Fabrication of Porous Nanostructures by Design

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***Abstract* — We report on the application of special design of masks for the purpose of electrochemical etching of InP single crystals which enables one to change in a controlled fashion the direction of propagation of pores, including those propagating in directions parallel to the top surface of substrates. The fabricated templates have been used to electrochemically deposit metallic nanostructures along predefined directions and to develop two-dimensional arrays of metallic nanotubes or nanowires embedded in semiconductor matrix.**

***Index Terms* — porous semiconductor, electroplating, Au nanodots, arrays of nanopores.**

I. INTRODUCTION

Porous materials enlarge continuously the area of their applications due to simple, accessible, and cost effective methods of fabrication. Over the last decade, different template-based nanofabrication approaches have been developed which offer the possibility to produce large assembles of nanowires and nanotubes of various materials with defined diameters and lengths [1-6]. Nowadays two types of templates are widely used for nanofabrication purposes, namely porous Al_2O_3 and etched ion track membranes based either on inorganic materials or on organic polymers [3-6]. Both porous Al_2O_3 and etched ion track membranes, however, exhibit high resistivity and therefore they often play a passive role in nanofabrication processes. In particular, templated growth of nanowires via electroplating is provided usually by the metal contact deposited on the back side of the high-resistivity membranes, while electroplating of metal nanotubes requires additional technological steps e.g. chemical modification of the inner surface of the pores prior to electrodeposition which leads to the incorporation of spurious phases in the nanotube walls [3]. Semiconductor nanotemplates which properties can be easily controlled by external illumination, applied electric fields, etc. provide wider possibilities for nanofabrication.

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 with different morphologies have been produced by electrochemical etching of InP, GaP, GaAs, CdSe and ZnSe [7-15], proving that porosity is an effective tool for engineering basic parameters of semiconductor compounds. In particular, porous semiconductor compounds were found to exhibit Fröhlich-type surface-related vibrations with porosity-tunable frequencies [16,17] and efficient optical second harmonic generation [18].

The electrochemical deposition of metal dots proves to be one of the most cost-effective and efficient, especially when the dots are to be created on semiconductor substrates or matrices exhibiting electrical conductivity. Using pulsed electroplating, Sato et al. demonstrated uniform deposition of Pt dots with the diameters ranging from 20 to 30 nm on *n*-GaAs and *n*-InP substrates with the free electron concentrations of 2×10^{16} and 5×10^{16} cm^{-3} respectively [19,20]. The authors found the Fermi-level pinning at the metal-semiconductor interface to be greatly reduced, resulting in a strong dependency of the Schottky barrier height on the metal work function.

Recently we demonstrated the possibility to cover the huge surface inherent to GaP and InP porous structures by a self-assembled monolayer of electrochemically deposited nanoscale Au nanodots [21]. After nucleation, each dot was found to increase in sizes up to a critical dimension, the process of pulsed electrodeposition of gold being continuously supported by the formation of new nanodots. The density of deposited Au dots was shown to be dependent upon the number and width of the applied voltage pulses. The deposition of "size-saturated" dots continues until the entire surface exposed to the electrolyte is covered by a monolayer of self-assembled Au nanodots. Due to the good electrical conductivity of the porous skeleton, different shapes of nanotubes deposited inside the pores was demonstrated [22].

Recently, we demonstrated that electroplating represents a simple and effective tool for assessing the conductivity of InP nanostructures fabricated by electrochemical etching of InP wafers [23]. The comparison of metal electrochemical deposition on InP nanowires and on bulk InP suggests that the electrical conductivity of nanowires is similar to that of bulk crystals. At the same time the comparison of gold electroplating on nanowires and nanowalls is indicative of a much less conductivity of nanowalls as compared to that of nanowires. We found that no metal electrodeposition occurs on InP nanobelts, due to the absence of free charge carriers in nanobelts with the thickness of several nanometers.

The goal of this paper is to demonstrate the possibility to control the spatial architecture of deposited metal nanostructures by modifying the direction of propagation of pores. Herein, we will focus on controlled templated deposition of metal dots and nanotubes by using the previously developed technology for preparing pores

parallel to the top surface of the as-grown semiconductor substrates [24].

II. Description of technological procedures

Crystalline 500-μm thick n-InP(100) substrates with the free electron concentration of $1.3x10^{18}$ cm^{-3} supplied by CrysTec GmbH were subjected to anodic etching in 500 ml of 5% HCl aqueous solution at 25 ^{o}C to fabricate porous layers, as described elsewhere [25]. A specific design was used, where some areas of the front surface of the substrate are covered by a photoresist, while other areas are exposed to the electrolyte in the electrochemical etching process. Under these conditions, the pores will start to grow from the surface exposed to the electrolyte in the direction perpendicular to the top surface. However, with further propagation of pores, they will be deflected in directions parallel to the top surface, and will grow under the regions covered by the photoresist. Both types of pores, perpendicular and parallel to the top substrate surface, can be produced in the InP substrate. The ohmic contact is deposited on the opposite surface of the substrate with respect to the surface exposed to the electrolyte for the growth of pores perpendicular to the substrate surface. In such a case, the current oriented pores grow from the surface exposed to electrolyte in the direction of the ohmic contact.

Electroplating of Au was realized at 25 ^{o}C in a common two-electrode plating cell with commercially available gold or platinum baths (DODUCO) where the porous sample served as working electrode, while a platinum wire was used as counter electrode. A pulsed voltage with pulse duration of 100 μs and a cathodic voltage of - 16 V was applied between the two electrodes to electrochemically reduce the metal species on the surface of the samples being in contact with the electrolyte. After each pulse, a delay time as long as one second was kept. The solution was magnetically stirred to provide appropriate conditions for the recovery of the ion concentration in the electrolyte confined in the areas of pores.

III. Results and discussions

Fig. 1 illustrates SEM images of a porous InP template after electrochemical deposition of Au nanodots. Two different regions are seen, namely where the electrochemical deposition was performed (left) and the region without metal deposition (right).

The pores grow under a thin surface layer, which remains intact during the electrochemical treatment. The thickness of this surface layer is of the order of the surface depletion region, i. e. from several tens to several hundreds of nanometers, depending on the conductivity of the anodized substrate. For our single crystals this value is around 20 nm. Fig. 1a and 1b shows that the electrochemical deposition of Au dots occurs on the surface of the pore walls situated under the thin surface layer. With the increase of duration of electrochemical deposition, the metal dots increase in diameter up to a threshold value, followed by the initiation of dot deposition in neighboring areas.

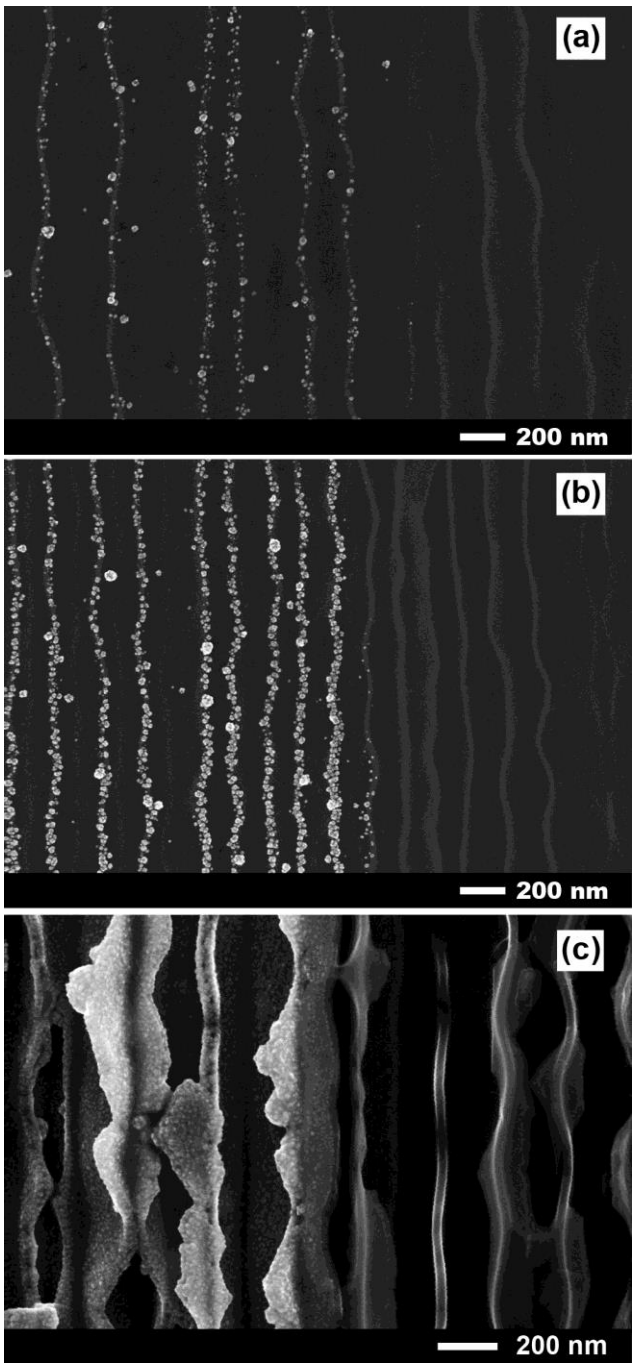

Fig. 1. SEM images of porous InP after electrochemical deposition of Au dots in the left side area (a) during 100 pulses, (b) 300 pulses, and protected porous InP (right). (c) SEM image with removed surface layer from (b) demonstrating the uniformity of the electrochemical metal deposition in the whole porous template due to the good electrical conductivity of the porous skeleton (left side). The right side was protected against electrochemical deposition.

It is to be noted that the electrochemical deposition of metal takes place uniformly in the whole porous structure due to the good electrical conductivity of the porous skeleton (see Fig. 1c).

One can easily see from Fig. 2 that the top surface layer has a good contact with the pore walls and is two times thinner that walls of the pores.

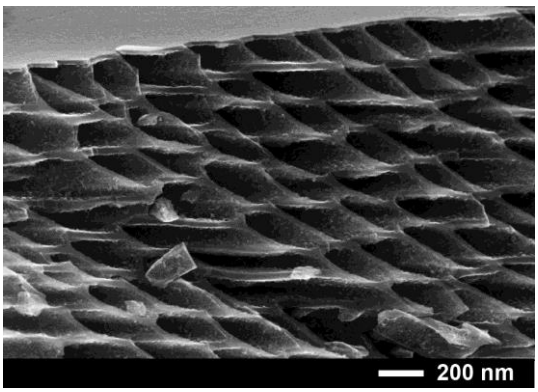

Fig. 2. Cross-sectional view of an indium phosphide porous layer.

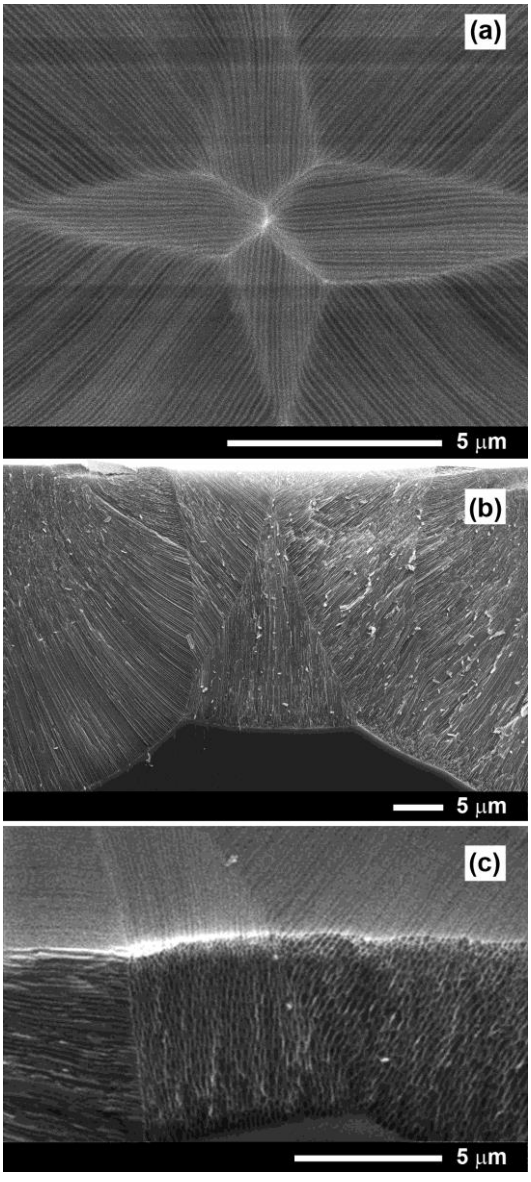

Fig. 3. SEM images of porous InP after anodization trough opened windows in photoresist: (a) – top view, (b) – cross-sectional view and (c) - tilted .

By applying a special design of mask, we demonstrated the possibility to obtain rather spectacular patterns of pores parallel to the top surface of the substrate, see Fig. 3. Note that the pores are forced to change their direction of propagation by design.

A special arrangement of pores was found not only in the areas near the top surface of the substrate, but also in the deepness of the crystal, as shown in Fig. 3 b,c. It was experimentally established that the deepness of pore formation by design depends on the width of opened windows in the photoresist, preliminarily deposited on the top surface, as well as on the duration of electrochemical etching.

Pulsed electrochemical deposition of Pt in porous layers with specially-designed morphology allowed us to demonstrate the possibility to fabricate arrays of metal nanotubes oriented along predefined crystallographic directions (see Fig. 4).

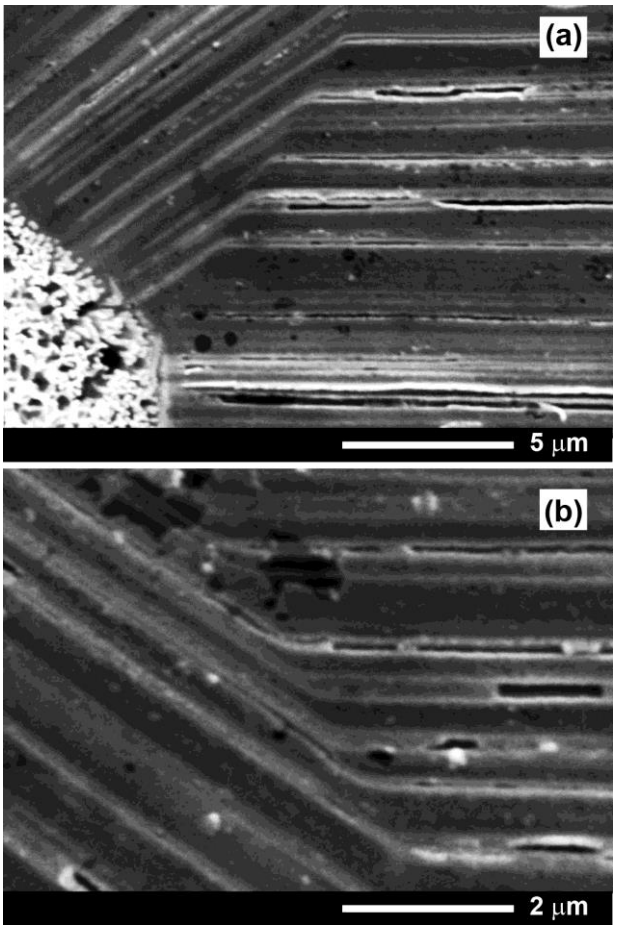

Fig. 4. (a) SEM top view of porous InP after Pt electroplating and the magnified view in (b).

IV. CONCLUSION

The results of this study demonstrate the formation of pores in semiconductor compounds by design. Electrochemical deposition of Au dots take place on inner surface of pores, and no dots are deposited on the top surface of the porous template. Prolonged pulsed electrochemical deposition of Pt leads to the formation of arrays of metal nanotubes embedded in semiconductor matrices fabricated by special design. The obtained results show that the combination of porous etching of semiconductor substrates and electrochemical metal deposition represents a powerful tool for the fabrication of

novel metal-semiconductor hybrid nanoarchitectures for various electronic and photonic applications.

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