Energy relaxation in optically excited Si and Ge nanocrystals
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CHAPTER 5

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Carrier multiplication in Ge nanocrystals

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Carrier multiplication is the phenomenon of creation of multiple electron-hole pairs in semiconductors upon absorption of a single photon. The potential usefulness of this phenomenon is immediately obvious for solar cells or photo-detectors when we realize that these devices typically operate on a single-photon-to-single-electron conversion basis. This chapter is dedicated to the observation of carrier multiplication in Ge nanocrystals by transient induced absorption spectroscopy. The experimentally determined lifetime of multiple carriers generated in the process is in the range of tens of picoseconds, typical for nanocrystals of a few nanometer diameters.
5.1 Introduction

High-energy photons create energetic electron-hole pairs that cool down first before they are extracted in the form of electric current; i.e., luminary power is converted into heat rather than electric power. The CM phenomenon inhibits generation of heat: the excess energy of the initially created electron-hole pairs is used to generate additional free carriers instead. These can then efficiently be extracted with fewer losses, either directly or through emission of photons of lower energy. In particular, in photovoltaics an overall increased efficiency can be expected (up to 45% [37]) for devices that make use of CM. Indeed, external quantum efficiencies – defined as the number of electron-hole pairs generated per absorbed photon – exceeding 100% have been observed [77] proving the usefulness and feasibility of the process. CM was first observed in classical crystalline bulk semiconductors - for instance silicon [78]. In bulk materials CM proceeds via impact excitation [79] by hot carriers and its efficiency is rather low, due to competition of the highly effective alternative carrier-cooling process – see Fig. 5.1 for a schematic illustration.

A quantum efficiency, defined as the number of electron-hole pairs extracted from the device for every absorbed photon, of 170% was found for photons with energies equal to 6 times the bandgap in bulk germanium [80]. An efficiency of 130% to generate an electron-hole pair by an absorbed photon has been reported for bulk Si irradiated with UV [78]. In spite of some initial doubts [81], CM turns out to be considerably enhanced in spatially-confined materials, like graphene [82] and PBS nanosheets [83] (2D confinement), C-nanotubes [67] and PbSe nanorods [84,85] (1D) and in nanocrystals (0D), where it is commonly labeled MEG [86]. In the latter case, CM was studied for NCs in a colloidal dispersion and embedded in a solid matrix [86-88]. Generally, in spatially-confined materials the Coulomb interaction between carriers is increased, thereby enhancing charge scattering processes, such as CM and Auger recombination. Therefore the stronger the confinement, the more efficient is the CM process [89]. Moreover, the same quantum confinement, apart from widening the electronic bandgap (in Si scaling with the square of the diameter [90]), relaxes the momentum conservation requirement in optical transitions through Heisenberg’s uncertainty relation, thus considerably enhancing the probability of band-to-band transitions for indirect bandgap materials (like Si and Ge), bringing the radiative recombination time constant down to the ten-microsecond range. Another effect of this relaxation of momentum conservation is enhancement of CM and Auger recombination [91].

Past research has demonstrated CM in NCs of many semiconductor materials, including PbSe, PbS, PbTe, CdSe, InAs, InP and Si [34,86]. Identification of CM in Si NCs is of particular significance in view of technological importance
of Si and its leading role in electronics industry [76]. CM in Ge NCs has not been reported until now. Ge is of interest, since it features unique properties, such as extreme chemical purity, great multiplicity of isotopes, and a very specific band structure, with close values of direct and indirect bandgaps and high sensitivity to stress, among others. Moreover, the technical importance of Ge is growing, with applications for detectors [92], and photovoltaics – not only for substrates, but also as an active material for tandem cells. The bandgap of (bulk) Ge, 0.67 eV, is nearly ideal for exploitation of CM in solar cells. The aforementioned theoretical 45% maximum efficiency of solar cells calculated by Nozik [37] is for semiconductors with bandgaps in the range of 0.6 eV to 1.0 eV, which is within reach of Ge NCs.

Figure 5.1: Schematic illustration of the processes described in this work. Upon absorption of a high-energy photon an energetic electron-hole pair is created. (a) These electrons and holes can ‘cool down’ to the band edges in a multi-step process of emission of phonons, from where they can be extracted in the form of electric current, or recombine either radiatively (emission of a photon with energy equal to the bandgap) or non-radiatively. (b) Alternatively, CM can occur and the ‘excess’ energy is used to excite a second electron-hole pair (for simplicity, only electrons are shown, while both electrons and holes can take part in CM). This process can take place when the energy of the electron or the hole is larger than the bandgap. (c) The opposite process is Auger recombination, where the electron recombines with the hole and the released energy is used to excite (a) carrier(s) further into the band. Because of the rapid occurrence of these two processes, one can imagine formation of a superposition state, indicated by the feathered arrow.
5.2 Optical characterization

The investigated materials have been prepared by radio-frequency co-sputtering using a multi-target chamber. Following deposition, the sputtered layers have been annealed in N₂ atmosphere at a temperature of 1100 °C for 30 min. During the annealing step, Ge segregates into small crystalline inclusions, embedded in the SiO₂ matrix.

The samples are optically characterized by measuring the steady-state absorption and PL spectra, the results are shown in Fig. 5.2 (a). The maximum of the PL spectrum corresponds to an optical band gap of 1.25 eV, which is characteristic for Ge NCs with a diameter of approximately 5-6 nm [8]. We note that the onset of the optical absorption is at lower photon energy than the PL. This low-energy absorption can either be attributed to excitation involving electronic states in the band gap of the NCs or to the presence of large NCs, which do not participate in emission. The NC diameter can also be estimated from the shift of the Raman spectrum, shown in Fig. 5.2 (b), which appears due to quantum confinement [93]. The value of the measured Raman shift is typical for a Ge NC diameter of 2 nm, which is not consistent with the size inferred from the PL. We attribute the measured shift to stress in the Ge NCs, rather than smaller NC diameter [94]. However the width (Γ) of the Raman peak is consistent with the sizes determined from the PL [94].

![Figure 5.2: (a) Absorption (blue) and PL (red) curves. (b) Raman spectrum (brown) with Lorentzian fit (dashed line) giving position and width as indicated. For comparison, the bulk Ge spectrum is shown in green.](image)
5.3 Discussion

5.3.1 Establishing single exciton dynamics: fingerprint of carrier multiplication

In order to investigate the CM in detail, we have measured the exciton multiplicity in Ge NCs as a function of excitation wavelength. Figure 5.3 shows the TIA (optical density (OD) vs. \( t \)) measured around a below-bandgap probe wavelength of \( \lambda = 1300 \) nm (obtained by integrating the signal from 1200 nm to 1400 nm), for two excitation pump wavelengths, \( \lambda^* = 800 \) nm, Fig. 5.3 (a) and \( \lambda^* = 400 \) nm, Fig. 5.3 (b). There is an initial negative signal (bleach) (not shown here). Apparently, the initial bleach of optical absorption is reduced after a relaxation process of about 20 ps. This is similar to previous results [95] and will be discussed in detail in chapter 7. The TIA signal on longer times is attributed to intraband absorption and proportional to the density of excited carriers in the entire band, independent of their energy.

![Figure 5.3: TIA dynamics measured at probe wavelengths \( \lambda \) near 1300 nm (obtained by integration of signal from 1200 nm to 1400 nm) for excitation wavelengths equal to \( \lambda^* = 800 \) nm (a) and \( \lambda^* = 400 \) nm (b), for three different pump pulse fluences and demonstrating the single-photon-absorption regime. The dashed lines are single- (a) and double-exponential (b) fits to the data. The double-exponential decay at the \( \lambda^* = 400 \) nm excitation wavelength is the fingerprint of CM. The insets show the maximum of the amplitude of the TIA transients (A) and its ratio to the amplitude of the single exciton decay tail (A/B) as a function of the absorbed photon fluence (see text for explanation).](image)

The TIA behavior at the two excitation wavelengths is remarkably different. Both show a tail with a relaxation time long compared to the time window (> 1
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However, for the short-wavelength excitation the absorption transient has an additional fast component on a timescale of hundred picoseconds. This is the fingerprint of CM, as will be discussed now. In this study we follow the reasoning of Schaller et al. [96] and Trinh et al. [97], and summarized by Smith and Binks [86]. The long tail TIA is due to NCs containing a single exciton. In the experimental procedure we made sure to be working in the low-fluence regime, so that the average number of absorbed photons (and thus excitons per NC) is very small, \(<N> \ll 1\). The initial exciton multiplicity directly after photoexcitation (and prior to CM) is in this case to a good approximation \(N_x = 1\), meaning that all excited NCs initially contains only one exciton. Under these conditions most of the NCs are not excited and do not contribute to the TIA signal. The TIA eventually decays on a timescale exceeding a nanosecond, as the total number of excitons decreases by radiative (PL) and non-radiative recombination (NRR) see Fig. 5.4 for a schematic illustration. In the case of short-wavelength high-photon-energy excitation, the hot carriers can induce CM. A single hot electron-hole pair decays by CM to yield two (or more) electron-hole pairs at lower energy (see step 2 Fig. 5.4(b)). The time scale of this conversion process is estimated to be 0.1-1 ps [98]. Consequently, the amplitude of the TIA signal is increased by the higher exciton multiplicity - see step 3 in Fig. 5.4(b). This multiple-exciton state, however, is rather short lived and decays through Auger recombination. Therefore in the assumed approach, the exciton multiplicity can be estimated by comparing the TIA dynamics obtained at a particular excitation energy with the single exciton dynamics [96,97]; this is most easily done by taking the ratio of the initial TIA magnitude, \(A\), where multiple excitons might have been generated, to the magnitude, \(B\), on long time when (eventual) Auger decay is completed. This \(A/B\) ratio is shown in both panels of Fig. 5.3.

In order to make sure that the measurements are conducted in the regime of single photon absorption per NC and to avoid multiple photon absorption per nanocrystal per pulse – which would obviously create multiple excitons per NC without the CM effect – our experimental procedure was to reduce the pump pulse intensity until the TIA transients (OD vs. \(t\)) remained invariant. This is illustrated in Fig. 5.3, where TIA dynamics measured for several pump pulse fluences (defined as number of photons per area per pulse) are shown for both excitation wavelengths. The \(\lambda^* = 800\) nm excitation wavelength (Fig. 5.3(a)) corresponds to an energy which is lower than twice the bandgap of the Ge NCs, so that CM is energetically not possible. The experimental traces exhibit identical decay dynamics with their amplitude depending linearly on the excitation power. The inset of Fig 5.3 shows the initial amplitude, \(A\), (left hand scale) and the \(A/B\) ratio (right hand scale) for the transients as a function of the
absorbed photon fluence. As expected, the initial magnitude of the transients, A, increases linearly with the number of absorbed photons. The observation that the ratio A/B is independent of the absorbed photon fluence demonstrates that the decay dynamics of the transients do not change upon pump laser fluence. This implies that a NC absorbs at most a single photon. We also note that the TIA dynamics measured for $\lambda^* = 800$ nm excitation can be fitted with a single-exponential decay with lifetime $\tau_1 = 3$ ns (dashed lines in Fig. 5.3a), featuring no fast component, which is consistent with the fact that for these energies no CM takes place.

Fig. 5.3(b) shows TIA dynamics for the $\lambda^* = 400$ nm excitation. Also in this case the transients at different pump fluences are depicted to demonstrate that the measurements are conducted in the regime in which a NC absorbs at most one photon. The traces can now be described by fitting a double-exponential to the data, as illustrated by the dashed lines with lifetimes $\tau_1 = 3$ ns and $\tau_2 = 170$ ps. The value of the delay time of the additional fast component $\tau_2$ is typical for Auger recombination in PbSe NCs [98,99] and in Si NCs in SiO$_2$ [100]. The higher A/B ratio as well as the steeper rise of the initial amplitude A upon increasing pump fluence for this short wavelength excitation confirm the occurrence of CM.

**Figure 5.4:** Difference between low pump photon energy and high pump photon energy experiments. (a) Electron-hole pairs produced by low pump photon energy (1) give rise to a long lived TIA (3) and eventually decay via photoluminescence (PL) non-radiative recombination (NRR) (5). (b) For high pump photon energy (1), CM takes place (2) doubling the TIA (3). Auger recombination causes the system to rapidly (< 200 ps) decay to a single electron-hole pair (4). The single electron-hole pair decays via PL/NRR (5).

Based on the results in Fig. 5.3, we conclude that the exciton multiplicity at higher-energy excitations can be determined by fitting a double-exponential to
the TIA dynamics. Experimentally, the CM yield $\phi_{\text{CM}}(h\nu)$ is found from the A/B ratio, scaled to the value measured for excitation at low-energy for which CM does not take place:

$$\phi(h\nu) = \frac{A(h\nu)/B(h\nu)}{A(1.55 \text{ eV}) / B(1.55 \text{ eV})},$$

(5.1)

### 5.3.2 Carrier multiplication efficiency

In order to investigate CM in detail, we have measured the exciton multiplicity in Ge NCs as a function of excitation wavelength. To do this, we first establish the low fluence regime for all the excitation energies. All low fluence transients are presented in Fig. 5.5.

![Figure 5.5: Transient absorption for different excitation wavelengths, obtained by integrating over the 1200 – 1400 nm probe range.](image)

Figure 5.6 presents the number of electron-hole pairs created per absorbed photon determined as described above. From this figure we can see a CM efficiency of nearly 190% at 3.5 eV; i.e. 1.9 electron-hole pairs are created for each absorbed photon with energy 2.8 times the optical bandgap. The lower panel of the figure shows the PL spectrum and its mapped multiplicities (‘2PL’ and ‘3PL’). In the most favorable case, i.e. when CM would proceed in the energy conservation limit, the onset of carrier duplication would appear at twice the PL energy, where free carriers in some NCs have exactly enough excess energy to create a second electron-hole pair. In summary, the CM efficiency should follow the integral of the normalized $n\text{PL}$ curves. The blue line in Fig. 5.6
is the integral of \( n_{PL} \). The dashed trace corresponds to the same curve scaled by a factor 0.9 to fit the data points. The quality of the fit corroborates the interpretation of the data discussed above.

![Figure 5.6: Relative CM efficiency (number of electron-hole pairs created per absorbed photon) as a function of pump photon energy, based on the ratio of fast and slow components of the TIA transients. The bottom panel shows the PL spectrum and scaled multiples of this spectrum. The blue line is the energy conservation limit which is the integral of the \( n_{PL} \) curve (the dashed line is the integral scaled by a factor 0.9 to coincide with the data points).](image)

A final question arises on how CM in the Ge NCs investigated in this study compares to CM in bulk Ge. For bulk Ge, Koc measured a CM efficiency of 170% for a photon energy of 4.15 eV, which corresponds to 6.2 times the bandgap [80]. In our measurements we find 190% CM for an energy of 3.5 eV (2.8 times the bandgap for our Ge NCs). In bulk Ge, at 3.5 eV, the efficiency is only 140%, while this energy is 5.2 times the bandgap. We therefore conclude that CM is substantially more efficient in Ge NCs than in bulk – both on the
absolute energy scale and in comparison to the bandgap. This finding offers the prospect of a new generation of highly efficient infrared detectors and perhaps even solar cells based on Ge NCs.