Optical properties of isoelectronic centers in crystalline silicon
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Chapter 1

Introduction

1.1 Optical centers in semiconductors

Recombination resulting from the annihilation of electron-hole pairs in semiconductors is called the photoluminescence (PL). This can be accomplished by a variety of ways. When semiconductor crystals are excited by a laser or other radiation, electrons are removed from the valence band and placed in the conduction band, leaving holes in the valence band. Because of the mutual attraction between the electrons and the holes, these particles can exist as pairs, excitons, which can move throughout the crystal. Free carriers and excitons can be trapped at donors or acceptors in either neutral or ionized states and subsequently recombine. Various electron-hole recombination processes produce an emission spectrum with many different components.

A useful distinction can be made between charged centers, i.e. donor or acceptor, and neutral (or “isoelectronic”) centers. A single donor has one excess electron (such as Si:P), meaning that the defect region has a net positive core charge. Similarly, a single acceptor (such as Si:B) has a net negative localized charge. An isoelectronic center (such as Si:C, Si:Cu) has no net charge in the local bonding region. A hole or an electron can be localized at such a center by a local (core) potential; subsequently, the secondary particle can be captured by Coulomb field into a shallow, effective-mass-theory (EMT) state. The main difference between neutral and charge centers is absence of the long-range Coulomb potential. This simple picture is adequate for single donors, acceptors and isoelectronic centers, but also for complex defects which involve more than one site, such as a pair of substitutional impurities, a substitutional-interstitial pair, a vacancy pair, a vacancy interstitial pair (if one constituent is a shallow donor or acceptor), etc. [1]. There are two systems of symbol which are used in literature to label these luminescence centers: these are given in the Table 1.1
Table 1.1: Common symbols for labelling recombination processes.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>Free exciton</td>
<td>X $\pm$ $\mp$</td>
</tr>
<tr>
<td>Donor</td>
<td>$D^0$ $\oplus$ $\ominus$</td>
</tr>
<tr>
<td>Acceptor</td>
<td>$A^0$ $\ominus$ $\oplus$</td>
</tr>
<tr>
<td>Exciton bound at neutral donor</td>
<td>$D^0$, X $\ominus$ $\oplus$</td>
</tr>
<tr>
<td>Exciton bound at ionized donor</td>
<td>$D^\pm$, X $\ominus$ $\oplus$</td>
</tr>
<tr>
<td>Exciton bound at neutral acceptor</td>
<td>$A^0$, X $\ominus$</td>
</tr>
<tr>
<td>Exciton bound at ionized acceptor</td>
<td>$A^\pm$, X $\ominus$ $\oplus$ $\ominus$</td>
</tr>
<tr>
<td>Exciton bound at isoelectronic center</td>
<td>$A^\pm$ $\ominus$</td>
</tr>
<tr>
<td>Free electron to acceptor transition</td>
<td>$c$, $A^0$</td>
</tr>
<tr>
<td>Donor to free hole transition</td>
<td>$D^0$, h</td>
</tr>
</tbody>
</table>

In the case of single donors or acceptors the ground state already contains one bound electronic particle, an electron or a hole, respectively. The excited states for these centers can usually be described in the EMT approximation [2.3] based on the hydrogen-like Coulomb potential. Localization of an exciton to these centers creates the bound exciton (BE) excitation. A BE consists of three carriers (two holes and one electron for acceptor BE, two electrons and one hole for donor BE) bound to a charged impurity. Fig. 1.1 (a,b). Because in a BE three carriers are localized in the same region of real space, an Auger transition, in which an electron recombines with a hole and the energy is carried off by the third carrier, can occur. Auger transitions are believed to limit the lifetimes of BEs in many cases.

The isoelectronic centers have no particle localized in the ground state, and the analog to the above-mentioned excitations for the donors/acceptors therefore does not exist. Such centers bind electrons (or holes) by a weak interaction (a strain field, or a local change of electronegativity). The cross section for capture of the first carrier is usually quite small for these centers. Upon localization of the primary particle, the secondary particle, a hole (or an electron) can be captured in Coulomb field of the first particle. This BE state containing two electronic particles associated with the isoelectronic center has usually very well defined electronic energy, corresponding to a sharp emission/absorption line in optical spectra (if the phonon coupling in the optical transition is not too strong). These systems have been classified as isoelectronic donors and isoelectronic acceptors on the basis of whether the impurity is attractive for holes or electrons, respectively, Fig. 1.1 (c,d).
1.2. Isoelectronic centers

The radiative decay of excitons bound to isoelectronic impurities is an important physical process in crystalline semiconductors. This is particularly true in indirect band-gap semiconductors like GaP and silicon, in which band-to-band radiative transitions are forbidden by the $\vec{k}$-conservation rule. The introduction of isoelectronic impurities into indirect band-gap semiconductors helps to improve the quantum efficiency of optical emission. Emission due to exciton bound to an isoelectronic center is characterized by a long radiative decay time, which indicates stability against nonradiative Auger processes, and high radiative quantum efficiency. The lifetime can be $\tau > 10^{-5}$ s compared to $\tau < 10^{-7}$ s for BE at single donors or acceptors. As a result of the relatively weak binding of both electron and hole, the luminescence from the isoelectronic centers usually has the photon energy close to the electronic gap, but considerably less than for an exciton bound to shallow donors or acceptors.

The isoelectronic bound exciton (IBE) emission from silicon has attracted considerable interest in the last few years and has now been observed for Si:S, Si:Be.
Si:In, Si:Tl, Si:Se, Si:Cu, Si:Ag as well as for some unidentified impurities in as-grown silicon [4]. IBEs are also the subject of some technological interest because larger exciton binding potential can lead to intense room temperature emission (for example, X in GaP for green LEDs). Indeed, high internal quantum efficiencies, $\eta_{\text{int}}$, have been observed [5]. Chalcogen complexes in silicon, in particular sulfur complexes, have the highest reported efficiencies; for S in Si an efficiency of $\eta_{\text{int}} = 2 - 5\%$ has been reported [6].

1.3 Silicon photonics

Silicon technology offers almost unlimited possibilities and pervades our everyday life. Silicon chips are in our homes, our cars and sometimes even in people’s bodies. Indeed, the scientific literature contains more than 250,000 papers relating to silicon. But bulk silicon is extremely inefficient for emitting light, and so could play only a minor role in optoelectronics - the high-speed alternative of electronic circuits. So, to make lasers and high-speed telecommunications devices, more complex semiconductors, such as GaAs, InP,... have been called upon. These are good light emitters but are more expensive than silicon and hard to integrate into silicon microchips. If an all-silicon light emitting device could be created it would lead to new types of optoelectronic devices and also revolutionize the design of supercomputers, among others.

Optical doping is an attractive method to tailor photonic properties of semiconductor matrices for development of solid state electroluminescent structures. In particular, rare earth (RE) and transition metal (TM) ions are frequently used for optical doping of semiconductor matrices. In this way, attractive systems are formed, which combine atomic-like properties of dopants with band structure of the host material.

1.3.1 Si:Ag, Si:Cu

There has been a great deal of recent interest in a number of long lifetime, impurity related photoluminescence lines observed in samples of crystalline silicon. It is thought that all of these lines arise from the recombination of excitons bound to various complex isoelectronic centers. The electronic structure of the optically active Cu (or Ag)-related center in silicon was confirmed to be well described by a model of an exciton bound to an isoelectronic center. This was evidenced by the temperature-dependence of luminescence, the time-resolved measurements, and Far-infrared (FIR) absorption spectrum. The electronic level scheme of the exciton bound to the isoelectronic center was developed. In that way, for the case
of copper and silver in silicon, an estimate of the thermal ionization energy of an
electron from the effective-mass-state of 33 meV has been given.

1.3.2 Si:Er

Rare earth doping of Si is known to result in the formation of luminescent centers
and is considered as a promising way to improve photonic properties of silicon.
Among the various rare earth elements, Er is of special interest since its atomic
transition in the 1.5 μm range coincides with the optical window of glass fibers
currently used for telecommunications. Devices based on Si:Er system can be easily
integrated within the highly successful standard silicon technology. Luminescence
at this wavelength from Er-implanted Si was already observed several years ago [7].
Meanwhile Er-based light-emitting diodes operating at room temperature have
been reported. The basic understanding of Er luminescence in Si, however, is
far from complete. While impact with hot carriers is responsible for generation
of efficient electroluminescence in reverse-biased diodes, localization or collisions
with excitons at Er-related donor centers is a generally accepted mechanism of
low temperature photoluminescence in crystalline Si:Er. The Auger process of
exciton recombination with a simultaneous energy transfer to the 4f-electron shell
of the Er$^{3+}$ ions has been modeled theoretically, but it has not been unambiguously
supported by experiment, all evidence in its favor being of an indirect nature.

1.4 This thesis

In this thesis fundamental investigations of excitation and de-excitation processes
of isoelectronic centers in crystalline silicon are described. The studies are carried
out by means steady-state and time-resolved photoluminescence, photolumines-
cence excitation spectroscopy, two-color spectroscopy using a free-electron laser,
and magneto-optical measurements.

The details of experimental techniques are discussed in Chapter 2. In Chapter
3, we report the results of a detailed study of optical properties of a silver-related
center in silicon. Perturbations of optical transitions by uniaxial stresses and
magnetic fields have been accurately described. With the developed energy-level
scheme, the total luminescence and the radiative decay time have been fitted over
the temperature range 4–50 K. It has been shown that from the data an estimate
can be given for the time necessary to thermally ionize an electron from the EMT
state. Using another isoelectronic center created by Cu dopant of silicon - Chapter
4, we have demonstrated that by two-color spectroscopy ionization cross section
can be determined for centers of unknown concentration. Further, we have pre-
presented evidence of a recapture of charge photo-ionized from the Cu-related center. In Chapters 5 and 6, we provide the most direct microscopic information on the structure of a prominent center responsible for optical activity of Er in crystalline silicon. We present specific results of a magneto-optical study of multilayer Si/Si:Er structures grown by sublimation molecular beam epitaxy technique. We show that the presence of Si spacer regions considerably increases emission intensity when compared to single layers. The PL from annealed multilayer structures is dominated by emission from the particular center, the Er-1 center, which is then preferentially formed. The PL spectrum of this center is characterized by ultra narrow, homogeneous lines. From analysis of Zeeman effect clearly observed on the main line of the Er-1 PL spectrum, the lower-than-cubic symmetry of the emitting center is conclusively identified as orthorhombic-I (C2). Based on this analysis, we propose that the microscopic structure of the Er-1 center comprises a single Er$^{3+}$ ion at a distorted interstitial T$_d$ site with multiple oxygen atoms in its direct vicinity. Subsequently, a detailed consideration of excitation mechanisms of the Er-1 center, carried out under cw and pulsed laser pumping, is made in Chapter 7. The overall excitation cross section and the total number of optically active Er$^{3+}$ ions present in Si/Si:Er nanolayers have been evaluated.

Finally, in Appendix A, we briefly discuss the role of exciton diffusion in the excitation process of Er in Si.