APPLIED PHYSICS LETTERS **96**, 251106 (2010)

Tuning the photoluminescence characteristics with curvature for rolled-up GaAs quantum well microtubes

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(Received 10 February 2010; accepted 17 May 2010; published online 23 June 2010)

III-V microtubes and nanotubes are formed by a strain-induced self-rolling process. We report room-temperature photoluminescence (PL) characteristics of such microtubes with embedded GaAs quantum-well structures and wall thickness as thin as 38 nm. Rolled-up tubes show dramatic PL intensity enhancement compared to their planar counterparts. Holey tubes, formed using patterned membranes, display further increase in intensity implying better light extraction efficiency with the air holes. Systematic shift of PL peak position as a function of tube curvature, attributed to strain induced band structure change, is established. © *2010 American Institute of Physics*. [doi:10.1063/1.3456098]

Strain induced self rolled-up semiconductor tubes is a recently discovered type of nanotechnology building block.[1–5] They are formed spontaneously through the mechanism of strain relaxation after releasing pseudomorphically strained epitaxial film from its native substrate. As illustrated in Figs. 1(a) and 1(b), for a GaAs–$In_xGa_{1-x}As$ bilayer epitaxial structure grown on a AlAs layer on GaAs substrate, the strained bilayer curves up and starts rolling upon releasing from the substrate by selectively removing the AlAs sacrificial layer, driven by the internal strain.

In contrast to the "bottom-up" growth and "top-down" fabrication approaches for other nanotechnology paradigms, the formation of self-rolling semiconductor microtubes and nanotubes exploits both. The bottom up aspect is the epitaxial growth of the strained layers with desired composition and thickness, which determines the tube diameter (from a few nanometers to a few tens of microns).[6–8] The top-down aspect is the definition of the mesa to expose sidewalls of the epitaxial film for lateral etching of the sacrificial layer in order to release the strained layer from the substrate. This mesa determines the tube location, orientation, and dimension (length, width, and number of rotations). As a result, self-rolling tubular micro- and nanostructures can be assembled in large arrays with uniform diameters and exceptional spatial placement controllability through postgrowth lithography, as demonstrated previously.[4,7] They can also be dispersed and transfer-printed to other substrates.[3]

Various types of active structures such as quantum well (QW) and quantum dots can be embedded in the tube wall by using the strained $In_xGa_{1-x}As$ layer as a wrapper while keeping the rest of the layers either lattice matched to the substrate or involving discrete structures. Photoluminescence (PL) studies of active light emitting tubes have been reported[9] and in some cases[10,11] optical modes from the microtube ring resonator and even lasing have been observed. Here we present a systematic study of room temperature optical properties of GaAs QW microtubes with ultrathin walls, controlled curvatures, and patterned with periodic holes.

The epitaxial growth of arsenide based III-V semiconductor heterostructures were carried out in an Aixtron 200/4 low pressure metal organic chemical vapor deposition reactor. The epitaxial structure consists of a strained $In_xGa_{1-x}As$ layer and a GaAs/AlGaAs stack. The microtube formation was done by postgrowth optical lithography and chemical etching using HF for the $Al_xGa_{1-x}As$ sacrificial layer and $H_2SO_4:H_2O_2:H_2O$ for other arsenide layers. The details of the growth and processing conditions have been reported previously.[8] For PL characterization, the microtubes were dispersed off the native GaAs substrate and redeposited onto a transparent substrate such as sapphire to minimize substrate optical absorption. Clusters of tubes were measured using a 532 nm Nd:YAG laser as the excitation source and a Si charge coupled device (CCD) as the detector. The excitation

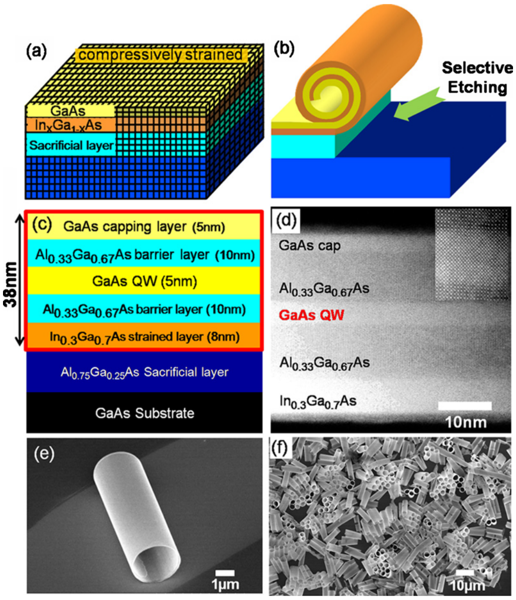

FIG. 1. (Color online) [(a) and (b)] Schematics illustrating the strained epitaxial structure and the self-rolling mechanism by selectively etching the sacrificial layer. [(c) and (d)] structure of a 38 nm thick epitaxial stack with 5 nm GaAs QW and the corresponding TEM image taken from the wall of a released tube (inset: high resolution of the GaAs QW region). [(e) and (f)] SEM images of a single rolled-up QW tube of 3 μm in diameter and a cluster of the same tubes dispersed onto a sapphire substrate.

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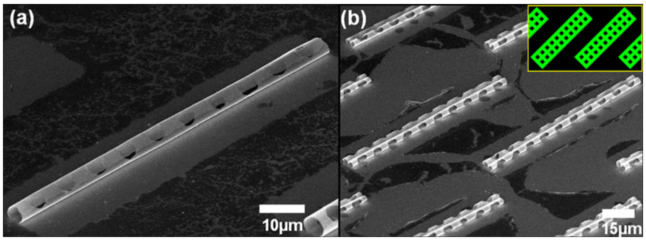

FIG. 2. (Color online) SEM images of (a) a single and (b) an array of rolled-up tubes formed from rectangular sheets of strained film with periodically patterned holes. Inset shows the mask pattern.

laser used was ~40 μm in spot size; when PL intensity comparison of different samples was made, effort was taken to ensure that the laser spot covered the same number of tubes or stripes. The excitation power density was in a range of 0.05 to 4.5 $\mathrm{kW/cm^2}$. Individual tubes were examined by micro-PL imaging with 1 μm step size using a Renishaw confocal system with a 633 He–Ne laser source (spot size was ~1 μm) and a CCD detector. Structural characterization was done using a Hitachi 4800 scanning electron microscope (SEM) and a JEOL 2200FS transmission electron microscope (TEM).

Shown in Fig. 1(c) is the epitaxial structure of a GaAs QW microtube for this study, which consists of a 5 nm GaAs QW cladded by 10 nm $\mathrm{Al_{0.33}Ga_{0.67}As}$ layers on each side on top of a strained 8 nm $\mathrm{In_{0.3}Ga_{0.7}As}$ layer and capped by a 5 nm GaAs layer. The total stack thickness is 38 nm. The corresponding TEM images taken from the wall of the rolled-up tube are shown in Fig. 1(d), confirming the epitaxial structure, thickness, and smooth interface with atomic resolution (inset) as well as the high crystallinity of the rolled-up tube. Figures 1(e) and 1(f) show SEM images of a single tube formed from this structure and clusters of these tubes dispersed randomly onto a sapphire substrate, respectively. The single tube shown has a diameter of 3 μm and the wall consists of 2.5 turns of the 38 nm membrane.

In addition to a regular solid layer of strained thin film, we demonstrate that patterned thin film membranes can be rolled up by the same mechanism and the patterns do not seem to affect the tube diameter. Shown in Fig. 2 are holey tubes formed from rectangular shaped thin films [same epitaxial structure as in Fig. 1(c)] with periodic holes patterned before the film was rolled-up (inset). The periodic array of holes not only serves as etching holes for faster release of the thin film from the substrate but also could add to the functionality of the tubes. It has been reported that the details of the tube geometry including the edge smoothness, intentionally created bottlelike notches, and periodic undulations have led to directional emission or better light confinement.[11–13] The demonstration of patterned rolled-up tubes provides new device prospects that involve spatial periodicity. For example, with proper design, the holes can be lined up after rolling for curved photonic crystal structures.

Not surprisingly, the PL spectrum from structure 1c before the thin film (38 nm) is released is dominated by emission from bulk GaAs substrate. The GaAs QW peak, which is supposed to be blueshifted from the bulk GaAs peak due to quantum confinement, is not observed at all. This is probably due to insufficient optical confinement from the ultrathin (20 nm) $\mathrm{Al_{0.33}Ga_{0.67}As}$ barriers and the strong absorption from the substrate. A weak PL peak at 817 nm is observed, however, when the GaAs QW structure is released from the native substrate and dispersed onto a transparent sapphire substrate, as shown in Fig. 3 (green curve). The planar film has the same structure as in Fig. 1(c) except without the 8 nm $\mathrm{In_{0.3}Ga_{0.7}As}$ strained layer (i.e., total thickness of 30 nm), thus no rolling action in this case. The peak position is consistent with the quantum confined band gap from a 5 nm GaAs QW. Eliminating the substrate associated absorption indeed enhances the QW emission.

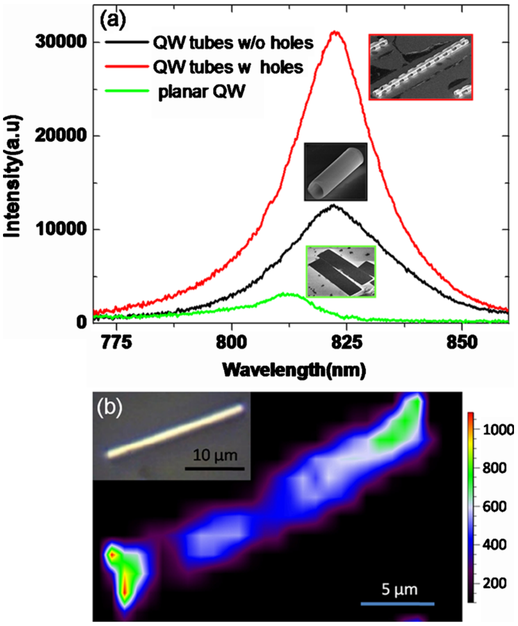

FIG. 3. (Color online) (a) Room temperature PL spectra taken from three geometries as labeled with the corresponding SEM images, demonstrating the intensity enhancement as a result of rolling up and further addition of air holes. (b) Room temperature micro-PL intensity mapping at 835 nm of a single tube that is 25 μm long and 3 μm in diameter (inset: white light image under 100× objective), demonstrating the intensity enhancement at the end of the tube compared to the center region.

The PL intensity from the QW structure is further enhanced dramatically once the planar sheet of strained film is rolled up along with the $\mathrm{In_{0.3}Ga_{0.7}As}$ strained layer. A strong and distinct peak at 834 nm is clearly observed, as shown in Fig. 3 (black curve). In addition, the PL peak position of QW tube shows a clear redshift relative to that from the planar sheet, which will be discussed later. Remarkably, further enhancement by a factor of ~3 has been observed for the holey tubes, as shown in Fig. 3 (red trace). Note that all three structures in Fig. 3 are fabricated from the same size rectangular sheets of the same epitaxial structure, except the planar sheets of thin films do not have the 8 nm $\mathrm{In_{0.3}Ga_{0.7}As}$ layer ($\mathrm{In_{0.3}Ga_{0.7}As}$ is actually a source of optical loss because it absorbs GaAs QW emission). The intensity enhancement observed here is consistent with other reports for rolled-up quantum dot and QW tubes and other curved/wrinkled structures.[9,14,15] Several factors could be responsible for the enhanced PL emission from the rolled-up tubular structures including internal reflection in the tube wall and interference contrast in the tube cavity, as suggested previously.[14] For the holey tubes demonstrated here, the loss of active gain material due to structural voids, not only does not lead to a decrease in PL intensity but to the contrary, a clear intensity enhancement. From planar sheets, rolled-up tubes with continuous films, to rolled-up tubes with air holes, more air-semiconductor interfaces and higher index contrast are created, which leads to better optical coupling and higher light

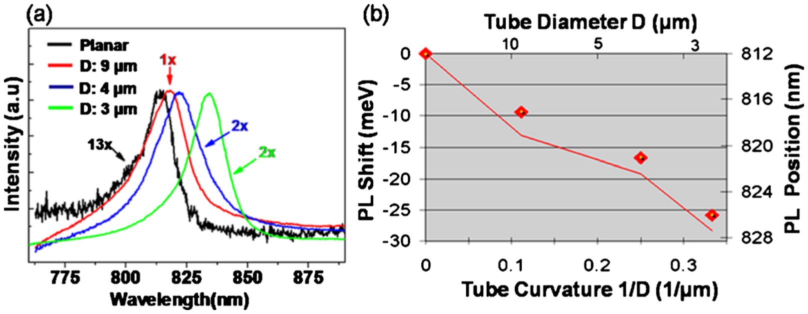

FIG. 4. (Color online) (a) Normalized PL spectra for a series of tubes with diameters (D) as indicated, showing a clear redshift as the tube diameter becomes smaller. (b) A plot of PL peak shift (milli electronVolt, left *y* axis) and position (nanometer, right *y* axis) as a function of tube curvature (1/D, bottom *x* axis) and diameter (D, top *x* axis). The data points are experimental results obtained from spectra in (a) and the line is calculated using the strain theory.

extraction efficiency and thus stronger PL intensity. For the same reason, the emission from the ends of the QW microtubes show stronger intensity compared to the center part of the tubes, as shown in the micro-PL map in Fig. 3(b) where the emission from the QW tube was collected at the same location (1 μm spot size) at which it was excited.

In addition to the enhancement of emission intensity, another unique effect of rolling up the QW thin film is the change in emission energy as a function of tube curvature. This can be seen clearly from Fig. 4 where a monotonic shift to lower energy with shrinking tube diameter is observed. For example, a 3 μm diameter tube results in 25 meV redshift compared to its planar (zero curvature) counterpart. Note that for all data points in Fig. 4, the GaAs QW and $Al_{0.33}Ga_{0.67}As$ barrier thickness and composition are all identical; and different tube curvatures are achieved by adjusting the composition of the strained $In_xGa_{1-x}As$ layer.

Before the thin film structure [see Fig. 1(c)] is rolled up, the only strained layer in the epitaxial stack is $In_xGa_{1-x}As$ (biaxial compressive strain). Once the film is released from its substrate, the lowest energy state is to roll up into tubular shape as observed experimentally, driven by the uniaxial strain in the tube tangential direction. The rolling action redistributes the strain by relaxing the compressive strain in the $In_xGa_{1-x}As$ layer partially and inducing tensile strain at the interface between $In_xGa_{1-x}As$ and the stack on top, and the strength of which gradually tapers off along the radial direction. The strain that the GaAs QW experiences can be determined by first locating the neutral strain plane which is calculated to be right at the middle of the stack when all layer thicknesses, compositions, and Young's moduli are considered; then calculating the strain ε based on the Matthews–Blackslee relationship.[16] The uniaxial strain induced band gap shift for a GaAs QW can then be calculated using $\delta E_{HH}=-7.7\varepsilon$, based on $k\cdot p$ perturbation theory and the example of Ohtani *et al.*[16,17] For example, the calculated strain for the GaAs QW ε in the structure shown in Fig. 1(c) is 0.37% (tensile), which corresponds to a band gap shift of 26 meV. Shown in Fig. 4(b) are the calculated band gap shifts as a result of strain for tubes with different curvatures and experimental PL peak shift. The good agreement between the two suggests that the PL peak shift observed due to curvature results directly from strain-induced change in band gap. It can be predicted based on this trend that, when the tube diameter is less than 500 nm, a structure with a 5 nm GaAs QW (817 nm band gap when unstrained) can emit light at a wavelength longer than 912 nm. The curvature-driven band gap engineering without changing either the composition or the thickness is systematically established.

No PL peak narrowing was observed for the power range studied at room temperature for these QW tubular structures. Several mechanisms could be responsible for the broad emission from these GaAs QW tubes, including optical loss through substrate (tubes were not suspended), absorption from layers in the tube wall that are not transparent to the QW energy (e.g., the $In_xGa_{1-x}As$ layer and GaAs cap), and the lack of 3D confinement as in quantum dot microtubes.

In summary, the tubular geometry, including patterned holey tubes, resulted from strain-induced self-rolling of III-V semiconductor ultrathin films dramatically enhances the PL intensity; by bending the film elastically without changing the composition or thickness, we are able to change the band gap continuously. It is clear that these III-V tubular structures provide a unique platform through their wall curvature for band gap engineering thus tailoring of effective mass, carrier mobility, and other associated properties, and could lead to devices that are smaller and more powerful, as well as new device concepts in both photonics and electronics.

We acknowledge support by NSF CAREER ECCS under Grant No. 0747178, NSF Nano-CEMMS under Grant No. 0749028 and DARPA YFA under Grant No. N66001-09-1-2107; and Dr. Jianguo Wen for kindly performing the TEM measurement.

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