Time-Resolved Spectroscopy of Energy Transfers in Optoelectronic Media

Izeddin Aguirre, I.

Summary

This thesis presents PhD promotion research on spectroscopy of optoelectronic media carried out at the Van der Waals-Zeeman Institute for Experimental Physics of the University of Amsterdam, during the years 2003 to 2007. Using a range of electro- and photoluminescence techniques, the investigations deal with various aspects of energy transfer processes in the material. These are studied from a fundamental point of view, and the conclusions are considered in view of prospective practical applications. The relevant theoretical modeling is developed in order to interpret the data and to propose microscopic models.

The Introduction starts by reflecting on the motivation of this research. After pointing out the importance of electronics—and therefore the element silicon—in modern society: the *silicon age*, its fundamental physical limits are presented. It is concluded that suitable alternatives need to be studied, and developed. In this context it is argued that *photonics – i.e.* the use of photons, instead of electrons, as information carriers – is an attractive field which could respond to the societal demand for ever smaller and faster devices. Doping of semiconductors with rare earth ions—and especially with erbium in view of its technologically important 1.5 μm emission—, and the use of nanostructured silicon are two prominent realizations of Si photonics. Both are considered in this thesis and several aspects are studied in detail.

After exposing the motivation for the research, the Introduction presents some basic concepts of condensed matter physics, necessary for the investigations: the definition of semiconductor materials and some considerations on their optical properties, a brief characteristics of the element silicon, and the concept of optical doping of a semiconductor describing the use of rare earth ions and silicon nanocrystals.

In Chapter 1, an in-depth study of optical properties of silicon doped with erbium ions is presented. The Section 1.1of the chapter deals with fundamental aspects of energy transfer between the host, silicon, and the optically active element, the rare earth ion erbium. Making use of a nanostructured sample consisting of a series of nanolayers of undoped and Er-doped silicon, and applying a Free Electron Laser for two-color spectroscopy, provides evidence that

proves the role of the erbium-related donor in the host-mediated optical excitation of erbium. Based on these results, a new excitation mechanism in this system is proposed and then confirmed by excitation spectroscopy.

While the first section of Chapter 1 is related to fundamental aspects of the optical excitation of erbium-doped crystalline silicon, Section 1.2 proves the potential of the multinanolayer system for applications. There, a fully CMOS compatible electro-optical converter with memory function is presented. Its electrically driven optical *write-read-erase* functionality is demonstrated outside cryogenic temperatures. A cross point memory array based erbium-doped silicon is proposed as a photonic memory device.

Chapter 2 focuses on the problem of sensitization of erbium in a silicon dioxide matrix with silicon nanocrystals. This system combines positive features of erbium-doped crystalline silicon with those of erbium-doped silicon dioxide. The key points are the high excitation cross section of the optical excitation of erbium via the silicon nanocrystals (similar to that of erbium excitation via the crystalline silicon host) and the thermal stability of the photoluminescence of erbium dispersed in a silicon dioxide matrix. Full understanding of the sensitization mechanism is of crucial importance for exploration of the potential of this material in the field of silicon photonics. In order to achieve that, a series of samples exhibiting simultaneous photoluminescence from both, erbium and silicon nanocrystals, were investigated by time-resolved spectroscopy with a high resolution obtained by implementation of a photon counting detection technique.

In the first Section 2.1 of Chapter 2, a fast erbium-related photoluminescence component, sensitized by silicon nanocrystals, is reported. Its a characteristic time decay is in the nanoseconds range – between five and six orders of magnitude faster than the usually reported radiative decay of erbium. Excitation and de-excitation, responsible for this fast component take place within the first microsecond after the laser excitation pulse, i.e., before the previously reported, microseconds excitation of erbium by the silicon nanocrystals takes place. An Auger process related to cooling and re-heating of confined carriers by transitions between the space-quantized levels of the silicon nanocrystals is proposed as the mechanism responsible for this fast photoluminescence band. With the new evidence at hand, a long-standing problem of apparent loss of optical activity of erbium dopants upon sensitization with silicon nanocrystals is cleared up, and it is shown that up to 50% of the total erbium content in the sample is excited via the newly proposed fast mechanism (while the excitation is immediately quenched by the reverse process).

The following Section 2.2 develops fully the model proposed in the previous Section 2.1 and exhaustively investigates the energy transfer processes between

silicon nanocrystals and erbium. All photoluminescence bands are identified and their kinetics investigated in detail. Accordingly, a comprehensive model of energy transfer mechanism for light generation and quenching in the system is proposed. The necessary theoretical framework is developed, yielding the microscopic understanding of the underlying physical mechanisms. The observed photoluminescence spectra, high-resolution dynamics, and excitation cross section measurements are combined with theoretical modeling and simulations rendering a consistent microscopic description of the sensitization effect and its limitations.

One of the consequences of the model proposed in Section 2.1 and developed in Section2.2 is the appearance of a second excitation mechanism when a photon with sufficient quantum energy is absorbed by a silicon nanocrystal. In this case, there exists a probability for this photon to "divide" its energy inducing two excitation processes of two erbium ions. In the so-called *quantum cutting* process, a high energy photon can be divided into two or more quanta of lower energy. The object of investigation of Section 2.3 is the photon cutting by silicon nanocrystals; nearby erbium ions and neighboring nanocrystals are used to enable this effect. The experiments demonstrate that above a certain energy threshold for the quantum energy of the incoming photons (defined by the sum of the silicon nanocrystal band gap and the energy necessary for excitation of the neighboring probe – either an erbium ion or another nanocrystal) the relative quantum efficiency of the excitation mechanism increases. This is explained in terms of two subsequent excitation processes: the primary one due to the intra-band cooling of the "hot" carrier within the quantized states of the nanocrystal, followed by a secondary excitation due to the inter-band recombination of the electron-hole pair.

The excitation increase by photon cutting process taking place between silicon nanocrystals is of paramount importance for photovoltaic applications. In solar cells, a substantial part of the incoming photon energy in the high-energy range of the solar spectrum is wasted to heat, as the excess energy of the absorbed photon is converted into kinetic energy of the electron-hole pair. This is one of the limiting factors for the maximum efficiency of solar cells. Therefore, as argued in Section 2.3, the space-separated quantum cutting process may lead the way to a substantial improvement of photovoltaic devices.

Finally, in Chapter 3, the optical properties of erbium-doped large band gap hosts are investigated. In Section 3.1, photoluminescence and photoluminescence excitation spectroscopies are applied to erbium-doped gallium nitride samples. Based on these results, the possible multiplicity of the erbium sites in this host is discussed. In Section 3.2, the potential of erbium doping for realization of mid-infrared emission at the wavelength of 2.7 μm, due to the

transition between the second and the first excited states, is studied. For that purpose, a large band gap fluoride crystal is used. In this material erbium occupies a well-defined substitutional site only, is used.. The results obtained for the fluoride serve to facilitate the understanding of the erbium-doped gallium nitride system. By recording the photoluminescence transients for several transition, lifetimes of the individual excited states are determined. The results indicate that erbium doping of both hosts should enable the mid-infrared emission.