

Comparison of Morphologies of Porous InP Layers Obtained in Different Electrolytes

V. SPRINCEAN^{1,2}, A. COJOCARU³, E. MONAICO², I. TIGINYANU^{1,2}, H. FÖLL³

¹ Laboratory of Nanotechnology, Institute of Electronic Engineering and Industrial Technologies, Academy of Sciences of Moldova, Chisinau 2028, Moldova

² National Center for Materials Study and Testing, Technical University of Moldova, Stefan cel Mare av. 168., Chisinau 2004, Moldova

³ Institute for Materials Science, University of Kiel, Kaiserstrasse 2, 24143 Kiel, Germany

Abstract — In this paper we present the possibility for nanostructuring of InP using an electrolyte based on aqueous solution of NaCl. A classical grow of columnar pores was obtained. In particular it was observed that there is no difference in the pore morphologies and the mechanisms of pore formation in case of NaCl electrolyte in comparison with HCl based solution. This environmentally-friendly electrolyte can be used for further exploration of pore formation in InP and related compounds.

I. INTRODUCTION

Significant progress has been made in understanding basic mechanisms for the formation of porous silicon and several models have been proposed to account for the variety of pore types [1,2]. Over the last decade, porous structure of InP has been systematically investigated by electrochemical etching techniques because of its great potential for applications in optoelectronic fields. For the formation of pores and porous structures in InP a variety of electrolytes has been explored. The nano-pore arrays of InP were fabricated by electrochemical etching of n-InP (100) in electrolytes based on HCl and other acidic solutions [3-12], more recently also liquid ammonia [13] or KOH were used [14,15].

At least the pores obtained in the HCl experiments can be classified into two different types with respect to their growth mechanism and morphology. At low current densities, the so-called crystallographically oriented pores (“Crysto pores”) are observed. They always grow along definite crystallographic directions, i.e. $\langle 111 \rangle_B$ directions of the single crystalline semiconductor, independent of the initial surface orientation. They tend to have a triangular cross-section and the pore walls and tips show a pronounced crystallographic anisotropy as well [16]. At high current densities the so-called current-line oriented pores (“Curro pores”) grow and they do not have preferential crystallographic directions of growth, i.e. they grow always perpendicularly to the equipotential lines of the electric field inside the sample, independent of the sample orientation. Depending on the etching conditions, they also can still have slightly triangular shape, but normally the shape tends to be round. The “crysto” pore growth mode may be changed to the “curro” pore growth mode by external causes, e.g. upon increasing the current or even in a self-organized way [16]. In this paper we will

present the results of pore formation in n-InP crystalline substrates in an environmentally friendly electrolyte, namely in aqueous solution of NaCl.

II. EXPERIMENTAL

Wafers used in this work were (100)-oriented n-type InP doped with S. The concentration of free electrons in bulk material was $3 \times 10^{17} \text{ cm}^{-3}$ at 300 K. The anodization was carried out in an electrochemical double cell as shown in Fig. 1 [17]. A four-electrode configuration was used; a Pt reference electrode in the electrolyte (REE), a Pt reference electrode on the sample (RES), a Pt counter electrode (CE), and a Pt working electrode (WE). The electrodes were connected to a Keithley 236 source measure unit. The temperature of the electrolyte was kept constant at $T = 20^\circ\text{C}$ with the help of a Julabo F25 thermostat only on that

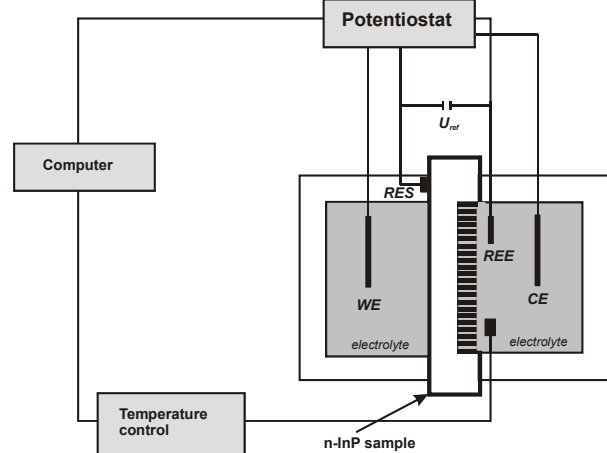


Fig. 1 Schematic illustration of the set-up with electrochemical double cell.

side of the double cell where pores were expected to grow. The electrolyte was pumped in a continuous mode through both cells with the help of peristaltic pumps. The

equipment involved in the experiments was computer controlled. The area of the sample exposed to the electrolyte was 0.12 cm². The anodic etching was performed using NaCl aqueous electrolyte (30 g NaCl, 300 ml H₂O) under potentiostatic conditions. The resulting pore structures have been investigated by scanning electron microscopy (SEM).

III. RESULTS

The porous layer was fabricated under potentiostatic conditions. The applied voltage was as high as 4 V. At the beginning, for a more uniform nucleation of the pores, a impulse of 15 V for half a second was applied. A classical

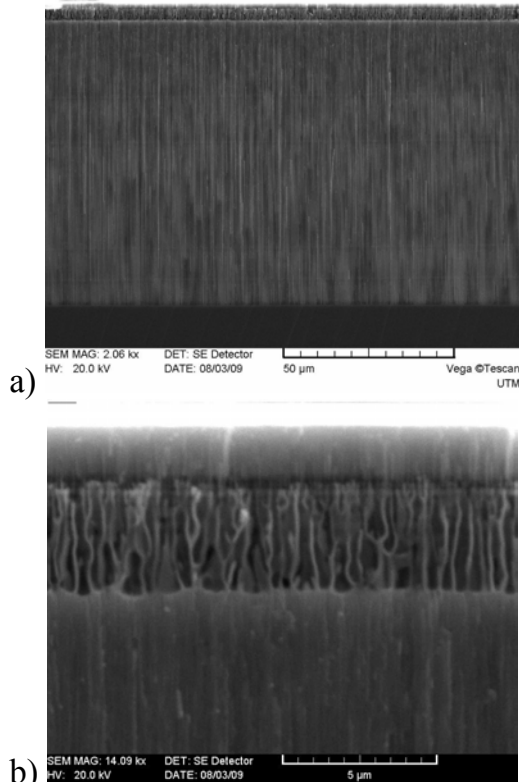


Fig. 2. SEM cross sectional view of a porous layer obtained on n-InP. a) general view of the porous layer, b) the nucleation layer followed by a stable current-line pore growth layer.

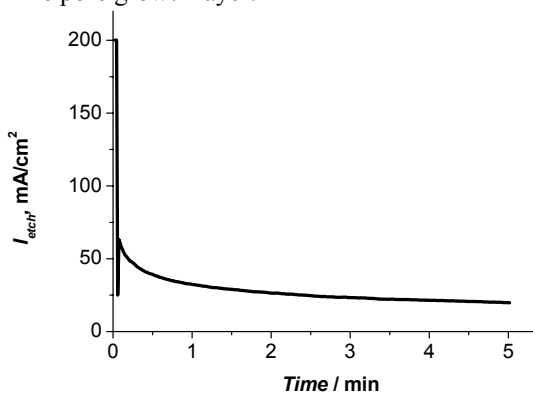


Fig. 3 Variation of the etching current during the growth of the porous layer on n-InP.

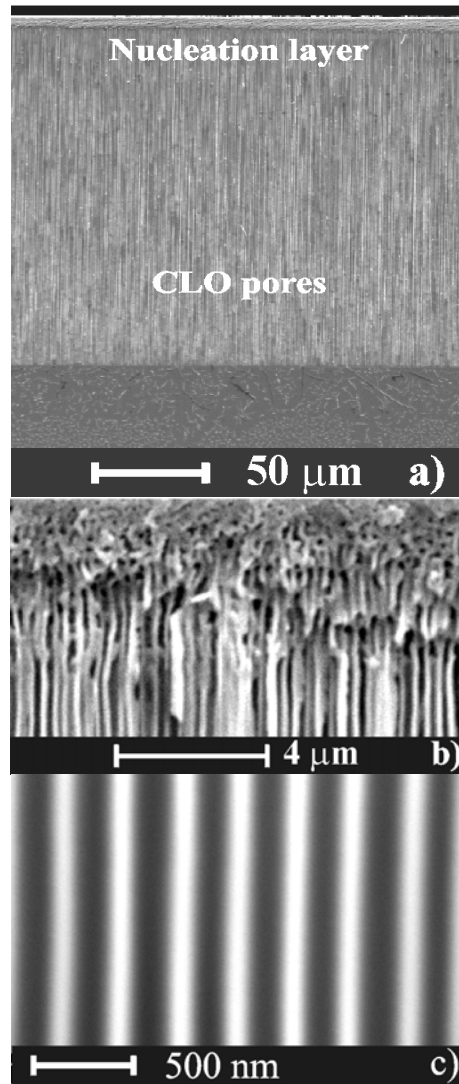


Fig. 4. Cross sectional views of porous layers fabricated on (100) n-InP substrates [19]. a) curved pores. b) Detail of nucleation layer. c) Detail of a).

growth with columnar aspect is obtained, the thickness of the layer being determined by the time of treatment. A specific cross sectional view of the layer is shown in Fig. 2, while the time evolution of the etching current is illustrated in Fig. 3. The strong increase of externally measured current in the beginning of the experiment corresponds to the formation of nucleation layer presented in Fig. 2 b) as a result of the applied high voltage impulse. Then, the exponentially decrease in the current is motivated by increasing of the pore depth and diffusion limitation of chemical species at the pore tips.

IV. CONCLUSION

The NaCl-based electrolyte provides conditions for the growth of crystallographically oriented pores and of arrays of parallel pores in n-InP, the morphology and the mechanism of pore formation being the same as in the case of anodic etching in HCl-based solutions. The environmentally-friendly electrolyte based on aqueous solution of NaCl can be used for further exploration of pore formation in InP.

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