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Enhanced luminescence from catalyst-free grown InP nanowires

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The surface effects in the optical properties of catalyst-free grown InP nanowires are investigated. Both as-grown nanowires and nanowires treated with hydrofluoric acid are studied using low- and room-temperature continuous-wave and time-resolved photoluminescence measurements and transmission electron microscopy. It is shown that the room-temperature photoluminescence intensity is increased by two orders of magnitude after the surface treatment, and that there is also a significant increase in the double-exponential photoluminescence decay time. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2431711]

While reaching towards the fabrication of one-dimensional semiconductor structures, a lot of effort has been put into studying the vapor-liquid-solid[1] growth of semiconductor nanowires. In metal organic vapor phase epitaxy (MOVPE), this is done using previously deposited catalytic metal nanoparticles (typically gold)[2] or, even better, *in situ* techniques without any substrate preprocessing.[3,4] These methods have provided an easy access for investigations of the structural, electrical, and optical properties of semiconductor nanowires. Especially properties related to their large surface-to-volume ratio are of great interest for, e.g., sensor applications. It has been demonstrated that the electrical[5] and optical[6] properties of semiconductor nanowires are rather sensitive to ambient gases or, more accurately, gas molecules adsorbed on the nanowire surface. Therefore, the surface properties of nanowires are essential background information for sensor design. In this study we have concentrated on the surface effects in the optical properties of InP nanowires fabricated using a catalyst-free (or self-catalyzed) MOVPE technique.[3,7] We show that the state of the nanowire surface significantly affects the photoluminescence emission efficiency and that it should, indeed, be taken into account in basic nanowire characterization and possible optoelectronic and gas sensor applications. Also, these results are direct experimental evidence of the effects predicted recently theoretically by Schmidt.[8]

The nanowire samples were fabricated in a horizontal reactor atmospheric pressure MOVPE system using *in situ* deposited indium droplets as seeds for nanowire growth.[3,7] Nanowires grow vertically on (111)*B* oriented InP substrates and are freestanding until removed for characterization. Some samples were immersed in 50% hydrofluoric acid (HF) for 1 min. Structural characterization of nanowires was performed using transmission electron microscopy (TEM). For photoluminescence (PL) measurements, the nanowires were detached from the substrate using clear double-sided adhesive tape. The PL measurements were carried out at 9 and 293 K. Sample excitation at 400 nm was created using a nonlinear bismuth triborate crystal at the output of a mode-locked titanium sapphire laser operating at 800 nm and a repetition rate of 76 MHz. The length of the excitation pulses was less than 1 ps, and the average excitation intensity was about 10 W cm^{-2}. A Peltier-cooled microchannel plate photomultiplier tube was used as detector in the optical measurements.

PL spectra measured from an ensemble of as-grown and HF treated InP nanowires at 9 and 293 K are shown in Fig. 1. The peak energies, widths, and relative intensities are listed in Table I. The 293 K PL intensity of HF treated nanowires is almost 100-fold compared to as-grown wires. At 9 K the HF treatment results in four times higher PL intensity. These results are in agreement with previous reports about InP surface passivation using HF containing solutions.[9,10] As the band gap energy for bulk InP at 9 and 293 K is 1.42 and 1.35 eV,[11] respectively, the as-grown nanowire emission is blueshifted by about 20 and 30 meV at 9 and 293 K, respectively. For the HF treated nanowires the blueshifts are 10 and 30 meV, respectively. This blueshift was independent from excitation intensity. It should be noted that the blueshifts seen here are lower bounds since it is possible that the local temperature on the excitation spot is higher than, e.g., 9 K, due to the low heat conductance of the adhesive tape. At 293 K the PL peak widths of as-grown and HF treated samples are almost equal (~100 meV), indicating that the
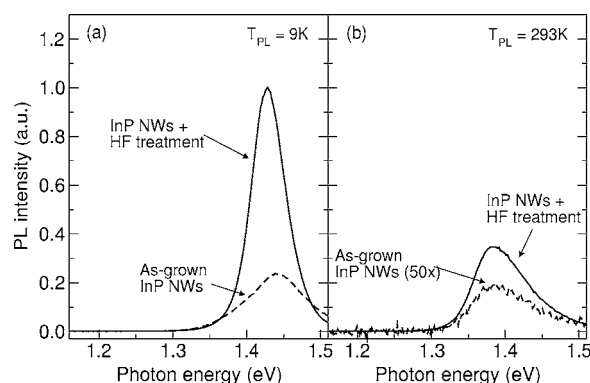

FIG. 1. Photoluminescence spectra from as-grown (dashed line) and HF treated (solid line) InP nanowires (NWs) at (a) 9 and (b) 293 K.

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TABLE I. Key figures of the PL spectra shown in Fig. 1. The PL intensity of as-grown nanowires at room temperature has been normalized to 1.

	Peak energy (eV)	FWHM (meV)	Relative intensity
As grown at 9 K	1.44	100	~60
HF treated at 9 K	1.43	58	~250
As grown at 293 K	1.38	100	1
HF treated at 293 K	1.38	90	~90

broadening is due to thermal effects. Of course, the fact that an ensemble instead of individual nanowires was measured also contributes to the PL peak width. The peak width of the as-grown sample remains the same at 9 K; however, the peak width of the HF treated sample is reduced. This is a signature effect of surface passivation.

To gain information on the carrier dynamics in the nanowires, time-resolved photoluminescence measurements were performed on an ensemble of as-grown and HF treated nanowires at 9 and 293 K. Figure 2 shows the resulting PL decay curves measured at the wavelength of maximum continuous-wave photoluminescence intensity. The background signal has not been subtracted from the data. There is clearly a significant difference in the PL decay times between as-grown and HF treated nanowires. A double-exponential function,

$$f(t) = \Gamma_1 \exp(-t/\tau_1) + \Gamma_2 \exp(-t/\tau_2) + C, \qquad (1)$$

was fitted to the data by adjusting Γ_i, decay times τ_i, and C $(i=1,2)$. The decay times can be expressed as $\tau_i^{-1} = \tau_{R,i}^{-1} + \tau_{NR,i}^{-1}$, where $\tau_{R,i}$ and $\tau_{NR,i}$ are the radiative and nonradiative decay times, respectively. Parameter C takes into account the noise background present in the measurements. Very good agreement between the fit and the data was
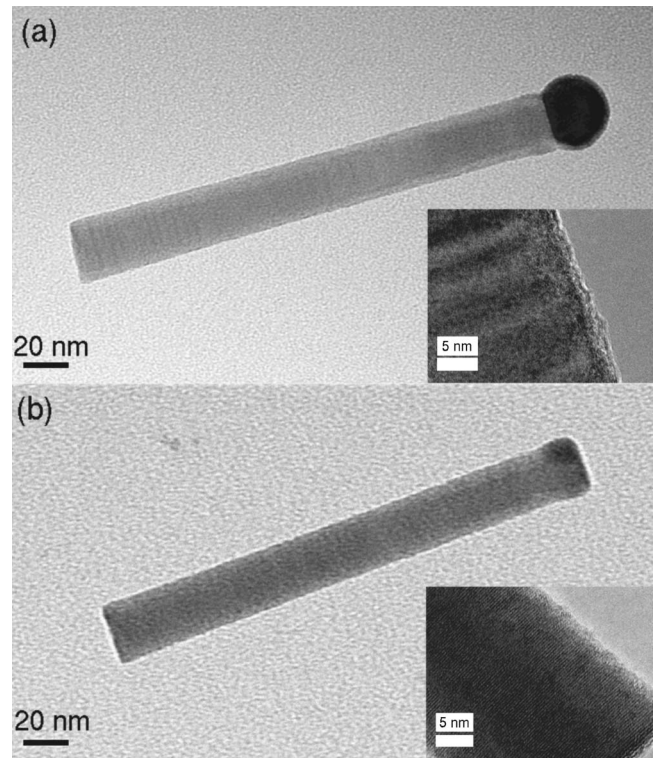
FIG. 3. TEM image of (a) an as-grown and (b) a HF treated InP nanowire. The insets show a close-up of the nanowire surface. The apparent difference in the crystal orientation between the nanowires is due to different observation angles.

achieved for the HF treated nanowires. However, there is more room for error in the fitting of as-grown nanowire data due their low luminescence intensity. Nevertheless, it was possible to extract one decay time from the as-grown nanowire data. The fitted curves and the extracted PL decay times are shown in Fig. 2.

The double-exponential decay curve shape, and thus the existence of two different decay times (τ_1 and τ_2), is probably related to band bending caused by surface states without excitation or at low excitation intensities.[12,13] The effects of band bending in InP nanowires have also been reported by van Weert *et al.*[14] At first, the bands are flattened out due to the large number of photoexcited carriers created by the high intensity excitation pulse from the mode-locked laser. At this point the charge carriers are free to diffuse to the surface of the nanowire and recombine nonradiatively via the surface states in addition to radiative recombination. This process corresponds to the fast decay observed in the data. After a while, when the concentration of photoexcited carriers has decreased, band bending prevents one carrier type from diffusing to the surface, and thus the PL decay is mainly due to radiative recombination away from the surface. The fact that the fast process is dominating in the as-grown nanowires means that either the density of surface states is higher than in the HF treated samples or that the nature of the defects is different in the as-grown and HF treated nanowires.

TEM imaging and diffraction analysis were carried out on as-grown and HF treated nanowires. The images are shown in Fig. 3. First, based on electron diffraction the nanowires have crystallized in the zinc-blende structure with the nanowire axis in the [111] direction (diffraction pattern not shown). Also, a large number of twin stacking faults were observed in the nanowires which is typical for growth in this
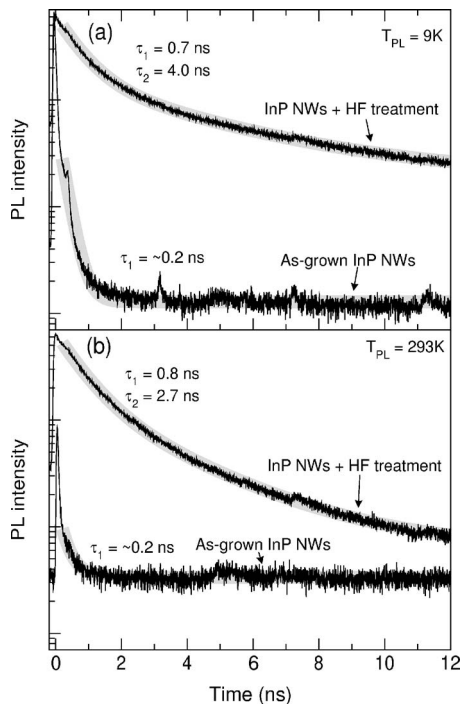

FIG. 2. Photoluminescence decay curves measured from as-grown and HF treated InP nanowires (NWs) at (a) 9 and (b) 293 K. The double-exponential fits are shown in gray.

direction,[15] although the orientation of the nanowire with respect to the electron beam is unsuitable for their observation in the images shown here. In the single-nanowire images in Figs. 3(a) and 3(b) it can be seen that the only large-scale difference between an as-grown and a HF treated wire is the absence of the In droplet after the treatment. The average nanowire diameter measured from an ensemble of nanowires is about 26 nm in both cases, with a standard deviation of 2 nm. The droplet diameter of as-grown nanowires is about 40 nm. Due to this rather large diameter of the nanowires, no blueshift with respect to bulk zinc-blende InP energy gap should be expected.[16] However, the PL results in Fig. 1 show that the nanowires exhibit a blueshift between 10 and 30 meV. Hiruma *et al.*[17] have proposed that the blueshift could be caused by a smaller effective nanowire diameter due to surface depletion. That can partially be the case here, too, since the HF treated nanowires exhibit 10 meV smaller blueshifts at 9 K than the as-grown nanowires. Another possible cause for this often-seen anomalous blueshift[16,17] could be the high density of twin stacking faults[18] or the presence of wurtzite sections in the nanowire.[19,20] However, also PL spectra from nanowires with twin stacking faults but without the blueshift have been reported.[21]

A closer look at the nanowire surface [insets of Figs. 3(a) and 3(b)] reveals no significant differences between the surface of an as-grown and a HF treated nanowire. There is a 1–2 nm thick amorphous layer visible on the surface of both nanowires. However, this layer became thicker during TEM imaging due to beam-induced damage. According to energy dispersive x-ray analysis (EDX), this layer consisted of carbon, otherwise as-grown and HF treated nanowires were stoichiometric InP. Nevertheless, we have shown that the surface treatment with HF has a significant effect on the PL intensity. As it is theoretically predicted by Schmidt,[8] a thin layer of hydrogen effectively passivates the InP surface. Such thin layers are not visible even by the high-resolution TEM used here. It has been proposed also that the passivation could be due to fluorine.[9] However, no signal from fluorine was detected here by EDX.

In summary, the optical properties of as-grown and HF treated InP nanowires were studied using continuous-wave and time-resolved photoluminescence measurements. It was found that the treatment led to a 100-fold increase in the room-temperature photoluminescence intensity and a significant increase in the double-exponential photoluminescence decay times. The longest decay time was 4.0 ns observed at 9 K. No macroscopic differences in the nanowire surface structure due to the surface treatment were observed in TEM imaging.

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