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**Time-Resolved Spectroscopy of Energy Transfers in Optoelectronic Media**

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# Introduction

*On s'engage et puis on voit*

Napoleon

The transistor is considered by many as one of the greatest inventions of the twentieth century. It is not the aim of this introduction to validate nor to refute this consideration, but to hint at the massive influence that the transistor—the fundamental building block of electronic devices and computers—, and therefore semiconductors, have on society and the recent History of mankind. Although the material with which the first practical transistor (built by William Shockley, John Bardeen and Walter Brattain in 1947) was germanium, it was thanks to the implementation of the silicon transistor—the basis of the integrated circuit—that miniaturization, cost reduction, and higher degrees of complexity could be achieved, giving rise to the so-called “silicon age”. It is not exaggerated to affirm that silicon is present in almost every aspect of our daily life.

However, the same dramatic pace of miniaturization that has translated into cheap production, popularization of electronic components and computers, and a seemingly unstoppable increasing computing speed, is bringing silicon technology towards its fundamental physical limits, and novel approaches need to be found, studied, and developed. The use of photons as information carriers—photonics—is an attractive way to overcome the forthcoming limitations and to open a whole new world of possibilities in a well known, cheap, environmentally friendly, and versatile technology. Doping of semiconductors with rare earth ions, and the use of nanostructured silicon are two prominent examples. In the last decade, semiconductor photonics and in particular silicon photonics have progressed significantly, but great effort remains yet to be done in the whole spectrum ranging from basic understanding of physical processes to design of devices for applications. From a purely experimental approach, based on optical time-resolved techniques—let us not forget that almost everything known in physics has been discovered or confirmed by look-

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ing at light (although almost everything in the Universe is utterly invisible)—, the work presented in this thesis deals with various aspects of energy transfer processes in optoelectronic media, studied from a fundamental point of view, but always considering the consequences of the drawn conclusions in view of the prospective practical applications. Theoretical modelling was developed within this framework, in order to support the proposed models.

### 0.1 Semiconductors. Silicon

A broad classification of materials can be established regarding the dependence of their resistivity with temperature: those materials whose resistivity increases linearly with temperature are classified as metals; those whose resistivity decreases exponentially with temperature are classified as semiconductors and insulators. The interpretation for the different behavior is the following: in metals, free carriers exist in the material, independently of the temperature; in semiconductors and insulators, it is necessary to provide a supplementary energy in order to create charge carriers. The *band gap* of a semiconductor or an insulator is the energy necessary to generate carriers which enable conductivity in the material. A semiconductor is commonly defined as a material whose energy gap for electronic excitation lies between zero and about 4 eV—there is no fundamental difference between a semiconductor and an insulator. Semiconductors occur in many different chemical compositions, as well as a large variety of crystal structures. Some semiconductors exhibit magnetic or ferroelectric behavior, others become superconductors when appropriately doped...

The best known semiconductor is element silicon (Si). Together with germanium (Ge), it is representative for a large group of semiconductors with similar crystal structures: the diamond structure. In this configuration, each atom is surrounded by other four nearest neighbors, forming a tetrahedron. Si and Ge are *elemental semiconductors*, other forms are *binary compounds*, *oxides*, *organic semiconductors*, etc. Together with the chemical composition, the crystal symmetry of the semiconductor will determine its band structure, *i.e.* the allowed energy range for an electron in the matrix, due to the overlap of the electronic wave functions, conveniently expressed in terms of the reciprocal space. The band structure of a semiconductor will ultimately determine the electronic and optical properties of the material. The valence band (VB) is the highest range of electron energies where electrons are present at the temperature of the absolute zero; the conduction band (CB) is the range of energies where an electron can move freely in the lattice structure, thus being susceptible to create electric current. The energy distance between the top of

the VB and the bottom of the CB determines the energy band gap  $E_g$  of a semiconductor. When the top of the VB and the bottom of the CB coincide in the reciprocal space, the semiconductor is called of direct band gap.

In an ideal semiconductor, where no defects or impurities are present (intrinsic semiconductor), light can not be absorbed when the incoming photon energy is smaller than the band gap  $E_g$  of the semiconductor. When the photons have sufficient energy, they can be absorbed by the semiconductor, promoting an electron from the VB to the CB, *i.e.* creating a free electron in the conduction band and a free hole in the valence band. In order to re-establish equilibrium, the electron-hole pair will recombine: radiatively by emission of a photon, or non-radiatively dissipating the energy in the form of phonons (collective lattice vibrations). When the semiconductor has an indirect band gap, electrons in the bottom of the CB and holes in the top of the VB have different  $\vec{k}$ -vectors, and the recombination can not take place without involving a third particle, in order to comply with the momentum conservation law; usually phonons are the third particle involved. In an indirect band gap semiconductor—as it is the case of Si—the probability of radiative recombination of an electron-hole pair is small compared to that of non-radiative recombination, and radiative recombinations of electron-hole pairs are only observed at low temperatures, where creation of phonons in the lattice is less probable.

When an electron-hole pair is created, due to the charge difference, Coulomb interaction appears between the two carriers; if the thermal energy  $k_B T$  is smaller than the attractive potential between the carriers (binding energy) a free exciton is formed. A free exciton can be considered as a pseudo-particle that can move in the crystal, and eventually recombine radiatively. The photoluminescence properties of intrinsic crystalline Si are basically limited to radiative recombination of excitons, and their replicas involving different types of phonons. As mentioned before, due to the indirect nature of the band gap of Si, the probability of this processes is negligible when compared to the non-radiative processes at room temperature, and only at cryogenic temperatures excitonic photoluminescence from Si can be observed.

## 0.2 Optical doping

The electrical properties of a semiconductor can be altered by adding impurity atoms to the crystal lattice; this is known as doping. Let us consider the case of Si, an element of the group IV of the table of elements, *i.e.* with four valence electrons. If one atom of Si is substituted in the lattice by an atom from the group V (N, As, P, Sb, Bi), with five valence electrons, the “fifth”

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electron will remain unbound, and the doped impurity “donates” an extra electron; these type of dopants are called “donors”. Substitutional Dopants from the group III (B, Al, Ga, In, Tl), with one less valence electron than Si, will “accept” an extra electron from the valence band, creating a hole; these dopants are therefore called “acceptors”. In general, all impurities added to a semiconductor can create energy levels within the band gap of the material. The appropriate choice of doping impurities and their concentration allows manipulation and tailoring of the properties of the semiconductor. In particular for Si, the ability to induce conductivity in the bands formed the basis for the development of active elements in semiconductors technology.

Impurities can also act as recombination centers, influencing the photoluminescence properties of the semiconductor. The alteration of the optical properties by addition of impurities is called optical doping. Optical doping is capable of influencing both, emission and absorption of the material, and plays a major role in optoelectronics; semiconductor lasers, optical discs, image sensors and optical fibers are key elements for the information industry.

### 0.2.1 Rare earth ions

Rare earth (RE) ions are used in a wide number of applications: from solid state lasers and full color displays, to magnetic refrigeration, paints, or catalysts... The RE atoms belong to the lanthanide series of the periodic table, comprising the elements from cerium (Ce, atomic number 58) to ytterbium (Yb, atomic number 70). Their electronic configuration can be expressed as  $[\text{Xe}]4f^{n+1}6s^2$ , with  $n$  ranging from 1 (Ce) to 13 (Yb); when a RE atom is incorporated into a solid, its configuration changes to  $[\text{Xe}]4f^n5s^25p^6$ . The “color” and paramagnetism of a RE are determined by the configuration in the  $4f$  shell, and due to the screening by the completely filled outer  $5s$  and  $5p$  shells, the environment have little influence on these properties. Therefore, optical transitions within this level are characterized by sharp spectral lines, with emission wavelength independent of the host material. This is a major advantage for practical applications, since a required wavelength can be selected by choosing the appropriate RE atom which can be incorporated in a variety of host materials—the most well-known example being perhaps the Nd:YAG lasers—; a careful selection of different RE ions can in fact cover the whole visible to near-infrared range.

Si is not a good optical emitter *per se*, due to the indirect nature of its band gap. RE doping of Si, and Er doped Si (Si:Er) in particular, is a possible way to achieve the silicon-based optical emitter. In  $\text{Er}^{3+}$ , the transition from the first excited state to the ground state of the  $4f$  shell ( ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ )—allowed after the inversion symmetry breaking by the crystal field—corresponds to an

energy of 0.8 eV, or emission of a 1.5  $\mu\text{m}$  photon when realized by a radiative transition. This is the preferred wavelength in telecommunications, since it coincides with the minimum losses of optical fibers. When  $\text{Er}^{3+}$  is incorporated in Si, only the first excited state  $^4\text{I}_{13/2}$  (0.8 eV) lies within the Si band gap (1.12 eV), and an Er-related donor level is created in the band gap of Si, as a consequence of the incorporation of Er ions in the lattice.

In order to emit light,  $\text{Er}^{3+}$  ions must be excited. Direct excitation into the  $^4\text{I}_{13/2}$  state is possible, but the effective excitation cross section is orders of magnitude smaller than the excitation via the host. The latter proceeds via creation of electron-hole pairs in the Si host, formation of a bound exciton connected to the Er-related donor level, and energy transfer to the  $\text{Er}^{3+}$  ion. In the first chapter of this thesis, the carrier mediated  $\text{Er}^{3+}$  excitation will be discussed in detail.

## 0.2.2 Silicon nanocrystals

Using the Si host as the excitation mediator for  $\text{Er}^{3+}$  offers the advantage of the high photoluminescence excitation cross section. However, light emission in this system is not thermally stable, due to energy back-transfer processes, activated by the thermal energy  $k_B T$ , and enabled due to the small band gap of Si. This is not the case in large band gap semiconductors—where many RE-based room temperature applications already exist— or insulators, like silicon dioxide ( $\text{SiO}_2$ ), with a band gap energy of 8.9 eV. One approach to combine the features of both systems is the use of Si nanocrystals (Si NCs) as sensitizers of  $\text{Er}^{3+}$  in  $\text{SiO}_2$ . Due to the confinement of the electron wave function in a nanocrystal of the order of the Bohr radius, the band gap energy of the Si NCs increases in respect to that of bulk Si, and the valence and conduction bands become represented by a series of discrete levels. Room temperature luminescence, and high excitation cross section are achieved in this system. The physical mechanisms underlying the energy transfer processes between Si NCs and  $\text{Er}^{3+}$  is investigated in detail in this thesis.

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References used for this introduction: [1], [2], [3], [4], and [5].

