Photon upconversion in highly doped InP substrates

Kilian Mergenthaler

kilian.mergenthaler@ftf.lth.se

FFF042: The Physics of Low-Dimensional Structures and Quantum Devices

December 2014
I. INTRODUCTION

In photoluminescence measurements (PL) a laser with a photon energy higher than the bandgap is used to excite electron-hole pairs in the studied semiconductor material. The luminescence is then typically detected at energies lower than the laser photon energy because, at first view, the detection of photons with higher energies seems to violate the laws of thermodynamics. However, there are some processes which create photons with higher energies than the absorbed photon, so called upconversion (UC) mechanisms\(^1\). One example of such a process is the absorption of two photons simultaneously or via an intermediate electronic state. Another example is the thermal excitation of photo-generated charge carriers or the absorption of phonons. The latter is for example seen as anti-Stokes lines in Raman measurements.

Additionally to the scientific interest UC mechanisms have several technological applications: For example upconversion lasers\(^2\), biological imaging\(^3\), and infrared detection\(^4\).

Recently a new UC mechanism was discovered in degenerately n-doped InP nanowires\(^5\), which relies on the absorption of photons with energies lower than the Fermi energy and the recombination of the photo-excited holes with electrons with higher |\(k\)|-values than the photo-excited electron. The purpose of this project was to investigate if this process is restricted to nanowires or if it can also be observed in degenerately doped InP bulk samples.

II. EXPERIMENTAL METHODS

The previously studied InP nanowires were grown by metalorganic vapor phase epitaxy (MOVPE) and n-doped with varying concentrations of sulfur (S). The studied bulk materials were commercially available S-doped n-type InP with donor concentration \(n = 6 \cdot 10^{18} \text{ cm}^{-3}\) and zinc (Zn) doped InP with acceptor concentration \(p = 3.4 \cdot 10^{18} \text{ cm}^{-3}\). The samples were optically characterized by photoluminescence spectroscopy (PL) and photoluminescence excitation spectroscopy (PLE). For the PLE measurements a tunable pumped Ti:Sapphire laser was used which enables photon wavelength from 750 nm (1.65 eV) up to 1000 nm (1.24 eV). For PL measurements the same laser was used low photon energy excitation and for high energy excitation a frequency doubled solid state laser emitting at 532 nm (2.33 eV). The measurements were performed at room temperature.

III. UPCONVERSION IN NANOWIRES

UC in highly doped semiconductor material was first discovered in highly sulfur doped InP nanowires\(^5\). An example of UC PL in such nanowires is shown in Figure 1, where the blue curve shows the more classical PL with excitation far above the detected luminescence and the lower curve shows the luminescence for excitation with laser energies below the Fermi energy: Luminescence is visible on both energy sides of the laser and the luminescence above the laser energy is the upconverted luminescence.

Here the upconversion process is based on absorption of photons with energies lower than the Fermi energy, which requires a hot conduction band electron gas. The ambient temperature is not high enough to enable the observed high energy UC, however the laser photon flux provides additional energy to the electron gas. The effect of laser heating is shown in Figure 2 (A) where the depicted PL spectra were measured with increasing laser intensity from bottom to top. It is clearly visible that the slope of the high energy side of the spectra is much steeper for low laser intensities and that it becomes less steep for higher laser intensities. The slope of the high energy side of the spectra is strongly determined by the Fermi distribution of the electrons and from a fit of the spectra with a Fermi distribution multiplied by a parabolic density of states the electron temperature can be calculated. The results of such calculations are shown in Figure 2 (B). For low laser intensities the electron temperature does not change with increasing laser intensity and the luminescence spectrum shows the equilibrium peak width without strong influence of the laser photon absorption. Around 1 % of the full laser intensity the region with strong laser heating begins and the intensity of the laser drastically changes the temperature of the electron gas.

In highly n-doped semiconductor material the recombination of charge carriers is limited by the number of photo-excited holes. The photo-excited electrons play only a minor role due to the large number of conduc-
upconversion in nanowires

Fig. 2: Laser intensity dependence: (A) Normalized PL spectra with increasing laser intensity ($\lambda = 532$ nm) from bottom to top. (B) electron temperature calculated from the spectra using as fitting function a parabolic density of states multiplied by a Fermi-Dirac distribution and convoluted by a Gaussian broadening peak. $4 \text{ K}$ was set as lower limit and the width of the broadening was calculated for the lowest laser intensity and then kept constant for the other laser intensities.

Fig. 3: Schematic image of absorption of $1.42 \text{ eV}$ photons in InP and the relaxation of the photo-excited light hole via LO phonon scattering. Scattering from the light to the heavy hole band by absorption of LO phonons creates high $k$ heavy holes. The phonon assisted transitions are indicated by green arrows. InP ZB masses were used for the bands. Band gap is not in scale.

doped materials ionized impurity scattering is the dominant scattering mechanism followed by scattering with optical phonons and then by scattering with acoustical phonons. The hole-electron scattering probability is typically comparably low and hole-hole scattering can be neglected in n-doped semiconductors due to low hole concentration and short life-time in highly doped material.

The scattering with ionized impurities can be considered to be elastic, which means the hole only changes its $|k|$-value, but not its energy during the scattering event. In scattering with phonons the hole changes $|k|$-value and gains or loses the energy of one phonon. In case of acoustical phonons the energy transfer is quite low and for optical phonons the energy transfer is $42.6 \text{ meV}$ and $38.1 \text{ meV}$ for LO and TO phonons, respectively. This also means that if the hole energy is less than one phonon energy lower than the valence band maximum the energy relaxation via emission of such a phonon is not possible. For example if the hole has an energy less than $42.6 \text{ meV}$ below the valence band maximum it cannot emit one LO phonon.
Intra-band scattering with ionized impurities and acoustical phonons does not lead to upconversion and upconversion from intra-band optical phonon scattering would only give peaks integer multiples of the optical phonon energy away from the laser energy. However, scattering from one valence band to another, for example from the light hole band to the heavy hole band, drastically changes the holes $|k_j|$-value and $k$-direct recombinations with conduction band electrons can have energies much larger than the absorbed photon. Figure 3 shows schematically the absorption of a photon with an energy \( E_{\text{laser}} \) lower than the Fermi energy \( E_F \) and one set of possible scattering transitions for light hole scattering with an LO phonon. For photon absorption from the heavy hole band the shown laser photon energy creates photo-excited hole less than one LO phonon energy away from the valence band maximum and energy relaxation via emission of one LO phonon is not possible. For photo-excited light holes the absorption and the emission of LO phonons is allowed and these transitions are shown as green arrows in Figure 3.

A comparison of the different scattering rates\(^6\) supports the theory that hole scattering to higher $|k_j|$-values can be the reason for upconversion in highly doped semiconductors: 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 $|k_j|$-values. These high-$k$ holes can recombine indirectly with electrons in the conduction band or during the inter-band energy relaxation process recombine directly with conduction band electrons with similar $|k|$-values.

**IV. UPCONVERSION IN BULK**

A literature study did not yield any reports on upconversion in bulk semiconductors and hence the upconversion was thought to be a nanowire specific feature. The PL measurements on a highly n-doped InP substrate seen in Figure 4 show that this is not the case: Photon upconversion is not limited to small dimensions, but also present in bulk semiconductors and from similar upconversion results observed in the studied p-doped InP substrate, it can be concluded that upconversion is a more general feature of highly doped semiconductors. Figure 4 shows the normalized PL spectra for different laser photon energies with increasing energies from bottom to top. All spectra exhibit a InP bandgap related peak around 1.32 eV and for higher laser photon energies the spectra additionally exhibit a broad state filling related peak with photon energies up to 1.5 eV.

Such a disappearance of the state filling related peak for lower laser photon energies was not observed for UC in nanowires (see Fig. 1) and is probably caused by a lower laser heating effect in bulk material. The excitation laser spot size can be in the order of hundreds of micrometer, but is usually not lower than about five micrometer, which means it is bigger than the nanowire. Thus, in nanowires the whole material is optically excited whereas in bulk material the heated sample spot is surrounded by a lower temperature reservoir. For higher laser energies the hole scattering with ionized impurities and acoustical phonons strongly contributes to the upconversion, but at low laser energies the absorption of optical phonons is the scattering mechanism that supports sufficient energy to scatter holes to $|k|$-values above the $|k|$-value of the Fermi energy \( k_F \). In bulk material the phonons can propagate away from the excitation volume, but in nanowires they are confined by the nanowire dimensions.

One interesting question about upconversion in highly doped bulk material is: why is there absorption with laser photon energies lower than the Fermi energy? In text books it is stated that the state filling causes the absorption edge to shift to higher energies with increasing doping concentration, the so called Burstein-Moss effect. Elias Burstein discovered the effect when he measured the absorption of highly n-doped InSb material where he observed a shift of the absorption edge to higher energies with increasing doping concentration,\(^7\) the so called Burstein-Moss effect. A second effect that influences the absorption edge is the bandgap renormalization which slightly lowers the bandgap with increasing doping concentration. A third effect is visible in some published absorption data (for example\(^8,9\)), but is usually not discussed. The absorption data show an increase towards lower photon energies, which gets more pronounced with increasing doping concentration. This effect is probably caused by absorption from the impurity band.

Absorption from the impurity band can be seen as local heating of the conduction band electron gas, which creates holes at energies very close to the conduction band minimum. Such conduction band holes allow the absorption of photons with energies much lower than the Fermi energy.
V. SUMMARY AND OUTLOOK

The measurements performed during this project showed that photon upconversion in highly doped semiconductors is not limited to nanometer-sized samples, but is a more fundamental property of highly doped semiconductors. Highly sulfur doped InP substrates were studied and showed photon upconversion for laser energies from 1.31 eV up to 1.46 eV. The change of the spectral shape of the upconversion was explained by the different scattering mechanisms of the photo-excited holes. The photon upconversion allowed to compare DC and UC PLE measurements with detection below, respectively, above the laser energy. The two PLE measurements showed very different spectra and the difference could be caused by the domination of \( \mathbf{k} \)-direct transitions.

For validation or falsification of the model of the upconversion mechanism the measurements should be repeated for low temperature and for samples with different doping concentrations. Furthermore, different semiconductor materials should be measured to verify that photon upconversion is not limited to InP. If this upconversion mechanism exists in all semiconductor materials it can be used to reveal more details about the charge carrier relaxation and the energetic band structure of semiconductors.