Nanoperforated Indium Phosphide for Terahertz Imaging Bio-applications

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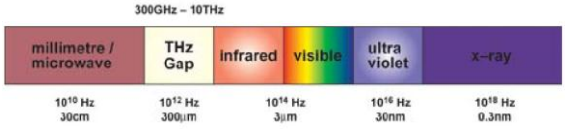
Abstract – We demonstrate the fabrication of thin InP membranes with porous compact packed structure that have been cut during electrochemical etching in the same anodic process. Besides, we show the possibility of pore filling with metal-organic composites. Chemical compounds have been identified by XRD method. The THz emitting characteristics of InP porous films were drastically changed after filling with sensitized metal-organic composites. We show that InP porous membranes filled with metal-organic composites are perfect materials for bio-applications. The experimental study and emulations based on Finite Element Model (FEM) show also that the obtained nanocomposite materials are promising for nonlinear optical applications, in particular for the development of THz emitters, THz imaging systems, MEMS, MOEMS, etc.

Index Terms – nanostructurated membrane, Terahertz (THz) spectroscopy, Indium Phosphide (InP), metal-organic composites, bio-materials.

I. INTRODUCTION

For many decades the terahertz frequencies that range between the infrared and millimeter wavelengths was one of the least explored regions of the electromagnetic spectrum.



While experimental techniques developed for both neighboring spectral ranges cannot be directly applied at terahertz frequencies many of the methods and theories have been adapted to the terahertz range. For instance, single-mode waveguides, widely used in the millimeter range, cannot be applied at terahertz frequencies because of strong damping, but oversized multimode waveguides are commonly used. On the other hand, glass is the standard material for optical components in the visible and near-infrared but in the terahertz range it cannot be used due to strong absorption. Instead, various crystalline and plastic materials are used for windows, filters, lenses, etc., in quasi-optical arrangements taking over all the advantages of visible optics. This mixture of optical and microwave techniques is a characteristic feature of terahertz technology. At the same time terahertz specific devices evolved which have no counterpart in other spectral range, like impurity semiconductor lasers, μ-photoconductivity detectors, metal mesh filters, grid polarizers, and others.

The spectroscopy at terahertz frequencies is of great importance for condensed matter physics and in particular for semiconductors and semiconductor structures because the characteristic energies of many elementary excitations lie in this spectral range [1]. Among them are plasma oscillations, ionization energies of typical shallow donors and acceptors, cyclotron resonance and spin-flip energies, the characteristic size-quantization energies of low dimensional electron systems, and optical phonon energies. Furthermore, the relaxation rates of free and bound excited carriers and scattering rates of free carriers coincide with the terahertz regime. The photon energies in this part of the electromagnetic spectrum range from about 1 to 35 meV being much smaller than the energy gap of usual semiconductors.

At the same time the terahertz technology has entered into an unprecedented revolutionary era with ever-growing applications in biology and medicine [2], monitoring and spectroscopy in pharmaceutical industry and science [3, 4], medical imaging [2], material spectroscopy and sensing, security, and high-data-rate communications.

Over the past few years, unprecedented progress has been made in the area of THz source technologies, which have played an important role in opening up the possibility of using THz waves in many real-world applications. Miniaturized electron beam sources have been demonstrated and the performances of the solid-state sources and frequency multipliers have been steadily improved by increasing their upper frequency limits and their power efficiencies. Terahertz quantum cascade lasers have

experienced a rapid progress over the last few years. Their output power level and operation temperatures have remarkably increased whereas their lowest operation frequencies have been continuously decreasing. Terahertz optoelectronic sources, including THz photomixers and THz parametric sources have seen a great improvement in their performances in terms of optical-to-electrical efficiencies and maximum output powers at frequencies above 1 THz. New material systems have been developed for photomixer sources allowing them to operate at optical telecommunication wavelengths. Taking the advantage of low-cost diode lasers and high-power fiber amplifiers and other telecommunication optical components, it is now possible to dramatically reduce the cost of the THz system.

II. EXPERIMENTAL SETUP

Crystalline (100)-oriented substrates of S-doped n-InP with 500 μm thickness (prior to anodic etching) and free electron concentration of 1.3×10^{18} cm^{-3} were used. The anodization was carried out in an electrochemical double cell as described elsewhere [5]. A four-electrode configuration was used: a Pt reference electrode in the electrolyte, a Pt reference electrode on the sample, a Pt counter electrode, and a Pt working electrode. The temperature was kept constant with a thermostat. The electrolyte was pumped continuously through both parts of the double cell with the help of a peristaltic pump. All equipment involved in the experiments was computer-controlled. The area of the sample exposed to the electrolyte was 0.5 cm^2. The anodic etching was carried out in 5 % HCl aqueous solution at room temperature in potentiostatic regime with the following range of values for obtaining gradient of diameter of pores: the applied voltage linearly and exponentially decreases from 8.0 to 1.0 V that leads to changing degree of porosity with depth. To have a thin porous film, we applied a shock pulse of bias from the potentiostat. The first pulse was used to remove the disordered layer of the porous structure (see Fig 1) and the next pulses were applied to fabricate membranes with ordered pores which were afterwards used in our experiments (see Fig 2). Further details of the anodic etching process can be found in [5]. A TESCAN scanning electron microscope equipped with an Oxford Instruments INCA energy dispersive x-ray (EDX) system was used to analyze the morphology and chemical composition of the porous samples. As previously shown [5], two types of pores can be introduced in III–V semiconductor compounds: crystallographically oriented or 'crysto' pores, and current-line-oriented or 'curro' pores. Crysto pores are usually generated at low anodization current densities or applied voltages, the mechanism of their formation being related to direct dissolution of the material. Curro pores are formed at relatively high anodic current densities or applied voltages, their growth being mediated by oxide formation and its dissolution at the pore tip [5].

Coordination compounds with structural formula $[Zn(C_3N_2(C_6H_5)_2NO_2)_2(CH_3OH)_2]$ and $[Ni(C_3N_2(C_6H_5)_2NO_2)_2(CH_3OH)_2]$ have been synthesized and characterized by X-ray crystallography (Fig. 3, upper part). These complexes have pseudopolimeric structures being connected to each other by hydrogen bonding (Fig. 3, middle part). This behavior made possible the introduction of these complexes in porous *n*-InP membranes. The complex deposition in the porous structure was carried out in a dark room. The monomers were incorporated into the porous layer from $Zn(C_3N_2(C_6H_5)_2NO_2)_2(CH_3OH)_2 : C_3H_6O$ and $Ni(C_3N_2(C_6H_5)_2NO_2)_2(CH_3OH)_2 : C_3H_6O$ solutions. Afterwards, the samples were dried for several days at room temperature. The morphology of the monomer nanowires in an InP template is illustrated in Fig. 3, lower part.

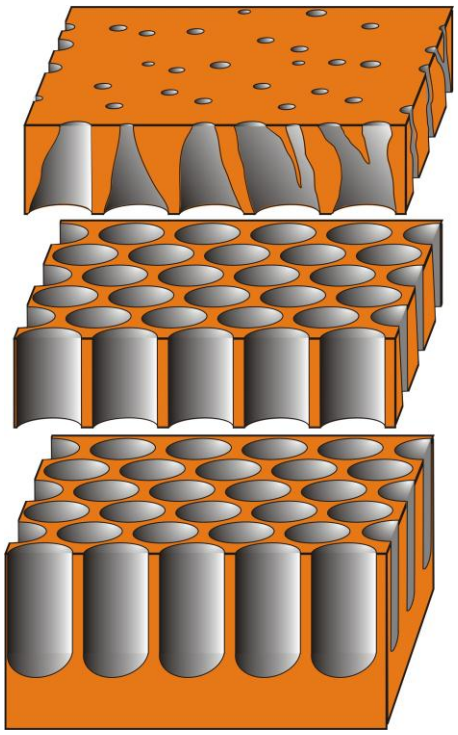


Fig. 1. Schematic representation of cutting membranes from the sample in the same anodic process.

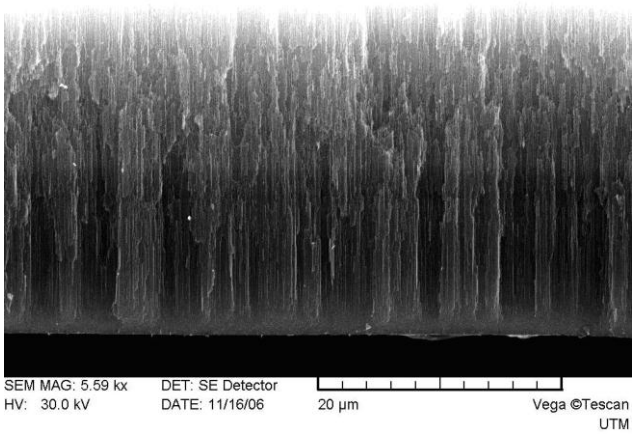


Fig. 2. SEM image of porous InP film.

The EDX analysis of coordination compounds demonstrates that they have fully filled the nanostructured template of n-InP along the entire depth of pores.

The setup used for characterization includes a THz time-domain spectrometer, and a laser amplifier-based optical-pump THz probe spectrometer [6]. The transmission through the sample in the time domain was recorded for each set of samples. Each sample was mounted on a piece of table having a hole with a diameter of 4 mm through which the transmission was measured. The terahertz electric field was linearly polarized for all measurements, and the terahertz beam was normally incident on the sample surface. All measurements were performed at room temperature (Fig. 4).

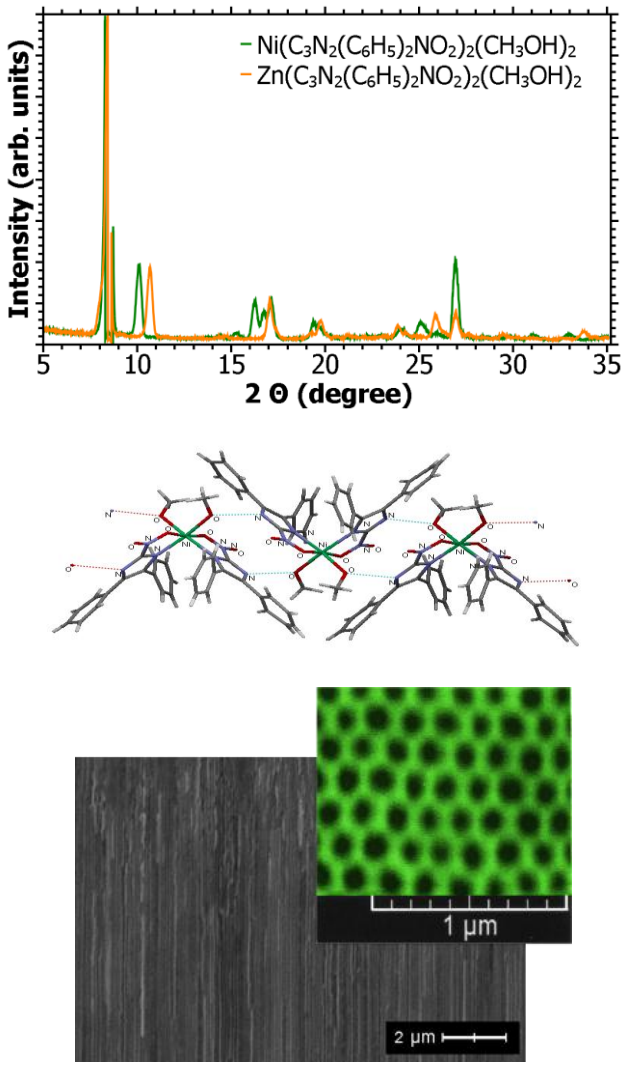


Fig. 3. XRD analyses of the complexes (upper part); hydrogen bonding inside $[Ni(C_3N_2(C_6H_5)_2NO_2)_2(CH_3OH)_2]$ structure (middle part); SEM image of an InP template filled with coordination compounds. The inset shows a top of view of the pores (lower part).

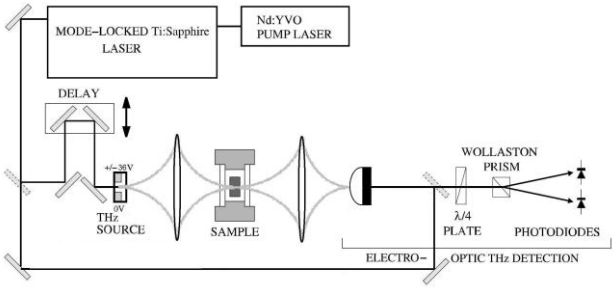


Fig. 4. Experimental setup for the investigation of THz emission from porous InP and composites samples. The samples are placed perpendicular to incident beam at room temperature.

The porous InP is one of the most promising material for the fabrication of THz devices [7, 8]. Recently we have reported a new technology [9] for the fabrication of membranes on InP (111) surfaces that can emit ultrafast coherent terahertz pulses under near-infrared optical excitation. The membranes irradiated by heavy noble gas Kr or Xe ions demonstrated enhanced terahertz emission.

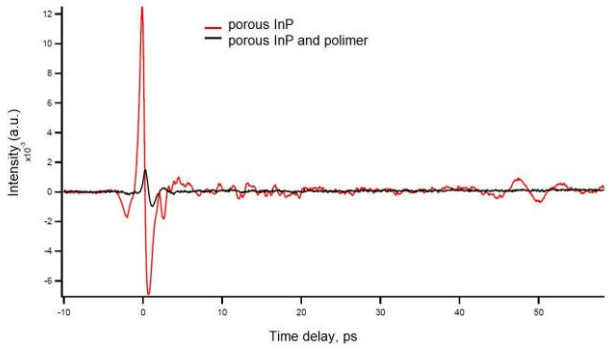


Fig. 5. THz signal from a pair of porous InP and composites samples.

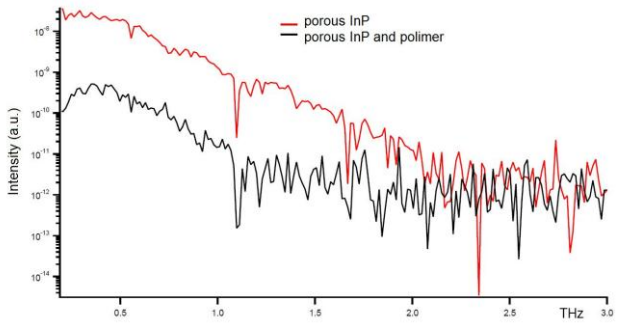


Fig. 6. THz spectrum measured in air. Several strong absorption lines due to water vapor are seen.

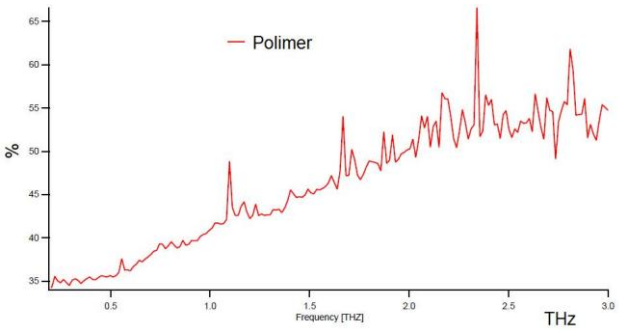


Fig. 7. Remodeled absorption spectrum. Several strong absorption lines due to water vapor are evident.

Porous InP has been taken as reference material in studying the THz emission and it has been compared with the same structure filled with polymer (Fig. 5) [10-12]. One can see from the THz spectrum that polymers increase the absorption of THz radiation (Figs. 6, 7). We suppose that the main impact on absorption is due to the presence of metallic atoms in this systemized metal-organic structure. Another contribution to the absorption comes from atmospheric water vapors, since the experiments were performed without using a nitrogen gas chamber.

III. SIMULATION MODEL FOR BIO APPLICATIONS

We investigated the terahertz characteristics of porous films with pores filled in with polymers. Two kinds of samples have been investigated: (i) clean poly- and monomers, and (ii) the ones containing metallic particles inside. We used FEM methods implying Mie theory and Drude model for the description of metallic nanoparticles dispersion. The model, defined in a cylindrical coordinate system, comprises a PML layer as thick as twice the wavelength used for excitation. The simulations were made for a single pore of 100 nm in diameter made in an A^3B^5 like

semiconductor. The pore was considered to be filled in with a highly contrast dielectric (our polymer) in terms of electric permittivity, with nanoparticles with various diameters in the range of 10 to 50 nm dispersed in it. We defined an excitation pulse of picoseconds replicating the LASER excitation for the real samples [12].

Fig. 8 represents a model for bio-applications, where the THz radiation is reflected from the surface of porous InP. In the specular direction we have absorption from the used bio sample (in our case a chemically synthesized metal-organic structure) that is going to be scanned.

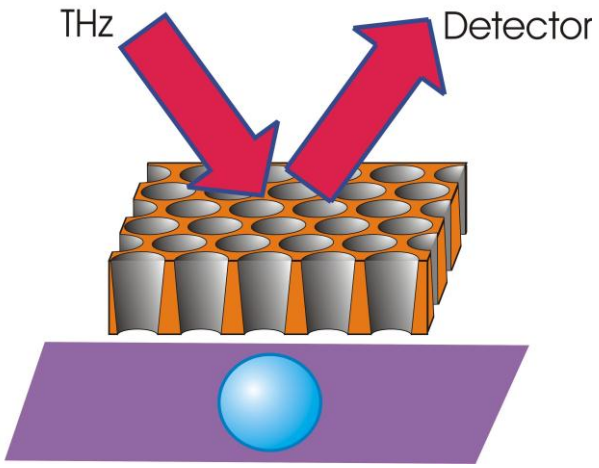


Fig 8. Model of bio-samples detector

IV. CONCLUSION

We carried out an experimental study of THz emission from new synthesized polymers as well as their THz absorption characteristics. We have developed a technique to obtain porous InP membranes with thicknesses in the range of 30-100 μm filled in with polymers. This technique is expected to be useful for medical applications, for instance in detecting and processing images like a huge lattice with thousands, millions, or even billions of detectors working simultaneously.

REFERENCES

[1] S.D. Ganichev. "Intense Terahertz Excitation of Semiconductors" Terahertz Science and Technology, ISSN 1941-7411 Vol. 1, No 3, Sept. 2008.

[2] Peter H. Siegel. „Terahertz Technology in Biology and Medicine" 2438 IEEE Transactions on Microwave Theory and Techniques, Vol. 52, NO. 10, Oct. 2004.

[3] Xin Wu, De Li, Wei-Hua Sun, Feng Gao, Zhi-Jian Zhang, and Ru-Wen Peng. „Coupling of THz Surface Plasmon Polaritons in Corrugated Stacks of Dielectric and Semiconductor" PIERS ONLINE, Vol. 5, no 2, 101, 2009.

[4] Yasser A. Hussein and James E. Spencer „Hybrid FDTD Analysis for Periodic On-Chip Terahertz (THz) Structures" SLAC-PUB-10908 Contributed to 2005 IEEE/ACES International Conference on Wireless Communications and Applied Computational Electromagnetics, April 3-7, 2005, Honolulu, HI, USA 2005.

[5] S. Langa, I. M. Tiginyanu, J. Carstensen, M. Christophersen and H. Foell „Self-organized growth of single crystals of nanopores" Appl. Phys. Lett. 82 278, 2003.

[6] A. Charles Schmuttenmaer "Using Terahertz Spectroscopy to Study Nanomaterials" Terahertz Science and Technology, ISSN 1941-7411 Vol.1, No.1, March 2008.

[7] M. Reid, I. I.V. Cravetchi, R. Fedosejevs, I.M. Tiginyanu and L. Sirbu. „Enhanced terahertz emission from porous InP(111) membranes" Appl. Phys. Lett., Vol. 86, 021904, 2005.

[8] M. Reid, I. I.V. Cravetchi, R. Fedosejevs, I.M. Tiginyanu, L. Sirbu & Robert W. Boyd. „Enhanced nonlinear optical response of InP(100) membranes" Physical Review B, Vol. 71, 081306, 2005.

[9] K. Radhanpura, S. Hargreaves, R. A. Lewis, L. Sirbu, and I. M. Tiginyanu „Heavy noble gas (Kr, Xe) irradiated (111) InP nanoporous honeycomb membranes with enhanced ultrafast all-optical terahertz emission" Appl. Phys. Lett. 97, 181921, 2010.

[10] Alexander M. Sinyukov and L. Michael Hayden „Efficient Electrooptic Polymers for THz Applications" J. Phys. Chem. B 108, 8515, 2004.

[11] Vittorio M. N. Passaro Francesco Dell'Olio, Biagio Casamassima 1 and Francesco De Leonardis „Guided-Wave Optical Biosensors" Sensors, 7, 508, 2007.

[12] V. Sergentu, D. Esinenco, L. Sirbu, I. Vodă, I. M. Tiginyanu, V. Ursaki. „Rayleigh scattering of a metal nanoparticle on a flat dielectric surface" Tereahertz & Mid IR Radiation: Basic Research & Practical Applications The NATO Science for Peace and Security Programme, Photonics Society, Turunç-Marmaris, Turkey 3-6 Nov. 2009.