Optical properties of InP nanowires on Si substrates with varied synthesis parameters

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We report the effect of the precursor V/III ratio on the shape and optical properties of InP nanowires (NWs) grown on Si substrates by metal-organic chemical vapor deposition. A strong dependence on the group V to III precursor ratio is observed on the NW shape and, consequently, its photoluminescence (PL). Narrow, uniform-diameter NWs are achieved with an optimized V/III ratio. The uniform NWs exhibit PL widths as low as 1.4 meV. Their peak wavelength does not vary much with excitation, which is important for NW lasers on Si. These characteristics are attributed to the one-dimensional density of states in uniform-diameter NWs. © 2008 American Institute of Physics. [DOI: 10.1063/1.2832643]

The integration of III-V compound materials with Si has been an important research area for monolithic integration of semiconductor diode lasers and Si-based electronic circuits. However, past attempts have not been successful because of poor laser reliability due to high defect densities resulting from a large lattice mismatch and process incompatibility with complementary metal-oxide semiconductor integrated circuits due to high temperatures required for epitaxial synthesis. III-V compound nanowires (NWs) grown on Si substrates have recently drawn much attention because they provide a means of circumventing these difficulties for integration. Recently, we showed dislocation-free III-V NWs with excellent optical properties grown at substantially lower temperatures (430–470 °C) using a metal-organic chemical vapor deposition (MOCVD) system. In this paper, we report the effect of the precursor V/III ratio on the shape and optical properties of InP NWs grown on (111) Si substrates. We show that the V/III ratio can be used to tailor the NW shape and optical properties. In particular, we report the growth of NWs with uniform diameters along the axial direction with a record narrow photoluminescence (PL) peak of 1.4 meV and a large blueshift of 178 meV due to quantization. These uniform NWs also have less power dependence for their PL emission peak wavelength. This wavelength stability is important for critical applications such as NW lasers. The PL intensity can also be maximized when using high V/III ratios.

Five InP NW on (111) Si samples were grown with V/III ratios equal to 15, 30, 67, 180, and 240. The Si substrates were first cleaned and then chemically deoxidized with buffered oxide etch followed by Au nanoparticle (NP) dispensing. Colloidal Au NPs with an average of 20 nm diameter were used as the catalysts for vapor-liquid-solid (VLS) NW growth. The growth procedure was the same as Ref. 7 using a MOCVD system. The group V and III precursors were tertiarybutylphosphine (TBP) and trimethylindium (TMIn), respectively. The TMIn mole fraction was held at 1.9 × 10^{-3} in a 12 l/min hydrogen carrier gas flow for all the growths. The TBP mole fraction was varied to attain the five V/III ratios: 15, 30, 67, 180, and 240 (samples A, B, C, D, and E, respectively). The V/III ratios we quote above are the supplied gas-phase mole ratios which are the input experimental parameters for the NW syntheses in this work. The growth time was 3 min for all the samples and the growth pressure was 76 Torr. The NW shape was characterized by field-emission scanning electron microscopy (FE-SEM). Optical properties were characterized by microphotoluminescence (μ-PL) measurements at both room temperature (RT) and at 4 K.

Figure 1 shows the FE-SEM images of the five InP NW/(111) Si samples. With increasing V/III ratio, a significant NW shape change was observed. With a low V/III = 15, NWs did not grow due to insufficient phosphorus [Fig. 1(a)]. Many indium-rich balls, whose composition was determined by SEM energy dispersive spectroscopy, were observed. The improvement for NW formation is seen for sample B with V/III = 30 [Fig. 1(b)]. NWs on sample C, with V/III = 67, have uniform diameters along the entire NW lengths [Fig. 1(c)]. Further increasing the V/III ratio resulted in tapered NWs with wider bases and narrow tips, shown in Figs. 1(d) and 1(e), with V/III ratios equal to 180 and 240, respectively. The tapering is attributed to an increase in the thin-film deposition rate on NW sidewalls compared to that of the vertical VLS growth. The dependence of thin film growth rate on V/III ratio has been previously reported for GaAs material in conventional thin film growth. Here, we observed the sidewall thin-film growth mechanism for InP NW growth, which has a similar V/III ratio dependence, as that shown in Ref. 13. The two tapered NW samples, D and E, appear to have slightly thinner tips than sample C. This might be due to the increased Au-catalyst diffusion into the NWs during the growth for the higher V/III ratio conditions. This phenomenon served as a secondary effect to make the NWs more tapered. Between the straight NW sample C (V/III = 67) and the tapered NW sample D (V/III = 180), two more V/III ratios, 90 and 120, were tested. While the V/III = 90 NW sample still looks straight, the V/III = 120 sample begins to show some taperness. The onset of NW tapering is then deduced as between V/III = 90 and 120.
PL characterization was performed on all samples at 4 K and RT (300 K) using a diode-pumped solid state laser at 532 nm focused to a ~2 μm spot. Figure 2 shows the 4 K μ-PL spectrum comparison for the five samples in Fig. 1. The emission wavelengths of samples A and B are expected to be very close to the bulk InP bandgap since there are very few NWs on both samples but only some larger InP blobs, which might contribute to this PL emission. The PL peak of sample C with uniform NWs shows a blueshift of 40 meV from the bulk InP bandgap due to quantum confinement.7 Single-wire peaks from the narrowest NWs are visible on the high-energy side of the ensemble spectrum. For example, a peak with a 178 meV blueshift and linewidth of 1.4 meV was observed (see inset of Fig. 2), which is the narrowest linewidth reported for a III-V NW.15 Sample D has a similar PL blueshift as sample C. However, the spiky features at the high-energy side are not observed for sample D. This can be explained by the following. At low temperature, the carrier diffusion length is longer.16 Hence, carriers originally generated at the tips of the very narrow NWs can diffuse to the wider parts of the NWs where they see less quantum confinement (smaller photon energy) and recombine there. For sample E, the carrier diffusion phenomenon is more pronounced for the strongly tapered NWs. As a consequence, for sample E, not only have the spiky features disappeared, the PL peak shifts significantly to the redder side of sample C, at 20 meV blueshift of the InP bulk bandgap.

The RT μ-PL spectra (Fig. 3) show significant differences with those at 4 K. First of all, the fine features are no longer visible for sample C. Second, sample E has the same PL peak energy and linewidth as samples C and D, instead of being 20 meV redder at 4 K. This is particularly interesting since the NW base is wider than 100 nm and emission at the bulk bandgap is expected. We attribute this observation to luminescence from the narrow NW tips, where at RT confined carriers recombine radiatively before being able to diffuse to the wider base region. Third, samples A to D all show an extra 60 meV blueshift from the bulk InP bandgap compared to the amount of blueshift at 4 K (see Fig. 2). The origin of this extra 60 meV blueshift is under further investigation.

The PL intensity for both 4 K (Fig. 2) and RT (Fig. 3) measurements increases with V/III ratio. A similar trend is observed for InP epilayers,17,18 where it has been shown that high V/III ratios result in epilayers with lower defect densities.18,19

Figure 4(a) shows the peak energy position as a function of the excitation power at 4 K. When the excitation power is swept from 600 nW to 1.6 mW, over a three-decade power increase, the straight (V/III=67) and most tapered NWs...
mized to 67, nontapered InP NWs were grown. These NWs show a record narrow PL peak and weak excitation-power dependence, resembling features of ideal one dimensional structures. In our experiments, non-tapered InP NWs could be synthesized for V/III ratios ranging from 60 to 90, hence, offering a reasonable growth window. We also showed that the PL peak intensity could be increased with the increase of V/III ratio.

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