Optical manipulation of excitation paths in RE-doped semiconductors

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We report on experimental verification of the proposed energy transfer mechanism responsible for photoluminescence of rare earth ions in semiconductors. Using two-color optical spectroscopy in the visible and the mid-infrared region, we demonstrate reversal of the most important step in the excitation process. This "back-transfer" effect was supported experimentally only in an indirect manner by measurements on thermal quenching of PL intensity and lifetime. In the current study on InP:Yb, formation of the intermediate state bridging atomic states of the RE ion and extended orbitals of a semiconducting host is explicitly confirmed and its characteristic energy spectroscopically determined. This finding will allow optimization of the efficiency of semiconductor:RE systems for applications.

Introduction

Semiconductors, which are doped or grown with rare earth (RE) -ions, have been a topic of study for many years. Due to the isolated character of the 4f-shell of RE-ions (which is surrounded by filled 5s- and 5p-shells), transitions from the excited states of this shell are generally energetically well-defined, which leads to spectroscopically sharp lines in the spectrum of RE's. The successful use of RE's in large bandgap semiconductors and insulators for the fabrication of laser systems have inspired people to take a similar approach with semiconductor:RE systems. While in an insulator and a large bandgap semiconductor excitation of the RE ion occurs in a direct manner (by optical pumping), excitation of the RE ion in a semiconductor host is accomplished via the host material. This indirect excitation pathway is believed to be similar for different combinations of semiconductor- and RE-species. The general model describes the RE-ion forming a (RE-related) level in the bandgap of the host. This level can bind a electron-hole pair, either by capturing an exciton or in a two-step process where a second carrier is attracted by the Coulomb force of a first carrier of opposite charge, captured at the RE-related level. Recombination of the pair provides the energy needed for excitation of the RE-ion into one of its excited states. Subsequent radiative decay of this state leads to photoluminescence (PL) from the RE-ion. The mismatch, which will generally exist between the recombination energy and the energy of excitation of the RE, is lost in a multi-phonon process. If this energy is supplied to the system when the RE-ion is in an excited state, it is generally believed that also the reverse of this excitation can occur, a process called (energy) "back-transfer". In this case, the excited RE-ion de-excites, and an electron-hole pair is formed on the RE-related level. This process is held responsible for the decreases in PL from RE-ions in semiconductors observed at elevated temperatures and hampers the construction of devices operating at room temperature. Although generally accepted, evidence for the model described above and, specifically, the "back-transfer" mechanism originates primarily from (indirect) measurements on thermal quenching of PL intensity and lifetime of the investigated RE-ions [1]. In this contribution, we describe how we have successfully used high-intensity mid-infrared radiation from a free-electron laser

(FEL) to induce the normally thermally activated "back-transfer" process, by tuning the FEL to the appropriate light quantum. In this way, we obtain spectroscopic information about the energy needed in this excitation-reversal mechanism which can be compared to theoretical predictions.

Experimental setup

The experiments were performed on p-type InP doped with Yb. Following a band-to-band excitation with a 100 ps pulse from a Nd:YAG laser (532 nm), PL from Yb^{3+} could be observed at 1 μm, corresponding to transitions from the first (and only) excited state of the 4f-shell of the Yb-ion (see fig.1).

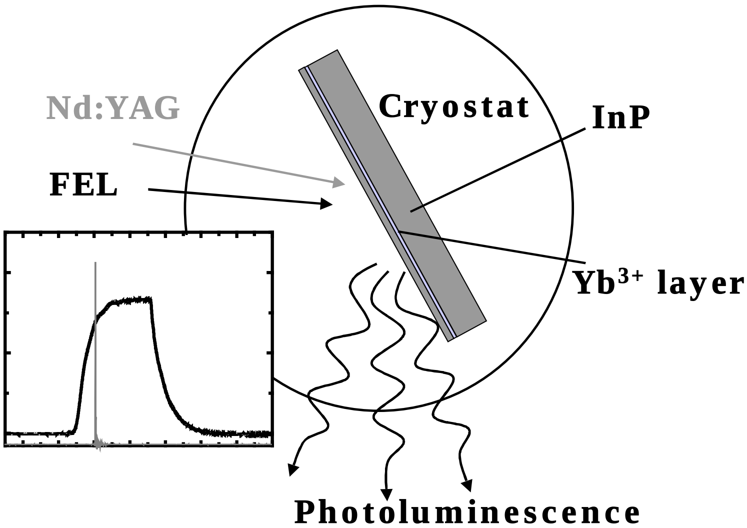

Fig.1 The InP:Yb sample is illuminated with both a Nd:YAG and a FEL laser. The sample is positioned in a flow-cryostat and kept at 4 K. The inset displays the time-relation between both laser pulses.

This PL was gathered with a system of lenses, dispersed with a single grating monochromator and measured with a photo-multiplier-tube with a flat response between 300 and 1600 nm. After a tunable delay, a second beam of pulse duration 4-6 μs from the FEL was activated to illuminate the same area on the sample as the Nd:YAG pulse. The FEL can be set to produce light with energy quanta of 65 to 175 meV. The photon density in the beam varies greatly with the selected wavelength, which has to be taken into account while analyzing dependencies on photon energy. It is known that Yb^{3+} forms an acceptor-like electron-trap about 30 meV below the bandgap of the InP host [2]. This trap captures an electron and subsequently binds a hole due to the resulting Coulomb potential. The binding energy of the hole is estimated to be of the order of 10 meV [3]. With a bandgap of 1.42 eV, and an Yb^{3+} 4f-shell excited state energy of 1.24 eV, we find a value of 0.14 eV for the expected "back-transfer" energy.

Results

We have observed effective quenching of PL of Yb^{3+} when applying the FEL pulse after the primary Nd:YAG excitation. The effective decay rate during this quenching process can be calculated from the ratio between the PL signal with and without the FEL applied [4].

Fig.2 shows this effective decay rate due to the FEL pulse as a function of the energy of the photons in the beam. Note that the rate of spontaneous decay for Yb in InP is approximately

$8.0 \bullet 10^4$ s^{-1}. The top curve has been shifted with $0.1 \bullet 10^5$ s^{-1} for clarity. At a photon energy of ~145 meV, a discontinuity can be observed in the measurement. For photons with higher energy than this value, quenching becomes more probable. This is the direct fingerprint of the "back-transfer" process induced optically by the FEL.

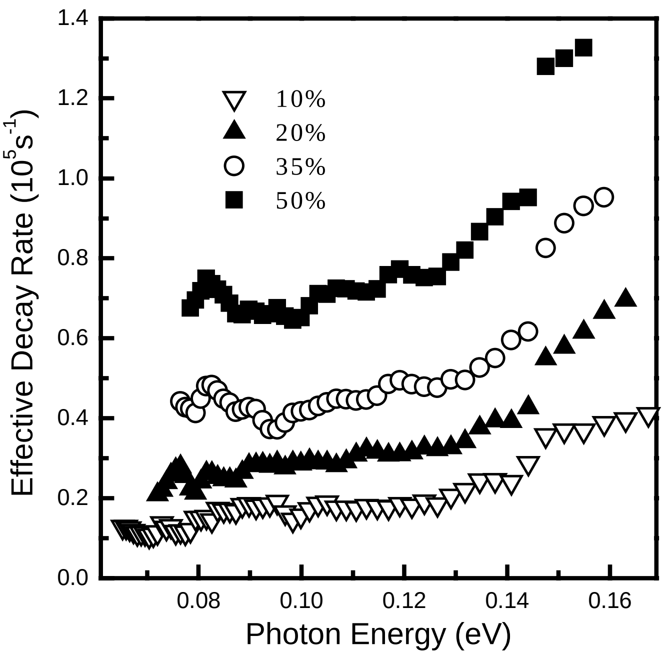

Fig.2 Effective decay rate during the FEL pulse as a function of FEL photon energy. A clear step can be observed around 145 meV..

A detailed study of the dependence on flux densities for both the regions of photon energy above and below 145 meV reveals a different behavior for these regimes (see Fig.3). For photons with energy smaller than 145 meV, we found a square root dependence on flux. The regime above 145 meV shows a linear dependence on flux.

Conclusions

We found that the application of a powerful mid-infrared beam from a free-electron laser induces quenching of PL of Yb^{3+} ions incorporated in InP. Upon measurement of the dependence of this effect on photon energy in the FEL beam, a stepwise increase of the decay rate was found for photon energies above 145 meV. This energy corresponds to the energy deficit in the "back-transfer" process described in the introduction, for the case of Yb^{3+} in InP. We therefore conclude that this "back-transfer" process can be activated optically with a highly intense laser beam of the appropriate energy. This validates the model as proposed and proves the existence of an intermediate level in the excitation mechanism in a direct spectroscopic measurement.

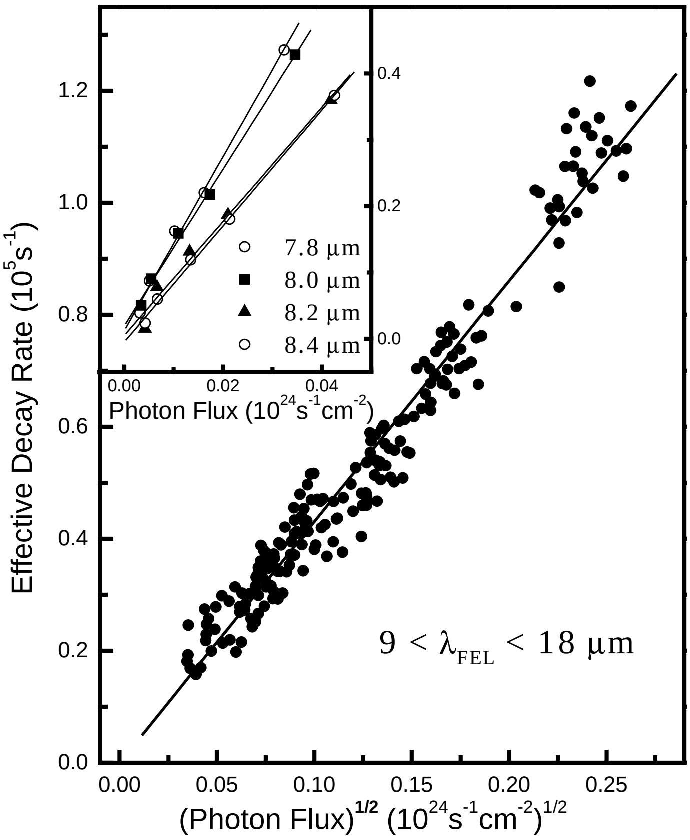

Fig.3 Dependence of the effective decay rate on photon flux in the FEL beam for the region with photon energy above 145 meV (<9 μm) and below 145 meV (>9 μm).

References

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