layers with mechanically stable skeletons exhibiting percolation, which easily detach from the substrate thus representing nanomembranes. At the same time the predominant formation of nanowires was evidenced at further increase of the applied voltage up to 15 V. Uniform deposition of Au dots on InP nanowires and nanowalls is demonstrated using electroplating.
37.	Prislopski, S.Ya.; Tiginyanu, I.M.; Ghimpu, L.; **Monaico, E**.; Sirbu, L.; Gaponenko, S.V. Retroreflection of Light from Nanoporous InP: Correlation with High Absorption. *Appl. Phys. A* **2014**, *117*, 467–470, doi:10.1007/s00339-014-8683-x.
	Abstract: Pronounced retroreflection behavior is reported for a fishnet nanoporous strongly absorbing semiconductor material. Retroreflection appears along with diffusive specular reflection for all angles of incidence

	for light wavelength corresponding to interband optical transitions, where absorption coefficient is of the order of 10^5 cm^{-1} (green and red light). Retroreflection is apparent by the naked eye with daylight illumination and exhibits no selectivity with respect to wavelength and polarization of incident light featuring minor depolarization of retroreflected light. Retroreflection vanishes for wavelength corresponding to optical transparency range where photon energy is lower than the InP bandgap (1.064 μm). The phenomenon can be classified neither as coherent backscattering nor as Anderson localization of light. The primary model includes light scattering from strongly absorptive and refractive super-wavelength clusters existing within the porous fishnet structure. We found that retroreflection vanishes for wavelength where absorption becomes negligible.
38.	**Monaico, E**.; Colibaba, G.; Nedeoglo, D.; Nielsch, K. Porosification of III–V and II–VI Semiconductor Compounds. Journal of Nanoelectronics and Optoelectronics 2014, 9, 307–311, doi:10.1166/jno.2014.1581.
	Abstract: We report on a comparative study of the pore growth during anodization of a narrow-bandgap III–V compound (InAs), a medium-bandgap III–V one (InP) and wide-bandgap II–VI semiconductors (ZnSe and $Zn_{0.4}Cd_{0.6}S$). According to the obtained results, the morphology of the porous layers can be controlled by the composition of the electrolyte and the applied electrochemical parameters. It was evidenced that in the narrow bandgap semiconductor InAs it is difficult to control the mechanism of pore growth. Both current-line oriented pores and crystallographically oriented pores were produced in the medium-bandgap material InP. The electrochemical nanostructuring of wide-bandgap semiconductors realized in single crystalline high-conductivity samples evidenced only current-line oriented pores. This behavior is explained in terms of difference in the values of electronegativity of the constituent atoms and the degree of ionicity.
39.	Colibaba, G.; Goncearenco, E.; Nedeoglo, D.; Nedeoglo, N.; **Monaico, E**.; Tiginyanu, I. Obtaining of II-VI Compound Substrates with Controlled Electrical Parameters and Prospects of Their Application for Nanoporous Structures. *Phys. Status Solidi C* **2014**, *11*, 1404–1407, doi:10.1002/pssc.201300590.
	Abstract: Substrates of II-VI semiconductor compounds may be widely used in fabrication of nanoporous matrices (NM), which give the possibility to obtain nanowires and nanotubes of various materials with good application

	prospects in various fields. The easiest and cost-effective method to obtain nanoporous matrices is electrochemical etching (ECE), which, however, depends on conductive properties of the substrates. The conditions of growing homogeneous ZnSe, ZnS, ZnSSe, ZnO, and ZnCdS single crystals by physical and chemical vapour transport methods are discussed. Based on the results of investigation of electrical, optical, and photoluminescence properties of the samples with various doping levels, the prospect of examined technology for manufacturing the substrates of these compounds with large area and controlled n-type electrical conductivity varied up to 20, 0.3, 0.3, 9, and 30 $\Omega^{-1}cm^{-1}$, respectively, is estimated. Possible utilization of these substrates for preparation of NM by ECE is analyzed. The results of nanostructuring using various electrolytes are shown. The prospect of using ZnSe and ZnCdS compounds for manufacturing nanopore arrays with diameter down to 30 nm and nanopo-rous structures with a specific morphology on ZnO substrates is demonstrated. Technological limitations for fabrication of the similar structures on the basis of ZnS and ZnSSe substrates are also analyzed. (© 2014 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)
40.	Colibaba, G.V.; **Monaico, E.V**.; Goncearenco, E.P.; Nedeoglo, D.D.; Tiginyanu, I.M.; Nielsch, K. Growth of ZnCdS Single Crystals and Prospects of Their Application as Nanoporous Structures. *Semicond. Sci. Technol.* **2014**, *29*, 125003, doi:10.1088/0268-1242/29/12/125003.
	Abstract: Substrates of wide band-gap II–VI semiconductor compounds are considered feasible for the fabrication of nanoporous matrices (NM) needed for templated growth of nanowires and nanotubes of solid-state materials promising for applications in various fields. An accessible and cost-effective approach to fabricate NM is based on electrochemical etching (ECE) which, however, depends on the electrical conductivity of the substrates. In this paper, growth of homogeneous $Zn_xCd_{1-x}S$ single crystals, with x varying from 0 to 1, is demonstrated and the influence of chemical composition on optical and electrical properties of the crystals is identified. The feasibility of using $Zn_xCd_{1-x}S$ alloys with x = 0–0.6 for the growth of nanopore arrays with pore diameter down to 30 nm is shown. The perspectives and limitations of the use of these semiconductor alloys for the fabrication of NM by means of ECE are discussed.
41.	Tiginyanu, I.; **Monaico, E**.; Ursaki, V. Two-Dimensional Metallo-Semiconductor Networks for Electronic and Photonic Applications. *ECS Trans.* **2012**, *41*, 67, doi:10.1149/1.4718392.

	Abstract: Two-dimensional metallo-semiconductor networks have been fabricated by pulsed electrochemical deposition of Pt inside porous GaP membranes with parallel pores possessing diameters in the micrometer and sub-micrometer ranges. The electrochemical parameters were optimized for a uniform metal deposition on the inner surface of the pores. This technology was applied for the fabrication of a variable capacitance device on the basis of Pt/GaP Schottky diodes formed on Pt/GaP interpenetrating networks. The capacitance density variation caused by the change in voltage applied to this device is much higher than that inherent to standard devices. Taking into account the quasi-ordered spatial distribution of pores in the GaP template, one can assume that the produced 2D metallo-semiconductor networks are promising also for specific photonic applications.
42.	Ioisher, A.M.; Badinter, E.Ya.; Postolache, V.; **Monaico, E.V**.; Ursaki, V.V.; Sergentu, V.V.; Tiginyanu, I.M. Filiform Nanostructure Technologies Based on Microwire Stretching. *J. Nanoelectron. Optoelectron.* **2012**, *7*, 688–695, doi:10.1166/jno.2012.1411.
	Abstract: A technological route allowing one to integrate huge amounts of electrically isolated metal, semiconductor, or semimetal nanowires in glass fibers with the diameter of up to a few hundreds of micrometers is presented, and the perspectives of implementation of these filiform nanostructures in concrete devices are described, particularly in photonic crystal lenses. The technology is based on a multiple stretching process. We found that a relationship between the main technological parameters including surface tension of the core material, tensile force and glass viscosity should be satisfied in order to provide continuity of the core. The possibility of integrating hundreds of thousands and even millions of glass-encapsulated nanowires is demonstrated.
43.	**Monaico, E**.; Tighineanu, I. Nanofire şi Nanotuburi: Tehnologii şi Perspective de Utilizare. *Fiz. Şi Tehnol. Mod.* **2012**, *10*, 4–12.
	Abstract: Lucrarea prezintă date privind activităţile de cercetare concentrate asupra formării nanostructurilor unidimensionale (1D) – fire şi nanotuburi, a căror dimensiune transversală nu depăşeşte 100 nm. Sunt descrise tehnologiile de obţinere a nanofirelor şi nanotuburilor metalice prin depunerea electrochimică în nanotemplate. Este elucidată, de asemenea, metoda de întindere a microfirelor îmbrăcate în fibră din sticlă, ce rezultă în formarea de nanofire metalice integrate cu lungimea de până la un metru.

44.	Langa, S.; Tiginyanu, I.M.; **Monaico, E**.; Föll, H. Porous II-VI vs. Porous III-V Semiconductors. *Phys. Status Solidi C* **2011**, *8*, 1792–1796, doi:10.1002/pssc.201000102.
	Abstract: In this work a morphological comparison of porous structures obtained by means of electrochemical etching in II-VI (ZnSe, CdSe) and III-V (InP, GaAs, GaP) semiconductors is presented. It is shown that in III-V semiconductors current-line and crystallographically oriented pores can be grown, whereas in II-VI semiconductors only current line oriented pores can form. The lack of crystallographically oriented pores in II-VI is a possible reason why no long-range order for the current line oriented pores was observed in these materials up to now.
45.	Tiginyanu, I.M.; Ursaki, V.V.; **Monaico, E**.; Enachi, M.; Sergentu, V.V.; Colibaba, G.; Nedeoglo, D.D.; Cojocaru, A.; Föll, H. Quasi-Ordered Networks of Metal Nanotubes Embedded in Semiconductor Matrices for Photonic Applications. *J. Nanoelectron. Optoelectron.* **2011**, *6*, 463–472, doi:10.1166/jno.2011.1197.
	Abstract: We report on templated fabrication of metal nanotubes by electrochemical pulsed deposition of Pt in InP and ZnSe porous layers with pore diameters from 40 to 400 nm. Ordered two-dimensional hexagonal arrays of pores are produced in *n*-InP crystalline substrates, and a uniform distribution of pores is realized in *n*-ZnSe substrates. We demonstrate the possibility to fabricate arrays of pores and networks of embedded metal nanotubes oriented parallel to the top surface of the template. The optical properties of the produced porous materials are studied using Raman scattering and photoluminescence spectroscopy. The prospects for the elaboration of photonic crystal lenses and beam splitters on the basis of two-dimensional metallo-semiconductor structures prepared on porous templates and tubular structures are demonstrated by means of calculation of their photonic properties.
46.	Ioisher, A.; Badinter, E.; **Monaico, E**.; Postolache, V.; Hartnagel, H.L.; Leporda, N.; Tiginyanu, I. Integration of Ge Nanowire Arrays in Glass Micro-Fibers. *Surf. Eng. Appl. Electrochem.* **2011**, *47*, 103–106, doi:10.3103/S1068375511020062.
	Abstract: We report on a technological route for the integration of large arrays of Ge nanowires (NWs) in a human-hair-like glass micro-fiber, the length of the micro-fiber reaching one meter. The route comprises (a) the formation of semiconductor microwire in glass insulation by capillary drawing from the bottom of a glass tube softened by a conducting Ge melt

	drop levitating in the high-frequency electromagnetic induction field; (b) mechanical assembly of a bundle from equal-length cut microwires which are distributed in a two-dimensional quasi-hexagonal densely packed lattice encircled by a joint glass envelope; (c) stretching of the obtained preform under proper heating conditions to reduce the diameters of the stacked together microwires; (d) repeating the cut-assembly-stretching processes for the purpose of further decreasing in transverse dimensions of constituents down to 150 nm. The fascinating incorporation of huge amounts of Ge nanowires in glass micro-fibers opens new possibilities for the development of highly integrated photonic and quantum electronic systems.
47.	Prislopski, S.Y.; Naumenko, E.K.; Tiginyanu, I.M.; Ghimpu, L.; **Monaico, E**.; Sirbu, L.; Gaponenko, S.V. Anomalous Retroreflection from Strongly Absorbing Nanoporous Semiconductors. *Opt. Lett.* **2011**, *36*, 3227–3229, doi:10.1364/OL.36.003227.
	Abstract: Pronounced retroreflection behavior is reported for a fishnet nanoporous strongly absorbing semiconductor material. Retroreflection features a half-cone about 0.35 rad0.35 rad along with diffusive specular reflection for all angles of incidence. Retroreflection is apparent by the naked eye with daylight illumination and exhibits no selectivity with respect to wavelength and polarization of incident light featuring minor depolarization of retroreflected light. The reflectance in the backward direction measures 12% with respect to a white scattering etalon. The phenomenon can be classified neither as coherent backscattering nor as Anderson localization of light. The primary model includes light scattering from strongly absorptive and refractive superwavelength clusters existing within the porous fishnet structure. A reasonable qualitative explanation is based on the fact that strict retroreflection obeys shorter paths inside absorbing medium, whereas all alternative paths will lead to stronger absorption of light
48.	Badinter, E.; Ioisher, A.; **Monaico, E**.; Postolache, V.; Tiginyanu, I.M. Exceptional Integration of Metal or Semimetal Nanowires in Human-Hair-like Glass Fiber. *Mater. Lett.* **2010**, *64*, 1902–1904, doi:10.1016/j.matlet.2010.06.002.
	Abstract: We report on a technological route allowing one to integrate huge amounts of electrically isolated metal or semimetal (Pb/Sn alloys and Bi) nanowires in glass fibers with the diameter of up to a few hundreds of micrometers and the length reaching 1 m, the nanowires exhibiting a two-dimensional hexagonal distribution in the cross-sectional plane. The

	obtained results are indicative of new challenges for the elaboration of photonic crystals based on metallo-dielectric periodic and quasi-periodic structures.
49.	Volciuc, O.; **Monaico, E**.; Enachi, M.; Ursaki, V.V.; Pavlidis, D.; Popa, V.; Tiginyanu, I.M. Morphology, Luminescence, and Electrical Resistance Response to H_2 and CO Gas Exposure of Porous InP Membranes Prepared by Electrochemistry in a Neutral Electrolyte. *Appl. Surf. Sci.* **2010**, *257*, 827–831, doi:10.1016/j.apsusc.2010.07.074.
	Abstract: Porous InP membranes have been prepared by anodization of InP wafers with electron concentration of 1×10^{17} cm^{-3} and 1×10^{18} cm^{-3} in a neutral NaCl electrolyte. The internal surfaces of pores in some membranes were modified by electrochemical deposition of gold in a pulsed voltage regime. Photoluminescence and photosensitivity measurements indicate efficient light trapping and porous surface passivation. The photoluminescence and electrical resistivity of the membranes are sensitive to the adsorption of H_2 and CO gas molecules. These properties are also influenced by the deposition of Au nanoparticles inside the pores.
50.	Gologan, V.F.; Bobanova, Zh.I.; **Monaiko, E.V**.; Mazur, V.A.; Ivashku, S.Kh.; Kiriyak, E. Peculiarities of the Influence of an Inductance-Capacitance Device on the Initial Stage of the Crystallization of Electrolytic Coatings of Copper. *Surf. Eng. Appl. Electrochem.* **2010**, *46*, 9–15, doi:10.3103/S1068375510010023.
	Abstract: It was experimentally determined that, depending on the conditions of the molybdenum monocrystal processing and due to the application of the inductance-capacitance device, crystals of various configurations and sizes are deposited first and significantly influence the copper formation with the deposition time increasing

- **Part II**

51.	**Monaico, E**.; Tighineanu, P.; Langa, S.; Hartnagel, H.L.; Tiginyanu, I. ZnSe-Based Conductive Nanotemplates for Nanofabrication. *Phys. Status Solidi RRL – Rapid Res. Lett.* **2009**, *3*, 97–99, doi:10.1002/pssr.200903026
	Abstract: We show that anodic etching of n-type ZnSe crystalline substrates leads to the formation of pores which, after nucleation at surface defects, prove to follow the current lines, exhibiting multiplication until the front of the porous network covers the whole available space. No growth of crystallographically oriented pores has been observed in ZnSe. The

	formation of multilayer porous structures is realized, including layers subjected to successive porosification at two different length scales. The electrochemical pulsed deposition of arrays of Pt nanotubes in the porous ZnSe matrix is demonstrated. The obtained results show that porous ZnSe structures are promising for use as conductive and optically transparent nanotemplates for nanofabrication, in particular for the important application of metal nanotubes. (© 2009 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)
52.	Irmer, G.; **Monaico, E**.; Tiginyanu, I.M.; Gärtner, G.; Ursaki, V.V.; Kolibaba, G.V.; Nedeoglo, D.D. Fröhlich Vibrational Modes in Porous ZnSe Studied by Raman Scattering and Fourier Transform Infrared Reflectance. *J. Phys. Appl. Phys.* **2009**, *42*, 045405, doi:10.1088/0022-3727/42/4/045405
	Abstract: Arrays of parallel pores with a diameter of around 60 nm have been introduced by anodic etching in ZnSe single crystals with a free electron concentration of 4×10^{17} cm^{-3}. Porosity-induced Fröhlich vibrational modes were studied by Raman scattering and Fourier transform infrared spectroscopy. The experimental data are compared with the results of theoretical simulation based on the effective medium theory. Traces of Se phase were evidenced at the surface of the porous matrix after anodization, the Raman active modes of this phase being incident in the region of the occurrence of Fröhlich vibrational modes inherent to porous ZnSe. To identify reliably the Fröhlich modes, Raman spectra of porous ZnSe layers were explored under different resonance conditions with several excitation wavelengths and various excitation power densities.
53.	Ursaki, V.V.; Zalamai, V.V.; Burlacu, A.; Klingshirn, C.; **Monaico, E**.; Tiginyanu, I.M. Random Lasing in Nanostructured ZnO Produced from Bulk ZnSe. *Semicond. Sci. Technol.* **2009**, *24*, 085017, doi:10.1088/0268-1242/24/8/085017
	Abstract: We propose to produce three-dimensional ZnO random laser media on the basis of bulk ZnSe. Bulk ZnSe wafers are transformed into granular ZnO media by thermal treatment in oxygen ambient at temperatures in the range of 700–800 °C. This technology ensures a high optical quality of the ZnO nanostructured material produced to act as a gain medium for stimulated emission in the ultraviolet spectral region in combination with high-quality factor random laser resonators indicated by narrow lasing peaks. The quality factor for the observed emission modes is estimated to be around 1500. The

	structures produced are expected to find applications in microlaser technologies for optoelectronics and photonics.
54.	Tiginyanu, I.M.; Ursaki, V.V.; Sirbu, L.; Enaki, M.; **Monaico, E**. Novel Phosphors Based on Porous Materials. *Phys. Status Solidi C* **2009**, *6*, 1587–1591, doi:10.1002/pssc.200881116
	Abstract: Technological conditions have been developed for the preparation of nanocomposite phosphors based on porous InP, GaP and GaAs semiconductor as well as Al2O3 and TiO2 dielectric templates doped with rare earth and transition metal ions.Semiconductor and dielectric templates are prepared by electrochemical treatment of bulk semiconductor substrates and metallic plates, respectively. Doping is performed by impregnation from liquid solutions followed by thermal treatment.
55.	Tiginyanu, I.; **Monaico, E**.; Monaico, E. Ordered Arrays of Metal Nanotubes in Semiconductor Envelope. *Electrochem. Commun.* **2008**, *10*, 731–734, doi:10.1016/j.elecom.2008.02.029
	Abstract: We report on fabrication of metal nanotubes in semiconductor nanotemplates possessing ordered two-dimensional hexagonal arrays of pores grown in *n*-InP crystalline substrates using anodic etching in neutral electrolyte. Electrochemical pulsed deposition of arrays of Pt nanotubes with diameters of 70 and 140 nm is demonstrated. The produced metallo-semiconductor tubular structure behaves like a layered nanomaterial allowing one to easily cleave thin films consisting of rows of Pt nanotubes in semiconductor envelope.
56.	Dikusar, A.I.; Bruk, L.I.; **Monaico, E.V**.; Sherban, D.A.; Simashkevich, A.V.; Tiginyanu, I.M. Photoelectric Structures Based on Nanoporous p-InP. *Surf. Eng. Appl. Electrochem.* **2008**, *44*, 1–5, doi:10.3103/S1068375508010018
	Abstract: The possibility of nanostructuring of surfaces of indium phosphide with hole conduction is confirmed. The technique of manufacturing and research of SnO2/InP heterostructures with a nanoporous surface at the interface is developed. It is shown that the investigated structure can form a basis for working out photovoltaic devices with an enlarged active surface.
57.	**Monaico, E**.; Tiginyanu, I.M.; Ursaki, V.V.; Sarua, A.; Kuball, M.; Nedeoglo, D.D.; Sirkeli, V.P. Photoluminescence and Vibrational Properties of Nanostructured ZnSe Templates. *Semicond. Sci. Technol.* **2007**, *22*, 1115–1121, doi:10.1088/0268-1242/22/10/007
	Abstract: Electrochemical etching of pores in as-grown and doped n-type ZnSe substrates is reported. To dope the samples the as-grown semi-

	insulating substrates were annealed in a Zn melt containing Al impurity at concentrations ranging from 0.1 to 40 at.%. We demonstrate the growth of arrays of parallel pores with diameters ranging from several hundreds of nanometers down to 40 nm. According to the dependence of the anodic current on the applied potential, the pore growth is found to be mediated by oxide formation. LO–phonon–plasmon coupling and the emergence of the Fröhlich-type surface phonon mode are studied by Raman spectroscopy of annealed and electrochemically treated samples. The position of the Fröhlich mode is found to be identical in porous samples with different diameters of pores and skeleton wall thicknesses, in accordance with the effective medium theory when applied to porous materials with identical semiconductor skeleton relative volume concentration. The photoluminescence analysis of the prepared porous structures is indicative of effective passivation of the porous skeleton surface during anodization while Raman scattering evidences a decrease in the free carrier concentration and neutralization of impurity centers in the porous skeleton walls.
58.	Tiginyanu, I.M.; Ursaki, V.V.; **Monaico, E**.; Foca, E.; Föll, H. Pore Etching in III-V and II-VI Semiconductor Compounds in Neutral Electrolyte. *Electrochem. Solid-State Lett.* **2007**, *10*, D127, doi:10.1149/1.2771076
	Abstract: We propose to use a neutral electrolyte based on an aqueous solution of NaCl instead of commonly used aggressive acids or alkaline electrolytes for the purpose of electrochemical nanostructuring of GaAs and CdSe substrates. It is shown that the process of material porosification can be controlled by the conditions of anodic etching. A photoluminescence analysis of the porous structures obtained and referenced to the as-grown substrate demonstrates that an effective passivation of the surface occurs during anodization in this electrolyte. The results obtained pave the way for the development of optoelectronic devices based on electrochemically nanostructured GaAs and CdSe compounds, particularly for high-efficiency solar cells.
59.	Tiginyanu, I.M.; **Monaico, E**.; Albu, S.; Ursaki, V.V. Environmentally Friendly Approach for Nonlithographic Nanostructuring of Materials. *Phys. Status Solidi RRL – Rapid Res. Lett.* **2007**, *1*, 98–100, doi:10.1002/pssr.200701007
	Abstract: Self-organized quasi-ordered two-dimensional hexagonal arrays of pores with diameters as low as 70 nm in n-InP substrates subjected to anodic etching in aqueous solution of NaCl are reported. We show that proper

	periodic modulation of the applied potential with time allows one to reach 3D nanostructuring of the material. Anodization in salty water proves to be a cost-effective and environmentally-friendly tool for spatial nanostructuring of materials and nonlithographic manufacturing of semiconductor nanotemplates for nanofabrication. (© 2007 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)
60.	**Monaico, E**.; Ubrieta, A.; Fernandez, P.; Piqueras, J.; Tiginyanu, I.M.; Ursaki, V.V.; Boyd, R.W. Intense Luminescence from Porous ZnSe Layers. *Mold. J. Phys. Sci.* **2007**, *6*, 129–134
	Abstract: We report on the possibility to prepare ZnSe porous layers with different degrees of porosity by means of electrochemical methods. The prepared porous structures were characterized using scanning electron microscopy (SEM), photoluminescence (PL) and cathodoluminescence (CL) techniques. The PL of the as-grown material and porous layers measured at low temperatures (10 K) was found to be dominated by an emission band at 2.796 eV as well as a band at 2.700 eV with several phonon replicas. The analysis of the dependence of these bands upon the excitation power density and temperature suggests that free-to-bound and respectively donor-acceptor electron transitions are responsible for the emission bands involved. The comparison of SEM and CL images taken from the same porous regions demonstrated that cathodoluminescence intensity from layers with small characteristic sizes of the porous entities (around 50 nm) is weaker than that inherent in bulk material, while porous layers with the pore diameter of around 500 nm exhibit much stronger luminescence.
61.	Albu, S.; **Monaico, E**.; Tiginyanu, I.M.; Ursaki, V.V. GaP Template Based Semiconductor-Metal Nanocomposite. *Mold. J. Phys. Sci.* **2007**, *6*, 135–141
	Abstract: Pulsed electrochemical methods are proposed for the deposition of Pt into porous GaP templates. It was found that short applied pulses result in a predominant metal deposition on the bottom of pores, while long pulses lead to predominant deposition on the top of pores. The electrochemical parameters were optimized for a uniform metal deposition inside the pores. Pt nanotubes and nanowires were produced by changing the duration of the deposition process. This technology was applied for the fabrication of a variable capacitance device. Optimal combination of semiconductor material parameters, morphology of the template and the metal used were analyzed for this purpose. Methods of pasivation of the internal metalsemiconductor interface were developed. The pasivation technology was optimized via the

	analysis of current-voltage and capacitance-voltage characteristics of the fabricated devices.
62.	**Monaico, E**.; Ursaki, V.V.; Tiginyanu, I.M.; Dashevsky, Z.; Kasiyan, V.; Boyd, R.W. Porosity-Induced Blueshift of Photoluminescence in CdSe. *J. Appl. Phys.* **2006**, *100*, 053517, doi:10.1063/1.2338833
	Abstract: Porous CdSe layers have been fabricated by anodic etching of *n*n-type single crystalline substrates with different values of conductivity. The morphology and porosity of the layers thus produced were found to be controlled by the conductivity of the material, anodization voltage, and conditions of *in situ* UV illumination. The porosity-induced changes in the photoluminescence spectra were studied. The decrease of the skeleton size down to 10–20nm was found to result in a blueshift of the excitonic emission lines by 10meV10meV which was attributed to quantum-size effects in the nanocrystalline CdSe porous skeleton. An increase of the exciton–LO-phonon interaction by a factor of 1.5 in a weak-to-intermediate confinement regime was deduced from the analysis of temperature dependence of the free exciton luminescence line
63.	Langa, S.; Sirbu, L.; **Monaico, E**.; Carstensen, J.; Föll, H.; Tiginyanu, I.M. Morphology and Chemical Composition Microanalysis of 2D and 3D Ordered Structures on Porous InP. *Phys. Status Solidi A* **2005**, *202*, 1411–1416, doi:10.1002/pssa.200461117
	Abstract: Porous InP proves to be promising for use in nanotechnologies due to the possibility to fabricate ordered structures like two-dimensional (2D) single crystals of nanopores. The main goal of this paper is to demonstrate that, along with 2D structures, one can fabricate 3D ordered porous structures on InP using alternative anodic current superimposed to a constant current or by pulsing the current. The dependence of the efficiency of pore diameter modulation upon the current frequency was explored. The stoichiometric composition of 2D and 3D porous InP structures was evidenced by chemical composition microanalysis. (© 2005 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)
64.	Tiginyanu, I.M.; **Monaico, E**.; Ursaki, V.V.; Tezlevan, V.E.; Boyd, R.W. Fabrication and Photoluminescence Properties of Porous CdSe. *Appl. Phys. Lett.* **2005**, *86*, 063115, doi:10.1063/1.1864240
	Abstract: We report the results of a study of the growth of pores in *n*-CdSen-CdSe single crystals using anodic etching techniques. Upon anodization in dark, a nonuniform distribution of pores was produced. However, anodic

	dissolution of the material under *in situ* UV illumination proves to result in uniform distribution of pores stretching perpendicularly to the initial surface of the specimen. The porous structures exhibit less luminescence than the bulk samples. These results pave the way for cost-effective manufacturing of CdSe-based semiconductor nanotemplates for nanofabrication.
65.	**Monaico, E**.; Ursaki, V.V.; Urbieta, A.; Fernández, P.; Piqueras, J.; Boyd, R.W.; Tiginyanu, I.M. Porosity-Induced Gain of Luminescence in CdSe. *Semicond. Sci. Technol.* **2004**, *19*, L121–L123, doi:10.1088/0268-1242/19/12/L04
	Abstract: Porous CdSe layers have been produced by anodic etching of crystalline substrates in a HCl solution. Anodization under *in situ* UV illumination resulted in the formation of uniformly distributed parallel pores with a diameter of 30 nm, stretching perpendicularly to the initial surface. At the same time, pronounced nonuniformities in the spatial distribution of pores were evidenced in samples subjected to anodic etching in the dark. Gain of luminescence was observed in some porous regions and attributed to the formation of ring microcavities for light in the porous network.
66.	Tiginyanu, I.M.; Langa, S.; Sirbu, L.; **Monaico, E**.; Stevens-Kalceff, M.A.; Föll, H. Cathodoluminescence Microanalysis of Porous GaP and InP Structures. *Eur. Phys. J. - Appl. Phys.* **2004**, *27*, 81–84, doi:10.1051/epjap:2004043.
	Abstract: Electron microscopy and cathodoluminescence (CL) microanalysis were used for a comparative study of porous layers fabricated by electrochemical etching of n-GaP and n-InP substrates in aqueous solutions of sulfuric and hydrochloric acids. Both the CL and morphology of porous layers were found to depend upon the anodic current density. At high current density (100 $mA \cdot cm^{-2}$) anodization leads to the formation of so-called current-line oriented pores while at low current densities the pores grow along <111> crystallographic directions. The porosity relief was found to give rise to spatial modulation of the CL intensity. The composition microanalysis proved the stoichiometry of porous GaP and InP skeletons, although we found considerable traces of oxygen in porous GaP layers. Self-induced voltage oscillations giving rise to a synchronous modulation of the diameter of pores and CL intensity were evidenced.