APPLICATIONS OF POROUS III-V SEMICONDUCTORS IN HETEROEPITAXIAL GROWTH AND IN THE PREPARATION OF NANOCOMPOSITE STRUCTURES
Dušan NOHAVICA\textsuperscript{a,b}, Jan GRYM\textsuperscript{a}, Petar GLADKO\textsuperscript{a,b}, Eduard HULICIUS\textsuperscript{b}, Jiří PANGRAC\textsuperscript{b}

\textsuperscript{a}Institute of Photonics and Electronics, ASCR, Chaberska 57, 182 51, Prague 8, Czech Republic
\textsuperscript{b}Institute of Physics ASCR, Cukrovarnicka 10/112, 162 00 Praha 6, Czech Republic

nohavica@ufe.cz

Abstract
Semiconductor epitaxial growth has progressed to pseudomorphic, lattice mismatched systems where a small amount of strain is accommodated in very thin layers. We investigate the concept of epitaxial growth on porous substrates, which can lead to the increased critical layer thickness and reduction of the density of threading dislocations. Both crystallographically oriented and current line oriented pore networks in InP and GaAs were created by electrochemical dissolution. Heat treatment of InP pores at 650 °C and GaAs pores at 700-850°C converted them into microcavities. The capability of improved structural quality homo- and heteroepitaxially overgrown films is demonstrated on InAs and GaInAs layers with a different composition grown on porous GaAs substrates. Another important application of porous semiconductors is related to the preparation of nanocomposite structures.

Keywords: Porous III-V semiconductors, Electrochemical etching, Pore conversion, Heteroepitaxial growth.

INTRODUCTION
A study of the heat treatment of micropores and their technological applications has not been thoroughly described in the literature yet. Transformation of both current-line oriented (CLO) and crystallographically oriented (CO) types of pores into microcavities was briefly discussed in Ref.[1], where micropores anodized at the InP surface were overgrown by the liquid phase epitaxy (LPE). Potential applications of such porous substrates in heteroepitaxial growth are promising since the resulting structures may present quite improved properties without the requirement of any graded transition layers or significantly extended nucleation barriers during growth. Furthermore, a detailed investigation of the pore interaction with strain fields and/or structural defects existing in the materials is of considerable interest.

1. EXPERIMENTAL
Two types of pores are formed during the process of electrochemical dissolution: (i) CO pores alongside the principal crystallographic axes and (ii) CLO alongside the applied electric field, Ref.[2]. Anodized micropores in InP substrates were produced at different conditions to realize: (i) CO micropores with pore orientations in [111], [221], and [322] directions, (ii) CLO micropores or (iii) their combination. Heat treatment of porous InP samples was realized in liquid phase epitaxy apparatus in hydrogen atmosphere under phosphorus overpressure. This overpressure was necessary at temperatures higher than 360 °C. Within 60 minutes at 640 °C, both CO and CLO pores produced hollow figures of different shapes. The correspondence between the orientation of CO pores and the final spherical figures (microbubbles) is evident. We suppose that Ostwald ripening connected with mass transport works as a transformation mechanism. Similar behaviour is observed in CLO pores, where spherical figures are vertically oriented. Pore anodization in GaAs was realized with the same experimental set up as in InP (see Fig. 1). Different electrolytes and intensities of illumination of the etched GaAs surfaces were tested. The best results were observed with the electrolyte containing diluted HF and KI. The HF electrolyte was originally used in Ref.[3]. The porous GaAs as well as InP layer retained single-crystalline structure of the initial monolithic substrate and had a mirror-smooth (InP) or pierced (GaAs) surfaces suited for epitaxial growth. Initial structures of the anodized GaAs plate and the structures after heat treatment at 850 °C are similar as in InP only the mass transport velocity is slower.
1.1. Epitaxial growth on porous substrates

InAs and InGaAs layers were prepared in an EpiRAS 200 TT equipped AIXTRON 200 machine by...
LP-MOVPE on Si doped GaAs substrates with (100) exact orientation. TMGa, TMIn and arsine were used as precursors. The following technological parameters were used: total growth pressure 70 hPa and H2 total flow 8 slpm. Prior to growth, substrate temperature was increased to 700°C for 5 min under arsine flow. The growth temperature of 560°C was used for both InGaAs and InAs layer growth. The partial pressure of the group III precursors was 0.3 Pa with the V/III ratio of 230. The epitaxial growth of GaxIn1-xAs (up to x~0.2) on porous GaAs substrates demonstrates the changes in the surface morphology (see Fig. 2). Instead of regular cross hatching observed on monolithic substrates, the morphology on porous substrates was similar to the one observed on homoepitaxial GaAs on porous substrates. At large lattice mismatch approaching 3.6 %, the surface “scales” were more pronounced. When the growth temperature exceeds 700 °C the pores do not annihilate unlike in InP. This observation corresponds to crucial influence of the mass transport velocity on pore annihilation at high stress conditions observed by us during LPE growth of InAs on InP. Cross-sectional images of the GaInAs (x=0.5) and InAs on porous GaAs substrates are documented in Fig.3 and surface morphologies of the InAs grown on porous and nonporous GaAs substrates are in Fig.4.

![Cross-sectional SEM image of the heteroepitaxial MOVPE layers of the GaInAs (x=0.5), (a/) and pure InAs on porous GaAs substrates (b/).](image)

![Surface morphology of the InAs grown on porous (a/) and nonporous (b/) GaAs substrate](image)

1.2. Photoluminescence measurements

Fig. 5 compares the PL spectra from InAs layers grown on porous GaAs substrates prepared at three different pores growth conditions and the PL from a reference sample. In Fig.6 the same comparison is demonstrated for GaInAs (x=0.5) grown on porous and reference (nonporous) GaAs substrates. The PL measurements were conducted at 4 K using a closed cycle He-cryostat. The PL was recorded with FTIR
spectrometer equipped with liquid nitrogen cooled InSb detector. The PL excitation density at 653 nm was 5 W/cm².

The following specific features have to be mentioned:
1. All PL spectra are recorded in identical experimental conditions
2. The PL Spectra have a composite character with at least three indicated components.
3. The reference sample shows the lowest integral luminescence compared to the layers grown on porous substrates.
4. The PL spectrum from samples 631 and 628 shows the highest integral intensity.

Fig. 5. PL spectra of InAs grown on three porous and one monolithic GaAs substrates. Luminous efficiency of the InAs layers grown on porous substrates is higher in comparison with nonporous-reference GaAs.

Fig. 6. PL spectra of In₀.₅Ga₀.₅As grown on porous and monolithic GaAs substrates. Luminous efficiency of the layers grown on porous substrates are higher in comparison with nonporous-reference GaAs.

Fig. 7. presents the deconvolution of the PL spectrum from the sample with four Gaussians. A consistent identification of the bands according to the known literature data is as follows: a/the band peaking at 0.404
eV originates from band to Sn-acceptor transitions; b/ the band with maximum at 0.396 eV is due to transitions donor-acceptor impurity bands; c/ the band at 0.384 eV correlates with the identification of PL from a deep impurity or defect related impurities. d/ with account to the uncertainty introduced by the deconvolution of the PL spectrum, the band with peak at 0.372 eV we identify as LO-phonon replica (LO-phonon 29.5 meV) of the band with maximum at 0.396 eV.

**CONCLUSION**

Preparation of porous substrates and their epitaxial overgrowth is a multifactorial process with large amounts of variables. We have been able to control the process of pore formation in GaAs and achieved different pore morphologies. Preparation of dense porous networks – and control over their conversion during the heat treatment in particular – is different in comparison with InP. Our results support the claim that porous substrates have potential to improve the structural quality of the deposited epitaxial layers, however a lot of work has to be done to gain full control over the all technological steps. At very high lattice misfit in InAs/GaAs the strain induced surface roughening as the dominant structural relaxation mechanism. Improvement of the PL intensities of the InAs and GaInAs, x=0.5 on porous versus conventional GaAs substrate could be explained by injection of dislocation loops deep to the softer porous substrates or by dislocations annihilation in pores (internal diameter is <100 nm).

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**REFERENCES**


