Effect of Substrate Orientation on the Growth Direction of $\text{In}_x\text{Ga}_{1-x}\text{As}$ Nanowires (NWs)

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Abstract. We have grown the $\text{In}_x\text{Ga}_{1-x}\text{As}$ NWs on GaAs(111), GaAs(100) and Si(111) substrates via Vapor-Solid-Solid (VSS) mode using MOCVD. We observed that the cylindrical NWs grow perpendicular to the GaAs(111) substrate. The straight line NWs with an angle of 50.60° to the normal were occurred on GaAs(100), while kinks NWs were perceived on Si(111). We found that the growth direction of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ NWs can be easily controlled using certain orientation of the substrate by considering its lattice mismatch and its surface energy.

1. Introduction
Semiconductor NWs have been continuously gaining interest among science, researcher and engineer communities since the late 1990s, pioneered by Wagner and Ellis [1]. The vapor liquid solid VLS is one of the most common model to grow NWs assisted by seed particles [2-5]. In this model vapor donates the phase of precursors, liquid the phase of particles, and solid the phase of NWs. Nevertheless, it has been reported that the particle could also be in a solid state when growth occurs, which is labelling as the vapor solid solid (VSS) model [4-15]. In particular, III-V nanowires can be epitaxially grown by metalorganic chemical vapor deposition (MOCVD) [2, 3]. In the NWs growth process using MOCVD, nanoparticle as a seed promotes NWs growth by either VLS or VSS mechanism [16, 17]. At growth temperature, the seed particles on the semiconductor substrate surface form a liquid (for VLS) or solid (for VSS) alloy with the group III species [2-5, 17]. Once the group III species precipitate out at the seed particle-semiconductor interface, nanowire growth occurs with seed nanoparticle a top each nanowires [1-10, 17]. In this paper, the effect of substrate materials and it’s orientation on the growth direction of gold seed-particles assisted growth of $\text{In}_x\text{Ga}_{1-x}\text{As}$ NWs are deeply investigated.
2. Experiment

The In$_{x}$Ga$_{1-x}$As NWs were grown by Au seed particles-assisted on GaAs(111)B and (100) as well as Si(111) substrates using MOCVD. The system uses low-pressure (0.1 atm) chamber with trimethylindium (TMI), trimethylgallium (TMGa) and arsine (AsH$_3$) as precursors. Palladium-diffused hydrogen (99.9999% pure hydrogen) is used as carrier gas. The TMGa and TMI are held in temperature controlled baths at -3.5 °C and 17 °C, respectively, while arsine is diluted to 10% in hydrogen. The temperature and pressure of the metal-organic precursors are fixed to control the vapor pressure in the bubbler. The substrates were functionalized by immersed it in 0.1 % poly-L-lisine (PLL) solution for 3 minutes. Then, it was cleaned with de-ionized water and subsequently dried with nitrogen (N$_2$). It was then treated with 50 % gold colloid solution for 30 seconds. The negatively charged of Au particles are attracted to the positively charged PLL layer thus are immobilized on the substrate surface [13, 14].

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 a constant partial pressure of AsH$_3$ gas for 10 minutes, and then cooled to desired growth temperature. Once the growth temperature was achieved, TMI, TMGa, and AsH$_3$ were flowed into the chamber and the growth begun. The growth time, growth temperature and V/III ratio were set at 30 minutes, 400 °C and 10, respectively. The growth temperature is below the pseudobinary eutectic point Au-GaAs (630 °C) [15]. Therefore, it can be obviously observed. For that reason, In$_{x}$Ga$_{1-x}$As NWs were grown via VSS rather than VLS mechanism. FESEM images of In$_{x}$Ga$_{1-x}$As NWs grown with different substrate orientation is shown in Figure 1.

Figure 1(a and b) show the In$_{x}$Ga$_{1-x}$As NWs grown on GaAs(111) grow perpendicular to the surface of substrate. The direction of In$_{x}$Ga$_{1-x}$As NWs can be determined using the relationship of crystallography plane and crystallography direction. For the cubic system, if the growth direction is perpendicular to an (h k l) plane then the orientation of the crystal is an [h k l] direction [17, 18]. It means the direction of In$_{x}$Ga$_{1-x}$As NWs grow perpendicular to the GaAs(111) substrate is [111]. Nonetheless, In$_{x}$Ga$_{1-x}$As NWs grown on GaAs (100) substrate did not grow perpendicular to the substrate but grow straight line form an angle of 50.60° to the normal.

By using the relationship of crystallography plane and crystallography direction, the growth direction of In$_{x}$Ga$_{1-x}$As NWs can be also identified i.e. [111]. This angle undergoes deviation of 4.14° from the theoretical reference [21]. On the reference, the angle between crystallographic plane of (100) and crystallographic direction of [111] should be 54.74°. The deviation of this value is likely contributed by the miss cut of GaAs(100) substrate. In addition, it can be obviously observed that the NWs are grown both on GaAs(111) and (100) substrate grow in the same orientation to [111] direction. This indicates that the [111] is the preferential growth direction of NW as its lower surface energy [18, 19]. Consequently, NWs grown on (111) grow perpendicular to the substrate while the NWs grown on GaAs(100) grow to form an angle of 50.60° to the substrate. Nevertheless, once the In$_{x}$Ga$_{1-x}$As NWs grown on Si(111) substrate, NWs did not grow upright as grown on GaAs(111) and it shape is not elongated, although the crystallography plane of Si and GaAs substrates is similar. This phenomena is assumed due to the surface energy differences between GaAs(111) and Si(111) as well as the lattice mismatch differences between In$_{x}$Ga$_{1-x}$As NWs and substrate. In practice, the surface energy of any surface material can be calculated by using Eq.1 as following:
Figure 1. FESEM images of In$_x$Ga$_{1-x}$As NWs grown with different substrate orientation: (a, b). on GaAs (111)B; (c, d). on GaAs (100)B and (e, f). on Si (111).

\[ \gamma = \frac{1}{2} N_b \varepsilon \rho_s \]

where $\gamma$ is the surface energy, $N_b$ is the number of broken bonds, $\varepsilon$ is the bond strength and $\rho_s$ is the surface atomic density i.e. the number of atoms per unit area on the surface [19]. Due to the crystal structure of GaAs is zinc blende and the crystal structure of Si is diamond, both of this material has
similarity on the number of atoms and the crystallography geometry. Therefore the number of broken bonds of this material \((N_p)\) on the \((111)\) plane is assumed equal. Moreover, based on the definition of the surface atomic density, the value of \(\rho_s\) is inversely proportional to the square of the lattice constant \((a)\). Hence to simplify the calculation, the surface energy \((\gamma)\) can be then expressed as function of \((\varepsilon)\) and \((a)\) as follow:

\[
\gamma \approx \frac{\varepsilon}{a^2}
\]  

Based on Eq. 2 it can be seen that the surface energy of material highly dependable on the bond strength and the lattice constant of material. In case of GaAs and Si substrate, the bond strength of GaAs\((111)\) is lower than Si\((111)\) \([20]\), whereas the lattice constant of GaAs \((5.6534 \, \text{Å})\) is higher than Si \((5.4307 \, \text{Å})\). Therefore, the surface energy of Si\((111)\) is higher than GaAs\((111)\), even though the crystallography plane both of those material is identical. Consequently, In\(_{x}\)Ga\(_{1-x}\)As NWs grown on Si\((111)\) substrate did not grow straight as NWs grown on GaAs\((111)\) substrate. Adachi has also reported that the surface energy of GaAs\((111)\) and Si\((111)\) i.e. 1.05 Jm\(^{-2}\) and 1.36 Jm\(^{-2}\), respectively \([20]\). Besides, the difference of lattice mismatch between In\(_{x}\)Ga\(_{1-x}\)As NWs to the substrate is another aspect that considered could contribute on the difficulty level of growth NWs on certain substrate. The range of the lattice constant of ternary alloy In\(_{x}\)Ga\(_{1-x}\)As is from \(5.6534\, \text{Å} \) (GaAs) to \(6.0585\, \text{Å} \) (InAs). It means the lattice constant of Si substrate is out of the range from the lattice constant of In\(_{x}\)Ga\(_{1-x}\)As, while the lattice constant of GaAs substrate still inside this range. As a result, the lattice mismatch In\(_{x}\)Ga\(_{1-x}\)As NWs to the Si substrate is higher than to the GaAs substrate. Therefore, In\(_{x}\)Ga\(_{1-x}\)As NWs are easier grown on GaAs substrate rather than on Si substrate due to its lower surface energy and lattice mismatch. Consequently, In\(_{x}\)Ga\(_{1-x}\)As NWs grow straight on GaAs\((111)\) substrate but grow with kinks morphology on Si\((111)\) substrate. So, the kinds and orientation of substrate are important aspect should be considered in order to epitaxially growth of In\(_{x}\)Ga\(_{1-x}\)As NWs. As well, the growth direction of NWs can be possibly controlled using certain orientation of the substrate by considering its lattice mismatch and surface energy.

4. Conclusion
The investigation of the effect of substrate orientation on the growth direction of In\(_{x}\)Ga\(_{1-x}\)As NWs were conducted. It can be seen that the growth direction of NWs is possible controlled. Cylindrical In\(_{x}\)Ga\(_{1-x}\)As NWs grow perpendicular to the substrate along \([111]\) direction when it is grown on GaAs\((111)\). On GaAs\((100)\), the NW’s orientation is straight line form an angle of 50.60° to the normal on the [111] direction, whereas kinks NWs are observed on Si\((111)\). The growth direction of NWs can be controlled using certain orientation of the substrate by considering its lattice mismatch and surface energy.

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