Highly Sensitive Arrayed Indium-Antimony Nanowires for Infrared Detection

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Abstract

The objective of this study is to achieve a high sensitive infrared detector by fabricating highly ordered array of indium-antimony (In-Sb) nanowires which is a semiconductor material. The approach is to investigate an infrared detector with arrayed nanowires which can transport signals in one dimension to obtain high efficiency and sensitivity compared with In-Sb by using traditional thin film fabrications. This research expects to provide an infrared detector by fabricating III-V alloy nanowires to highly improve the resolution of infrared signal. To develop scaled-up functional devices, highly ordered nanowire arrays are essential building blocks. Many candidate materials (metals, alloys, oxides and semiconductors) have been studied for various potential applications in nanotechnology and have shown some promising results. The solid metallic nanowires have been exploited for a wide range of applications to take the advantages of their large length/diameter aspect ratio. Further development to synthesize nanowires efficiently at lower cost is the direction for manufacturing next generation nanodevices. In this study, various diameters of ordering nanowires, from 10 nm to 500 nm, were fabricated and evaluated the performance of the sensitivity of infrared detection. Moreover, a 1 inch plate, which can be regarded as a device, with nanowires array was fabricated by designing a new type of processing chamber.

Keywords: InSb, nanowires, AAO, infrared

Introduction

Photoelectric materials in the infrared applications are very important in military, aerospace, industry and medical and health work. In 1950s, indium-antimony (InSb) was discovered it had the smallest bandgap of any semiconductor known at that time and it can be applied as middle wavelength infrared detector. The bandgap of InSb is matched to the 3000-5000 nm wavelength at high operating temperatures, and better performance can be achieved from HgCdTe, which is a common material for infrared detection. Zndian compared HgCdTe and InSb photodiodes their dependence of dark current on temperature. [1] However, InSb is still an interesting material for infrared detection due to the difficulties in growing HgCdTe. Traditionally, the standard fabrication of InSb starting with n-type silicon wafer with donor concentration about 10^{15} cm^{-3}. The molecular beam epitaxy (MBE), liquid phase epitaxy

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growth (LPE) and metal-organic chemical vapor deposition (MOCVD) technologies were usually utilized to yield products with impeccable performance. However, these technologies require very expensive equipment and raw materials. For the infrared focal plane array (FPA), the size of the mostly used currently is about 1024×1024 and 2048×2048 (4,000,000 pixel). [2-3] The most important way to enhance the resolution and recognition ability is to increase the density of detection unit, which can be obtained by reducing the size of single unit. Therefore, the etching technique was also needed to fabricate ultra-high-density pixel array is an important method to achieve better performance FPA devices.

Recently, the development of fabrication technique of well-aligned and vertical pixel array by using nanomaterials for infrared detection have received great attentions. The nanomaterials arrayed photoelectric devices have great potential to obtain high sensitivity, fast response, and low energy consumption. The highly ordered array nanostructure can be achieved with high-aspect-ratio template. Anodic Aluminum Oxide, also known as Al_2O_3 or AAO, is a ceramic with a high melting point and high hardness. Anodic alumina is known by various names: anodic aluminum oxide (AAO) [4-9], anodic alumina nanoholds (AAN), anodic alumina membrane (AAM), or porous anodic alumina (PAA). According to Chen's report [10], AAO has an ordered nano-structure arrangement. When aluminum is anodized in an acid electrolyte under suitable conditions, it forms a porous oxide called AAO with very uniform and parallel cell pores. Each cell contains an elongated cylindrical sub-micron, or nanopore, that is normal to the aluminum surface and extends from the surface of the oxide to the oxide/metal interface. Aluminum and AAO are sealed by a thin barrier oxide layer with approximately hemispherical geometry. The structure of AAO can be described as a closely packed array of columnar cells. Schematic diagrams of AAO are shown in Fig. 1. Fig. 1a shows a schematic diagram of AAO template on Al substrate and the barrier layer was between AAO and Al. The pore diameter and pore density can be controlled by applied voltage, and the film thickness can be controlled by anodizing time. Fig. 1b, a side view of the AAO structure, shows an open pore on the top, a closed pore or barrier layer on the bottom, and the Al substrate under the AAO film. Each cell that is extending from the surface of the oxide to the oxide/metal interface contains an elongated cylindrical sub-micron or nanopore that is normal to the aluminum surface where it is sealed by a thin barrier oxide layer with approximately hemispherical geometry.

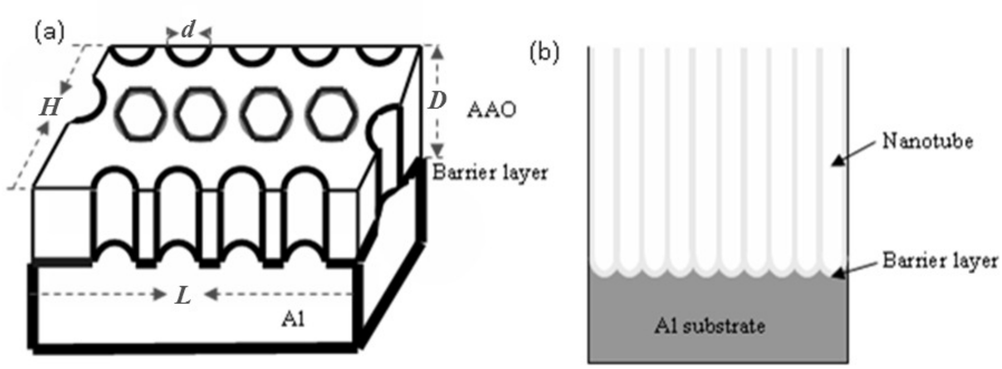


Fig. 1 The schematic diagram of AAO template.

Infrared detecting materials can be filled into the AAO template to obtain highly ordered pixel array.

However, traditional processes mentioned above have difficulties to perform conformal coating in the high-aspect-ratio template. Therefore, solution-based methods, such as electrodepositioin and sol-gel deposition, have been utilized to obtain highly ordered pixel arrays. The pore density of AAO template is generally 10^{10}-10^{11}/cm^2. Photoelectric materials can be filled into the AAO template to build a maximum billion or ten billion pixel device. So the resolution of the FPA could be greatly improved with a simpler process by AAO template assisting. Currently, infrared photoelectric materials using AAO template have been reported. InSb has a narrow bandgap as a direct bandgap semiconducting material. Adding other elements is a possible method to adjust its bandgap, but it is very difficult to achieve doping during the electrodeposition and sol-gel deposition processes. Unlike electrodeposition and sol-gel deposition, InSb nanowires can be doped by adding a few amount of supplemental metals through heat injection molding process. [11-13]

In this paper, we fabricated the InSb nanowire arrays by heat injection molding with AAO template assisted. We also investigated its infrared detecting performance which showed the potential for further infrared detection application.

Experimental

The experimental procedures listed as below, including manufacturing of AAO template and fabrication of highly ordered InSb nanowires array.

(1) Fabrication of a nanotubular template by anodization process.

(2) Modification of the tube diameter of the oxide template by a chemical etching process.

(3) Formation of a bulk material of InSb with a desire composition.

(4) Filling a liquid phase of InSb into the oxide template by a die casting process in order to form a highly ordered nanowire array.

The high quality AAO template fabrication steps are: Al foil (99.999%) → mechanical-polishing → annealing → electro-polishing → 1st anodization → remove AAO → 2nd anodization → remove aluminum substrate → remove barrier layer → both sides pore widening. the detail experimental operation and parameters as discuss in the following.

The AAO quality depends on the purity of Al substrate. The higher Al purity, such as 99.999% (5N), the better quality of AAO with uniform pore diameter can be obtained. The AAO templates with 15 nm, 60 nm, and 400 nm diameters are manufactured by anodizing a pure aluminum (Al) substrate (99.999%) in acid solutions of sulfuric acid (H_2SO_4), oxalic acid $(COOH)_2$, and phosphoric acid (H_3PO_4), respectively. The Al substrate was first polished to #1000 by SiC water proof paper, then annealed in the air furnace at 550℃ for 1 hr. The sample was then electrochemically polished in a bath consisting of 15 vol.% perchloric acid ($HClO_4$, 70%), 70 vol.% ethanol (C_2H_6O, 99.5%) and 15 vol.% monobutylether (($CH_3(CH_2)_3OCH_2CH_2OH$), 85%) applied 42 volt (DC) for 10 min. The 60 nm-diameter template was fabricated by anodizing the polished Al substrate at 40V in 3 vol.% $(COOH)_2$ at room temperature for 20 min, which is called the first anodization. In order to obtain an order pattern on the substrate for the second anodization, the first anodization film was removed in the 1.8 wt.% chromic acid (CrO_3) + 6 vol.% H_3PO_4 solution at 60℃ for 40 min. The substrate with regular pattern on the surface was used for the second anodization for hours to form a highly ordered AAO film. The Al substrate can be removed when the sample was put in a saturated copper chloride ($CuCl_2$) + 10 vol.% hydrochloric acid (HCl) for 30 min. Finally, the AAO template can be pore-widened in the 5 vol.% H_3PO_4 at 25 ℃ for 90 min. Fig. 2 showed the AAOs have nano-pore of 10 nm and the sub-micron pore of 357 nm structure. Finally, the highly ordered nanotubular template was ready to assist the InSb nanowire array synthesis.

Indium antimony tablet was first prepared in a 1:1 molar ratio in a vacuum quartz tube, and it was melted at 610 ℃ for 30 min. After InSb ingot was obtained, mechanical polishing was conducted to remove surface oxide. The InSb-ingot-covered AAO template was placed between the two plates as shown in the insert in Fig. 3b. The entire chamber (Fig. 2b) was vacuumed and heated to 610 ℃ again, then load 50 kgf / cm^2 for 5 min to press melting InSb into AAO template to form InSb nanowire array. Finally, the entire chamber was cooled down under air atmosphere.

A field-emission scanning electron microscope (FESEM; Hitachi SU-8010) with a 15 keV operating voltage was used to observe the top view and cross-sectional view of the InSb nanowire array. An energy dispersive X-ray spectroscopy (EDX; Inca Energy System) was used to analyze the elemental composition of the InSb nanowire array. A Fourier transform infrared spectrometer (FTIR) was used to measure the infrared absorption ability of the InSb nanowire array.

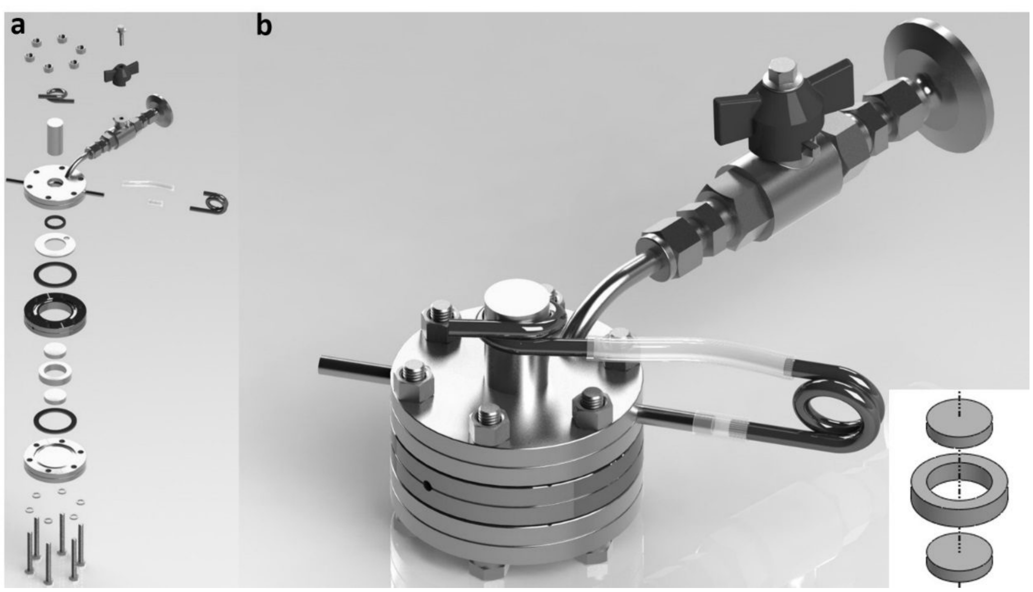


Fig. 2 The chamber design for the heat injection molding process.

Results and discussion

Fig. 3 shows the SEM images of InSb nanowires in AAO template. Fig. 3a and 3b show the top-view images, and the filling ratio of InSb nanowire was over 90 % which means the die casting process was successful. Fig. 3c and 3d are the cross-sectional view of the arrayed InSb nanowires. Fig. 4 shows the compositional analysis result by EDS. The composition of the InSb nanowire array was slightly changed compared to the composition of the InSb ingot. It is because that indium is easier to evaporate than antimony and the vapor would be extracted by the vacuum system in the chamber. Therefore, the final composition shows more antimony in the nanowire array. Fig. 5 shows the FTIR results of the InSb nanowire array. This result present a high absorption ability to the infrared. Moreover, the die casting process in this study has the advantage of the high capability of composition modification than any other processes. Fig. 6 show the XRD results of the doped InSb alloys. Fig. 6a shows XRD results for different amounts of Ni-doped InSb, and Fig. 6b presents the XRD results for different amount of Mn doping. These results confirms that the composition is adjustable, therefore, it is potential to fine tune the bandgap of the InSb nanowire without any complicated procedure in conventional fabrication processes.

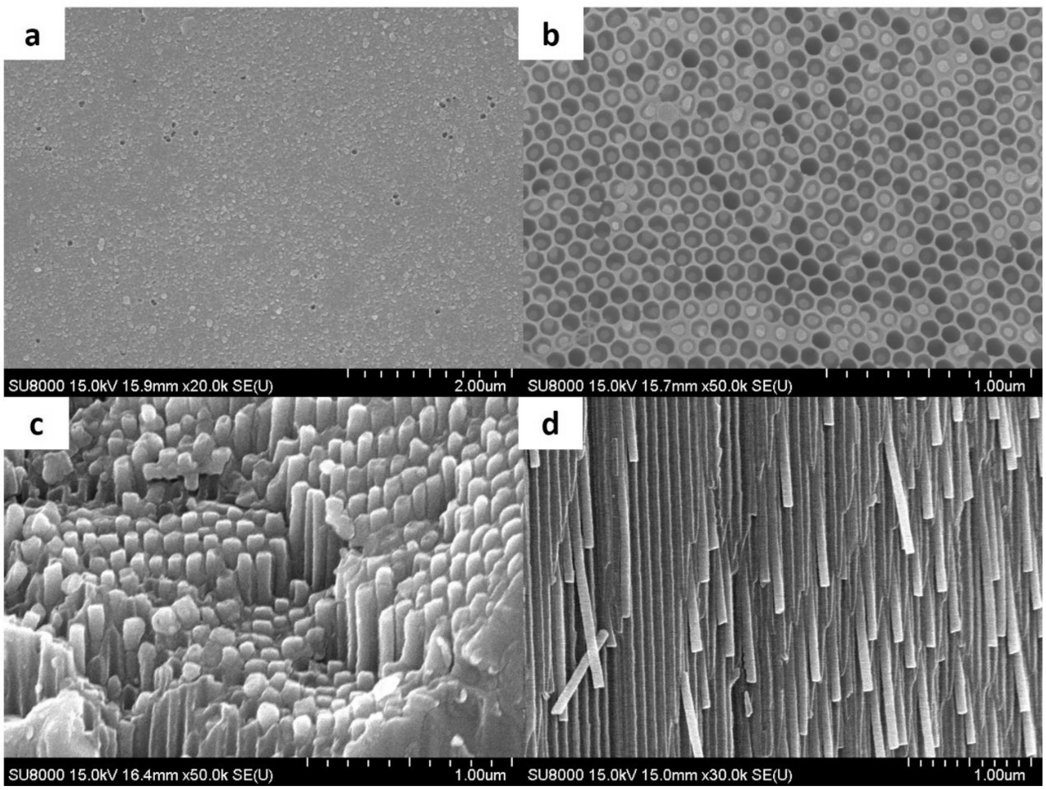
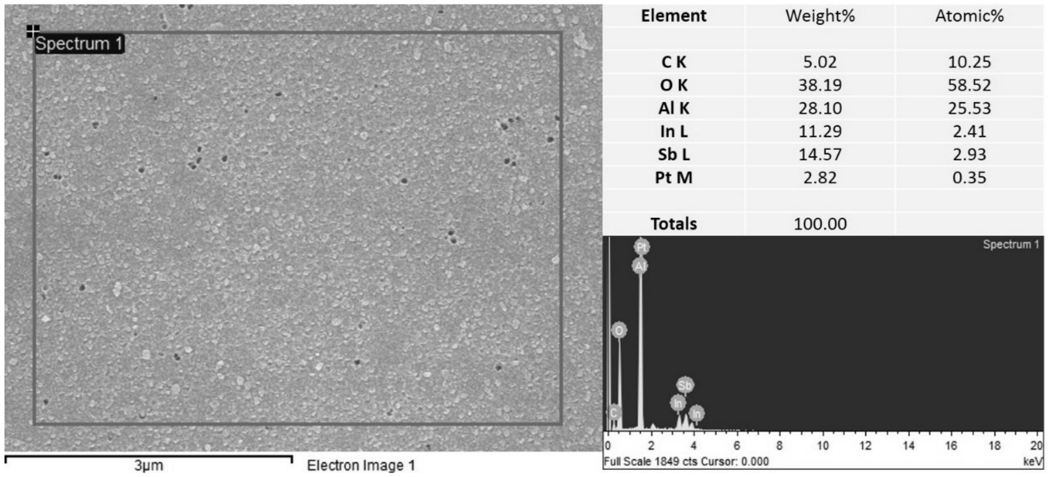


Fig. 3 The SEM images of InSb nanowire array; (a) top view in 20,000 X, (b) top view in 50,000 X, (c) cross-sectional view in 50,000 X, and (d) cross-sectional view in 30,000 X.



Element	Weight%	Atomic%
C K	5.02	10.25
O K	38.19	58.52
Al K	28.10	25.53
In L	11.29	2.41
Sb L	14.57	2.93
Pt M	2.82	0.35
Totals	100.00	

Fig. 4 The EDS analysis of the InSb nanowire array.

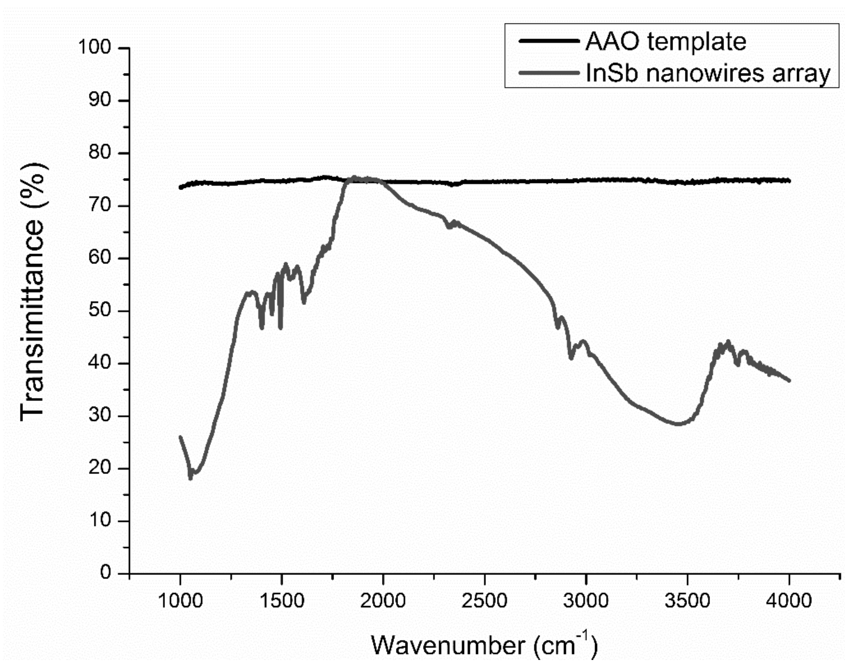


Fig. 5 The FTIR transmission spectra.

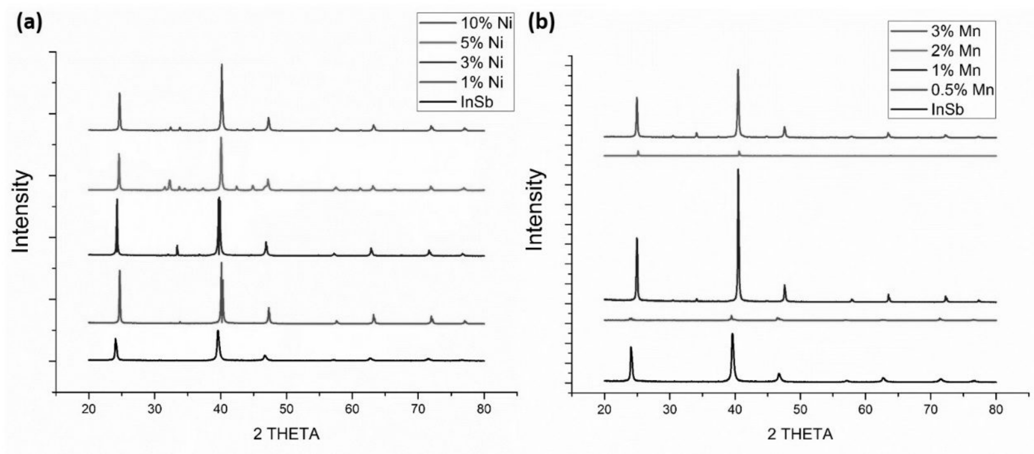


Fig. 6 The XRD results for doped InSb alloys; (a) doping Ni and (b) doping Mn.

Conclusions

In this study, we successfully designed and fabricated a die casting system for synthesizing InSb nanowire array with AAO template assisted. It shows high sensitivity to infrared, and it has potential to develop a new generation of infrared detection device.

Acknowledgement

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