Energy relaxation in optically excited Si and Ge nanocrystals
Saeed, S.

Citation for published version (APA):

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: http://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.
CHAPTER 6

Self-assembled Ge nanocrystals grown by PECVD

Structural and optical study of solid-state dispersions of Ge nanocrystals prepared by plasma-enhanced chemical vapor deposition is presented. Two prominent emission bands centered around 2.6 eV and 3.4 eV are reported. Decay dynamics of the observed emission contains fast (nanosecond) and slow (microsecond) components, indicating contributions of several relaxation channels. Based on these material characteristics a possible microscopic origin of the individual emission bands is discussed.
6.1 Structural characterization

The sample used in this study is ~300 nm thick SiGe rich oxide layer grown on a Si substrate in a parallel plate PECVD reactor using N\textsubscript{2}O (23 sccm), SiH\textsubscript{4} (15 sccm), GeH\textsubscript{4} (20 sccm) and N\textsubscript{2} (777 sccm) as precursor gasses. The deposition was followed by annealing in N\textsubscript{2} for 1 hr. at 1200 °C. The sample is characterized using scanning electron microscopy (SEM) together with energy-dispersive X-ray spectroscopy (EDS) for atomic composition, high resolution transmission electron microscopy (HRTEM) for determining the nanocrystal size and shape, Raman spectroscopy for the chemical bonds, and Rutherford back-scattering spectroscopy (RBS) for the atomic composition.

6.1.1 Scanning electron microscopy and electron-dispersive X-ray spectroscopy

SEM together with EDS is used to obtain morphological information together with site-specific atomic composition. EDS can determine the elements present in a certain volume by looking at the characteristic X-ray emission after an electron is kicked out of a specific atomic orbital. SEM imaging reveals that the sample contains a diverse morphology. Figure 6.1 gives an overview of the different structures present in the sample. The sample consists of micrometer size chunks of Ge, together with several oxide structures. These oxide structures are either SiO\textsubscript{2} or GeO\textsubscript{2}. The most interesting structure is perhaps the structure in Fig. 6.1 (d). It presents differently sized spherical particles containing oxygen together with both Si and Ge.

6.1.2 High resolution transmission electron microscopy

Figure 6.2(a) shows the full HRTEM images of the investigated material. The region marked in black is amplified in Fig. 6.2(b) which shows crystalline inclusions. The white marked regions in Fig. 6.2 (b) points out the crystalline structures with a diameter of 8-10 nm. The areas of these structures are obtained by filtering the images in the Fourier domain and transforming back to the real space, Fig. 6.2(c). A lattice spacing of 0.326(4) nm is obtained by analyzing the lattice fringes in Figs. 1(c) and 1(e), which is close to bulk Ge, and clearly different from 0.314 nm characteristic for crystalline Si.

6.1.3 Raman Spectroscopy

Raman spectroscopy is used to characterize the specific bonds present in the sample. Figure 6.3 shows the Raman spectra for as-grown and 1200 °C annealed samples obtained with an excitation wavelength of \( \lambda_{\text{exc}} = 514.5 \) nm, at RT. A clear change from amorphous to crystalline Ge is visible. A Ge-Ge bond-related peak around 297 cm\textsuperscript{-1} is observed and is clearly shifted from 302 cm\textsuperscript{-1} of the bulk crystalline Ge. In addition, a weak peak around 450 cm\textsuperscript{-1} also appears upon
annealing; this has been attributed in the past to Si-Ge bond [101], and could indicate the formation of SiGe alloy. It is nevertheless fair to mention that broad Raman peaks appearing in that range have also been attributed in the past to amorphous Si [102,103]. However in the present case the peak observed around 450 cm⁻¹ is rather narrow, and therefore unlikely to arise due to amorphous Si inclusions.

Figure 6.1: SEM images and EDS spectra showing a crystalline piece of Ge (a), oxide with predominantly Si (b), GeO₂ (c) and nanometer sized spherical particles (d).

Figure 6.1: SEM images and EDS spectra showing a crystalline piece of Ge (a), oxide with predominantly Si (b), GeO₂ (c) and nanometer sized spherical particles (d).
Figure 6.2: Full HRTEM image of the sample annealed at 1200 °C (a). Crystalline structures (b) along with its frequency filtered Fourier space image (c) of the region marked in black in full image. High resolution image of one of the crystalline area (d) and its frequency filtered Fourier space image (e).

Figure 6.3: Raman spectra of as-grown (black solid line) and 1200 °C annealed (red solid line) sample compared with bulk Ge (blue dashed line). The characteristic fingerprint of Ge-Ge bond is present around 297 cm⁻¹ in the annealed sample, indicating formation of a crystalline Ge inclusions. In addition, a peak around 450 cm⁻¹ can also be seen which might be associated with Si-Ge bonds.
6.1.4 Rutherford back-scattering spectroscopy

RBS is an ion scattering technique used for compositional thin film analysis. During these measurements high energy iodine ions (38 MeV) are directed onto the sample and the energy distribution and yield of the back scattered ions at a given angle is measured. Since the backscattering cross section of each element is known, it is possible to get information about the sample composition. The RBS measurement for the sample annealed at 1200 °C shows that it contains 20% Ge, 50% Si and 30% O which is different from the non-annealed sample that contains 70% Ge, 20% Si and 10% O. There is the huge difference between the non-annealed and annealed sample; the reason could be that large amount of Ge is evaporated during the annealing process.

6.2 Optical characterization

In order to have a detailed insight on the quantum confinement effects in this material different optical measurements are performed. These measurements will be discussed in the context of the results obtained from structural analysis of the material.

6.2.1 Linear absorption

Figure 6.4 shows the linear absorption of the annealed layers. The results reveal measurable absorption already for energies starting at approximately 0.5 eV. Also the range of excitation energies for the observed PL bands is indicated.

![Figure 6.4: Linear absorption of the annealed sample. The black arrow indicates the range of the excitation energies for which three PL bands are observed.](image-url)
6.2.2 Photoluminescence
Figure 6.5(a) compares PL spectra of the annealed sample as obtained under continuous wave excitation at different energies. Two prominent peaks can be distinguished around 2.6 eV and 3.4 eV, further referred to as #1 and #2, respectively, both showing a blue shift upon increase of the excitation energy. For the highest excitation energies also an emission peak at approximately 3.3 eV, referred to as #3, can be distinguished. In contrast to PL bands #1 and #2, its position does not depend on excitation energy. Decomposition of the total PL spectrum into three bands for one of the highest excitation energies is shown in Fig. 6.5(b).

![Figure 6.5: (a) PL spectra obtained for the annealed material upon different excitation energies. Dashed lines indicate the excitation-related shift of PL peaks #1 and #2 and the steady PL peak #3. (b) PL spectrum for one of the highest excitation energies, where PL peak #3 is clearly visible. The decomposition of the total spectrum into 3 bands of a Gaussian shape is illustrated.](image)

6.2.3 Photoluminescence lifetime
To get more information about the visible emission, the PL decay dynamics have been investigated. This has been done under pulsed excitation with a photon energy of 4.1 eV. Figure 6.6(a) shows the high-resolution transient taken at a detection energy of 2.8 eV. As can be seen, the decay is dominated by a fast component, with the decay time constant $\tau_{\text{fast}} \approx 30 \text{ ns}$, superimposed on a slowly decaying background (about 1% of the initial signal amplitude), characterized by the time constant of $\tau_{\text{slow}} \approx 200 \mu\text{s}$. We note that in spite of its small amplitude, the slow component dominates the time-integrated PL spectrum. Figure 6.6(b)
shows the PL dynamics in the 1.5 ms range, illustrating the slow component. As can be seen, the actual value of the slow decay time constant varies, becoming smaller towards higher emission energies – see the inset to the Fig. 6.6(b).

Figure 6.6: Dynamics of PL band #1 at an emission energy of 2.8 eV, upon excitation at 4.1 eV. (a) The full dynamics reveal clearly the presence of fast (ns) and slow (µs) components. (b). Dynamics of the slow component of PL band #1 at different emission energies; the inset shows the average PL lifetime versus emission energy as obtained by fitting with a stretched exponential function $I_{PL}(t) = I_0 \exp\left[-\left(t/\tau\right)^{0.8}\right]$.

6.2.4 Time-resolved photoluminescence

Figure 6.7 illustrates the investigations of the fast PL dynamics. Panel (a) shows time evolution of the PL intensity in the 2.3-3.55 eV range within the first 18 ns after the excitation pulse. The initial developments of PL band #1 peaking around $E \approx 2.6$ eV, and a superposition of bands #2 and #3 at around $E \approx 3.3$ eV are illustrated in panel (b), by showing PL spectra at $t_1 = 1$ and $t_2 = 18$ ns. We note that the initial intensity decrease of PL band #1 is characterized by a very fast decay of a few nanoseconds (as indeed seen in the dynamics depicted in figure 6.6(a)) which is faster than the decay of PL band #2 at the higher energy. The situation changes for PL dynamics obtained with the ultrahigh resolution PL setup using 140 fs laser pulses – see figure 6.8. In that case, the very short laser pulse of 140 fs has a high repetition rate of 4 MHz; consequently the slow microsecond component of PL band #1 does not fully decay between consecutive pulses and appears in the measured dynamics.
Figure 6.7: (a) Time-resolved PL spectra obtained with a nanosecond excitation source at 4.1 eV. (b). Decomposition of the PL spectra at $t_1 = 1$ ns and $t_2 = 18$ ns showing the initial fast decay of the PL band #1. Spectra are fitted with two Gaussian components, indicated in green, whereas their superposition is depicted in red. For clarity, the vertical scale in the lower panel has been amplified, as indicated.

Figure 6.8: (a) TR-PL spectra of the fast component obtained with 140 fs excitation source and the excitation energy of 4.1 eV. (b). Decomposition of PL spectra at $t_1 = 1$ ps and $t_2 = 18$ ns. For clarity, the vertical scale in the lower panel has been amplified, as indicated.
6.2.5 Power dependent photoluminescence

The co-existence and sequential dynamics of a slow and fast PL band suggests an intricate interplay between these two emission/recombination channels. This was further investigated by varying the excitation power. Figure 6.9 shows the evolution of the PL spectra excited at $E_{\text{exc}} = 4.1$ eV as a function of excitation power. While the high energy band does not show any change, the band #1 shows a blue-shift of about 300 meV upon increase of the excitation flux, accompanied by the linewidth reduction on the low-energy side.

![Figure 6.9: Influence of excitation power on PL spectrum: a power dependent blue shift of 300 meV for PL peak #1 can be seen.](image)

6.3 Discussion

In order to discuss the possible microscopic origin of the observed emission, we first consider the structural characterization of the material. First of all, the RBS measurements show that following the annealing procedure, the sample contains 50% of Si. However Raman spectra reveal no traces of pure Si – neither in crystalline nor in amorphous form. This is consistent with HRTEM images which do not show any crystalline structures with the lattice spacing matching that of Si. We remark that presence of amorphous Si clusters, which would not be revealed by HRTEM, is also unlikely in view of the high annealing temperature of 1200 °C. On the other hand, the Raman spectrum shows a clear fingerprint of the Ge-Ge bond, as well as a weaker resonance which can possibly be due to the Ge-Si bond. This, again, is consistent with HRTEM, where
Self-assembled Ge nanocrystals grown by PECVD

crystalline inclusions with lattice spacing close to that of crystalline Ge are identified, embedded within an amorphous matrix. We therefore conclude that the investigated material contains Ge and/or Si-Ge crystalline inclusions embedded in Si-rich SiO\textsubscript{2}. Judging from the HRTEM images (Fig. 6.2) the crystalline clusters have a rather broad size distribution, with grains reaching diameters in excess of 10 nm. This large range of sizes is consistent with the linewidth of the Ge-Ge Raman peak [11], in Fig. 6.3, although it is fair to mention that the broadening of the Raman peak can also arise due to temperature and strain.

Before we turn our attention to the emission characteristics of the investigated material, we first link the observed PL with the information provided from Raman spectroscopy. In order to do that we conducted micro PL measurements and results are shown in Fig. 6.10. In that way we have explicitly confirmed that the previously considered Raman spectra are characteristic for the regions of the sample responsible for the observed emission.

![Figure 6.10: Comparison of micro PL with PL spectrum from Fig. 6.6 at E\textsubscript{exc} = 3.8 eV. This confirms that the Raman and emission spectra are measured at the same region of the sample.](image)

As discussed in the experimental section, the PL spectrum contains three components. The two bands shift with pump energy – lines #1 and #2 – and one with pump flux (#1). Such a behavior is characteristic for an ensemble of emitters and is typically observed for NCs [17]. Figure 6.11 displays characteristics of the 3 PL bands found in the investigated material as a function of excitation energy, with panel (a) showing peak positions and panel (b) the
intensity for all the three components. As can be seen, line #2 appears for excitation energies exceeding \( \sim 2.5 \text{ eV} \) and its peak position shifts from \( E_{#2} = 2.4 \) to \( 3.6 \text{ eV} \). Line #1 shifts in a much smaller range, between \( E_{#1} \approx 2.4 \) and \( 2.8 \text{ eV} \), and exhibits a large Stokes shift, appearing only for excitations above \( 3.55 \text{ eV} \). Line #3 is seen for the highest excitation energies and its position remains constant at \( E_{#3} \approx 3.3 \text{ eV} \). This emission band has been frequently reported in the past [9] and assigned to Ge/O-related defect. Detailed investigations uniquely linked this band to the formation of Ge NCs but proved that the emission energy remained fixed regardless of the Ge NC size, thus excluding its excitonic origin.

![Figure 6.11](image)

**Figure 6.11:** (a) Peak position and (b) integrated intensity versus excitation energy for the three observed emission bands.

As mentioned, the excitation-induced PL shift is a fingerprint of an ensemble of emitting centers, and has in the past been observed for NCs of different semiconducting materials and also for molecules. In the first case, its origin is traced to the size, and therefore exciton energy, dispersion and in the latter, to the minute differences in the local environment of individual molecules. In case of NCs, at small excitation energies only large NCs with smaller bandgap can be excited; when the excitation energy is increased, it becomes also possible to excite smaller NCs with larger bandgaps. At shorter excitation wavelengths, the smaller NCs make a substantial contribution to the PL which is then blue shifted. In the present case, the ensemble origin of line # 1 is further confirmed by the power dependence of its peak position – Fig. 6.9 – and the lifetime shift – Fig. 6.6(b). A possible interpretation of the results in Fig. 6.9 is the gradual saturation
of emission from larger grains due to their larger absorption cross-section [104]; this leads to the effective linewidth narrowing and therefore the blue-shifting of the maximum intensity, as indeed observed. Again, in the past these effects have been theoretically modelled and experimentally observed for Si NCs [105]. We also recall that a similar power-dependent blue shift has been reported for well-defined Si/SiGe multilayers prepared by chemical vapor deposition and by molecular beam epitaxy [106,107], and emitting in the near-IR. Also the lifetime shortening at higher excitation energies is consistent with the enhancement of quantum confinement and/or enhanced surface recombination for smaller NCs whose relative contribution increases for shorter excitation wavelengths.

Before we discuss the possible microscopic origin of the observed excitation-dependent emission, we first compare the current results to those obtained in some previous investigation of Ge and Si-Ge NCs [9,18,108]. Figure 6.12 shows the PL energies and lifetimes as obtained in the present study and those published earlier. For completeness, we include there also data for amorphous Si nanoparticles where PL at high energies has also been reported in the past [109]. As can be seen, emissions with characteristics of bands #1 and #2 have not been reported thus far.

![Figure 6.12: Comparison of PL characteristics (peak energy and lifetime) of emission bands #1 and #2 observed in this study with those reported before for Ge and GeSi NCs [9,18,108] and amorphous Si nanoclusters [109].](image)

In an attempt to identify the microscopic origin of PL bands #1 and #2, we confront the results revealed in the present study with what is known on emission from ensembles of Ge and Si NCs. Figure 6.13(a) gives the theoretical
dependence of the bandgap of Ge NCs as a function of the diameter [8]. The energy ranges of PL bands #1 and #2 are marked. We conclude that if the observed emission would be coming from Ge NCs, then their diameters should be small, in the 1-2 nm range, i.e. much smaller than those revealed by the HRTEM measurements, Fig. 6.2. For reference, also some experimental results obtained in previous investigations are shown [9,10,12,110-113]. We see that qua emission energy, PL band #1 is similar to the blue-green PL reported in Refs. [9,12,110]. In figure 6.13(b) a similar comparison is made for the decay time constants; again, we conclude that the experimentally measured lifetimes do not agree with those expected for the large Ge NCs, as identified by HRTEM. Although the presence of Si NCs in the investigated materials has not been revealed, in figures 6.13(c&d) we compare the parameters of bands #1 and #2 with the values theoretically calculated for core emissions from H-terminated Si NCs [114] and experimentally observed for crystalline [115-118] and amorphous Si nanoclusters [109,119]; it is clear that the observed combination of emission energy and lifetime is not likely to be realized with Si. Following on the above considerations, we propose to identify band #2 with exciton core emission from small Ge NCs, with diameters in the 1-2 nm range. NCs of these sizes are beyond detection capabilities of HRTEM, but their presence in our material is certainly plausible; in previous investigations of Ge NCs formed by annealing of supersaturated dispersions in SiO$_2$/GeO$_2$ typically very broad size distributions have been observed [9,19]. We propose further, that this emission is quenched by a strong non-radiative recombination. This notion follows from the very low external quantum efficiency of PL. Figure 6.14 shows PL quantum efficiency of approximately 1%, as determined for the PL peak #1 for several excitation energies. Since the PL peak #2 has a lower intensity than #1, its efficiency will be even smaller. Interestingly, we note that a similar value of PL quantum efficiency can be deduced from the decay transient in Fig. 6.6(a), with an assumption that the fast and the slow components represent the (mostly) non-radiative and purely radiative contributions, respectively. The excitonic origin of band #2 is consistent with the very small Stokes shift, and is supported by the fact that it appears at the energy of ~2.4 eV. Theoretical modelling predicts that for Ge NCs of this bandgap energy and larger, indirect and direct bands equalize [121], thus boosting radiative recombination which can now compete better with non-radiative channels. We also note that the excitonic energy of Ge NCs can be strongly influenced by the presence of a surrounding Si shell [122]; while the presence of such a shell is not revealed in this study – neither in HRTEM nor by Raman – it certainly cannot be excluded. Also investigations of chemically synthesized Ge NCs [123] confirm great surface sensitivity of their optical properties.
Self-assembled Ge nanocrystals grown by PECVD

Figure 6.13: (a) Comparison of the experimentally measured PL peak position versus NC diameter – Refs [9-10,12,110-113] with values modelled theoretically for H-terminated Ge NCs [8], solid dark-blue line. PL peak position (pink) versus expected distribution of NC diameter (dark green) is marked for peak # 1 and peak position (blue) versus expected distribution of NC diameter (light green) is marked for peak # 2. (b) PL life times versus Ge NC diameter, the red points are taken from the theoretical calculation for H-terminated Ge NCs from Ref. [8]. The experimentally observed lifetime ranges for PL bands #1 and #2 and are also indicated. (c) and (d) Similar plots as in panels (a) and (b) but for Si NCs [114-118]. Also results for amorphous Si nanoclusters are indicated for completeness [109,119]. For a more complete review - see Ref. [120].

The microscopic origin of band #1 remains unclear. The two characteristic features of this band are the large Stokes shift, well in excess of 1 eV, and a relatively long lifetime. At the same time, the excitation dependencies of peak intensity and decay time prove multiplicity of emitting centers contributing to this band. Similar emissions have been observed previously and were assigned to “molecule-like” recombination centers at the interface between Ge NCs and the
matrix [16]. One speculation could be to relate PL band #1 to the previously investigated blue-green luminescence [9,19] arising due to excitonic recombination at defect centers introduced by Ge NCs, but with no size relation. In the present case the somewhat higher energy range at which band #1 appears might be related to different material specifications than in Refs [9,19] and the longer lifetime could mark switching between singlet and triplet recombination states, as frequently discussed [121]. Other possibilities include Si-Ge and amorphous Si nanoclusters; these are however less likely due to the high Ge contents and the high annealing temperature, respectively, but cannot be totally excluded based on the evidence at hand. Finally, for the sake of completeness, we recall that a recent report relates PL of characteristics very comparable to that observed in our material to formation of GeO₂ NCs [124].

![Figure 6.14: Quantum yield versus photon excitation energy for PL peak #1.](image)

### 6.4 Conclusion

We report on the possible identification of the excitonic emission from very small Ge NCs dispersed in an amorphous matrix of sub-stoichiometric SiO₂. The relevant PL band is widely tunable, covering the whole visible range. Its external quantum efficiency is low due to strong non-radiative quenching, which precludes its observation at lower energies, for larger NC sizes. The overall emission from the investigated material is dominated by two other bands which were investigated in the past and related to defects and/or recombination centers induced upon formation of NCs.