GROWTH OF BINARY, TERNARY AND QUATERNARY III-V COMPOUNDS NANOWIRES BY MOCVD

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ABSTRACT

Various III-V compounds semiconductor Nanowires (NWs) have been grown by using vertical camber MOCVD. The morphology of the NWs has been characterized using FESEM and SEM. In addition to binary and ternary NWs such as GaAs, InP, In_xGa_{1-x}As and Al_yGa_{1-y}As NWs, the quaternary compounds InGaAsP NWs have been successfully grown. The growth of NWs has been assisted by gold nanocolloids as seed particles. Besides this technique, seed free-assisted growth of NWs has also been demonstrated. In_xGa_{1-x}As NWs have been successfully grown without gold seed-particle assisted.

Keywords: III-V compounds NWs; MOCVD; gold seed particles assisted; seed free-assisted;

INTRODUCTION

Semiconductor NWs based on III-V compound have been receiving attention as base components for next generation electronic and optoelectronic devices due to their direct band gap and high carrier mobility [1-4]. One of the most popular techniques used to fabricate NWs is metal-organic chemical vapor deposition (MOCVD). MOCVD has been developed as the technique to grow various III-V and II-VI compounds materials. Therefore by using this technique a wide range of III-V semiconductor compounds NWs including those containing P, As and Al are possible to fabricate. The easiness of controlling in fabricating more complex structures such as radial and axial NWs is a great additional advantage which confirms MOCVD as versatile NWs growth technique.

III-V NWs can be epitaxially grown using seed particle-assisted by MOCVD. In the NWs growth process using MOCVD, seed particle such as gold promotes anisotropic wire-like growth by either via vapour-liquid-solid (VLS) or vapor-solid-solid (VSS) mechanism [5-7]. At the growth temperature, the Au nanoparticles on the semiconductor substrate surface form a liquid (in case of VLS) or solid (in case of VSS) alloy with the group III species [5]. Using this technique, various compounds NWs
including binary and ternary compounds such as GaAs, InP, In\textsubscript{x}Ga\textsubscript{1-x}As and Al\textsubscript{y}Ga\textsubscript{1-y}As NWs as well as quaternary compounds InGaAsP NWs have been successfully fabricated. In addition, seed free-assisted growth of In\textsubscript{x}Ga\textsubscript{1-x}As NWs has also been successfully demonstrated.

**EXPERIMENTAL DETAILS**

The binary, ternary and quaternary III-V compounds NWs have been grown on various substrates using vertical chamber MOCVD system. The chamber is low pressure (0.1 atm) with hydrogen as carrier gas. The NWs were grown using trimethylindium (TMIn), trimethylgallium (TMGa), trimethylaluminium (TMAI), phosphine (PH\textsubscript{3}) and arsine (AsH\textsubscript{3}) as precursors. For seed particles assisted growth of NWs, the substrate was functionalized by immersing it in 0.1 % poly-L-lysine (PLL) solution for 3 minutes prior to NWs growth on the surface of substrate. After that, substrate was cleaned with de-ionized water and subsequently dried with nitrogen (N\textsubscript{2}). It was then treated with 50 % gold colloid solution for 30 seconds. The negatively charged Au particles are attracted to the positively charged PLL layer thus are immobilized on the substrate surface [1,2]. After Au seed particles were deposited on substrate surface, the substrate was placed in MOCVD chamber. Substrate was heated at temperature of 600 °C under constant partial pressure of AsH\textsubscript{3} gas for 10 minutes, and then cooled to desired growth temperature. Once the growth temperature was achieved, the precursors were flowed by automatically controlling into the chamber following the recipe of respective NWs. Binary NWs were grown by simultaneously injecting TMGa with AsH\textsubscript{3} for GaAs NWs and TMIn with PH\textsubscript{3} for InP NWs. In\textsubscript{x}Ga\textsubscript{1-x}As NWs were grown by injecting TMGa, TMIn and AsH\textsubscript{3}, whereas Al\textsubscript{y}Ga\textsubscript{1-y}As NWs were grown by injecting TMGa, TMAI and AsH\textsubscript{3}. Quaternary InGaAsP NWs were grown by injecting TMIn, TMGa, TMAAs and PH\textsubscript{3}. Finally, for free gold seed particles assisted, the NWs were grown on sterile substrate without pre treatment before growth process. Samples were investigated using Scanning Electron Microscopy (SEM) and Field Emission-Scanning Electron Microscopy (FESEM) located at Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia to investigate the morphology and the chemical composition of the NWs, respectively.

**RESULTS AND DISCUSSION**

**Binary GaAs and InP Nanowires**

Figure 1 shows SEM images of GaAs NWs grown at temperature of 420 °C on GaAs (111) and (100) substrate. The growth temperature was below the pseudo-binary eutectic point of Au-GaAs (630 °C) [7]. Therefore, the state of Au seed particle was either solid or molten - its surface and interface were liquid, while the core of the seed particle was solid [8]. For that reason, the NWs have been grown via VSS rather than VLS mechanism. Based on Figure 1(a) and (b) it can be observed that the NWs that were grown on GaAs (111) and (100) substrate were in the same [111] direction with cylindrical shape [9]. This indicates that the [111] direction is the preferential growth direction of NWs due to its lower surface energy [10, 11]. Consequently, NWs grown
on (111) grew perpendicular to the substrate while the NWs grown on GaAs(100) grew at an angle of 50.60° to the substrate [9]. Cylindrical NWs indicate that NW’s growth was by direct impinging mechanism via VSS at 420 °C. In this mechanism, source atoms (precursor) directly fall onto Au seed particle to form a liquid solution (partially molten state) of an alloy (stable or unstable). This serves as a preferential site for the decomposition of the source atom via absorption and diffusion mechanism of precursors into alloy seed particles [12]. The amount of precursor in the vapor near the seed particle is then locally increased compared to elsewhere on the substrate [13].

Figure 1: SEM images of GaAs NWs seeded by 30 nm diameter Au particles and grown for 30 minutes at temperature of 420 °C on a) GaAs (111) and b) GaAs (100) substrate. Samples were tilted at 45°.

At a certain point when enough precursor materials have been incorporated into the seed particle it will become supersaturated. In this case, saturation of seed particle with the growth precursor or the formation of the proper combination may lead to an induction period before the growth [6]. Then, the super saturation leads to precipitation of the semiconductor material at the particle-substrate interface referred to as nucleation and GaAs NWs starts to grow. Due to a continuous supply of growth precursors the growth occurs at the particle-wire interface to form GaAs NWs.

InP NWs that were grown on GaAs (111) substrate at temperature of 400 °C for 30 minutes is shown in Figure 2. As can be seen, even though they were grown on similar GaAs (111) substrate as GaAs NWs, these InP NWs did not grow perpendicular to the substrate but in random direction. This phenomenon is due to the greater lattice mismatch between InP NWs and GaAs substrate [9]. The lattice constant of InP material is 5.8686 Å, while that of GaAs is 5.6533 Å [14]. GaAs NWs on GaAs substrate grew with uniform shape and direction because the lattice constant of the NWs and substrate are similar. Consequently, InP NWs grew with random direction on GaAs substrate. Therefore, the high level of lattice mismatch between NWs and the substrate is one aspect which should be considered that could contribute to the difficulty level of growing NWs with controllable shape and direction.
Figure 2: SEM images of InP NWs seeded by 30 nm diameter Au particles and grown for 30 minutes at temperature of 400 °C via VSS mechanism on GaAs (111) substrate. Samples were tilted at 45°.

**Ternary In\textsubscript{x}Ga\textsubscript{1-x}As and Al\textsubscript{x}Ga\textsubscript{1-x}As Nanowires**

Ternary III-V compounds semiconductor NWs were successfully grown using MOCVD. Figure 3 shows FESEM images of In\textsubscript{x}Ga\textsubscript{1-x}As NWs grown at temperature of 400 °C with different indium mole fraction (x). The growth time and V/III ratio were set 30 minutes and 10, respectively. In\textsubscript{x}Ga\textsubscript{1-x}As NWs that were grown with x equals to 0.41 and 0.47 are shown in Figure 3(a) and (b), respectively. Even though they are not uniform, almost NWs were grown with cylindrical shape without any kinking and perpendicular to GaAs (111) substrate indicating that the growth of NWs were mainly controlled by direct impinging mechanism. It can be observed that the tapering degree of NWs is proportional to the increasing indium mole fraction. NWs grown at indium mole fraction of 0.47 have higher degree of tapering. This is due to the fact that In species have a much larger diffusion length on (111)B surfaces, compared to Ga species. The diffusion length of In and Ga species are 6 µm and 2 µm, respectively [15]. By increasing the value of indium mole fraction the growth mechanism of NWs has changed from via the direct impinging mechanism to the combination of direct impinging and diffusion source atoms from the substrate, therefore, resulting in tapering of NWs.

Figure 4 shows SEM images of In\textsubscript{x}Ga\textsubscript{1-x}As NWs grown on GaAs (111) substrate for 30 minutes at high growth temperatures (480 and 520 °C) with indium mole fraction and V/III ration were set at 0.47 and 10, respectively. For comparison, In\textsubscript{x}Ga\textsubscript{1-x}As NWs were then grown on Si (111) substrate as shown in Figure 5. For NWs that were grown on GaAs (111) substrate, its morphology looks very different compared to the NWs grown at low growth temperatures. At growth temperature of 400 °C, In\textsubscript{x}Ga\textsubscript{1-x}As NWs were grown perpendicularly to the substrate with cylindrical shape. At 480 °C, different
phenomenon was observed. In$_x$Ga$_{1-x}$As NWs underwent evolution and grew with short tapering like an array of uniform size mountains. Surprisingly, when growth temperature was further increased to 520 °C the mountain wires grew higher than those at 480 °C. This phenomenon can be interpreted as due to different mechanism of NWs growth when the growth temperature was changed. The growth mechanism of NWs assisted by seed particle such as Au particle is highly determined by growth temperature.

Figure 3: FESEM images of In$_x$Ga$_{1-x}$As NWs grown at temperature of 400 °C with different indium mole fraction ($x$), a) 0.41 and b) 0.47. Samples were tilted at 45 °

Figure 4: SEM images of highly tapering In$_x$Ga$_{1-x}$As NWs grown at temperatures of a) 480 °C and b) 520 °C. Samples were tilted at 45 °

Increasing the growth temperature can give additional energy to source atoms (precursors), therefore precursor atoms that fall onto the substrate surface obtain extra energy to move through substrate surface via diffusion mechanism. Since the seed particles act as the preferential sites (lower energy barrier than elsewhere) for the decomposition of the source atoms which lead to nucleation, source atoms from the substrate surface tend to move towards the seed particles and contribute to the growth of the NWs via diffusion mechanism and cause tapering. At certain growth conditions
(high temperature) however, adatom diffusion mechanism from substrate surface could be highly dominant compared to the direct impinging mechanism. Therefore, In$_x$Ga$_{1-x}$As NWs grown by this mechanism are highly tapered, whereby the top of the NWs is highly small compared to the base of the NWs as shown in Figure 4.

Figure 5 shows In$_x$Ga$_{1-x}$As NWs that were grown on Si (111) substrate at two different magnifications. As can be seen In$_x$Ga$_{1-x}$As NWs grown on Si (111) substrate did not grow upward with uniform direction as on GaAs(111), although the crystallographic plane of Si and GaAs substrates is similar. This phenomenon is slightly similar with the growth of InP NWs on GaAs substrate. Therefore, the surface energy differences between GaAs(111) and Si(111) substrate as well as the lattice mismatch differences between In$_x$Ga$_{1-x}$As NWs and substrate are considered as causing the differences in the morphology and orientation of NWs which grown on both substrates.

**Figure 5:** SEM images of highly tapered In$_x$Ga$_{1-x}$As NWs grown on Si (111) substrate at temperature of 480 oC with magnifications of a) X3,000 and b) X7,000. Samples were tilted at 45°

Al$_y$Ga$_{1-y}$As NWs were also successfully grown on GaAs (111) substrate using MOCVD. The NWs were grown at temperature of 530 °C for 30 minutes with aluminum mole fraction, $y$, and $V/III$ ratio were set at 0.41 and 10, respectively. High density Al$_y$Ga$_{1-y}$As NWs grew perpendicular to the substrate with mostly uniform size is shown in Figure 6. This indicates that at temperature of 530 °C Al$_y$Ga$_{1-y}$As NWs were grown by direct impinging mechanism via VSS model. The similarity of lattice constant between Al$_y$Ga$_{1-y}$As NWs (the possible range is between 5.6533 Å to 5.6605 Å) and GaAs substrate (5.6533 Å) is the reason why Al$_y$Ga$_{1-y}$As NWs are easy to grow on GaAs substrate with controllable morphology and direction. This phenomenon is contrast to the growth of NWs, which has high lattice mismatch with its substrate such as InP NWs on GaAs (111) as well as In$_x$Ga$_{1-x}$As NWs on Si (111).
Figure 6: FESEM images of high density AlyGa1-yAs NWs on GaAs (111) substrate. Samples were tilted at 45°.

**Quaternary InGaAsP NWs and Gold Free Seed Particles Assisted InxGa1-xAs NWs**

More complex III-V compounds InGaAsP semiconductor NWs have also been successfully grown using MOCVD. The NWs were grown on GaAs (111) substrate at temperature of 400 °C for 30 minutes using gold seed particles. Similar to GaAs, InxGa1-xAs and AlxGa1-yAs NWs, on GaAs (111) substrate, InGaAsP NWs grew straight up and its morphology can be considered as cylindrical shape which is shown in Figure 7. This trend is expected to be extended to other NWs of quaternary III-V compound with various material compositions. More importantly, the successfullness of growing various compound semiconductor NWs ranging from binary till quaternary is a great evidence that shows that MOCVD is one of the most versatile techniques to grow nanowires.

Advance study on growth of III-V compounds NWs has been done by growing InxGa1-xAs NWs without using gold particles as foreign metal catalyst. The experiment was carried out by replacing gold particles with Ga or In droplets which is provided by injecting TMGa or TMIn as one of precursors InxGa1-xAs compounds. GaAs (111) was used as substrate because the InxGa1-xAs NWs will grow in upward direction from the surface. The substrate was heated to a growth temperature of 400 °C in AsH3 flow. After the growth temperature was stabilized, the AsH3 flow was turned off and TMGa was injected for NWs growth which were seeded by Ga droplets. For NWs growth which were seeded by In droplets, TMGa injection was replaced by TMIn injection. In this study the duration of Ga or In injection was 90 seconds. Without interrupting the growth after the deposition of Ga or In droplets, TMGa, TMIn and AsH3 precursors were flowed simultaneously for InxGa1-xAs NWs growth. The indium mole fraction and V/III ratio were set at 0.41 and 10, respectively. After 30 minutes, the sample was cooled down in AsH3 flow until NWs growth is finished. Ga droplet assisted and In droplet assisted InxGa1-xAs NWs are shown in Figure 8(a) and (b), respectively. As can be seen, InxGa1-xAs NWs growth that was assisted by Ga droplets has produced cylindrical morphology with relatively uniform size, whereas NWs which was grown
by In droplet assisted has tapering shape. Hence, it can be noted that foreign seed particles catalyst was not necessarily required for growing NWs. NWs can also be seeded using one of precursors compound of desirable NWs. As a result, disadvantage of NWs growth using foreign seed particles in the form impurities on the NWs can be avoided thus free-impurities NWs can be produced. These impurities are believed can reduce the NW’s performance. Meanwhile, impurities free NWs are expected able to enhance the NW’s appearance and its properties.

Figure 7: FESEM images of quartenary InGaAsP NWs on GaAs (111) substrate with different magnification. a) x10,000 and b) x20,000. Samples were tilted at 45°

Figure 8: FESEM images of Ga droplet assisted and In droplet assisted InₙGa₁₋ₙAs NWs on GaAs (111). (a) Ga droplet assisted and (b) In droplet assisted. Samples were tilted at 45°
CONCLUSION

GaAs, InP, In_xGa_{1-x}As, Al_yGa_{1-y}As and InGaAsP NWs have been successfully grown by MOCVD using gold seed nanoparticles as catalyst. Besides, foreign free seed-particles-assisted growth of In_xGa_{1-x}As NWs has demonstrated. In_xGa_{1-x}As NWs were successfully grown by using Ga or In droplet which was provided by injecting TMGa or TMIn before desirable NWs growth process. Therefore, the impurities from foreign materials which are believed able to reduce the NW’s performance could be avoided. The successfulness on the NWs growth ranging from binary till quaternary is other great out come that highly MOCVD as one of the most versatile method in fabricating various compound semiconductor NWs.

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REFERENCES
