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Free-electron laser studies of energy transfer mechanisms in semiconductors doped with transition series ions

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Abstract

Shallow levels determine electrical and optical properties of semiconductors. Mid-infrared radiation from a free-electron laser can be used for an effective ionization of shallow impurities, leading to a variety of effects. In contrast to thermal ionization, the optically induced ionization process can be tuned to a particular level by adjusting the wavelength. In this way, different impurity and defect levels can be selectively addressed. The short-pulsed output of the free-electron laser allows the experiments to be performed in a manner, which utilizes its unique characteristics.

In this contribution, we show how two-color spectroscopy with a free-electron laser can be used to unravel energy transfer between different centers in semiconductor matrices. In particular, energy storage at shallow centers in silicon and mid-infrared-induced Auger recombination process of long-living optically active centers will be discussed. Specific examples for rare earth- and transition metal-doped silicon and rare earth-doped III–V semiconductors will be presented. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The formation of shallow levels, well described with the effective mass theory, is the most characteristic feature of semiconductors and is the main reason for the widespread application of these materials for electronics. The shallow levels, which can be readily introduced by doping, are fully thermally ionized at room temperature and provide for either n or p conductivity type of the material, enabling device construction. At low temperatures, carriers trapped at shallow levels can be ionized optically by photons of an appropriate energy. A free-electron laser (FEL) provides tunable pulsed radiation in this mid-infrared (MIR) spectral range and can therefore be conveniently used for manipulation of the shallow level population.

Deep levels positioned close to the middle of the band gap of a semiconductor are responsible for non-radiative recombination of electrons and holes generated into the bands and therefore control the free carrier lifetime. In some cases, deep centers can have isoelectronic character, i.e.

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appear as neutral with respect to the host. Such isoelectronic centers can possess a local potential, e.g. due to core polarization, capable of short-range binding of an electron or a hole. Once the so-called primary particle is localized, a charged center is formed with a long-range Coulomb potential. Subsequently, a secondary particle of an opposite charge can be bound by this potential in a shallow, effective-mass-theory state. The carrier pair localized by the isoelectronic center may interact to form an exciton. In contrast to excitons localized at (shallow) donors or acceptors, an exciton bound to an isoelectronic center forms a two-, and not a three-particle system. This suppresses non-radiative Auger recombination and photon emission can take place. For an indirect band-gap semiconductor, this radiative recombination is not readily allowed, and relatively long lifetimes, of the order of 100 μs, are observed.

A special class of deep levels is formed by doping with elements, which are characterized by incomplete inner electron shells—transition metals (TM) and rare earths (RE). Electronic centers formed by these dopants frequently have isoelectronic character and their electronic configuration allows for a special kind of relaxation, where part of the recombination energy is transferred to the core, promoting it to an excited state. Such a non-radiative recombination is generally accepted as the main excitation mechanism responsible for photoluminescence of RE ions imbedded in semiconductor matrices.

2. MIR-induced ionization of shallow traps

If the optical ionization takes place in an equilibrium situation, a certain steady concentration of free carriers ionized from shallow states will be present in the band during the pulse. These carriers will be recaptured at the shallow states once the MIR radiation is turned off. For materials with an indirect energy band gap, a non-equilibrium situation may occur when free carriers generated by, e.g. band-to-band excitation may relax to shallow states, but then cannot recombine with non-equilibrium carriers of the opposite charge due to momentum conservation. The recombination involves thermalization into the band continuum and therefore will be delayed. For silicon, where technology allows for a precise impurity control and therefore for a very effective suppression of alternative recombination channels, thermalization at cryogenic temperatures may take tens of ms or more, depending on the ionization energy of a particular trapping center. Application of an MIR pulse in a non-equilibrium situation will result in repopulation of carriers towards equilibrium. In this case, preferential carrier capture at deep levels, not influenced by the MIR radiation, will take place. Luminescence due to radiative recombination at deep centers serves as a convenient monitor of carrier transfer induced by the MIR pulse.

3. Experimental

The two-color experiments were performed at the Dutch free-electron laser user facility FELIX in Nieuwegein. The second harmonic of a pulsed Nd : YAG laser at $\lambda = 532\,\text{nm}$ was used for primary band-to-band excitation. A pulse from the FEL was fired with a variable delay with respect to that of the Nd : YAG pump pulse. For details of the experimental configuration see, e.g. Ref. [1].

Several different semiconductor samples were used in this study. These are listed below.

1. Si : Er—Er-implanted Si, showing emission at $\lambda = 1.54\,\mu\text{m}$ due to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of Er^{3+}.
2. Si : Ag—silver-diffused Si.
3. InP : Yb—MOCVD-grown, Yb-doped during growth.
4. GaAs : Er—MBE-grown, Er- and O-doped during growth.

4. Optical storage effect in silicon

It has been observed that emission from Er^{3+} ions embedded into crystalline silicon can be excited using MIR photons with energy quanta

of 70–170 meV, i.e. several times smaller than the absorption frequency of the $^4I_{15/2} \rightarrow {}^4I_{13/2}$ transition [2]. The effect was found to take place when the MIR pulse was applied within a short delay time after band-to-band excitation of the sample. The enhancement disappeared with a relatively large time constant τ_D of several ms. A comprehensive treatise of the MIR-activated Er PL has been given [3] and recombination of carriers (temporarily) stored at shallow levels as a result of the prior band-to-band excitation, has been identified as the mechanism responsible for this effect. By scanning the wavelength of the MIR beam, ionization energies E_i of traps responsible for carrier storage have been determined [4]. It has been established that the particular values of both E_i and τ_D were sample-dependent, being influenced by substrate parameters and Er-doping procedure.

The MIR-induced enhancement of the Er PL is illustrated in Fig. 1. The wavelength and the characteristic decay time uniquely identify the FEL-generated PL as originating from the same Er-related optical centers that can also be excited by the visible laser pulse. As can be concluded from the inset to Fig. 1, the magnitude of the effect depends on the delay time Δt between the visible (Nd : YAG) and the MIR (FEL) pulses.

The experimentally observed slow increase of the enhancement effect is unexpected in view of our previous [3] identification of energy storage at

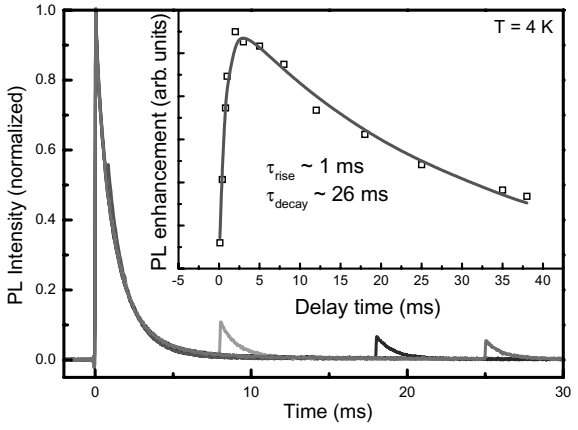

Fig. 1. MIR-induced enhancement of the Si : Er PL for a high pump-excitation density.

shallow levels as being responsible for the MIR-induced Er PL. Since the typical lifetimes of free carriers in Si are of the order of ns, the shallow traps will localize carriers immediately after their generation by the Nd : YAG pulse. They will then be prepared for the energy transfer and practically no delay should be observed. We note further that the rise time τ_{rise} of the magnitude of the "additional" PL is relatively slow: τ_{rise} values in a range of 1 ms can be obtained by numerical fitting—see inset to Fig. 1. Based on results obtained for several differently prepared samples, we concluded that the "incubation" time τ_{rise} of the MIR-induced Er PL is related to the life time of the $^4I_{13/2}$ excited state of the Er^{3+} ion, τ_{Er}, in a given sample. The observation of a rise time is then naturally explained by saturation of the Er PL. We note that saturation might easily set in due to the very short duration of the Nd : YAG laser pulse. Indeed, dedicated experiments revealed that at a low pumping rate, the MIR-induced enhancement of the Er PL sets in immediately following the pump pulse, is in full agreement with the microscopic mechanism proposed in Ref. [3].

The influence of saturation on the initial magnitude of the MIR-induced Er PL signal allows one to use this effect to measure the lifetime of the excited state responsible for the observed emission, since now $\tau_{rise} = \tau_{Er}$. The value of τ_{Er}, which is determined, can then be compared with the time dependence of the PL signal intensity measured directly under identical experimental conditions, but without the FEL. Fig. 2 shows the experimentally measured PL signal fitted with a single exponential decay with a time constant determined from the saturation behavior of the FEL-induced enhancement. Good agreement can be obtained only for the initial part of the experimental trace; for longer times a second, slower component is necessary. As illustrated in the figure, the kinetics can be satisfactorily reproduced over the entire recorded time range with a double exponential decay, when τ_{rise} and τ_D are used as time constants.

Fig. 3 shows the time dependence of the PL signal before and after the FEL pulse. In both cases, the kinetics can be well described with the same two time constants (τ_{Er}, τ_D) but with a

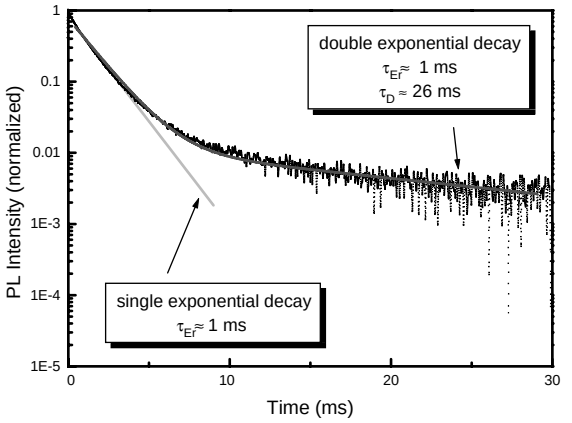

Fig. 2. Kinetics of the Er PL signal fitted as a single- and a double-exponential decay.

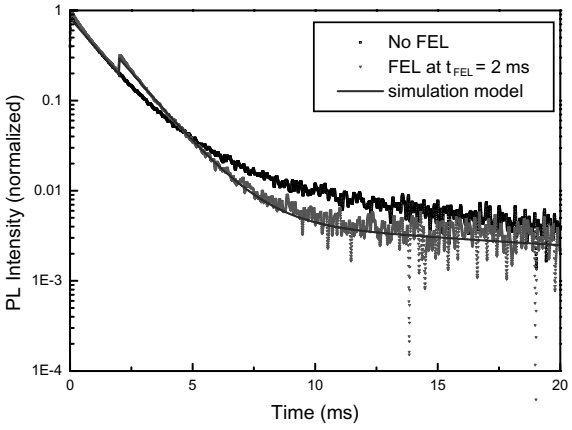

Fig. 3. Double exponential fit of the Er PL signal following the FEL pulse.

different amplitude ratio of the two components. The FEL pulse leads to an enhancement of the Er PL component, characterized by the τ_{Er} time constant, accompanied by a simultaneous quenching of the "slow" component. We conclude therefore that the application of the MIR pulse leads to excitation transfer from the "slow" (τ_D) to the "fast" erbium component (τ_{Er}). Following the FEL pulse, the system can then be described by a similar set of rate equations as used for the band-to-band excitation [3], but taking a new generation term G_{FEL}, proportional to the concentration of "slow" traps at the time when the FEL is fired, $N_D(t_{FEL})$. Using this model, we can now predict the amplitude of the FEL-induced effect for different delay times. This is illustrated for a specific delay time with a solid line in Fig. 3. Good agreement with the experimental data is obtained [5].

Addressing the question of the microscopic origin of the "slow" component identified from the PL kinetics, we note that its characteristic decay time, equal to τ_D of the enhancement effect, is extremely long. Depending on particular parameters of a sample, τ_D values in the 20–100 ms range are commonly found [5]. Such a time constant exceeds the radiative lifetime of the Er^{3+} ion $^4I_{13/2}$-multiplet [6]. On the other hand, the wavelength dependence of the "slow" component (not shown here) clearly links it to Er emission. Taking into account the available evidence, we attribute the "slow" component to excitation of Er ions by thermal emission from non-equilibrium traps. These traps are populated by the Nd : YAG pump pulse and, while returning to equilibrium, will thermally emit carriers, which can then recombine leading to excitation of Er ions. Since the time constant of thermal emission exceeds the Er relaxation time, this slow excitation process will directly reproduce in kinetics of the Er-related PL signal. Alternatively, carriers localized at these traps can be rapidly ionized by the FEL, as discussed in the introductory paragraph, resulting in an abrupt increase of Er PL. The proposed mechanism provides a natural explanation for the fact that the MIR-induced enhancement of the Er PL is observed only at low temperatures $T \leqslant 50$ K. As the temperature is increased, thermal emission from traps becomes more efficient and the enhancement effect disappears.

According to the explanation outlined above, the optical storage effect is not related to Er doping, but, rather, represents an intrinsic feature of silicon. In order to confirm this important conclusion, we searched for the MIR-induced enhancement in Er-doped GaAs, where also an intense Er-related PL at $\lambda \approx 1.5\,\mu$m was observed, but whose direct band-gap structure makes temporary storage at shallow trapping levels less probable. Indeed, we could not detect any increase

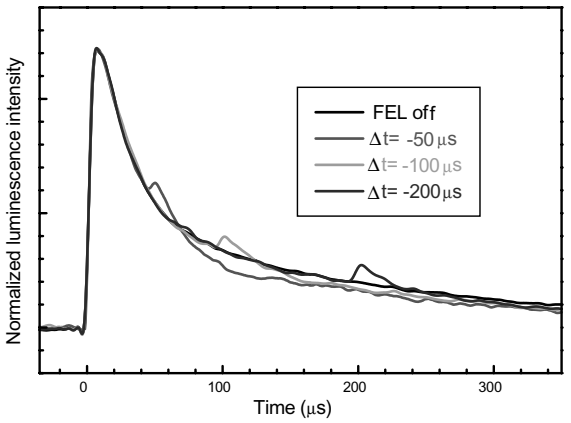

Fig. 4. MIR-induced enhancement of the silver-related 780 meV PL band in Si : Ag.

of the Er PL intensity upon application of the MIR pulse from the FEL. Consequently, we returned to silicon and looked for another recombination center that could serve as a recipient of the stored excitation. As discussed earlier, an isoelectronic center is especially suited for that purpose, as it can localize primary particle, and then produce emission only after a secondary particle becomes available. This allows, in principle, an arbitrarily long time separation between both excitation steps.

In particular, silver doping of silicon is known to create an isoelectronic center, giving rise to a PL band at $\sim$780 meV [7]. Fig. 4 illustrates the effect of the FEL pulse applied shortly after the Nd : YAG excitation on the Ag-related band. As can be concluded, similar to the Si : Er sample, a clear enhancement of Ag-related PL follows. This observation confirms that the effect of excitation storage is an optical property of silicon crystal.

5. Optically induced Auger quenching of PL

In addition to luminescence generation, carriers liberated from shallow levels can give rise to non-radiative recombinations. As a result, excitation induced by the pump laser pulse might be quenched, leading to a reduction of the PL

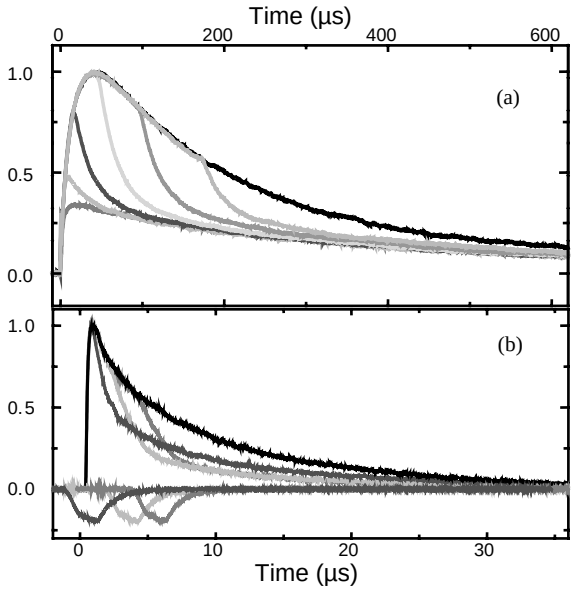

Fig. 5. MIR-induced quenching of the PL of (a) Er^{3+} in silicon and (b) Yb^{3+} in InP.

intensity. In particular, the Auger process of energy transfer to free carriers or ''on-site'' Auger quenching can occur. These effects might be induced by ionization of carriers temporally stored at shallow traps, as well as in equilibrium, when the traps will be repopulated after the pulse. We note that, in the first case, the quenching will compete with the earlier discussed effect of MIR-induced excitation. RE ions can also be conveniently used to reveal the quenching process, since Auger recombinations are known to efficiently terminate their excitation [8,9]. Fig. 5(a) illustrates the MIR-induced Auger quenching of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition of the Er^{3+} ion in Si. As can be seen, the magnitude of the effect diminishes as the time delay between the pump and the FEL pulse increases. This is a characteristic fingerprint of a non-equilibrium situation when the concentration of temporarily stored carriers decreases with time. In Fig. 5(b), the same effect for InP : Yb is shown. Since the PL intensity for this system is considerably larger than for Si : Er, a higher time resolution could be obtained; in this way, it could be conclusively established that the quenching effect takes place only during the MIR pulse. On

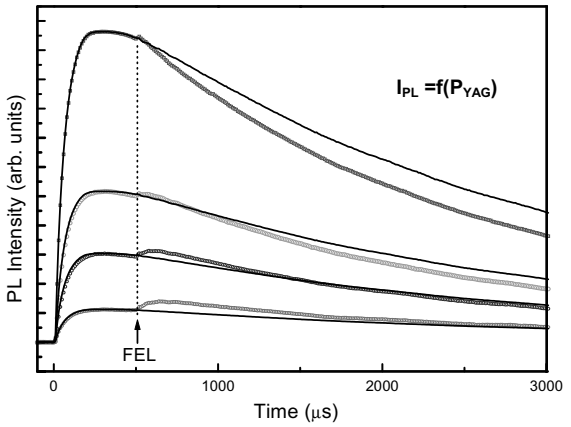

Fig. 6. Effect of the MIR-pulse on the PL of Si : Er as a function of Nd : YAG excitation density.

the other hand, the direct band gap of InP does not permit temporary storage of non-equilibrium carriers. In agreement with this, no delay-time dependence of the quenching magnitude is observed, in contrast to the Si : Er case depicted in Fig. 5(a). The quenching effect is related (in this case) to ionization of equilibrium traps, generating a certain concentration of free carriers into the band during the FEL pulse. Auger energy transfer to free electrons quenches the Yb PL. The experimentally measured dependence of the quenching magnitude on the FEL pulse energy could be successfully reproduced, confirming the model that we assume [5].

Competition of quenching and enhancement effects in the non-equilibrium situation is best illustrated for a Si : Er sample in Fig. 6, where the influence of the FEL pulse is shown as a function of the pump excitation density. For low powers of the Nd : YAG laser, the erbium absorption is not saturated, and carriers released by the FEL from shallow traps can increase the Er excitation level, thus enhancing the PL signal. At a high pump power density, the excitation cannot be increased, but, when the concentration of free carriers liberated by the FEL is sufficiently high, relaxation via Auger process will occur [10],[1] as is apparent in the experiment.

6. Conclusions

We have shown that MIR radiation from an FEL can effectively ionize shallow levels available in a semiconductor. By adjusting the FEL wavelength, specific shallow states can be selected. The FEL-induced ionization can affect not only levels occupied in equilibrium, but also those involved in temporal carrier storage, an important effect for indirect band-gap materials at low temperatures. In both cases, the released carriers will influence the energy transfer paths, and therefore two-color spectroscopy can be used to track them. As illustrated, both RE and TM ions can serve as convenient monitors of the free carriers appearing in the system.

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[1] Such a situation is possible, since excitation of Er in Si is a two-stage process, involving formation of an intermediate state—for a more complete discussion, see Ref. [10].