Nanowire growth

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Excess Indium and Substrate Effects on the Growth of InAs Nanowires**

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Semiconductor nanowires (NWs) have been studied extensively over the past decade for a variety of electronic and photonic applications.[1,2] Understanding the growth mechanisms and key growth processes is of critical importance for control and optimization of NW synthesis and their electronic and optical properties. NW growth by a variety of mechanisms including vapor–liquid–solid (VLS),[3] vapor–solid–solid (VSS),[4] vapor–solid (VS),[5] oxide-assisted growth (OAG),[6] and group III mediated growth,[7,8] has been reported. Among different semiconductor materials, InAs NWs have been widely studied[9,10,11,12] for potential applications in nanoelectronics due to their small effective mass, which allows strong quantum confinement and high electron mobility. Despite the similarity in most of their synthesis techniques, the mechanisms governing InAs NW growth, both in the presence[13,14,15] or absence[16,17] of Au nanoparticles, remain the subject of active debate.

In this study, we examine nucleation and growth of InAs NWs from excess In with and without Au nanoparticles. Au nanoparticles on SiO_2/Si substrates were found to facilitate AsH_3 pyrolysis[18] but not to be necessary to nucleate NWs, while excess In, supplied from either the input group III precursor source or the III–V substrate, was found to nucleate InAs NWs. We show that due to the catalytic effect of Au nanoparticles on substrate decomposition, NW growth in a closed chemical vapor deposition (CVD) tube is possible without any additional source other than the growth substrate itself.

InAs NWs for these studies were synthesized in a horizontal metal-organic chemical-vapor-deposition (MOCVD) system using Arsine (AsH_3) and trimethylindium (TMIn) precursors in H_2 carrier gas at a chamber pressure of 100 Torr. In the first set of experiments, we studied the effects of TMIn flow on the nucleation density and growth rate of InAs NWs grown on InAs(111)B substrates on which 40 nm Au nanoparticles had been dispersed. The growth time, substrate temperature, and input AsH_3 flow rate were 6 min, 500 °C, and 45 μmol min^{-1}, respectively, while the input TMIn flow rate was varied between 0.75–7.5 μmol min^{-1}. Figure 1 a–f shows 45° field-emission scanning electron microscopy (FESEM) images of the grown NWs, and the corresponding growth rate is plotted in Fig-

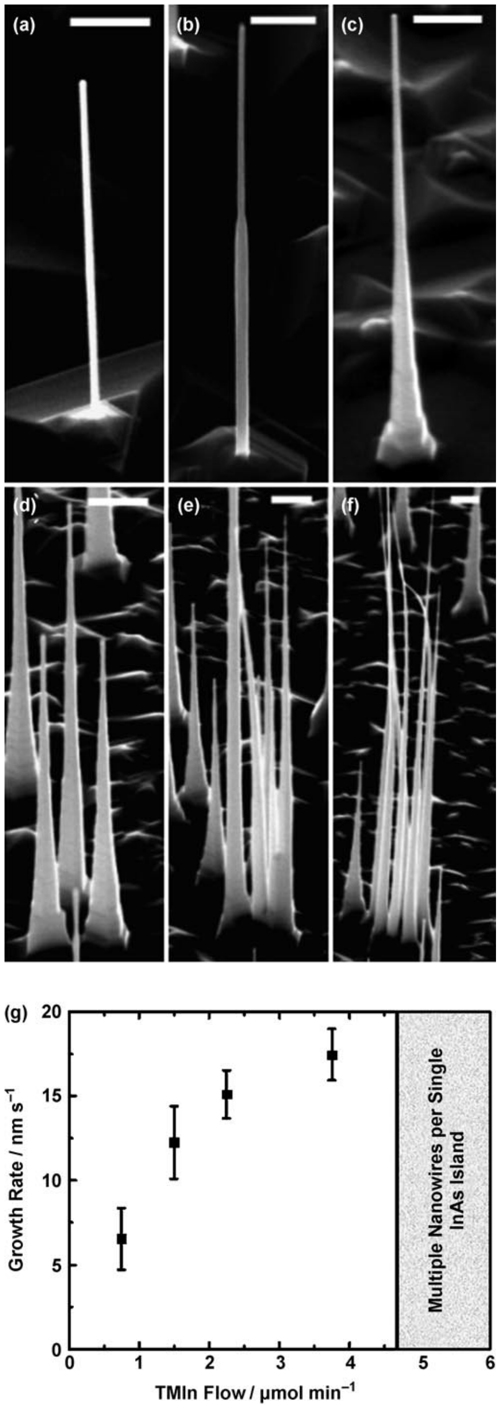

Figure 1. 45° FESEM images of InAs NWs grown on InAs(111)B at 500 °C with AsH_3 flow rate of 45 μmol min^{-1} and TMIn flow rates of a) 0.75, b) 1.5, c) 2.25, d) 4.7, e) 6, and f) 7.5 μmol min^{-1}. Scale bars are 500 nm. g) Growth rate of InAs NWs versus TMIn flow rates. At TMIn flow rates ≥ 4.7 μmol min^{-1}, multiple InAs NWs grow per single Au nanoparticle.

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ure 1 g. First, we observe that the lengths of the NWs increase as the TMIn flow rate is increased, although with different morphologies. Second, InAs NWs grow with uniform diameter determined by that of the Au nanoparticle ($\approx$40 nm) when the TMIn flow rate is low (0.75 μmol min^{-1}). With increased TMIn flow rate, the NWs are tapered with the diameter at the base of the NWs being larger than that at their tips. Third, for TMIn flow rates $\geq$ 4.7 μmol min^{-1}, multiple InAs NWs grow in the vicinity of a single Au nanoparticle.

We explain these observations as follows. The growth rate follows the universal dependence on group III input precursor flow rate (TMIn), which is normally consumed at the growth interface for a V/III ratio greater than 1.[19] As the TMIn flow rate increases, the axial NW growth rate increases, as shown in Figure 1 g, at a rate of 0.34 μm μmol^{-1} for TMIn flows of 0.75-2.25 μmol min^{-1}. Also, the concentration of In adatoms at the surface of the substrate will increase as the TMIn flow rate increases. Due to the In concentration gradient between the substrate surface and NW, diffusion of In adatoms from the substrate surface to the NW becomes prominent at TMIn flow rates greater than 1.5 μmol min^{-1}. Excess In available at the base of the InAs NW, where the mobility of In diffusing on the substrate surface to the NW tip is most impeded, allows radial growth and tapering at their bases. The base diameter thus increases steadily with increasing TMIn flow until the In concentration near the base is sufficiently high to form liquid In droplets and nucleate multiple NWs in the vicinity of the Au-catalyzed InAs NWs. Figure 1 d–f also shows evidence of surface growth due to excess available In on the substrate surface. The growth of multiple InAs NWs from a single nucleation site cannot be explained through the common VLS or VSS mechanism from a AuIn alloy particle but rather suggests additional nucleation from In droplets made available from the input precursor.

This effect of excess In was also observed during NW growth under identical growth conditions both with and without AsH_3 flow during temperature ramp-up. AsH_3 is typically introduced in the reactor during temperature ramp-up to counteract As sublimation and maintain the surface stiochiometry of the InAs substrate. Thus, one would expect that As sublimation would lead to the formation of an In rich surface and the excess In responsible for NW growth could be supplied from the substrate itself. We have therfore performed growth experiments on an InAs(111)B substrate with Au nanopaticles 40 nm in diameter on its surface, where the growth temperature was kept constant at 520 °C, and the AsH_3 and TMIn flow rates were fixed at 150 μmol min^{-1} and 6 μmol min^{-1}, respectively, for a growth time of 6 min. When AsH_3 flow was maintained during temperature ramp-up, a single InAs NW is grown per single Au nanoparticle, as shown in the side-view FESEM image in Figure 2 a and the top-view FESEM image in Figure 2 b. A few islands show two InAs NWs due to the presence of two Au nanoparticles in close proximity. In the absence of AsH_3 during temperature ramp-up, multiple NWs grow from a single InAs island formed around a single Au nanoparticle, as shown in the side-view FESEM image in Figure 2 c and top-view FESEM image in Figure 2 d. It is known that the decomposition temperature of InAs to produce As_x in the form of As_2 and As_4 is lowered by $\approx$300 °C in the presence of Au.[20] The presence of AsH_3 in the growth chamber during the temperature ramp compensates the decomposed As_x and prevents the formation of In droplets that can initiate NW growth. In the absence of AsH_3 during temperature ramp-up, As sublimation leaves an In rich surface, especially around the Au nanoparticle where the decomposition is most effective, allowing formation of In droplets that initiate multiple InAs NW growth.

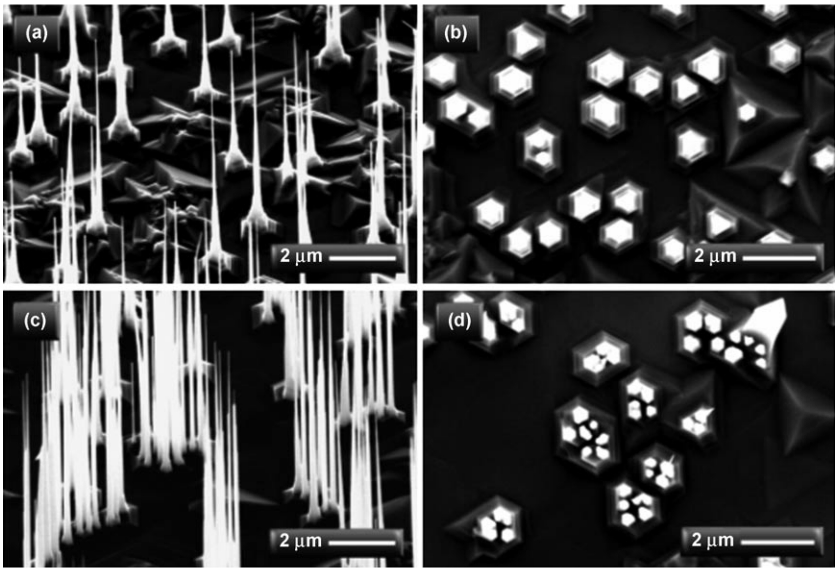

Figure 2. Representative FESEM images of a) 45° angle view and b) top view of InAs NWs grown on InAs-(111)B substrate at 520 °C, while AsH_3 flow was maintained during temperature ramp-up. FESEM micrographs of c) 45° angle view and d) top view of multiple InAs NWs per single Au nanoparticle grown under the same conditions as in (a) and (b) with no AsH_3 flow during temperature ramp-up.

The catalytic decomposition of the InAs substrate by Au nanoparticles is further illustrated in Figure 3 a and b, which clearly shows that deep-etch pits form only around Au nanoparticles on the InAs(111)B substrate when the substrate temperature was ramped up to 500 °C and cooled down in AsH_3 flow. It can be clearly seen in Figure 3 b that Au nanoparticles are present at the bottom of the etch pits.

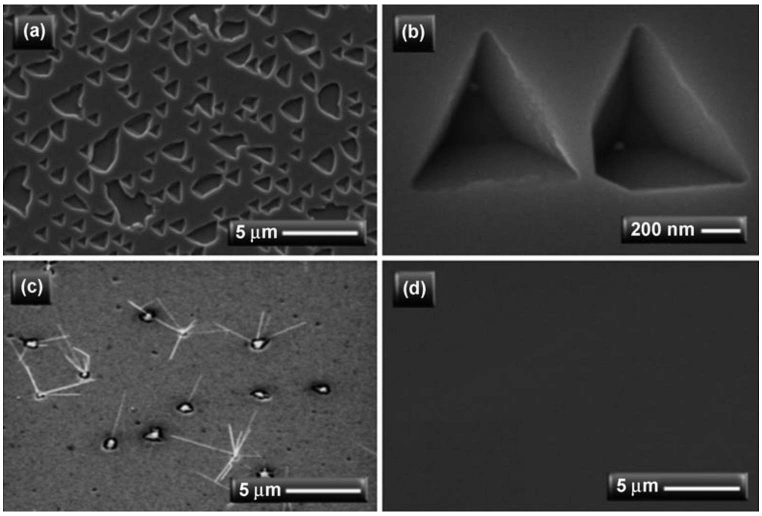

Figure 3. FESEM images of a) InAs(111)B surface with Au nanoparticles atop heated to 500 °C under AsH_3 flow. b) Zoomed-in view of etch pits formed on the InAs(111)B surface around Au nanoparticles. c) InAs NWs grown on InAs(111)B surfaces in a closed tube in the presence of Au nanoparticles. d) InAs-(111)B substrate without Au nanoparticles atop subject to the same growth conditions as in (c). No NWs were observed.

No such severe decomposition was found on a substrate without Au nanoparticles when subjected to identical conditions.

To further illustrate the catalytic decomposition of the InAs substrate, we performed growth in a simple closed CVD tube containing an InAs(111)B substrate with Au nanoparticles at 550 °C for 5 min and a pressure less than 0.1 Torr. From Figure 3c, it is evident that substrate decomposition is enhanced in the vicinity of the Au nanoparticles where single or multiple NWs grow. This result, in the absence of any additional source other than the growth substrate itself, is different from previously reported InAs NW growth using a two-temperature-zone closed CVD tube.[13] Under identical growth conditions but without Au nanoparticles on the InAs(111)B substrate, no severe surface decomposition was found, as shown in Figure 3d. These results further demonstrate the catalytic effect of Au nanoparticles on decomposition of the InAs substrate and suggest that substrate material incorporation of both group III and group V can occur in the grown NWs—an observation with important consequences for purity and doping control in III–V NW growth on a III–V substrate. However, during MOCVD NW growth, the abundant material constituents from the input precursors dominate material incorporation into the NW and minimize substrate decomposition. These results also highlight the importance of maintaining AsH_3 flow during temperature cool down to prevent NW decomposition after growth.

As the growth temperature is increased in a closed system, the growth density and the length of the NWs decrease. Growth using this technique was observed up to temperatures greater than 600 °C with a nanoparticle density of $\approx 0.04\ \mu m^{-2}$, above which no NWs were observed on top of the substrate. If the density of the Au nanoparticles increases, the upper limit of the growth temperature decreases (e.g., 550 °C for a nanoparticle density of $\approx 0.5\ \mu m^{-2}$). Higher growth temperature and larger Au nanoparticle density both enhance the substrate decomposition and As sublimation, and thus increase the local V/III ratio during growth. As a result, the NW growth rate is reduced, as discussed in detail elsewhere.[21]

To further illustrate InAs NW growth from In droplets in the absence of a foreign metal catalyst, we performed growth experiments on a bare InAs(111)B substrate. The substrate was heated to a growth temperature of 400 °C in AsH_3 flow of 44.6 $\mu mol\,min^{-1}$. After the temperature stabilized, the AsH_3 flow was switched off and TMIn (6 $\mu mol\,min^{-1}$) was introduced for 90 s. Figure 4a shows a typical SEM image of In droplets with diameters ranging from 50 to 200 nm formed atop the InAs(111)B substrate from TMIn decomposition. Without interrupting the growth after predepositing In droplets, the AsH_3 and TMIn input precursors were introduced for NW growth at 400 °C, followed by temperature cool down in AsH_3 flow. Figure 4b shows InAs NWs grown for 15 min, with diameters in the range of 200–300 nm. The growth density of these NWs does not correspond to the In droplet density obtained in Figure 4a due to the continual supply of In throughout the growth experiment. Note that all NWs grown for 15 min have flat tips, smooth surfaces, and hexagonal facets, as shown in the top-view inset of Figure 4b, similar to prior reported growth of InAs NWs on SiO_x surfaces.[16,17] The absence of a globule on the NW tips can be attributed either to In consumption when the TMIn precursor is shut off and AsH_3 flow is maintained during temperature cool down, or to In evaporation from the globule during growth.[22]

Figure 4c shows InAs NWs grown for 30 min using identical growth conditions as in the 15 min growth (Figure 4b). Two kinds of NW morphologies were observed: 1) short NWs with flat tips and smooth surfaces, as shown in the top inset of Figure 4c, and 2) long NWs with faceted tips, where the bases of the NWs have smooth surfaces and the upper sections show periodic variation in diameter, as seen in Figure 4c. The globular tips are typically larger than the NW diameter and have irregular shapes, except for a few where a spherical globule is maintained, as shown in the bottom inset of Figure 4c. The faceted tips formed during temperature cool down where AsH_3 flow is maintained and excess In at the NW globule is consumed after the TMIn supply was stopped. This was also suggested for Ge whiskers that showed faceted tips when grown from Au seeds.[22] Periodic instability in NW/whisker growth is typically observed due

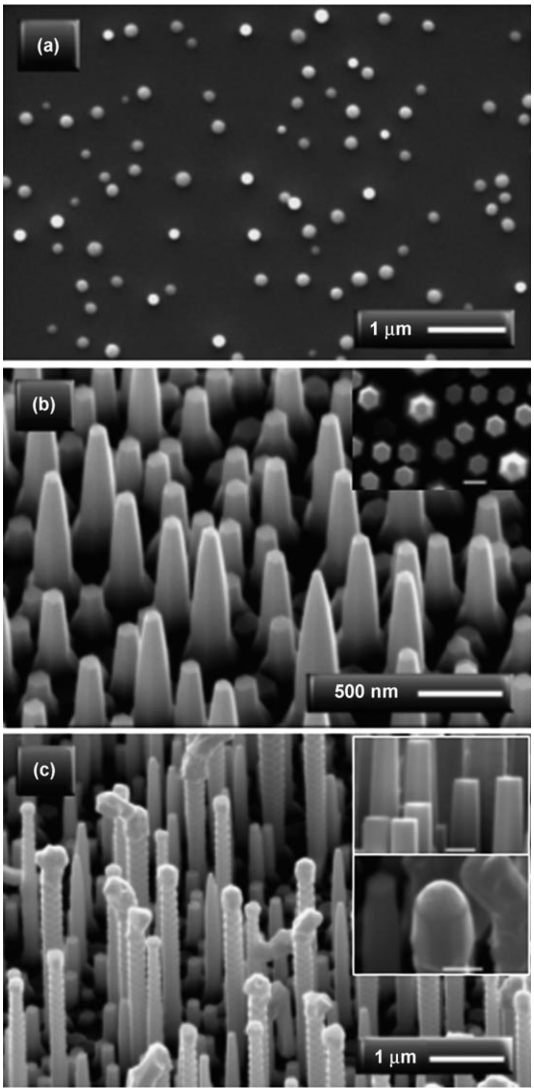

Figure 4. InAs NW growth from In droplets: a) Top-view FESEM image of In droplets formed on InAs(111)B substrate after 90 s TMIn exposure. 45° angle view of (b). b) InAs NWs grown for 15 min. Inset is a top-view image showing hexagonal facets of InAs NW sidewalls. c) InAs NWs grown for 30 min, top inset shows flat tips for shorter NWs and bottom inset shows a globule at the longer NW tip.

to variation in the supersaturation of the growth droplet at the tip of the NW.[22] Givargizov proposed a self-oscillation model to explain the periodic instability in Si whiskers with a positive feedback due to fluctuation in the curvature of the growth droplet that alters its supersaturation, surface roughness at the liquid–solid interface, and the droplet contact angle.[23] Such periodic oscillations were also observed in InAs whiskers grown at 800 °C on GaAs(111)B, and disappeared as the growth temperature was decreased.[24] In the case of the InAs NWs shown in Figure 4c, it is highly plausible that higher In concentrations, available from TMIn source, in globules of some NWs lead to longer growth after the cessation of the shorter wires. The periodic instability in their diameters can thus be explained by Givargizov's model. In general, there is no diameter dependence for cessation of the NW growth. Therefore, instability[25] in NW growth or Ostwald ripening behavior,[26] where the smaller-diameter NWs lose their caps either to the bottom of the NW[25] or to the larger-diameter NWs,[26] could be excluded as possible reasons for the cessation in the NW growth and formation of flat tips. Toward the edge of the substrates, a few thin NWs show globules at their tips, and the globule size decreases as the NW length increases and finally vanishes, resulting in needlelike NWs.

Without the in situ In predeposition step through exposing the InAs(111)B surface to TMIn flow, no InAs NW growth was observed. InAs NWs can grow at certain sites where excess liquid In is formed. A low temperature of 400 °C is required to maintain the liquid In on the substrate. At higher temperatures, excess In is subject to crystallization, resulting in surface growth rather than NW growth. For example, at a growth temperature of 460 °C, fewer NWs, which are generally needle shaped, are grown. We have noted earlier that growth from excess In droplets can occur at 520 °C when Au nanoparticles are present on the substrate surface (Figure 2c and d). In the latter case, the Au nanoparticle not only catalyzes the decompostion of AsH_3 but also acts as a material sink for both In and As. When high TMIn flow is maintained during growth, NWs can grow from In droplets in the presence of Au at even higher growth temperatures of $\approx$500 °C.

To summarize, we have shown that excess liquid In nucleates InAs NWs on an InAs(111)B substrate during MOCVD growth through the VLS growth mechanism. The liquid In can be supplied either from the input precursor or from substrate decomposition that is enhanced in the presence of Au nanoparticles. InAs NW growth in a closed system confirms the catalytic decompositon of the InAs substrate by Au nanoparticles and also shows that both group III and group V constituents decomposed from the growth substrate can be incorporated into the NWs. InAs NWs were also observed to grow from predeposited In droplets. Faceted tips and periodic instability in the diameter of long NWs were observed due to fluctuations in the curvature of the In droplet. Since In is one of the growth constituents, short NWs with flat tips or needlelike NWs were formed due to In consumption during growth. These insights reveal new key processes during the growth of III–V semiconductor nanowires and aid the understanding of their growth mechansim.

Keywords:
chemical vapor deposition · indium · nanoparticles · nanowires

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