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Formation of Porous n-A_3B_5 Compounds

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Porous layers of A_3B_5 compounds were formed on n-type wafers by electrochemical anodic etching. The morphology of nanostructured layers was studied by scanning electron microscopy and atomic force microscopy techniques. The optimal conditions of the formation of porous layers were determined by varying the composition of etching solution, current density and etching time. Large area (1.5×1.5 cm^2) porous layers of uniform porosity were produced by anodization process of n-type A_3B_5 semiconductors, GaAs, InP, and GaP.

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1. Introduction

In recent years, nanocrystalline semiconductors have been widely studied because of their particular physical and chemical properties and perspectives for applications. Nanocrystalline structures are the systems, in which the size of structural elements varies from 1 to 100 nm [1]. The technology of nanocrystalline semiconductors is rapidly developing and presents the most actual area in materials science. These materials play an important role in many technologies, including optical and photonic devices, sensors chemical reactors [2, 3], etc.

A cheap and simple technology of electrochemical etching is one of the most versatile techniques for fabrication of nanocrystalline or porous materials. Formation of pores during anodization process has been widely reported for various types of crystalline silicon. The compound semiconductors such as GaAs [4], GaN [5], SiN [6], InP [7, 8], and GaP [9–11] have also been investigated in the form of porous layers and many different properties relative to the corresponding bulk materials have been revealed. For instance, a photoluminescence emission was observed [7] at 2.2 eV in InP dots of size around 2 nm prepared by colloidal chemistry. It was found [8] that the amount of the blueshifted energy depended

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on the microstructure of porous InP. From the theoretical [12] and experimental [4] studies it followed that the nanocrystalline structures of direct band gap semiconductors like GaAs possessed even higher-energy luminescence in a visible wavelength region.

Gallium phosphide has a large refractive index (3.2) and the band edge at 2.24 eV [13]. Thus, macroporous GaP represents an interesting photonic material for the visible spectral range as well. Micrometer-thick light-yellow layers were produced by etching GaP in a 50% HF solution and ultraviolet luminescence up to 3.3 eV was observed [9]. Pore walls of thickness about 100 nm were formed in aqueous solution 0.5 M H_2SO_4 [10]. Raman study of porous GaP revealed a surface-related optical phonon near longitudinal optical (LO) phonon [11]. However, in these works the dependence of the morphology on the etching conditions was not carefully studied.

In this work we would like to show that large-area porous structures of A_3B_5 semiconductors GaAs, InP and GaP can be prepared by electrochemical etching. The influence of various anodization conditions on the morphology of porous layers was studied as well. The optical properties of these porous films will be investigated in future studies.

2. Experimental

The wafers used were n-type Te-doped ($n \approx 10^{18}$ cm^{-3}) (100)-oriented GaAs, n-type ($n \approx 10^{17}$ cm^{-3}) (100)-oriented InP and n-type ($n \approx 10^{17}$ cm^{-3}) (111)-oriented GaP. Before anodization procedure, the samples placed in ultrasound bath were degreased by treating with acetone, isopropanol, and ethanol, and afterwards rinsed with distilled water. In order to remove a native oxide film, etching solutions $NH_4OH : H_2O_2 : H_2O$ (3:1:400; 30 s) and HCl:H_2O (1:1; 2 min) have been subsequently used. Back contact was made by deposition of In/Ga eutectic. The electrochemical etching was accomplished in different electrolytes: HF:$C_2H_5OH : H_2O$ (2:1:1) for GaAs, 1 M HCl for InP, and 0.5 M H_2SO_4 for GaP. The porous layers were prepared by etching the samples varying from 10 to 60 min at current density of 4–50 mA/cm^2. During anodization process the samples were either illuminated or kept in the dark.

The morphology of obtained structures was investigated by the scanning electron microscope (SEM) BS300 in the electron beam induced current (EBIC) mode and in the secondary electron image mode (with a primary beam energy up to 26 keV) and by atomic force microscope (AFM) Dimension 3100 (Digital Instrument).

3. Morphology of porous structures

The observations performed have shown that the surface morphology strongly depended on various parameters of anodization process such as etching time, current density, composition of etching solution and illumination during the

etching procedure. During formation of porous layers on n-type semiconductors, additional charge carriers within the semiconductor electrolyte boundary can be generated by light.

The morphology of n-type porous GaAs is presented in Fig. 1. The surface of layer is quite uniform and consists of crystallites. During anodization process, the substrates were illuminated from the top and the current density was 20 mA/cm^2. The crystallites vary in size in the range $\approx 0.5-2.0$ μm (Fig. 1a). When the wafers were illuminated from bottom and etched at a lower current density, the crystallites were not formed (Fig. 1b). In the second case, the pores of diameter about 1–4 μm were observed on the surface of the samples. It seems that the porous layer has cracked during the drying process, most likely due to the strain in film. The thickness of porous GaAs layer is ≈ 4 mm.

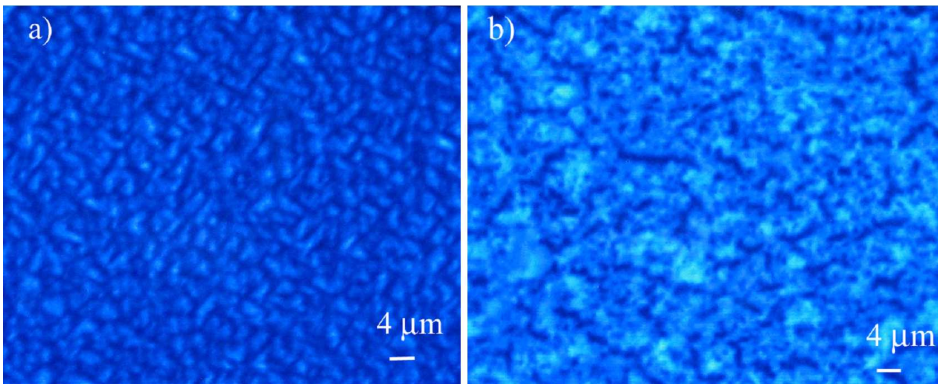

Fig. 1. SEM top view of n-GaAs (100) substrates anodized for 10 min at 20 mA/cm^2 (a), 10 min at 5 mA/cm^2 (b). The substrates during anodization were illuminated from top (a) and from bottom (b).

Figure 2 illustrates the morphology of n-type porous InP samples formed at various current densities during anodization process. The surface network is oriented along crystallographic axes in all cases. At the lowest current density of 4 mA/cm^2 (Fig. 2a) the structure consists of microrods with ≈ 1 μm in width and ≈ 20 μm in length. Two-layer structure of porous InP was found in the SEM micrograph of the sample cross-section (Fig. 2d). The top layer is of a few micrometers in thickness and consists of InP oxides and products of reaction. The bottom layer is porous InP and consists of microrods. The bottom layer with thickness up to 20 μm and the microrods width in the range of 0.2–1.0 μm were formed on the surface of the crystalline substrate. At high current density 30 mA/cm^2 (Fig. 2b) the larger structures form with the size of microrods up to 8 μm in width. The change of the size of microrods on the surface with an increase in current density is clearly illustrated in Figs. 2a–c.

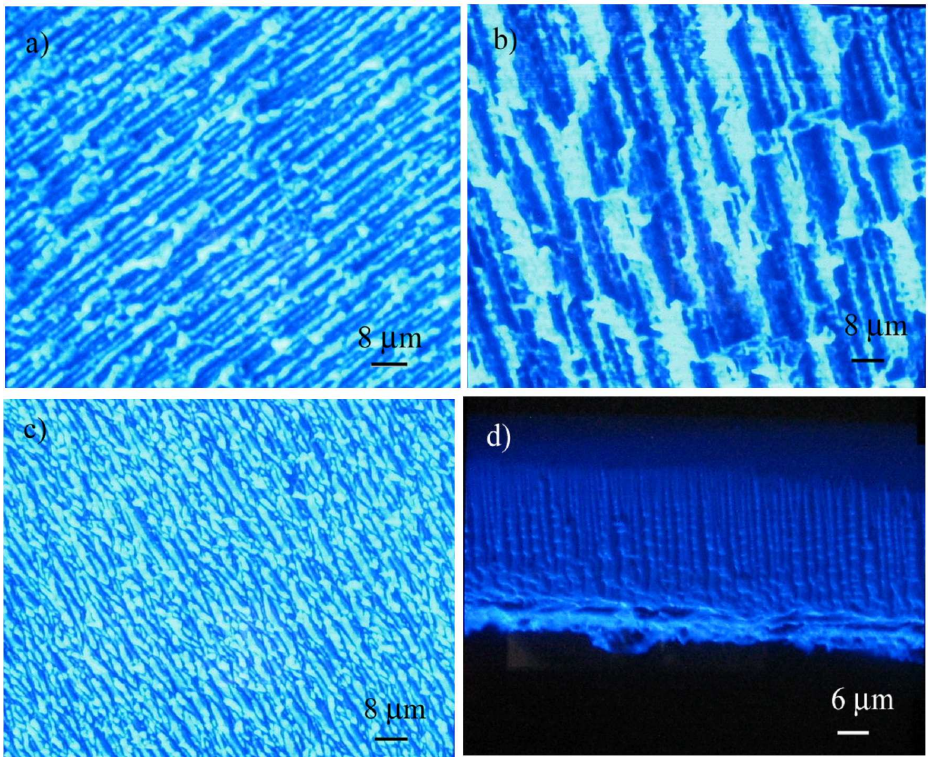

Fig. 2. SEM top view of n-InP (100) substrates anodized for 10 min at 4 mA/cm^2 (a), 30 mA/cm^2 (b), and 20 mA/cm^2 (c) and the cross-sectional view (d) of samples (a). All substrates were illuminated from bottom during anodization.

The structures of porous GaP are presented in Fig. 3. The porous layer with micropores and grains of up to 2 μm is formed at higher current density and shorter anodization time (Fig. 3a). The pores and grains are distributed chaotically. The presence of such disordered structure HH follows also from AFM investigations (Fig. 4). The thickness of porous GaP layer is about 0.4 μm. The morphology of porous structure changes and larger pores developes with increase in etching time (Fig. 3b). In this case the pores are up to 8 μm in length and 2 μm in width. The pores in the layer seem to be oriented along crystallographic axes. This phenomenon has also been observed in [14]. The results indicated a strong dependence of morphology on current density and etching time during anodization process of n-type GaP.

In summary, the large area (1.5×1.5 cm^2) porous layers of uniform porosity were produced by anodization process of various n-type A_3B_5 semiconductors. The structure investigations showed that the morphology of porous layers strongly depended on technological conditions such as etching time, current density, and illumination.

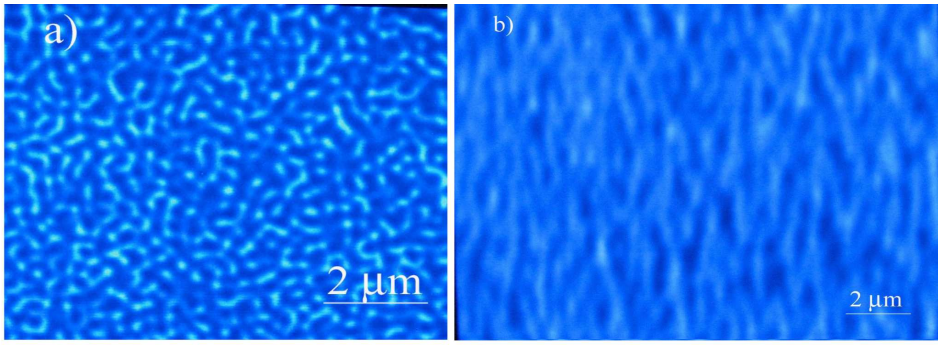

Fig. 3. SEM top view of *n*-GaP (111) substrates anodized for 10 min at 10 mA/cm^2 (a) and for 20 min at 5 mA/cm^2 (b). The samples during anodization were in the dark.

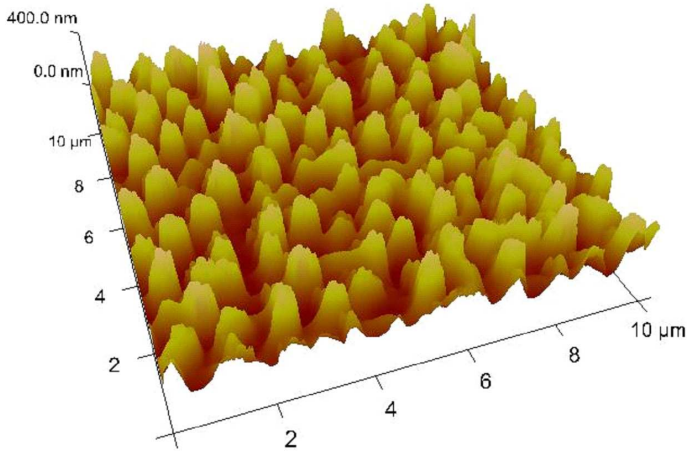

Fig. 4. AFM image of *n*-GaP (111) sample etched for 10 min at 10 mA/cm^2.

Acknowledgments

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