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Journal of Luminescence 102–103 (2003) 85–90
JOURNAL OF LUMINESCENCE
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Two-color mid-infrared spectroscopy of optically doped semiconductors

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Abstract

Optical doping is an attractive method to tailor photonic properties of semiconductor matrices for development of solid-state electroluminescent structures. For practical applications, thermal stability of emission obtained from these materials is required. Thermal processes can be conveniently investigated by two-color spectroscopy in the visible and the mid-infrared. Free-electron laser is a versatile high-brilliance source of radiation in the latter spectral range. In this contribution, we briefly review some of the results obtained recently by the two-color spectroscopy with a free-electron laser in different semiconductors optically doped with rare earth and transition metal ions. Effects leading to both enhancement and quenching of emission from optical dopants will be presented. For InP:Yb, Si:Er, and Si:Cu activation of particular optically induced non-radiative recombination paths will be shown. For Si:Er and Si:Ag, observation of a low temperature optical memory effect will be reported.

Keywords: Photoluminescence; Semiconductors; Rare earths; Free-electron laser

1. Introduction

Rare earth (RE) and transition metal (TM) ions are frequently used for optical doping of semiconductor matrices. In this way, attractive systems are formed, which combine atomic-like properties of dopants with band structure of the host material. In particular, narrow emission lines with temperature-independent wavelengths due to transitions within the 4f-electron core of the RE ion can be activated by efficient band-to-band absorption of the matrix, or by carrier injection. This makes RE-doped semiconductors (Sc:RE) interesting for applications.

Due to separation of absorption and emission processes, energy transfers are of crucial importance for optically doped semiconductors. These are best facilitated by formation of intermediate stages bridging the highly localized states of the doping ion with extended orbitals of the matrix. During the transfer process, the difference between absorbed energy (comparable with the bandgap energy of the host) and emission energy characteristic for the ion core is dissipated. This is usually accomplished in several steps. As a result, reverse processes are characterized by relatively small activation energies and the transfer process

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0022-2313/02/$ - see front matter
PII: S0022-2313(02)00498-2

responsible for excitation of an optical dopant is sensitive to temperature variations. The resulting thermal quenching of emission efficiency of Sc:RE systems is the major drawback for their practical applications in solid-state light-emitting devices.

Alternative to thermal activation, intense mid-infrared (MIR) radiation from a tunable free-electron laser (FEL) can be used to access directly individual steps of the energy transfer process [1]. In that way unique information on optically doped semiconductors is obtained. In this contribution, we concentrate on selected findings recently revealed in optically doped semiconductor systems by two-color spectroscopy with the FEL. For InP:Yb, we will demonstrate the optically induced "*back-transfer*" effect reversing excitation mechanism of the 4f-electron RE core. For Si:Er and Si:Ag we will show an optical memory effect, similar to that observed in the past for some of the III–V materials. Finally, optically activated non-radiative recombination processes will be presented for Si:Cu and Si:Er.

2. Experimental approach

Formation of shallow, effective mass states is an inherent feature of semiconductors and the most important reason of the domination of these materials in device manufacturing. In case of silicon, the state-of-the-art technology offers a total control over shallow states. Therefore, it should be possible to eliminate, or even positively engineer, thermal effects, once their role in the energy transfer processes has been understood. Investigation of thermal effects is, however, experimentally difficult due to their indeterminate activation. A free electron laser generates photons whose energies are comparable to kT. Consequently, two-color mid-infrared (2C-MIR) spectroscopy with FEL provides a convenient tool to investigate thermal effects.

The idea of the 2C-MIR experiment is presented in a cartoon depicted in Fig. 1. A sample placed in a variable temperature cryostat is exposed to two correlated laser beams operating in different wavelength ranges. The pump beam from a laser operating in the visible (2nd or 3rd harmonic of a

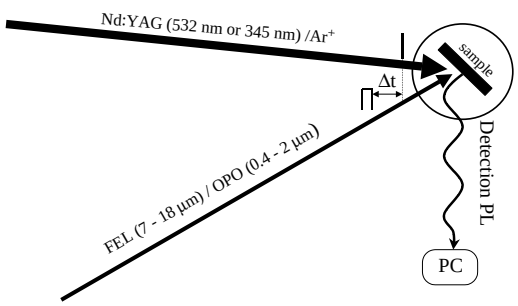

Fig. 1. Experimental configuration for two-color experiments. The band-to-band excitation is provided by a laser operating in the visible: for that purpose 2nd or 3rd harmonics of Nd:YAG pulsed laser or cw Ar^+ ion laser is used. The MIR beam is provided by FEL. Alternatively, OPO can be used to access deeper levels.

Nd:YAG laser, or a cw Ar^+-ion laser) provides band-to-band excitation leading to emission from the optical dopant. A secondary pulse from the FEL ($\lambda_{FEL} = 7$–$18\,\mu m$), with an adjustable time delay, impinges at a MIR wavelength of choice. Alternatively, an optical parametric oscillator OPO ($\lambda_{OPO} = 0.4$–$2\,\mu m$) can be used in order to access deeper levels. The change of intensity and dynamics of photoluminescence (PL) is then recorded as a function of wavelength, timing, and power of the MIR pulse and can be subsequently analyzed in a computer. Intense radiation from the FEL (OPO) allows optical spectroscopy of (shallow) energy levels in the gap of the semiconductor host. In combination with the band-to-band excitation, it offers a possibility to investigate thermal effects in the ground and excited states of an optical dopant, and to probe non-equilibrium and metastable states.

3. Possible effects of MIR radiation in a (doped) semiconductor

The most important effects of the MIR radiation on a semiconductor matrix are related to ionization of (shallow) traps and to optical generation of lattice and local phonons. Although the latter process is not very probable—e.g. multiphonon absorption bands in Si are weak—phonon generation must be taken into

account in experiments with FEL due to the high photon flux.

Optical ionization of shallow traps by FEL (or OPO) beam is schematically depicted in a diagram in Fig. 2. In a semiconductor host optically doped with RE or TM ions, other impurity levels are also present. The free carriers generated in the material upon primary excitation (Ar^+, Nd:YAG) are trapped at these levels while recombination of other carriers at specific centers will follow an appropriate energy transfer process and lead to excitation of the optical dopant. Optical ionization of the trapping centers gives information on the energy transfers (labeled 1 and 3). In this way, identification of specific levels and their role in the excitation mechanism can be selectively accomplished. Such a situation is in clear contrast to the indiscriminate activation occurring in the system upon thermal excitation. Also, role of Auger de-excitation process of the energy transfer between optical dopant and free carriers (labeled 2), or backtransfer processes of excitation reversal from the optical dopant to the host (theoretically postulated and but never proven experimentally) can be investigated in a spectroscopic manner.

Ionization of carriers from the trapping levels can result in an additional excitation of the optical dopant, leading to an increase of emission. On the other hand, liberated carriers can induce nonradiative processes, leading to PL quenching. In what follows, examples of both FEL-induced enhancement as well as quenching of the optical dopant related emission will be presented.

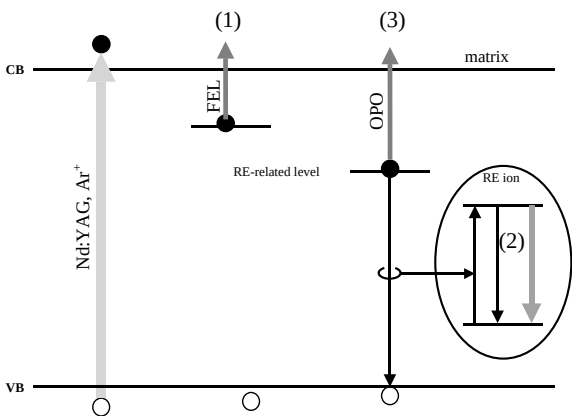

Fig. 2. Optical ionization of (shallow) levels in an optically doped semiconductor.

4. Selected experimental results

4.1. Excitation reversal of the optical dopant: InP:Yb

InP:Yb is considered to be the most simple Sc:RE system featuring a direct bandgap host and the $4f^{13}$-electron configuration of the dopant. We have investigated the photoluminescence of Yb^{3+} ion on an InP matrix after band-to-band optical excitation of the host. The Yb^{3+} ion is brought into its excited state by means of an indirect excitation mechanism, which is believed to involve the capture of an electron–hole pair at an acceptor-like electron trap, located 30 meV below the conduction band. Recombination of this pair excites the RE ion from which a characteristic emission with photon energy of 1.24 eV follows [2].

As depicted in the inset to Fig. 3, we have observed a strong quenching effect in the PL of the Yb^{3+} ion upon application of a powerful MIR pulse from an FEL [3]. Closer investigation revealed this quenching to occur only during the

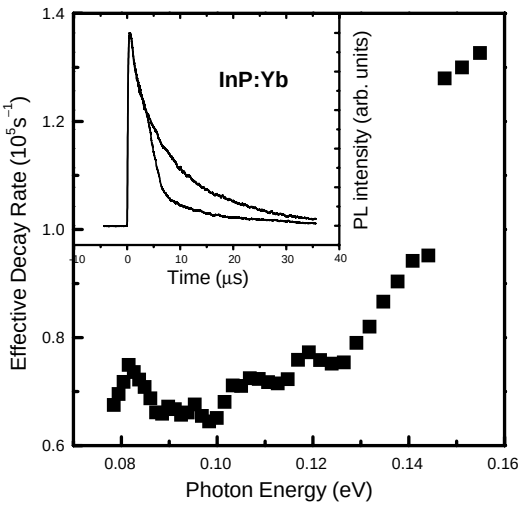

Fig. 3. Optical "backtransfer" in InP:Yb. The FEL-induced quenching of Yb^{3+}-related PL (1.24 eV) as a function of FEL photon energy. The inset shows the effect of the FEL pulse on the decay dynamics of the PL signal.

FEL pulse. PL quenching does not take place when the FEL beam is applied before the band-to-band excitation of the host. Both experimental results indicate the mechanism of quenching to be a fast process with a characteristic time constant being equal to or shorter than the detection speed of the setup (300 ns).

We have determined the magnitude of the PL quenching effect as a function of FEL photon energy—see Fig. 3. This reveals a discontinuity in the photon energy dependence at 140 meV, corresponding to the energy needed to reverse the last step of the excitation mechanism [4]. This measurement shows that by illumination of the excited Yb^{3+} ion with a powerful flux of photons of the appropriate energy, an electron–hole pair can be generated on the acceptor-like electron trap. In that way, this particular experimental result proves the existence of the intermediate excitation state of an electron–hole pair bound and a Yb-related level and confirms the theoretically proposed excitation model for InP:Yb identifying the energy levels involved in this process.

4.2. Optical memory effect

Erbium-containing crystalline silicon c-Si:Er is probably the most important Sc:RE system, as doping with Er is a promising approach to the highly desired silicon photonics [5]. 2C-MIR spectroscopy reveals for this material an interesting effect (omnipresent for all investigated samples) of, the so-called, "optical memory" [6]. In the past, similar memory effects were reported for optically active III–V semiconductors GaAs and GaN [7]. The optical memory effect is illustrated in Fig. 4 which depicts the dynamics of Er PL at 1.54 μm upon the excitation with a nanosecond pulse of a Nd:YAG laser operating at 532 nm. As can be seen, FEL fired at different delay times of $\Delta t = 20$, 40, and 80 ms leads to MIR-induced enhancement of Er PL. In a dedicated study [6], temporal characteristics of the MIR-induced Er PL amplitude has been investigated and participation of non-equilibrium carriers in this excitation process has been deduced. Carriers, temporally stored at shallow acceptor or acceptor-like levels, are ionized optically by MIR radiation and

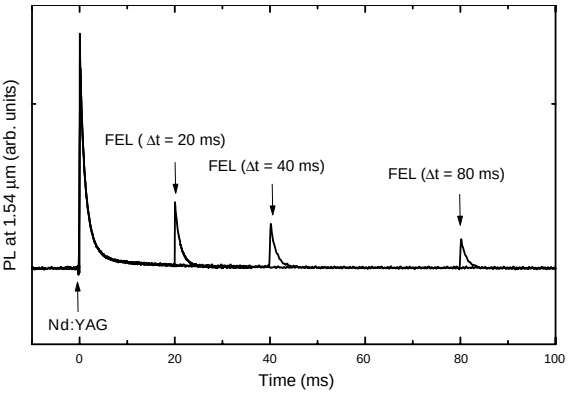

Fig. 4. Optical memory effect observed for Si:Er at low temperature: application of FEL pulse at a delay Δt with respect to the band-to-band pump pulse induces additional excitation of Er^{3+} ion. Amplitude of this effect diminishes as the delay time increases, resulting in the optical memory "archival time" of ~100 ms.

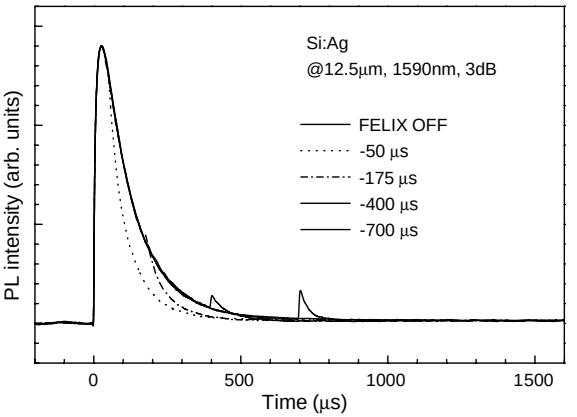

Fig. 5. Optical memory effect for Si:Ag. Additional emission at 1590 nm due to electron–hole recombination at a silver-related center appears upon MIR pulse following band-to-band excitation pump. The illustrated PL dynamics was measured at $T = 4.2$ K and for FEL set at $\lambda_{FEL} = 12.5$ μm.

recombine with electrons captured at an Er-related level. In that way, an additional excitation process occurs and Er emission follows.

A similar optical memory effect, but of a smaller magnitude and a shorter archival time, has also been observed for the silver optical dopant in silicon [8], as illustrated in Fig. 5. Yet another example of a medium exhibiting the optical storage effect is ZnSe:Cr. For this particular

system, non-linear optical effects are present due to two-photon absorption and occurrence of anti-Stokes luminescence (ASL) [9].

4.3. Optically induced non-radiative recombination of the optical dopant

Since the excited RE ion has a long lifetime, it can transfer its energy to a free carrier in the band. Indeed, such an Auger process of non-radiative recombination has been observed for Si:Er and InP:Yb at an elevated temperature [10]. In a 2C-MIR experiment, this process can be activated optically by ionization of carriers at traps. In Fig. 6 such an effect is shown for Si:Er prepared by implantation and high-temperature anneal at 1000°C. After band-to-band excitation by a Nd:YAG (532 nm), FEL is fired at short delay times of 50 or 180 μs. As can be seen, Er PL clearly reduces upon FEL pulse. The quenching time, in the figure limited by the time constant of the detector (75 μs in the illustrated experiment), is likely to be of the order of nano- to few microseconds. Since an Auger process concerns energy transfer to a single carrier, the quenching amplitude has to be proportional to the square root of FEL power, as is in deed confirmed experimentally.

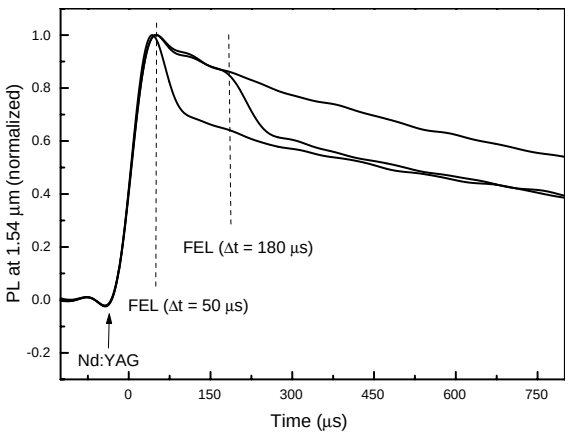

Fig. 6. Optically induced quenching of Er-related emission in Si. FEL pulse applied with a small delay time Δt with respect to the band-to-band excitation results in an abrupt reduction of the PL signal at $\sim 1.54\,\mu m$.

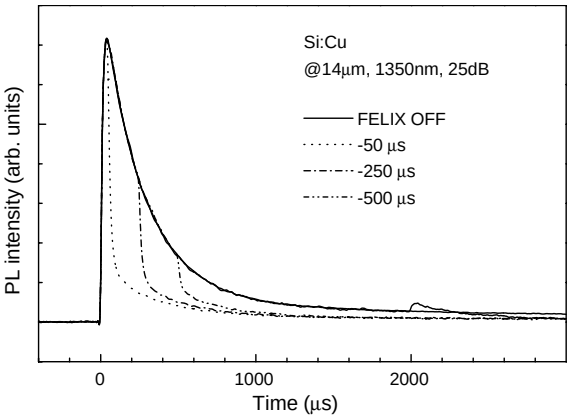

Fig. 7. Optically induced quenching of copper-related PL band in Si. Application of the FEL pulse subsequent to the band-to-band excitation results in an almost complete quenching of the emission.

A similar quenching effect has been observed for Si:Cu—see Fig. 7 [11]. Experiments currently on the way will decide whether also in that case the PL quenching is due to an Auger mechanism, or rather, due to optically induced dissociation of an electron–hole pair bound at a Cu-related level in the silicon bandgap.

5. Conclusions

The briefly discussed examples of several research projects illustrate how the two-color spectroscopy in the mid-infrared can be used to unravel optical properties of materials. In particular, this technique appears to be very useful for tracking energy transfer paths in semiconductor matrices optically doped with rare earth and transition metal ions. Ionization of shallow centers by the MIR pulses accelerates slow energy transfers, which otherwise easily escape detection, thus allowing convenient investigation of thermally activated recombinations, both radiative and non-radiative. In this way, application of the free-electron laser for the two-color spectroscopy allows a truly spectroscopic approach to thermal effects, which are of crucial importance for optical processes of semiconductors and for practical application of Sc:RE systems.

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