Photoluminescence spectroscopy on erbium-doped and porous silicon
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Summary

Among various possibilities, rare-earth doped- and porous silicon aim at one common goal in semiconductor applications that is the developing of light emitting of silicon-based materials with high efficiency. The research described in this thesis presents an optical study on these two systems.

Chapter 1 gives a brief introduction about the main technique, photoluminescence, which is used in this thesis, and the necessity to eliminate the limitation of the low radiative efficiency of silicon. The aim and outline of the thesis are given.

Chapter 2 discusses the participation of weakly bound states in the energy transfer processes between rare-earth ions and host semiconductors for two systems, i.e., ytterbium in indium phosphide (InP:Yb) and erbium in silicon (Si:Er). This links the atomic-like states of the inner core of the rare-earth ion with states in the band of the host crystals. The multi-stages excitation mechanism is discussed for the Si:Er system, where the weakly bound states control both excitation and de-excitation paths. Experimental results supporting the involvement of these states are reviewed.

In chapter 3 photoluminescence spectra of different crystalline silicon samples doped with erbium by ion implantation with and without oxygen co-dopant, by molecular beam epitaxy method and an erbium-doped amorphous silicon sample are analyzed. In the multiple-component spectra the presence of erbium-related centers of different symmetry, cubic and non-cubic, is confirmed. The dependencies of the luminescence intensities on the laser excitation power were measured and analyzed on the basis of a physical model involving free and bound exciton intermediate states. It was found to be necessary to include Auger processes, by which erbium-bound excitons and excited erbium ions decay nonradiatively, in the model. The results showed a remarkable similarity for erbium-doped crystalline implanted samples of float-zoned and Czochralski origin. This conclusion was revealed by the consistent use of normalized units for both excitation and luminescence intensity. A good quantitative agreement is obtained for suitable values of the model parameters.

More information on excitation and de-excitation mechanisms can be deduced from thermalization behaviors of the photoluminescence inten-
sity, which is described in chapter 4. The dependencies of the erbium photoluminescence intensity on temperature of different kinds of samples and at different excitation powers were measured in the temperature range from 4.2 to 200 K. The experimental results were analyzed and compared with the excitonic excitation model with involvement of Auger processes as mentioned in chapter 3. The model provides good quantitative agreement with the experimental data. In the temperature range below 100 K the thermal quenching of erbium luminescence intensity is controlled by the binding of excitons to erbium centers. At higher temperatures, above 100 K, the activation energy, which is associated with the energy transferred from an excited erbium ion back to an erbium-bound exciton becomes more prominent. In some particular samples the binding energy 1 – 3 meV of excitons bound to shallow centers of the silicon host is obtained in a low-temperature range from 10 to 30 K. The optically active erbium ions are estimated to be a small fraction, in the order of 1% of the total erbium concentration.

Chapter 5 deals with two-beam excitation experiments, a pulsed laser, Nd:YAG, operating in the visible range and a free-electron laser providing an intense mid-infrared illumination, to investigate individual stages in the energy transfer process of erbium-doped silicon system. Two effects induced by the mid-infrared radiation on erbium-related photoluminescence are observed. The first one is the quenching effect, which is related with lower-than-cubic symmetry centers of erbium ions at short delay times of the mid-infrared excitation beam. The effect is propounded to be a consequence of disruption of the energy transfer processes by the mid-infrared beam. The second effect is an enhancement of photoluminescence intensity upon the excitation of the mid-infrared beam. The enhancement effect is obtained for all samples; with long delay times for samples dominated by low-symmetry centers and with all delay times for samples in which cubic symmetry erbium-related centers predominate. The origin of the enhancement effect is concluded to be related to energy storage at shallow, effective-mass-theory characteristic centers. These centers are ionized by the mid-infrared pulse, thus promoting extra carriers into the excitation path of the erbium ions. Dependencies of the enhancement effect on wavelength and power of the mid-infrared beam are investigated in detail as spectroscopic evidences for the participation
Summary

of shallow centers in the energy transfer processes in the erbium-doped silicon system. A theoretical description is proposed in good agreement with the experimental data.

The observation of visible photoluminescence from the so-called free-standing yellow silicon-based fibers and the remaining porous silicon wafers is presented in chapter 6. In these fibers silicon nanocrystallites embedded in an imperfect silicon oxide are identified by various structure analyses. The Raman scattering spectra of the yellow silicon-based fibers are well reproduced by a theoretical calculation using the spherical model for the silicon nanocrystals. From this an average diameter of 2.5±0.5 nm is obtained for the nanocrystalline grains in the fibers. Quantum confinement effect accounts for the light emission of these materials. Besides that, the influence of surface states on the radiative recombination via chemical treatments in HF-solution has been concluded.