Core-shell InGaAs/GaAs quantum well nanoneedles grown on silicon with silicon-transparent emission

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Abstract: In$_x$Ga$_{1-x}$As wurtzite nanoneedles are grown without catalysts on silicon substrates with $x$ ranging from zero to 0.15 using low-temperature metalorganic chemical vapor deposition. The nanoneedles assume a 6˚-9˚ tapered shape, have sharp 2~5 nm tips, are 4 $\mu$m in length and 600 nm wide at the base. The micro-photoluminescence peaks exhibit redshifts corresponding to their increased indium incorporation. Core-shell InGaAs/GaAs layered quantum well structures are grown which exhibit quantum confinement of carriers, and emission below the silicon bandgap.

OCIS codes: (250.5230) Photoluminescence; (250.5590) Quantum-well, -wire and -dot devices

1. Introduction

Integration of III-V optoelectronic materials with Si CMOS processing is an important area of research for realizing active optoelectronic devices integrated with Si electronics, particularly those that operate at silicon-transparent wavelengths. Devices such as lasers, LEDs and photodetectors require low defect densities and the ability to grow heterostructures. Vapor-liquid-solid grown nanowires have proved promising for this application, but their size is limited to critical diameters by their lattice-mismatch with the substrate and crystal phase transitions [1,2].
Recently we reported a new growth technique yielding ultra-sharp, catalyst-free GaAs/AlGaAs nanoneedles (NNs) with sharp taper angles of 6°-9° and tips less than a few nm wide, which can be grown up to 4 μm long and 0.6 μm wide at the base [3]. The NNs are grown via metal-organic chemical vapor deposition (MOCVD) on both GaAs and Si substrates at low temperatures of 380~420 °C. The NNs are single-crystal wurtzite, free of twinning defects, and are not constrained by lattice-mismatch critical diameters, contrary to nanowire vapor-liquid-solid growth. They also can be large enough to facilitate device fabrication using top-down, standard processing techniques. This was the first observation of such large samples of wurtzite GaAs outside of high-pressure experiments. The single needles exhibited bright room-temperature photoluminescence. These ultrasharp NN tips may also be of interest due to the effect of electric field enhancement at sharp tips [4–6]. This effect is useful for applications such as tip-enhanced Raman spectroscopy [7], second harmonic and THz generation [8], or for field emission devices.

Here, we report the growth of pure InGaAs NNs with indium composition up to 15%, and InGaAs/GaAs quantum well (QW) heterostructures grown on GaAs NNs on silicon substrates. The NNs retain their sharp tips, narrow tapers and are single-crystal wurtzite. These QW structures exhibit 8 x brighter photoluminescence (PL) than our typical GaAs NNs, indicating quantum confinement of carriers. The QW NNs can be tuned for emission even below the silicon band edge by increasing the indium composition further. The ability to grow these III-V heterostructures on silicon with bandgaps below the silicon band edge paves the way for bandgap tunability of integrated optoelectronic devices for applications such as lasers, detectors, and other devices, which allow for use of silicon waveguides.

2. Growth

The InGaAs NNs were grown via MOCVD at 76 torr and 400-420 °C on Si substrates for 60 min, resulting in ~4 μm long NNs with ~600 nm wide bases. The metal-organic precursors were trimethylindium (TMIn), triethylgallium, and tertiarybutylarsine. The growth conditions were the same as in our previous report of GaAs NN growths [3] except for the addition of the TMIn flow. The growth is initiated via mechanical roughening of the substrate surface, without the need for metal catalyst particles, contrary to nanowire growth.

Three different growths were conducted, with their scanning electron microscope (SEM) images shown in Fig. 1. The first NN shown in Fig. 1(a) had a TMIn flow rate of zero. The second growth, shown in Fig. 1(b), had a TMIn flow rate which resulted in InGaAs material with a nominal 5% indium incorporation. The third growth in Fig. 1(c) had further increased TMIn flow, resulting in a nominal 15% indium incorporation. The indium incorporation was estimated based on photoluminescence experiments via the following method. The wurtzite GaAs NNs have photoluminescence peaks at 1.509 eV, which is lower than the typical zincblende 1.519 eV by 0.7%. In Eq. (1), we utilize the quadratic bandgap vs. indium composition equation from Ref. [9], with the 0.7% reduction factor to determine the indium composition vs. bandgap for the NNs.

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0.993 \times [0.419 + 7(1-x) + 4(1-x)^2] \text{ (eV)} = E_g (\text{In}_x\text{Ga}_{1-x}\text{As}).
\] (1)

As the indium incorporation increases, the NNs become shorter with a curved taper, and take on a more rounded cross-section rather than the hexagonal shape of the pure GaAs NN. Figures 1(d)-1(f) show the top-down views of the 0%, 5% and 15% indium NNs, respectively.
Fig. 1. (a)-(c): SEM images of In$_x$Ga$_{1-x}$As NNs with indium concentrations of $x = 0$, 0.05 and 0.15. The images are tilted 30° from the normal view. The pure GaAs NN was grown on a 4° off-cut (111)Si wafer. The scale bar (middle) is 500 nm and applies to all the SEM images. (d)-(f): top-down views of the $x = 0$, 0.05 and 0.15 In$_x$Ga$_{1-x}$As NNs, respectively. The GaAs NN has a hexagonal cross section, which becomes more rounded for higher indium concentrations.

3. Micro-Photoluminescence Characterization

The optical properties of single InGaAs NNs from these growths were characterized using micro-photoluminescence ($\mu$-PL) with a 532 nm laser focused to a 2 $\mu$m diameter spot with the sample at a temperature of 4 K. The results are shown in Fig. 2. Quantum confinement effects from the tip are not expected to contribute to the emission, since the quantum confined regions with radius < 10 nm makes up less than 1% of the NN, and are likely dominated by non-radiative surface recombination.

The peak wavelength of the typical GaAs NNs is at 1.509 eV, redshifted only slightly from bulk zincblende GaAs at 1.519 eV. For the lower TMIn flow sample, the $\mu$-PL peak is at 1.430 eV due to the increased indium incorporation. This peak corresponds to approximately 5% indium composition based on Eq. (1). The higher flow rate NN has a $\mu$-PL peak at 1.294 eV, corresponding to approximately 15% indium incorporation. The $\mu$-PL peak full-width at half-max (FWHM) for the In$_{0.15}$Ga$_{0.85}$As (61 meV) is approximately twice that of the pure GaAs (35 meV), and the intensity is reduced by 50%. The $\mu$-PL peak does not vary when the excitation laser spot is moved from the base to near the tip of a NN, which shows the indium distribution is fairly uniform.

Fig. 2. $\mu$-PL spectra of In$_x$Ga$_{1-x}$As NNs with $x = 0$, 0.05 and 0.15.
4. Transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) was performed on the InGaAs NNs. Figure 3 shows the tip of an In$_{0.15}$Ga$_{0.85}$As NN imaged on the [1-100] zone axis. The InGaAs NNs have sharp tips and are free of twinning just like the GaAs NNs. The lattice constant of the In$_{0.15}$Ga$_{0.85}$As NNs measured at the tips and sidewalls is larger than in the GaAs NNs by 0.9 ± 0.1%. The wurtzite structure is very similar to zincblende, except that instead of the zincblende ABCABC repeating (111) plane stacking of atoms, wurtzite has ABABAB (0002) plane stacking [10]. For our GaAs NN TEM measurements, these wurtzite and zincblende interplanar spacings are equal [3]. If one assumes this trend is similar for InAs, which in zincblende phase is 7.16% larger than GaAs, then the 0.9% lattice mismatch corresponds to 13% indium incorporation, close to our estimate of 15% based on photoluminescence.

![HRTEM image](image)

Fig. 3. HRTEM image at the tip of the In$_{0.15}$Ga$_{0.85}$As NN imaged on the [1-100] zone axis. Comparisons with the GaAs NNs show that the lattice constant is 0.9 +/- 0.1% larger.

5. Quantum well structures

Previously, growth of the NN structure was shown to be via preferential deposition along the c-axis [3]. We also reported a core-shell NN structure with sharp heterojunction interfaces in AlGaAs/GaAs NNs [3]. Here, we first determined the growth rate of InGaAs and GaAs NNs with several runs having different growth times. The NN radii and lengths have a linear dependence on growth time, and the growth rate on the NN sidewalls is approximately 5 nm/min. We grew three quantum well (QW) core-shell layered structures with nominal well region thickness of 15, 10 and 5 nm using the 15% indium TMIn flow rate, as shown in Fig. 4(a). In this InGaAs heterostructure case, the growth steps start with a 60-minute GaAs core, In$_{0.15}$Ga$_{0.85}$As for one to three minutes, and 10 more minutes of GaAs to form an outer shell to confine carriers in the InGaAs region. All growth conditions were held constant, except for the flow of TMIn.

µ-PL measurements were performed on the single QW NNs at 4K. The results are shown in Fig. 4(b), compared with a typical GaAs NN and the In$_{0.15}$Ga$_{0.85}$As bulk NN. The 15 nm QW NN peak is at 1.339 eV, redshifted from the typical bulk GaAs peak, due to carrier recombination in the lower-bandgap InGaAs region. The 15 nm well is blueshifted by 45 meV from the bulk In$_{0.15}$Ga$_{0.85}$As NN emission, which may be due to strain resulting from lattice mismatch with the GaAs core. The exact contribution of strain is unknown though since the properties of bulk wurtzite InGaAs are yet to be determined, and the tapered NN sidewalls...
make it difficult to predict the strain relaxation in the heterostructure, and the strain contribution to bandgap shift. There is also a possibility that reduced indium incorporation compared to the InGaAs NNs contributes to this blueshift.

The 10 nm QW NN PL peak is at 1.351 eV, 12 meV higher. This QW NN emission is ~8 x more intense than the typical GaAs NN, indicating that the carriers are confined to the well region, reducing the effects of non-radiative surface recombination. TEM images of these 10 nm In$_{0.15}$Ga$_{0.85}$As layers grown on GaAs show that they are coherent to the GaAs core lattice.

The 5 nm QW NN has its peak at 1.458 eV, blueshifted further due to additional quantum confinement. In this case the carriers are less confined, and relatively more radiative recombination can be seen from the GaAs core at higher energy. The FWHM for the 5 nm QW is 34 meV.

![Fig. 4.](image)

(a) Three NN samples were grown, starting with a 4 µm long GaAs core for 60 min, then coating with In$_{0.15}$Ga$_{0.85}$As for 1-3 min (~5-15 nm width), and capping with a GaAs barrier for 10 min. The schematic shows a three dimensional side-view of the NN growth steps with one third of the needle cut away to show the heterostructure layers. (b) µ-PL spectra of the 60-minute bulk GaAs NN, bulk In$_{0.15}$Ga$_{0.85}$As NN and the three QW NNs.

A third QW NN sample was grown with the same recipe as the 10 nm QW NN, except with the TMIn flow rate doubled. The resulting µ-PL spectrum is shown in Fig. 5 along with the 15% indium QW NN and pure GaAs NN normalized spectra for comparison. The peak emission energy is at 1.119 eV, 390 meV below the GaAs peak. The indium composition is estimated to be 30% based on the PL emission. The emission peak energy shows the ability to tune the PL wavelength over a wide range, even below the absorption edge of silicon at 1.17 eV (at T = 4 K). This is important for integrated optoelectronic devices on silicon which operate at wavelengths for which silicon waveguides are transparent.
Fig. 5. The μ-PL emission spectra of single NNs comparing the 30% and 15% indium QW NNs to the pure GaAs NN. All spectra are shown in normalized arbitrary units. The emission can be tuned from 1.509 eV to 1.119 eV, a range of 390 meV. The 30% indium QW NN emission is below the silicon band edge.

6. Conclusion

To summarize, we report the optical and crystalline properties of single wurtzite-phase, InGaAs NNs and InGaAs QW on GaAs NNs grown on silicon substrates for the first time. The catalyst-free NN growth can facilitate integration of III-V heterostructures with silicon electronic devices, as we demonstrated with the core-shell quantum well structure. In particular, we have shown quantum well emission which is tunable over a 390 meV range, even below the silicon bandgap. Achieving such a large range of bandgap tunability and efficient carrier confinement is necessary for realizing optoelectronic devices on silicon and guiding the light via silicon waveguides.

Acknowledgments

This work was supported by DARPA HR0011-04-1-0040 (CONSRT) and HP-CITRIS grants. The authors acknowledge the fellowship support from the UC Berkeley EECS Fellowship Program, NSF-IGERT Program, and NSF Graduate Research Fellowship Program. TEM work was performed at the National Center for Electron Microscopy (NCEM), Lawrence Berkeley National Laboratory, and was supported by the Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02—05CH11231. The authors would like to thank Christian Kisielowski at the NCEM for his assistance.