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Photon upconversion in degenerately sulfur doped InP nanowires

K. Mergenthaler,*† S. Lehmann,† J. Wallentin,‡ W. Zhang,¶ M. T. Borgström,†
A. Yartsev,¶ and M.-E. Pistol†

Department of Solid State Physics/The Nanaometer Structure Consortium, Lund University, Box 118, 221 00 Lund, Sweden, Institute for X-ray Physics, University of Göttingen, Friedrich-Hund-Platz 1, 37077 Göttingen, Germany, and Division of Chemical Physics, Lund University, Box 124, 221 00 Lund, Sweden

E-mail: kilian.mergenthaler@ftf.lth.se

Abstract

Radiative recombination in degenerately n-doped InP nanowires is studied for excitation above and below the Fermi energy of the electron gas, using photoluminescence. Laser-induced electron heating is observed, which allows absorption below the Fermi energy. We observe photon upconversion where photo-excited holes recombine with high |k|-values, and the temperature dependence of this process is measured. We show that hole relaxation via phonon scattering can be observed in continuous wave excitation luminescence measurements.

Introduction

The relaxation of photo-excited carriers in semiconductors is highly relevant for the development of optoelectronic devices and has been extensively investigated, both theoretically and experimentally.¹⁻⁵ However, for intrinsic semiconductors the measured results contain averaged data over the electron and hole distribution⁶ and the electron response typically dominates the measured signal.² Consequently the electron relaxation process is relatively well characterized, but comparably little is known about hole thermalization dynamics. These obstacles are circumvented when studying highly n-doped semiconductors where the radiative recombination is limited by photo-excited holes and the emitted photon energy is strongly determined by the hole relaxation process. The hole relaxation process may involve scattering to higher |k|-values, which for a range of excitation wavelength in highly n-doped sample leads to emission of photons with higher energies than the absorbed photon: i. e. photon upconversion.

Photon upconversion can occur through different physical mechanisms⁷ and is of significant technological importance for the realization of upconversion lasers,⁸ for biological imaging,⁹ and for infrared detection.¹⁰ Examples for upconversion mechanisms are: the simultaneous absorption of two photons, the sequential absorption of several photons, for instance via electronic states in the semiconductor bandgap, and the thermal excitation of charge carriers where the emission energy is within a few kT of the excitation energy.¹¹ Photon upconver-
sion has so far been realized in zero-dimensional systems such as quantum dots and in two-dimensional systems such as type II heterojunctions, CdS nanoribbons, and GaAs quantum wells. Recently we reported on an efficient new upconversion (UC) mechanism in degenerately n-doped InP nanowires. The UC mechanism relies on the absorption of photons with energies less than the Fermi energy of the degenerately doped material, followed by recombination of the photo-excited holes with electrons with higher $|k|$-values than the photo-excited electron. In this work we demonstrate, that the reported UC mechanism is not only of potential technological interest, but also allows the exploration of hole relaxation processes in heavily doped semiconductor materials during continuous wave excitation. We show that the UC in highly doped nanowires is determined by scattering of the photo-excited holes to higher $|k|$-values, in which absorption of optical phonons is the dominating scattering process. Charge carriers are confined in nanowires and we expect that laser heating of carriers is easier than in bulk facilitating absorption into an electron gas.

### Experimental Methods

The nanowires for this study were grown in a low-pressure (100 mbar) metal organic vapor phase epitaxy (MOVPE) system with trimethylindium (TMIn), phosphine (PH$_3$) and dihydrogensulfide (H$_2$S) as precursors utilizing the vapor-liquid-solid method whereby gold aerosol particles were used as a catalyst. More details on the growth can be found in Ref. 18. From the state filling related blue-shift of the high energy side of the luminescence spectra, the doping concentration was estimated to be $3 \cdot 10^{18}$ cm$^{-3}$ to $8 \cdot 10^{18}$ cm$^{-3}$. A zinc blende (ZB) dominated crystal structure with stacking defects was confirmed by transmission electron microscopy (TEM) analysis.

For optical measurements the nanowires were mechanically transferred onto thin gold layer covered silicon substrates which, for the photoluminescence measurements (PL), were mounted on the cold finger of a continuous flow liquid helium cryostat system. The samples were optically excited by a continuous wave (cw) frequency doubled solid state laser emitting at 532 nm (2.33 eV) or a tunable optically pumped cw Ti:Sapphire laser. The laser light was focused on the sample reaching a maximum power density of about 400 W/cm$^2$. For measurements close to the laser line a triple stage monochromator was used where the first two stages were used as a tunable band pass filter and the last stage dispersed the emission on a charge-coupled device (CCD) camera. A mechanical chopper was used to lower the average excitation power density. The chopper lowered the total transmission to 8%.

### Laser heating

The upconversion process studied in this paper is based on absorption of photons with energies lower than the difference between the electron Fermi energy and the valence band maximum. This is allowed in two cases: if the conduction band electron gas is hot and thus contains empty states, or if the sample has a spatially varying doping concentration and thus a spatially varying valence band maximum energy. Recent studies of doping concentrations in nanowires reported on spatially varying doping concentrations along the wire axis. For large-energy-shift upconversion based on doping level fluctuations the doping level gradient must be very steep. It requires absorption in non-degenerately doped material followed by spatially indirect recombinations of the hole with electrons in a heavily doped region or drift of the photo-excited holes from the non-degenerately doped region into a neighboring heavily doped region. Such steep doping concentration changes are not expected for samples grown with constant doping precursor flow and spatial diffusion of the holes is negligibly small at the timescale of hole life times.

For upconversion relying on absorption below the electron Fermi energy the temperature of the electron gas is a crucial factor. The ab-
sorption depends on the number of un-occupied conduction band states and to reach, for example, a fraction of $10^{-6}$ unoccupied states 50 meV below the Fermi energy, an electron gas temperature of at least 42 K is required. More discussion on the temperature dependent absorption can be found in the supplementary information.

To study the laser induced change of the electron temperature, we performed laser intensity dependent PL measurements. The results of such a measurement are shown in Figure 1 (a) where the laser intensity was changed within seven orders of magnitude. The high energy side of the spectra becomes steeper for lower excitation intensities. Since the Fermi-Dirac distribution is a main contributor to the shape of the high energy tail, the electron temperature can be estimated from the steepness using a fitting procedure. The spectra were fitted with a parabolic density of states multiplied by a Fermi-Dirac distribution and convoluted by a Gaussian broadening peak. 4 K was chosen as lower limit of the temperature variable, because the measurements were performed at liquid helium temperature. More details on the fitting procedure can be found in the supplementary information.

The calculated electron temperatures for all laser intensities are depicted in Figure 1 (b) as a function of the relative laser intensity. The clear onset at about 1 % of the highest laser intensity shows the effect of laser heating and a laser-induced shift of the Fermi energy to higher energies. For intensities below 1 % of the highest laser intensity, no qualitative change of the spectrum was observed, meaning that the number of photo-generated electrons is too small to contribute significantly to the temperature of the conduction band electrons.

The dependence of the integrated luminescence intensity on the excitation power density can be expressed by the relation $I \propto P^{\alpha}$, where $I$ is the PL intensity, $P$ is the excitation power density, and $\alpha$ is a parameter. From a power law fit to the experimental data shown in Figure 1 (b) $\alpha = 0.5$ was determined. $\alpha < 1$ is usually attributed to three particle Auger generation-recombination processes,\textsuperscript{19} and thus is consistent with an Auger electron gas heating

Figure 1: Laser intensity dependence at a cryostat temperature of 4 K: (a) Normalized PL spectra with increasing laser intensity ($\lambda = 750$ nm, 1.65 eV) from bottom to top. (b) Integrated PL intensity and electron temperature. The latter was calculated from PL spectra using a parabolic density of states multiplied by a Fermi-Dirac distribution and convoluted by a Gaussian broadening peak as fitting function. 4 K was set as lower temperature limit. The width of the broadening was assumed to be a sample specific constant, which was fitted for the lowest laser intensity and then kept constant for the other laser intensities.
process driven by absorbed laser photons.

Figure 2: Normalized PL spectra measured at 8% of the full laser intensity ($\lambda = 532$ nm) using a gray filter (blue spectrum) or a chopper (red spectrum) to reduce the average laser intensity. The cryostat temperature was 4 K.

To further investigate the influence of the laser intensity on the electron temperature we compared cw excitation PL measurements with chopped excitation with similar average heat load. The spectra are shown in Figure 2. Both spectra were measured at about 8% of the full laser intensity. For the blue spectrum in Figure 2 a gray filter was used to lower the intensity, while for the red spectrum a chopper was used, which generated pulsed excitation with an average intensity equal to about 8% of the full laser intensity. The average heat load was thus the same in both experiments, but the instantaneous excitation power density was about 12 times higher when using the chopper.

The spectra in Figure 2 are normalized to allow a better comparison of the spectral shape. Before normalization the luminescence intensity for pulsed excitation was about one fifth of the intensity with cw excitation. While the spectral shape below the peak maximum is identical for both excitation methods there is a clear difference at higher photon energies. From fits of the spectra we calculated that the Fermi level was only about 5 meV higher when the chopper was used, but the electron gas temperature was increased about 10 K.

We thus conclude that the luminescence during the laser pulse originates from an Auger-heated non-equilibrium electron gas, while for cw excitation the electron gas is in a quasi-equilibrium state with (but possibly at a higher temperature than) the crystal lattice. The electron gas temperature difference of only about 10 K (compare with about 100 K at comparable intensities in Fig. 1 b) and the five-times higher intensity for cw excitation, show that the electron gas relaxes to a much lower temperature between the laser pulses and that most of the absorbed pulsed laser energy is heating the electrons rather than causing radiative recombination.

Previous investigations have shown that the upconversion is not caused by two-photon absorption.\textsuperscript{16} We will argue that a high electron temperature allows excitation into the electron gas. A temperature-dependent momentum change of the holes, due to optical phonon scattering, will then cause the upconversion. Figure 3 shows PL spectra of nanowires as a function of temperature. We show spectra, both for excitation above the Fermi energy (2.33 eV) as well as for excitation directly into the electron

Figure 3: Normalized PL spectra for different cryostat temperatures. (Light gray) for 532 nm laser excitation, (color) for excitation with a tunable laser, where the laser photon energy was adjusted to the PL peak energy for 532 nm laser excitation. The excitation energy is indicated with a vertical line.
gas. The tunable laser energy was chosen to be at the luminescence maximum (for 532 nm laser excitation), which compensates for the temperature dependence of the band gap. The upconversion intensity at 4 K is comparably low, but its existence implies an electron gas heating similar to the laser heating presented in Figure 1, even for low energetic laser photons, but with lower effect.

The intensity of upconverted luminescence increases strongly with increasing temperature (as shown later), but even more interesting is the shift of the luminescence maximum to lower energies compared to 532 nm laser excitation (fig. 3). For excitation into the electron gas we observe a negative slope right below the laser energy even if there was a positive slope at that energy for 532 nm excitation. The strength of this effect is more pronounced at lower temperatures and becomes less significant for temperatures above 100 K. To verify that the observed sign change of the slope is not simply an artifact related to the laser energy, we measured the laser energy dependence of the luminescence at 4 K, which is shown in Figure 4 (a). As a way to quantify the observed slope change, we calculated the ratio of the slopes in the respective luminescence spectra about 28 meV below the laser energy and at around 1.400 eV. As comparison the identically calculated slope ratios of the same energy regions were calculated for the spectrum with 750 nm excitation. These relative local slopes are plotted in Figure 4 (b) together with the spectrum measured with 750 nm excitation. For laser energies above the Fermi energy the relative slopes are very similar, but below the Fermi energy there is a big difference and a sign change for laser energies below the 750 nm peak maximum until the laser energy is less than one optical phonon energy higher than the band gap. To explain this effect we will, in the following, discuss the hole relaxation processes in degenerately n-doped semiconductors.

Figure 4: Laser energy dependence at a cryostat temperature of 4 K: (a) Normalized PL spectra with increasing laser energy from bottom to top. (b) the relative local slopes of the spectrum with 750 nm (1.65 eV) excitation and the relative slopes for excitation with 770 nm, 790 nm, 810 nm, 830 nm, 850 nm and 870 nm. The slope was calculated around the photon energy of detection, which was 28 meV below the laser energy, and normalized by the slope around 1.40 eV of the respective spectrum.
Hole relaxation

In the highly degenerate n-type doped InP nanowires the hole relaxation process is of utter importance for the electron-hole recombination process, since the recombination is determined by energy and momentum of the hole. Photo-excited holes relaxe via scattering and the main scattering mechanisms are ionized impurity scattering, optical phonon scattering, acoustic deformation potential scattering and carrier carrier scattering. We will argue that scattering with optical phonons is responsible for both the peak shift in downconversion as well as for the upconversion. We will support our hypothesis by experiments.

One possible reason for photon upconversion is inelastic scattering of the photo-excited hole to higher energies. In highly doped materials ionized impurity scattering is the dominant scattering mechanism, however, due to the elastic nature of this process the hole does not change its energy in the scattering process. The most important inelastic hole scattering mechanism is the scattering with optical phonons. For hole energies more than the optical phonon energy below the VBM, the emission of phonons dominates. However, for holes with energies less than the optical phonon energy below the VBM the phonon emission is energetically forbidden and the absorption of optical phonons has the highest inelastic scattering rate at temperatures above 100 K. The scattering with acoustic phonons is important at low temperatures and for hole energies less than the optical phonon energy below the VBM, where it is at all temperatures the dominating scattering process for hole energy relaxation.

Hole-hole scattering can be neglected for low hole concentrations and due to the short carrier life-times in highly doped InP material. Electron-hole scattering plays only a minor role in hole energy relaxation because: For heavy holes the significant difference in effective masses between holes and electrons makes the hole energy gain negligible. For light holes the similar effective masses between holes and electrons makes an average energy transfer from electrons to holes unlikely. And, above about 100 K electron-hole scattering can be neglected in comparison to the other scattering mechanisms. In summary, hole energy change through inelastic scattering is not sufficient to explain the observed high energy upconversion.

The laser energies for the luminescence results shown in Figure 3 allow transitions from the heavy hole band and the light hole band to the conduction band, however the energy was too low to excite holes to the split-off band. We will thus neglect holes in the split-off band in the following discussion. Transitions from the heavy hole band create hole energies less than the optical phonon energies below the valence band maximum while transitions from the light hole band leave a hole more than one E\textsubscript{LO} from the valence band maximum.

A second possible reason for photon upconversion is scattering of the photo-excited holes to higher |k|-values. For elastic and nearly elastic scattering such as scattering with ionized impurities and acoustic phonons, inter-subband scattering causes no, or very little change of |k| for isotropic hole effective masses. Intersubband phonon scattering changes the hole energy by the energy of the absorbed or emitted phonon and the influence on the |k|-value depends on the hole mass. For light holes the change of |k| is rather low and it enables upconversion of not more than about two phonon energies above the absorbed photon. For heavy holes the scattering with (optical) phonons has a much stronger effect and phonon absorption scatters holes to high |k|-values.

Intra-band scattering has, due to the mass differences between the heavy and the light hole band, a strong effect on the energies of the emitted photons. We illustrate these effects in Figure 5, where the bands are computed using realistic effective masses and the Fermi level energy is taken from our experiments. The rates for scattering from the light hole band to the heavy hole band is almost always higher than the reversed process and scattering from the light to the heavy hole band typically leads to holes at very high |k|-values. The high |k| holes can recombine with electrons in the conduction band and emit photons with a higher energy than the absorbed photon energy. Scattering
Figure 5: Illustration of different scattering paths involving optical phonons. The figure is to scale (effective masses and band edge energies for ZB InP were used), apart from the bandgap which has been decreased for clarity. The absorbed photon energy is 1.52 eV and the optical phonon energy was taken to be 42.6 meV, which corresponds to the LO phonon energy. We neglect the $k$ dependence of the LO phonon energy and the carrier masses. Left panel: If holes are created in the light hole band, they may scatter to lower energy by emission of an optical phonon causing downconverted luminescence. Absorption of an optical phonon causes scattering to the light hole band or to the heavy hole band and both can be seen as photon upconversion, but only scattering to the heavy hole band enables photon emission at energies much higher than the absorbed photon. Right panel: Illustration of holes created in the heavy hole band. Scattering by optical phonons can only cause photon upconversion.
with optical phonons can also cause downconversion if the hole is in the light hole band. The discrete hole energy change of such scattering is visible as reduced luminescence intensity right below the laser. Downconversion caused by optical phonon scattering cannot occur if the hole is in the heavy hole band.

Figure 6: Integrated upconversion PL intensity divided by the integrated downconversion intensity of the spectra shown in Figure 3 (a) and phonon absorption rate divided by phonon emission rate calculated from Equation 1.

The temperature dependence of the phonon absorption versus emission ratio can be calculated from the phonon occupation via

$$P_{\text{abs}} \over P_{\text{em}} = \left( \frac{E_{\text{laser}} + E_{\text{ph}}}{E_{\text{laser}} - E_{\text{ph}}} \right)^4 \exp \left( -\frac{E_{\text{ph}}}{k_B T} \right).$$

Where $E_{\text{laser}}$ is the laser photon energy, $E_{\text{ph}}$ the phonon energy, $k_B$ the Boltzmann constant and $T$ the absolute temperature. The results of this equation are plotted in Figure 6 together with the relative integrated upconversion intensity of the PL spectra shown in Figure 3 (a). The comparison shows a qualitative agreement with an onset below 100 K which indicates a strong dependence of the upconversion efficiency on the phonon absorption rate. For a fully quantitative comparison the calculation of the relative phonon absorption rate is insufficient since it neglects for example other scattering mechanisms and the energetic position of the laser relative to the band edge and the Fermi energy. Nevertheless, the agreement between theory and experiment support our hypothesis that scattering of holes from low to high momenta by optical phonons cause the observed upconversion.

Figure 7: Excitation intensity dependence of integrated upconversion (UC) and downconversion (DC) intensity for 840 nm (1.48 eV) laser excitation, measured at 4 K.

In Figure 1 we showed the laser intensity dependence of the integrated PL intensity for excitation above the Fermi energy. Figure 7 shows in a similar plot the integrated upconversion and downconversion intensity for excitation below the Fermi energy. At high laser intensities both the upconversion and the downconversion intensity saturate (see also previous work\(^\text{16}\)) when the absorption of laser photons exceeds the stimulated emission and state filling suppresses an increase of absorption. Below the saturation upconversion and downconversion show a very different slope and from power law fits $\alpha = 0.7$ was retrieved for downconversion and $\alpha = 1.34$ for upconversion. The difference shows different dominating processes: The downconverted luminescence is dominated by Auger generation-recombination processes ($\alpha < 1$),\(^\text{19}\) but the upconverted luminescence is dominated by Shockley-Read-Hall processes ($\alpha > 1$),\(^\text{19}\) processes which may be caused by the absorption or emission of phonons.\(^\text{23}\) This agrees well with our proposed mechanisms for upconversion and downconversion.
Summary and Conclusions

We find that laser induced heating of the conduction band electrons in degenerately doped semiconductor nanowires enables absorption of photons with energies lower than the Fermi energy. Such absorption can create a hole in the light or the heavy hole band with $|k| < |k_F|$. We find that these hole may scatter to higher $|k|$-values and thus allow $k$-conserving recombination with energies higher than the energy of the absorbed photon, i. e. we have photon upconversion. By measuring the temperature dependence of the luminescence we identified absorption of phonons as the dominating process for this photon upconversion mechanism for sample temperatures higher than 100 K. The observed photon upconversion at temperatures below 100 K, where phonon absorption is strongly suppressed, shows that other scattering mechanisms contribute as well. These scattering mechanisms contribute only weakly although almost all scattering (even elastic scattering) from the light hole to the heavy hole band leads to photon upconversion.

At temperatures below 100 K and hole energies higher than the optical phonon energy the emission of optical phonons is the dominating hole relaxation process. This is visible in continuous wave PL spectra as suppressed luminescence close to the laser energy. At higher temperatures, and thus higher phonon occupation numbers the suppression disappears as scattering to higher $|k|$-values distributes the holes over a wider range in reciprocal space.

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