NANOPOROUS MEMBRANES AND HETEROSTRUCTURES ON III-V COMPOUNDS FOR MICRO- AND OPTOELECTRONIC APPLICATIONS

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***Abstract* - High-quality nanoporous membranes and heterostructures of III-V compounds have been fabricated by using MeV-ion-implantation-assisted or photon-assisted electrochemical etching. They were found to exhibit short-wavelength luminescence, Fröhlich-type surface-related vibrations and enhanced nonlinear optical response. The obtained results are discussed in connection with various possible applications of nanoporous structures.**

I. INTRODUCTION

Nanoporous materials are characterised by nanometer sized structural units and high surface-to-volume ratio. Under definite circumstances, these characteristics lead to unique and often greatly enhanced proprieties in comparison with the bulk materials. Bulk Si, for instance, has an indirect band gap, and, therefore, the probability of band-to-band radiative transitions in the material is low. At the same time nanoporous Si exhibits intense visible luminescence resulting in the development of electro-luminescent structures and displays [1-3]. Among other potential applications of porous Si one can mention graded reflection mirrors, photonic crystals, alphanumeric displays, photovoltaics, biological and chemical sensors, etc [1-4].

Over the last years, increasing attention has been paid to porous structures of some III-V compounds [5-10]. Important advantages of III-V materials are related to the possibilities of changing the chemical composition and further extending the fields of applications of porous structures towards the UV region of the spectrum. Apart from that, the shift from element to compound leads to the occurrence of new physical properties, specific to acentricity, like Fröhlich-type surface-related vibrations [8]. A strongly enhanced photoresponse and birefringence at the wavelength of optical communication systems were reported for some of III-V compounds [6,7].

It is well established that porous III-V layers fabricated by anodic etching are optically inhomogeneous, resulting in multiple scattering of the visible light in the porous network [7,11,12]. Obviously, the porous medium will become optically homogeneous providing that the dimensions of both the pores and skeleton are much lower than the wavelength of the electromagnetic radiation. To fulfil this requirement, one has to introduce in the semiconductor materials uniformly or quasi-uniformly distributed pores at sufficiently high densities. In this work, we developed a technological basis for an electrochemical manufacturing of optically homogeneous porous layers and free-standing membranes of III-V compounds pre-implanted by MeV-energy ions or illuminated in-situ. The porous samples have been characterised by scanning electron microscopy, photoluminescence (PL), micro-Raman spectroscopy and second harmonic generation (SHG) technique. The obtained results are discussed in connection with possible device applications of nanoporous structures.

II. EXPERIMENT

The (100)- and (111)-oriented n-GaP substrates used in the present study were cut from liquid-encapsulation – Czochralsky-grown S- or Te-doped ingots with the free electron concentration of $(0.5 - 1) \times 10^{18}$ cm^{-3} at 300 K. Porosity was introduced by anodic etching of samples in an aqueous solution of sulphuric acid. Free standing membranes of porous GaP were fabricated by subjecting the (100)- and (111)A-oriented samples to a 5-MeV Kr^+ ion implantation with subsequent anodic etching or anodising the as-grown substrates under proper conditions of in-situ illumination. The porous membranes with the thickness up to tens of micrometers were transparent to the visible light.

GaAs/GaP heterostructures have been produced by Molecular Beam Epitaxy (MBE), 1-µm thick GaAs layers were therefore grown on (100)–oriented GaP substrates at 600 °C in a Riber 32P system, using a valved-cracker cell for arsenic in order to provide molecular beams of As_2. The porosity was introduced subsequently by anodization of samples for 60 min in the dark. The formation of the pores was evidenced by images taken with a Scanning Electron Microscope (SEM).

III. MORPHOLOGY OF POROUS STRUCTURES

The formation of the pores in III-V compounds results from the nonuniform dissolution of the material owing to ever present uncontrolled surface defects such as dislocation loops emergencies. In (100)-oriented n-GaP, for instance, after the initial pitting of the surface, further etching proceeds in the direction both perpendicular and parallel to the surface [7,13]. Since the extension of the porous structure occurs underneath the surface, this is termed a 'catacomb'- like porosity [13]. The border between the porous layer and the substrate is hilly rather than flat.

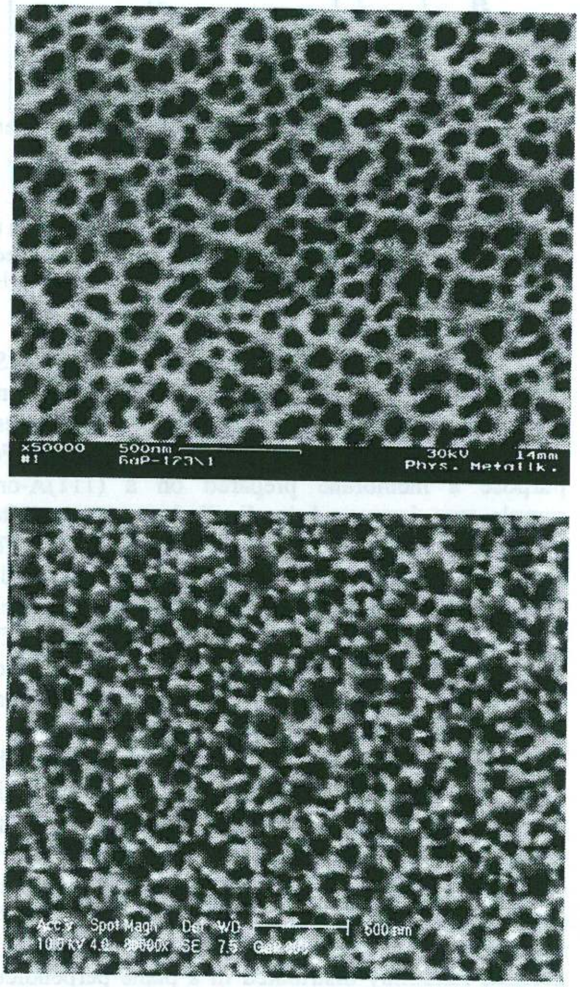

Fig. 1. SEM-images of porous GaP membranes prepared on substrates with (100) and (111)A orientations.

Only two attempts to prepare uniformly sized porous-like structures on III-V materials have been undertaken so far. Takizawa et al [14] fabricated a pillar-like porous structure on (111)A-oriented n-InP using electron beam lithography. Recently [13] we have demonstrated that a 5-MeV Kr^+ implantation in n-GaP substrates enables the control of the surface defect density, irrespective of its initial value determined by the crystal growth. The pores left by the dissolved material stretch perpendicularly to the surface and thus leave a network-shaped porous structure whose average lateral dimensions are comparable to the depth of the carrier-depleted surface layer before anodization. Under suitable etching conditions lateral dissolution can be achieved, thus yielding a way to prepare free-standing membranes of porous material. Fig. 1 shows SEM images of the top surface for two membranes prepared by Kr^+ ion implantation at the dose $3 \cdot 10^{10}$ cm^{-2} with subsequent anodization of (100)- and (111)A-oriented substrates. One can see that the porous membrane prepared on GaP substrate with a (100) orientation (Fig. 1, upper image) shows a grid-shaped or honeycomb structure. In contrast, electrochemical etching of a (111)A-oriented GaP surface (Fig. 1, lower image) leads to a top layer with a pillar structure characterised by lightly interconnected columns stretching perpendicularly to the initial surface.

Further improvement of the morphology of porous GaP was possible to achieve under proper conditions of in-situ illumination. We succeeded to fabricate optically-transparent free-standing porous membranes with the thickness up to tens of micrometers. As one can see from Fig. 2, the pores are uniformly distributed and no pronounced fluctuation in their lateral dimensions is observed.

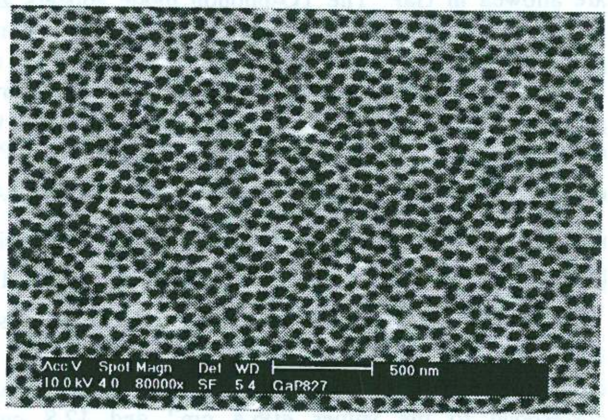

Fig. 2. SEM-image of a porous GaP membrane fabricated on a (111)A-oriented substrate illuminated in-situ.

The anodization of the GaAs/GaP heterostructure led to a non-uniformly distributed porosity along the top GaAs MBE-layer. We observed clusters of pores (Fig. 3) with an average distance between them of about 3 μm. Nevertheless, underneath GaAs a uniform porous layer of GaP was produced due to the formation of porous domains[13]. The possibility to introduce porosity in GaP through channels in MBE-grown GaAs layers is a strong indication to the reasonability of using nanolithography for the purpose of producing ordered nanostructures on GaP by wet etching.

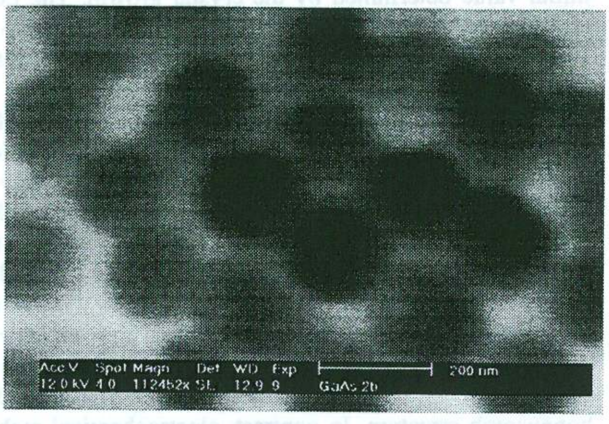

Fig. 3. SEM micrograph of the top GaAs epilayer after anodic etching of the GaAs/GaP heterostructure.

IV. PROPERTIES AND POSSIBLE APPLICATIONS

A. *Optical phonon engineering*

The micro-Raman spectroscopy of the as-grown bulk sample, as shown in Fig. 4a, displays the typical behaviour of highly n-type doped GaP. According to the selection rules for a (111)-oriented surface, both the transverse optical (TO) and longitudinal optical (LO) phonon modes are allowed in GaP. The TO-phonon mode appears at a frequency of 365 cm^{-1}. The inherent to undoped material pure LO-phonon is no longer observed due to the interaction of lattice vibrations with the free carrier plasma. This kind of interaction gives rise to the observation of LO-phonon-plasmon-coupled (LOPC) modes, denoted by L_+ and L_-. Unlike the case of GaAs, the L_--mode cannot be observed due to strong damping [15] caused by the low mobility of the free carriers. The L_+- mode is shifted upwards in frequency in comparison with that of pure LO-phonon and its line-width is considerably broadened. The peak position and line-width correspond to the values 406.4 cm^{-1} and 12.8 cm^{-1}, respectively.

Measurements of the Raman scattering (RS) on free-standing porous membranes (Fig. 4b) show quite a different behaviour. Whereas the TO-phonon is nearly unaffected, proving the good crystalline quality of the GaP-skeleton, we observe instead of the LOPC-mode a strong peak of LO-phonon related scattering at 402 cm^{-1}, nearly at the position of LO-phonon in undoped samples. Moreover, between the TO and LO peaks, an additional broad structure is observed, which can be interpreted as the surface-related Fröhlich-type vibrational mode (marked "S" in Fig. 4b). A downward frequency shift of this mode was observed when filling in pores with a methanol-ethanol mixture (Fig. 4b).

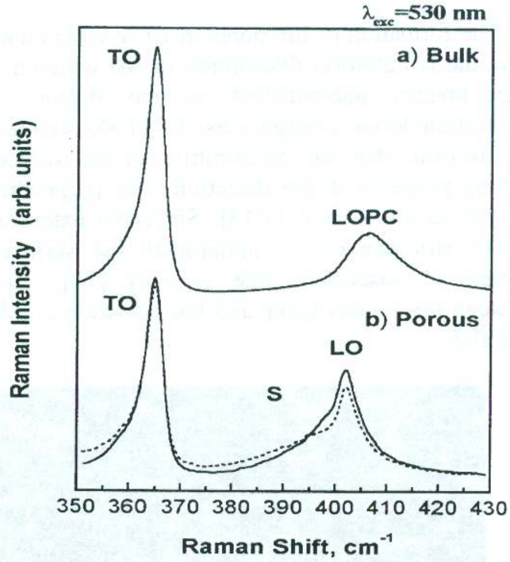

Fig. 4. Micro-Raman spectra from as-grown (111)-oriented bulk (a) and porous (b) GaP. The porous samples were measured under different conditions: in air (solid curve) and in methanol-ethanol mixture (dashed curve) environments.

To demonstrate the Fröhlich character of the RS peak centred in the frequency gap between the TO and LO phonons, a Raman analysis of porous membranes with pores filled in with air and water was undertaken. For this purpose a membrane prepared on a (111)A-oriented sample was immersed in distilled water just after the fabrication and stored there for several hours. The RS spectra of porous membranes with empty and filled pores are shown in Fig. 5. One can see that filling in the pores with water has no influence on the position of bulk TO and LO phonons. At the same time, the spectral decomposition evidenced a low-frequency shift of the surface-related phonon from 397 to 388.2 cm^{-1}.

The TO, LO and Fröhlich modes are given by the maxima of $Im(\varepsilon(\omega))$ and $Im(- 1/ \varepsilon(\omega))$. On the basis of a one-pole approximation for the calculation of an effective dielectric constant [16] of a heterogeneous material we obtain for a disordered arrangement of parallel pores with circular cross-section interpolated according to [17] to a percolating GaP-skeleton simulated by planes with normals randomly distributed in a plane perpendicular to the pore direction

$$\varepsilon_{eff}(\omega) = \varepsilon_1 \left(1 - \frac{c-\beta}{s} - \frac{\beta}{s-s_0} \right) \qquad (1)$$

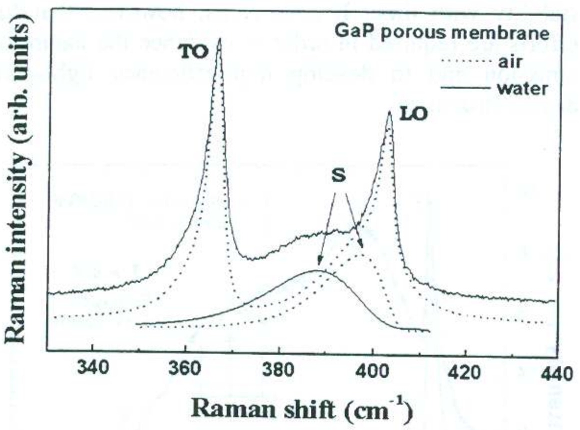

Fig. 5. Micro-Raman scattering spectra of a porous GaP membrane before and after filling in the pores with water. In both cases the surface related band was derived from spectral decomposition.

where $s = \varepsilon_1 / (\varepsilon_1 - \varepsilon_2)$, $\beta = (1 / 2s_0) \cdot c \cdot (1 - c)$, and $s_0 = (1 - c/2)$, and c – denotes the GaP concentration, $\varepsilon_2 = \varepsilon_2(\omega)$ is the dielectric function of gallium phosphide in the phonon region and ε_1 – is the dielectric constant of material filling the pores ($\varepsilon_1 = 1$ in the case of air and $\varepsilon_1 = 2.3$ in the case of water [18]). From the poles and zeros of $\varepsilon_{eff}(\omega)$ one can deduce unchanged (compared with the bulk value) TO and LO phonons and a Fröhlich mode which splits into TO-like and LO-like surface related modes for *c* # 1 (Fig. 6). The TO-LO components of the Fröhlich mode show a frequency shift with increasing the degree of porosity, the gradient of this shift being higher for the LO-component. Moreover, the actual frequencies of the Fröhlich mode components prove to depend upon the dielectric constant of the material in the pores. As one can see from Fig. 6, the LO-component, expected to prevail in the Raman spectra, shows a downward frequency shift of 7-8 cm^{-1} for intermediate degrees of porosity (40 - 50 %) which is in good agreement with the experimental data (Fig. 5).

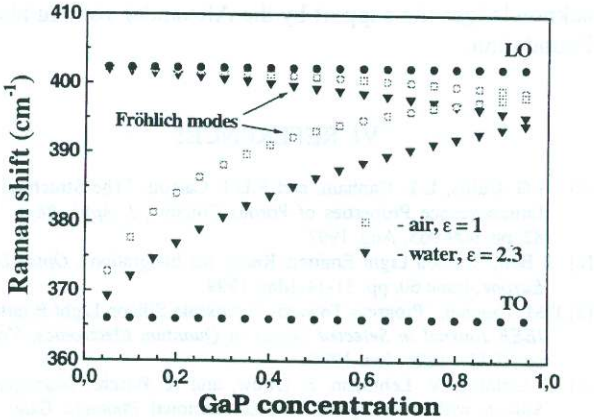

Fig. 6. Calculated dependence of TO, LO and Fröhlich mode frequencies upon the GaP concentration in GaP/air and GaP/water nanocomposites.

The dependence of the Fröhlich mode frequencies upon the degree of porosity and the dielectric constant of the surrounding medium is of real practical importance. Since the frequency of a Fröhlich mode can be changed in a controllable manner within the frequency gap of the bulk optical phonons (TO-LO), one can propose completely new design of phonon-assisted optoelectronic devices. In quantum well structure devices [19,20], for instance, the wells can be made porous. This will allow one to use the Fröhlich-vibration-assisted tunnelling as an operating principle, taking the advantage of the unique possibility to control this process by optical means.

B. Applications Related to Anisotropy, Optical Homogeneity and Ordered Distribution of Pores

Porosity changes drastically the optical properties of semiconductor materials. The formation of parallel pores stretching perpendicularly to the initial surface leads to a pronounced anisotropy in the material properties. As mentioned above, porous InP was found to exhibit birefringence at the wavelength of optical communication systems (λ = 1.55 μm) [6]. The value of the anisotropic refractive index in the directions parallel and perpendicular to the pore axis equals respectively 2.82 and 2.66, which is 10-20 % lower than the refractive index of bulk InP (3.17).

The possibility to control the morphology and porosity of III-V compounds at high density of pores seems to be a strategy for a variety of applications. First, in spite of the statistical distribution of pores, the relatively small dimensions of both pores and skeleton entities make the porous material optically homogeneous and the light propagates through it without scattering (since the wavelength is much greater than the characteristic dimensions of pores and skeleton, it "sees" a homogeneous medium). The degree of porosity defines the value of refractive index and, in case of a uniform distribution of parallel pores, the optical anisotropy of structures which can be easily integrated in optoelectronic systems.

Recently the porosity-based approach was found to meet the requirements for fabricating infrared (5 μm) photonic band-gap material on crystalline Si [4]. In that case usual photolithography was used to define the ordered distribution of etching pits. Taking into account the E_g value of GaP, it may be considered as a promising material for manufacturing photonic band-gap structures covering the near infra-red and red/green regions. A combination of electron beam lithography with the possibility for leaving flat surfaces of definite orientations after anodic etching would be of particular interest for designers of new photonic band-gap materials.

It is important to note that the photonic band-gap structures on III-V materials may find different microwave applications, in particular as perfectly reflecting substrates for planar dipole antennas [21].

C. Surface-Enhanced Phenomena and Luminescence

Along with the ability to support Fröhlich-type surface-related vibrations, porous GaP was found to exhibit a high nonlinear response. In fact, μm-thick porous membranes show SHG signals of the same order of magnitude as bulk samples. The nonlinear optical processes on the surface seem to be enhanced by the excitation of surface phonon-polaritons since the coupling between light and lattice vibrations often leads to the formation of mixed light-polarization states. Fig. 7 shows the SHG rotation dependence for a (111)-oriented membrane of porous gallium phosphide (a Q-switched Nd-YAG laser was used as a pump beam source). It reflects adequately the crystallographic features of (111)-oriented GaP demonstrating the high crystalline quality of the porous skeleton.

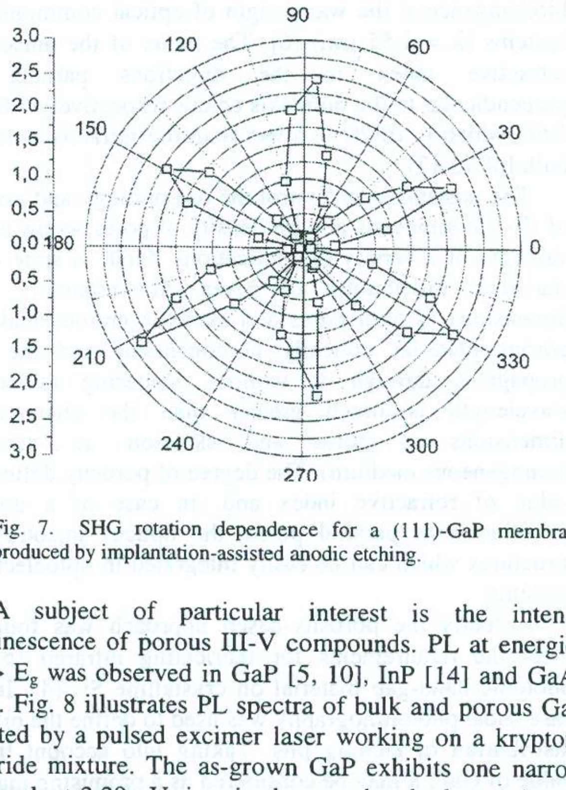

Fig. 7. SHG rotation dependence for a (111)-GaP membrane produced by implantation-assisted anodic etching.

A subject of particular interest is the intense luminescence of porous III-V compounds. PL at energies $h\nu > E_g$ was observed in GaP [5, 10], InP [14] and GaAs [22]. Fig. 8 illustrates PL spectra of bulk and porous GaP excited by a pulsed excimer laser working on a krypton-fluoride mixture. The as-grown GaP exhibits one narrow PL peak at 2.29 eV, i.e., in the near-band-edge region of GaP. The spectrum of porous gallium phosphide consists of several bands which cover a wide spectral range from 2 to 4 eV. Apart from the peak at 2.29 eV and a wide band with the maximum at 2.7 eV, UV structures are observed. The occurrence of several UV peaks may be attributed to the size distribution of quantum structures in porous GaP. An important advantage of short-wavelength PL in porous GaP in comparison with that of porous Si is the high stability with time. It is obvious, however, that further efforts are required in order to evidence the nature of the emission and to develop high-efficiency light-emitting device structures.

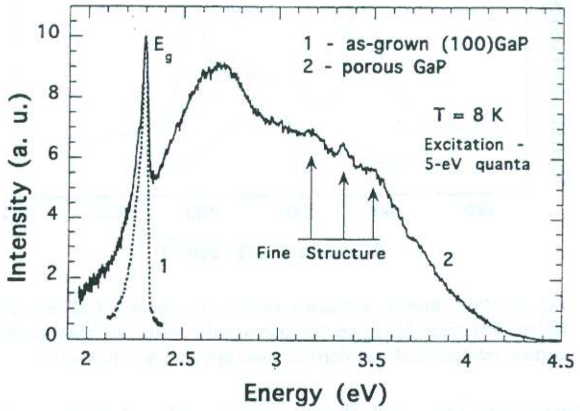

Fig. 8. PL spectra of bulk GaP and porous layer fabricated by implantation-assisted anodization.

V. CONCLUSION

We have developed technological conditions for producing porous membranes and heterostructures based on III-V compounds. Anodic etching of pre-implanted or in-situ illuminated substrates was found to be promising for the purpose of manufacturing optically-transparent free-standing porous membranes for different schemes of optoelectronic application. The porosity-based approaches show the exciting possibilities for engineering the band gap, refractive index, phonon spectrum, emission and nonlinear optical characteristics.

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