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Photoluminescence from Single Hexagonal Nano-Wire Grown by Selective Area MOVPE

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Abstract We demonstrate formation of nano-wires with GaInAs/GaAs double hetero-structures using selective area metal-organic vapor phase epitaxy (SA-MOVPE) on SiO_2 masked GaAs (111) B substrates with periodic circular openings. Hexagonal nano-wires with six vertical {110} sidewall facets and a lateral size of around 70 to 260 nm are successfully fabricated on the masked GaAs (111) B substrates. Using microscopic area photoluminescence (μ-PL) measurements, PL emission from single GaInAs/GaAs double hetero-structure nano-wires is clearly identified at energy of around 1.28 eV. Full width at half maximum (FWHM) of the PL emission spectra from nano-wires is as narrow as around 10 meV.

1. Introduction

Nano-structures, such as carbon nano-tubes and semiconductor nano-wires, have been intensively investigated because of their enormous potential for new functional electronic and photonic device applications in the next generation. As a new technique to realize ultra small logic circuits [1], lasers [2], photo-detectors [3] and field effect transistors [4], semiconductor nano-wires have been intensively studied in recent years, and nano-wire superlattice (or hetero-) structures have been demonstrated for further electronic and photonic device applications. [5, 6] So far, almost all of the semiconductor nano-wires have been fabricated by vapor-liquid-solid (VLS) growth [7] or chemical vapor deposition (CVD) with metal catalysts, such as gold (Au) particles. However, these growth techniques with metal catalysts substantially have a poor controllability of positioning and size uniformity of nano-wires because it depends on the position and size of metal particles randomly deposited on semiconductor substrates. In previous studies, we have proposed and demonstrated a novel fabrication technique for semiconductor nano-wire arrays by using selective area metal-organic vapor phase epitaxy (SA-MOVPE) on partially masked semiconductor substrates without any small particles of metal catalysts. [8 - 10] SA-MOVPE is very promising epitaxial growth techniques for fabricating not only nano-wires but also other nano-structures, e.g. quantum dots [11], photonic crystals [12, 13] and two-dimensional artificial Kagome lattices [14], because we can expect better controllability for crystal quality, abruptness of hetero-structure interfaces, doping as well as positioning and size uniformity of nano-structures. In this paper, we report on successful fabrication of GaInAs/GaAs double hetero-structure nano-wires with well defined vertical facets by utilizing SA-MOVPE growth. We also show strong photoluminescence emissions from single nano-wire, which indicate good crystal qualities of nano-wires. These characteristics of double hetero-structure nano-wires are quite important for future applications to ultra small nano-wire light emitters and single photon emitters.

2. Experimental Procedures

SA-MOVPE growth was carried out in horizontal low pressure MOVPE systems at a working reactor pressure of 76 Torr. Arsine (AsH_3), tri-methyl-gallium (TMGa) and tri-methyl-indium (TMIn) were used as group V and III source materials. Schematic cartoons of a fabrication process for nano-wire arrays were depicted in Fig. 1(a). SiO_2 masked GaAs substrates with periodic circular openings were formed using electron beam (EB) lithography and wet chemical etching techniques. The shape of the openings of SiO_2 mask pattern is circular because of the resolution limit in EB lithography and wet chemical etching process, although the shape of the designed ones was hexagonal. Diameter of initial circular openings, d_0, was around 100 nm. These circular openings were arranged to form triangular lattice with a lattice constant (period of the holes), a, as defined in Fig. 1(b). We changed a period of the holes, a, from 0.65 to 3 μm. GaInAs/GaAs double hetero-structures were grown on partially SiO_2 masked GaAs (111) B substrates. Planar GaAs (001) and (111) B substrates were also used as a reference at the same growth runs for nano-wire fabrications. Figure 1(c) shows a schematic of layer sequence and estimated layer thickness of GaInAs/GaAs double hetero-structures on planar GaAs (001) surfaces. Indium contents and layer thickness of GaInAs layers on planar GaAs (001) substrates were 2.4 % and 10 nm, respectively. Typical growth temperatures, Tg, for nano-wires were 750 and 600 °C for GaAs and GaInAs layers, respectively. AsH_3 partial pressures during GaAs and GaInAs layer growth were 2.5×10^{-4} and 6.3×10^{-5} atm, respectively. Estimated growth rates of

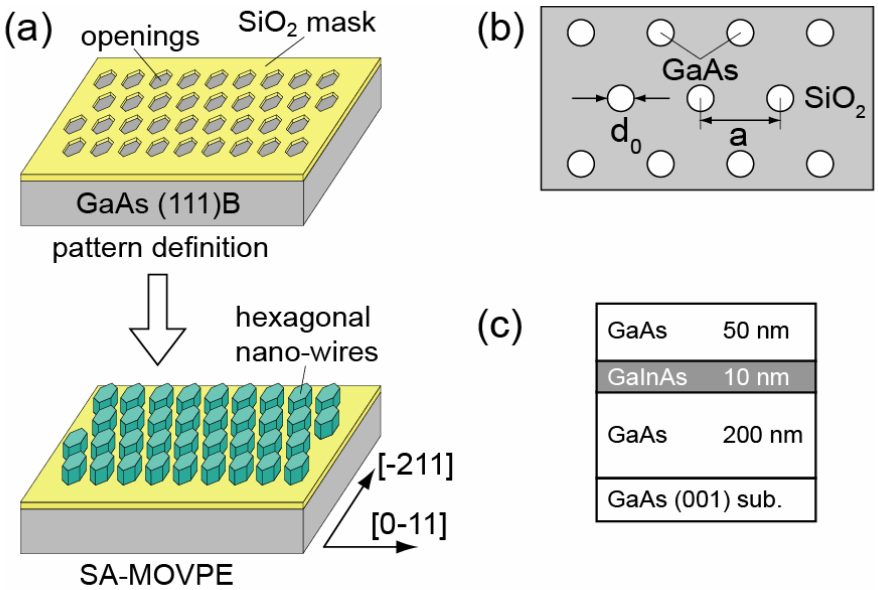

Figure 1. (a) Cartoons of SiO_2 mask pattern and SA-MOVPE on GaAs (111) B substrates. (b) Definition of diameter, d_0, and period, a, of initial openings on SiO_2 masked GaAs substrates. (c) Schematic of layer sequence and nominal layer thickness estimated on planar GaAs (001) substrates.

GaAs layers on reference planar GaAs (111) B surfaces were 0.16 and 0.08 nm/s. Growth rate on masked and reference planar (111) B surfaces strongly depends on growth conditions, e.g. V/III ratios and Tg, because of a well-known surface reconstruction of arsenic trimers on arsenic-terminated GaAs (111) B surfaces.

Scanning electron microscope (SEM) observations and microscopic area photoluminescence (μ-PL) measurements were carried out as structural and optical characterizations, respectively. He-Ne lasers operating at the wavelength of 632.8 nm was used as an excitation light source for μ-PL measurements. Spot size of the focused excitation light was around 2 μm. The experimental set-up for μ-PL measurements was described in detail in Ref. 8.

3. Results and Discussion

Figure 2(a) shows a bird's eye view of SEM images of GaInAs/GaAs nano-wire arrays with a = 0.65 μm. A highly magnified image of a typical nano-wire was also observed, as shown in Fig. 2(b). Hexagonal wires consisting of six vertical {110} sidewall facets were successfully formed. Typical lateral size of the nano-wires was around 200 nm. Some of the nano-wires had larger lateral size and lower height. That is presumably due to inhomogeneous lateral over-growth of GaAs and GaInAs layers grown under relatively low Tg conditions (600 °C) and/or due to diameter size fluctuations of initial circular openings, d_0, caused by unintentional fluctuation of EB lithography conditions. The μ-PL spectra for the nano-wire arrays with a = 0.65 μm show several peaks, which probably come from different size of nano-wires. Figure 2(c) shows dependence of PL emission spectra on excited areas of the nano-wire samples shown in Figs. 2(a) and (b). PL peaks at the energies of around 1.48 eV were attributable to shallow acceptor levels in GaAs layers. Therefore, peak energies below 1.42 eV were originated from GaInAs layers of the nano-wires. PL emission peaks observed at various energies for the nano-wires with a = 0.65 μm were probably caused by different incorporation efficiencies of indium atoms into GaInAs layers in the nano-wires with different size shown in Fig. 2(a).

We also formed GaInAs/GaAs nano-wires with larger period of the initial openings under various growth conditions. Figure 3 shows typical SEM bird's eye view of GaInAs/GaAs nano-wire arrays with a = 3 μm. Typical lateral size of the hexagonal

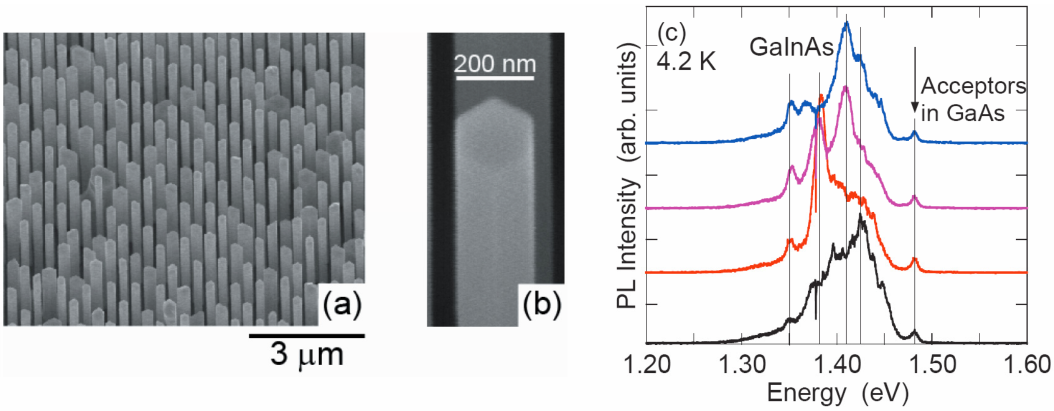

Figure 2. (a) Bird's eye view of SEM images of GaInAs/ GaAs hexagonal nano-wire arrays with a = 0.65 μm, and (b) highly magnified images of a nano-wire. (c) Typical PL spectra from nano-wire arrays. Spot size of a focused excitation light was around 2 μm.

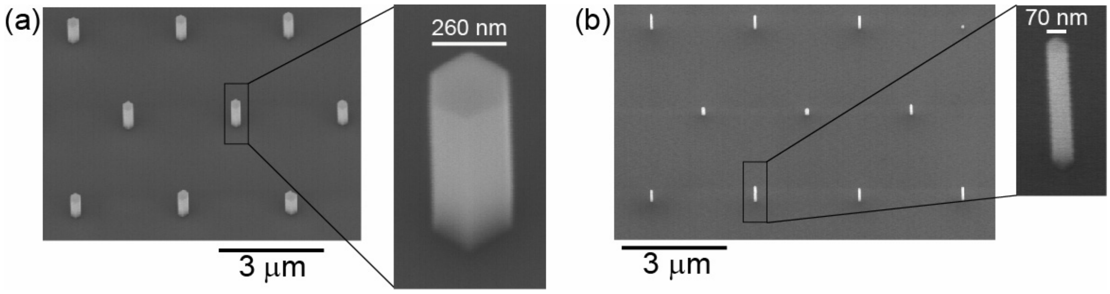

Figure 3. Bird's eye view of typical SEM images of GaInAs/GaAs hexagonal nano-wire arrays with a = 3 μm, and highly magnified images of the nano-wires. Nano-wires were grown under the growth conditions for GaAs layers of (a) V/III = 173 and (b) 86, respectively. Typical lateral size of nano-wires is around (a) 260 nm and (b) 70 nm, respectively.

nano-wires observed in Fig. 3(a) was around 260 nm. In our previous studies [8 - 10], it was revealed that the shape of the wires was independent of initial shape of the openings on partially masked substrates, but depended on growth conditions, such as growth temperatures and V/III ratios (or AsH_3 partial pressures) during SA-MOVPE growth. The lateral size of the wires depends on not only diameter of the initial circular openings, d_0, on partially masked substrates but also the growth conditions. These facts mean that lateral size of the nano-wires can be controlled by changing the growth conditions and/or EB lithography conditions. As shown in Fig. 3(b), much narrower GaInAs/GaAs hexagonal nano-wires with typical lateral size of 70 nm were formed. For the nano-wires shown in Figs. 3(a) and (b), the V/III ratios during SA-MOVPE growth of GaAs nano-wires were 173 and 86, respectively, and those of GaInAs layers were 42 and 21, respectively. In the present growth conditions, lateral growth on six vertical {110} surfaces was supposed to be higher for the nano-wires shown in Fig. 3(a) than for the ones shown in Fig. 3(b). Therefore, nano-wires with much smaller lateral size were formed under lower V/III ratio conditions during SA-MOVPE growth. Here, it should be noted that the deference in the lateral size of nano-wires involved some amount of the deference in diameters of the initial circular openings, d_0, between these two samples because of unintentional fluctuation in EB lithography conditions.

In order to clarify PL emission from single nano-wire, μ-PL measurements were carried out at 4.2 K for the nano-wires shown in Fig. 3(a). Figure 4(a) shows an optical microscope image through objective lens of the μ-PL measurement systems. Solid black circles (b) to (d) in the image represent the areas actually excited by He-Ne lasers in μ-PL measurements. At positions of (b) and (d), nano-wires are observed, while there are no wires at a position of (c). PL spectra obtained for each of the excited areas were shown in Figs. 4(b) to (d), respectively. PL peaks at energies of around 1.48 eV were originated from shallow acceptor levels in GaAs layers, and the ones observed at energies of around 1.52 eV were due to the band edge emissions of GaAs. In Figs. 4(b) and (d), PL emission spectra from GaInAs/GaAs nano-wires were observed at the energies of around 1.28 eV. Full width at half maximum (FWHM) of the spectra was as narrow as around 10 meV. In the case of Fig. 4(c), however, no additional PL emission spectra were detected. These results clearly show that relatively strong PL emission from single GaInAs/GaAs nano-wires can be identified by using μ-PL measurements, and the nano-wires with good crystal qualities were successfully formed by SA-MOVPE growth. From PL peak energies of GaInAs layers at 1.28 eV, incorporation

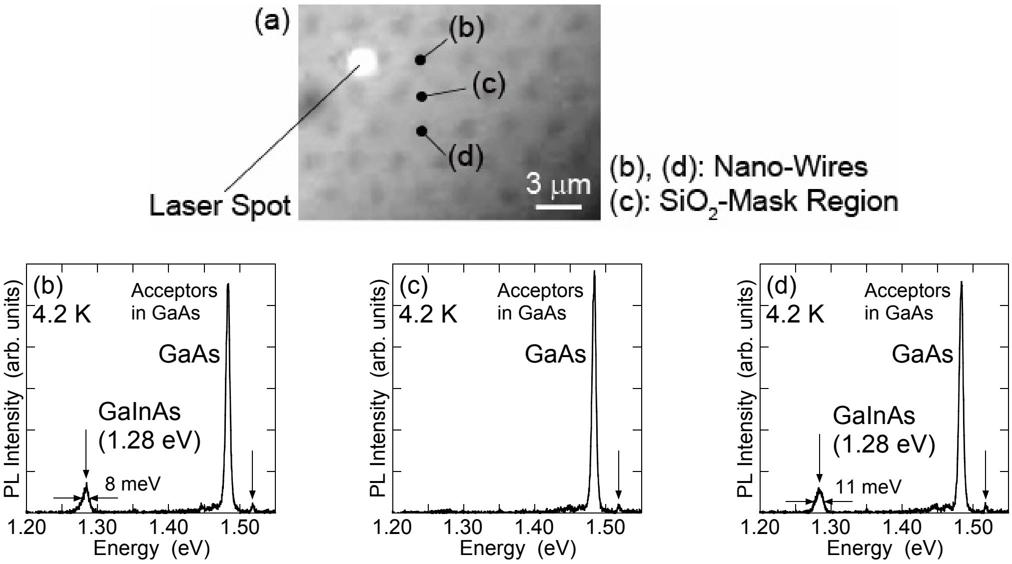

Figure 4. (a) Optical microscope image observed for μ-PL measurement sample of the nano-wires shown in Fig. 3 (a). The bright spot in the image is a focused excitation light (< 2 μm) of He-Ne laser. Solid black circles (b), (c) and (d) in the image represent the areas measured by μ-PL, and PL spectra from each of the measured areas are shown in Figs. 4 (b), (c) and (d), respectively.

of indium atoms seemed to be drastically enhanced in GaInAs layers of the nano-wires. Indium contents in the nano-wires were about 16 %, which were roughly estimated excluding strain effects in the GaInAs layers, although indium contents in the GaInAs layers on the reference planar GaAs (001) surfaces were only 2.4 %. In order to discuss indium contents and layer thickness of GaInAs layers in the nano-wires in detail, further experiments to investigate piezoelectric field effects for GaInAs/GaAs quantum wells on GaAs (111) B surfaces are needed. [15]

For the nano-wires with a lateral size of 70 nm shown in Fig. 3(b), μ-PL measurements have also been carried out at 4.2 K. In area with nano-wires on the samples, PL emissions were observed at the energies of around 1.30 eV as well as PL emissions from GaAs layers. The emissions at the energies of 1.30 eV were probably originated from single GaInAs/GaAs nano-wires with a lateral size of 70 nm. Detailed studies combing structural characterizations and μ-PL measurement techniques are underway to investigate growth condition dependences of nano-wire formation for the samples with GaInAs/GaAs double hetero-structures in order to fabricate ultra small nano-wire light emitters and single photon emitters using SA-MOVPE.

4. Summary

Using SA-MOVPE growth on SiO_2 masked GaAs (111) B substrates with periodic circular openings, we demonstrated formation of hexagonal nano-wires with six vertical {110} sidewall facets and GaInAs/GaAs double hetero-structures. Nano-wires with a lateral size from 70 to 260 nm were successfully fabricated. Using μ-PL measurements, relatively strong PL emissions from single GaInAs/GaAs nano-wires were identified. These results indicated that GaInAs/GaAs nano-wires had good crystal quality, and that SA-MOVPE growth techniques are very promising for realizing ultra small nano-wire devices. To investigate characteristics of single nano-wire in detail, controllability of positioning and density uniformity of nano-wires is a crucial issue to be solved. Therefore, these results here suggest that SA-MOVPE growth techniques combining μ-PL measurements are quite powerful and useful methods to form and characterize nano-wires.

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