Journal of Alloys and Compounds 479 (2009) 832–834

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

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

Shuzhen Yu [a,b], Guoqing Miao [a,*], Yixin Jin [a], Tiemin Zhang [a,b], Hang Song [a], Hong Jiang [a], Zhiming Li [a], Dabing Li [a], Xiaojuan Sun [a]

[a] *Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, The Chinese Academy of Sciences, Changchun 130033, China*
[b] *Graduate School of the Chinese Academy of Sciences, Beijing 100049, China*

ARTICLE INFO

Article history:
Received 18 September 2008
Received in revised form 16 January 2009
Accepted 21 January 2009
Available online 31 January 2009

Keywords:
Semiconductors
Nanostructures
Nanofabrications
Vapor deposition

ABSTRACT

Catalyst-free InP nanowires were grown on Si (1 0 0) substrates by metal organic chemical vapor deposition. In this method, *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.

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 [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 [8–17].Au nanoparticle is the most common catalyst to grow nanowires by various methods such as metal organic chemical vapor deposition (MOCVD) [12,13], pulsed laser deposition (PLD) [18], molecular beam epitaxy (MBE) [19] and chemical beam epitaxy (CBE) [20]. But Au catalyst can result in unintentional incorporation into nanowires or produce unwanted effect in nanowires [21,22]. It has been demonstrated by Allen et al. [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 [21]. They demonstrated the catalyst-free growth of InP nanowires on InP (1 1 1) B substrates using *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_3) were used as indium and phosphorus sources with hydrogen as the carrier gas. The TMI flow was kept constant at 4.8×10^{-6} mol/min and the PH_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_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)

* Corresponding author. Tel.: +86 431 84627073; fax: +86 431 84627073.
E-mail address: miaogq@ciomp.ac.cn (G. Miao).

0925-8388/$ – see front matter
doi:10.1016/j.jallcom.2009.01.073

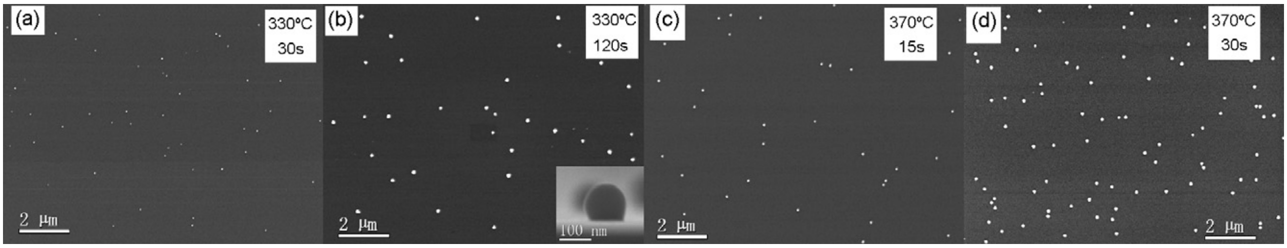

Fig. 1. SEM images of In droplets grown at different temperature with varied growth time (a) 330 °C, 30 s; (b) 330 °C, 120 s; (c) 370 °C, 15 s; (d) 370 °C, 30 s. Inset in (b) shows an image of single In droplet taken at a tilt angle of 90°.

are about 50, 120, and 85 nm, respectively. The average diameters of the In droplets in Fig. 1(b) and (d) are similar. Obviously, the diameter of the In droplets can be varied by controlling the In droplets deposition time or the growth temperature. Growth rate of the In droplets increases rapidly when the growth temperature increases from 330 to 370 °C (in Fig. 1(a) and (d)), resulting from the rapid increase in TMI decomposition efficiency and diffusion length of In atoms on the substrate surface with increasing temperature.

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 and the substrate 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 temperature of nanoparticles is always lower than that of bulk materials [28]. So the In droplets were indeed in molten state during the growth. This means that the growth mechanism of the wires is vapor–liquid–solid (V–L–S). When the PH_3 and TMI were supplied into the reactor, the In droplet absorbs In and P atoms from the vapor phase, then In atoms combine with P atoms to form crystalline InP directly. Since 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 In droplets need the 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 PH_3 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 time.

The TMI flow was kept constant and the flow of PH_3 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-

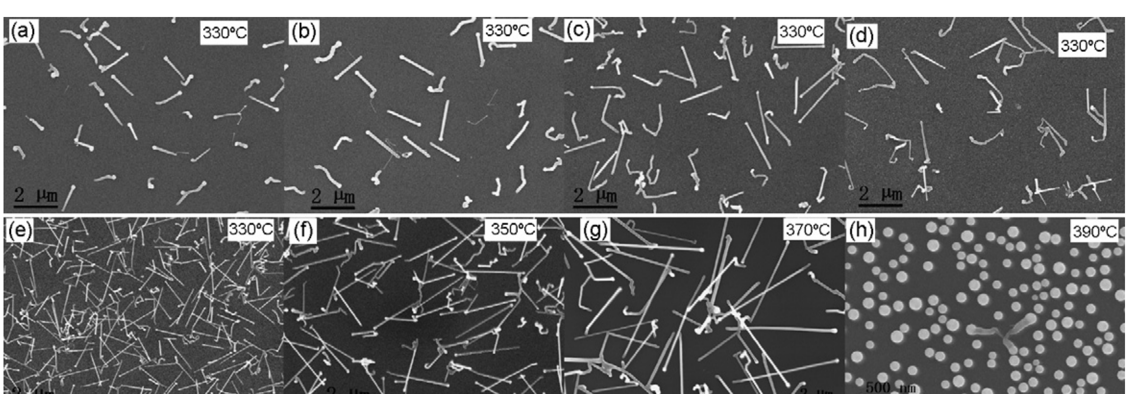

Fig. 2. (a)–(d) SEM images of InP nanowires grown at 330 °C with varied V/III ratio (a) 15; (b) 30; (c) 50; (d) 100. (e)–(h) SEM images of InP nanowires grown at different temperature (e) 330 °C; (f) 350 °C; (g) 370 °C; (h) 390 °C with the same V/III ratio of 30. The In droplets deposition time for (a)–(d) and (e)–(h) are 120 s and 30 s, respectively.

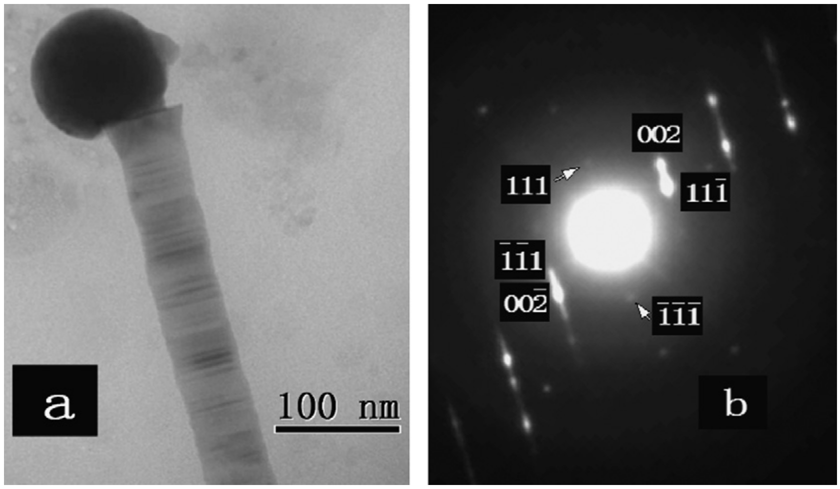

Fig. 3. TEM image (a) and corresponding TED pattern (b) of single InP nanowire.

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 nanowire 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 invariable diameter of the In droplet determines the uniformity of the nanowires. That is why in the temperature range of 330–370 °C, different diameters of the In droplets need the similar optimal 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 these of In atoms absorbed by the In droplet. So In atoms consumed by P atoms 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.

Acknowledgement

This work is supported by Projects of National Natural Science Foundation of China under grant no. 50632060.

References

[1] K. Haraguchi, T. Katsuyama, K. Hiruma, K. Ogawa, Appl. Phys. Lett. 60 (1992) 745–747.
[2] X. Duan, Y. Huang, Y. Cui, J. Wang, C.M. Lieber, Nature 409 (2001) 66–69.
[3] X. Duan, Y. Huang, R. Agarwal, C.M. Lieber, Nature 421 (2003) 241–245.
[4] M.T. Bjork, B.J. Ohlsson, C. Thelander, A.I. Persson, K. Deppert, L.R. Wallenberg, L. Samuelson, Appl. Phys. Lett. 81 (2002) 4458–4460.
[5] C. Thelander, T. Martensson, M.T. Bjork, B.J. Ohlsson, M.W. Larsson, L.R. Wallenberg, L. Samuelson, Appl. Phys. Lett. 83 (2003) 2052–2054.
[6] O. Hayden, R. Agarwal, W. Lu, Nanotoday 3 (2008) 12–22.
[7] Y. Hu, J. Xiang, G. Liang, H. Yan, C.M. Lieber, Nano Lett. 8 (2008) 925–930.
[8] K.A. Dick, K. Deppert, L. Samuelson, W. Seifert, J. Cryst. Growth 297 (2006) 326–333.
[9] S. Bhunia, T. Kawamura, S. Fujikawa, H. Nakashima, K. Furukawa, K. Torimitsu, Y. Watanabe, Thin Solid Films 464–465 (2004) 244–247.
[10] P. Paiano, P. Prete, N. Lovergine, A.M. Mancini, J. Appl. Phys. 100 (2006) 094305–094308.
[11] M. Tchernycheva, J.C. Harmand, G. Patriarche, L. Travers, G.E. Cirlin, Nanotechnology 17 (2006) 4025–4030.
[12] K. Tateno, H. Hibino, H. Gotoh, H. Nakano, Appl. Phys. Lett. 89 (2006) 033114–033116.
[13] U. Kim, H.K. Seong, M.H. Kim, H.J. Choi, Mater. Lett. 63 (2009) 97–99.
[14] T. Stoica, R. Meijers, R. Calarco, T. Richter, H. Luth, J. Cryst. Growth 290 (2006) 241–247.
[15] M.S. Gudiksen, J. Wang, C.M. Lieber, J. Phys. Chem. B 105 (2001) 4062–4064.
[16] X.M. Cai, F. Ye, S.Y. Jing, D.P. Zhang, P. Fan, E.Q. Xie, J. Alloys Compd. 467 (2009) 472–476.
[17] K.A. Dick, K. Deppert, L. Samuelson, W. Seifert, J. Cryst. Growth 298 (2007) 631–634.
[18] E.P.A.M. Bakkers, M.A. Verheijen, J. Am. Chem. Soc. 125 (2003) 3440–3441.
[19] D.M. Cornet, V.G.M. Mazzetti, R.R. LaPierre, Appl. Phys. Lett. 90 (2007) 013116–013118.
[20] P.J. Poole, J. Lefebvre, J. Fraser, Appl. Phys. Lett. 83 (2003) 2055–2057.
[21] C.J. Novotny, P.K.L. Yu, Appl. Phys. Lett. 87 (2005) 203111–203113.
[22] M. Mattila, T. Hakkarainen, H. Lipsanen, H. Jiang, E.I. Kauppinen, Appl. Phys. Lett. 89 (2006) 063119–063121.
[23] J.E. Allen, E.R. Hemesath, D.E. Perea, J.L. Lensch-falk, Z.Y. Li, F. Yin, M.H. Gass, P. Wang, A.L. Bleloch, R.E. Palmer, L.J. Lauhon, Nat. Nanotechnol. 3 (2008) 168–173.
[24] M. Mattila, T. Hakkarainen, H. Jiang, E.I. Kauppinen, H. Lipsanen, Nanotechnology 18 (2007) 155301–155305.
[25] M. Moewe, L.C. Chuang, V.G. Dubrovskii, C.C. Hasnain, J. Appl. Phys. 104 (2008) 044313–044316.
[26] K. Hiruma, M. Yazawa, T. Katsuyama, K. Ogawa, K. Haraguchi, M. Koguchi, H. Kakibayashi, J. Appl. Phys. 77 (1995) 447–462.
[27] X. Xu, W. Wei, X. Qiu, K. Yu, R. Yu, S. Si, G. Xu, W. Huang, B. Peng, Nanotechnology 17 (2006) 3416–3420.
[28] N. Wang, Y. Cai, R.Q. Zhang, Mater. Sci. Eng. R 60 (2008) 1–51.
[29] Y. Cui, L.J. Lauhon, M.S. Gudiksen, J. Wang, C.M. Lieber, Appl. Phys. Lett. 78 (2001) 2214–2216.