Time resolved microphotoluminescence studies of single InP nanowires grown by low pressure metal organic chemical vapor deposition

S. Reitzenstein, a S. Münch, C. Hofmann, and A. Forchel
Technische Physik, Physikalisches Institut, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

S. Crankshaw
Applied Science and Technology Group, University of California at Berkeley, Berkeley, California 94720

L. C. Chuang, M. Moewe, and C. Chang-Hasnain
Department of Electrical Engineering and Computer Sciences, University of California at Berkeley, Berkeley, California 94720

(Received 26 June 2007; accepted 6 August 2007; published online 27 August 2007)

The authors report optical studies of InP nanowires (NWs) grown by metal organic chemical vapor deposition. By means of low temperature microphotoluminescence experiments, the authors determined the optical properties of as-grown NWs. The emission of individual NWs is characterized by small linewidths as low as 2.3 meV. Blueshifts of the NW emission energy between 25 and 56 meV with respect to bulk InP are related to radial carrier confinement in nanowires with diameters between 15 and 50 nm. Time resolved investigations reveal a low surface recombination velocity of \(6 \times 10^{5} \text{ cm/s} \) and indicate thermally activated nonradiative surface recombination above approximately 20 K. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2776358]

The study of semiconductor nanowires (NWs) has been a field of growing interest in recent years. High quality semiconductor nanowires are reported based on material systems such as GaAs, GaN, or InP using various growth methods.1–4 Optimization of catalyzed patterning and growth control enabled the growth of NWs with controlled size and composition, which is crucial for the application of NWs in nanoelectronic or nanophotonic devices.5–7 Nanowires exhibit interesting electronic and optical properties due to quantum confinement effects. However, the large surface to volume ratio of these quasi-one-dimensional systems makes them sensitive to surface states and may result in a low luminescence quantum yield in photonic wire structures. Nonradiative recombination due to surface states is most severe in thin wires, which leads to a major trade-off between quantum efficiency and strong quantum confinement effects. For instance, detrimental nonradiative processes are observed for GaAs NWs, which thus require effective surface passivation.8,9 In contrast to GaAs NWs, InP NWs have shown to be good candidates for optoelectronic devices with both high quantum efficiency and strong quantum confinement.10

In the present work, we performed optical studies on individual InP NWs in order to assess important properties such as confinement energies and nonradiative surface recombination relevant for nanowire based devices. In particular, photoluminescence experiments reveal ultralow emission linewidths and a very low surface recombination velocity of high quality, as-grown InP NWs. The NWs were grown on B-doped (100) Si substrates by low pressure metal organic chemical vapor deposition (MOCVD). After cleaning the Si substrate, 10 Å Au was evaporated as the vapor-liquid-solid catalyst. The substrate was annealed for 3 min at 640 °C in the MOCVD reactor to form the Au catalyst droplets. For the subsequent 10 min nanowire growth, the reactor temperature was reduced to 460 °C, using tert-butylphosphine and trimethylindium with a V/III ratio of 60 as the metal-organic sources. To characterize the NWs, spatially and temporally resolved microphotoluminescence (\(\mu\text{PL}\)) studies were performed on as-grown, individual InP nanowires. For continuous-wave experiments, the NWs were excited by an argon-ion laser at 514 nm. The laser beam was focused by a microscope objective with a numerical aperture of 0.4 to a spot size of about 3 μm on the sample. A computer-controlled x-y-z-piezo stage with an accuracy of 0.1 μm in each direction allowed a precise addressing of single NWs. The photoluminescence (PL) was collected by the same microscope objective, dispersed by a 0.55 m monochromator, and detected by a nitrogen cooled charge coupled device. For time resolved measurements, a mode locked Ti-sapphire laser tuned to 790 nm providing pulses with a width of about 150 fs at a repetition rate of 82 MHz was used. The decay curves were recorded by a photon-multiplier tube in combination with single photon counting electronics after spectral filtering with a 0.55 m monochromator.

The structural quality of individual as-grown InP NWs was analyzed by transmission electron microscopy (TEM) imaging and diffraction analysis. A TEM image of a NW with a diameter of about 35 nm is shown in Fig. 1(a). From the electron diffraction (not shown) of the nanowires, we conclude that the NWs crystallized in the wurtzite structure with the nanowire axis in the [0001] direction. For studies on individual NWs, sample positions with a low surface density of approximately 1 wire/μm² were chosen. A typical \(\mu\text{PL}\) spectrum of individual NWs recorded at 10 K with an excitation power of 2 μW is depicted in Fig. 1(b). The spectrum shows two NW emission peaks at 1.452 and 1.460 eV, respectively. We observe remarkably small linewidths of 4.7 and 2.3 meV, which are significantly narrower than reported

---

aElectronic mail: stephan.reitzenstein@physik.uni-wuerzburg.de
1.460 eV are displayed in Figs. 1a and 1b. Using an effective mass model for electrons and holes confined in a cylindrical potential, we obtained estimates for the wire diameters of nanowires NW1–NW5.

We relate the different peak emission energies of NW1–NW5 to size dependent radial confinement energies of the respective wires. Lacking consistent experimental data on the bandgap of wurtzite InP, we estimate this size dependence using zinc-blende InP parameters. In this case, the emission peaks of NW1–NW5 show confinement induced blue-shifts of about 25 to about 56 meV. In order to explore the size dependence of the nanowire luminescence quantitatively, we applied an effective mass model for electrons and holes confined in a cylindrical potential. Using the InP effective masses of electrons and holes and the reduced effective mass, we obtain estimates for the wire diameters ranging from 50 to 15 nm. The values agree well with the results of TEM and scanning electron microscopy investigations, which show typical wire sizes in the calculated range of diameters. These results are tabulated in Table I.

The optical properties of the NWs were investigated in more detail by time resolved measurements. These types of measurements reveal important information on the free carrier dynamics which in turn allows one to estimate the contribution of radiative and nonradiative channels on the free carrier decay. Since surface states usually introduce nonradiative recombination centers, time resolved investigations are a direct tool to assess the surface quality of the NWs. In order to gain information on the surface properties of the present NWs, we performed time resolved studies on the emission associated with NW4 at 1.463 eV as it could be well separated from the other peaks. The temporal evolution of the luminescence from NW4 is depicted in Figs. 3a and 3b for a temperature of 4 and 27 K, respectively. We observe a monoexponential dynamics associated with a decay time of \( \tau = 2.6 \text{ ns} \). This long decay time together with the monoexponential decay reflect again the high surface quality of the as-grown NWs and indicate that nonradiative surface recombination is negligible at low temperature. In particular, the decay time of as-grown NWs investigated in the present work is much higher in comparison to 0.2 ns reported for as-grown InP NWs on InP substrate and are comparable to decay times after HF passivation of these catalyst-free grown NWs. The monoexponential decay characteristic is sustained up to about 20 K above which a transition to biexponential free carrier decay evolves. As

Previously and indicate a low density of surface states for the as-grown NWs. The spatial distribution of the PL intensity was investigated by taking PL spectra at different positions over a scan area of about 50 \( \times \) 50 \( \mu \text{m}^2 \). Corresponding surface maps of the integrated intensity associated with peak A at 1.452 eV and peak B at 1.460 eV are displayed in Figs. 1c and 1d. It is clearly seen that the PL originates from distinct positions associated with two wires centered at (arbitrary) positions \((x_1, y_1) = (22, 17 \mu \text{m})\) and \((x_2, y_2) = (24, 23 \mu \text{m})\), respectively. We would like to point out that no signatures of optical transitions due to Au from the catalyst droplets have been observed in the PL spectra.

The emission of a few InP NWs recorded at 10 K with an excitation power of 15 \( \mu \text{W} \) at a position with a slightly higher surface density is displayed in Fig. 2. The emission consists of a group of five features denoted as NW1–NW5.

By changing the excitation spot position in a micrometer range, the relative contribution of the components can be varied strongly, indicating that each feature has a different spatial origin, i.e., is due to a different NW. The intensity of all lines depends on a good approximation linearly on the excitation power. This demonstrates that the lines are due to ground state transitions in NWs of different diameters.

We would like to point out that no signatures of optical transitions due to Au from the catalyst droplets have been observed in the PL spectra.

The optical properties of the NWs were investigated in more detail by time resolved measurements. These types of measurements reveal important information on the free carrier dynamics which in turn allows one to estimate the contribution of radiative and nonradiative channels on the free carrier decay. Since surface states usually introduce nonradiative recombination centers, time resolved investigations are a direct tool to assess the surface quality of the NWs. In order to gain information on the surface properties of the present NWs, we performed time resolved studies on the emission associated with NW4 at 1.463 eV as it could be well separated from the other peaks. The temporal evolution of the luminescence from NW4 is depicted in Figs. 3a and 3b for a temperature of 4 and 27 K, respectively. We observe a monoexponential dynamics associated with a decay time of \( \tau = 2.6 \text{ ns} \). This long decay time together with the monoexponential decay reflect again the high surface quality of the as-grown NWs and indicate that nonradiative surface recombination is negligible at low temperature. In particular, the decay time of as-grown NWs investigated in the present work is much higher in comparison to 0.2 ns reported for as-grown InP NWs on InP substrate and are comparable to decay times after HF passivation of these catalyst-free grown NWs. The monoexponential decay characteristic is sustained up to about 20 K above which a transition to biexponential free carrier decay evolves. As

![Figure 1](image1.png)

**FIG. 1.** (Color online) (a) TEM image of an InP NW with a diameter of about 35 nm. Inset: zoom in of the upper part of the NW. (b) \( \mu \text{PL} \) spectrum of two nanowires with emission energies of 1.452 eV (labeled A) and 1.460 eV (labeled B), respectively (\( P = 2 \mu \text{W}, T = 10 \text{ K} \)). Intensity maps showing the spatial distribution of the integrated intensity of nanowire A [panel (c)] and B [panel (d)], respectively.

![Figure 2](image2.png)

**FIG. 2.** \( \mu \text{PL} \) spectrum of individual nanowires (NW1–NW5) recorded at an excitation power of 15 \( \mu \text{W} \) at 10 K.

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Emission energy (eV)</th>
<th>Confinement energy (meV)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NW1</td>
<td>1.445</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>NW2</td>
<td>1.452</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>NW3</td>
<td>1.460</td>
<td>40</td>
<td>23</td>
</tr>
<tr>
<td>NW4</td>
<td>1.464</td>
<td>44</td>
<td>20</td>
</tr>
<tr>
<td>NW5</td>
<td>1.476</td>
<td>56</td>
<td>15</td>
</tr>
</tbody>
</table>
shown in Fig. 3(b) for $T=27$ K the biexponential is associated with a fast decay shortly after the laser pulse and a slower decay at longer delay times. We relate the fast decay with a time constant of $\tau_1=1.1$ ns to nonradiative surface recombination while the longer component with $\tau_2=2.6$ ns observed also for $T=4$ K [c.f. Fig. 3(a)] is attributed to radiative recombination in the NWs.\textsuperscript{12}

In order to describe the time resolved data more quantitatively, we take into account a model introduced to describe carrier decay in GaAs NWs.\textsuperscript{16} In this model, the carrier decay rate depends via

$$\frac{dn}{dt} = -\left( \frac{1}{\tau_{\text{rad}}} + \frac{2S}{d_{\text{NW}}} \right) n$$

on the radiative lifetime $\tau_{\text{rad}}$, the surface recombination velocity $S$, and the wire diameter $d_{\text{NW}}$. Charged surface states cause band bending $\varphi$ which repels carriers from the wire surface and leads to deviations from the flatband value $S_0$ at high carrier densities when band bending is suppressed due to screening effects,

$$S = S_0 e^{-\varphi/\varphi_0}.$$  \hfill (2)

In relation to this model, we associate the fast decay observed in Fig. 3(b) to nonradiative surface recombination, which is most prominent at short delays after photon excitation where band bending is partially screened out due to high free carrier concentration in the wire.\textsuperscript{12} By calculating the logarithmic derivation $\frac{d\ln I}{dt}$ of the decay curve at short delays, we estimate a surface recombination velocity $S = -(\frac{d\ln I}{dt})d_{\text{NW}}/2$ of about $6 \times 10^2$ cm/s ($d_{\text{NW}}=20$ nm). This value is comparable to surface recombination velocities on the order of $10^3$ cm/s reported for InP bulk\textsuperscript{17} and significantly lower than values on the order of $10^6$--$10^7$ cm/s observed for GaAs wires.\textsuperscript{16,18} The fast decay is only observed at elevated temperatures and is attributed to a thermally activated process according to Eq. (2). In fact, the appearance

of the fast decay component at higher temperatures is associated with a strong decrease of PL intensity which is shown in the Arrhenius plot in Fig. 3(c). The temperature dependence of the emission intensity allows us to estimate the characteristic activation energy and yields a band bending of $\varphi=2.8$ meV.

In summary, spatially and temporally resolved $\mu$PL spectroscopies have been used to address physical properties of single InP nanowires. We observed a size dependent blue-shift of up to 56 meV for the nanowire emission energy with respect to InP bulk band gap emission and narrow linewidths as low as 2.3 meV which indicates a nonradiative surface recombination in the as-grown nanowires. This interpretation is confirmed by temperature and time resolved investigations which reveal a low surface recombination velocity of about $6 \times 10^2$ cm/s and point to thermally activated nonradiative surface recombination above approximately 20 K.

This work was partly supported by the European Commission through the IST Project Node and the State of Bavaria. Support is also acknowledged from DARPA HR0011-04-1-0040 (CONSRT) and HP-CITRIS grants, with author fellowship support from the NSF Graduate Research Fellowship Program to one of the authors (S.C.), and NSF-IGERT Program to two of the authors (L.C.C. and M.M.).

\textsuperscript{1}X. Duan, J. Wang, and C. M. Lieber, Appl. Phys. Lett. 76, 1116 (2000).
\textsuperscript{2}C. M. Park, Y. S. Park, H. Im, and T. W. Kang, Nanotechnology 17, 952 (2006).