



Thermally activated luminescence in InN nanowires

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ABSTRACT

The photoluminescence from InN nanowires is known to decrease in magnitude with increasing temperature up to 300 K. Here it is shown that the luminescence reappears at higher temperatures, and continues to increase in intensity with increasing temperature up to 600 K. The high temperature luminescence has similar features as the low temperature spectrum, however the magnitude of the high temperature peaks show activated temperature dependence not observed at low temperatures. This suggests that the high temperature luminescence is due to the thermal excitation of charge from long-lived trap states into the conduction band where it then relaxes radiatively.

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1. Introduction

Indium nitride nanowires show promise for near-infrared photovoltaic and sensing applications due to their relatively low energy band-gap [1]. An ongoing challenge is the prevalence of midgap states in the nanowires [2] due to nitrogen deficiencies and surface defects. The photoluminescence (PL) spectrum of indium nitride nanowires shows a peak near 0.7 eV which has been ascribed to electron–hole recombination across the band-gap [3]. Additional transitions are also observed below the band edge at 0.5 eV [5] and 0.62 eV [4] that have been attributed to LO-phonon replica and recombination of degenerate electrons with holes trapped in low lying states [6] respectively. In addition, Hall Effect measurements [7] show that the surface carrier concentration increases exponentially above room temperature, due to thermal activation from electron trap states lying just below the conduction band edge. Evidence for these shallow lying states has not been observed optically since the energies are well below the range of standard near-IR spectroscopy techniques. Nevertheless, their presence can influence optical absorption efficiencies and opto-electronic device operation. Thermal luminescence techniques have been used to probe such shallow defect states in other material systems, such as ZnS [8] and CdTe [9].

Here, photoluminescence of indium nitride nanowires is reported for measurements made both above and below room temperature. At cryogenic temperatures, the photoluminescence

decreases with increasing temperature, as has been reported in the literature [10]. After reaching a minimum value near room temperature, the PL signal reappears with increasing temperature, showing activated temperature dependence up to 600 K. Surprisingly, the luminescence peak positions measured at high temperatures are very similar to those observed at low temperatures. The peak positions are also uninfluenced by surface passivation. This suggests that the high temperature luminescence is due to thermal excitation from long-lived electron trap states into the conduction band, where radiative recombination can occur.

2. Experimental

The InN nanowires used in this study were grown by a reactive vapor transport process [11]. A boron nitride crucible is filled with In metal and loaded on top of a ceramic heater. A quartz substrate rinsed in ethyl alcohol is then mounted on top of the crucible. Prior to growth, the In metal is cleaned with HCL to ensure synthesis of oxide free InN nanowires. The heater temperature is raised to 550 °C under a flow of Ar gas, after which NH₃ is introduced at a rate of 310 sccm. The reactor pressure is maintained at 1–2 Torr. The growth time is typically 2 h. The reactor is then adiabatically cooled to room temperature in the ammonia atmosphere. The resulting nanowires grow along *c*-crystallographic direction and have an average diameter about 50 nm and are a few microns long as shown in Fig. 1(a). Energy dispersive X-ray spectroscopy (EDS) analysis indicates the presence of In and

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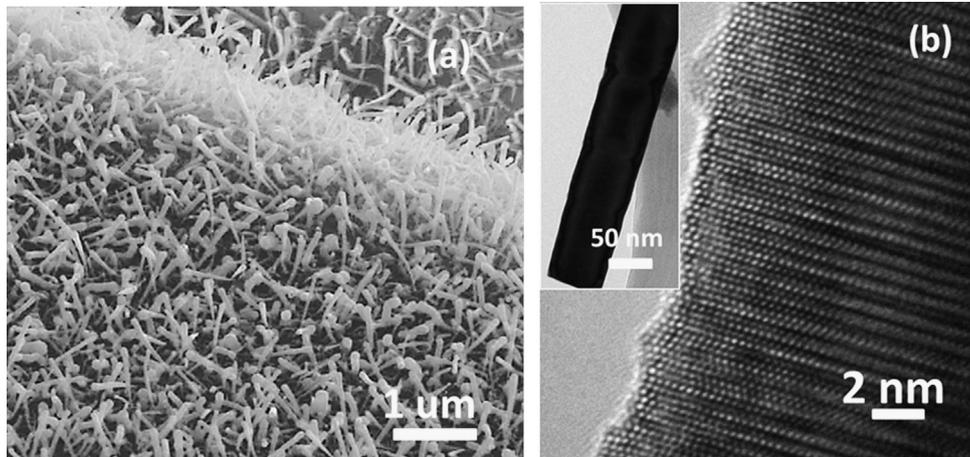


Fig. 1. (a) SEM image of an InN nanowire array on a quartz substrate. (b) [2110] high-resolution TEM image of an InN nanowire showing the *c*-axis growth direction and a high density of basal stacking faults. Inset: bright-field TEM micrograph of an InN nanowire.

N only, while the XRD measurements shows peaks corresponding to InN (shown in [Supplementary material](#)).

The photoluminescence is measured with a Renishaw RL633 spectrometer having an InGaAs detector and using 5 mW excitation from a HeNe laser emitting at 633 nm. As-grown nanowires are removed from the substrate and deposited onto a closed LINKAM THMS 600 temperature control stage which uses a combination of a heating element and liquid nitrogen cooling to allow for temperature control between 100 K and 600 K. Prior to each scan the temperature is stabilized for 10–15 min to allow the sample temperature to equilibrate. The laser spot is $\approx 1 \mu\text{m}$ in diameter so that the luminescence is detected from approximately 3–4 nanowires per measurement.

3. Results and discussion

Fig. 2(a) shows the photoluminescence spectrum measured for five different temperatures between room temperature and 90 K. Two main peaks are observed at 0.62 eV and 0.67 eV. The higher energy peak has been ascribed to the band-to-band transition while the lower energy peak is thought to be caused by the recombination of electrons with holes occupying deep level states [4]. As shown in the inset of **Fig. 3(a)**, the magnitude of the signal increases with decreasing temperature, in agreement with the temperature dependence for the PL reported in the literature [12]. **Fig. 2(b)** shows the PL spectrum measured for five different temperatures above 300 K. Once again, two main peaks are observed in the photoluminescence whose positions are virtually unchanged from those observed at low temperature. The magnitude of the 0.62 eV peak increases more rapidly with increasing temperature than the 0.67 eV peak, making the spectrum more heavily weighted toward lower energies.

Indium nitride is known to have a high concentration of mobile carriers at its surface [13], and it is possible that excitation of the plasma formed by these carriers is the source of the high temperature photoluminescence. Chen et al. observed an increase in the electroluminescence [14] of indium nitride nanowires above room temperature, and attributed this to the light emitted by the electrically excited electron plasma at the nanowire surface. In this case, the high temperature electroluminescence spectrum broadens and shifts to higher energy as the temperature increases. This agrees with the expectation that the surface plasma resonance frequency should increase as the carrier concentration on the surface increases with increasing temperature. In contrast, the luminescence spectrum that

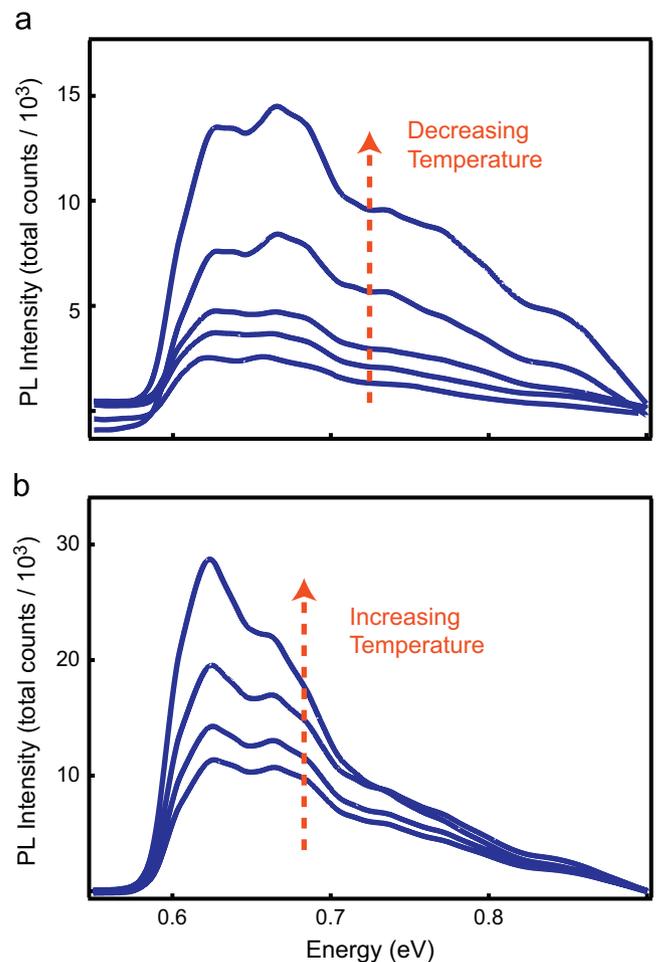


Fig. 2. Photoluminescence spectra of as-synthesized InN nanowires (a) measured from 90 K to 300 K, and (b) measured from 300 K to 643 K.

we observe becomes somewhat sharper with increasing temperature and the peak positions remain constant.

To explore the role of the surface carriers on the luminescence, indium nitride nanowires were passivated with a standard sulfur surface treatment [15]. First, to remove the native oxide layer on the surface, as-grown samples are treated with HCl, followed by a DI water rinse. The samples are then annealed in vacuum at 240 °C for 2 h, and then dipped into $(\text{NH}_4)_2\text{S}_x$ solution for one hour. Finally, the samples

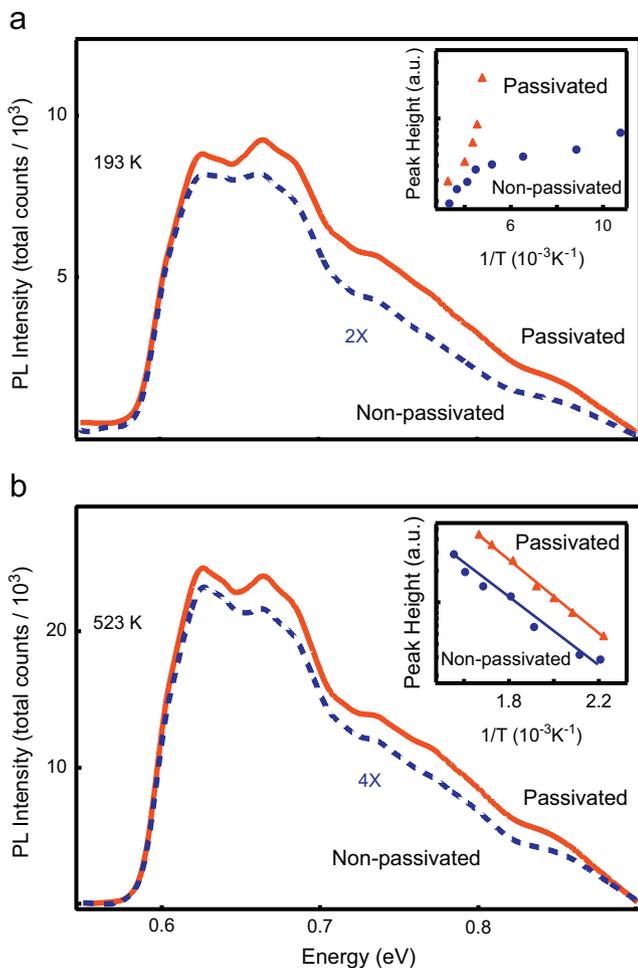


Fig. 3. (a) Photoluminescence spectra of passivated (solid) and non-passivated (dashed) nanowire samples at 193 K. Inset: Photoluminescence peak height versus inverse temperature from 90 K to 300 K. (b) Photoluminescence spectra of passivated (solid) and non-passivated (dashed) nanowire samples at 523 K. Inset: Photoluminescence peak height versus inverse temperature from 300 K to 600 K.

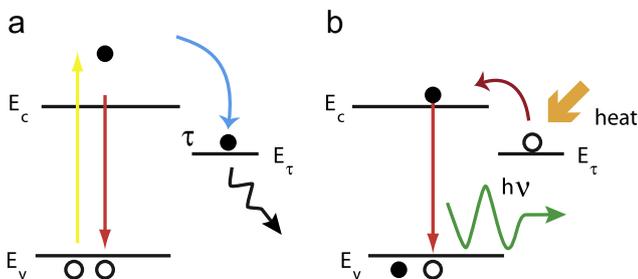


Fig. 4. Model for the observed luminescence: (a) some of the photo excited carriers are captured by long-lived trapped states close to the conduction band edge. (b) At high temperature, the trapped charge is thermally excited into the conduction band where it can radiatively recombine.

are annealed again in vacuum at 330 °C for 2 h. It has been demonstrated that this process results in a reduction in the carrier concentration on the surface of the sample as evidenced by a decrease in surface Fermi level [15]. This should result in a shift in the luminescence spectrum due to plasma emission.

Photoluminescence measurements of the surface passivated samples are shown in Fig. 3(a) and (b) for temperature below and above 300 K, respectively. The main difference between the passivated and non-passivated samples is that the PL signal increases in magnitude following passivation. This shows that the passivation reduces non-radiative recombination pathways, and increases the luminescence

efficiency. However, there is no shift in peak position as would be expected for a change in the plasma carrier concentration [16]. This result strongly suggests that the luminescence we observe is not due to plasma luminescence. Additional measurements made on TiO₂ coated InN nanowires (Supplementary material), also show that the surface layer does not have a strong influence on the high temperature luminescence spectrum.

In the inset of Fig. 3(b), the peak luminescence intensity is plotted on a log scale as a function of $1/T$ for temperatures ranging from 300 K to 600 K. The PL intensity is well described by an activated temperature dependence, with an activation energy $E_{act}=0.26$ eV. Both passivated and non-passivated samples show similar temperature dependence and activation energy. This suggests that thermal charge excitation is involved in the high temperature luminescence. An energy diagram for the proposed mechanism is shown in Fig. 4. Incident light excites electron/hole pairs above the band-gap. A percentage of the electrons relax into long-lived mid-gap states approximately 0.26 eV below the conduction band edge (indicated as E_T). Because there is no optically allowed recombination path available, relaxation from E_T to the ground state occurs slowly, and does not produce any light. Above room temperature, the charge from E_T can be thermally excited into the conduction band. Once in the conduction band, radiative recombination becomes the dominant relaxation path. If the population of thermally generated charge is greater than the loss in radiative recombination due to phonon assisted relaxation, an increase in light with increasing temperature occurs. This model predicts that the luminescence peak positions will be independent of the temperature, since the same optical transitions occur at both low and high temperature. The transition at 0.62 eV grows most quickly with increasing temperature because thermal activation occurs preferentially into the lowest energy states. This causes the narrowing of the spectrum around low energies at higher temperature. Although the precise source of the E_T states is not known, it appears to be due to a bulk defect, since it is not influenced by surface modification. These bulk defects most likely have the same origin as the shallow electron trap states identified through Hall measurements.

4. Conclusion

In conclusion, the high temperature photoluminescence of InN nanowires reveals the contribution of shallow electron trap states, lying approximately 0.26 eV below the conduction band. Surface passivation increases the luminescence intensity, but does not modify the spectral features, showing that surface carriers or defects are not the primary source for the luminescence. The strong high temperature luminescence signal suggests that a large percentage of excited carriers are captured by these defects, thus limiting luminescence efficiencies at low temperature.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jlumin.2013.03.041>.

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