Interband optical transitions in GaP nanowires encapsulated in GaN nanotubes

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This work investigates the optical properties of cylindrical GaP nanowires encapsulated inside GaN nanotubes (GaP@GaN). Many absorption structures are observed in the range of 2.0–4 eV. Calculations are performed to determine the quantized energy levels of electrons and holes confined in the GaP well. Analytical results indicate that the absorption peaks are attributable to interband optical transitions due to the confined carriers in the heterostructure.

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A remarkable feature of one-dimensional (1D) systems is that the density of states has a singularity at the bottom of each subband. Such divergences lead to interesting transport properties and collective excitations. For example, theories predict strong mutual interactions in a 1D system, and a Tomonaga-Luttinger liquid phase is expected. 1 Scattering is expected to be suppressed in a 1D system because of the small scattering probability, which may cause high mobility. 2

The physical properties of 1D systems have emerged as a field of research in the last two decades. Advanced technology for processing two-dimensional-electron-gas (2DEG) systems can be used to fabricate 1D quantum wires by etching a 2DEG structure by nanoscale lithography procedures. 3 Quantum wires with square or rectangular cross sections are formed on the substrate. The problem with this lithographic method for forming a quantum wire is that the etching process leaves behind rough wire sidewalls/air interfaces, exhibiting in places a roughness of several nanometers, increasing carrier scattering by the sidewall and reducing mobility. Furthermore, the singularities in the density of states are widened. The problem of surface roughness hinders experimental efforts to observe the interesting effects expected in a 1D system.

Recently, great progress has been made in synthesizing semiconductor nanowires using various growth methods. These synthesized nanowires show a good crystalline structure and their interfaces are smooth to one or two atomic layers. This work investigates the optical absorption spectra of GaP nanowires encapsulated inside GaN nanotubes, referred to hereafter as GaP@GaN heterostructure nanowires. Many absorption structures are observed in the visible range. An analysis is performed to determine the eigenenergies for carriers confined in the cylindrical well. The results show that the absorption peaks are attributable to interband transitions due to the confining of carriers in the heterostructure. The clear optical features observed here reveal the high quality of the nanowires, which may therefore be used to investigate the interesting physical properties of 1D systems.

The GaP@GaN nanowires were prepared on the basis of a vapor-liquid-solid mechanism. 4 Details of the synthesis procedure are described elsewhere. 5 At the first stage, GaP nanowires were grown on a silicon substrate from the reaction of gallium and red phosphor in the presence of metal catalysts in a tube furnace. X-ray diffraction analysis revealed the structure of GaP nanowires to be zinc blende with a lattice constant of 5.44 Å. The resulting GaP nanowires were then continuously reacted under a flow of ammonium. 6 Figure 1(a) shows a typical scanning electron microscope image of an as-grown GaP@GaN nanowire sample on a silicon substrate. The materials observed on the substrate were almost all wire like. Figure 1(b) shows the high-resolution TEM image of a single GaP@GaN nanowire. Double layer structures were observed in the image and the clear lattice fringes, shown in the inset, confirmed that GaP nanowires were indeed encapsulated inside GaN layers. X-ray diffraction analysis revealed the diffraction peaks of both GaN and GaP crystals. The GaN outer shell has the wurzite structure with lattice constants of a = 3.15 Å and c = 5.13 Å. Optical transmission measurements were taken with a grating monochromator over the energy range 1.5–4 eV. Absorption spectra were obtained by taking the ratio of the transmission spectrum of the sample to that of the background. The incident light was moved around the sample to search for locations with good optical signals since the distribution of nanowires over the substrate was not uniform. 7

Figure 2(a) presents the absorption spectrum of GaP@GaN heterostructure nanowires at room temperature. Six pronounced absorption peaks appear over the spectral range of 2–4 eV. This result is in strong contrast to that obtained for bulk GaP, which exhibits only a fundamental absorption at 2.26 eV and two weak peaks at 2.75 and 2.85 eV due to $E_0$ and $E_0 + \Delta_0$ transitions, respectively. 8 Figure 2(b) shows the absorption spectrum for a different sample position. The absorption-peak energies are slightly different from those in Fig. 2(a). The absorption spectrum generally varies slightly with the sample position, which is due to a dispersion in the nanowire diameter. Figure 2(c) displays the absorption spectrum at 4 K. As the temperature is reduced, the absorption peaks become sharper and better resolved; the peak energies increase slightly, and the number of absorption peaks increases. The baseline of the absorption spectrum in Fig. 2(c) is removed to better display these low-temperature absorption peaks, and the resulting weak structures are shown in Fig. 2(d). Thirteen discernible absorption peaks appear at $E = 2.08, 2.26, 2.37, 2.43, 2.5, 2.56, 2.66, 2.76, 2.87, 3.14, 3.6, 3.68 and 3.8 eV.
The origin of the absorption peaks in Fig. 2 is now addressed. Consider a bare GaP quantum wire with a circular cross-section of radius $a$ and whose axis along the $z$ axis. For simplicity, an infinite potential well is assumed; that is, $V(r) = 0$ for $r < a$ and $V(r) = \infty$ for $r \geq a$. The electron eigenstates are the eigenenergies of the Schrödinger equation $-\frac{\hbar^2}{2m_e} \nabla^2 \psi = E \psi$, where $m_e$ is the effective mass of the conduction-band electron. In cylindrical coordinates, the wave function $\psi(r, \varphi, z) = R(r)Y(\varphi)Z(z)$. Since the electrons move freely in the $z$ direction, the $z$-component solution $Z(z)$ is simply a plane wave $e^{\pm ik_z z}$ with energy $\hbar^2 k_z^2 / 2m_e$. Confinement in the $(r, \varphi)$ plane yields quantum effects. Inserting the $(r, \varphi)$ plane wave function $R(r)Y_n(\varphi)$ into the Schrödinger equation, the solution in the $\varphi$ direction is a periodic wave $Y_n(\varphi) = (1/\sqrt{2\pi}) e^{\pm i n \varphi}$, and the radial equation becomes

$$\frac{d^2 R}{dr^2} + \frac{1}{r} \frac{dR}{dr} + \left( \frac{2m_e E^*}{\hbar^2} - \frac{\nu^2}{r^2} \right) R = 0. \quad (1)$$

The energy $E^*$ is related to the wave vector $k_r$ by $E^* = \hbar^2 k_r^2 / 2m_e$. Expressing $E^*$ in terms of $k_r$ and letting $x$
TABLE I. Calculated interband-transition energies \( E_{vn} \) for heavy holes and light holes confined in a GaP@GaN heterostructure nanowire with a radius of 3.7 nm. The experimental results are shown for comparison. The letters that precede the calculated energies refer to the labels in Fig. 2(d).

<table>
<thead>
<tr>
<th>Index</th>
<th>Calc. (eV)</th>
<th>Expt. (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu n )</td>
<td>( E_{vn} )</td>
<td>( E_{vn} )</td>
</tr>
<tr>
<td>01</td>
<td>2.4 ( a ) 2.37 ( b ) 2.42 ( b ) 2.37 ( b )</td>
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<tr>
<td>11</td>
<td>3.8 ( c ) 2.43 ( e ) 2.57 2.43 2.56</td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>5.5 ( d ) 2.55 ( g ) 2.82 2.56 2.83</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>7.0 ( f ) 2.68 ( j ) 3.13 2.66 3.14</td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>8.7 ( h ) 2.86 ( l ) 3.54 2.87 3.6</td>
<td></td>
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</table>

\[ \frac{d^2 R_y}{dx^2} + \frac{1}{x} \frac{dR_y}{dx} + \left(1 - \frac{\nu^2}{x^2}\right) R_y = 0, \]

which is just the Bessel equation. The radial solution \( R_y(x) \) is the Bessel function of integral order \( J_\nu(x) \). The infinite potential well requires the wave function \( J_\nu \) to vanish at the boundary. For \( \nu = 0 \), \( J_0(x) = 0 \) at specific values of \( x_{nn} = 2.40, 5.52, 8.65, and 1.79 \); for \( \nu = 1 \), \( J_1(x) = 0 \) at \( x_{1n} = 3.83, 7.02, 10.17 \), and 13.32, where the subscript \( n \) denotes the \( n \)th index. The energy of a wire of radius \( a \) becomes \( E_{vn} = h^2 \nu^2 / 2m_e \). The discrete \( x_{nn} \) values yield discrete energy levels \( E_{vn} \), revealing the quantum-size effect.

The discrete energy levels \( E_{01}(x = 2.40), E_{11}(x = 3.83), E_{02}(x = 5.52), E_{12}(x = 7.02), E_{03}(x = 8.65), E_{13}(x = 10.17), \) and \( E_{04}(x = 11.79) \). The energy \( E_{vn} \) is the increase in electron energy due to confinement. Holes in the valence bands exhibit the same effect:

\[ E_{vn} = \frac{\hbar^2 \nu^2}{2m_h a^2}, \]

where \( m_h \) is the effective mass of a hole. The interband-transition energy from the \( \nu n \)th heavy hole subband to the \( \nu n \)th conduction subband equals the bulk gap \( E_g \) plus the increase due to the quantum effect:

\[ E_{vn} = E_g \text{(bulk)} + E_{vn} + E_{nbn} = E_g \text{(bulk)} \]

\[ + \frac{\hbar^2 \nu^2}{2a^2} \left( \frac{1}{m_e} + \frac{1}{m_{bh}} \right). \]

A similar equation for a light hole is determined by replacing the hole mass by \( m_{lh} \). The transition energy thus depends on the index \( \nu n \) (or \( x_{nn} \)). Only transitions that correspond to the same indices \( \nu n \) are considered here.

Several pronounced absorption peaks were selected from the absorption spectrum of Fig. 2(c), assigned indices \( \nu n \), and then their energies were fitted by Eq. (3). For fitting, the following bulk GaP parameters are used: \( m_e = 0.02 m_0, m_{hh} = 0.57 m_0, m_{lh} = 0.18 m_0, \) and \( E_g(300 \text{ K}) = 2.26 \text{ eV} \). The best fit yields radius \( a = 3.7 \text{ nm} \). The radius was then used to determine the transition energies for various values of the indices, \( \nu n \). Table I presents the calculated results.

Figure 2(d) plots these results as long (short) solid bars for heavy (light) holes. Table I also presents experimental results for comparison. According to this table, the calculations effectively account for the experimentally observed absorption peaks in the range 2.3–3.6 eV. To confirm the calculation, the radii of nanowires were examined under a scanning electron microscope. Figure 1(c) reveals the image of a nanowire with a radius of approximately 6 nm. Similar nanowires were also observed at many different sample positions. After subtracting the thickness of the GaN barrier, the radius of the GaP well is approximately 4 nm, in excellent agreement with the calculated value. The good agreement between the experimental and calculated results supports the interpretation of interband transitions in the heterostructure nanowires.

The above discussion assumes an infinitely high barrier potential. In reality the GaN-barrier height is finite and the band-edge alignment must be considered. The band-edge lineups in the GaP@GaN heterostructure is unknown at present and its determination is a difficult experimental problem. For simplicity, the system is assumed to be a type-I heterostructure. Then, interband transitions due to the confined states must lie between the energy gap of the well and the barrier [as the inset of Fig. 2(b) depicts]; that is, \( E_g \) (GaP) = 2.26 eV \leq E_{vn} \leq 3.45 \text{ eV} = E_g \) (GaN). This fact may explain the finding in Fig. 2(c), that the absorption peaks are concentrated mainly between 2 and 3.5 eV. Notably, no absorption peak appears in the range 3.2–3.5 eV, implying that the system reaches the continuum (delocalized) states in this range and thus yields negligible absorption.

The remaining absorption peaks in Fig. 2(c) are now considered. An important optical effect is excitonic transition. Previous calculations showed that \( E_{hh}(2\text{D}) = 4E_{hh}(3\text{D}) \). The 1D case is more complex and must be solved numerically, but the result can be approximated by \( E_{hh}(1\text{D}) \approx 2E_{hh}(2\text{D}) \). The exciton binding energy for bulk GaP is around 15 meV. Hence, \( E_{hh}(1\text{D}) \approx 8E_{hh}(3\text{D}) = 8 \times 15 \text{ meV} = 0.12 \text{ eV} \). The absorption peak at 2.26 eV in Fig. 2(c), which is 0.11 eV lower than the interband-transition energy of the ground state \( (E_{01} = 2.37 \text{ eV}) \), is therefore attributed to the ground state transition of the exciton. Three high-energy peaks are present at 3.6, 3.68, and 3.8 eV. These energies are close to the energy gap of the GaN barrier. Hence the high-energy peaks are tentatively attributed to interband transitions due to confined states in the GaN barrier.

Another evidence for quantum-confinement effect is presented in Fig. 2(e). This absorption spectrum was taken with an incident-light spot three times larger in area than that used in Fig. 2(c). There are only two broad absorption peaks at 2.25 and 3.4 eV. This spectrum is in striking contrast to Fig. 2(c) in which many weak absorption peaks are observed. The two broad peaks are consistent with the fundamental absorption edges (valence to conduction) of bulk GaP (2.26 eV) and bulk GaN (3.45 eV). With a large incident beam spot, the light sees a larger number of nanowires, many of them having thick diameters near 50 nm [as revealed in Fig. 1(a)]. Thick wires have large volumes and yields large optical absorption. Hence the absorption spectrum is predominated by the signals from thick wires. Since thick nanowires exhibit no quantum-size effect, the absorption spectrum of thick wires is similar to those for bulk samples. The weak absorption structures due to quantum-confined thin wires are buried.
in the signals from the thick wires. The lack of weak absorption structures in thick wires of Fig. 2(c) is strong evidence that the optical structures in Fig. 2(c) are due to optical transitions in quantum-confined nanowires.

The absorption peaks in Fig. 2(c) are relatively weak. This can be attributed to several characteristics of the 1D samples: (1) GaP is an indirect-gap semiconductor. Matrix elements for indirect optical transitions are much smaller than for direct transitions. (2) Optical absorption is characterized by optical density \( d \), where \( d \) is the absorption coefficient, and \( n \) is the sample thickness. The absorption coefficient \( \alpha \) is proportional to the number of carriers, \( n \), that participate in the interactions with light. In low-dimensional systems, \( n \) is small due to small sample volumes, leading to weak optical absorption. In 2D quantum wells, multiple quantum-well structures, fabricated by stacking several arrays on top of each other, are used to produce larger absorption. In 1D nanowires, the wires are randomly stacked and there is large empty space between wires. The incident light traversing through nanowires sees mostly empty space. This greatly reduces the carrier density \( n \) and the effective thickness \( d \) seen by the incident light, leading to weak absorption features. (3) Single spectroscopy techniques such as transmission and absorption measurements normally reveal optical structures as weak features superimposed on a broad background. This is because the absorption at a given energy may include contributions from several allowed transitions in the \( k \) space. To better resolve these weak structures one needs to use modulation spectroscopy such as electroreflectance or piezoreflectance techniques, which requires the attachment of electrical leads to the sample. However, it is still difficult at present to make reliable electrical contacts to nanowire samples.

In conclusion, this work has examined the optical properties of GaP@GaN heterostructure nanowires. The absorption spectra reveal many absorption structures in the visible range. These absorption features are attributed to interband optical transitions due to carriers confined in the GaP quantum well. The nanowires can be used to explore various interesting properties of 1D systems.

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