Photoconductivity Relaxation in Nanostructured InP

Vitalie POSTOLACHE[1], Eduard MONAICO[1,2], Eugeniu BORODIN[1], Oleg LUPAN[3,5], Veaceslav URSAKI[4], Rainer ADELUNG[5], Kornelius NIELSH[2], Ion TIGINYANU[4]

[1]*National Center for Material Study and Testing, Technical University of Moldova, Stefan cel Mare av. 168, Chisinau MD-2004, Republic of Moldova, e-mail: monaico@mail.utm.md*
[2]*Institute of Applied Physics, University of Hamburg, Jungiusstrasse 11, 20355 Hamburg, Germany*
[3]*Department of Microelectronics and Semiconductors Devices, Technical University of Moldova, Stefan cel Mare av. 168, Chisinau MD-2004, Republic of Moldova*
[4]*Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, Academy str. 3/3, Chisinau MD-2028, Republic of Moldova*
[5]*Functional Nanomaterials, Institute for Materials Science, University of Kiel, Kaiserstr.2, 24143 Kiel, Germany*

***Abstract* — We show that long-duration-photoconductivity decay (LDPCD) and persistent photoconductivity (PPC) in porous InP structures produced by anodization of InP substrates can be controlled through the control of their 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.**

***Index Terms* — Porous InP, anodization, ultrathin walls, photoconductivity decay, persistent photoconductivity.**

I. INTRODUCTION

Porous materials enlarge continuously the area of their applications due to simple, accessible, and cost effective methods of fabrications ensured by electrochemical etching. A variety of porous semiconductor architectures have been demonstrated by electrochemistry. Because of the nanoscale nature of light absorption and photocurrent generation in solar energy conversion, the advent of methods for controlling inorganic materials on the nanometer scale opens wide opportunities for the development of future generations of solar cells.[1-5] InP and GaAs are among the most suitable materials for these purposes since their bandgap fits very well the maximum of the solar energy distribution. The applicability of a porous GaAs electrode in a photoelectrochemical solar cell was demonstrated.[6] It was shown that the introduction of porosity in the photoelectrode leads to a considerable photosensitivity increase in the longwavelength region near the bandgap which results in an increase of the output power by a factor of four in comparison with the cell based on bulk electrodes. Nanostructured semiconductors are show also enormous potential for their use as active components in photodetectors,[7] light-emitting diodes,[8] ultrahigh-density transistors,[9] and gas sensors.[10-13] A a high-speed polarization-insensitive photoconductor has been demonstrated based on intersecting InP nanowires synthesized between a pair of hydrogenated silicon electrodes deposited on amorphous SiO2 surfaces prepared on silicon substrates.[14,15] Long long-duration-photoconductivity decay (LDPCD) and persistent photoconductivity (PPC) have been shown to be inherent to porous materials.16 These phenomena can have a significant effect on the characteristics of device structures such as UV detectors, field effect transistors, gas sensors, etc in terms of their sensitivity, noise properties, dark level, and response speed. Different mechanisms were considered as origin of PPC, such as defects with bistable character,[17,18] AX,[19] or DX centers,[20,21] as well as random potential fluctuations caused by inhomogeneities, which lead to spatial separation of charge carriers, therefore their recombination being hindered by potential barriers.[22-26]

The goal of this paper is to investigate the LDPC and PPC phenomena in nanostructured InP and to demonstrate the possibilities of controlling these phenomena by the control of sample morphology.

II. SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

Crystalline (100)-oriented substrates of sulfur doped *n*-InP with 500 μm thickness and a free electron concentration of $1.3x10^{18}$ cm^{-3} were supplied by CrysTec GmbH, Germany. Before the anodization process, conventional photolithography was used to open windows in the photoresist covering the top surface of the samples. Anodic etching was applied to these samples through opened rectangular windows with a breadth of 35 μm. An electrical contact was made on the backside of the anodized samples with a silver paint. The anodization of the InP substrates was carried out in 500 ml of a 5 % HCl aqueous solution at 25°C in a common two-electrode cell where the sample served as working electrode. A platinum wire (0.5-mm diameter) mesh with the surface of 6 cm^2 was used as counter electrode. A Keithley's Series 2400 Source Measure Unit was used as potentiostat.

The morphology and chemical composition have been investigated by microanalysis in a Scanning Electron Microscope (SEM) Zeiss Sigma and TESCAN Vega TS 5130MM equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV.

Radiation from a mercury lamp or from an Ar+ laser was used for the photoconductivity (PC) excitation. Neutral density filters were used to reduce the intensity of the light

at the sample. The current through the samples was measured by means of Keithley's Series 2400 Source Measure Unit. Since the PC decay time is long enough, a mechanical shutter was used in the PC relaxation experiments. The signal from the Source Measure Unit was introduced in an IBM computer via IEEE-488 interface for further data processing. The experiments were performed in a temperature interval 30 – 300 K, the samples being mounted in LTS-22-C-330 Workhorse-type optical cryogenic system.

III. RESULTS AND DISCUTIONS

A porous structure with the thickness of skeleton walls comparable with pore diameters is produced at low applied voltages during anodization as shown in Fig. 1a. III–V compounds, and InP in particular, are characterized by the existence of a surface depleted layer with the thickness

$$L_D = (2\varphi_0\varepsilon_0\varepsilon_S/eN_D^+)^{1/2} \quad (1)$$

where $e\varphi_0$ is the surface potential, $\varepsilon_0\varepsilon_S$ is the static dielectric constant of the material and N_D^+ is the concentration of ionized donors. For the given concentrations of free carriers, at room temperature the L_D is equal to ~20 nm.

As shown in Fig. 1b, the free carrier distribution in porous InP structures is highly inhomogeneous, which leads to potential fluctuations across the sample.

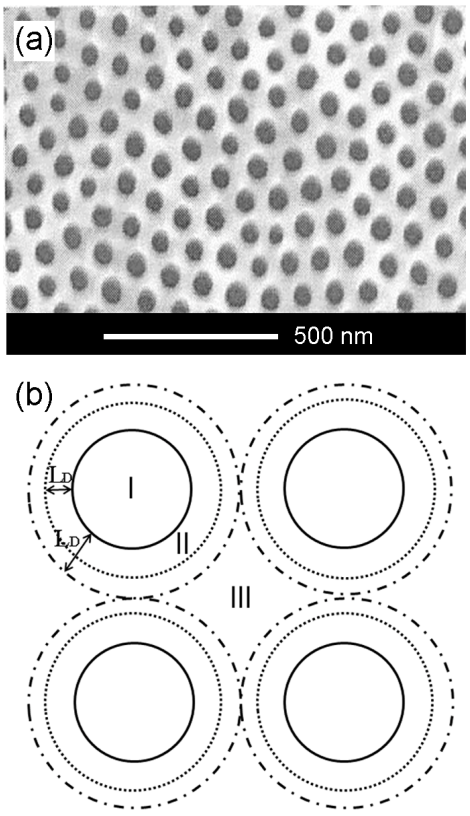

Fig. 1. (a) SEM image of a porous InP sample produced at low applied voltages during anodization. (b) Representation of the volume distribution within a porous membrane: (I) pore volume; (II) depleted InP volume; (III) InP volume containing free charge carriers. The dotted line shows the depletion layer at room temperature, the dash–dot line that at low temperatures.

At room temperature the exhausted areas do not touch each other thus leaving space for free carriers to move freely along the honeycomb-like structure. With decreasing temperature, the width of L_D increases which leads to overlapping of exhausted areas and to confinement of carriers in the region 'III'. This results in the increase of potential barriers.

Figs. 2 and 3 show the PC transient in a porous InP sample at T = 150 K and 120 K, respectively. One can observe that the PC decay consists of two components: fast and slow. The slow component manifests the characteristics inherent to LDPCD:

1. long relaxation time;
2. the PC relaxation is asymmetric in light on – light off;
3. the transient time after the light turned on depends on the light intensity, it being decreased by the intensity increase, while the transient time after the light turned off is independent of the light intensity;
4. the instantaneous transient time is temperature activated.

At low temperature the relaxation time can reach too high values that the conductivity apparently doesn't change, i.e. the phenomenon of PPC is observed (Fig. 3). All these peculiarities are well explained on the basis of a spatial potential barrier model.[22-24] The formation of a spatial barrier pattern in porous samples is naturally expected as described above.

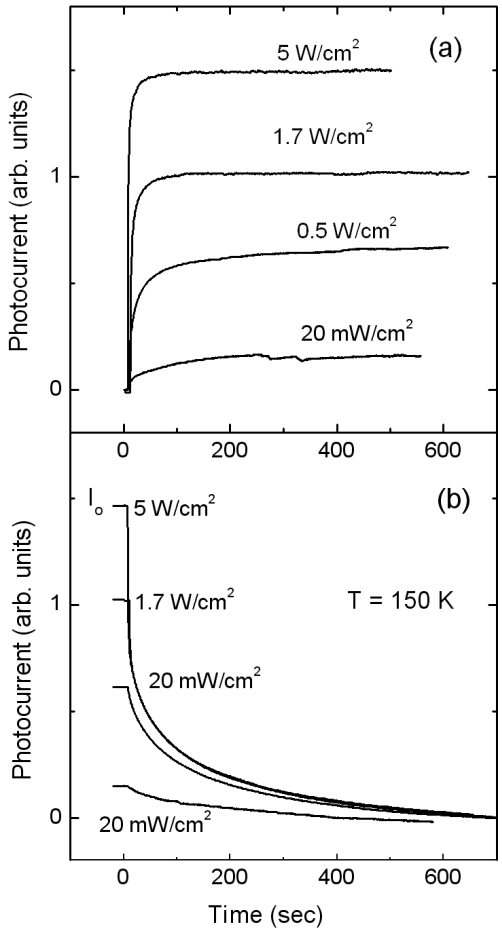

Fig. 2. PC decay in porous InP at different light intensities and T = 150 K. a) light on; b) light off.

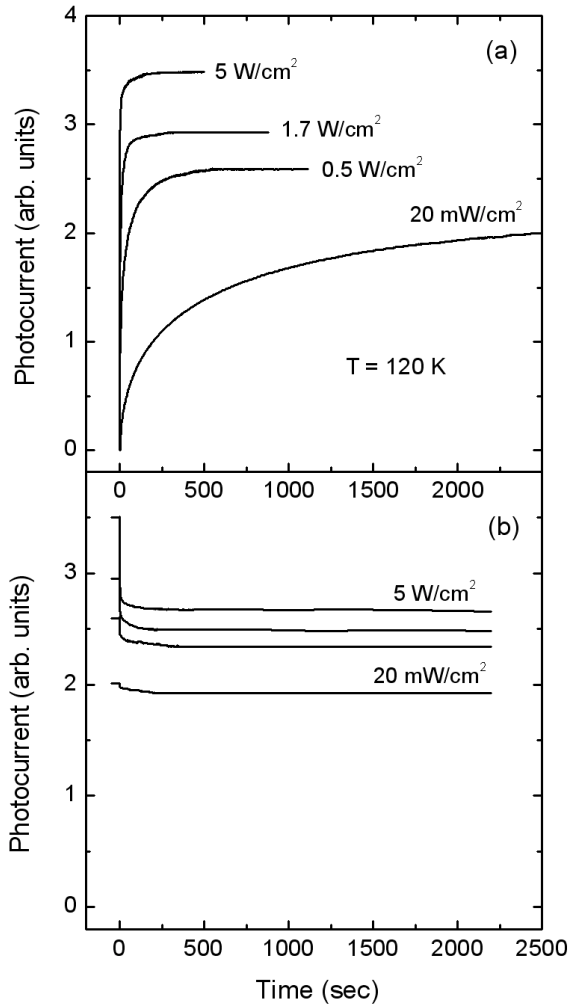

Fig. 3. Fig. 1. PC decay in porous InP at different light intensities and T = 120 K. a) light on; b) light off.

The increase of the applied voltage up to 10 V was found to modify drastically the morphology of the anodically etched layer.[27] As one can see from Fig. 4a, the etching results in the formation of mosaic structures consisting of ultrathin walls.

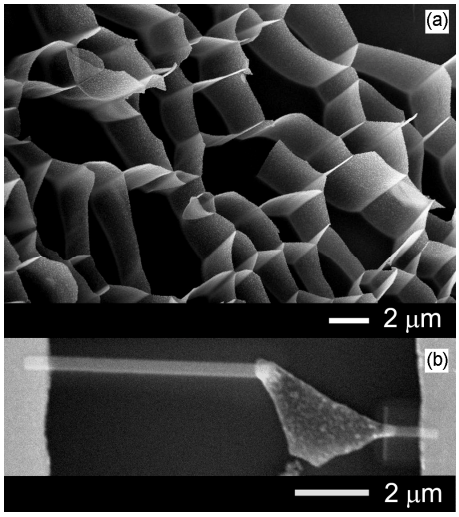

Fig. 4. (a) SEM images taken from *n*-InP subjected to anodic etching at U = 10V. (b) A photodetector prepared on a piece of this mosaic structure.

A piece of ultrathin membranes constituting this mosaic structure was used for the preparation of a photodetector as illustrated in Fig. 4b. One can see from Fig. 5 that the relaxation of photocurrent in this ultrathin membrane is substantially different from that observed in the porous sample. As compared to porous sample, there is no persistent photoconductivity in the membrane even a very low temperature (30 K). One should mention that the membrane is totally exhausted of carriers due to its small thickness as compared to the depleted layer thickness L_D. Therefore, it is homogeneous from the point of view of free carrier distribution, and the relaxation of photoconductivity is not governed by the existence of potential barriers. Due to the extremely big surface of the membrane as compared to its volume, one can suggest that the photoconductivity relaxation processes are governed in this case by surface states. The influence of the environment on the photoconductivity as deduced from a comparison of curve 1 measured in air, and curve 2 measured in vacuum (Fig. 5), supports this assumption.

On the other hand, the photoconductivity decay in the ultrathin membrane is also different from that observed in the initial bulk materials (see Fig. 6). In the bulk material, the relaxation of photoconductivity is similar to that observed in the porous sample. However, the relaxation times are much shorter. The PC relaxation is also asymmetric in light on – light off sequences, and the transient time after the light turned on depends on the light intensity, it being decreased by the intensity increase, while the transient time after the light turned off is independent of the light intensity. That means that, in contrast to the ultrathin membrane, the photoconductivity relaxation in the initial bulk InP is governed by potential barriers induced by potential fluctuations caused by inhomogeneities. However, the nature of these potential fluctuations is different from those inherent to porous samples. While potential fluctuations in porous samples are induced by porosity, the formation of randomly distributed potential barriers in bulk InP is due to the high doping level and partial compensation.

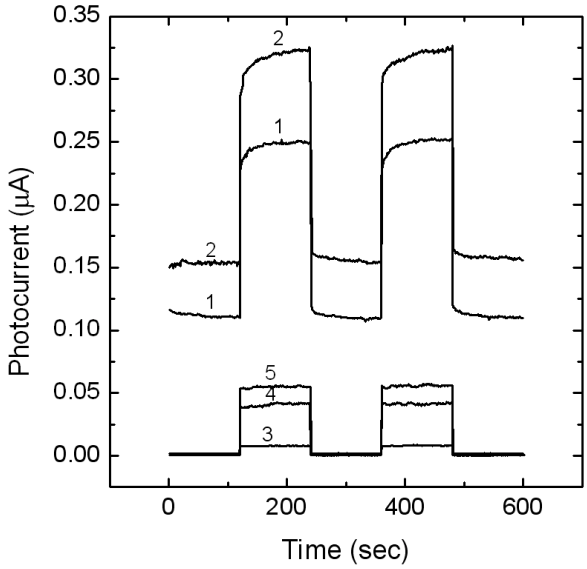

Fig. 5. Photocurrent measured at various temperatures in the sample illustrated in Fig. 4b: 1 - 300 K in air; 2 - 300 K in vacuum; 3 - 200 K, 4 - 100 K; 5 - 30 K.

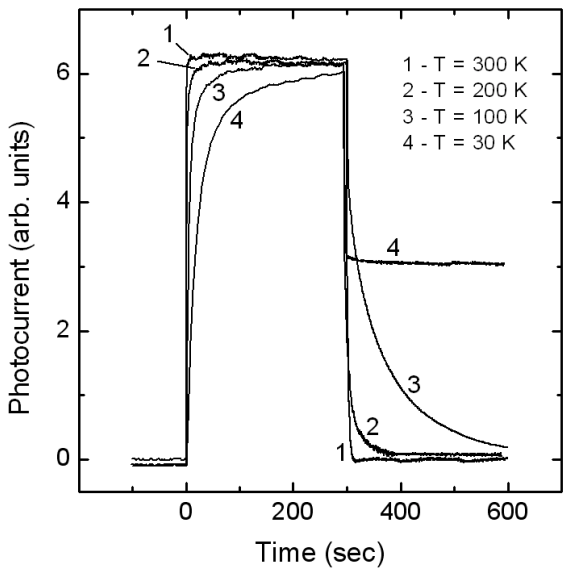

Fig. 6. Photocurrent measured at various temperatures on the bulk InP sample.

The amplitude of the potential relief in doped semiconductors is proportional to $(1\text{-}K)^{-1/3}$, where K is the compensation degree[22]. With lowering the temperature the compensation degree increases and the potential relief becomes more pronounced, which leads to PPC as demonstrated by curve 4 in Fig. 6.

IV. CONCLUSION

The results of this study demonstrate possibilities to control the persistent photoconductivity in porous InP structures produced by anodization of InP substrates through the control of their morphology. In porous InP samples with the thickness of skeleton walls comparable with pore diameters the photoexcited carriers should overcome the porosity induced potential barriers in order to recombine, that leads to persistent photoconductivity al low temperatures. Persistent photoconductivity is also observed at low temperatures in bulk InP samples. However, the potential barriers are lower as compared to porous samples, and the nature of the potential fluctuations producing these potential barriers is different from that of porous samples, it being determined by the high doping level and partial compensation. The persistent photoconductivity is quenched in ultrathin InP membranes, the photoconductivity relaxation processes being governed by surface states in this case.

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