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High density near amorphous InSb nanowire arrays and its photo-electric performance



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1. Introduction

Photo-electric (PE) materials in the infrared field are very important in military, aerospace, industry and medical and health work [1]. To obtain the infrared detection material, the molecular beam epitaxy (MBE), liquid phase epitaxial growth (LPE) and metallo-organic chemical vapor deposition (MOCVD) technologies was usually utilized. The products obtained by those techniques usually had perfect performance, but suffered the expensive equipment and raw material, sophisticated technology, etc. For the focal plane array (FPA), the etching technique was also needed [2]. Currently, the size of the mostly used infrared FPA is about 1024×1024 and 2048×2048 (4,000,000 pixel). Only a few reports had achieved 4096×4096 pixels. Limited by the diffraction limit, it is difficult to reduce the size of single unit of the pixels. But a most important way to enhance the resolution and recognition ability is by increasing the density of detection unit, which could be achieved by reduction of the size of single unit. So, the development of the fabrication technique of well-aligned and vertical nanowire (NW) array is of great importance for the future micro-PE devices [3].

Infrared (IR) detectors using nano materials have received great attentions recently [4,5] because of their high sensitivity photodetection, fast response speed and low energy consumption. The nanomaterial array obtained by anodic aluminum oxide (AAO)

ABSTRACT

In this paper, we report the fabrication of high density near amorphous InSb nanowire arrays with using 30, 55 and 70 nm diameter anodic alumina oxide (AAO) template by electrodeposition method. The near amorphous structure was proved by combining the results of X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM). Different from the bulk material, these nanowires are black and could not be analyzed by the traditional method, and the reason was discussed. By testing of the photo-electric performance, the 30 nm diameter InSb nanowire showed the best performance, which could be used at about 260 K. The formation of the near amorphous structure was also discussed. Such high density nanoarrays may found potential application in the infrared detection field.

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assisted method (electro-deposition [6,7], sol-gel method [8,9], vapor deposition [10,11], etc.) was a recently most utilized method toward high density nano arrays. The density of the pore of AAO is usually 10¹⁰–10¹¹/cm². So if we could assemble nanomaterial that could be potentially used as photo-electric material in the pore of AAO template, a maximum billion or ten billion pixel density chip may be obtained. (Actually, it is difficult to use the technology right now to obtain a butt joint circuit to this, but we could utilize more than one nanounit to as a single pixel. At the current level of the electrode fabrication, it is easily to obtain 10 million pixels.) So the resolution of the FPA could be greatly enhanced, and at the same time the simplified technological process may make the expansion of the production easily. Currently, people have begun to fabricate infrared PE materials by the AAO assisted method, but only a few of them was related to the PE performance. [4,9,12–18] So, utilized the AAO template to fabricate high density array of infrared PE nanomaterial and investigate the infrared PE performance is of great value both in theory and application.

As a direct bandgap semiconductor, indium antimonide (InSb) has a narrow band gap, measuring 0.17 eV at 300 K and corresponding to IR wavelength ($6.2 \mu m$) [12,19,20]. The exciton Bohr radius of InSb is about 65.5 nm [21], and the quantum confinement effect will dominate when the diameter of the InSb nanowire is less than its Bohr radius. These properties make it an ideal material for PE and long-wavelength detectors, field-effect transistors (FETs), quantum devices, etc. [22–33]. Most of the reported InSb nanowires were crystallinity [14,20]. But reducing the crystal size may be considered as another way toward disorder, which seems



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favorable as a detector. So, what would happen while the maximum disorder – amorphous?

Therefore in this paper, we fabricated the near amorphous InSb nanowire arrays and investigated its infrared PE performance, which showed the potential application in infrared detection.

2. Materials and methods

2.1. Materials

The reagents were purchased from Shanghai Runjie Chemical Reagent Co., Ltd. All chemicals were analytical grade and used without any further purification.

2.2. Synthesis

The details of the fabrication of AAO template could be found elsewhere [6–8]. In a typical fabrication, an aluminum disk with 99.999% purity and 0.5 mm in thickness was firstly washed with acetone, alcohol, respectively for several times. And then it was used as anode and against a graphite cathode in the 0.3 mol/L oxalic acid solution. Different voltage (30, 40 and 50 V direct current (DC) was used in this experiment) was added on to achieve different diameter of the holes. After that, it was subject to dissolving of the back aluminum and the Al_2O_3 barrier layer, and AAO template with open holes was obtained. To be used in this experiment, an Au film was evaporated on one side as electrode.

The fabrication of InSb nanowire arrays was performed under the air condition. Firstly, appropriate amount InCl₃, SbCl₃, tartaric acid ($C_4H_6O_4$), citric acid ($C_6H_8O_7$ ·H₂O), glycerol ($C_3H_8O_3$), sodium citrate ($C_6H_5O_7$ Na₃·H₂O) and NaCl were dissolved in water to obtain 0.02 mol/L, 0.02 mol/L, 0.05 mol/L and 0.6 mol/L solution, respectively. After that, an AAO template with Au film was used as negated electrode and 1.4 V DC was added. 10 h later, the template was taken out and washed with deionized water for several times.

2.3. Characterization

Different treatment on nanowire arrays-AAO template was performed to satisfy the need for different characterization. For XRD, TEM, uv–vis–NIR absorption and FTIR investigations, the Au film of the sample was firstly grinded off, then it was soaked in the NaOH solution (5%) for a long time enough dissolved the Al₂O₃ (about 10 min or longer as heating at 60 °C). As the uv–vis–NIR absorption and FTIR investigations, the samples were redissolved in the alcohol, and then spread on a CaF₂ glass. For FESEM investigation, it was only dissolved in NaOH for about 5 min without grinding off the Au film. As for the PE measurements, the template was floated on the NaOH (5%) solution for 3 min with the Au film side up. After that, it was dried at 60 °C for 5 h before evaporated with an Au film on the other side (a plastic ring (4 mm in diameter) was used as mask to avoid short circuit). Then the template was cut by a knife grinder into two pieces. A gold wire was glued on the hall fround Au electrode with conducting resin, and put into the oven at 80 °C for 10 h.

The phase of the powder was identified by X-ray diffraction (XRD) using a Philips X'Pert Pro MPD with Cu K α (λ = 1.5406 Å) radiation. The morphology, crystalline size, and crystal structure of the sample were determined by Field Emission Scanning Electron Microscopy (FESEM; FEI Sirion-200), transmission electron microscopy (TEM) and high resolution Transmission Electron Microscopy (HRTEM; JEOL JEM-2010, 200 kV). The optical absorption spectra and the fourier-transform infrared (FTIR) transmission spectra were measured by uv-vis-NIR spectrophotometer (Shimadzu, UV-3600) and FTIR spectrometer (Nexus), respectively. The photoelectric performance measurement was performed in a low-temperature probe station (TTPX, Linkphysics Corporation) with a CaF₂ glass window with a transparence range covers from 130 nm to 11 µm. Liquid nitrogen was used as refrigerant. The temperature range was from 80 K to 380 K. A SiC lamp was put at 30 cm from the sample with illumination power of 0.046 mW/cm². The electric measurement was utilized with a Keithley digital source meter (2400). A mechanical switch was used to control the optical path. All the photo-electric measurement experiment was placed in a closed box to reduce the stray light.

3. Results and discussions

Fig. 1 is the XRD pattern of the InSb nanowire array obtained at 1.4 V electro-deposition utilizing the 30 V AAO membrane. A broad dispersion peak with 2θ from 20° to 50° should mainly ascribe to the amorphous glass substrate. Besides, only two weak peaks locate at 39.4° and 46.6° Could be distinguished. By considering the standard InSb JCPDS card no. 731985, these two weak peaks indicate the near amorphous phase of InSb, and which would be further proved. Fig. 2 presents the FESEM images of the product. The nanowire is about 30 nm in diameter, which is corresponded



Fig. 1. XRD pattern of the InSb nanowire.

to the pore diameter of the AAO template. The nanowire is about 3 μ m in length and has a very high fill ratio in the template.

Fig. 3(a) is the TEM image of a single nanowire. It could be seen that the nanowires are uniform. From Fig. 3(b), the nanowire does not present obvious lattice fringe, indicating the near amorphous, which could be further proved by the SAED pattern in Fig. 3(c). The results are consistent to the XRD result. Fig. 3(d) is the EDS pattern of the nanowire. Only In, Sb, C and Cu elements are found. (The Cu and C originate from the Cu net.) The atomic ratio of In and Sb is \approx 1:1. This further proves the product is InSb.

Fig. 4 shows the XRD and HRTEM images of the nanowire obtained in 40 V and 50 V AAO membranes, respectively are 55 and 70 nm in diameter. From the XRD pattern, their intensity is a little higher than that of the 30 nm nanowire. The peak at about 24° is observed. However, from the HRTEM images, both of the nanowires do not show obvious lattice fringe, meaning the near amorphous structure.



Fig. 2. FESEM images, (a) the enlarged topview, (b) the topview, (c) the large scale view of the arrays and (d) the side view of the nanoarrays.

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