Comparative study of porosification in InAs, InP, ZnSe and ZnCdS

Eduard MONAICO[1,2], Ion TIGINYANU[2,3], Kornelius NIELSCH[1], Veaceslav URSAKI[4], Gleb COLIBABA[5], Dmitrii NEDEOGLO[5], Ala COJOCARU[6], and Helmut FÖLL[6]

[1] *Institute of Applied Physics, University of Hamburg, 20355 Hamburg, Germany*

[2] *National Center for Materials Study and Testing, Technical University of Moldova, MD-2004 Chisinau, Republic of Moldova*

m_eduard_y@yahoo.com, Kornelius.Nielsch@physik.uni-hamburg.de

[3] *Institute of Electronic Engineering and Nanotechnologies, Academy of Sciences of Moldova, MD-2028 Chisinau, Republic of Moldova*

tiginyanu@asm.md

[4] *Institute of Applied Physics, Academy of Sciences of Moldova, MD-2028 Chisinau, Moldova*

ursaki@yahoo.com

[5] *State University of Moldova, MD-2009 Chisinau, Republic of Moldova*

GKolibaba@yandex.ru, nedeoglo@usm.md

[6] *Faculty of Engineering, Christian-Albrechts-University of Kiel, 24143 Kiel, Germany*

alasprin@yahoo.com, kb@tf.uni-kiel.de

Abstract — **We report on a comparative study of the pore growth during anodization of a narrow-bandgap III-V compound (InAs), a medium-bandgap III-V one (InP) and wide-bandgap II-VI semiconductors (ZnSe and $Zn_{0.4}Cd_{0.6}S$). According to the obtained results, the morphology of the porous layers can be controlled by the composition of the electrolyte and the applied electrochemical parameters. It was evidenced that in the narrow bandgap semiconductor InAs it is difficult to control the mechanism of pore growth. Both current-line oriented pores and crystallographically oriented pores were produced in the medium-bandgap material InP. The electrochemical nanostructuring of wide-bandgap semiconductors realized in single crystalline high-conductivity samples evidenced only current-line oriented pores. This behavior is explained in terms of difference in the values of electronegativity of the constituent atoms and the degree of ionicity.**

Index Terms — **anodization, crystallographically oriented pores, current-line-oriented pores, ionicity degree, porous layer.**

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 have been 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 [8] and efficient optical second harmonic generation [9,10]. 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 of 0.35 eV. The indium containing narrow-gap III-V semiconductors such as InAs and InSb may have 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 semiconductor materials is the appropriate choice of the electrolyte composition. This problem is solved individually for each material. Due to the narrow band gap of InAs it is very difficult to reach nanostructuring in this compound via electrochemical etching techniques. Nevertheless, the formation of InAs micro- and nano-pencils was reported [11]. It was found that pulsed anodization in a mixture of H_3PO_4:HNO_3 in proportion of 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 a NaCl electrolyte was realized and the results of a comparative study of the morphology of etched InAs crystals in this environmental friendly electrolyte and electrolyte based on acids at pulsed potential were reported [12]. The obtained results demonstrated that the nature of the electrolyte does not

influence significantly the morphology of the InAs porous structures.

II-VI semiconductors are prospective candidates for nanotemplates taking into account their large bandgap, high electron mobility, transparency in the visible region of the spectrum etc. ZnS is a relatively large band-gap II-VI compound (E_g=3.6 eV at 300 K) and has prominent luminescence proprieties that opens opportunities to use it in optoelectronics and photonics. However, electrical parameters of this material are not as good as those of the other compounds of the same group. The maximum concentration of free charge carriers in n-ZnS is less than 10^{17} cm^{-3} because of the compensation effect, and this material has extremely high contact resistance due to surface states [13, 14]. In case of CdS (E_g ~ 2.4 eV), it is easy to obtain the concentration of free charge carriers up to 10^{20} cm^{-3} [13]. As a result, ZnCdS solid solution crystals are of great interest, because they may have wider band-gap and good electrical parameters necessary for efficient electrochemical treatment.

II. EXPERIMENTAL

The studied materials are (100) oriented n-type InAs, InP and ZnSe substrates with free carrier concentration $n=3\cdot10^{17}$ cm^{-3} at 300 K. To obtain ZnSe crystals with carrier concentration of $3\cdot10^{17}$ cm^{-3}, the substrates were subjected to annealing in a Zn+Al melt with a content of 30 % of Al at 950 °C for 100 h, as described elsewhere [10,15].

$Zn_{0.4}Cd_{0.6}S$ single crystals were grown by physical vapor transport using HCl as transport agent. The as grown ZnCdS:Cl crystals possess high resistivity (>10^8 $\Omega\cdot$cm) that was decreased by annealing in Zn + Cd vapors. The electrical parameters of $Zn_{0.4}Cd_{0.6}S$ samples are as follows: concentration of charge carriers is $2\cdot10^{18}$ cm^{-3}, electrical conductivity is 20 $(\Omega\cdot cm)^{-1}$, and mobility of charge carriers is 70 $cm^2/(V\cdot s)$.

Before the anodization process, the InAs 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°C). A potentiostat capable to deliver up to 1 A and 100 V was used. The anodization of ZnSe crystals was performed in a $K_2Cr_2O_7$:H_2SO_4:H_2O electrolyte as described in [4]. InP and $Zn_{0.4}Cd_{0.6}S$ crystals were anodized in an aqueous solution of 5 % HCl as described in [5]. After etching the morphology and chemical composition microanalysis of samples have been investigated by Scanning Electron Microscope (SEM) TESCAN Vega TS 5130MM equipped with an Oxford Instruments INCA Energy EDX system and Zeiss Sigma operated at 20 kV.

III. RESULTS AND DISCUSSIONS

Figure 1a presents the top view morphology of 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. 1a). At these etching parameters the thickness of the obtained porous InAs layer is around 1 μm.

With increasing the electrolyte concentration, the morphology can be essentially changed in sense of the increased porosity (see Fig. 1b). However, it is difficult to grow thick porous InAs layers, since uniform electrochemical dissolution proves to occur simultaneously with the pore growth.

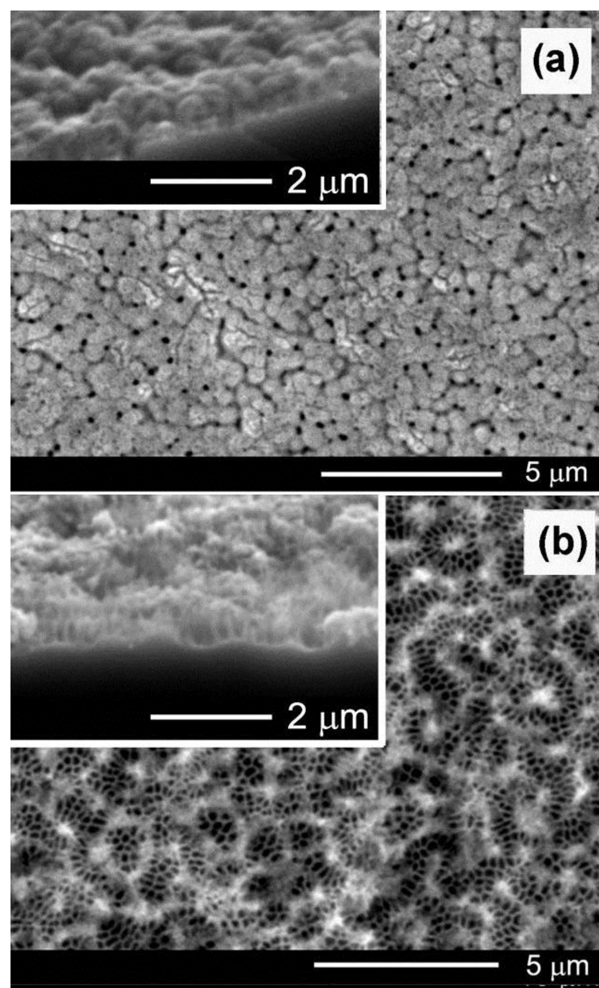

Fig: 1 SEM images of InAs samples etched during 5 minutes with an applied potential of 35 V: in a 2M KOH solution (a) in a 4M KOH solution (b). Inserted is the cross sectional view.

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 μm x 5μm. 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 thick porous layers with uniform porosity, since isotropic electrochemical etching occurs simultaneously with the pore growth process in narrow band gap semiconductors.

In premiere, $Zn_{0.4}Cd_{0.6}S$ crystals were subjected to the electrochemical etching. This composition was chosen, since its bandgap is nearly equal to that of ZnSe. The polarization curve measured for $Zn_{0.4}Cd_{0.6}S$ crystals, see the insert in Fig. 2, shows that the formation of pores starts at voltage around 5 V. The characteristic size of the obtained porous structure can be changed by the applied voltage and it increases up to around 30 nm with the increase of the applied voltage up to 18 V (see Fig. 2).

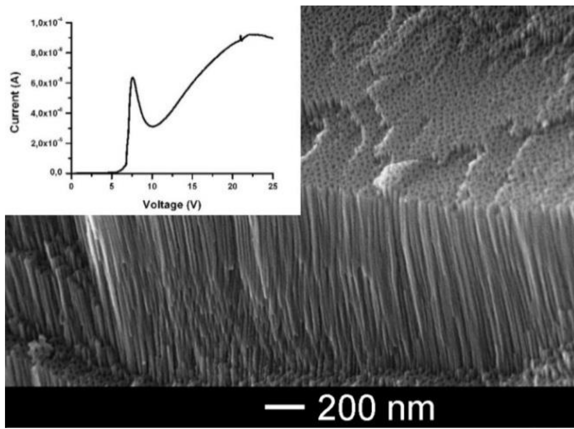

Fig.2 SEM image of porous $Zn_{0.4}Cd_{0.6}S$ layer anodized in a 5 % HCl electrolyte with an applied potential of 18 V. Inserted is the polarization curve measured at the beginning of electrochemical etching.

It was previously reported [16] 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. This observation is corroborated by the present investigation of the pore growth in $Zn_{0.4}Cd_{0.6}S$ crystals. The impossibility of growth of the crystallographically oriented pores in II-VI compounds is a reasonable explanation of the absence of long-range order in the spatial distribution 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 [17].

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

	II-VI					III-V				
Compound	ZnO	ZnS	CdS	ZnSe	CdSe	InP	InAs	GsAs	InSb	GaP
Electro-negativity 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

The electronegativity is an indicative of the strength with which atoms attract electrons. The difference in electronegativities of the constituent elements is therefore an indicative of the ionicity, as shown in Table 1 [18]. 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.

Figure 3 presents SEM images of electrochemically etched InP, ZnSe and $Zn_{0.4}Cd_{0.6}S$ crystals with the anodization potential intentionally changed during the pore growth.

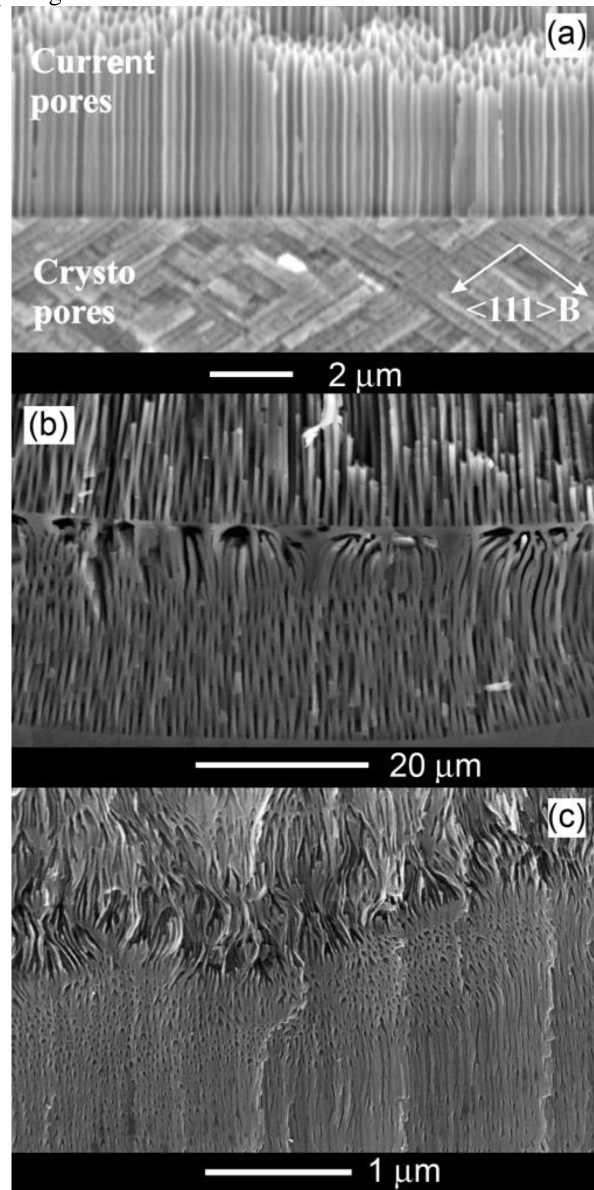

Fig. 3 SEM image of porous InP (a), ZnSe (b), and $Zn_{0.4}Cd_{0.6}S$ (c) layers anodized with changing the applied potential [from 7 V to 1 V in (a); from 15 V to 13 V in (b); and from 18 V to 16 V in (c)].

One can deduce from Fig. 4 that changing the applied potential from 18 V to 16 V during the anodization of $Zn_{0.4}Cd_{0.6}S$ crystals leads to the change of the mean pore diameter from 30 nm to around 15 nm.

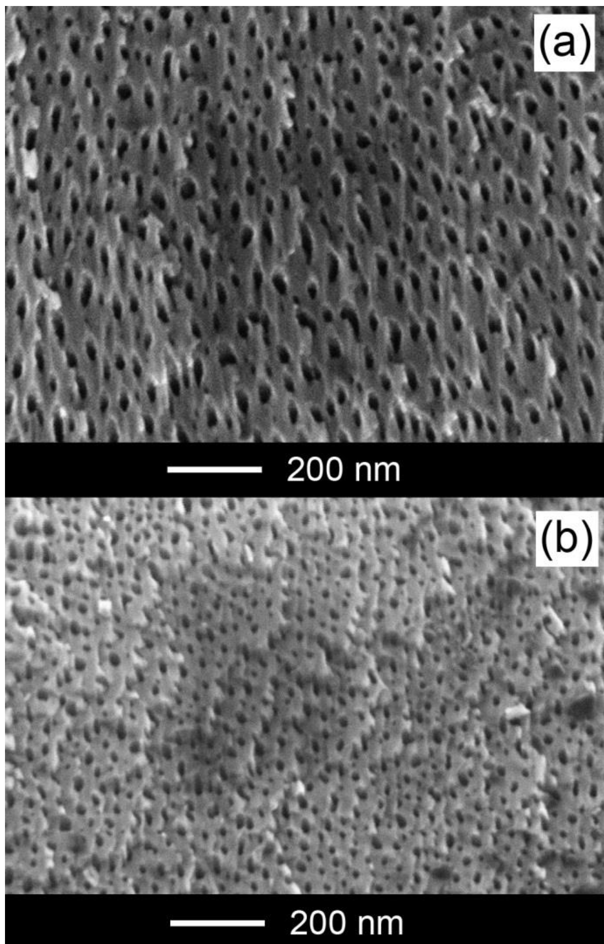

Fig. 4 SEM image of porous Zn0.4Cd0.6S (c) layers anodized with the applied voltage of 18 V (a) and 16 V (b) illustrating the change of the pore diameter.

IV. CONCLUSION

The results of this study demonstrate that the mechanism of pore growth is strongly dependent upon the parameters of the anodized material, particularly upon the ionicity of the material, in addition to the dependence on the composition of the electrolyte and the technological conditions applied for porosification. 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 bandgap semiconductors, therefore leading to the limitation of the achieved depth of the produced porous layer. 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 and $Zn_{0.4}Cd_{0.6}S$.

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