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Influence of Growth Temperature on the Selective Area MOVPE of InAs Nanowires on GaAs (111) B Using N_2 Carrier Gas

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ABSTRACT

The influence of temperature on selective area (SA) InAs nanowire growth was investigated for metal-organic vapor phase epitaxy (MOVPE) using N_2 as the carrier gas and (111)B GaAs substrates. In contrast to the growth temperature range – below 600°C – reported for hydrogen ambient, the optimal growth temperature – between 650° and 700°C was 100K higher than the optimal ones for H_2 carrier gas. At these temperatures nanowires with aspect ratios of about 80 and a symmetric hexagonal shape were obtained. The results found are attributed to the physical and chemical properties of the carrier gas.

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Keywords: A1. Nanostructures; A3. Metalorganic vapor phase epitaxy; A3. Selective epitaxy; B1. Nanomaterials; B2. Semiconducting III-V materials

1. Introduction

III-V compound semiconductor nanowires have received much attention as base components for next generation electronic devices. Especially, InAs nanowires are very promising to realize high-speed and low-power-consumption electronic nanodevices [1-2], spintronic nanodevices [3], and single-electron spin-qubit quantum dots with multi-gates [4]. This is because InAs has a narrow gap, a surface accumulation layer, a high mobility and a large spin-splitting. Moreover nanowires are ideal one-dimensional structures due to their small diameters and sufficient lengths, which become very important for the application to multi-gated nanodevices as mentioned above. For this application the wire definition needs to be controllable in width and length with dimensions of a few ten nanometers and several micrometers, respectively.

Selective area (SA) growth in metal-organic vapor phase epitaxy (MOVPE) is the preferable method when defining the location and width of nanowire growth. It is a good alternative to the frequently used catalyst assisted methods [1-3, 5-6], since no extrinsic impurities can be incorporated by the growth method. The catalyst assisted growth temperatures are typically also much lower than for bulk and selective area growth leading to unintentional intrinsic impurity incorporation. In the case of the MOVPE of InAs nanowires with the typical Au catalyst, the growth temperature was limited by the eutectic melting point of the Au-In alloy (455℃) [6]. The formation of InAs nanowires by using SA-MOVPE on (111) B surfaces which have been partially masked by amorphous materials has already been carried out using H_2 as the carrier gas [7-9]. However the optimum growth temperatures were still lower than 600°C and growth suppression was observed at higher growth temperatures. It is also well known that twinning can occur due to the increasing stabilization of the hexagonal wurtzitic structure with respect to the cubic zinc blende [8, 9], but high temperature annealing at 800°C can converse hexagonal InAs to cubic [10]. Therefore, InAs nanowire growth at higher temperatures than 600°C is of interest to obtain cubic InAs. In this paper we will investigate the influence of growth temperature on InAs nanowire formation where N_2 is used as the carrier gas and ambient during MOVPE. The carrier gas N_2 in MOVPE has an influence on the hydrodynamics as well as the chemical reactions and will therefore change the gas phase and possibly the surface diffusion [11] as well as the temperature window for InAs nanowire growth.

2. Experimental procedure

For SA-MOVPE, we first prepared masked substrates. We chose a spin-on-glass technology for thin-film preparation as follows. We coated a GaAs (111)B substrate with hydrogen silsesquioxane (HSQ) [12] and then heated it up to 275°C in air. The typical thickness and refractive index of the film after heating are 30 nm and 1.50, respectively. Next, we patterned it with a hole-array by using electron-beam lithography with positive resists and anisotropic reactive ion etching with CHF_3 gas. The typical diameter of the mask openings was 50 nm. The mask openings were arranged hexagonally, so that the distance from one hole to all the surrounding holes was the same and 500 nm. We note that

this procedure is well-defined by the resist pattern and more suitable for small diameters openings than typical wet chemical etchings [7-9, 19], which show isotropic etching behavior. After patterning the samples were cleaned by organic chemicals to remove the resist. Immediately before growth the templates were deoxidized by a 5 minute concentrated H_2SO_4 treatment followed by rinsing in de-ionized water and drying in a nitrogen stream.

We used a low-pressure MOVPE system and N_2 as the carrier gas and growth atmosphere at a working pressure of 2 kPa. The total flow rate in the reactor was fixed to 3.1 slm. These are the optimized conditions in our reactor with N_2 carrier gas to obtain a uniform distribution of temperature and chemical species [13]. We used trimethylindium (TMIn) and arsine (AsH_3) as precursors, and the partial pressures of TMIn and AsH_3 were fixed to 0.118 and 12.9 Pa, respectively. Therefore the V/III ratio was about 110. Figure 1 shows a schematic diagram of the growth sequence. The substrates were heated up to 750°C once with AsH_3 flow in order that the native oxide is desorbed within the opening areas. At this temperature we confirmed that the mask openings were preserved as well as that uniform growth of GaAs homoepitaxial nanowires was successful with N_2 carrier gas [14], thus this desorption step seemed to be sufficient. Then the substrates were cooled down to growth temperature T_G followed by 3 minutes stabilization at T_G. Then TMIn flows set into the reactor i.e. nanowire growth was commenced. We varied T_G from 550°C to 700°C, which corresponds to optimal temperature used for growth to extremely high temperature when H_2 carrier gas is used on GaAs (111) B substrates [8, 9]. The samples were characterized by scanning electron microscopy (SEM).

3. Experimental results and discussions

The influence of growth temperature on InAs nanowire morphology is presented in figure 2. For all the samples the growth time was fixed to 10 minutes, and the tilt angle for each SEM image was 40°. The InAs nanowires exhibit vertical {110} facets for every growth temperature. Although it is difficult to compare the absolute wire length from the images at the growth temperatures above 600°C, it is apparent that the nanowires grown at 550°C, are however, obviously much shorter than those grown at higher temperatures. Moreover, the top shapes vary and only a few hexagonally shaped nanowires at growth temperatures lower than 600°C are observed. It should be noted that the initial opening holes were of almost circular shape. The possible reason of such randomness is the nucleation on the GaAs (111)B, which generally needs high temperatures around 800°C as well as low arsenic supply for typical the MOVPE of GaAs homoepitaxial planar growth [15, 16]. In fact, symmetric hexagonally top shaped wires were only successfully obtained for the two highest growth temperatures – 650°C and 700°C – under investigation.

In order to understand growth in more detail, we plotted the average length and the average diameter taken from SEM images. The results are shown in figures 3(a) and 3(b), respectively. The error bars indicate the standard deviations. In figure 3(a), we found that the length of the nanowires becomes longer as the growth temperature increases up to 650°C, and that it then decreases slightly at

700°C. Additionally, we observed that the deviation of the length becomes shorter as the growth temperature increases from 600°C to 700°C. In figure 3(b), we also found a clear suppression of the nanowire diameter increase above 650°C. The deviation of the diameter also becomes smaller as the growth temperature increases. Therefore, high growth temperatures result in long length, small diameter and high uniformity nanowires. Obviously they are better for the SA-MOVPE of InAs nanowires with N_2 as the carrier gas.

Here we note that the observed diameter of the nanowires is larger than the typical diameter of the initial opening (~ 50 nm), and we could not observe fringes of the opening edges at the bottom of the nanowires. This indicates that there is a slight lateral growth on the {110} side facets. Additionally, if shorter growth times are employed at 650°C, the growth rates are not linear with time: a smaller diameter d (= 87 nm) and a longer wire length L (= 4.3 µm) are confirmed than expected. A Similar time evolution tendency has been discussed in the SA-MOVPE of InGaAs nanowires [17]. The present result indicates that the diffusion length of In adatoms on {110} side facets are shorter than the nanowire lengths. This causes lateral growth of the nanowires. The interpretation also qualitatively agrees with the temperature dependence of nanowire length and diameter because increasing growth temperature gives a larger diffusion coefficient, thus an enhancement of the preferential growth on top of the (111)B surface – the wire top – as well as a suppression of lateral growth on {110} side facets. We also note that growth performed at 650°C with a low V/III ratio of 27 shows shorter L (= 8.2 µm) and larger d (= 143 nm) wires. It seems to be a similar tendency to the result obtained at 700°C, where the wires become slightly shorter and slightly larger than those obtained at 650°C. Moreover we confirmed that growth performed at 650°C with a high V/III ratio of 221 shows longer L (= 12.1 µm) and smaller d (= 87 nm) wires than at 110. Generally, low V/III ratios as well as high growth temperatures can lead to high growth rates on planar (111) B surfaces [7, 16]. Under the conditions in SA-MOVPE at which tetrahedrons grow on (111) B planes, the top facet is extended by a high diffusion length of III-group adatoms on (111) B [18]. Our SA-MOVPE deposition of hexagonal nanowires is different situation, however the observed larger diameter might originate from the diffusion length of In adatoms on (111) B in a similar manner as in tetrahedron growth.

Figure 4 shows an Arrhenius plot of growth (here the average nanowire volume ($V = \frac{3\sqrt{3}}{8} d^2 \times L$)) and of the average aspect ratio (L / d) calculated from the results shown in Figs. 3a and 3b as a function of reciprocal temperature. Two growth regimes can be seen: at temperatures at and above 600°C, growth is nearly temperature independent indicating that gas phase diffusion of the reactive species to the nanowire limits growth. A saturation volume of $V = 6.7\text{-}6.9\times10^7$ nm^3 was observed. We found a small V indicating that here the kinetics of the growth determining step - precursor decomposition on the growth surface - determines growth. The aspect ratio is determined by surface diffusion. At a temperature of 600°C and below, the surface diffusion length decreases so that it becomes smaller than the wire length. The maximum aspect ratio of over 100 at 650°C slightly

decreases to over 80 at 700°C. Our present results differ from the former works on nanowires deposited with H_2 carrier gas, in which the optimum growth temperature was below 600°C [7, 9]. In Ref. [7] a clear drop of vertical growth and strong enhancement of lateral growth were clearly observed at 600°C and at 510°C, respectively. In contrast, our results with N_2 carrier gas show no strong drop of nanowire volume or aspect ratio even at the highest temperature investigated. The smallest volume was observed at the lowest temperature of 550°C. Additionally, in our case the growth performed at 650°C with a V/III ratio of 27 shows the largest V (= 1.1×10^8 nm^3) under investigation, although usually a lower V/III ratio results in a growth suppression of InAs nanowires in Ref. [7]. It seems that the AsH_3 supply assists the axial growth of InAs nanowires in H_2 carrier gas, even though this does not seem to be the normal growth mode on planar (111) B surfaces [7, 15, 16]. Our present results correlate with the tendency observed for planar (111) B growth as well as for the SA-MOVPE of GaAs nanowires using H_2 as the carrier gas [9, 19]. Here growth can be limited by excess AsH_3 supply. We also note that the volume of our InAs nanowires grown at 550°C exhibits almost the same order of magnitude as for the H_2 carrier gas case at 540°C when taking into account the difference in TMIn partial pressure (0.118 Pa: 0.050 Pa) and growth time (10 minutes: 20 minutes) between our case and Ref. [7]. The AsH_3 partial pressures were almost the same (12.9 Pa: 13.2Pa). The difference in chemical nature of the carrier gas is expected to have a big influence on growth. The decomposition of AsH_3 to AsH_x with $x < 3$ is enhanced due to the absence of H_2 from the carrier gas in the equilibrium reaction [20]. Therefore, our present results might originate from As-rich conditions induced by the N_2 carrier gas, which can result in a shift and an extension of growth windows towards high temperatures. Moreover, an increased surface diffusion of growth determining species as well a stabilization of As-containing surfaces can be expected. An increase in surface diffusion can lead to long nanowire lengths and small diameters as mentioned before and then result in high aspect ratios. Especially at higher temperatures the etchant nature of H_2 becomes prominent, which then in turn has a detrimental effect on. Therefore, we conclude N_2 as the carrier gas is very helpful for growing indium containing III-V nanowires with high aspect ratio and the conventional diffusion controlled growth mode without a desorption of materials. It remains to be seen, if the advantage to be able to grow wires at high growth temperatures may also lead to cubic structures. An investigation to this end will be carried out and will be the topic of a future paper.

4. Summary

In summary, we carried out SA-MOVPE of InAs nanowires on GaAs (111) B masked substrates with N_2 carrier gas. We investigated the growth temperature dependence between 550°C and 700°C. We successfully demonstrated uniform InAs nanowires with hexagonally shaped tops at high growth temperatures of 650°C and 700°C. The nanowires grown at the high temperatures also exhibited very high aspect ratios above 80. The calculated average volume of the nanowires saturates as the growth temperature increased above 600°C. The result indicated that the growth rate was determined mainly

by diffusion for the higher temperatures. All in all, we successfully achieved high temperature growth of InAs nanowires by using N_2 carrier gas in SA-MOVPE.

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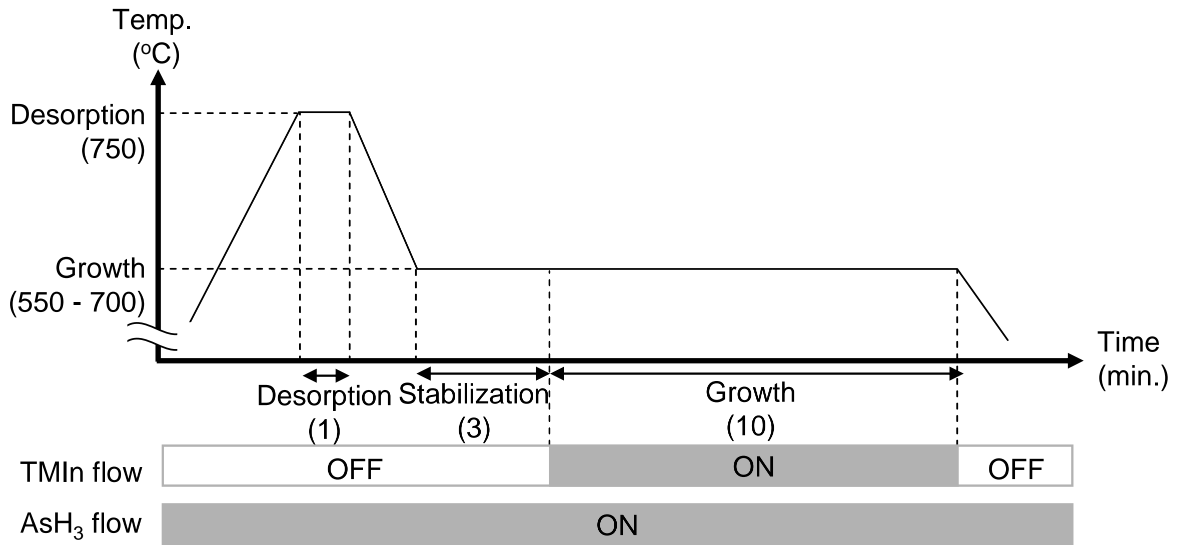


Figure 1. Schematic diagram of the growth sequence.

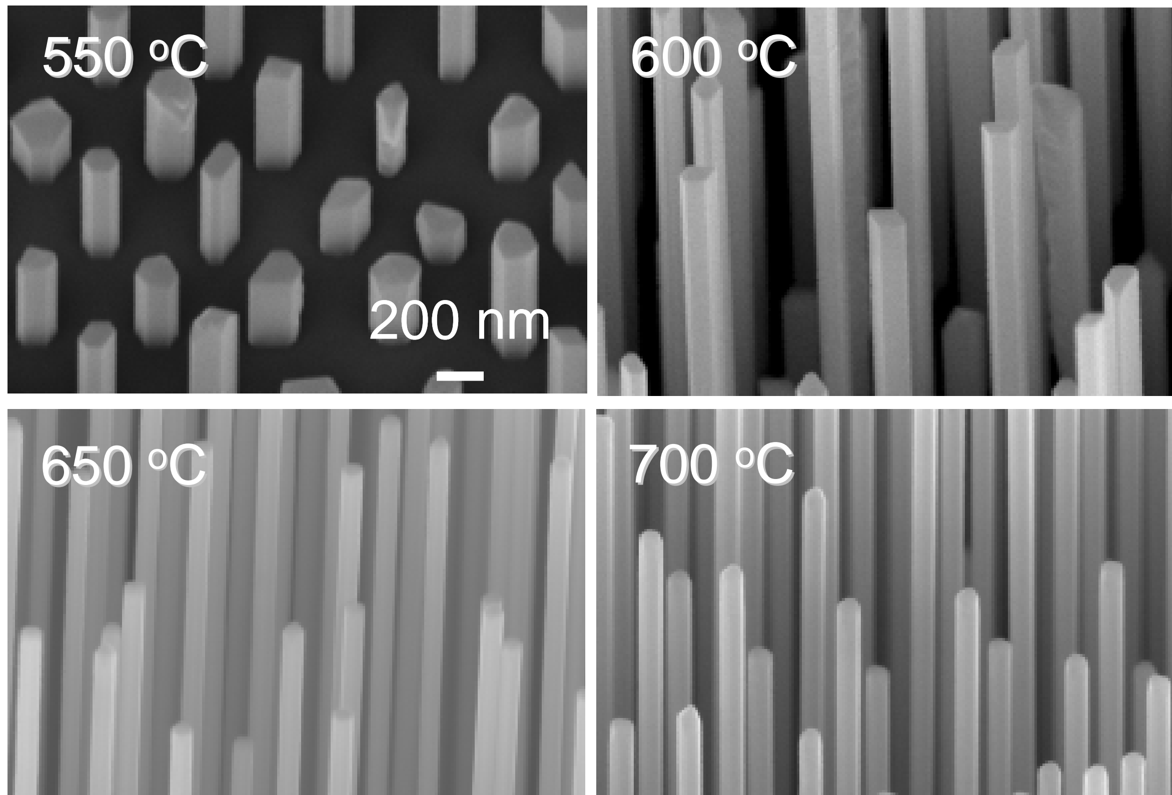
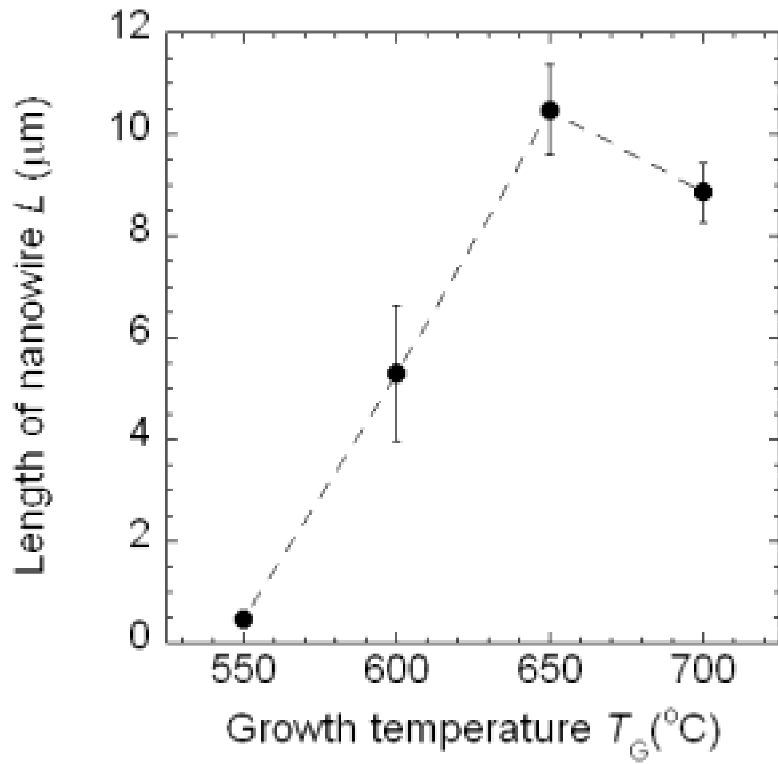
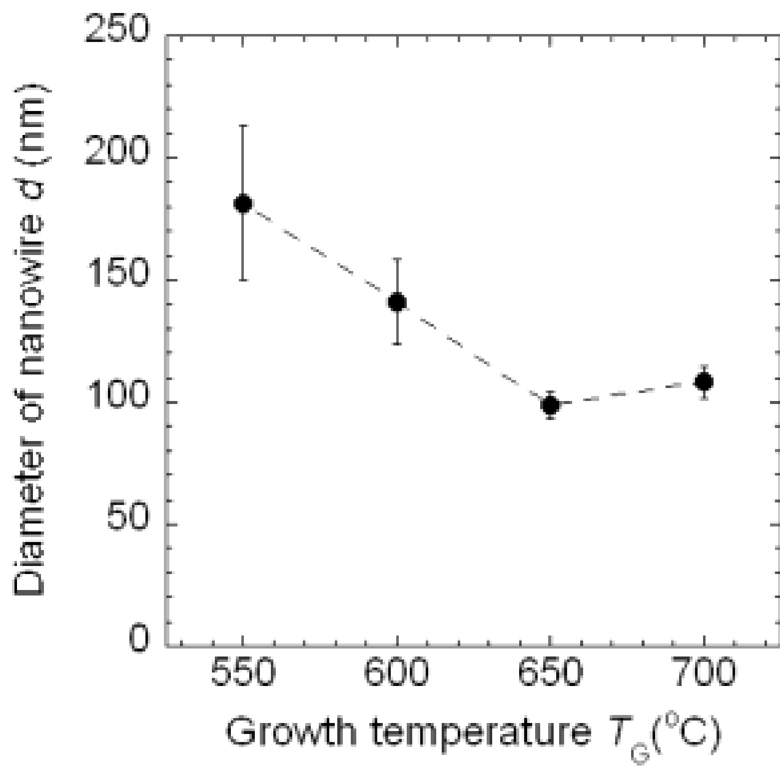


Figure 2. Scanning electron micrographs showing the morphology of InAs nanowires grown at various temperatures. The magnification is the same for all micrographs.



(a)



(b)

Figure 3. Trend of (a) length (L) and (b) diameter (d) of InAs nanowires as a function of growth temperatures (T_G) taken from SEM images. Error bars indicate the standard deviations.

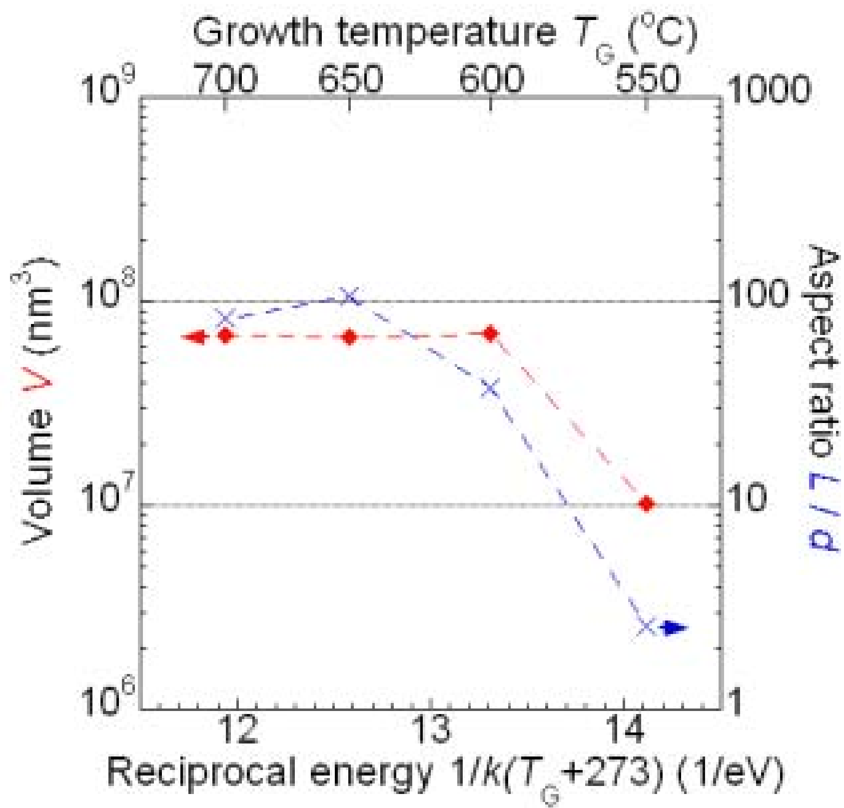


Figure 4. Average volume (*V*, diamonds) and aspect ratio (*L* / *d*, crosses) of InAs nanowires calculated from length and diameter shown in Fig. 3a and 3b.