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Improving the composition uniformity of Au-catalyzed InGaAs nanowires on silicon

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ABSTRACT

Spatial distribution of indium (In) atoms in ternary $In_xGa_{1-x}As$ nanowires (NWs) was investigated by the energy-dispersive X-ray spectroscopy, which were grown on Si (111) by metal-organic chemical vapor deposition. The NWs have a tapered morphology with thicker diameter and higher In composition in the bottom of NWs. However, decreasing growth temperature and V/III ratio resulted in straight NWs with constant In composition throughout the NWs. This was attributed to enhanced deposition on the sidewall of the NW with higher In composition through the vapor–solid mode, leading to a core-shell structure consisting of low and high In-content layers.

1. Introduction

One-dimensional (1-D) nanostructures such as nanorods, nanowires (NWs), and nanobelts have been successfully synthesized using a wide range of semiconductors and demonstrated new design concepts for novel electronic and optoelectronic devices. Especially, hetero-structured 1-D nanostructures, including coaxial core-shell, axially-modulated, and alloyed NWs, have attracted much attention because of their controlled morphologies and multi-functional optoelectronic properties [1–4]. Among them, alloyed semiconductor NWs can offer more unique properties than the corresponding elemental or binary ones by engineering the bandgap energy, which is one of the most important parameters of a semiconductor and determines its electronic and optical properties [5–8]. III–V compound semiconductor NWs based on binary materials (e.g., GaAs, InP, GaN) have been fabricated for optical devices such as solar-cells and light-emitting-diodes [9,10]. For example, the ternary $In_xGa_{1-x}As$ can cover the wavelength range from near- to mid-infrared (0.87–387–3.5 μm) by adjusting indium (In) composition, as demonstrated by the heterojunction solar cells [8] and light-emitting diodes (LEDs) for medical applications [11]. Several recent works had reported the successful growths of high quality III-V semiconductor NWs by using selective-area epitaxy (SAE) in metal-organic chemical vapor deposition (MOCVD) reactor [12–14]. In the SAE-grown NWs, the growths were defined by the openings formed by various lithography methods resulting in highly-order NWs [12–14]. The fabrication of these patterns had been reported by using electron-beam lithography, and other self-assembled lithography methods (i.e. 2-D close-packed monolayer colloidal deposition [15,16], or diblock-copolymer methods [17,18]). Vapor–liquid–solid (VLS) method, which facilitates one-dimensional (1-D) crystallization using metal catalyst, is also well-known method to synthesize semiconductor NWs [19,20]. The ternary NWs grown via VLS method, however, are suffered from large variation of the alloy composition along the NW height [4,21]. For example, the In composition of the ternary $In_xGa_{1-x}As$ NW varies from 0.2 to 0.6 with NW position [4]. Formation of ternary $In_xGa_{1-x}As$ NW as a result of gallium (Ga) diffusion from GaAs substrate have shown relatively uniform alloy composition along the NW height [22]. However, the tunable range of the alloy composition is very limited (i.e., $x=0.81–1$).

In this paper, we have investigated the distribution of In atoms in the ternary $In_xGa_{1-x}As$ NWs grown at different process parameters such as growth temperature and V/III ratio, aiming to minimize the composition variation of the NW. In addition to the VLS, we have found that vapor–solid (VS) growth mechanism played important role for the composition variation along the NW heights. The VS growth mechanism is nearly deactivated with the decrease of growth temperature and V/III ratio, resulting in

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single-crystalline, ternary $In_xGa_{1-x}As$ NWs possessing very uniform alloy composition along the NW height.

2. Experimental methods

Metal-organic chemical vapor deposition (MOCVD, Aixtron inc.) with horizontal reactor has been used for the growth of $In_xGa_{1-x}As$ NWs. For the growth, *p*-type Si (111) wafer were immersed in poly-L-lysine (PLL) solution (Sigma-Aldrich inc.) for 2 min, rinsed in deionized water for 10 s and dried with N_2 gun. Thin PLL layer which is positively charged promotes the uniform distribution of Au nanoparticles (NPs) on Si surface by preventing the agglomeration of negatively charged Au NPs [23]. Afterwards, Au NP colloid (Ted pella inc.) containing Au NPs of 20 nm diameter was dropped on the Si surface and blown by N_2 gun after 30 s. Then, the Si substrate was immediately loaded into the MOCVD chamber and annealed at 620 °C for 10 min in the H_2 ambient to form eutectic alloy at the interface between Au colloids and Si. After that, the reactor temperature was reduced to the growth temperature (i.e., 430–500 °C). Once temperature was stabilized, Trimethylindium [$(CH_3)_3In$, TMIn] and trimethylgallium [$(CH_3)_3Ga$, TMGa] and AsH_3 sources were simultaneously supplied into the reactor. The growth time was fixed to 10 min for the growth of the nanowires in this experiment. The molar flow rate (mol/min) was 1.3×10^{-5}, 2.4×10^{-5} and 4×10^{-4} for TMIn, TMGa, and AsH_3, respectively. The In molar ratio [i.e., TMIn/(TMIn+TMGa)] was 0.36, and the V/III [i.e., AsH_3/(TMIn+TMGa)] was 10. The molar flow rate of AsH_3 increases to 1.1×10^{-3} mol/min to change the V/III ratio to 30. Structural properties of the $In_xGa_{1-x}As$ NWs were examined by scanning electron microscope (SEM, Hitachi inc.) and transmission electron microscope (TEM, FEI inc.). The compositional variation along the NW height was investigated by energy-dispersive X-ray spectroscopy (EDX) equipped in TEM. The error range of alloy composition is less than 10% and the X-ray spot size for EDX was ~0.1 nm. In composition, *x* of the $In_xGa_{1-x}As$ NW was calculated from the atomic ratio of EDX spectra.

3. Results and discussion

Fig. 1(a–c) shows the SEM images of ternary $In_xGa_{1-x}As$ NWs on Si (111) substrate grown at 440, 470, and 500 °C, respectively. One can see that most $In_xGa_{1-x}As$ NWs were vertically grown on the substrate. The number density of the NWs is in the range of $1–5\times10^7/cm^2$ while that of the Au nanoparticles is $2\times10^9/cm^2$. The surface of Si is known to be easily oxidized upon exposure to air. The de-oxidation process performed by a thermal annealing at 620 °C under H_2 ambient was found to be an important step to have dense and vertically aligned $In_xGa_{1-x}As$ NWs on Si substrates. Without thermal annealing process, the number density of the NWs significantly decreases. Insets in Fig. 1 are high-magnification SEM images of the representative NWs. The $In_xGa_{1-x}As$ NWs grown at 440 °C have straight morphology, which is one of typical characteristics of VLS mechanism (i.e., 1-D growth). However, increase of growth temperature causes $In_xGa_{1-x}As$ NWs to taper off towards the tips with a simultaneous decrease of the NW length. The growth rate of the nanowires in height is ~0.46, 0.36, and 0.22 μm/min at the growth temperature of 440, 470, and 500 °C, respectively. The tapering-off of $In_xGa_{1-x}As$ NWs is a result of crystallization of In, Ga, and arsenic (As) species on the sidewall of NWs via so-called vapor–solid (VS) mechanism [24]. Paiano et al. reported that the GaAs NW growth in the axial direction via VLS mechanism is thermally activated with an activation energy of 17 ± 1.0 kcal/mol [25], which is slightly lower than 20.7 ± 3.2 kcal/mol for low-temperature planar growth of GaAs via VS mechanism from TMGa and AsH_3 [26]. In other words, the lateral growth of GaAs via VS mechanism becomes dominant at higher temperature region because of higher activation energy.

Similar tapering-off has been observed in both elemental Si [24,27] and binary NWs (e.g., InAs or GaAs) grown at higher growth temperature [26,28]. In these tapered-off elemental and binary NWs, the composition along the axial direction should be constant irrespectively of different mechanisms for the axial and lateral NW growths. In alloyed ternary/quaternary NWs, however, this tapering phenomenon might have a critical impact on the uniformity of constituent elements of NWs and thus their corresponding bandgap energies. Thus, we characterize atomic distribution of $In_xGa_{1-x}As$ NWs using EDX analysis. The NWs were grown at different temperatures while other growth parameters are fixed (i.e., V/III ratio = 10). $In_xGa_{1-x}As$ NWs are divided into three different areas for EDX measurements (Fig. 2a); base (area 1), center (area 2), and tip (area 3). EDX measurements were performed more than 10 points in each area to get averaged In composition along the NW height. As seen in the Fig. 2(b), the In composition varies from 0.6 to 0.3 along the NW height for the NW grown at 500 °C. Similarly, In composition changes from 0.6 to 0.4 for the NW grown at 470 °C. In contrast, the composition variation is less than ~10% (i.e., from 0.67 to 0.6) for the NW grown at 440 °C. The NW has very uniform diameter along the NW height, indicating that the sidewall growth via VS mode is nearly minimized at the growth temperature of 440 °C. The EDX analysis shows that the composition variation is strongly related to the tapered shape of the NW. Taking into account activation energies needed for the lateral growth of InAs and GaAs, it were reported that the activation for the growth of InAs thin film is approximately 10 kcal/mol, which is much lower than 19.7 kcal/mol for GaAs [29,30]. As a result, more In atoms are incorporated into the sidewall of NWs, leading to higher In composition at the NW shell than in the NW core. It is interesting to note that the In composition of the nanowires is much higher than the molar ratio of the gas phase [i.e., TMIn/(TMIn+TMGa)] during the growth. This can be explained that the pyrolysis efficiency of TMIn is much higher than that of the TMGa in the growth temperature range of 400–500 °C [31].

We also have investigated the effects of the V/III ratio on the change of NW morphologies as shown in Fig. 3. The NWs were

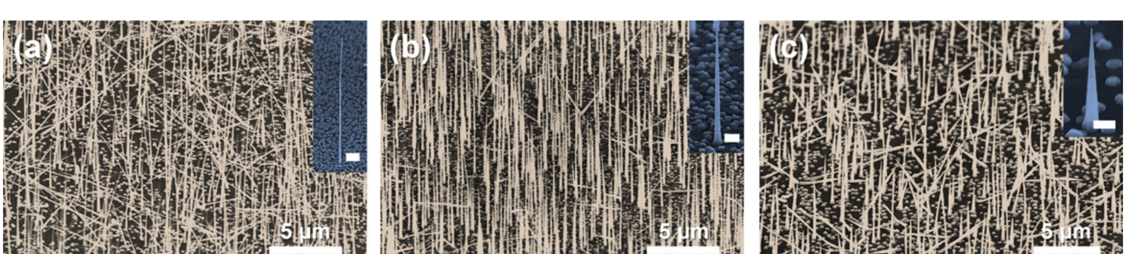

Fig. 1. SEM images of ternary $In_xGa_{1-x}As$ NWs grown at: (a) 440, (b) 470, and (c) 500 °C, respectively. Insets in the figure are the high magnification SEM image of the NWs with 500 nm of scale bar. The NWs are more tapered as the growth temperature increases indicating that more sidewall growth is activated.