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Gold Electroplating as a Tool for Assessing the Conductivity of InP Nanostructures Fabricated by Anodic Etching of Crystalline Substrates

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Electroplating is shown to represent a simple and effective tool for assessing the conductivity of InP nanostructures fabricated by electrochemical etching of InP wafers. A mixture of nanowalls, nanowires and nanobelts was fabricated by anodic etching of crystalline bulk *n*-InP with free electron concentration of 1.3×10^{18} cm^{-3} under applied voltage of 13 V. We found that electroplating of Au occurs differently on these three nanostructures under identical electroplating conditions. A monolayer of densely packed Au nanodots with the diameter of around 20 nm is deposited on nanowires, while the density of Au nanodots deposited on nanowalls proves to be much smaller. At the same time no electroplating occurs on nanobelts. The evidenced distinctive features of electroplating processing are determined by different electrical conductivities of InP nanostructures. The produced materials are characterized by scanning electron microscopy (SEM), high-resolution scanning transmission electron microscopy (HR-STEM), electron nano-diffraction, selected area electron diffraction (SAED), and energy dispersive X-ray analysis (EDAX).

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Considerable research efforts have been focused in the last decade on one-dimensional (1D) and quasi-1D nanostructures, such as nanorods, nanowires, nanobelts, and nanotubes with well-controlled sizes, morphologies, and geometries. Due to quantum size effects and huge surface-to-volume ratio, these nanostructures show fascinating properties feasible for a myriad of applications in various fields. In particular, semiconductor nanowires are predicted to drive new generations of compact, ultrafast, and high efficiency electronic and optoelectronic device structures. III–V semiconductor nanowires, such as those based on GaAs, InAs and InP, show enormous promise as active components in solar cells,[1,2] photodetectors,[3] light-emitting diodes,[4] and ultrahigh density transistors.[5] Among nanowire materials, InP is of special interest due to its high electron mobility and direct bandgap of 1.34 eV, ensuring absorption of light over a broad range of solar spectrum wavelengths.

Semiconductor nanostructures, particularly nanowires, have been prepared by a variety of methods including laser ablation,[6] template-assisted electrochemistry,[7] chemical transport reactions,[8] chemical vapor deposition,[9] and solvothermal methods.[10] However, the nanomaterials obtained using these techniques exhibit crystallographic defects generated by impurities from electrolytes, precursors and different transport gases in the growth process. On the other hand, we recently demonstrated formation of InP nanowalls and nanowires under fast anodic etching of bulk substrates.[11] The advantage of this newly developed approach opens the possibility to avoid the contamination of obtained nanowires due to direct electrochemical dissolution of the crystalline material around the emerging nanostructures.

Data about conductivity and dynamics of charge carriers in nanomaterials is essential for the design of nanodevices. Particularly important are the effects of nanowire size, surfaces, and crystal structure on nanowire electronic properties. The unique structural features of 2D nanomaterials, such as ultra-small thickness and selectively exposed specific crystallographic planes, prove also to be advantageous for charge transport and surface interaction/reaction oriented applications, such as electrodes in dye-sensitized solar cells,[12] gas sensors,[13] supercapacitors, photocatalytic water splitting, photocatalysis,[14] etc. However, a limited number of reports on 2D semiconductor nanosheets and related devices based on non-layered crystalline materials has been published. The main reason is related to difficulties in growing high quality 2D semiconductor nanosheets with appropriate electron or hole concentrations required for device applications.

Electrochemistry is a cost-effective tool for nanostructuring of semiconductors, including III–V and II–VI materials. A variety of porous semiconductor structures have been produced by electrochemical etching of InP, GaP, GaAs, CdSe and ZnSe,[15–21] 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,[22] efficient optical second harmonic generation,[23] and porosity-enhanced Terahertz emission.[24,25] We demonstrated the controlled fabrication of semiconductor nanotemplates with self-organized quasi-ordered distribution of nanochannels using anodic etching of III-V (InP, GaAs) and II-VI (CdSe) crystalline substrates in a neutral electrolyte.[18,26,27]

In this paper, we propose an original method of the electrical conductivity estimation in 1D and 2D nanostructures by means of pulsed electrochemical deposition of metal nanodots.

Experimental

Crystalline (100)-oriented substrates of sulfur doped *n*-InP with 500-μm thickness and free electron concentration of $1.3 \cdot 10^{18}$ 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 back side 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. A mesh with the surface of 6 cm^2 from platinum wire with 0.5-mm diameter was used as counter electrode. To avoid the damage of nanostructures, no steering was used. A Keithley's Series 2400 Source Measure Unit was used for the control of the applied voltage and current during the anodic etching.

Electroplating of Au was realized in a commercially available gold bath containing 5 g · dm^{-3} Au (DODUCO). The electrochemical deposition of Au was performed at T = 25°C for 100 s in a

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