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# Understanding the Mechanisms that Affect the Quality of Electrochemically Grown Semiconducting Nanowires

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#### Abstract

Template-assisted synthesis of nanowires is a simple electrochemical technique commonly used in the fabrication of semiconducting nanowires. It is an easy and cost-effective approach compared to conventional lithography, which requires expensive equipment. The focus of this chapter is on the various mechanisms involving mass transport of ions during successive stages of the template-assisted electrochemical growth of indium antimonide (InSb) nanowires. The nanowires were grown in two different templates such as commercially available anodic aluminum oxide (AAO) templates and polycarbonate membranes. The chapter also presents the results of characterizing the InSb nanowires connected in a field effect transistor (FET) configuration. The Sb-rich InSb nanowires that were fabricated by DC electrodeposition in nanoporous AAO exhibited hole-dominated transport (p-type conduction). Temperature-dependent transport measurement shows the semiconducting nature of these nanowires.

**Keywords:** semiconducting nanowire, InSb, electrodeposition, anodic aluminum oxide (AAO), nanowire growth mechanism

## 1. Introduction

In recent years, anodic aluminum oxide (AAO) templates have been used extensively for fabricating myriads of nanostructures. AAO is a self-organized nanostructured material containing a high density of uniform cylindrical pores that are aligned perpendicular to the surface and extend over the entire thickness of the template. AAO is also optically transparent, electrically insulating, thermally and mechanically robust and chemically inert. Nanowire arrays that are grown in AAO template pores are used in many applications such as energy conversion [1], energy-storage devices [2, 3], electronics [4], metamaterials [5],



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optoelectronics [6], photonics [7], and piezoelectrics [8]. Template-assisted electrochemical growth of large-scale nanowire arrays is attractive because they are readily scalable to mass production. Moreover, it is possible to obtain an array of uniform diameter and length and a surface that can be engineered by nonuniformity of the template tubes.

This chapter reviews the various processes that govern the filling of the nanochannel alumina template pores resulting in a systematic growth of nanowires within the pores. We also discuss the challenges faced in achieving uniform growth including effects of pore-wetting and aeration. Any nonuniformity in the alumina template tubes also result in nanowires with rough surfaces, an exploitable result for use of nanowires in thermoelectric applications.

Over the last decade, there has been increasing interest in nanostructures of III–V semiconducting materials due to their potential applications in electronic and optoelectronic devices [9]. After identifying the various mechanisms of electrochemical growth of semiconducting nanowires, we present the specific growth process conditions for growth of indium antimonide (InSb) nanowires. Indium antimonide (InSb) bulk is a promising III–V direct bandgap semiconductor material with zinc blende (FCC) structure [10–14]. InSb has a high room temperature mobility (electron and hole mobility [15] of 77,000 and 850 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively), low electron effective mass [16] of 0.014, and low direct bandgap ( $E_g = 0.17 \text{ eV}$ , at 300 K), and large Lande g-factor of 51, [17] making it suitable for use in applications such as high speed, low-power transistors, tunneling field effect transistors (FETs), infrared optoelectronics [18], and magnetoresistive sensors [19].

Nanowires can be grown via electrodeposition in different nanoporous templates like anodic aluminum oxide (AAO) and ion track-etched polycarbonate. Every template type has its own advantage, disadvantage, and application.

## 2. Growth process: convection, migration, and diffusion

The benchmark method for synthesis of nanowire was suggested in 1986 by Martin et al. [20], where nanowires were grown inside polycarbonate membranes. This method has since been widely used to synthesize nanowires in both polycarbonate and anodic aluminum oxide (AAO) membranes. These membranes contain a high density of cylindrical pores that are perpendicular to the membrane surface and in most cases, these pores penetrate the entire membrane thickness. There have been several studies on electrochemical growth of nanowires but very small number of investigations on understanding the growth mechanism of nanowires in AAO pores.

Template-assisted nanowire growth process consists of two major steps: electrochemical reduction of the cation inside the pore, followed by removal of the template. Several studies [21, 22] have shown that during the pore-filling stage (nanowire growth), the total constant current density is independent of flux variation inside the pore and concentration of electrolyte at the mouth of pore during electrodeposition. Recently, another study [23] showed that the electrolyte concentration at the mouth of the pore remains constant and current decays

with time; a fact that contradicts the previous study where current remains constant. Here, we discuss the more realistic model that describes a situation where the electrolyte concentration at the mouth of the pores is different than the bulk during electrodeposition.

The electrodeposition growth process of nanowires in porous templates has been modeled by considering different mechanisms of mass transport at different stages of the growth process [24]. There are mainly three different mechanisms that could explain the growth process: (i) diffusion process (arising from concentration gradients existing between electrolyte in the template pores and in the solution), (ii) convection process (arising from movement of deposition ions in the electrolyte), and (iii) migration of ions into the template pores. Contribution of each process can be controlled by modifying the cell design, reducing depositing ion concentrations compared to mixing electrolyte, and stirring the electrolyte during growth process to avoid the concentration gradient.

#### 2.1. Diffusion mechanism in nanowire growth process

Mass transport of ions during nanowire growth is mainly controlled by a diffusion process. The three main stages of this process are shown in **Figure 1**. **Figure 1(a)** shows the earlier stage of diffusion where diffusion front propagates in only one dimension inside the pores.

**Figure 1(b)** shows the second stage where diffusion front reached the mouth of the pore and opens in three-dimensional hemispherical front. As soon as diffusion front reaches at the mouth, then there is a concentration gradient builds up between the mouth and the bulk. **Figure 1(c)** shows the third stage where linear diffusion happens inside and outside of the pores. This diffusion-limited electrodeposition results in a morphological instability driven by individual nanowires [25]. In template-assisted electrodeposition, nanowire length must follow the length of AAO pore, but some nanowire grows fast compared to others and ends up mushroom-like structures at the top surface of AAO template [26–31]. Recent study [25] also showed that this growth instability can be avoided by introducing temperature gradient between bottom and top of the AAO pores.



**Figure 1.** Schematic of growth of nanowire in a single nanopore: (a) linear diffusion, (b) linear and semi-infinite hemispherical diffusion, and (c) semi-infinite planar diffusion outside the pore (Adapted from Ref. [24]).

The diffusion mechanism during various stages of nanowire growth is described by the S-curve of current-time plot, as shown in **Figure 2(a)**.

The entire mechanism involves three consecutive growth stages: (i) one dimensional diffusion front inside AAO pores; (ii) linear diffusion inside the pores and hemispherical diffusion at the mouth of the pores; and (iii) merging of hemispherical diffusion front and resulting in planned front over the surface of the mouth. The electrodeposition time and average length of wire have been controlled by monitoring the deposition current versus time at given deposition voltage –1.5 V which was maintained with respect to reference electrode. Inset of **Figure 4(a)** shows the schematic of the various stages of electrodeposition.

In first stage of growth process, concentration of the electrolyte at the mouth of pores matches the concentration of the bulk of the electrolyte (c<sup>b</sup>). The linear diffusion front passing through pore length results in transportation of In and Sb ions inside the pores of the AAO template. The diffusion fronts between individual pores have not been overlapped at this stage. The concentration within the pore changes as nanowire growth starts and it has been expressed by Fick's law as:  $c(x, t) = c^{b} \operatorname{erf}\left[\frac{x}{2\sqrt{Dt}}\right]$ , where  $2\sqrt{Dt}$  is the diffusion length (L) that corresponds how far concentration varies along the pore length at time t. The initial pore length is L<sub>0</sub> at t = 0. There is a sharp decrease in electrodeposition current during this time, as is expected for diffusion-controlled process. The current was observed to decrease from 35 to 20 mA in region (I) of the plot in **Figure 2(a)** which corresponds to region (i) of growth process. In region (i), In and Sb ions diffuse to the bottom of the pore in the tubular column of AAO template to initiate nanowire growth.

During region (II) of the growth process, initial linear diffusion front reaches the mouth of the pores and three dimensional hemispherical diffusion front develops at the mouth. During this stage in region (II) of plot **Figure 4**, the steady increase in current has been observed and is believed to increase the diffusion of ions to the nanowire growth front. During the final stage in region (III), the nanowires have filled the pore completely and the hemispherical cap merges with each other and formed a continuous rough film on the surface of template. In the



**Figure 2.** Evolution of nanowire growth in the AAO template pores: (a) current-time plot of InSb nanowire growth showing different growth regions; (b) cross-sectional SEM image of the template in region I. The thin bottom layer is a gold film. The pores are partially filled with InSb. This region corresponds to a planar diffusion inside the pore; and (c) cross-sectional SEM image of region III where NWs have filled the pores and the dome-shaped tips collapse to form mushroom-shaped clusters, corresponding to semi-infinite planar diffusion at the mouth of the pore [32].

region (III) of the S-curve plot, current does not increase significantly and tends to saturate, as compared to region (II) of the plot. **Figure 2(b)** and **(c)** shows cross-sectional SEM images of template in the region (I) and (III), respectively. **Figure 2(b)** shows partially filled pores, which correspond to a linear diffusion in region (I) of the S-curve. **Figure 4(c)** shows the completely filled pores and hemispherical caps that merge to form a dense mushroom-like overgrowth on the surface of the pores.

#### 2.2. Convection mechanism in growth of nanowires

The effect of convection on nanowire growth process is dependent on cell design. The three electrodes in an electrochemical cell are: (i) working electrode (substrate); (ii) counter electrode (Pt wire/mesh); and (iii) reference electrode. To minimize the mechanism of natural convection, electrodeposition cell configuration is an integral part of nanowire growth in nanoporous templates. In **Figure 3(a)** and **(b)**, the cathode and anode are placed vertically above each other, whereas in **Figure 3(c)**, the cathode and anode are placed parallel to each other. The effects of convection are considered to be minimal for the design in **Figure 3(c)**. Konishi et al. [33] reported that the electrodeposition current increases in the case of anode over cathode **Figure 3(b)** configuration, and current decreases in the case of cathode over anode configuration **Figure 3(a)** during early stages of the electrodeposition. They have found the considerable difference in the transient behavior of the current in 100- and 200-nm-sized pores in certain stage of electrodeposition, which is caused by the electrolytic cell configuration.

The effects of natural convection are proven to be significant and reported in Ref [32] for the schematic shown in **Figure 4**, where an increase in convection current because of this mechanism is shown for pores size as small as 100 nm. This effect was observed during Cu electrodeposition.

#### 2.3. Migration of ions during growth of nanowires

To explain the InSb nanowire growth process in the following section, the effect of migration of In and Sb ions has not been considered in this discussion. Since concentration of these ions in supporting electrolyte is low, the contribution of ion migration is considered to be lower than diffusion.



**Figure 3.** Schematic of cell designs: (a) cathode over anode; (b) anode over cathode; and (c) cathode and electrode placed laterally and parallel to each other. Letter A represents working electrode (Cathode), C represents secondary electrode (Anode), and B represents reference electrode.



Figure 4. Schematic diagram convection in and around nanoporous pores in the configuration of anode over cathode.

To conclude the discussion on mechanisms affecting nanowire growth in template pores, we can say that there are various parameters that affect the nanowire growth such as cell design, pH of electrolyte, applied bias as well as various growth mechanisms like convection, migration and diffusion. However, of these, diffusion-controlled mass transfer flux is more important. Influence of migration can be ignored by lowering the concentration of depositing metal and increasing the concentration of supporting electrolyte. The contribution due to natural convection can be avoided by electrodeposition cell design in which working electrode can be placed in up or vertical positions.

Commercial self-organized porous AAO templates purchased from Synkera Technologies, Inc., have AAO pore length and diameter of  $\sim$ 50  $\mu$ m and  $\sim$ 100 nm, respectively. Figure 5 shows the



**Figure 5.** SEM image of commercial anodic aluminum oxide (AAO) template purchased from Synkera Technologies Inc. (a) SEM image of top surface of AAO template at 500-nm scale bar and inset shows 1-µm scale bar. These pores are nonuniform pores. (b) SEM image of bottom surface of AAO template at 500-nm scale bar.

SEM images of the (a) top and (b) bottom surfaces of commercial AAO templates. Inset shows higher magnification of the same surfaces. It is obvious from these images that the top and bottom pores do not have the same diameter, and the top surface pores are larger in diameter compared to the bottom pores. It is this difference in pore diameters that leads to most researchers depositing gold on the lower diameter side of the AAO template, thus preventing overfilling of the pores.

# 3. Fabrication and characterization of InSb nanowires in commercial AAO template

Using the commercial AAO templates discussed in the previous section, one surface of the AAO template was coated with a thin film of Au (~150 nm) using thermal evaporation. Prior to Au evaporation, the pores were widened nominally by soaking the template in 5% phosphoric acid (H3PO3) for 2 min at 30°C. The electrodeposition process was conducted in a three-electrode cell with the AAO template Au side as the working electrode, platinum electrode as the counter electrode and Ag/AgCl as the reference electrode. Crucial part of deposition process was to cover the edges of the AAO template with an insulating material and then attaching it to a conducting copper tape. The side of the AAO pore, which was covered with thin film of Au, was attached to conducting glue side of copper tape. After that, insulating polymer was applied to avoid any conducting path except through the open AAO pores which terminates at the Au film at the bottom of the pores. The entire electrodeposition process was controlled and carried out by a potentiostat (Princeton Applied Research, model: Potentiostat/Galvanostat 263A). The deposition parameters used for electrolyte in this experiment are as follows: 0.15 M InCl<sub>2</sub>, 0.1 M SbCl<sub>2</sub>, 0.36 M C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>H<sub>2</sub>O, and C<sub>6</sub>H<sub>5</sub>Na3O<sub>7</sub>. The pH value of the electrolyte was adjusted to 1.7 and electrodeposition was performed at room temperature (200°C). The citrate ions have been used as complexing agents that bring the deposition potential of In and Sb closer to maintain a binary growth during the deposition of the InSb nanowires. The complete electrodeposition process was performed for 50 min at a potential of -1.5 V with respect to the reference electrode (Ag/AgCl). Also, magnetic stirring was used to maintain the uniform concentration of electrolyte during growth of nanowires. On completion of the deposition process, the AAO template was carefully rinsed several times with DI water, and then AAO template was removed from copper tape for further processing.

Following steps are involved in extraction of nanowires from AAO template: (a) AAO template was placed in a clean 80 ml beaker with the gold side facing upward and gold film was removed by 1 M potassium iodide (KI). To dissolve the AAM template, a few drops of 1 M KOH solution was used. This was done with vigorous shaking for about 20 min (b) following dissolution of the template; 15 ml of DI water was added to the solution, which was then sonicated for 10 min. The sonication step helps to dissolve the AAO completely, while breaking the InSb nanowires off the InSb crust (overgrown areas). (c) DI water as added to wash out the precipitates in the bottom of the beaker into the vial; the process was repeated until there was no visible precipitate in the beaker. This step was extremely important, since most of the nanowires were obtained from these precipitates. (d) To further dilute the KOH and AAO in the solution, both vials were placed in a centrifuge (Fisher Scientific Centrifuge, model: 228)

Benchtop Centrifuge) at 3000 rpm for 10 min. Eighty percent of the solution was then carefully removed from the top of the centrifuge vial. Dilution step was repeated until there was no residue of KOH and AAO left, a fact that was verified by SEM. The final dark solution was found to contain a high density of InSb nanowires that could then be drop-cast for making devices. After growth, overgrown part is removed by a gentle mechanical polishing. Average length and diameter of InSb nanowire after processing have been found to be 20–30 µm and 100 nm, respectively.

**Figure 6(a)** is an SEM image of dispersed InSb nanowires, which show that they have a rough surface. This surface roughness is attributed to nonuniform pores and roughness inside the pores of the AAO template. This roughness can be avoided by using homemade AAO template or track-etched polycarbonate membranes where the tubular pores are uniform resulting in smooth and uniform nanowires as compared to those grown in commercially available AAO templates. The nanowire composition was verified by energy dispersive X-ray spectroscopy (EDX) in **Figure 6(b)**, which shows Sb-rich composition, with an average In:Sb weight ratio of 40:60.

To verify the composition and crystallinity, Raman spectroscopy and X-ray diffraction studies were made on the as-grown InSb nanowires. **Figure 7** shows the Raman spectrum obtained from two crossed InSb nanowires that were dispersed on a Si substrate. Optical image of the region where the spectrum was collected from is shown in the inset of **Figure 7**. Room temperature Raman spectrum shows two distinct peaks at 178 and 188 cm<sup>-1</sup>, which correspond to TO and LO phonon modes, respectively. These peaks are matched to prior studies on InSb nanowire [9]. Additional peaks at 150 (TO-TA) and 110 cm<sup>-1</sup> have been reported earlier in InSb nanorods by Wada et al. [34].

Above InSb NWs was characterized with high-resolution X-ray diffraction system from Rigaku model Ultima III. **Figure 8** shows the X-ray diffraction spectrum of as-grown InSb nanowires in AAO template. All strong peaks were indexed to  $2\theta = 23.0$ , 39.0, and 46 identify



Figure 6. SEM images of (a) InSb nanowires that were removed from the AAO template and dispersed on a cleaned Si substrate. Inset shows a single nanowire with roughened surface and (b) EDX spectrum of Sb-rich InSb nanowires [32].

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**Figure 7.** Raman spectrum obtained from two crossed InSb nanowires; inset shows the region from where the Raman spectrum was collected. The two peaks at 150 and 110 cm<sup>-1</sup> are most likely related to surface roughness and defects in the nanowire. The characteristic TO and LO peaks attest to crystallinity of the InSb nanowires [32].

![](_page_9_Figure_3.jpeg)

**Figure 8.** XRD spectrum of InSb NWs grown in AAO template in the scan range of  $2\theta = 20-60^{\circ}$ .

the dominant phase as zinc blende InSb. No other crystalline impurities peaks, such as In2O3, were detected in the XRD pattern. Similar XRD pattern has been reported earlier for electrochemically grown InSb nanowires [35–37].

To obtain additional information on the electronic quality of the as-grown InSb nanowires, electron transport measurement was performed on individual nanowires by connecting them in a back-gated FET type structure as shown in **Figure 9**. To determine type, concentration and mobility of carriers in the nanowire, 2-terminal and 3-terminal current–voltage measurements were performed on the fabricated device. **Figure 9(a)** shows the device schematic where back-gate has been used and **Figure 9(b)** shows the SEM image of the InSb nanowire contacted by Cr/Au as a source and drain.

![](_page_10_Figure_1.jpeg)

**Figure 9.** (a) Schematic of back-gated InSb nanowire field effect transistor and (b) SEM image of a single InSb nanowire contacted by two Cr/Au contacts [32].

**Figure 10** shows the results of electron transport measurements made on the back-gated nanowire at different  $V_{ds}$  (from 0.2 to 1.0 V, in steps of 0.2 V). The transfer characteristic at  $V_{ds} = 1.0$  V was found to have a subthreshold region between -0.5 and +0.5 V in both linear and log scale (Inset of **Figure 10**.). These values most likely correspond to complete depletion of the nanowire. The conductance of InSb nanowire has been shown to decrease with the increasing  $V_{g'}$ , that is, confirmation of a p-channel FET behavior. The p-type behavior is attributed to the Sb-rich nature of the InSb nanowire and attributed to the two common defects in Sb-rich InSb and Sb antisite and In interstitial defects [38].

The equilibrium hole concentration  $p_0$  in the nanowire was determined by using the Eq. (1) [39, 40]:

$$p_0 = \frac{C V_T}{q \pi R^2 L} \tag{1}$$

where the gate capacitance (C) has been determined from the Eq. (2) [40]:

$$C = \frac{2\pi \varepsilon_0 \epsilon_{eff} L}{\cosh^{-1}\left(\frac{t_{ex} + R}{R}\right)}$$
(2)

where  $\epsilon_{\text{eff}} \sim 2.2$  is the effective dielectric constant of the SiO2 dielectric,  $\epsilon_0$  is the permittivity of free space,  $t_{\text{ox}} = 250$  nm is the thickness of dielectric, R = 50 nm is the nanowire radius, and L = 10 µm is the length of nanowire channel, which is used for this measurement. Using Eqs. (1) and (2), the hole concentration has been calculated to be  $1.96 \times 10^{16}$  cm<sup>-3</sup>. From the linear part of the I<sub>ds</sub> versus V<sub>gs</sub> as shown in **Figure 10**, the field effect mobility (µFE) was determined at different constant V<sub>ds</sub> using Eq. (3):

$$\mu_{FE} = \left(\frac{L^2}{C V_{ds}}\right) \times \left(\frac{d I_{ds}}{d V_{gs}}\right)$$
(3)

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![](_page_11_Figure_1.jpeg)

**Figure 10.** Transfer characteristics of InSb nanowire back-gated FET at increasing  $V_{ds}$  from 0.2 to 1.0 V. Inset shows a logarithm plot of the  $I_{ds}$  vs.  $V_{gs}$  curve at  $V_{ds}$  = 1.0 V. The ON–OFF current ratio is estimated to be of the order of 10<sup>3</sup> [32].

where transconductance  $g_m = \left(\frac{d I_{ds}}{d V_{gs}}\right)$  has been deduced at different constant Vds. The field effect mobility was determined to be 507 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at V<sub>ds</sub> = 1.0 V. The lowest mobility has been found to be 277 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at V<sub>ds</sub> = 0.2 V, which is higher than the previously reported [11] value of 57 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> obtained at V<sub>ds</sub> = 0.1 V on unintentionally doped 5-µm long p-type InSb nanowire grown by electrochemical method. Similarly, carbon-doped p-type InSb nanowire of length 1.8 µm has been reported to be has the mobility of 127 ± 21 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at V<sub>ds</sub> = 0.05 V [41]. Inset of **Figure 10** shows p-type nanowire FET has been shown a relatively high ON/OFF ratio of 10<sup>3</sup>. One possible cause for the Sb-rich nature of these nanowires is the lower pH (1.7) of the electrolyte. This most likely causes an increase in adsorption of Sb anions on the growing crystalline nanowire.

![](_page_11_Figure_4.jpeg)

**Figure 11.** (a) Temperature-dependent I-V shows current increasing with temperature, which is characteristic semiconducting behavior. (b) Temperature-dependent conductivity measurements (Arrhenius plot) for the extraction of activation energy from a single InSb nanowire. Inset shows normalized resistance versus temperature, which shows the exponential decrease of resistance with increasing temperature [32].

The results of temperature-dependent I-V have been shown in **Figure 11(a)**. Linear I-V shows that the Cr/Au contacts (source-drain) to the nanowire are ohmic contacts. The InSb nanowire resistivity was determined to be 248  $\Omega$  cm<sup>-1</sup>, which is higher than the value reported for bulk InSb. The reasons for higher resistivity of the nanowire compared to bulk are as follows: (i) Sb antisite and In interstitials and (ii) surface roughness of nanowire (**Figure 6(a)**). The increased resistivity has been also reported in the references [15, 42], attributed to a significantly reduced hole mobility caused by the scattering at nanowire surface. The nanowire resistance was found to decrease with increasing temperature (inset of **Figure 11(b)**). This large temperature dependence of resistance of InSb nanowire has been reported previously in Ref.s [15, 43]; this is the characteristic behavior of a semiconductor where carrier concentration varies exponentially with temperature. The nanowire conductivity has been measured using device geometry. **Figure 11(b)** shows that below T = 200 K, the nanowire conductivity ( $\sigma$ ) exhibits the characteristics of thermal activation which can be analyzed using Eq. (4):

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{k_B T}\right) \tag{4}$$

where  $\sigma_0$  is the pre-exponent factor,  $E_a$  is the activation energy,  $k_B$  is Boltzmann's constant (8.617 × 10<sup>-5</sup> eVK<sup>-1</sup>), and T is the absolute temperature.  $E_a$  has been estimated to be about 0.1 eV corresponding to carrier generation across the bandgap with activation energy equal to half of the bandgap. The roughness of the nanowire surface can be exploited to control phonon transport. Future work can be directed toward reducing the intrinsic point defects within the nanowire so that electrical conductivity can be enhanced, while the surface roughness can impede transport of phonons to reduce the lattice contribution to thermal conductivity, making it a promising material for thermoelectric applications.

# 4. Homemade AAO template fabrication for semiconducting nanowire growth of desired dimensions

Anodic films on aluminum have received considerable attention due to their extensive application as templates for synthesizing various nanostructures in the forms of nanowires and nanotubes [44–46]. To obtain a higher control of the nanowire dimensions and surface quality, an electrochemical self-assembly technique was used to fabricate a hexagonally ordered array of cylindrical nanopores on an aluminum substrate. Starting with high purity, unpolished and annealed aluminum (99.997%, AlfaAsar) foil with thickness of ~250  $\mu$ m, the unpolished samples were first chemically polished [47] using 15 parts of 68% nitric acid and 85 parts of 85% phosphoric acid for 5 min at 850°C. The samples were then neutralized in 1 M sodium hydroxide (NaOH) for 20 min. This was followed by a multistep anodization process using 3% oxalic acid and 40 V DC at room temperature. Final step of anodization is carried out for 5 min, which produces pore length of ~1  $\mu$ m [48]. **Figure 12** shows SEM images of top surface at a scale bar of 500 nm and **Figure 12(b)** is the top surface with a scale bar which shows the pore diameter of AAO template is approximately 50 nm. Understanding the Mechanisms that Affect the Quality of Electrochemically Grown... 37 http://dx.doi.org/10.5772/intechopen.71631

![](_page_13_Figure_1.jpeg)

**Figure 12.** SEM images of AAO template top surfaces (a) at scale bar of 500 nm and (b) with scale bar in pore diameter which shows that diameter of pore is approximately 50 nm.

After second step anodization, aluminum is dissolved in 1 M mercury chloride ( $H_gCl_2$ ) saturated solution. We have achieved ~50 µm pore length in about 4 h 16 min with pore diameter of ~50 nm. One advantage for the home-grown route of synthesizing templates is the possibility of obtaining smaller pore diameters. In this chapter, results of pore widths of ~50–70 nm are presented, in contrast to the larger diameter ~100 nm obtained from the commercial templates. Nanowires of different diameters will enable a study of its dependence on the electrical, magnetic, and thermoelectric properties of nanowires.

A noteworthy challenge in homemade AAO templates is the presence of a thin barrier layer comprising aluminum oxide. Following fabrication of the alumina layer and removal of the underlying metallic aluminum, the bottom layer of the template was found to exhibit bulges or protrusions. **Figure 13(a)** shows an SEM image showing the capped protrusions (hemispherical caps) of the barrier later at the bottom of the pore. Inset shows an enlarged image of the barrier caps. **Figure 16(b)** shows the completely opened barrier later after etching in 5% phosphoric acid at 30°C for 30min. It has also been observed that if etching time in 5% phosphoric acid is increased from 30min to 35 min, the thin membrane tears in sections from the top surface and the pores merge together as their walls collapse. Such membranes cannot be used for nanowire growth via electrodeposition, since the collapsed walls will result in direct contact with the underlying metal layer. **Figure 14** shows SEM images of bottom and top

![](_page_13_Figure_5.jpeg)

**Figure 13.** SEM images of bottom side of AAO template: (a) hemispherical cap of barrier layer formed during anodization and (b) complete barrier layer etching in 5% phosphoric acid at 30°C for 30min.

![](_page_14_Picture_1.jpeg)

**Figure 14.** SEM images of bottom and top surfaces after etching in 5% phosphoric acid  $(H_3PO_4)$  for 35 min at 30°C. (a) SEM image of bottom surface, which shows all the barrier layers are etched and pores are uniformly open and (b) SEM image of the same sample as in (a), which shows over etching of top surface which looks like pores are bundled together.

surfaces after etching in 5% phosphoric acid ( $H_3PO_4$ ) for 35 min at 30°C. **Figure 15(a)** shows SEM image of bottom surface, which shows all the barrier layers are etched and pores are uniformly open and **Figure 15(b)** shows SEM image of the same sample as shown in **Figure 13**, which shows over etching of top surface which looks like pores are bundled together.

To check the anodization rate, cross-sectional image of AAO template has been taken at two different times of second anodization, 5 and 250 min, respectively. **Figure 15** shows SEM images of cross-section of homemade templates. **Figure 15(a)** shows ~50- $\mu$ m long pore which was obtained after 250 min of second anodization, and inset shows smooth and straight pore and; **Figure 15(b)** shows ~ 5- $\mu$ m long pore which was obtained after 15 min of second anodization. Based on **Figure 15**, anodization rate in the abovementioned condition for the growth of homemade AAO template is 1- $\mu$ m long in 5 min, which is a faster rate than any other anodization conditions reported before [49].

As mentioned earlier, removal of the barrier layer from the bottom of the AAO membrane is very challenging; if the etching time is not well controlled in most cases, it results in collapse of the tubular walls and destruction of the pores from the top surface of the template. Results of barrier removal using 1 M  $H_3PO_4$  at 30°C at different times are presented for

![](_page_14_Figure_6.jpeg)

**Figure 15.** SEM images of cross-section of homemade template: (a) shows ~50-µm long pore which was obtained after 250 min of second anodization, and inset shows smooth and straight pore and (b) shows ~5-µm long pore which was obtained after 15 min of second anodization.

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![](_page_15_Figure_1.jpeg)

**Figure 16.** SEM images of top surface of AAO template: (a) shows nonporous hexagonal AAO pores without any etching, (b) after 17 min etching in 1 M phosphoric acid at 30°C and, (c) after 20 min etching in 1 M phosphoric acid at 30°C.

comparison. **Figure 16** shows the SEM images of AAO top surface (a) as-grown and without etching, (b) after 17 min etching in 1 M phosphoric acid at 30°C and (c) after 20 min etching. It is clear from SEM image in **Figure 16(b)** that after 17 min of etching in 1 M phosphoric acid, the AAO template top pores are widened to its maximum capacity, and any increase in etching time will result in merging of the pores. **Figure 16(c)** shows that 20 min of etching is over etching and the pores are merged. After appropriate time etching, barrier layer is thinned and pore diameter is widened. Now, pores can be filled with cobalt by AC electrochemical deposition using a 5%  $CoSO_4.7H_2O$  solution stabilized with 2%  $H_3BO_3$  at 20 V AC and 250 Hz [50].

Barrier layer thinning is an alternative technique to remove the barrier layer formed at the end of second anodization process. After thinning of barrier layer, individual pores terminate in the metallic aluminum layer at the bottom of the template. Such membranes grown directly on aluminum foil are suitable for electrodeposition since the bottom aluminum layer works as one electrode.

As discussed in Section 3, nanowire growth can also be carried out in the pores of a tracketched polycarbonate membrane.

# 5. Semiconducting InSb nanowires grown in polycarbonate template

Following the pioneering work of pore creation in track-etched mica by Possin [51], metallic (Ag) nanowires were grown in 8 nm wide pores by Williams and Giordano [52]. Penner and Martin [53–55] subsequently created pores in polycarbonate membranes by track-etch method. In this work, polycarbonate membranes were purchased from Whatman and had pore lengths of 20  $\mu$ m and diameter of the order of 200 nm. Following metal deposition on one surface of this template, InSb nanowires were grown in its pores. Unlike the pores in the AAO template, the polycarbonate pores were of uniform diameter and had smooth surfaces. This results in a very smooth surface for the as-grown InSb nanowires.

As-grown InSb nanowires in polycarbonate were first dissolved in dichloromethane and then in chloroform. After InSb nanowires were also grown in track-etched polycarbonate membranes and an SEM image of the as-grown nanowires is shown in **Figure 17**. The biggest

![](_page_16_Picture_1.jpeg)

Figure 17. SEM image of a piece of InSb nanowire bundle which was drop-casted on the silicon wafer after dissolving as-grown InSb in polycarbonate template.

challenge in the polycarbonate membrane growth process is the clumping of the nanowires into bundles. This is most likely caused by the residues of the polymer membrane which tends to hold the nanowires together. Dissolution of the membrane is typically done using dichloromethane and chloroform, followed by cleaning in alcohol and DI water, and the nanowires grown by this technique were found to have very smooth surfaces and a length of approximately 20  $\mu$ m. Electrolyte concentration and cell design were same as used to grow the InSb nanowire in AAO template as discussed in Section 3 except for the pH of solution was maintained at 1.9 instead of 1.7.

**Figure 18(a)** and **(b)** shows the SEM images of dispersed on silicon substrate at different places and **Figure 18(c)** shows the EDX spectrum of the InSb nanowires and they are In-rich.

![](_page_16_Figure_5.jpeg)

**Figure 18.** SEM image of InSb nanowire after drop casting on silicon wafer after ultrasonication for 1 min and 1 min oxygen plasma etching: (a) showing broken nanowire due to ultrasonication which resulted in reduced lengths of nanowire from ~20 micron to average 5 micron and (b) showing reduced bundle with approximately 20  $\mu$ m long InSb nanowires. Average diameter of the nanowires are approximately 150 nm and (c) energy dispersive X-ray (EDX) spectrum of in-rich (54.4 wt% In and 45.6 wt% Sb) electrochemically InSb nanowires grown in polycarbonate template with ~1.5 V potential at room temperature and pH = 1.9.

Major challenge is the pore wettability, if this step is not optimized prior to nanowire growth, then even if all other conditions are met, this will result in either no growth or in nonuniform growth in some pores and formation of a mushroom-like crust. To avoid this, it is important that a few basic steps to be performed prior to nanowire growth. Pore-wetting can be achieved by: (i) sonication of nanoporous template in water to remove any air bubbles at the bottom of the pores and (ii) aeration of nanoporous template in vacuum chamber to remove any air bubbles at the bottom of the template. Another challenge is the nonuniform growth which can be avoided by maintaining a temperature gradient between working electrode and mouth of the pore.

#### 6. Conclusions

The growth process of semiconducting nanowires in template pores is a relatively simple process that can be used for synthesizing a high density of well-ordered nanowires in an array. However, the growth process involves several complex basic mechanisms that are affected by cell design, pore wettability, and electrolyte condition. This chapter presents a brief review of work done in this area. It has been experimentally found that commercial AAO template pores have rough tubular surfaces and this results in nanowires with jagged edges. Most commercial AAO templates with narrow pores (of the order of 100 nm) are sometimes tapered and therefore, the metal evaporation and pore-wetting of the pores in these templates are very critical. To circumvent this problem, homemade templates with controlled thickness and pore diameters can be used. However, in this case, the challenge is with the barrier layer formed on the backside of the template. A controlled etching process typically achieves barrier layer removal, where the etching time and etchant concentration as well as temperature are controlled. If the process is not optimized, this will cause the template to tear along the top surface. The tear does not extend over the entire template thickness. The advantage of homemade templates is the pores are relatively uniform and therefore, the nanowires grown in these pores have smooth surfaces. Such smooth nanowires can also be grown in track-etched polycarbonate membranes.

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