FORMATION OF LOW-DIMENSIONAL STRUCTURES ON InP UNDER FAST ANODIC ETCHING.

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Abstract: *In this paper, we report on the possibility of cost-effective fabrication of InP nanomembranes and nanowires using fast anodic etching of n-InP single crystalline substrates under potentiostatic conditions. Fast anodic etching means that 2-мм long nanowires are obtained in just 3 s of anodization, i.e., the rate of etching in depth direction is about 40 μm/min. Uniform electrochemical depositions of Au dots on InP nanowires is demonstrated.*

Keywords: *low-dimensional structures, nanowires, fast electrochemical etching, pulsed electrochemical deposition.*

1. Introduction

Considerable research efforts have been focused in the last decade on one-dimensional (1-D) nanostructures, such as nanorods, nanowires, nanobelts, and nanotubes with well-controlled sizes, morphologies, and geometries due to the quantum size effects which resulted in fascinating properties and novel applications in nanooptoelectronic and nanosensor devices. In particular, semiconductor nanowires are predicted to drive new generations of compact, ultrafast, and high efficiency electronic and optoelectronic devices. III–V semiconductor nanowires, such as GaAs, InAs and InP nanowires, show enormous promise as active components in solar cells [1-4], photodetectors [5], light-emitting diodes [6] and ultrahigh density transistors [7].

Among nanowire materials, InP is of special interest due to its direct band gap of 1.34 eV, which means that it can absorb light over a broad range of solar spectrum wavelengths and has a high electron mobility. A multitude of prototype InP nanowire devices have been demonstrated including photodetectors [5,8], light-emitting diodes [6], waveguides [9], solar cells [1-4, 10,11] and field effect transistors [6,12].

At the same time, two-dimensional (2-D) nanomaterials which are characterized by a thickness of the order of nanometers and a lateral scale much bigger than that of nanobelts, including nanosheets and nanoplates, receive much less research attention than 0-D (nanoparticles and quantum dots) and 1-D materials. The unique structural features of 2-D nanomaterials, such as ultrathin thicknesses and selectively exposed specific crystalline planes, prove however to be advantageous for charge transport and surface interaction/ reaction oriented applications, such as electrodes of dye-sensitized solar cells [13-15], gas sensors [16,17], supercapacitors, photocatalytic water splitting, photocatalysis [18] etc. A small number of reports on 2D semiconductor nanosheets and related devices have been published. The main reason is related to the difficulty to obtain high quality 2D semiconductor nanosheets with appropriate electron or hole concentrations required for device application.

2. Experimental data

Crystalline (100)-oriented substrates of sulfur doped *n*-InP with 500 μm thickness and free electron concentration of $1.3 \times \Box 10^{18}$ cm^{-3} were used. The samples were supplied by CrysTec GmbH, Germany. Before the anodization process, conventional photolithography was used to open windows in photoresist covering the top surface of samples. Anodic etching was applied to these samples through opened rectangular windows with the breadth of 35 μm. An electrical contact was made on the backside of the anodized sample with a silver paint. The anodization of InP substrates was carried out in 500 ml of 5 % HCl aqueous solution at 25°C in a common two-electrode cell where the sample served as working electrode. The mesh with the surface 6 cm^2 from platinum wire with diameter 0.5 mm was used as counter electrode. To note, that no steering was used to avoid the destruction of nanostructures. As potentiostat the Keithley's Series 2400 Source Measure Unit was used.

Electroplating of Au was realized in a commercially available gold bath containing 5 g/l Au (DODUCO). The electrochemical deposition of Au was performed at T = 25°C for 100 s in a common two-electrode plating cell where the porous sample served as working electrode, while a platinum wire was used as counter electrode. A pulsed voltage regime with rectangular pulses was provided by a home-made

generator. During the 50-μs pulse time a cathodic potential of 12 V was applied between the two electrodes to electrochemically reduce the metal species on the surface of the sample in contact with the electrolyte. After each pulse, a delay time as long as one second was applied. The morphology and chemical composition microanalysis of samples have been investigated by Scanning Electron Microscope (SEM) Zeiss Sigma and TESCAN Vega TS 5130MM equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV.

3. Results and discussion

The cost-effective approaches of nanowire growth based on electrochemical etching of n-type single crystalline InP substrates is reported. This method is still at early stage of development, but it proves to be very promising for a range of applications that require the generation of 1D nanostructures rapidly and at low cost.

It was found that anodization at 5-7 V via photolithographically defined windows (windows with the breadth of 35 μm) leads to the formation of highly-porous layers, the porous skeleton being characterized by percolation, see Fig. 1. Note that the thickness of nanowalls is much smaller than the diameter of pores, and overall the morphology changes with the increase of the applied voltage. Anodization at 5V leads to the formation of pores with nearly the same diameters (Fig. 1 a,b), while further increase in the applied voltage gives rise to pronounced fluctuations in the pore diameters (Fig. 1 c,d). By application of a high-voltage pulse it is possible to detach the porous structure from the substrate and, as a result, to fabricate a highly porous membrane.
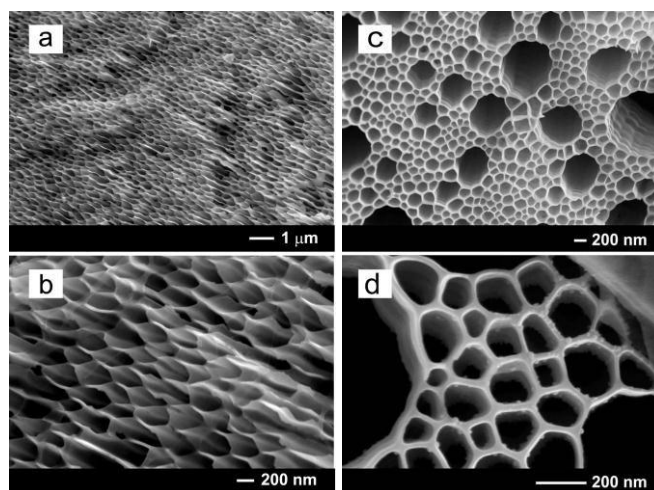

Fig. 1 SEM images taken from porous layers fabricated by anodization of bulk *n*-InP
at U = 5 V (a,b) and U = 7 V (c,d).

Increase of the applied voltage up to 10 V was found to modify drastically the morphology of the anodically etched layer. As one can see from Fig. 2, the etching results in the formation of mosaic structures consisting of ultrathin walls. Besides, a relatively large number of nanowires are simultaneously formed with the diameters of about 50 nm (Fig. 2).
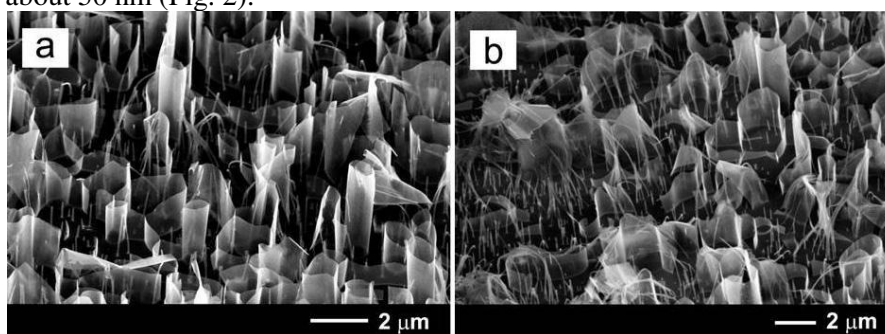

Fig. 2 SEM images taken from *n*-InP subjected to anodic etching at U = 10 V.

The formation of nanowires proved to predominate with further increase of the applied voltage. Fig. 3a illustrates a uniform network of parallel nanowires with the diameters of about 50 nm fabricated by anodic etching at U = 15 V. The nanowires are oriented along the crystallographic direction [001].
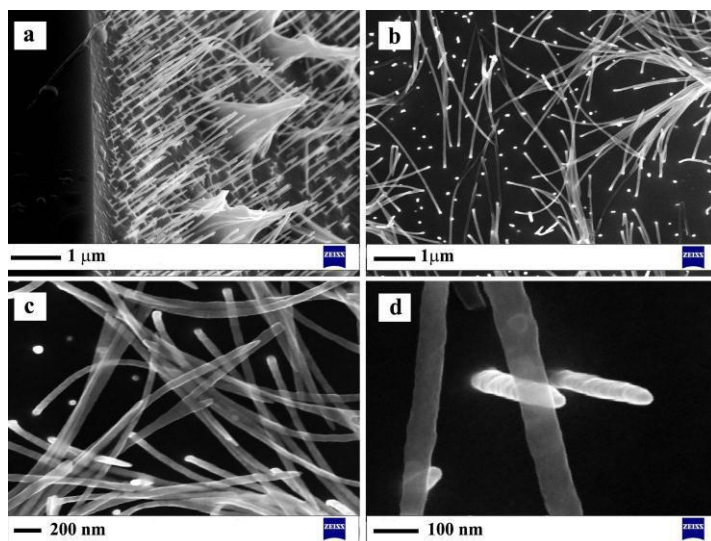
Fig. 3 SEM images of InP nanowires (a) – tilted view, (b) – top view, (c) – mix of nanowires and nanobelts and magnified view in (d).

Besides nanowires, InP nanobelts can be fabricated in the same process, see e.g. Fig. 3c,d. Fig. 3d shows that the thickness of nanobelts is very small in comparison with diameters of nanowires (50 nm). From SEM images, it was established that nanobelts are transparent, and the nanowires can be easily seen through nanobelts. According to our preliminary estimations, the thickness of nanobelts is of about several nanometers. Electrical and other properties of nanowires are expected to be different from those of nanobelts.

The development of nanowire-based devices requires a deep understanding of charge carrier dynamics and transport in 1-D structures. Progress in understanding these properties has, however, been hampered because conventional techniques for measuring electrical transport require lithographically placed electrical contacts to individual nanowires, and the measurements are subject to artifacts arising from the electrical contacts.

Having experience in pulsed electrochemical deposition in porous semiconductor nanotemplates, I have previously obtained arrays of metal nanotubes in semiconductor envelope [19]. The walls of the porous skeleton which exhibits good electrical conductivity in comparison with the walls of other dielectric nanotemplates (porous Alumina, etched ion track membranes, etc), create good conditions for uniform nucleation of metal dots. As a result nanotubes, without any activation of the pore's wall, can be electrochemically deposited on inner surface of pores. Further evidence of good electrical conductivity is provided by the uniform deposition of Pt on the inner surface of pores regardless of the pore shape (e.g. circular, triangular-prism like pores etc.) [20].
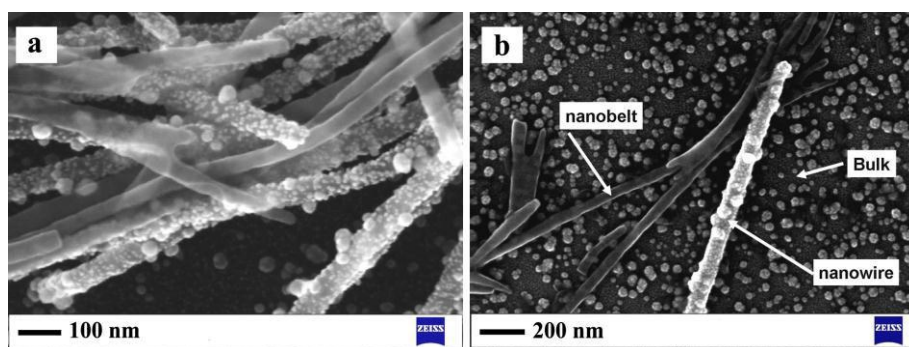

Fig. 4 (a) SEM image of n-InP 1-D nanostructures (nanowires and nanobelts) on bulk InP substrate after pulsed electrochemical deposition. (b) Enlarged view of one nanowire and a few nanobelts.

This technique was used to explore how the electrical conductivity of 1-D nanostructures is affected by the geometrical dimensions. In Fig. 4a one can see a mixture of bundle of nanowires and nanobelts on bulk InP substrate. It is clearly seen that the surface of nanowires, after pulsed electrochemical deposition of Au, is uniformly covered with gold nanodots, in contrast to the nanobelts, where no electrochemical deposition occurs.

4. Conclusions

In this work, was demonstrated that anodic etching of n-InP crystalline substrates at voltages as high as 15 V via photolithographically defined rectangular windows leads to the formation of membranes and nanowires with diameters of about 50 nm. Comparing the results of electrochemical deposition of metal on InP nanowires and on bulk InP substrate from Fig. 2b, one can conclude that electrical conductivity of nanowires is similar to that of bulk crystals, in contrast to nanobelts which seem to exhibit low electrical conductivity.

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