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Optical spectroscopy of carrier dynamics in semiconductor nanostructures

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Citation for published version (APA):

de Jong, E. M-L. D. (2017). Optical spectroscopy of carrier dynamics in semiconductor nanostructures

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Introduction

Semiconductors can be found in many forms in our society and have a big impact on it. They are the building blocks of many devices, ranging from electronics to light sources. In this Chapter, an introduction to the fundamental optical properties of semiconductors is given. The concept of nanocrystals, a semiconductor nanoform, and their properties are also described and important carrier dynamics processes, which can take place in these materials are discussed.

1.1 Semiconductors

Based on their resistance as function of temperature, materials can roughly be divided in three groups: metals or also called conductors, semiconductors and insulators. Metals have a very large number of free electrons and therefore a high conductance, whereas insulators have no free electrons and zero conductance. The resistivity of semiconductors and insulators decreases with temperature, while on the contrary that of metals increases. Semiconductors have conductance properties between metals and insulators. For insulators and semiconductors, there is a supplementary energy necessary, which is at least equal to the so-called material-specific bandgap, in order to create charged carriers and enable conductivity. For insulators the bandgap is much larger than that of a semiconductor (depending on the nomenclature, usually when it is larger than $\sim 5\text{eV}$). The highest electron occupied valence band and the electron unoccupied conduction band (at 0K) are separated from each other by the bandgap energy.

Upon optical excitation, an electron is excited to the conduction band, leaving a vacancy in the valence band behind, which is called a hole. A photon is only absorbed when its energy exceeds the bandgap energy of the ideal intrinsic semiconductor with no defects or impurities. After absorption of an above-bandgap photon, an electron-hole pair (free electron and hole) will be created with an excess energy equal to $E_{\text{excess}} = E_{\text{exc}} - E_{\text{gap}}$, where E_{exc} and E_{gap} are the excitation and the material-specific bandgap energy, respectively. Since cooling to lower excited states is generally several orders of magnitude faster than recombination across the bandgap, the excess energy will quickly be lost and eventually converted into heat by the emission of phonons.

After optical excitation, the excited electron can recombine radiatively with a valence band hole by emitting a photon of an energy, which is (generally) equal to the material-specific bandgap (with state-filling and alike transient non-equilibrium effects being neglected). The process is called photoluminescence (PL). Besides, non-radiative recombination can occur, whereby the energy is released through the emission of phonons (through, e.g., carrier trapping at defects).

1.2 Bulk Si

Silicon is a frequently used semiconductor in many applications due to its advantages, such as large abundance (it is the second most abundant element after O in the Earth's crust, on a weight basis), possibility of high-purity, large monocrystals, easy doping, convenient bandgap energy (close to the optimal bandgap for maximum conversion efficiency for single-junction photovoltaic cells[1]), availability of a matching insulator (SiO_2) and non-toxicity. The element Si can be found in many forms, such as clay, granite, quartz and sand, and it is frequently used in many applications, such as hard concrete

and fragile glass, but also in the electronic industry as integrated circuits, and in photovoltaics as the dominant material for solar panels.

The name Si originates from the Latin word *silex* or *silicis*, which means flint or hard stone. The element Si has atomic number 14 and can be found together with C, Ge, Pb and Sn in group IV of the periodic table. All these elements have four valence electrons in their outmost shell. The most common dopants are group III elements (e.g. B, In and Ga) for acceptors and from group V elements (e.g. P, N and As) for donors, since they contain three and five valence electrons, respectively.

Despite the great advantages of Si, its light emission is relatively poor, even at liquid He temperatures, due to its indirect bandgap electronic structure. For direct bandgap materials, the conduction band minimum and the valence band maximum are located at the same position in k (momentum) space, whereas they are shifted from each other for indirect bandgap materials. In the latter case, radiative band-to-band recombination between a state in the valence band and a state in the relatively shifted conduction band requires the absorption or emission of at least one photon in order to conserve momentum and to accommodate the momentum mismatch. Since a third particle needs to be involved, the probability of radiative emission, which is in competition with non-radiative recombination, in indirect bandgap materials (like Si and Ge) is therefore relatively low compared to direct bandgap materials (such as GaAs, CdTe and GaN). Indirect bandgap materials are therefore not frequently used as light-emitting devices, but the relatively long free-carrier lifetime of these materials (in the bulk form) can be beneficial for photovoltaic applications, since it prolongs the carrier extraction window (up to milliseconds versus nanoseconds for direct bandgap materials).

In Fig. 1.1, the band structure of bulk Si is schematically presented in momentum space. The top of the valence band is located at the Γ point and the bottom of the conduction band close to the X point, corresponding to an indirect bandgap of $\sim 1.14\text{eV}$, while the difference between the conduction and valence band at the Γ point is $\sim 3.32\text{eV}$ for bulk Si (standard ambient pressure and room temperature conditions), representing the direct transition for which absorption and emission of photons can occur without the help of one or multiple phonons.

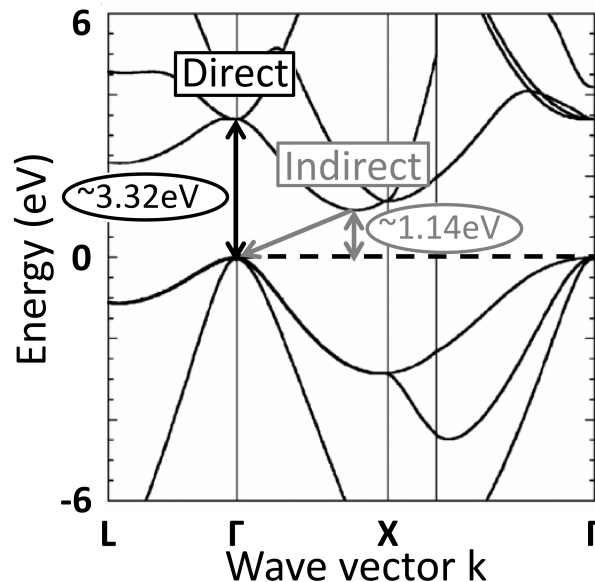


Figure 1.1: **Banddiagram of bulk Si** (a) *Bandstructure in reciprocal space of bulk Si. Its direct ($\sim 3.32\text{eV}$, black) and indirect ($\sim 1.14\text{eV}$ at $T=300\text{K}$, gray) transitions are indicated with black and gray arrows, respectively. (The Fig. is edited from Ref. [2].)*

1.3 Quantum confinement

The optical properties of semiconductors, among which Si, might be improved by using nanostructures. When the size of the structure becomes comparable to the size of the material-specific exciton Bohr radius, which is about 5nm for Si[3], quantum confinement effects start to play a role. A nanocrystal (NC), or also often called quantum dot, has the size of several nanometers and experiences quantum confinement in all 3 dimensions, i.e., is 0-dimensional. The quantum confinement effects modify the electronic and optical properties of the material and interesting quantum phenomena emerge. One effect is the relaxation of the momentum conservation, which can be explained using the Heisenberg's uncertainty principle:

$$\Delta x \Delta p \geq \frac{\hbar}{2}, \quad (1.1)$$

where Δx and Δp are the uncertainties in position and momentum, respectively and \hbar is the reduced Planck constant. As the position of the particle can be determined more precisely (Δx smaller), the less certain the momentum (Δp larger) determination becomes, and vice versa. In case of nanostructures, the particles become more localized in a small volume (Δx smaller), resulting in a larger momentum uncertainty compared to the bulk (Δp larger). Consequently, the relative probability of radiative recombination compared to non-radiative recombination increases, allowing for brighter emission.

Quantum confinement modifies also the energy structure. In contrast to bulk semiconductors with a continuous distribution of energy overlapping levels, the density of states decreases and the energy levels become separated from each other. As a result of the larger distance between individual states, the relaxation of hot carriers through phonon emission (also called phonon cooling) is expected to slow down compared to bulk[4, 5, 6, 7]. This effect is commonly referred to as phonon bottleneck[8, 9].

In addition, quantum confinement offers the possibility to tune the bandgap of the material by changing its size, enlarging its application perspective. Moreover, the bandstructure can be altered through the surface termination, as has been shown for, e.g., Si NCs[10], or by changing the chemical compositions of the material (e.g. perovskite NCs[11], see also Chapter 8).

With decreasing size of the nanostructure, the surface-to-volume ratio decreases, amplifying the importance of the surface. Dangling bonds or other surface defects can cause the PL to quench via non-radiative recombination involving these defect sites. Passivating the surface reduces the number of defects, hence resulting in brighter light emission (and for photovoltaic applications, a longer carrier lifetime and extraction window).

Moreover, Coulomb interactions are enhanced in NCs as a result of the confinement, which greatly influence multicarrier interactions, such as Auger recombination (AR) and carrier multiplication (CM). These processes will be discussed in the next Sections.

1.4 Auger recombination

During the multiparticle AR process an excited carrier does not recombine radiatively by emitting a photon, but non-radiatively by transferring its energy to a third particle (electron or hole), promoting it to a higher excited state. This process is schematically depicted in Fig. 1.2(a) and reduces the free-carrier concentration. The efficiency of this process is relatively low in bulk and is greatly enhanced in NCs as a result of the enhanced Coulomb interaction[12, 13]. The AR rate speeds up with decreasing NC size and/or increasing free-carrier concentration (i.e. excitation power or number of electron-hole pairs per NC)[14]. The AR process (usually in the picoseconds range) is typically much faster than the radiative recombination in NCs, setting an upper limit to their PL intensity at high excitation powers[15], limiting the semiconductor NCs application potential.

1.5 Carrier multiplication

The reverse process to AR is also possible. After the absorption of a high-energy photon by a semiconductor material, an electron-hole pair with large excess energy is created. This excess energy can be converted into heat through the emission of phonons when the electron cools down to the bottom of the conduction band (or the hole to the top of the valence band), but it can also be used to create an additional electron-hole pair instead (see Fig. 1.2(b) for a schematic illustration). This process is commonly referred to as CM, multiple exciton generation (MEG) or impact excitation in case of bulk materials and can only take place if the excess energy is at least as large as the bandgap energy ($E_{excess} \geq E_{gap}$). Efficient CM is very beneficial for the photovoltaic conversion of ultraviolet (UV) photons, whose energy is predominantly wasted as heat in standard solar cells. The CM process is in competition with carrier cooling and therefore has to occur on short timescales in order to be efficient. Similar to AR, impact excitation is inefficient in bulk systems with high CM threshold energies (multiple times the bandgap energy) and low CM conversion efficiencies[16, 17]. Due to the just-discussed quantum confinement-induced effects of the slowdown of carrier cooling and increased Coulomb interaction, this process can be greatly enhanced in NCs[18, 19]. Following the MEG process, whereby multiple excitons are generated in a single NC, AR can take place, resuming to the situation of a single electron-hole pair in the NC with a lot of excess energy. This cycle of MEG followed by AR can continue until the excess energy becomes insufficient for MEG to take place due to cooling or until the carriers have recombined[20]. At the end, the maximum number of emitted photons per NC is (generally) still limited to 1 due to the AR process being fast compared to the radiative recombination rate.

A specific type of MEG, namely space-separated quantum cutting (SSQC), has been reported for Si NCs embedded in an SiO_2 matrix[21, 22]. During the SSQC process, the excess energy of a hot carrier is used to excite a neighboring NC (see Fig. 1.2(c)). Due to the spatial separation, the two electron-hole pairs do not undergo AR and they can both recombine radiatively. This SSQC process offers perspective for many applications. For example, it can lead to an enhanced photovoltaic conversion since the excess energy of the electron-hole pair generated after the absorption of an UV photon, which is otherwise lost before it can be extracted, can now be used to create another long-living free carrier and hence additional photocurrent. Besides transferring to a neighboring NC, rare earth ions, which will be discussed in the next Section, can also be introduced into the material as energy recipients in the SSQC process, as will be considered in Chapter 6.

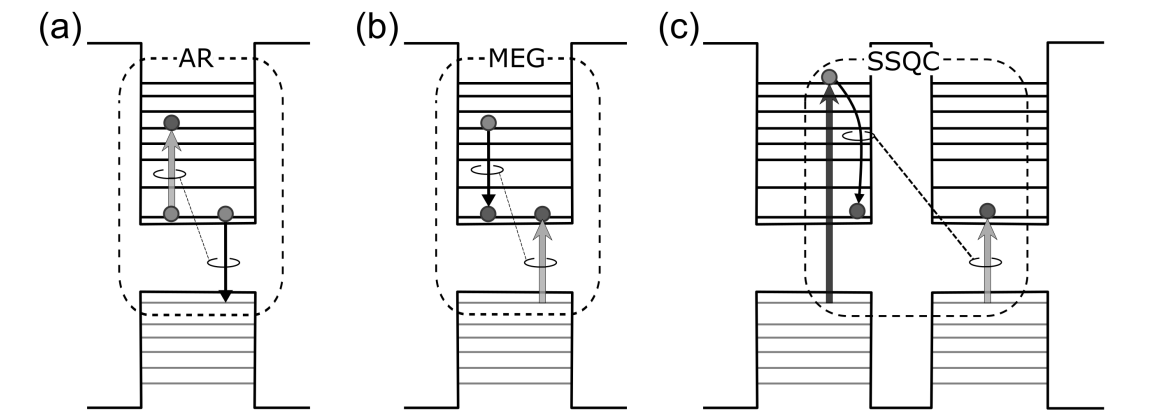


Figure 1.2: **Schematic illustration of multicarrier processes in semiconductor nanocrystals.** (a) Schematic illustration of the AR process of two electron-hole pairs in a single NC, whereby one pair transfers its energy to the other one promoting it to a higher excited state. (b) During the MEG process a hot carrier cools down by generating a second exciton in the same NC. (c) Special case of the MEG process, whereby the hot-carrier excess energy is used to generated an exciton in a neighboring NC.

1.6 Doping semiconductors with rare earth ions

Doping of semiconductors is generally used to enhance their optical, magnetic and electrical properties. Lanthanides are frequently referred to as rare earths, together with the elements Sc and Y, which feature similar chemical properties. Unlike the rare earth name would suggest, most of these elements are less rare than some other industrial metals. Their individual abundances in the Earth can vary by two to five orders of magnitude and their name probably originates from the fact that they are usually not concentrated in exploitable ore deposits[23]. Doping a semiconductor with rare earth ions can lead to the formation of an optical material, whose emission usually features sharp, practically temperature-independent emission lines, which, for a specific dopant, varies only slightly with the semiconductor host. Rare earth ions are therefore frequently used to develop laser materials (e.g. Nd:YAG) and for optoelectronic applications. The ions can be excited directly, by resonant energy absorption within the 4f-electron core, but also indirectly by energy transfer via the host, as will be discussed further for the systems of SiO₂ co-doped with Si NCs and Er and GaN doped with Eu in Chapters 6 and 7, respectively.

1.7 Synergy of the thesis

In this thesis, the carrier dynamics in three semiconductors are described. An overview of the fundamentals of semiconductors is just presented in the previous Sections of this Chapter. The next five Chapters are dedicated to nanostructures of the best known and most used semiconductor in the electronic and photovoltaic industries, Si. In Chapter 2, Si NCs are discussed with an eye on photon management in future photovoltaics. Currently a large part of the solar spectrum is not utilized by single-junction photovoltaic devices based on Si. At least 19% passes through a crystalline Si solar cell, because the photon energy is too low, and more than 33% of the solar energy is after absorption converted into (useless) heat[24]. Therefore strategies are proposed to decrease these losses and to reach high photovoltaic efficiencies above the Shockley-Queisser limit[1]. The power-dependent PL properties of Si NCs embedded in an SiO₂ matrix are presented in Chapter 3, which could be relevant for the application potential of this material for spectral conversion layers in concentrator photovoltaics. Chapter 4 is dedicated to the carrier dynamics of this system, with the focus on the self-trapped exciton (STE) state on the surface of the Si NCs. The PL properties of slightly larger Si nanoparticles (NPs) of a size of ~100nm, so outside of the quantum confinement regime, are studied and discussed in Chapter 5. The next two Chapters are devoted to the optical doping with rare earth ions of semiconductors with the focus on the energy transfer between the semiconductor and the dopant. The rare earth ion Er³⁺ is added to the system of Si NCs in SiO₂ and its optical properties are compared to the Er-free system (Chapter 6). For the development of full color displays of the new platform of the wide-bandgap semiconductor GaN, efficient red light-emitting devices are still needed. For that purpose, GaN doped with Eu could be a promising alternative and the carrier dynamics of this system is therefore studied in Chapter 7. Finally, recently developed and now widely investigated NCs, featuring high PL quantum yields (QYs) and narrow, tunable emission in the visible range are studied: all-inorganic cesium lead halide perovskite NCs (Chapter 8). Due to its advantageous properties, this material has great potential for many applications. The research field of these perovskite NCs is still relatively young, but theoretical as well as experimental knowledge is quickly developing. The presented study contributes to this dynamic research field.

The experimental details differ per study and are briefly given at the beginning of each Chapter. Generally, in view of the application-driven character of the research described in this thesis, all the experiments have been performed at room temperature.