

EFFECT OF DEPOSITION TIME ON THE MORPHOLOGY AND STRUCTURAL PROPERTIES OF INDIUM ANTIMONIDE (InSb) NANOWIRES BY TEMPLATE ASSISTED ELECTRODEPOSITION

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ABSTRACT

Semiconductor InSb nanowire have been synthesized by the typical three-electrode electrochemical cell. The deposition is from tartaric acid aqueous solution into anodic alumina oxide (AAO) at different time deposition varies from 15 to 40 mins with constant deposition potential of -1.5 V. The morphology and structural properties of InSb nanowires were studied using XRD and FESEM equipped with EDX. The nanowires have diameter varying and the length of the template assisted InSb nanowires varied from the deposition time of 15 to 40 mins, from 100 to 200 nm respectively. The length of synthesized InSb nanowires increases from 1.8 to 5.5 μm with the increasing deposition time of 15 to 40 min. The XRD analysis shows that the diffraction peaks of nanowires are on a plane (111) and (220). Based on the elemental composition from the EDX, almost stoichiometric composition with ratio 1:1.1 was achieved for the samples deposited for 35 and 40 minutes.

INTRODUCTION

Several consideration progress has been achieved in III-V nanowires based optoelectronic devices such as photodetector [1], solar cell [2], photovoltaic [3] and light emitting diode (LEDs) [4]. Indium antimony (InSb) nanowire is a III-V semiconductor compound has attracted consideration potential since it is recognized for its direct narrow band gap (0.18 eV at 300 K), very high-electron mobility ($8 \times 10^4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at 300 K), and thermal conductivity ($16.0 \text{ Wm}^{-1}\text{K}^{-1}$). Typical example method for fabrication of III-V semiconductor nanowires are include CVD, [5,6] MOCVD [2,7] and MOVPE [8]. Though, the major disadvantages of this method are its requires high vacuum, high temperature, and even expensive and toxic metal organic precursors. Hence template assisted electrodeposition is being considered since its potentially more cost-effective, because no expensive vacuum equipment is needed. In addition, the lower growth temperatures, typically at room temperature, make electrodeposition attractive for semiconductor processes not compatible with higher temperatures [9]. It is one of the promising methods to synthesis InSb nanowires with

controlled shape and size based on electrochemical synthesis that had widely been reported [1], [10-14]. However, there are several limitation faced by the experiment reported before such as they does not able to reach a right stoichiometric In to Sb ratio and the existence of structural defects [10], [12-14]. Thus, achievement of better control of stoichiometry and NWs structures is favourable and will be important for future device application. Time of deposition is one of the parameters in an electrochemical experiments that might give an important response for the result obtained. Therefore, in this paper, we report the fabrication and structural characterization of InSb NWs arrays in the AAO template by the electrodeposition technique at different time of deposition.

EXPERIMENTAL

The InSb nanowires were synthesis by electrochemical deposition inside the AAO template. The electrodeposition were carried out in a typical three-electrode electrochemical cell equipped with a platinum (Pt) electrode as the counter electrode, Ag/AgCl as references electrode, and the AAO template with Au layer as the working electrode controlled by a potentiostatic. The AAO template was purchased from the Whatman Inc. Florham Park. The diameters of the pores in the AAO are 200 nm. Initially, 200 nm a layer of gold was sputtered on the bottom sides of AAO to serve as a conduction contact for nanowires growth. The electrolyte used composed of 0.02 M SbCl_3 , 0.03 M InCl_3 , 0.1 M tartaric acid, and 0.002M HCl. The InCl_3 and SbCl_3 provide metal ion source. While the tartaric acid is used as a complexing agents to bring the deposition potential of In and Sb closer to maintain binary growth. The deposition was conducted at different deposition time: 15, 25, 30, 35 and 40 mins, under the fixed deposition potential of -1.5 V at room temperature. After the deposition, the sample was washed several times in distilled water and rinsed with acetone. After rinsing with distilled water, the samples were immersed in 3 M NaOH solution for 20 minutes until all the AAMs completely dissolve. Then, the samples were centrifuged washed with distilled water to remove the NaOH solution.

The morphological and structural properties of nanowires were characterised by Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-7600F) equipped with energy dispersive X-ray spectroscopy (EDX) and X-ray Diffraction (XRD-Hitachi X'Pert Pro Panalytical).

RESULTS AND DISCUSSION

Figure 1 shows the FESEM images of the InSb nanowire deposited at different time of deposition after detaching from AAO template. Clearly the deposition time has a significant effect on the nanowires morphology, which changes from bundled to single nanowires with deposition time. The image show in Figure 1 (a) and (b) indicates the nanowires deposited for 15 and 25 minutes are poorly aligned and the nanowires arrays were stuck together, resulting in the formation of nanowires bundle especially for nanowires deposited for 25 mins (Figure 1 (b)). It is possible that the poorly aligned

nanowires might be due to loss of support from AAO membrane during the etching process in NaOH [14]. While the formation of coalescence nanowire bundles may due to surface tension arises from perturbations in the drying process [15]. If the bending force overwhelms the stiffness of the nanowire during the drying process, then the nanowire will bend toward the other nearby nanowires which can be intensified by inhomogeneities in nanowire sizes and spacing [16]. Figure 1 (c) to (e) shows the FESEM image of InSb nanowires deposited at 30, 35 and 40 mins. The InSb nanowires shows are singles nanowires with uniform diameter. At least five nanowires were measured for every sample. The average length of InSb nanowires varies from 1.767 μm to 5.493 μm as shown in Table 1, which corresponds with the deposition time. The average values of the nanowires length and growth rate as the function of deposition time are plotted in Figure 2. An obvious trend shown by this plot is that the nanowires length increases with increasing deposition time, similar of nanowires also increasing. Hence, it can be said that the length of the nanowires is strongly affected by time deposition similar to the previous report [9].

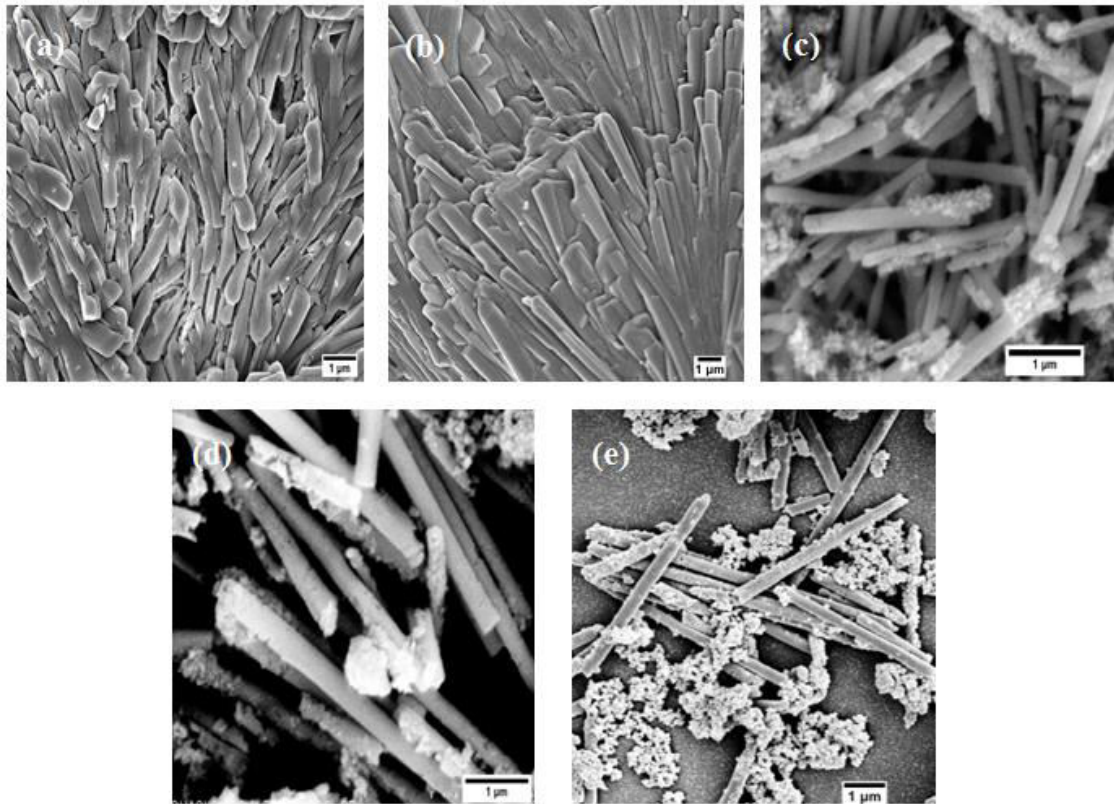


Figure 1: Top view FESEM image of the InSb nanowire array deposited at different time deposition; (a) 15min, (b) 25min, (c) 30min, (d) 35min and (e) 40min

Table 1: Average length of InSb nanowires and atomic composition based on EDX analysis

Time (min)	Length of nanowires ($\pm \mu\text{m}$)	Growth rate ($\mu\text{m}/\text{min}$)	Atomic %		Ratio In:Sb
			In	Sb	
15	1.767 ± 0.5	0.118	85.2	14.8	6.1:1
25	3.219 ± 0.6	0.129	86.7	13.3	3.0:1
30	3.602 ± 0.45	0.120	58.23	41.74	1.5:1
35	4.349 ± 0.5	0.124	47.0	53.0	1:1.1
40	5.493 ± 0.3	0.137	45.33	54.76	1:1.1

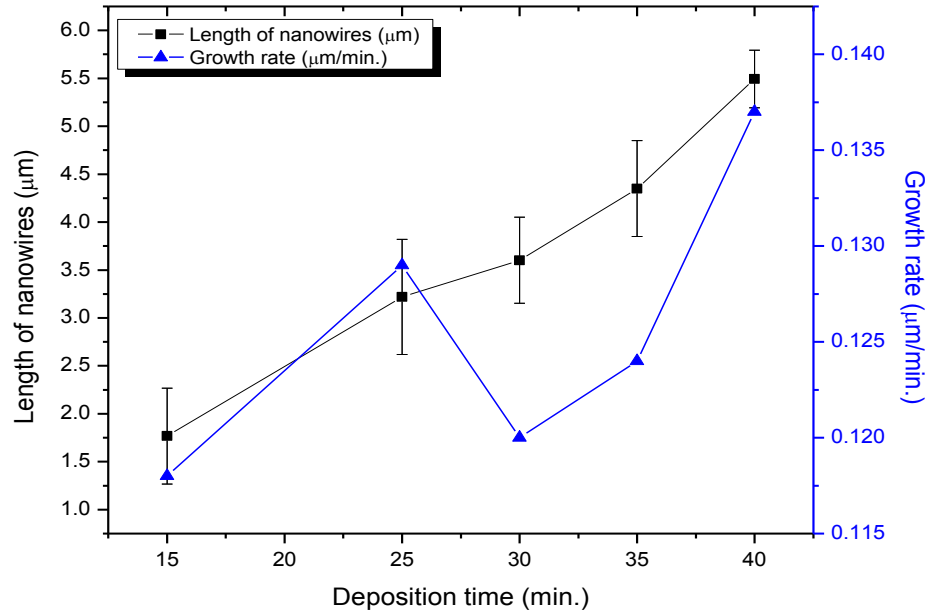


Figure 2: Graph of deposition time as a function of average length of nanowires and growth rate of nanowires

To determine the influence of deposition time on the atomic ratio, the EDX analysis under FESEM observation was performed. Table 1 shows that, the ratio of indium to antimony start to achieve a right stoichiometry ratio with increasing deposition time. At deposition time of 30, 35 and 40 minutes the atomic ratio of indium to antimony were nearly to 1 as shown in Table 1. The atomic composition at lower deposition time are not stable maybe due to the solubility limit beyond which is low solubility of Sb in In makes it becomes thermodynamically unstable at lower deposition time [5].

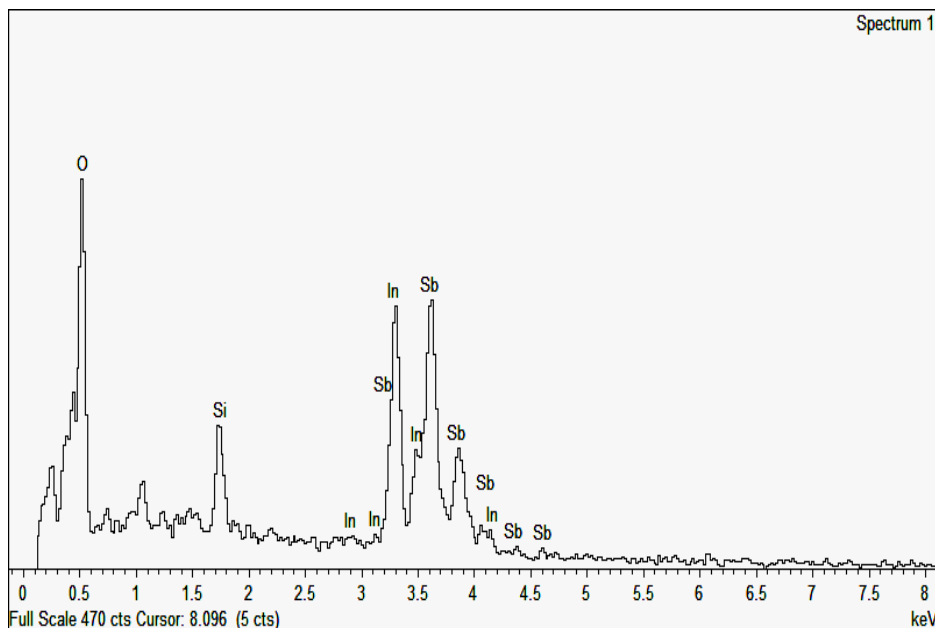


Figure 3: The EDX spectrum of near stoichiometric InSb nanowires deposited at 40 min

Figure 4 shows the XRD pattern of the InSb nanowires that were obtained by changing the deposition time at a constant deposition voltage. At 15 minutes deposition time, there is no pure InSb peak was observed. While for the InSb nanowires deposited at 25, 30, 35 and 40 mins deposition time, the XRD pattern showed InSb (111) and (220) peaks are identified at $2\theta = 23.7^\circ$ and 39.4° according to (ICDD-PDF Card No: 01-089-4299). It is clearly seen that the intensity of diffraction peak at $2\theta = 39.4^\circ$ relatively stronger than the other diffraction peak for InSb. Thus demonstrating that the InSb nanowires deposited in AAO grow preferentially along (220) crystal structures, with good agreement with the previous work [12],[14]. The XRD data show not only a pure InSb phase was form, but also In_2O_3 (ICDD-PDF Card No: 98-000-4257), Sb_2O_3 (ICDD-PDF Card No: 98-009-0443) and Al_2O_3 (ICDD-PDF Card No: 98-003-2934) denoted with symbol *, # and X respectively observed in diffraction peak especially at deposition time of 15 and 25 mins. The indium oxide and antimony oxide may formed during preparation of the electrolyte or formed on nanowires during drying processes and post storage before XRD analyses. Hence, carefulness for handling nanowires before and after the deposition should be include for optimization of electrodeposition technique to overcome the oxidation problem [10]. While peak Al_2O_3 corresponding to the AAO template that are not completely dissolved during etching process. The quality of crystallinity of InSb nanowires may be improve by conducted the annealing treatment [10],[11],[1](K. E. Hnida et al. 2015; Zhang et al. 2005; K. Hnida, Mech, and Sulka 2013) and can be considered for future study.

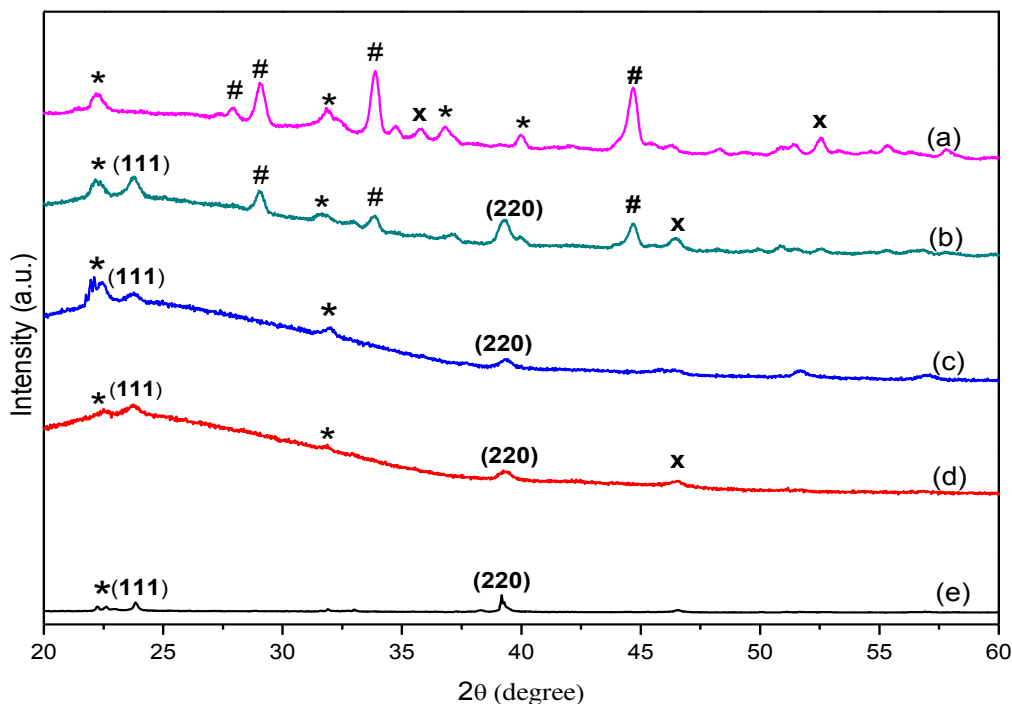


Figure 4: The XRD diffraction pattern of the InSb nanowires deposited at different time of deposition (a) 15 min, (b) 25 min, (c) 30 min, (d) 35 min, (e) 40 min

CONCLUSION

In summary, template assisted electrodeposition using AAO for fabrication of InSb nanowires allow to control their composition and morphology. The length of InSb nanowires is strongly dependent on the value of a time deposition. With the increase of deposition time the length of InSb nanowires also increases. Besides that deposition time also had influence on stoichiometry of the deposited InSb nanowires. The atomic ratio of indium to antimony was nearly to 1 form at the time deposition time of 30, 35 and 40 minutes. It was found that the single-crystalline InSb nanowire with right stoichiometric composition can be fabricated by proper controlling of the time deposition from 30min and above. Additionally, the InSb nanowires grow preferentially along (220) crystal direction. Achievement of better crystallinity of InSb nanowires than demonstrating here are possibles and very beneficial for future device application.

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