Demonstration of InP/InAsP/InP axial heterostructure nanowire array vertical LEDs

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Abstract

Semiconductor nanowires (NWs), which have nanoscale footprints, enable us to realize various quantum structures with excellent position and size controllability, utilizing a wide range of materials for heterostructures. In addition, enhancing light extraction and controlling spontaneous emission by modifying their size and shape are possible. Thus, NWs are promising materials for nanoscale light sources applicable from visible to telecommunication bands. In this study, we grew InP/InAsP/InP axial heterostructure NWs, where the InAsP layer was embedded to serve as an active layer, by selective-area growth and demonstrated vertical NW array light-emitting diodes (LEDs) as a step towards realizing on-demand single photon sources. The NW array LEDs showed rectifying characteristics and electroluminescence originating from the embedded InAsP layer in the near-infrared region.

Keywords: nanowire, light-emitting diode, selective-area growth, metal-organic vapor-phase epitaxy, indium phosphide

(Some figures may appear in colour only in the online journal)

1. Introduction

Semiconductor nanowires (NWs), which have nanoscale footprints, have been used to form various heterostructures with confinement in either the axial or radial direction or both directions. The NW structure can reduce strain energy induced by lattice mismatch in both the radial [1] and axial directions [2, 3], making it possible to utilize a wider range of materials for heterostructures than for their planar counterparts. An NW structure can also enhance light extraction efficiency and control spontaneous emission by optimizing its size and shape [4–9], so NWs are suitable materials for light emitting devices in various wavelength bands. In particular, nanoscale light sources in telecommunication bands are a promising application of NWs for the development of information technology. However, very few studies on light emission in the near-infrared region by current injection have been reported [10–13].

A single photon source is necessary for quantum cryptography communication [14]. One of the promising single photon sources is quantum states of quantum dots (QDs) self-assembled on substrates by the Stranski-Krastanow (S-K) growth mode or droplet epitaxy. Single photon sources using QDs excited by current injection in the near-infrared region [14–17] and telecommunication wavelength bands, such as in the 1.3 μm [18, 19] and 1.55 μm [20] bands, have been reported. Emission in the 1.55 μm band by an entangled single photon from a QD has also been reported [21]. Regarding self-assembled QDs, however, it is difficult to control their positions and number because of the nature of their formation, and previous reports used complex structures such as an aperture electrode to select emission from only one QD [19, 21]. This makes current injection as well as the fabrication process...
inefficient, which might be an obstacle to the application of self-assembled QDs to on-demand single photon emitters.

As an alternative, NW-based light sources are attracting interest as quantum light sources [22]. Among them, NW-QDs consisting of InAsP QDs embedded in InP NWs are the most suitable for light emitters operating in telecommunication wavelength bands because their bandgap can cover the bands by controlling the alloy composition [7, 23–27]. We have reported the growth of site-controlled NWs by selective-area growth and NW-QDs in which QDs are embedded in a single NW [28, 29]. Single photon emission has been confirmed from density and site-controlled InP-based NW-QDs, where an embedded InAsP layer in an InP NW acts as a QD [30, 31], presumably owing to its thickness fluctuation. Emission in the S band from a QD by controlling the As/P composition has also been confirmed [32]. We have also succeeded in fabricating InP vertical NW array light-emitting diodes (LEDs) and demonstrated electroluminescence (EL) in the near-infrared region [33, 34]. In this study, we report InP/InAsP/InP axial heterostructure NWs with axial p-i-n structures as a step towards the application of NW-QDs as single photon sources in telecommunication bands, and fabricated NW array vertical LEDs. EL from the InAsP active layer was clearly confirmed by current injection.

2. Experimental procedure

Figure 1(a) shows a cross-sectional schematic illustration of the InP/InAsP/InP axial heterostructure NW in the present study. An InAsP active layer is embedded in the undoped segment of the InP NW. As we explain later, InP/InAsP/InP heterostructure NWs have a top larger than their bottom. The NWs were grown by selective-area metal-organic vapor-phase epitaxy (SA-MOVPE). The growth was carried out on a p-InP(111) A substrate partially masked with 20-nm-thick SiO$_2$ [35]. The mask pattern of periodic openings was made by electron beam lithography and wet chemical etching. The pitch of the openings $a$ was from 600 to 3000 nm and the openings were defined within 100 µm × 100 µm regions. Trimethylindium (TMIn), tertiarybutylphosphine (TBP), and AsH$_3$ were used as source materials. We first grew Zn-doped and undoped InP for 12 and 2 min, respectively, at 660 °C with a V/III ratio of 16. These growth conditions were expected to yield an InP crystal with a wurtzite (WZ) structure having low twinning without Zn doping [36], but with Zn doping, the formation of a zincblende (ZB) structure was promoted. As a result, the Zn-doped segment of InP NWs was expected to contain rotational twins or a mixture of these crystal structures [37]. The undoped InP was considered to contain unintentional impurities and Zn due to segregation or diffusion, but it is referred to as i-InP hearafter. The partial pressure [TMIn] of TMIn was 4.4 × 10$^{-6}$ atm throughout the growth. After the growth of p-InP and i-InP, the growth temperature was decreased to 580 °C and an InAsP layer was grown for 3 sec with a V/III ratio of 304. The ratio of the AsH$_3$ partial pressure [AsH$_3$] to the total vapor pressure of the V-source materials was set to $p_{As} = [AsH_3]/([AsH_3] + [TBP]) \sim 4 \%$. Then, an i-InP capping layer was grown for 2 min to suppress As/P exchange at the interface. The V/III ratio for the i-InP capping layer was...
36. Finally, a Si-doped n-InP layer was grown for 12 min after the growth conditions were set to those for the initial \( p \)-InP and \( i \)-InP growth. We used diethylzinc (DEZn) and silane (SiH\(_4\)) as \( p \)-type and \( n \)-type dopants, respectively. The doping densities were estimated to be \( 1.4 \times 10^{18} \) and \( 1.1 \times 10^{19} \) cm\(^{-3} \) from the result of \( p \)- and \( n \)-InP planar growth, respectively.

After the NW growth, NW vertical LEDs (NW-LEDs) were fabricated following our previous report \([33]\), as shown in figure 2. The NW array was buried with benzocyclobutene (BCB) as an electrical separation layer with spin coating (figure 2(a)). After burying the NW array, BCB was etched by reactive ion etching (RIE) to expose the top part of the NWs (figure 2(b)). Indium tin oxide (ITO) was sputtered to a thickness of 100 nm on the surface of the substrate as a transparent surface electrode. The electrodes were patterned by photolithography and wet chemical etching to isolate individual NW arrays. Finally, 100-nm-thick AuZn (Zn:5%) was evaporated on the back side of the substrate and annealed for 3 min at 420 °C in N\(_2\) gas (figure 2(c)). The two-terminal current density-voltage (\( J-V \)) characteristics were measured with standard source measurement units. EL from the LEDs was focused on an optical fiber and the collected light was dispersed by a spectrometer equipped with a cooled InGaAs array photodetector. Current density-light output (\( J-L \)) characteristics were obtained by integrating EL spectra in designated spectral ranges under a fixed bias.

3. Results and discussion

3.1. Selective-area growth of InP/InAsP/InP axial heterostructure NWs

Figure 1(b) shows a scanning electron microscopy (SEM) image of grown NWs. The average height of the NWs, \( h \), was about 1.5 \( \mu \)m. The diameter of the n-InP segment of the NWs was larger than that of the bottom segments. The average top diameters of the top and bottom of the NWs were 230 and 180 nm, respectively. NWs with this shape have already been observed in undoped InP/InAsP/InP axial heterostructure NWs \([30, 32]\), but not in Zn-doped InP NWs. Thus, the change and nonuniformity originated from the InAsP layer. This is considered to be due to the different preferential growth directions of NWs; InP NWs tend to grow in the \( <111> \) A direction, but InAs NWs tend to grow in the \( <111> \) B direction \([38]\), and the top shape of the NWs was roughened by the insertion of the InAsP layer. The detailed mechanism of the change in NW shape is under investigation.
Figure 3. (a) J-V characteristics of an NW-LED. The inset shows the illustration of NW-LED structure and the direction of the bias voltage. (b) Optical microscopy image of NW-LEDs isolated in each NW array (left side) and emission image under a vidicon camera at a forward bias of 1.5 V (right side). The area encompassed by the broken line is covered by ITO. (c) EL characteristics of NW-LEDs at room temperature. The bias voltage was changed from 1.0 to 1.5 V in 0.1 V steps. The current density $J$ for each spectrum is shown in the legend. (d) Results of fitting EL spectrum for bias voltage of 1.5 V (dotted line) with six Gaussian curves. Red and blue solid lines are the individual components of the fitting result shown by the dotted line. Red curves are assigned as emission from InAsP and blue curves are assigned as emission from the InP layer. (e) Integrated EL intensity $L$ of an NW-LED as a function of current density $J$. Black squares, red triangles, and blue circles indicate the integrated intensity of the total EL, the EL from InAsP, and the EL from InP, respectively.

3.2. Electrical characteristics of NW-LEDs

Figure 3(a) shows J-V characteristics of a fabricated NW-LED. We converted the measured current $I$ into the current density $J$ using the area of the NW array region ($100 \, \mu m \times 100 \, \mu m$). Rectifying characteristics with some leakage were confirmed. The reason for the leakage is not clear at present. The turn-on voltage $V_{on}$ was 1.24 V, the ideality factor of the diode, $n$, was calculated to be 2.97, and the series resistance $R_s$ was estimated to be 0.031 $\Omega \, cm^2$. $R_s$ was of a similar order of magnitude to the value reported in a previous report [39]. The ideality factor of a pn-junction is typically in the range from 1 to 2 but is larger if the tunneling current becomes dominant [34]. Therefore, similarly to that observed in our previous study on homojunction InP NW-LEDs, the conduction in the present heterostructure NW-LEDs is also considered to be dominated by tunneling.

3.3. EL spectra of NW-LEDs

The microscopy image of fabricated NW-LEDs is shown on the left side of figure 3(b). Light emission from the NW array LED at forward bias was confirmed by vidicon camera observation as shown on the right side of figure 3(b). The surface electrode is located inside the broken line in figure 3(b) and one can see that the area with the NW array emitted light. Figure 3(c) shows EL spectra of NW-LEDs under different current injection levels. Broad emission from 1.0 to 1.5 eV consisting of several peaks was observed. From the peak deconvolution
of the EL with Gaussian lineshapes, it was found that these peaks were located at around 1.44, 1.36, 1.31, 1.19, 1.08, and 1.02 eV, as shown in figure 3(d). The peaks at 1.31, 1.36, and 1.44 eV were considered to originate from InP for the following reasons. InP NWs form two types of crystal structures, namely, ZB and WZ, according to the growth conditions and impurity doping [40], and have different band gaps. The EL at 1.36 eV was close to the band gap energy of ZB InP (1.353 eV) and was thus assigned to the peak from ZB InP. The peak at 1.44 eV is about 80 meV higher than that of ZB InP, which is consistent with the predicted difference in the band gap energy of WZ and ZB InP NWs [41]. Furthermore, we have reported room-temperature EL with two peaks from homojunction InP NW-LEDs [33, 34, 42] in a similar energy range. The positions of the peaks are not identical in these reports and the present study, and show variation among the samples. This might be due to the mixing of the two crystal structures and to the formation of a type-II band structure, in which the band edge energy of the conduction (valence) band is lower (higher) in the ZB (WZ) segments. In this case, it is possible to produce emission corresponding to the energy gap between the conduction band edge of ZB-InP and the valence band edge of WZ-InP. It is also likely that indirect transition between the band edge states and the confined energy states occurs. These results in emission with energy between the ZB and WZ band gaps or slightly below the band gap of ZB [43]. Therefore, the EL at 1.31 eV is also considered to originate from InP.

On the other hand, the EL peaks at much lower energies (1.19, 1.08, and 1.02 eV) have not yet been observed from InP NW-LEDs. In particular, the peak at 1.19 eV dominates the spectrum under each injection condition. Thus, these EL peaks are considered to be emissions from the InAsP layer. On the basis of the growth rate of InAsP NWs on InP, the thickness of the InAsP layer was estimated to be about 8 nm: thus, the formation of an InAsP quantum well (QW) was expected. For InAsP/InP QWs with a well width of 8 nm, the As composition of the InAsP well was 22 %. Furthermore, assuming that the EL at 1.08 eV corresponds to emission originating from the InAsP layer, it is possible to produce emission corresponding to the energy gap between the conduction band edge of ZB-InP and the valence band edge of WZ-InP. It is also likely that indirect transition between the band edge states and the confined energy states occurs. These results in emission with energy between the ZB and WZ band gaps or slightly below the band gap of ZB [43]. Therefore, the EL at 1.31 eV is also considered to originate from InP.

Figure 4. Pitch dependence of the EL spectrum of NW-LEDs biased at 1.5 V.
from the band edge energy of InAs$_x$P$_{1-y}$, $y$ is calculated to be 22 %. Although these rough estimates ignore the strain effect, the results indicate that the solid-phase composition $y$ of As in InAsP was much larger than the partial pressure ratio $p_{As}$ in the vapor phase. This means that the distribution coefficient [44] of As is larger than that of P. A smaller distribution coefficient of P than of As was reported in References [44–46], but this was attributed to the low thermal decomposition efficiency of PH$_3$, and TBP is known to have a much higher decomposition efficiency than PH$_3$. The reason for the smaller distribution coefficient in the present study is not understood yet, but the higher desorption rate of P than of As is a possible reason for the difference. The origin of the EL at 1.02 eV is not clear, but it is possible to form the donor-acceptor level by the segregation or diffusion of unintentional impurities and Zn.

3.4. Properties of EL intensity

Figure 3(e) shows the J-L characteristics of an NW-LED. The total integrated EL intensity saturates with increasing injection current. To clarify the origin of the saturation, the spectrum at each injection current was separated into the emissions from InP and InAsP by fitting with Gaussian lineshapes, as described in the previous section. The results are shown in figure 3(d). The EL intensity from the InP NW increased linearly with the current density $J$, while that from InAsP showed a sublinear increase and saturation with increasing $J$. NW-LEDs operating at a high current density tend to show a decrease in internal quantum efficiency caused by carrier overflow because of band filling or by inefficient carrier injection into the active region [47]. In the present sample, the small volume of the active InAsP layer was considered to be the main reason for band filling and inefficient carrier injection, resulting in efficiency droop. Moreover, the existence of emission from the InP layer also indicates inefficient carrier injection into the InAsP layer. One of the reasons for this might have been the formation of a p-i-n junction without InAsP insertion, for instance, at the sidewall of InP NWs. Clarifying and eliminating the origin of inefficient injection are required for efficient single photon sources with high quantum efficiency and are left for future study.

3.5. Pitch dependence of EL spectrum

Figure 4 shows the EL spectra of LED arrays with different NW pitch $a$. The pitch dependence showed that the dominant EL peak, originating from InAsP, red-shifted with increasing the pitch. This indicates that the As composition $y$ in InAs$_x$P$_{1-y}$ or the well width of the InAsP QW increases with $a$. In the former case, the As composition $y$ in the solid phase was estimated to increase from about 20%–23 % when $a$ increased from 600 to 3000 nm from assuming a well width of 8 nm and the composition dependent band gap energy reported in References [48, 49]. This estimation also ignores the strain effect, but an increase in As incorporation by about 4% would account for the difference. The difference is considered to have originated from the local concentration difference of the group V material sources and the higher incorporation probability of As than of P in InAsP. On the other hand, the latter indicates a higher growth rate for a larger $a$. Such dependence of the growth rate on the NW pitch has not been reported for InAsP but has been reported for InP at a lower growth temperature [36].

One of the requirements for a single photon emitter is to separate emissions from individual NW-QDs, and the control of the pitch or density of the NW array is necessary for this purpose. Thus, the above results show the necessity of taking into account the shift of the emission wavelength originating from the pitch of the NWs towards realizing single photon emission in the telecommunication bands. Further investigation is required to clarify the origin of the peak shift.

4. Conclusion

InP nanowires with a p-i-n structure and an InAsP active layer were grown by selective-area growth, and vertical nanowire LEDs were fabricated using the grown nanowire arrays. Electrical characterization confirmed the rectifying characteristics of the p-i-n junction, and electroluminescence was demonstrated at room temperature. Spectral analysis revealed that the dominant emission was in the near-infrared region and that it originated from the InAsP layer.

Towards realizing on-demand single photon emitters operating in the telecommunication bands, we previously reported single photon emission from a quantum dot in nanowires [30, 31], emission from quantum dots in a telecommunication band [32], and electrical injection and emission in homostructure nanowires [33, 34]. We consider these achievements to be important for quantum-dot-based single photon emitters, and their combination is expected to lead to the demonstration of our target devices. This work is an extension of these studies and focuses on electrical injection into nanowires with heterostructures. Although a more efficient carrier injection into InAsP and the control of the emission wavelength are required, the present study is an important step towards realizing nanowire quantum-dot-based single photon emitters operating in telecommunication bands.

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