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Morphology and Chemical Composition of $In_xGa_{1-x}As$ NWs Au-assisted Grown at Low Growth Temperature Using MOCVD

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Abstract: Cylindrical $In_xGa_{1-x}As$ NWs have been successfully grown at low growth temperature using MOCVD. Field Emission-Scanning Electron Microscopy (FE-SEM) characterization and Energy Dispersive X-ray (EDX) analysis have been used to investigate the morphology and chemical composition of NWs, respectively. Both characterization results consistently reinforce that the NWs growth were via direct impinging mechanism and NW have relatively uniform chemical composition.

Key words: $In_xGa_{1-x}As$ NWs, Au-assisted grown, direct impinging mechanism and chemical composition

INTRODUCTION

One-dimensional semiconductor nanowires (NWs) are expected to play to key-role not only for testing of fundamental phenomena but also for potential nanotechnology applications (Sano *et al*., 2007; Regolin *et al*., 2007; Dick *et al*., 2007). Due to the direct band gap and high carrier mobility of materials, III-V compound semiconductor NWs have been receiving high attention as base components for next generation electronic and optoelectronic devices (Cornet and La Pierre, 2007). The flexibility to modify the lattice constant and energy band gap by adjusting the relative composition of the alloy leads to ternary alloy Nws have been gaining interest over elemental and binary compound NWs (Lim *et al*., 2008).

$In_xGa_{1-x}As$ NWs is one of the most amazing III-V ternary alloy NWs to be further elaborated due to some fascinating importance of this material system for application in long wavelength optical transmission and integrated photonics applications (Lim *et al*., 2008; Kim *et al*., 2006). In addition, due to low electron effective mass of the material, $In_xGa_{1-x}As$ is considered to be one of the fascinating materials suitable as transistors channel (Sato *et al*., 2008a, b). For large scale device application, the dimension of the NW (diameter and length), its crystalline structure, chemical composition as well as the surface coverage of Nws needs to be uniform and fully controlled (Joyce *et al*., 2006; Messing *et al*., 2009). To pursue these objectives, $In_xGa_{1-x}As$ NWs must be grown not only at suitable condition but also by appropriate growth mechanism.

Recently, semiconductor NWs with different composition have been successfully grown using seed particle via vapor-liquid-solid (VLS) (Lim *et al*., 2008; Wagner and Ellis, 1964; Park, 2008; Kodambaka *et al*., 2006; Jishiashvili *et al*., 2009; Schwalbach and Voorhees, 2008; Greytak *et al*., 2004; Hoffmann *et al*., 2006), vapor-solid-solid (VSS) (Adhikari *et al*., 2006; Lensch-Falk *et al*., 2007; Wang *et al*., 2008; Omari *et al*., 2008), and solid-liquid-solid (SLS) based on self-organized growth mechanism (Kolasinski, 2006). Those mechanism depend on the growth technique, growth condition as well as the material of NWs that grown (Kolasinski, 2006). In particular, III-V NWs seed particle-assisted can be epitaxially grown by metal-organic chemical vapor deposition (MOCVD) (Joyce *et al*., 2007). In the growth process, a seed particle such as gold promotes anisotropic wire-like growth by either VLS or VSS mechanism (Dick, *et al*., 2007; Kolasinski, 2006; Joyce *et al*., 2006). At the growth temperature, 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 (Joyce *et al*., 2006). As the group III species precipitate out at the nanoparticle-semiconductor interface, highly NW growth occurs, with

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Au nanoparticle a top of each NWs (Wagner and Ellis, 1964; Park, 2008; Kodambaka *et al*., 2006; Jishiashvili *et al*., 2009; Schwalbach and Voorhees, 2008; Greytak *et al*., 2004; Hoffmann *et al*., 2006; Joyce *et al*., 2006). Usually, the diameter of NW is mainly determined by the size of the seed particle and its length is determined by the growth time and conditions (Wagner and Ellis, 1964; Lauhon *et al*., 2004; Samuelson *et al*., 2004).

The challenges in the growth ternary compound NWs such as $In_xGa_{1-x}As$ NW is still difficult to produces Nws with uniform size and chemical composition (Kim *et al*., 2006; Joyce *et al*., 2007). NWs grow with tapered shape (bigger size on the bottom) have non-uniform chemical composition along the wire. In this study however, cylindrical $In_xGa_{1-x}As$ NWs with relatively uniform chemical composition have been successfully grown. The growth temperature was below the pseudo-binary eutectic points of Au-GaAs (630°C) (Duan and Lieber, 2000). Consequently the state of Au seed particle is solid or molten state. Its surface and interface are liquid, while the core of the seed particle is solid (Kim *et al*., 2006). Therefore, in this case, $In_xGa_{1-x}As$ NWs were grown via VSS rather than VLS mechanism.

MATERIAL AND METHODS

$In_xGa_{1-x}As$ NWs have been grown on undoped GaAs (111)B substrates in vertical chamber MOCVD system. The system uses low-pressure (0.1 atm) chamber with trimethylindium (TMIn), trimethylgallium (TMGa) and arsine (AsH_3) as precursors and 99.9999% pure hydrogen as carrier gas. GaAs (111)B substrate was chosen due to low surface energy which is the energetically favorable growth direction (Kim *et al*., 2006; Cau, 2003). Prior to the NWs growth on the substrate surface, the substrate was functionalized by immersed it in 0.1% poly-L-lysine (PLL) solution for 3 min. The substrate was then cleaned with de-ionized water and subsequently blow-dried with nitrogen (N_2). It was then treated with 50% gold colloid solution (30 nm diameter Au particle) for 30 sec. It was then loaded into the MOCVD chamber. The substrate was heated up to 600°C under constant partial pressure of AsH_3 gas for 10 min to desorbed surface contamination and then cooled down to the desired growth temperature. Once the growth temperature was reached, TMIn, TMGa, and AsH_3 was flowed into the chamber for the NWs growth. The growth time, growth temperature and V/III ratio of Nws growth were set at 30 min, 400°C and 10.0, respectively. The morphology and chemical composition of NWs were investigated using Field Emission-Scanning Electron Microscopy (FE-SEM) and Energy Dispersive X-ray (EDX) analysis, respectively.

In this growth process NWs were seeded by 30 nm diameter Au particles. Gold was chosen to initiate NWs growth due to many of the precursor materials used for growth are soluble in gold. Secondly, gold is a very soft metal and therefore is more probable to form particles with reasonably uniform shape even in the solid form. Furthermore, for many materials, growth with a solid particle would be impractically slow, but for gold however, the diffusivities of In and Ga through a solid particle are very high and therefore should give a reasonably high growth rates (Joyce *et al*., 2007).

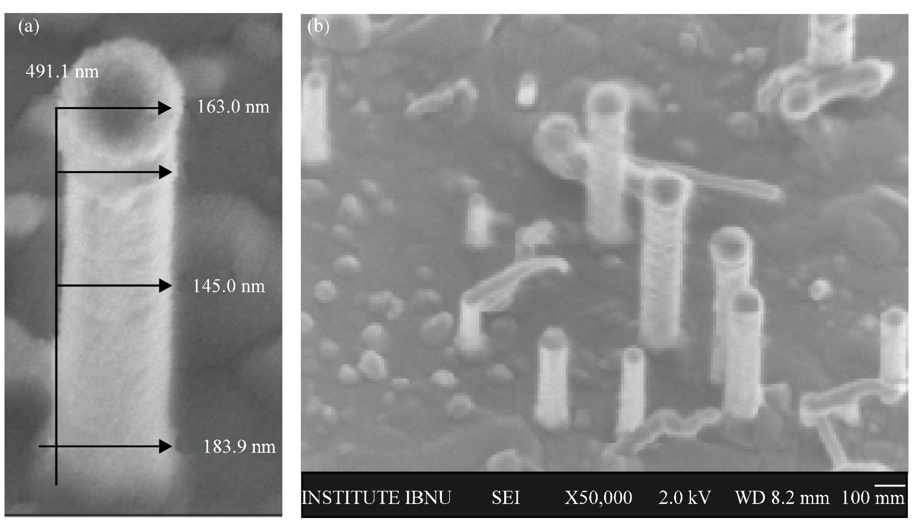


Fig. 1: FE-SEM images of $In_xGa_{1-x}As$ NWs seeded by 30 nm diameter Au particles and grown for 30 min at 400°C. The images were viewed at 45° angle from the surface normal

RESULT AND DISCUSSION

FE-SEM images in Fig. 1 shows cylindrical $In_xGa_{1-x}As$ NWs grow perpendicular to the substrate. It indicates at temperature of 400°C, NWs were grown by direct impinging mechanism via VSS models. In this mechanism, source atoms (precursor) directly fall onto Au seed particle (Fig. 2a) to form a true eutectic or liquid solution (partially molten state) of an alloy (stable or unstable). This is serves as a preferential site for the decomposition of the source atom via absorption (stage 1 of Fig. 2a) and diffusion mechanism (stage 2 of Fig. 2a) (Wang *et al*., 2008). The amount of precursor in the vapor near the seed particle is then locally increased compared to elsewhere on the substrate (Dick, 2008). At a certain point when enough precursor material has 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 (Kolasinski, 2006). Then, the super saturation leads to precipitation of the semiconductor material at the particle-substrate interface referred to as nucleation (stage 3 Fig. 2a), and $In_xGa_{1-x}As$ NW starts to grow (Fig. 2b). Due to a continuous supply of growth precursors the growth occurs at the particle-wire interface to form $In_xGa_{1-x}As$ NW (Fig. 2c). The growth rate of NW depends to a large extent on the precursor concentration and growth temperature (Joyce *et al*., 2007).

It can be observed that $In_xGa_{1-x}As$ NWs grown were different in diameter and length. The distribution of diameter and surface density of NWs were likely due to the annealing effect (temperature and time) on the distribution of Au particles on the surface of substrate before the growth precursors were injected. Since they can obtain some extra energy, the adjacent particles could combine together to form the larger size through the Ostwald ripening mechanism (Cau, 2003). On the other hand, Au particle that did not combine together did not change their size. Besides, the incorporation of significant amount of precursor into the seed particle is another way to change the size (volume) of seed particle. As a result, NWs grown with seed particle-assisted have different diameter. Therefore, Ostwald ripening and incorporation of growth precursor can both conspire to change the size of the Au seed particle. Due to those mechanisms some NWs were grown with diameter around six times than the diameter of Au seed particle as shown on Fig. 1b. Furthermore, NWs with smaller diameter grow shorter than the bigger ones due to different growth rate. The classical analysis of Givargizov concluded that narrower wires grow more slowly due to Gibbs-Thomson effect (Dick *et al*., 2006). Other studies, however, show the opposite (Givargizov, 1975), with narrow wires growth more rapidly. The difference is likely due to the different growth conditions, different growth mechanism and different material of the Nws.

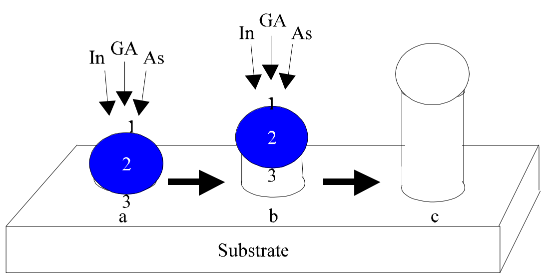
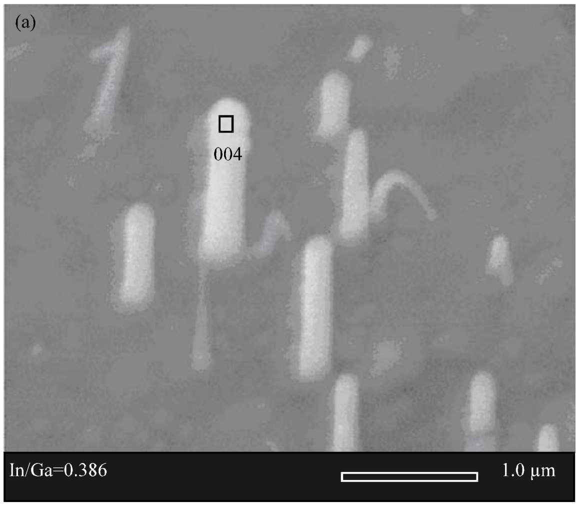


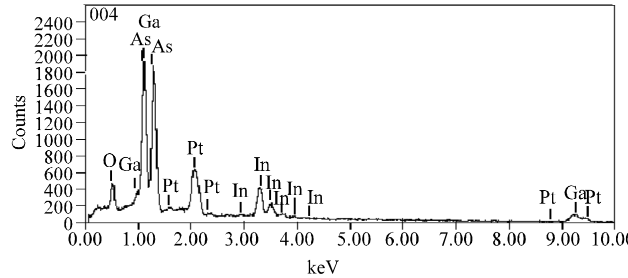
Fig. 2: Schematic diagram of a direct impinging growth mechanism of $In_xGa_{1-x}As$ NWs. The metal droplet (see particle) is in solid or partially molten state (liquid solution)

EDX analysis has been used to investigate the chemical composition of individual $In_xGa_{1-x}As$ NWs from various detection positions; tip, middle and bottom of NW as shown on Fig. 3. Surprisingly, Au was not detected from various detection positions, even on the tip of the NW. This is most likely due to the amount of Au was very small compared to the elements of the NW. From EDX measurement the ratio of In/Ga compositional at the tip, middle and bottom of the $In_xGa_{1-x}As$ NW was 0.386, 0.323, and 0.319, respectively. These ratios, especially the one at the tip of the NW is close to the value of In vapor composition, x_v of 0.41. The diverse In/Ga compositional ratios along the NW were due to (In,Ga) As source atoms (precursor) fall onto the tip of the NW then move downwards to the bottom of the NW. The EDX results is the evidence that NWs grow were via direct impinging mechanism. Even though the compositional ratio from these three detection positions were not exactly the same, but all values were around of 0.3. This means that straight NWs with uniform diameter, height and a chemical composition are possible to produce.

CONCLUSION

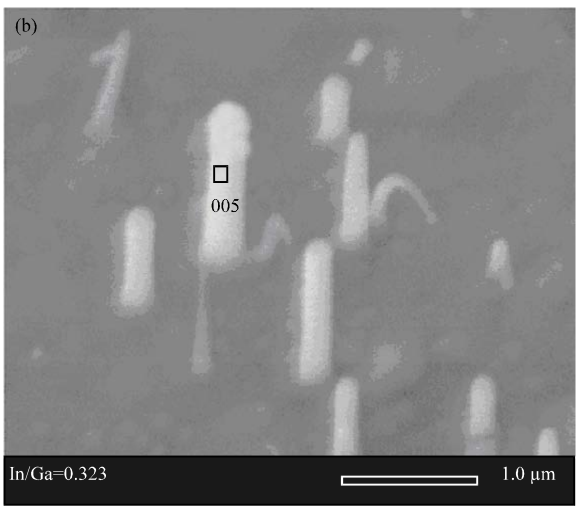
$In_xGa_{1-x}As$ NWs have been grown at low growth temperature using MOCVD. FE-SEM images show cylindrical shape $In_xGa_{1-x}As$ NWs grow perpendicular to the substrate, indicating NWs growth via direct impinging mechanism. EDX results show (In/Ga) ratio on the tip, middle and bottom of NW was not precisely same, but all values were around of 0.3. EDX results also indicate that NWs grow via direct impinging mechanism tends to have uniform chemical composition.

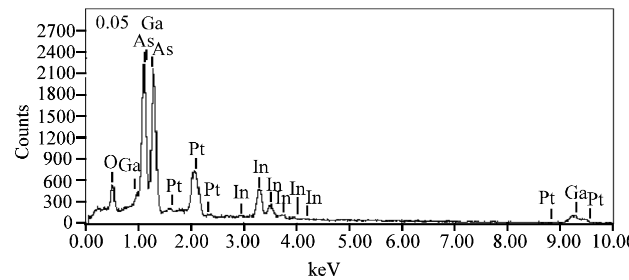




ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.2188

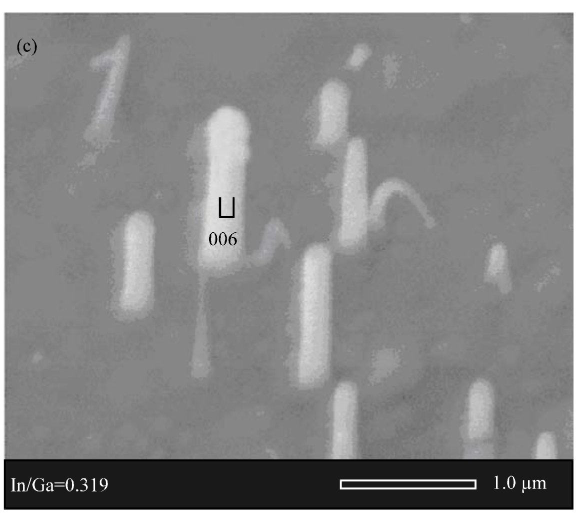
Elem.	(keV)	Mass%	Error%	Atom%	Comp.	Mass%	Cation	K
0K	0.525	8.77	0.10	35.72				7.3587
Ga K	9.241	27.61	1.82	25.79				35.6948
As K	10.530	24.57	4.45	21.36				25.9381
In L	3.285	17.56	0.25	9.96				17.9427
Pt M	2.048	21.49	0.28	7.17				14.9333
Total		100.00		100.00				

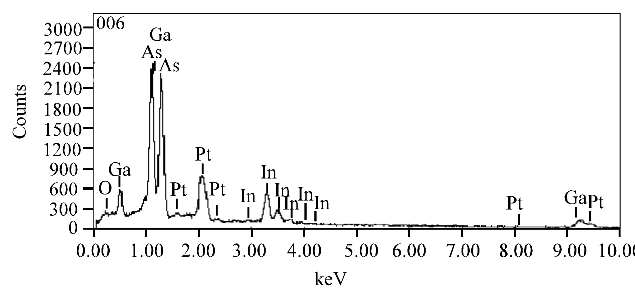




ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.2188

Elem.	(keV)	Mass%	Error%	Atom%	Comp.	Mass%	Cation	K
0K	0.525	5.39	0.09	23.98				4.6159
Ga K	9.241	24.35	1.69	24.86				31.58888
As K	10.530	37.96	4.21	36.07				39.5337
In L	3.285	12.96	0.24	8.03				12.9606
Pt M	2.048	19.33	0.28	7.05				12.6825
Total		100.00		100.00				





ZAF Method Standardless Quantitative Analysis
Fitting Coefficient: 0.2188

Elem.	(keV)	Mass%	Error%	Atom%	Comp.	Mass%	Cation	K
0K	0.525	4.55	0.09	20.54				3.8065
Ga K	9.241	27.07	1.80	28.05				34.3989
As K	10.530	37.76	4.48	36.40				38.5100
In L	3.285	14.21	0.25	8.94				14.0574
Pt M	2.048	16.41	0.30	6.08				10.4604
Total		100.00		100.00				

Fig. 3: EDX measurements of $In_xGa_{1-x}As$ NWs from various detection positions, seeded by 30 nm diameter Au particles and grown for 30 min. At 400°C. Determined In/Ga ratios are also shown

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