Investigation on growth related aspects of catalyst-free InP nanowires grown by metal organic chemical vapor deposition

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A B S T R A C T
Catalyst-free InP nanowires were grown on Si (1 0 0) substrates by metal organic chemical vapor deposition. In this method, \textit{in situ} deposited In droplets are seeds of the InP nanowires growth. In order to control the growth of epitaxial InP nanowires, a detailed investigation on the growth related aspects such as the In droplets deposition time, growth temperature, and V/III ratio has been made. The experimental results indicate that the diameter, shape, and length of the nanowires can be controlled by growth conditions.

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1. Introduction

Interest in one-dimensional systems such as nanowires and nanorods has been sparked by a desire to offer a way to fabricate devices with a bottom-up approach instead of conventional top-down methods. Nanodevices based on semiconductor nanowires have already been demonstrated\cite{1–7}. Controlled growth of semiconductor nanowires is a key requirement for the development of future nanoscale optoelectronic and nanoelectronic devices. Actually, growth conditions have great impact on controlling nanowires growth. For example, many semiconductor nanowires are sensitive to catalysts diameter, growth temperature, and reactants pressure\cite{8–17}. Au nanoparticle is the most common catalyst to grow nanowires by various methods such as metal organic chemical vapor deposition (MOCVD)\cite{12,13}, pulsed laser deposition (PLD)\cite{18}, molecular beam epitaxy (MBE)\cite{19} and chemical beam epitaxy (CBE)\cite{20}. But Au catalyst can result in unintentional incorporation into nanowires or produce unwanted effect in nanowires\cite{21,22}. It has been demonstrated by Allen et al.\cite{23} that Au catalyst atoms are detected in Si nanowires by high-angle annular dark-filed scanning transmission electron microscopy. In order to avoid the contamination from Au atoms, a new growth method has been proposed by Novotny and Yu\cite{21}. They demonstrated the catalyst-free growth of InP nanowires on InP (1 1 1) B substrates using \textit{in situ} deposited In droplets as seeds for nanowires growth.

In this paper, we study the growth related aspects of InP nanowires by varying the In droplets deposition time, growth temperature, and V/III ratio to control the diameter, shape, and length of the nanowires. Nanowires are characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM) and transmission electron diffraction (TED).

2. Experiments

The InP nanowires were grown on Si (1 0 0) substrate in a horizontal MOCVD reactor with a constant system pressure of 76 Torr. Trimethylindium (TMI) and phosphine (PH\textsubscript{3}) were used as indium and phosphorus sources with hydrogen as the carrier gas. The TMI flow was kept constant at 4.8 \times 10^{-6} mol/min and the PH\textsubscript{3} flow varied with V/III ratios during the growth. Prior to the growth, Si (1 0 0) substrates were cleaned with ultrasonic using organic reagent to remove organic residues and particles. Native oxide was not removed from the substrates intendedly before nanowires growth. After putting the substrates into the reactor, the substrates were heated to growth temperature. Then the TMI was introduced into the reactor to deposit the In droplets. The nanowires growth commenced by supplying the PH\textsubscript{3} and TMI simultaneously after the In droplets deposition. The growth temperature of the InP nanowires was the same as that of the In droplets.

3. Results and discussion

Fig. 1(a)–(d) shows SEM images of In droplets deposited at 330 and 370 °C, respectively, with different growth time. The Inset in Fig. 1(b) shows an image of a hemispherical In droplet taken at a tilt angle of 90°. The average diameters of the In droplets in Fig. 1(a)–(c) ...
The nanowires in Fig. 2(a)–(d) were grown at 330°C. The growth times for all the nanowires were 7 min. The nanowires in Fig. 2(a)–(d) were grown at 330°C with the V/III ratio of 15, 30, 50, and 100, respectively. Their In droplets seeds were deposited for 120 s. The SEM images of nanowires grown at 330, 350, 370, and 390°C with the V/III ratio of 30 are shown in Fig. 2(e)–(h), respectively. Their In droplets seeds were deposited for 30 s. From the images, it can be found that the lengths of the wires are different from each other. Some of them have lengths up to five micrometers. The angles between the wires are constant, the length of the nanowires is determined by the In droplets deposition time, growth temperature, and V/III ratio.

SEM images of InP nanowires grown at different V/III ratios and temperatures are shown in Fig. 2(a)–(h). The growth times for all the nanowires were 7 min. The nanowires in Fig. 2(a)–(d) were grown at 330°C with the V/III ratio of 15, 30, 50, and 100, respectively. Their In droplets seeds were deposited for 120 s. The SEM images of nanowires grown at 330, 350, 370, and 390°C with the V/III ratio of 30 are shown in Fig. 2(e)–(h), respectively. Their In droplets seeds were deposited for 30 s. From the images, it can be found that the lengths of the wires are different from each other. Some of them have lengths up to five micrometers. The angles between the wires are diverse.

Fig. 3 shows TEM image and corresponding TED pattern of the InP nanowire. These reveal that the nanowires have a rotational twin structure, which appears as alternate dark and bright contrasts along the length of the nanowires. The rotational twin structure is usually observed in III-V semiconductor nanowires such as InP [9,24,25], GaAs [26], and InAs [27] nanowires. The TED pattern shown in Fig. 3(b) confirms that the nanowires growth direction is [1 1 1]. The two sets of spots originate from rotational twin zinc-blende crystal structure.

The In droplet can be found at the top of each nanowire. The melting point of bulk In is only 156.6°C. Due to nanosize effect, the melting point of InP (1070°C) is much higher than that of the nanowire growth temperature, InP precipitates at the liquid–solid interface, and the liquid droplet rises from the Si substrate surface. Under this growth mechanism, we can understand the tendency of the diameter, length, taper, and reverse taper of the nanowires which are affected by In droplets deposition time, growth temperature, and V/III ratio.

The diameters of the InP nanowires in Fig. 2(b), (e), and (g) are consistent with those of the In droplets in Fig. 1(b), (a), and (d). This means that the diameters of the nanowires can be controlled by the diameters of the In droplets, in agreement with previous reports [29]. As seen in Fig. 2(a)–(d), the kink, taper, and length of the nanowires can be controlled by varying the V/III ratio and growth temperature. High V/III ratios cause frequent wires kink and taper, whereas low V/III ratios cause problems associated with low nanowires growth rate and reversely tapering nanowires. Uniform diameter of nanowires can be achieved by optimizing the input V/III ratio. Obviously, the V/III ratio of 30 is suitable for InP nanowires grown at 330°C. Furthermore, in the temperature range of 330–370°C, different diameters of InP nanowires exhibit similar optimal V/III ratio [Fig. 2(b) and (e)–(g)]. While InP nanoparticles deposition occurs at 390°C, and the area density of the nanowires at 310°C are too low. Another important observation from Fig. 2(e)–(g) is that the InP nanowires growth rate increases with increasing growth temperature, because the decomposition efficiency of PH3 and TMI are increased with increasing growth temperature. When the In droplets deposition time, growth temperature, and V/III ratio are constant, the length of the nanowires is determined by the nanowires growth temperature.

The TMI flow was kept constant and the flow of PH3 which provides P atoms for growing the nanowires varied with V/III ratios during the growth. When the V/III ratio is high, quantities of P atoms absorbed by the In droplet are much more than these of In atoms absorbed by the In droplet. A large amount of In atoms which con-
tain the absorbed In atoms and part of the In droplet are consumed by these P atoms. The diameter of the In droplet becomes small. The diameter of nanowires becomes smaller gradually. Then the tapering nanowires are formed.

When the V/III ratio is 30, equal quantities of In and P atoms are absorbed by the In droplet. No In atoms in the In droplet are consumed by the absorbed P atoms. So the diameter of the In droplet at the top of the nanowire is invariable, during the growth process. The V/III ratio (Fig. 2(b) and (e)–(g)).

When the V/III ratio is lower than 30, quantities of P atoms absorbed by the In droplet are fewer than those absorbed by the In droplet. The absorbed In atoms are surplus. So the diameter of the In droplet at the top of the nanowire becomes larger and larger gradually and the reversely tapering nanowires are formed. Also lacking P atoms decrease the growth rate of nanowires. It can conclude that the shape of the wires is affected by the relative quantities of In and P atoms which are absorbed by the In droplet.

4. Conclusions

Catalyst-free growth of InP nanowires with control over the diameter, shape, and length of the nanowires has been investigated in detail. The diameter of wires can be controlled by the diameter of In droplets. The effect of V/III ratio on the shape of the InP nanowires attributes to the relative quantities of In and P atoms which are absorbed by In droplets. The growth rate of InP nanowires increases with increasing growth temperature. The growth of InP nanowires can be controlled, which leads to a reproducible process, and can potentially offer high throughput for the fabrication of nanodevices in large scale.

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References


Fig. 3. TEM image (a) and corresponding TED pattern (b) of single InP nanowire.