

Porous morphologies in Si, III-V and II-VI compounds: a comparative study

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Abstract

Porous morphologies obtained during the anodization of semiconductors are mainly determined by particular characteristics of the semiconductor-electrolyte interfaces and the bulk properties of the semiconductor itself. This paper discusses the types of porous structures obtained in Si, III-V and II-VI semiconductors: crystallographically oriented pores, current line oriented pores and fractal pores.

I. INTRODUCTION

Over the last decade, a great deal of research was focused on manufacturing and studying porous nanochannel-array semiconductor materials attractive for applications in photonics, micro- and optoelectronics, catalysis, separations and environmental-technologies. Considerable progress was achieved in semiconductor nanostructuring using electrochemical etching technique. This approach offers new possibilities for the fabrication of large area arrays of nanopores on semiconductor substrates, which in turn opens new ways for efficient optical phonon engineering and modification of luminescence properties, leads to occurrence of artificial birefringence, increased optical second harmonic generation and Terahertz emission, etc [1]. From the practical point of view, electrochemical etching technique is cost-effective, easy to implement and totally compatible with the state of the art microelectronic technology.

Morphology of porous layers obtained during the anodization of semiconductors [2, 3] is one of the main characteristics which must be investigated in detail before any other properties should be considered. By morphology of porous structures it is meant the form of pores as individual units and the structure of porous layers as a whole. The form of pores is characterized by the shape, size and the direction of pore growth. The morphology determines the main properties of the resulting porous structure and the most evident in this context are the mechanical properties, however, optical, electrical, and thermal properties can be influenced by morphology as well. Three types of pores have been

observed up to now in Si, III-V and II-VI semiconductors: crystallographically oriented pores (crysto), current line oriented pores (curro) [3] and fractal pores.

II. CRYSTALLOGRAPHICALLY ORIENTED PORES

Typical cross section and top views of crysto pores on (100) oriented substrates are presented in Fig. 1 and 2. Such pores are called crysto due to the fact that the direction of growth is a definite crystallographic direction. It can be observed that the crysto pores in Si are totally different from crysto pores in III-V semiconductors [4]. The typical crysto pores obtained in (100)Si grow perpendicular to the surface of the sample, i.e. along one [100] direction (Fig. 1a), whereas the crysto pores observed in III-Vs (Fig. 1b) grow along two $\langle 111 \rangle_B$ directions and form an angle of approximately 109° between them [5].

The difference between the crysto pores in Si and III-Vs is mainly caused by the anisotropy of III-V compounds. Namely, the difference in the dissolution rates between the so called $\{111A\}$ and $\{111B\}$ facets in III-V compounds strongly influences the shape and the direction of pore growth.

The experiments done in III-Vs for very short anodization times (1-2 seconds) and low current densities ($< 10 \text{ mA/cm}^2$) show that, during the first step of pore formation, pits with two sharp tips oriented along $\langle 111 \rangle_B$ directions are formed on the surface of the sample (Fig. 2a). Due to the small radius of curvature at the tips of the pits the electrical field strength is much higher there as compared to the electric field on a flat surface. Thus,

electron-hole pairs are more easily generated at the two tips and consequently the dissolution will be enhanced. The tips of the pits will start to move into the substrate, due to dissolution, along $\langle 111 \rangle B$ directions (Fig. 2b).

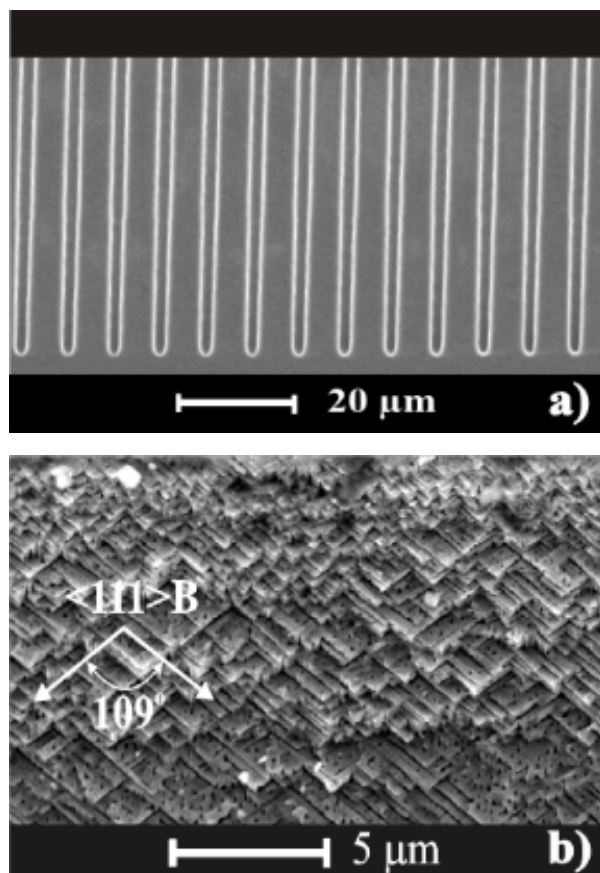


Fig. 1: Typical crystallographically oriented pores in (100)-oriented; a) Si and b) InP

The pores formed in III-Vs according to this mechanism have a triangular shape, whereas in Si are squared. A very important property of the cristo pores is their ability to intersect each other and thus opening a new way for semiconductor 3D structuring. Cristo pores have been observed in Si, GaP, InP and GaAs, however no cristo pores have been observed up to now in ZnSe.

III. CURRENT LINE ORIENTED PORES

Fig. 3 presents the cross section micrograph of a (100)-oriented n-InP sample anodized at high current densities $>10 \text{ mA/cm}^2$. Pores obtained at these conditions obviously do not grow strictly perpendicular to the surface of the sample as in the case of Si, or along $\langle 111 \rangle B$ directions for III-Vs, but follow some wavy lines. More than that, the obtained pores look similar to the pores presented in Fig. 3 even if samples with different crystallographic orientations are anodized, e.g. (111) or (110). Thus, at high anodization current densities the crystallographic dependence of pore growth seems to be completely lost [5,6].

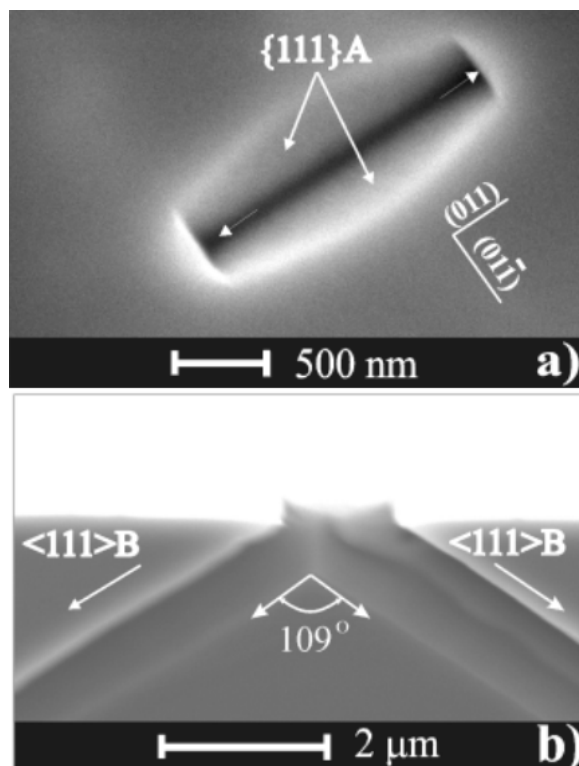


Fig. 2: Crysto pores in III-Vs : a) Pits observed at the beginning of the anodization process; b) Pore growth along $\langle 111 \rangle B$ directions;

At high current densities the system is trying to minimize the ohmic losses by minimizing the path for the current and thus "forces" the pores to grow perpendicular to the equipotential lines of the electrical field inside the substrate. Therefore, such kind of pores, i.e. which grow perpendicularly to the equipotential lines, are called current-line oriented pores or curro pores.

At optimized anodic conditions the so called current-line oriented pores can self-arrange and form two-dimensional (2D) single crystalline porous structures.

One can conclude that a change in the current density from low to high values leads to a switch in the pore growth mechanism from being crystallographically oriented to current-line oriented (see Fig. 3b). Curro pores have been observed in Si, GaP, InP and ZnSe, however no curro pores have been observed up to now in GaAs. No intersection of curro pores was observed up to now as well.

IV. FRACTAL PORES

Fractal pores are the third type of pores observed in Si, III-Vs and II-VI compounds. A fractal is normally defined as an object that can be divided into parts and each of these parts will be similar to the original object. The structures presented in Figure 4 are not perfect fractals, but the pores are called fractal due to their fractal-like way of growth, i.e. each point of a pore in such a structure can be a source for one or more similar pores growing in totally different directions.

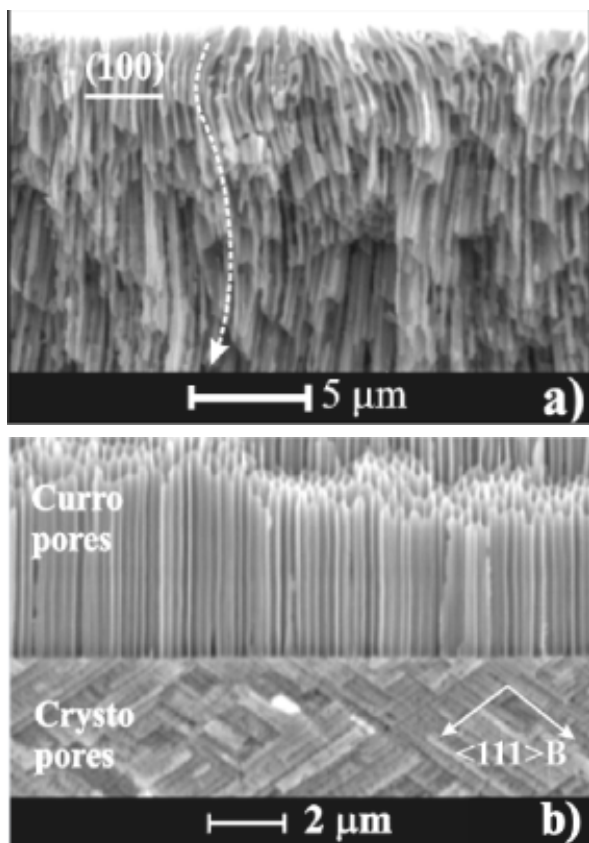


Fig. 3: a) Typical current-line oriented pores; b) A switch from cristo to curro pores by modulating the anodization current density

The fractal structures observed during the anodisation of semiconductors can be divided in two categories: a) surface fractal structures (2D) and b) volume fractal structures (3D). Examples of both types are presented in Figure 4. It is interesting to note that in Si as well as in ZnSe the fractal structures are observed at very low anodization current densities, which could be a hint that both types of fractals (2D and 3D) are based on the same mechanism. On the other hand, the fractal like pores in GaAs need a very high current density in order to be generated, therefore a different mechanism is supposed to take place in this case.

The existence of fractal pores not only opens new insides regarding the mechanism of pore formation in semiconductors, but is also interesting for optical applications, for example non-linear optical effects.

V. DISCUSSION

In Table 1 a summary of all types of pores and the corresponding semiconductors is presented. The lack of pore anisotropy in ZnSe is one of the most striking observations revealed by Table 1. This is very interesting because ZnSe has the same zinc-blend structure as GaAs, GaP or InP have. Nevertheless no cristo pores are observed in ZnSe.

According to the current burst model (CBM) for pore formation, the anisotropic/crystallographic behavior of semiconductors during the pore formation process is mainly determined by the so called hydrogen passivation (H-passivation). On the other hand, H-passivation can

also influence the hydrophobic/hydrophilic behavior of a surface.

It is well known that a surface with perfect covalent bonds (symmetric bonds) should be hydrophobic, e.g. in Si. On the other hand a surface with polarized covalent bonds should have a hydrophilic behavior, e.g. in III-V and II-V. A hydrophilic surface can be interpreted in our case as an easy to attack and dissolve the surface, whereas a hydrophobic surface is much more difficult to attach and dissolve due to the fact that water can not reach and oxidize the surface. Let have a look in more detail how the H-passivation will change the surfaces behavior in the case of GaAs and ZnSe.

GaAs surfaces tend to be hydrophilic due to their polarized bonds. If these surfaces will be H-passivated the behavior will change. A Ga-H terminated surface will remain hydrophilic, due to the fact that Ga and H have different electronegativities. However, As-H will become hydrophobic - As and H have nearly the same electronegativity (see Table 1) and the surface will become non-polarized. In this way in GaAs the Ga-H surfaces will dissolve easily, whereas As-H surfaces will be perfectly protected against dissolution. This explains the mechanism of cristo pore formation in III-Vs.

In ZnSe, however, H-Passivation will not change the behavior of Zn-H and Se-H surfaces. Zn, Se and H have different electronegativities and the H-passivated surfaces will remain polarized. Due to this fact in ZnSe no hydrophobic, i.e. protected against dissolution, crystallographic planes can be obtained in aqueous solutions. This seems to be the reason why no cristo pores are observed in this compound.

VI. CONCLUSIONS

Three types of pores have been observed up to now in Si, III-V and II-VI semiconductors: cristo, curro and fractal pores. The cristo pores grow along definite crystallographic directions, the curro pores grow perpendicular to the equipotential lines of the electrical field inside the sample and the fractal-like can grow in 2D or 3D geometries. The only semiconductor which does not show cristo pores is ZnSe. This behavior can be explained by the lack of perfectly passivated against dissolution crystallographic planes in this compound.

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TABLE I: TYPES OF PORES IN SEMICONDUCTORS

Types of pores		Crysto pores	Curro pores	Fractal pores (2D and 3D)	Electro - negativity	Type of H-bonds	Type of surface
IV	Si						
	Si	Yes	Yes	Yes (2D)	1,9	Polarized	Less-hydrophobic
III-V	InP	Yes	Yes	No	1,78/2,19	Polarized/No n-polarized	Less-hydrophobic/strongly hydrophobic
	GaP	Yes	Yes	No	1,81/2,19	Polarized/Non-polarized	Less-hydrophobic/strongly hydrophobic
	GaAs	Yes	No	Yes (3D)	1,81/2,18	Polarized/No n-polarized	Less-hydrophobic/strongly hydrophobic
II-VI	ZnSe	No	Yes	Yes (3D)	1,65/2,55	Polarized/Pol arized	Less-hydrophobic/ess-hydrophobic
Comments		Can intersect each other	Cannot intersect each other	Cannot intersect each other	H electro-negativity = 2.2		

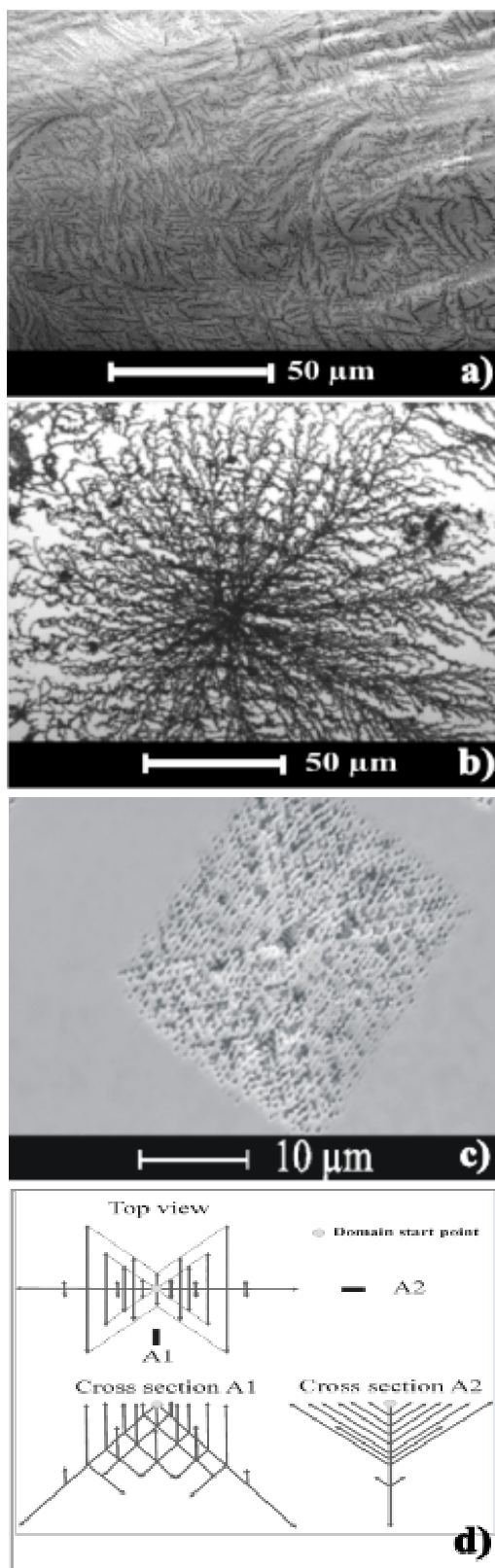


Fig. 4: a) 3D volume fractal pores in ZnSe, cross section; b) 2D surface fractal pores in Si; c) 3D volume fractal like pores in GaAs, top view; d) Schematic view of fractal pores in GaAs presented in c.