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Growth and Characterization of Wurtzite InP/AlInP Core-Shell Nanowires

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Abstract

Wurtzite AlInP is predicted to have a direct band gap and is therefore promising for light-emitting device applications. Here, we report on growth and characterization of InP/AlInP core-shell nanowires. The X-ray diffraction measurements showed that the wurtzite AlInP was grown in the radial direction on wurtzite InP core nanowires, while zinc blende in the axial direction.

1. Introduction

Semiconductor nanowires (NWs) have attracted considerable interest in recent years because of their potential applications in electronic and photonic devices. The most surprising feature of nanowires is that they can be grown with a wurtzite (WZ) crystal structure by properly adjusting the growth conditions [1], even though they are stable in the zinc blende (ZB) phase of the bulk crystal. Recently, band-structure calculations for indirect band gap materials such as GaP, AlP, and AlAs predict that when their crystal phases are changed from ZB to WZ, their band gaps also change from indirect to direct [2]. The predictions for GaP and AlGaP have been experimentally proven by using WZ GaP and AlGaP nanowires, showing the possibility of increasing the efficiency of light-emitting diodes (LEDs) [3]. However, there have been few experimental studies on other materials. According to the band structure calculations [2], because WZ AlP and InP have direct band gaps, WZ AlInP ternary alloys are expected to have direct band gaps in the entire compositional range. Therefore, WZ AlInP is promising for the amber-yellow (580–595 nm) LEDs, which would be used for the fourth LED to achieve a high color-rendering index (CRI) [4]. However, structural and optical properties of WZ AlInP have not been investigated until now. Here, we report on growth and characterization of WZ InP/AlInP core-shell nanowires by selective-area metal organic vapor phase epitaxy (SA-MOVPE).

2. Experimetal

As for the process for fabricating the nanowires, a 20-nm-thick SiO_2 film was first deposited on an InP (111)A substrate by plasma sputtering, and hexagonal-opening patterns were defined by electron-beam (EB) lithography and wet chemical etching using buffered hydrofluoric acid (BHF). The SiO_2 patterns were designed to be a periodic array of openings with a diameter of 140 nm and a pitch of 1.0 μm. The SA-MOVPE of nanowires was carried out in a horizontal low-pressure MOVPE system using trimethylaluminum (TMAl), trimethylindium (TMIn), and tertiarybutylphosphine (TBP) as source materials. For WZ InP core growth, the partial pressures of TMIn and TBP were respectively 2.7×10^{-6} and 4.9×10^{-5} atm. The growth temperature and growth time were 660°C and 15 min. For AlInP shell growth, the partial pressures of TMAl, TMIn and TBP were respectively $0–1.5\times10^{-6}$, $0.8–1.5\times10^{-6}$ and 3.1×10^{-4} atm. The partial pressure ratio of TMAl, X_{TMAl} = [TMAl]/([TMAl]+[TMIn]), was changed to 0, 0.33, 0.46, 0.57 or 0.66. The growth temperature and growth time were 600°C and 30 min.

X-ray diffraction (XRD) measurements were carried out using Cu Kα_1 radiation (λ = 1.54059 Å). The investigated sample area was about 4 mm^2, where more than 1 million nanowires were included. Cathode luminescence (CL) measurements were performed at 34K on a single nanowire. The electron beam was spotted on the top and middle of the nanowire.

2. Results and discussion

A total of five samples were grown with different X_{TMAl} values. 30°-tilted SEM images of the grown InP/AlInP core-shell nanowires for X_{TMAl} = 0 and 0.46 are shown in Figs. 1(a) and 1(b). The average height and total diameter of the core-shell nanowires were approximately 2.6 μm and 360 nm, respectively. Since WZ InP nanowires have almost the same diameters as opening diameters under the similar growth condition [1], we estimated that the diameter of InP core was about 140 nm and that the thickness of AlInP shell was about 110 nm. As shown in Figs. 1(a) and 1(b), the shell growth of InP (X_{TMAl} = 0) was homogeneous, but that of AlInP (X_{TMAl} = 0.46) was inhomogeneous. The morphologies of the other samples for X_{TMAl} = 0.33, 0.57, and 0.66 are similar to that for X_{TMAl} = 0.46. Thus, this inhomogene-

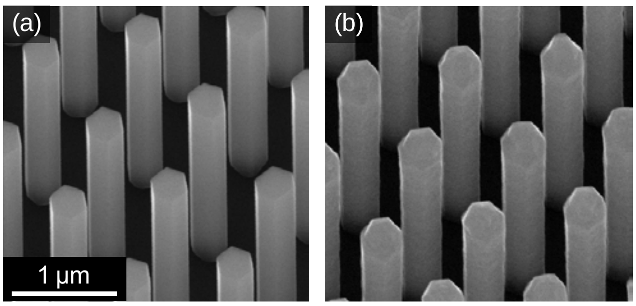

Fig. 1 30°-tilted SEM images of (a) InP/InP (X_{TMAl} = 0) and (b) InP/AlInP (X_{TMAl} = 0.46) core-shell nanowires.

ous shell growth was due to the lattice mismatch of InP core and AlInP shell.

A reciprocal space map (RSM) of InP/AlInP core-shell nanowires for X_{TMAl} = 0.46 around the ZB (331) reflection of the InP (111)A substrate is shown in Fig. 2(a). The strong intensity of the WZ InP (10-15) peak indicates that the InP core has a high crystalline quality of the WZ structure. It can be also seen that there are WZ AlInP (10-15) and ZB AlInP (224) twin peaks. In the case of InP/GaP core-shell nanowires [5], WZ GaP was grown on the side of the InP nanowires, while ZB GaP was grown on the top. Therefore, we think that the AlInP shell on the side has mainly WZ structures and that the AlInP shell on the top has ZB structures, as summarized in Fig. 2(b). Figure 3 shows lattice constants of the WZ InP core and AlInP shell calculated from the maximum peak position of (10-15) reflections. The calculated lattice constants of the InP core agree with the relaxed InP lattice constants regardless of X_{TMAl}. However, at low X_{TMAl}, the calculated lattice constant of the AlInP shell is larger than the relaxed AlInP lattice constants. This result shows the presence of strain between the core and shell at low X_{TMAl}.

To investigate the optical properties of WZ AlInP, we fabricated InP/AlInP core-multishell nanowires with quantum well structures in the AlInP shell. The barrier layer and quantum well layer were grown with X_{TMAl} = 0.57 and 0.33. The thickness of quantum well was estimated from its growth time to be about 4 nm. CL spectra of a single core-multishell nanowire are shown in Fig. 4. The emission peaks at the middle and top of the nanowire appear around 1.8–2.0 eV and 1.8–2.2 eV, respectively. As compared to the reference sample of planar AlInP on the InP (001) substrate, the emission energy at the top was almost the same, while that at the middle was lower. The same tendency was found in other two nanowire samples. The energy difference between the top and middle is probably related to the WZ and ZB structures of AlInP.

4. Conclusions

We fabricated WZ InP/AlInP core-shell nanowires with changing the supply ratio of TMAl. XRD measurements showed that the AlInP shell was grown with a WZ structure at the side, while a ZB structure at the top. The difference of CL emission energies between the WZ and ZB AlInP was observed, which is probably related to the difference of crystal structures. Further structural and optical studies are required to clarify this point.

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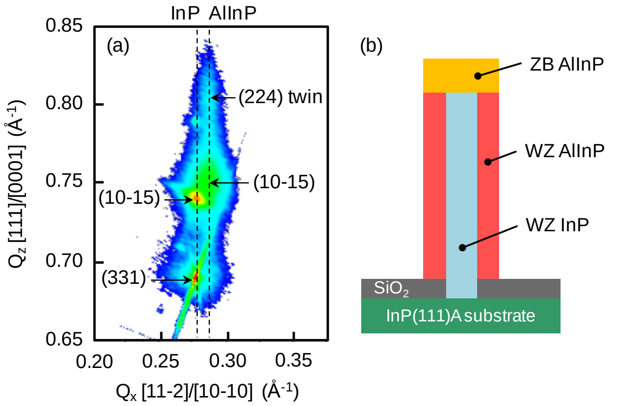

Fig. 2 (a) XRD reciprocal space map of InP/AlInP (X_{TMAl} = 0.46) core-shell nanowires. (b) Schematic view of grown crystal structures.

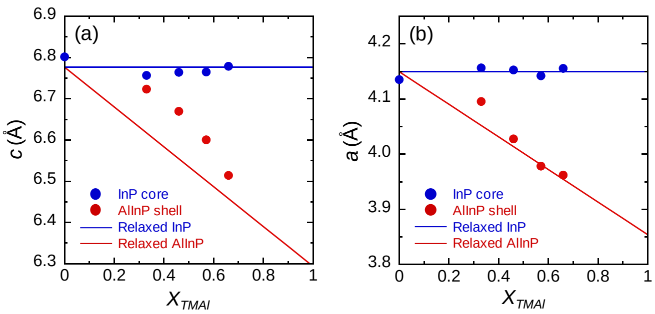

Fig. 3 (a) Axial and (b) radial lattice constants of the WZ InP core and AlInP shell. Blue and red solid lines represent the WZ lattice constants of relaxed InP and AlInP calculated from their ZB lattice constants when they are converted from ZB to ideal WZ.

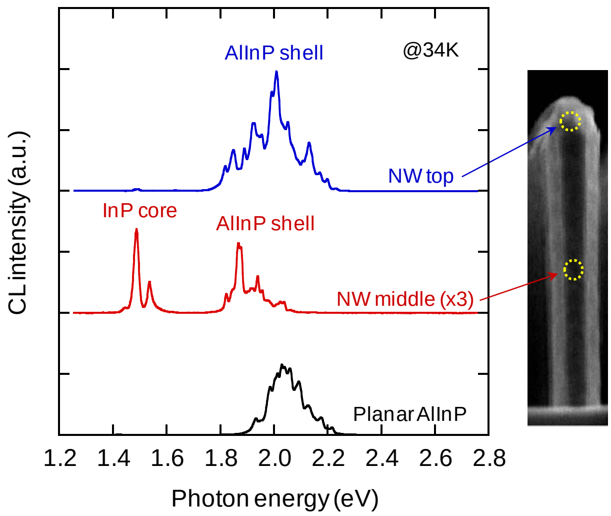

Fig. 4 CL spectra of a single InP/AlInP core-multishell nanowire measured at 34 K. The electron beam was spotted on the top and middle of the nanowire. The planar AlInP was grown on the InP (001) substrate as a reference.