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InGaP Nanowires grown by Selective-Area MOVPE

Fumiya Ishizaka[1], Keitaro Ikejiri[1], Katsuhiro Tomioka[1, 2], and Takashi Fukui[1]

[1] Graduate school of Information Science and Technology and Research Center for Integrated Quantum Electronics, Hokkaido University, North 13 West 8, Sapporo 060-8628, Japan
[2] JST-PRESTO, Japan Science and Technology Agency, 4-1-8 Honcho Kawaguchi, Saitama 332-0012, Japan
Phone: +81-11-706-7173, Fax: +81-11-716-6004, E-mail: ishizaka@rciqe.hokudai.ac.jp

1. Introduction

Semiconductor nanowires (NWs) have attracted increasing attention because of their potential to develop ultrahigh-efficiency electronic and photonic devices, such as field-effect transistors, light-emitting diodes, and solar cells. We have reported on the growth of III-V compound semiconductor NWs using catalyst-free selective-area metal organic vapor phase epitaxy (SA-MOVPE). This method has a great advantage in the crystal quality and the controllability of size, shape, and position of NWs, compared to catalyst-assisted vapor-liquid-solid growth. Therefore, selectively grown NWs are free from catalyst contamination and suitable for nanoscale device applications. By using SA-MOVPE of NWs, we have also fabricated light-emitting diodes on Si operated in the near-infrared region [1]. Combined use of these techniques provides the feasibility of visible light-emitting diodes on low-cost and large-area Si substrates. However, there have been little investigation of SA-MOVPE of InGaP NWs which can emit lights in the visible (red) region though much research has been done on another materials, such as InAs [2], InGaAs [3], GaAs [4], and InP [5]. Here, we report on the growth of InGaP NWs on InP(111)A substrates by SA-MOVPE and discuss their structural characterization and composition by using scanning electron microscope (SEM), X-ray diffraction (XRD), and micro-photoluminescence (μ-PL).

2. Experimental

The fabrication process of NWs started by preparing patterned InP(111)A substrates partially covered with a SiO_2 mask for SA-MOVPE. After a 25-nm-thick SiO_2 film was deposited on the InP(111)A by plasma sputtering, hexagonal-opening patterns were defined using electron beam (EB) lithography and wet chemical etching based on buffered hydrofluoric acid (BHF). The SiO_2 patterns were designed to be periodic array of openings with the diameter d_0 from 30 to 200 nm and the pitch a from 0.5 to 5.0 μm. The SA-MOVPE of NWs was carried out in a horizontal low pressure MOVPE system, in which trimethylgallium (TMGa), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) were used as source materials. The partial pressure of TBP, [TBP], was 8.1×10^{-5} atm and the total of the partial pressures of TMGa, [TMGa], and TMIn, [TMIn], was 4.5×10^{-6} atm. TMGa partial pressure ratio, x_{supply} = [TMGa]/([TMGa]+[TMIn]), were changed to 0%, 3.2%, and 6.5%. The growth temperature, growth time, and V/III ratio were 650°C, 20 minutes, and 18, respectively.

XRD measurements were carried out using Cu $K\alpha_1$ radiation (λ = 1.54 Å) with a Ge(400) double crystal monochromator. The μ-PL was measured at 4.2 K. The excitation light from a He-Ne laser with a wavelength of 632.8 nm was focused on the NW arrays using ×50 microscope objectives with 0.42 numerical aperture, which were also used to collect the PL from NWs. The excitation power was 1.0 kW/cm^2 and the laser spot was less than 2 μm in diameter.

3. Results and discussion

Figures 1(a)-(c) show SEM images of SA-MOVPE of InP and InGaP NWs with various x_{supply}. The mask opening d_0 and the pattern pitch a are 100 nm and 1.0 μm, respectively. For x_{supply} = 0% (Fig. 1(a)), uniform hexagonal structures were formed in the mask openings. However, the uniformity and surface flatness of NWs become worse with increasing x_{supply} (Figs. 1(b) and (c)). Moreover, sidewall

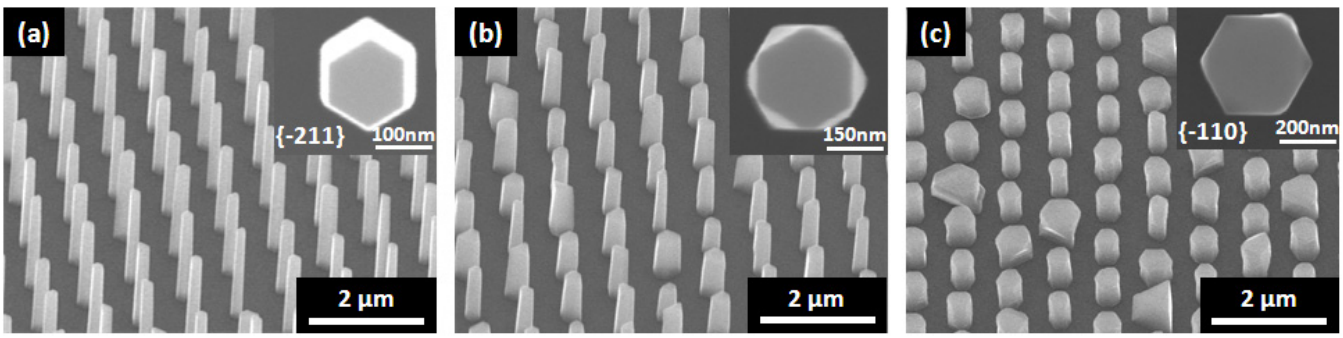

Fig. 1. SEM images of InP and InGaP NWs for x_{supply} = (a)0%, (b)3.2%, and (c)6.5%. Each inset shows a top view of the NW, showing the difference in orientation of hexagonal side facets. The mask opening d_0 and the pattern pitch a are 100 nm and 1.0 μm, respectively.

facets of NWs changed from {-211} to {-110} with increasing x_{supply}, as shown in the insets of Figs. 1(a)-(c). This result implies the possibility of structural transition from wurtzite (WZ) to zinc blende (ZB) [6].

The average heights and diameters of NWs as a function of x_{supply} are shown in Fig. 2. The NW heights decreased and the NW diameters increased as x_{supply}. We consider that this is probably caused by the decrease in effective growth temperature due to the increase in Ga composition (described in the next paragraph). In general SA-MOVPE, low-temperature growth below the optimum temperature contributes to the enhancement of lateral growth and the suppression of axial growth [4].

Figure 3 shows XRD patterns of reference InGaP planar layers on InP(001) substrates, which were grown simultaneously with InGaP NWs for each x_{supply}. From the peak positions of the XRD patterns, the calculated Ga compositions of the planar layers for x_{supply} = 3.2% and 6.5% are 8% and 11%, respectively, assuming the lattice without any relaxation. We think that Ga compositions of InGaP NWs can be slightly higher than those of the planar layers because selective-area growth enhances absorption of Ga atoms due to the lower desorption rate of Ga from the mask surface compared to In [3].

PL spectra of InP and InGaP NWs are plotted in Fig. 4. From the higher peak energies, the estimated Ga compositions of NWs for x_{supply} = 3.2% and 6.5% are 12.2% and 14.3%, respectively, assuming that these NWs are completely ZB and the PL peak energies correspond to the band-to-band emission. The Ga compositions estimated from the PL spectra of the NWs are higher than those from XRD of the planar layers because of the effect of ZB and WZ phase mixing [6].

4. Summary

We fabricated InGaP NWs on InP(111)A substrates using SA-MOVPE and analyzed the dependence of diameter, height, and sidewall facets on the TMGa supply ratios. We also estimated composition ratios of the InGaP NWs from XRD of reference InGaP planar layers and PL spectra of the NWs, indicating ZB and WZ phase mixing in the InGaP NWs.

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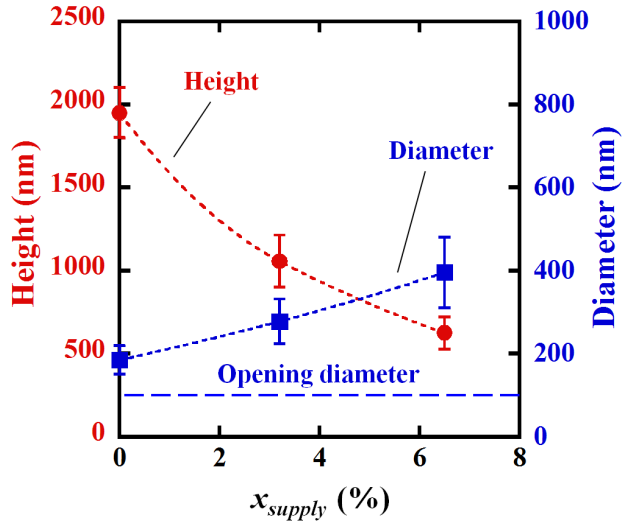

Fig. 2. NW heights and diameters versus TMGa partial pressure ratio. All error bars denote the standard deviations.

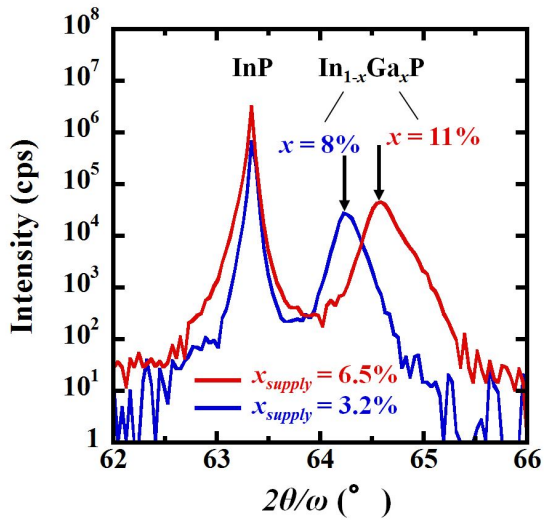

Fig. 3. XRD patterns of reference InGaP planar layers on InP(001) grown simultaneously with InGaP NWs.

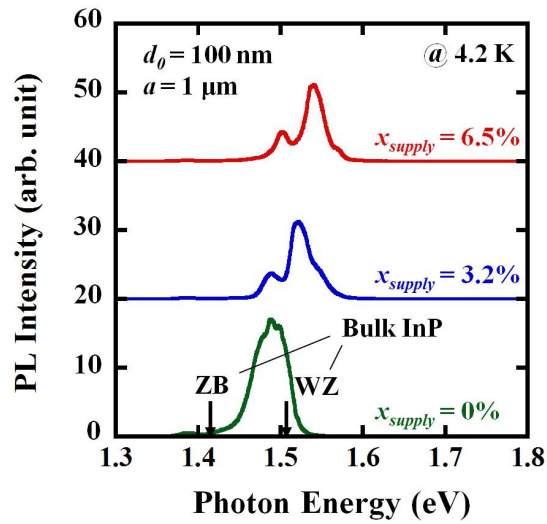

Fig. 4. PL spectra of InP and InGaP NWs. The base of each spectrum is shifted along the vertical direction for clarity.