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FABRICATION OF DIAMETER MODULATED GALLIUM ARSENIDE NANOWIRES VIA ANODIZATION

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In this paper, the technological approach for diameter modulated GaAs nanowires fabrication via electrochemical etching representing simple and cost-effective technology is demonstrated. At optimized applied potential, in the same technological process, the growth of GaAs nanowires oriented perpendicular to the crystal surface occurs. At the same time, simultaneously growing tilted pores penetrate the nanowires resulting in modulation of nanowires along the whole length. In 40 min of anodization the as long as 200 μm nanowires were obtained. A selective modulation of nanowires via anodization at two different applied potentials is demonstrated. The tree-dimensional modulation of diameter will give the possibility to increase the area of their applications.

Key words: gallium arsenide; porous GaAs; electrochemical etching; morphology; current line oriented pores; perforated nanowires.

INTRODUCTION

Gallium arsenide represent an important technological material due to its electrical and optical properties finding in a variety of electronic and optoelectronic at high-speed applications. The reduction of size of the material give rise to enhanced or even new unusual properties. During the two decades a lot of technological approaches were elaborated for low-dimensional materials obtaining. The electrochemical etching proved to be the most cost-effective and simple technology for nanostructuring of III-V and II-VI semiconductor materials [1]. Different morphologies of porous GaAs were reported [2, 3] including the formation of nanowires via anodization [4–7]. The nanostructuring of GaAs via anodization in NaCl based electrolyte proved to be environmentally-friendly approach [7, 8]. It is worth to mention that up to now, no current line oriented pores were reported in anodized GaAs.

To increase the area of GaAs nanowires application a lot of effort have been focused to modulation of diameter along the nanowire length aiming to improve the thermoelectric properties [9] as well as their functionalization with metals [10, 11] or semiconductor materials [12].

The goal of this paper is to demonstrate a simple and cost-effective in one-step approach for diameter modulated GaAs nanowires fabrication.

MATERIALS AND METHODS

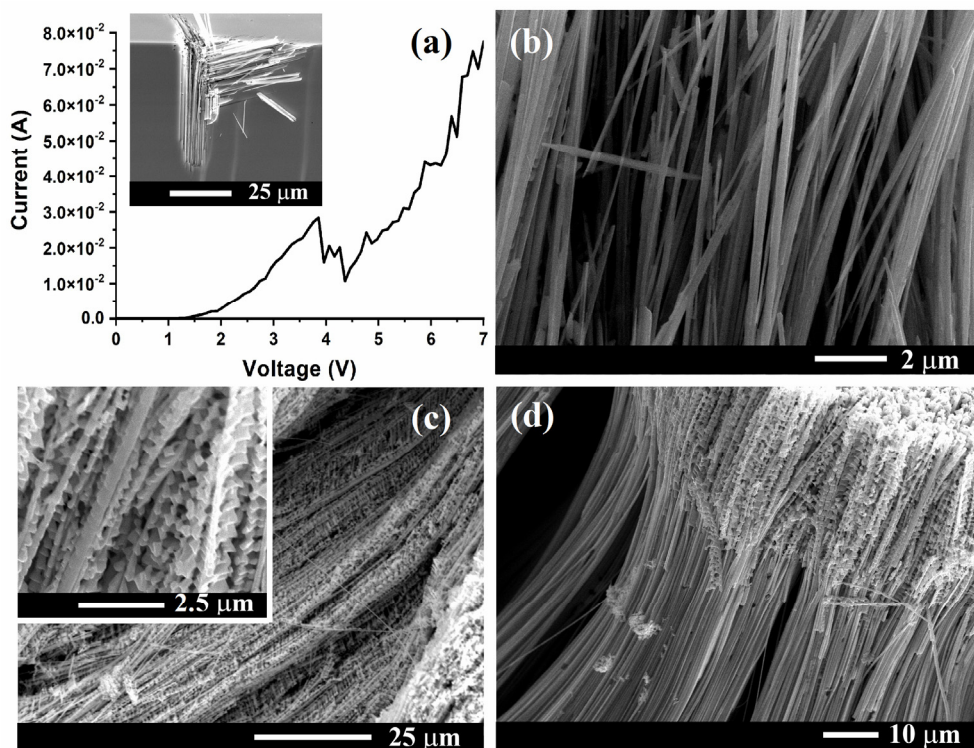
Crystalline 500 μm thick (111)B-oriented n-GaAs substrates with a free electron concentration of $2 \times 10^{18} \text{ cm}^{-3}$ were used. The samples were sonicated in acetone for 15 min, cleaned in distilled water and dried. In order to remove the native oxide from the surface, the samples were dipped in a HCl:H₂O solution with ratio (1:3) for 2 min. The anodization of GaAs crystals was carried out in a common two-electrode cell, where the sample served as working electrode. The design of electrochemical cell and description can be found in early published paper [2]. A Keithley's Series 2400 Source Measure Unit was used as potentiostat. The current – voltage polarization curve was measured at a slope scan of $10 \text{ mV} \cdot \text{s}^{-1}$. A Vega Tescan 5130 MM Scanning Electron Microscope (SEM) equipped with an Oxford Instruments INCA Energy EDX system operated at 20 kV was used to investigate the morphology and chemical composition analysis of anodized GaAs crystals.

RESULTS AND DISCUSSION

In Figure 1a the current-voltage (I–V) curve of the electrochemical dissolution behavior of (111)B GaAs substrate is presented. From the I–V curve clearly can be seen that the interval of pore formation in from 2 V up to 5 V followed by exponential increase of the current leading to the electropolishing. The mechanism of pore formation and transition from the porous GaAs structures to nanowire arrays was discussed in early published papers [2,7]. It should be mentioned that in semiconductor compounds three types of pores were reported: crystallographically oriented pores; current line oriented pores; and fractal pores. Up to now, no current line oriented pores were reported for anodized GaAs. The characteristic for GaAs crystallographically oriented pores, in contrast to current line oriented pores, can intersect each other and grow at low applied potentials or current densities.

The inset image in Figure 1a demonstrate the formation of pores during the anodization at applied voltage 2 V that grow perpendicular to the (111)B oriented GaAs surface. As mentioned above, the crystallographically oriented pores can intersect each other and at optimized anodization parameters the formation of GaAs pores occurs concomitantly with

the grow of pores that intersect the primary pores. With the further increase of the applied potential interval 3–4 V the formation of GaAs nanowires with the diameter 200–300 nm occurs (see Figure, *b*). At a certain applied voltage, 4.5 V in our case, a combination of cristo pores aligned perpendicularly to the sample surface and tilted pores intersecting them occurs; similarly to the pores growth from the inset in Figure, *a*. As a result, the diameter modulated nanowires or perforated nanowires are obtained as is presented in Figure, *c*. The anodization process strongly depends upon the applied voltage. Taking into account this behavior, the formation of perforated and smooth GaAs nanowires arrays in the same technological process at two different applied voltages is demonstrated as is presented in Figure, *d*.



(a) The polarization curves measured at the beginning of the electrochemical anodization of (111)B oriented GaAs substrate in 1M HNO_3 electrolyte. The inset in (a) represent SEM image of anodized GaAs at applied potential 2 V. (b) SEM image of anodized GaAs sample at 3 V resulting in formation of nanowires with a smooth wall. (c) SEM image of diameter modulated GaAs nanowires with a length of 200 μm produced at 4.5 V with the enlarged SEM view in the inset. SEM image of anodized GaAs substrate at 4.5 V for 5 min with formation of perforated GaAs nanowires followed by reducing the applied potential to 3 V for smooth nanowires obtaining

CONCLUSIONS

The formation of diameter modulated GaAs nanowires via anodization of (111)B oriented GaAs substrates is demonstrated in a single step process. The morphology and chemical composition were systematically investigated by means of scanning electron microscopy. The approach is based on anodization at optimized applied potential allowing simultaneous growth of pores oriented perpendicular and tilted to the GaAs surface. The key factor allowing to modulate the GaAs nanowire diameter is the feature of crystallographically oriented pores to intersect each other. A selective modulation of nanowires via anodization at two different applied potentials is demonstrated. The three-dimensional modulation of diameter will give the possibility to increase the area of their applications.

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