Auger-decay dynamics of germanium nano-islands in silicon

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Abstract
The decay dynamics of self-assembled germanium islands is studied by time-resolved fluorescence spectroscopy. The scaling behavior of the decay rate with the number of excitons in the islands is shown to agree with expectations for an Auger-recombination-dominated process in the asymptotic limit of high exciton numbers. The multi-excitonic decay time and spectral behavior are compared to theoretical estimates.

1. Introduction
Self-assembled germanium (Ge) islands embedded in silicon (Si) have attracted considerable interest because the emission wavelength of the luminescence can be tuned in the range around 1.5 μm used by standard fiber communication technology. The spectral dependence of the luminescence from Ge (or SiGe) islands has been studied as a function of various growth parameters [1–11], and for various experimental parameters such as sample temperature, laser excitation power and wavelength, and stress [8, 12–17]. Most of these studies have been conducted under continuous-wave optical pumping conditions, while detailed time-resolved experiments have been rare [15, 17]. Recently, we studied the luminescence decay dynamics with nanosecond time resolution under high-fluence pumping conditions [17] and identified the characteristic time scale of the Auger processes within the nano-islands to be of the order of 10 ns. In the present work we elaborate on this Auger-recombination dynamics. In particular, by varying the pump fluence the initial number of excitons in the nano-islands can be controlled while the corresponding decay dynamics is examined. Theoretical models from the literature are adapted to our particular nano-island configuration, and the validity of this adaptation is discussed.

2. Experimental methods
A Ge-island sample was prepared by molecular beam epitaxy on a Si(100) wafer (≈100 Ω cm). A 200 nm thick Si buffer layer was grown followed by a layer of Ge with a nominal thickness of 9.75 Å. Ge islands were thus formed in the Stranski–Krastanow growth mode. The islands were subsequently covered by a 50 nm Si capping layer. The growth temperature was 530 °C, the growth rate of the Ge layer was 0.5 Å s⁻¹, and a growth interrupt of 10 s was present immediately before and after deposition of the Ge layer. A surfactant [11] of approximately 0.01 monolayer (estimated by secondary ion mass spectrometry) of antimony (Sb) was used. A cross-sectional transmission electron micrograph is displayed in figure 1(b), which shows the typical island diameter of 20 nm and height of a few nanometers. While this island diameter is somewhat smaller than reported in [8], it agrees well with the findings of [18] for islands with a Ge-to-Si fraction approaching unity (this near-unity fraction has not been confirmed by independent measurements).

The optical characterization setup is shown schematically in figure 1(a). The sample was mounted in a closed-cycle cryostat, which was cooled down to 16 K. The Ge islands were excited optically using the second harmonic at 400 nm of an amplified Ti:sapphire femtosecond laser system (pulse duration 100 fs, repetition rate 1 kHz). The pump fluence was varied by a combination of translating a cylindrical lens and inserting neutral density filters into the pump beam. By collecting the Ge-island fluorescence from the sample edge, a significant amount of light was detected for all settings of the pump beam focusing (the experiments do not rely on a fixed collection efficiency). A McPherson 218 monochromator was used to spectrally disperse the fluorescence, while a liquid-nitrogen-cooled photo-multiplier tube (Hamamatsu R5509-73)
If $\partial n$ term is:

the radiative transition rate is of electrons and holes if we assume charge-neutral excitons),

$d t$ is the probability of finding on the number of charged particles, as demonstrated in [19].

is collected from the edge of the sample, dispersed by a pump light normal to the sample surface. The Ge-island fluorescence sample is placed inside a closed-cycle cryostat and subjected to

(a) Schematics of the optical characterization setup. The

(b) Transmission electron micrograph revealing Ge-island diameters of the order of 20 nm and heights of 1–2 nm.

was used for the detection. The temporal resolution of the detection setup was 1 ns.

3. Theory

The radiative recombination rate of confined excitons depends on the number of charged particles, as demonstrated in [19]. If $n$ denotes the number of excitons (and thereby the number of electrons and holes if we assume charge-neutral excitons), the radiative transition rate is $\Gamma^{(1)} n^2$, where $\Gamma^{(1)}$ is the radiative recombination rate of the single-exciton state. This follows from the fact that there are $n^2$ ways of choosing one electron and one hole. For an ensemble of nano-islands with a distribution of exciton numbers, such that $p_n$ is the probability of finding $n$ excitons, the probability $dp$ of light emission from each nano-island within the time $dt$ must be: $dp = \sum_{n=0}^{\infty} p_n \Gamma^{(1)} n^2 dt = \Gamma^{(1)}(n^2) dt$, i.e. the observed luminescence yield must be proportional to the average radiative rate, $\Gamma^{(1)}(n^2)$.

Now, if radiative recombination (or possibly another non-radiative two-body mechanism) is the dominant process, we may calculate the expected change in the luminescence yield (being proportional to $(n^2)$). The time evolution of each $p_n$ term is: $\partial p_n / \partial t = 2 \Gamma^{(1)} [p_{n+1}(n+1)^2 - p_n n^2]$, i.e. the first term populates the $n$-exciton state by recombination of the $(n+1)$-exciton state, while the second term models the $n$-exciton-state recombination. It then follows that:

$$\frac{\partial (n^2)}{\partial t} = - (n^2(2n-1)) \Gamma^{(1)}$$

(radiative). (1)

In contrast, if Auger processes dominate the decay dynamics, we must consider the recombination rate for an $n$-exciton state, which by a combinatorial argument [20] must be $\frac{4 \Gamma^{(2)} n^2}{n(n-1)}$, where $\Gamma^{(2)}$ is the recombination rate for a bi-exciton. The time evolution of each $p_n$ term can be deduced in a similar way as above:

$$\frac{\partial p_n}{\partial t} = \frac{1}{4} \Gamma^{(2)} [p_{n+1}(n+1)^2 - p_n n^2(n-1)]$$

Here we assumed that the recombination of the electron or hole, which becomes excited (possibly to the continuum) by the energy released in the recombination process, is re-captured to maintain charge neutrality. The time evolution of $(n^2)$ then becomes:

$$\frac{\partial (n^2)}{\partial t} = - \frac{\Gamma^{(2)}}{4} (n^2(n-1)(2n-1))$$

(Auger). (2)

Although the detailed dynamics in these two cases depends on the specific distribution, we may estimate the approximate asymptotic behavior of the luminescence yield for large $n$. The instantaneous decay rate, $\Gamma_{\text{inst}} = -(n^2)^{-1} \partial (n^2) / \partial n$, scales as $2\Gamma^{(1)} n$ when radiative processes dominate and as $\frac{1}{4} \Gamma^{(2)} n^2$ for the Auger-dominated case. We emphasize that these scaling behaviors follow essentially from the two- and three-body nature of radiative and Auger processes, respectively. For a low exciton population the instantaneous radiative decay rate is $\Gamma^{(1)}$ independent of $(n)$.

In order to investigate the scaling behavior of the luminescence decay dynamics in experiment, an independent measure of the number of excitons, $n$, is needed. In [14] the luminescence from Ge/Si islands was investigated for various excitation powers and it was found that an increasing number of excitons gave rise to an energy-shifted luminescence peak. This shift was explained as state-filling effects of the confined holes, and a crude estimation of the density of states (per unit area) was proposed from a two-dimensional hole gas: $dn / dE = m_i^* / \pi \hbar^2$. Here $m_i^*$ is the in-plane effective mass of the holes, which can be interpolated between 0.22$m_0$ for pure Si and 0.058$m_0$ for pure Ge. This model suggests a linear scaling of the shift in luminescence peak position, $\Delta x_c$, with the number of excitons, $n$. While more elaborate calculations showed that the density of states was grossly overestimated in the two-dimensional hole-gas model, the linear scaling is approximately retained (a slight sub-linearity can be seen from figure 5 of [14]). The luminescence peak shift was estimated to be 60 meV for 180 holes in a Si$_{50}$Ge$_{50}$ nano-island ($m_i^* = 0.136m_0$) of diameter 100 nm and height 6 nm, i.e. on average they found $\Delta x_c \approx 7$ meV. The two-dimensional hole-gas model suggests how this number can be scaled to our particular nano-island configuration (diameter around 20 nm, Ge fraction taken to be unity). The island area is 25 times smaller, and by accounting for the change in effective mass, we expect the average energy spacing to be increased by a factor of $25 \times 0.136/0.058 \approx 59$. For our islands the estimate is thus $\Delta x_c \approx 20$ meV.

4. Results

Time-resolved emission spectra have been obtained from the sample and examples are presented in figures 2(a) and (b) for two different time windows and for optical pump fluences varied among five values between $10^{-4}$ and $5 \times 10^{-4}$ J cm$^{-2}$. It is evident that the luminescence peak shifts toward lower energies with time and that the initial peak position is moved
significantly toward higher energies when the pump fluence attains the highest values. In order to analyze the luminescence dynamics, we fit the spectra with Gaussian functions (with the height, width, peak center, and background as free parameters). These fitting parameters present a convenient tool for understanding the general behavior of the nano-island ensemble luminescence. For instance, the shift of the peak center position, $\Delta x_c$, presents a measure of the mean number of excitons $\langle n \rangle$ in the islands. Similarly, the fitted peak area must be proportional to the total detected luminescence intensity, which again is an approximate ensemble-averaged measure of $\langle n^2 \rangle$.

In figure 2(c) we present the peak position as a function of time. For times well above 10 ns, the behavior is very similar for the different pump fluences, while at early times the dynamics depends strongly on the fluence. A similar behavior is seen in figure 2(d), in which the Gaussian peak area is displayed as a function of time: the early-time decay is much more rapid for the highest pump fluences. This early-time dynamics was previously attributed to Auger recombination [17], which, in agreement with the observation that higher pump fluences lead to larger shifts in the peak position (higher exciton populations) together with faster decays. In the following we examine whether the theoretical scaling predictions can be observed in the dynamics.

To this end, the central peak position is examined, as exemplified in figure 3(a). The shift, $\Delta x_c$, in the early-time dynamics is extracted by subtracting the linear function (dashed line) obtained by a linear fit to the late-time part of the data. Next, the instantaneous decay rate of the total luminescence yield (the Gaussian peak area) is extracted by triple-exponential fits of the peak area versus time (see figure 2(d); the three terms are adequate for modeling the entire curves). By modeling, $\text{area} = \sum A_j \exp(-\Gamma_j t)$, the instantaneous decay rate is:

$$\Gamma_{\text{inst}} = \frac{\frac{1}{\text{Area}} \sum \frac{\partial \text{area}}{\partial t}}{\sum A_j \Gamma_j \exp(-\Gamma_j t)/\sum A_j \exp(-\Gamma_j t)}.$$  

By evaluating this rate at the particular times of the data points, we may directly compare the instantaneous decay time $\Gamma_{\text{inst}}^{-1}$ and $\Delta x_c$ as shown in figure 3(b). From the theory we expect $\Gamma_{\text{inst}}^{-1}$ to scale with the exciton population as $n^{-2}$, and by approximating $\Delta x_c \propto n$, the
expectation becomes $\Gamma_{\text{inst}}^{-1} \propto \Delta x_c^{-2}$. This behavior can indeed be observed in figure 3(b) for the circles (i.e. the highest pump fluences) with the highest $\Delta x_c$-values (i.e. for the earliest times only)—the solid line represents a fit to a power law with the exponent fixed at $-2$. Hence, a fingerprint of an Auger process is indeed found for the highest pump fluence, where the effect should be most clear; for the lower pump fluences we see that the characteristic power-law exponent changes from $-2$ to less negative values. We also note that the averaging inherent in equation (2) was neglected in estimating the scaling behavior, i.e. it is only valid in the asymptotic limit for high exciton populations.

Since the Auger process is seen most clearly for the highest pump fluence, we will elaborate further on this particular data set. Consider once again the peak area versus time in the lower graph of figure 2(d). The early-time part must correspond to a significant number of charges in each Ge island, whereas for times larger than the 50 ns scale the number of excitons must largely be one or less since the Auger processes have vanished. The single-exciton borderline must then be crossed somewhere between these two time limits. By fitting a single-exponential function to the data in the range 60–200 ns and extrapolating the model back to zero time (dashed line in figure 2(d)), we obtain a characteristic peak area, which must correspond reasonably to this borderline. Now, in figure 3(c) the same data are presented but normalized to this characteristic peak area. The vertical scale thus presents (in absolute numbers) an estimate of $\langle n^2 \rangle$. The initial data point attains the value of $\langle n^2 \rangle \approx 36$, i.e. the initial number of excitons must be of the order of six.

With an estimate of the exciton number at hand, the density of states can also be examined. In a first step, we estimate $\langle n \rangle$ from $\langle n^2 \rangle$. The most naive approximation, $\langle n \rangle^2 = \langle n^2 \rangle$, is valid if the distribution is narrow, as can be seen from the well-known relation $\text{Var}(n) = \langle n^2 \rangle - \langle n \rangle^2$. In order to be more specific, knowledge of the exact distribution is required. It might be reasonable to argue that the initial distribution is Poissonian, and for simplicity we assume this to be the case for all times (which is not justified but is most likely a better approximation than assuming zero variance). It can

Figure 3. For all panels the symbols are similar to those of figure 2. (a) The peak position versus time including a linear fit in the range 60–200 ns (dashed line). (b) The instantaneous decay time, $\Gamma_{\text{inst}}^{-1}$, as a function of the peak position shift, $\Delta x_c$. The solid line is fitted to the three circles with the highest $\Delta x_c$ leading to: $\Gamma_{\text{inst}}^{-1} = 1.1 \times 10^{-2}$ ns eV$^2$ $\Delta x_c^{-2}$. (c) The normalized peak area (from figure 2(d); the lower graph normalized to the dashed-line asymptotic limit at $t = 0$). (d) The peak position shift as a function of $\langle n \rangle$ inferred from the normalized area of panel (c). The solid line is a linear fit to the three data points with the highest $\Delta x_c$ giving $\Delta x_c = 2.3 \times 10^{-2}$ eV $\langle n \rangle_{\text{Area}}$. 
then be shown that \( \langle n \rangle = \frac{1}{4}(1 + \frac{1}{4}n^2 - 1) \), which also presents the correct asymptotic limits when \( n^2 \ll 1 \) and \( n^2 \gg 1 \). By this formula, we estimate from the normalized area (figure 3(c)) the mean number of excitons, \( \langle n \rangle_{\text{Area}} \). In figure 3(d) we plot the observed peak position shift, \( \Delta x_c \), as a function of \( \langle n \rangle_{\text{Area}} \). The three data points with the highest \( \Delta x_c \)-values (the earliest times with most pronounced Auger effects) are fitted reasonably to a linear function, resulting in the rough experimental estimate of \( \Delta x_c \approx 23\langle n \rangle \text{meV} \). Despite the rather approximate approach to this estimate, we find a very reasonable agreement with the calculations from [14] scaled to our Ge-island configuration, \( \Delta x_c \approx 20\text{meV} \). This indicates that interpreting the vertical scale of figure 3(c) as \( \langle n \rangle^2 \) is reasonable.

We may also combine the solid-line fits from figures 3(b) and (d) in order to obtain the asymptotic behavior: \( \Gamma_{\text{inst}}^{-1} \approx 20 \text{ns}/\langle n \rangle^2_{\text{Area}} \). From theory we expect \( \Gamma_{\text{inst}}^{-1} = \Gamma_{\Delta}^{(2)} n^2 \), which leads to an estimate of the bi-excitonic lifetime: \( \tau_{\text{2}} = (\Gamma_{\Delta}^{(2)})^{-1} \approx 10 \text{ns} \).

5. Discussion

The entire analysis in the present work deals with the general trends of the nano-island luminescence and is rather approximate. For instance, inhomogeneous effects from the nano-island size dispersion are neglected and constant charge neutrality is assumed. Anyway, for the highest pump fluence it is still possible to identify the expected scaling behaviors, which of course is a consequence of the three-body nature of Auger processes and the two-body nature of radiative recombination.

Effects of inhomogeneity can be seen, though. In figure 3(b) the individual data sets seem to follow their own path; i.e. there is no unique correspondence between \( \Delta x_c \) and \( \Gamma_{\text{inst}} \). A possible explanation could be that for low pump fluences, a moderate number of electron–hole pairs are available, and predominantly the largest nano-islands with the largest capture cross-section are populated, while for higher electron–hole concentrations the smaller islands will contribute more [9]. This hypothesis agrees with the fact that the luminescence spectra are red-shifted in general for low pump fluences after the initial Auger processes, as can be seen from figure 2(b) and (c), and at the same time the Auger processes would be less dominant due to the larger size. An alternative explanation suggests that for higher initial electron–hole concentrations, the electrons start to populate the interior of the Ge island leading to a higher photon energy in the luminescence from spatially direct transitions [8], which would also lead to faster Auger processes due to the increased wavefunction overlap.

In the literature there exist some specific studies on Auger-recombination processes; however, most studies deal with strongly confined excitons. For instance, it has been demonstrated [21] that the Auger-recombination time of free-standing spherical Ge nano-crystals is proportional to the nano-crystal volume, and in particular a nano-crystal radius of 5 nm leads to a bi-excitonic decay time of 110 ps. This is 100 times faster than the recombination time in our Ge islands despite the fact that the island volume is similar. The discrepancy is not surprising since: (1) the islands are embedded in Si and are not free standing, (2) the geometry is very different and quantum confinement is only an issue along the growth direction, and (3) the band alignment between Si and Ge is type-II leading to charge separation of electrons and holes. In fact, it has been demonstrated that the reduced wavefunction overlap between electrons and holes together with smooth potential barriers may slow down the Auger process by orders of magnitude [22, 23]. This explains qualitatively the observed rates of the 10 ns scale; however, detailed calculations for the specific Ge/Si islands (taking any possible Si–Ge intermixing into account) would be very desirable. We also note that experimental studies on an ‘Auger fountain’, in which charges interact across the Ge/Si interface, also presented a characteristic Auger lifetime of 10 ns [24]. In other words, this time scale seems to be characteristic for Auger processes in a type-II configuration, and if type-I excitons recombine much faster by the Auger process it then remains an open question whether type-I single excitons would even exist after the Auger processes for high pump fluences. Further experimental investigations along the lines of the present work on very narrow size distributions [9] could be very fruitful in clarifying this issue.

6. Conclusions

In conclusion, we have demonstrated that the luminescence from Ge islands embedded in Si shows the correct asymptotic scaling behavior for Auger-recombination processes when considering the recombination time scales as a function of the number of excitons per nano-island. Furthermore, a rough estimate of the density of states was found to be in agreement with previously published calculations [14] scaled to our nano-island geometry. Specific theoretical investigations of Auger processes for both type-I and type-II excitons within Ge islands are still lacking in the literature and would be desirable for a better understanding of the luminescence characteristics.

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