

POROSIFICATION OF NARROW AND WIDE BAND GAP SEMICONDUCTOR COMPOUNDS: COMPARATIVE STUDY OF InAs, InP AND ZnSe

Eduard Monaico^{1,2}, I.M. Tiginyanu^{2,3}, V.V. Ursaki⁴, G. Colibaba⁵, D.D. Nedeoglo⁵,
A. Cojocaru⁶, and H. Föll⁶

¹⁾ Institute of Applied Physics, University of Hamburg, Jungiusstr. 11, 20355 Hamburg, Germany

²⁾ National Center for Materials Study and Testing, Technical University of Moldova, MD-2004 Chisinau, Moldova

³⁾ Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

⁴⁾ Institute of Applied Physics, Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova

⁵⁾ State University of Moldova, MD-2009 Chisinau, Moldova

⁶⁾ Faculty of Engineering, Christian-Albrechts-University of Kiel, 24143 Kiel, Germany
m_eduard_y@yahoo.com

Abstract. *A comparative study of the pore growth during anodization of a narrow-bandgap III-V compound (InAs), a medium-bandgap III-V compound (InP) and a wide-bandgap II-VI semiconductor (ZnSe) is performed. It was found that the morphology of the porous layers can be controlled by the composition of the electrolyte and the applied electrochemical parameters. Difficulties in controlling the mechanism of pore growth in InAs were evidenced. Both current-line-oriented pores and crystallographically oriented pores can be produced in InP, while only current-line-oriented pores can be obtained in ZnSe.*

Keywords: *porous layer, anodization, current-line-oriented pores, crystallographically oriented pores, ionicity degree.*

I. Introduction

Electrochemistry is a cost-effective tool for introducing porosity in semiconductors, including III-V and II-VI materials, and offers an accessible and cost-effective approach for “drilling” holes in semiconductor materials. A variety of porous semiconductor structures have been produced by electrochemical etching of InP, GaP, GaAs, CdSe and ZnSe [1-4]. Porosity is an effective tool for engineering basic parameters of semiconductor materials [5]. Porous III-V and II-VI compounds are less investigated as compared with porous Si [6,7]. In particular, porous materials were found to exhibit Fröhlich-type surface-related vibrations with porosity-tunable frequencies and efficient optical second harmonic generation [8-10]. Most experiments investigating emission characteristics of porous III-V materials have been restricted to photoluminescence. The photoluminescence of porous GaP, GaAs and InP at energies above the band gap of the bulk material has been attributed to quantum size effects.

InAs is a material with crystal structure of Zinc Blende type and energy gap $E_g = 0,35$ eV. The indium containing narrow-gap III-V semiconductors such as InAs and InSb play an important role for many potential applications in photonic and electronic devices. Their electronic characteristics (high carrier mobility and saturation drift velocities, band gap in the infrared region of the spectrum, and low effective masses) make these materials attractive for infrared detectors and emitters as well as for high-speed electronic devices.

One of the key problems with electrochemical methods of introducing porosity in semicon-

ductor materials is the appropriate choice of the electrolyte composition. This problem is solved individually for each material. Due to the small band gap of InAs it is very difficult to subject these samples to nanostructuring via electrochemical etching technique. Nevertheless, the formation of InAs micro- and nano-pencils was reported. It was found that pulsed anodization in a mixture of $\text{H}_3\text{PO}_4:\text{HNO}_3$ in proportion 1:1 leads to the nanostructuring of InAs surfaces and the authors succeeded to demonstrate their application in field emitters [11]. However, the obtained structures are inhomogeneous. Later, the nanostructuring of InAs substrates in NaCl electrolyte and comparative study of morphology of etched InAs crystals in this environmental friendly electrolyte and electrolyte based on acids at pulsed potential was reported [12]. These results demonstrated that the nature of the electrolyte does not influence significantly the morphology of the porous structures.

II. Experimental

The studied materials are (100) oriented n-type InAs, InP and ZnSe substrates with free carrier concentration $n=3 \cdot 10^{17} \text{ cm}^{-3}$ at 300 K. Before the anodization process, the samples were degreased in acetone, ethanol and rinsed in distilled water. An electrical contact was made on the backside of the anodized crystal with a silver paint. The copper rod and edges of the crystal were insulated from the solution with nonconductive epoxy. The anodization of InAs substrates was carried out in 2M and 4M KOH aqueous solutions at room temperature ($T = 25^\circ\text{C}$). A potentiostat was used, capable to deliver up to 1 A and 100 V. The anodization of ZnSe crystals was performed in a $\text{K}_2\text{Cr}_2\text{O}_7:\text{H}_2\text{SO}_4:\text{H}_2\text{O}$ electrolyte as described in [4], and InP was anodized in an aqueous solution of HCl as described in [5]. After etching the morphology and chemical composition microanalysis of samples have been investigated by TESCAN Vega TS 5130MM Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV.

III. Results and discussion

Figure 1a presents the top view morphology of an InAs porous layer anodized in 2M KOH aqueous solution. A potential of 35 V was applied between the sample and the Pt electrode for 5 min. The electrolyte was stirred during the experiment to ensure the recovery of electrolyte concentration at the electrolyte-semiconductor interface. The sample was analyzed in cross-section in order to estimate the deepness of the produced porous layer (see Fig. 1b). At these etching parameters the thickness of the obtained porous InAs layer is around 1 μm .

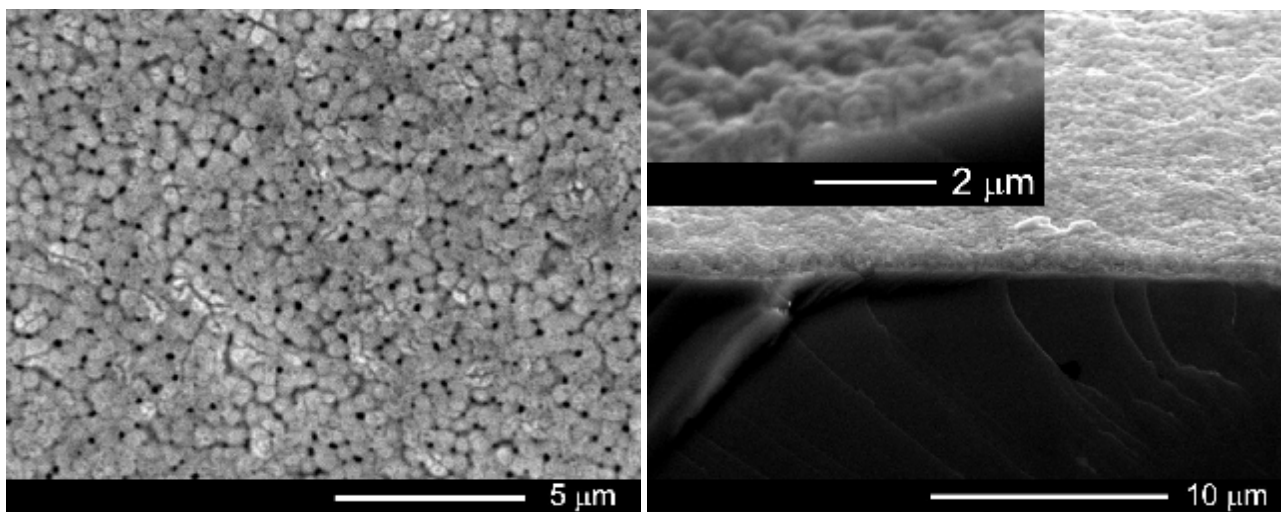


Fig. 1. SEM images of InAs samples etched in 2M KOH: top view (a) and cross sectional view (b).

Figure 2 shows the results of anodization with the same value of the applied potential and the same duration of electrochemical etching, but carried out in 4M KOH electrolyte. The resulted diameter of pores is about 250 nm and the thickness of the pore walls was estimated to be as high as 80 nm.

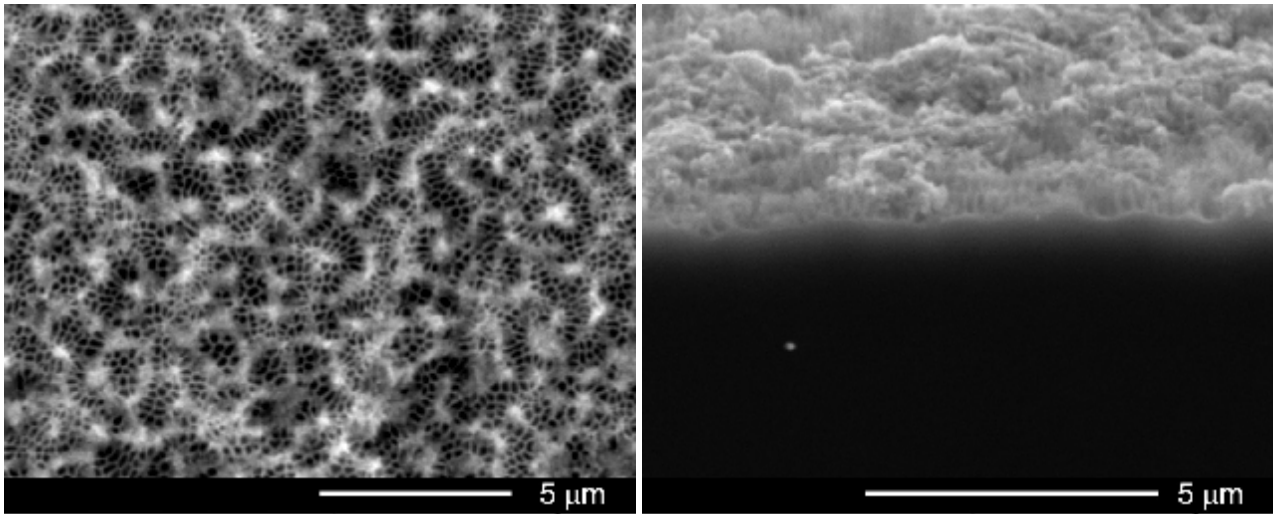


Fig.2. SEM images of indium arsenide samples etched in 4M KOH, top view (a) and cross sectional view (b).

The composition of the films and the atomic ratio of In to As in the etched samples were investigated by EDX measurements. The diameter of the focused electron beam in the EDX analysis is about 100 nm, and the scanning area is of $5\mu\text{m}\times 5\mu\text{m}$. The EDX measurements demonstrated that the chemical composition of the porous InAs skeleton is stoichiometric. Therefore, the morphology of the porous InAs layer can be controlled by the composition of the electrolyte and the applied electrochemical parameters. However, it is difficult to control the mechanism of the pore growth and to produce deep porous layers with uniform porosity, since isotropic electrochemical etching occurs simultaneously with the pore growth process in narrow band gap semiconductors.

It was previously reported [13] that current-line and crystallographically oriented pores can be grown in III-V semiconductors, whereas in II-VI (e.g. ZnSe and CdSe) semiconductors only current line oriented pores can be produced. The impossibility for formation of crystallographically oriented pores in II-VI compounds is a reasonable explanation of the absence of long-range order of current-line oriented pores in these materials if one takes into account the model for the formation of pores proposed previously [5]. The absence of crystallographically oriented pores can be explained by the type of atomic bonds in these semiconductors. Covalent tetrahedral bonds due to sp_3 hybrid orbitals are inherent to elemental semiconductors such as Si and Ge. Tetrahedral bonds are also inherent to compound semiconductors. However, these bonds can be both covalent and ionic, since the compound semiconductors consist of atoms with different electronegativities. Table 1 presents the atom electronegativity difference for some semiconductor compounds calculated by Pauling's law [14].

The electronegativity is an indicative of the strength with which atoms attract electrons. The difference of electronegativities of the constituent elements is therefore an indicative of the ionicity as shown in Table 1 [15]. The higher is the ionicity, the stronger is the attraction between the atoms. One can see from Table 1 that the degree of ionicity of III-V semiconductor compounds is lower as compared to that inherent to II-VI compounds. As a result, crystallographically oriented pores can be obtained in III-V compounds in contrast to II-VI compounds.

Table 1. Values of electronegativity difference and degree of ionicity in II-VI and III-V semiconductor compounds.

Compounds	II-VI					III-V				
	ZnO	ZnS	CdS	ZnSe	CdSe	InP	InAs	GaAs	InSb	GaP
Electronegativity difference	2	1	1	0,9	0,9	0,6	0,5	0,5	0,3	0,32
Ionicity [%]	63	22	22	19	19	11	9	9	2	2

Figure 3 presents SEM images of electrochemically etched ZnSe and InP crystals under conditions when the anodization potential is intentionally changed during the pore growth. It is evident from Fig. 3b that a change of the applied potential during anodization from high to low value leads to a switch in the pore growth mechanism from current-line oriented pores to crystallographically oriented pores. In contrast to this, the change in the applied potential for ZnSe single crystals does not change the pore growth mechanism, current-line oriented pores being produced under both high and low values of the applied potential (see also Refs. 16-18).

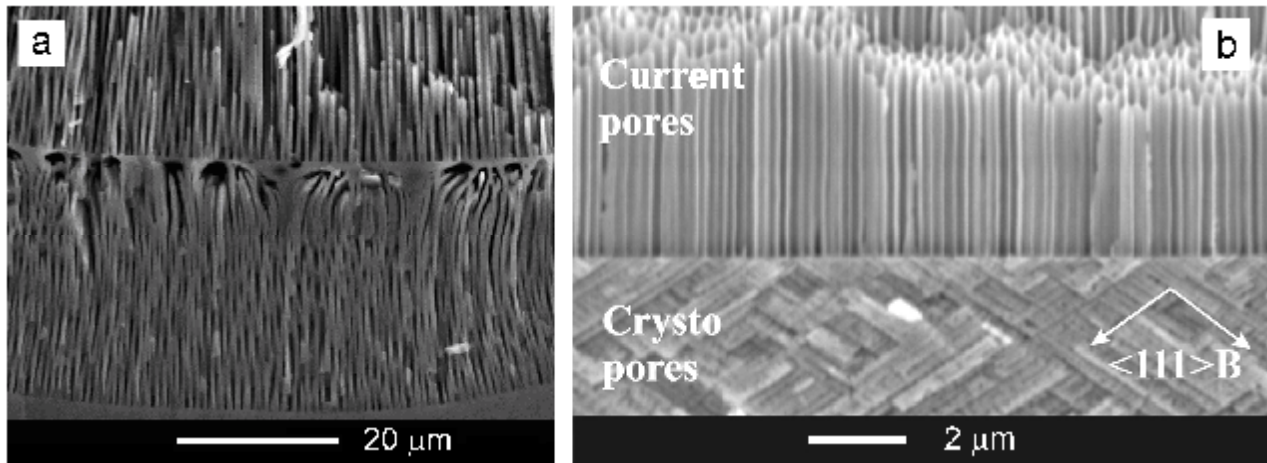


Fig. 3. SEM image of porous ZnSe (a) and InP (b) layers anodized at different values of the applied potential

IV. Conclusions

The results of this study demonstrate that, apart from the composition of the electrolyte and the technological conditions applied for porosification, the mechanism of pore growth is strongly dependent upon the parameters of the anodized material, particularly by the ionicity of the material. The morphology of the porous InAs layer can be controlled by the composition of the electrolyte and the applied electrochemical parameters. However, it is difficult to control the mechanism of pore growth in InAs since uniform electrochemical etching proves to occur simultaneously with the pore growth in narrow band gap semiconductors. On the other hand, the pore growth mechanism in wide-band gap semiconductors is determined by the difference in the values of electronegativity of the constituent atoms and the degree of ionicity. Since the degree of ionicity of III-V semiconductor compounds is lower as compared to that inherent to II-VI compounds, both current-line-oriented pores and crystallographically oriented pores can be produced in InP, while only current-line-oriented pores can be obtained in ZnSe.

V. Acknowledgments

This work was supported financially by the Alexander von Humboldt Foundation and by the Supreme Council for Research and Technological Development of the Academy of Sciences of Moldova under the State Program on “Nanotechnologies and Nanomaterials”.

VI. References

1. Tiginyanu I.M., Langa S., Sirbu L., Monaico E., Stevens-Kalceff M.A. and Föll H. Cathodoluminescence microanalysis of porous GaP and InP structures. *European Physical Journal – Applied Physics*, Vol. 27, 2004, pp. 81-84.
2. Tiginyanu I.M., Monaico E., Ursaki V.V., Tezlevan V.E. and Boyd Robert W. Fabrication and photoluminescence properties of porous CdSe. *Applied Physics Letters*, Vol. 86, 2005, 063115.
3. Tiginyanu I.M., Ursaki V.V., Monaico E., Foca E., and Föll H. Pore Etching in III-V and II-VI Semiconductor Compounds in Neutral Electrolyte. *Electrochem. Solid-State Lett.*, Vol. 10, Issue 11, 2007, pp. D127-D129.
4. Monaico E., Tighineanu P., Langa S., Hartnagel Hans L. and Tiginyanu I.M. ZnSe-based conductive nanotemplates for nanofabrication. *Phys. Stat. Sol. (RRL)*, Vol 3, No 4, 2009, pp. 97-99.
5. Föll, H., Langa, S., Carstensen, J., Christophersen, M. and Tiginyanu, I.M. Pores in III-V Semiconductors. *Adv. Mater.*, Vol. 15, 2003, pp. 183–198.
6. Lehman V. *Electrochemistry of silicon*. Wiley-VCH, Weinheim, 2002.
7. Genereux F., Leonard S.W., H.M. van Driel, Birner A. and Gösele U. Large birefringence in two-dimensional silicon photonic crystals *Phys. Rev. B* Vol. 63, 2001, 161101.
8. Sarua A., Monecke J., Irmer G., Tiginyanu I.M., Gärtner G., Hartnagel H.L. Fröhlich modes in porous III–V semiconductors. *J. Phys.: Condens. Matter* Vol. 13, 2001, pp. 6687-6706.
9. Tiginyanu I.M., Kravetsky I.V., Monecke J., Cordts W., Marowsky G., Hartnagel H.L. Semiconductor sieves as nonlinear optical materials. *Appl. Phys. Lett.* Vol. 77, 2000, pp. 2415-2417.
10. 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. *Journal of Physics D: Applied Physics*, Vol. 42, 2009, 045405.
11. Litovchenko V., Evtukh A., Semenenko M., Grygoriev A., Yilmazoglu O., Hartnagel H.L., Sirbu L., Tiginyanu I.M. and Ursaki V.V. Electron field emission from narrow band gap semiconductors (InAs). *Semiconductor Science and Technology*, Vol. 22, 2007, pp. 1092-1096.
12. Sirbu L., Ursaki V.V., Monaico E. and Tiginyanu I.M. Electrochemical porosification of InAs substrates. *Proceedings of the 5th International Conference on Microelectronics and Computer Science*, Vol. 1, pp. 95-98. September 19-21, 2007, Chisinau, Republic of Moldova.
13. Langa S., Tiginyanu I. M., Monaico E. and Föll H. Porous II-VI vs. porous III-V semiconductors. *Physica status solidi (c)*, Vol. 8, 2011, pp. 1792–1796.
14. Pauling L. *The nature of the Chemical Bond*. Cornell University Press, New York, 1960.
15. Osamu Oda. *Compound Semiconductor Bulk Materials and Characterizations*. World Scientific, 538 Seiten, 2007, pp. 3-6.

16. Christophersen M., Langa S., Carstensen J., Tiginyanu I.M. and Föll H. Porous III-V compound semiconductors: formation, properties, and comparison to silicon. *Phys. Status Solidi A*, Vol. 197, 2003, pp. 197-203.
17. Tiginyanu Ion, Monaico Elena, and Monaico Eduard. Ordered arrays of metal nanotubes in semiconductor envelopes. *Electrochemistry Communications*, Vol. 10, 2008, pp. 731-734.
18. Tiginyanu I. M., Ursaki V. V., Monaico E., Enachi M., Sergentu V. V., Colibaba G., Nedeoglo D. D., Cojocar A., and Föll H. Quasi-ordered networks of metal nanotubes embedded in semiconductor matrices for photonic applications. *Journal of Nanoelectronics and Optoelectronics*, Vol. 6, 2011, pp. 463-472.