Photoluminescence spectroscopy on erbium-doped and porous silicon
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Chapter 1

Introduction

1.1 Luminescence

In semiconductors, as well as in other solids, luminescence results from radiative transitions of an electron from a higher- to an empty lower-energy state. The emission spectra are characteristics of the materials and their dopands. They are usually in the visible or near-infrared ranges of wavelength. According to the source of excitation different kinds of luminescence are distinguished. Chemoluminescence is caused by light emission during a chemical reaction. Luminescence following irradiation by X-rays is termed X-ray luminescence. Cathodoluminescence results from bombardment by energetic electrons. Electroluminescence is luminescence excited by applying a voltage to the material. Photoluminescence is a result of an optical excitation. In semiconductor spectroscopy, photoluminescence is a useful technique for the study of optical and dynamical processes in the materials. Together with other types of experiments, like optical absorption spectroscopy, secondary-ion mass spectroscopy, Hall effect experiments and many others, the gathered knowledge will give a detailed picture of the electrical and optical properties of the investigated system. In the photoluminescence technique, free carriers or excited states in the semiconductor are generated by absorption of optical photons with an energy above the band gap of the semiconductor. When the equilib-
rium in the sample is perturbed the system tends to return to its initial state and relaxation processes like the recombination of carriers may be observed. The photoluminescence spectra contain information about impurity and defect constituents, quality of the material and recombination mechanisms which are involved. A certain fraction of the recombination occurs with emission of a photon (radiative recombination), while the other recombinations involve the emission of one or several phonons or occur by an Auger process involving an electron; the last processes are nonradiative recombinations. The luminescence efficiency, $\eta_L$, is given by the following formula:

$$\eta_L = \frac{r_r}{r_r + r_{nr}},$$

(1.1)

where $r_r$ and $r_{nr}$ are the radiative and the nonradiative transition rates, respectively.

### 1.2 Luminescent recombinations in silicon

While the first transistor, invented in 1948 [1], was based on germanium, silicon has since then become the main material for microelectronic applications because of its ideal 1.12 eV band gap for room-temperature operation. In fact, a number of optoelectronic integrations on silicon-based materials have been achieved, such as high-quality optical detectors, light-emitting diodes, semiconductor lasers and so on. The radiative recombination rate in pure silicon is, however, very low since electron and hole are not located at the same wave vector in $\mathbf{k}$-space due to the indirect band gap of silicon. Their recombination necessarily involves a third particle, which is accomplished by the absorption or emission of a phonon with a correct wave vector $\mathbf{k}$. Although semiconductor applications in optoelectronics tend to use the direct-band gap compound semiconductors like indium phosphide and gallium arsenide, which have higher optical recombination rate than that of silicon, silicon materials are strongly dominant in the field and thus it is necessary to eliminate the limitation of the radiative efficiency in silicon. There is a number of ways that have been suggested to achieve this goal which can be classified as follows:
Photoluminescence via impurities in silicon. Radiative impurities in silicon create recombination centers in the band gap through which the recombination of electron-hole pairs can be accomplished without phonon required. The most common impurity-radiative centers are the isoelectronic centers. For instance, sulfur-, selenium- or beryllium-doped silicon by implantation or diffusion [2, 3, 4, 5] with subsequent rapid quenching. The impurities can also be rare-earth ions which show intra-shell transitions independently of the host environment. Centers of rare-earth metals (Dy, Ho, Yb, Er), which are commonly donors, have been reported recently [6]. Erbium-doped silicon is a particular case where the light emission at 1.5 μm wavelength is coincidental with the maximum energy-transfer range of silica optical fibers applicable to the long-distance communication technique and to silicon-based integrated optoelectronics [7, 8, 9]. Applications of erbium-doped crystalline silicon in light-emitting diodes (LED) operating at 77 K [10] and at 300 K [11, 12] have also been developed.

- Strong radiative transitions are given by systems of two IV-group elements, such as Si$_{1-x}$Ge$_x$ (0 ≤ x ≤ 1) and their alloys [13, 14], because of the statistical disorder which breaks the selection rules. Some theoretical predictions [15, 16] have attributed the strong absorption and emission of the Si/Ge superlattices to the quasi-direct band gaps but the experimental evidences are still very weak.

- The formation of luminescent silicon-based materials with high concentration of hydrogenated amorphous silicon [17, 18, 19], synthesized siloxene [20] and related compounds, which produce strong visible luminescence due to transitions in adsorbed molecules.

- Reducing the dimensions of bulk silicon crystals to become quantum wires or quantum dots leads to an enlarged and direct band gap of silicon [21]. As a result of the quantum confinement effects, the probability of the direct recombination is increased. Porous silicon is a special case where a system of few-nanometers silicon grains is produced by etching of crystalline silicon in a solution containing of hydrofluoric acid. This material gives photoluminescence in the visible range with intense emission efficiency at room temperature.
Applications of nanocrystalline silicon materials have focused on the development of a stable electroluminescence system for integrated circuit processing and $p-n$ junction fabrication [23]. A structural example of a porous-silicon-based device was presented in Ref. [24], however, a better understanding of electrical activity and carrier-transport mechanisms of the materials is required.

The aim of the research presented in this thesis is to study silicon-based luminescent materials which are suitable to perform functions in telecommunications and optoelectronic applications. Two systems, erbium-doped silicon by implantation and silicon nanocrystals prepared by an electro-chemical method, have been chosen. Energy transfer in excitation and de-excitation processes of the two systems is investigated. The light-emission mechanisms are studied and discussed in detail.

### 1.3 Erbium in silicon

All rare-earth elements have a similar atomic configuration $[\text{Xe}]4f^{n+1}6s^2$ with $n = 1 \div 13$ from Ce to Yb. When incorporated into a solid the rare earths generally tend to form ions of trivalent charge state for which the electronic configuration is given by $[\text{Xe}]4f^n$. For erbium $n = 11$ leads to a ion configuration $[\text{Xe}]4f^{11}$. The radius of the $4f$ shell and the Er$^{3+}$ ion are 0.431 and 0.881 Å, respectively. Following the Russell-Saunders scheme the orbital and spin momenta of the individual electrons couple separately to total $L = 6$ and total $S = 3/2$. Spin-orbit interaction determines the ground state as $^4I_{15/2}$, the first excited state as $^4I_{13/2}$ and the higher excited states as $^4I_{11/2}$ and $^4I_{9/2}$. The most useful techniques for incorporation of erbium in silicon are ion implantation and molecular beam epitaxy (MBE). The erbium concentrations which can be achieved with these methods are $3 \times 10^{20} \text{ cm}^{-3}$ and $10^{19} \text{ cm}^{-3}$, respectively [25, 26]. Co-implantation of other impurities (C,F,N) and in particular of oxygen (O), forms impurity-erbium complexes which enhance the solubility of erbium in silicon and hence the erbium photoluminescence intensity at low temperatures [27, 28].

A most effective experimental method to investigate erbium in silicon is luminescence, because among the other methods the most informative technique, electron paramagnetic resonance (EPR), up to now has given
only a very limited set of results contributing to the elucidation of the
electronic structure of erbium-related centers in silicon. The erbium ion is
optically excited from the ground state only to the first excited state sepa-
rated by approximately 0.8 eV because the distance between the ground
state and the higher excited states exceeds the band gap energy of silicon.
The emission of erbium is characterized by the lines corresponding to the
$^4I_{13/2}$ to $^4I_{15/2}$ transitions within the $4f$ shell. Following the crystal-field
analysis the spectrum of a particular symmetry can be established; the
positions of all the spectral components can be fitted taking into account
the symmetry of the erbium-related optically active complexes. When er-
bium is incorporated in silicon at a cubic-symmetry ($T_d$) site, the ground
state is split into three quartet $\Gamma_8$, one doublet $\Gamma_7$ and one doublet $\Gamma_6$ and
the first excited state is split into one $\Gamma_7$, two $\Gamma_8$ and two $\Gamma_6$ levels. The
Er-related photoluminescence lines at low temperature are then ascribed
to transitions from the lowest level of the first excited state to levels of
the ground state. For a cubic center this will give rise to five lines in the
1.5–1.6 $\mu$m range. For a crystal field of lower symmetry every quartet
$\Gamma_8$ will split into two doublets; the spectrum, therefore, will exhibit eight
lines. The crystal-field splitting of erbium ions and possible transitions
in the $4f$-shell have been investigated theoretically and experimentally
[29, 30, 31]. The radiative recombination rate of erbium is influenced by
the interaction between $4f$ shell and crystal field, which can mix in states
of opposite parity. It is generally small and thus the emission efficiency or
oscillator strength of the intra-$4f$ shell transition is small and its radiative
lifetime is relatively long [32, 33].

1.4 Porous silicon

Porous silicon is a disordered system which consists of silicon nanocryst-
talline clusters of a few hundreds to a few thousands of atoms. The
main technique to fabricate porous silicon materials is electro-chemical
whereby the crystalline silicon is anodized in a HF-ethanol solution un-
der a constant current density. The shapes and sizes of the nanocryst-
tallites depend very much on the experimental parameters of the sample
preparation procedure [34]. Porous silicon has an enlarged direct band
gap which increases with decreasing size of the nanocrystals. Theoreti-
cal calculations of the dependence of the silicon band gap on the size of nanocrystals are presented and discussed in Ref. [35]. According to these calculations a band gap, for example, of about 2 eV is obtained for silicon nanocrystallites of 2.5 nm. The large surface-to-volume ratio in porous silicon indicates the important role of surface states in the luminescence processes of porous silicon. The radiative efficiency of porous silicon at room temperature is in the order of $0.01 - 0.1$ compared with $10^{-4}$ of bulk silicon.

1.5 About the thesis

This thesis focuses on two systems: rare-earth erbium-doped silicon and porous silicon investigated by photoluminescence. The experimental and theoretical results are shown to reveal insight into the mechanisms of the light emission from erbium-doped silicon by implantation (chapters 3 - 5) and from porous silicon fabricated by a chemical-electronic anodization method (chapter 6). Chapter 2 presents an overview on the role of weakly bound states in light emission processes of rare-earth ions doped semiconductors in the two most prominent systems: ytterbium in indium phosphide and erbium in silicon. Carriers related to the weakly bound states of the host crystals interact with the atomic-like states associated with the inner core of the rare-earth ions. The energy transfer processes involving such states control both excitation and de-excitation paths of the systems. The weakly bound states also dominate nonradiative mechanisms leading to the quenching of luminescence of rare earths in semiconductors, especially at high temperatures.

Chapter 3 concerns the dependence of erbium photoluminescence intensity on excitation power. The experiments have been performed on different samples implanted with erbium and co-implanted with oxygen ions. The power dependencies of luminescence intensity were measured under the excitation by an Argon-ion laser with power in the range of 0.1 mW to 1 W. The experimental results were analyzed based on theoretical calculations of energy-transfer kinetics of erbium in silicon, which were basically developed by Bresler et al. [36]. The theoretical calculations are performed with and without Auger processes in the erbium-related bound-exciton and excited erbium ions states with the aim of
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verifying the quantitative agreement.

Since valuable information on energy transfer mechanisms can be deduced from the temperature dependence of erbium photoluminescence intensity and decay time, in chapter 4 the theoretical calculations of the temperature dependence of photoluminescence intensities will be presented and compared with the experimental results for different kinds of samples and with different excitation powers. From that, analyses the activation energies responsible for individual paths of the energy transfer processes are obtained. The relation between erbium and silicon band-edge photoluminescence will also be presented and discussed in this chapter.

In chapter 5 double-beam experiments with a pulsed Nd:YAG laser operating at 532 nm or a continuous wave (cw) solid state laser operating at 820 nm wavelength and a mid-infrared pulse provided by a free-electron laser are applied to investigate in detail characteristic individual energy-transfer paths in luminescence processes of erbium in silicon. Two effects, quenching and enhancement of the erbium photoluminescence intensity induced by the mid-infrared illumination are observed and discussed. The intermediate states including shallow-state centers of effective-mass-theory characteristics are found to be involved in the energy transfer mechanisms of erbium in silicon, whose occupations are influenced by the mid-infrared pulse from the free-electron laser.

Results on the optical properties of the yellow silicon-based fibers which are prepared by an electro-chemical anodization process are reported in chapter 6. The crystalline structures of the yellow silicon-based fibers have been analyzed by several structure sensitive techniques, such as X-ray Diffraction, optical and Atomic Force Microscopy and X-ray Photoelectron Spectroscopy. The conclusion has been drawn that the yellow silicon-based fibers consist of nanoscale silicon crystals which exhibit intense luminescence in the visible region at room temperature. Chemical treatments in a hydrofluoric solution and Raman scattering spectroscopy measurements have been performed and analyzed. The average diameter of the spherical silicon nanocrystals in the yellow silicon-based fibers is found to be 2–3 nm. The nanocrystals are embedded in an imperfect silicon oxide.
References


Introduction


