Energy relaxation in optically excited Si and Ge nanocrystals
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Citation for published version (APA):
CHAPTER 2

Experimentals

This chapter describes the details of the sample preparation techniques - sputtering deposition and plasma enhanced chemical vapor deposition - along with the experimental methods used for optical characterization of these samples. Optical characterization includes photoluminescence and absorption (linear and induced) spectroscopies and quantum yield determination.
2.1 Magnetron sputtering deposition

The samples investigated in this work are mostly fabricated by sputtering deposition technique. In this method a target, or source of the material desired to be deposited, is bombarded with energetic argon (Ar\textsuperscript{+}) ions. Electrically neutral Ar atoms are introduced into a vacuum chamber at a pressure of 1 to 10 mTorr. A DC voltage applied between target and substrate ionizes the Ar atoms creating plasma, which consists of ions and electrons. The Ar\textsuperscript{+} ions are accelerated towards the target where forceful collision ejects target atoms into the space. These ejected atoms then travel towards the substrate and condense into a film. As more and more atoms reach the substrate, they begin to bind to each other at the molecular level, forming a tightly bound atomic layer. The electrons released during Ar ionization are accelerated towards anode substrate and on their way ionize more Ar atoms, creating an avalanche of ions and free electrons in the process. The thickness of the deposited layer depends on the specific sputtering rate of the target material, which can be controlled by changing the Ar gas pressure, power applied to the gun containing target, and the time of deposition. There are number of ways to enhance this process. One common way is to use magnetron sputtering. In such systems, a strong magnetic field is applied near the target area. This field forces the electron to spiral around the magnetic flux lines near the target and ionize more Ar atoms. In this way, a stable plasma is created which contains high density of ions, which helps in increasing the efficiency of the sputtering process. A DC power supply is generally used to sputter conducting targets, whereas radio-frequency (rf) power supply with an automatic or manual impedance matching network between the power supply and sputtering guns is usually required for insulating or semiconducting target materials. Figure 2.1 shows a schematic for the magnetron sputtering unit.

Different batches of samples, prepared using the rf magnetron sputtering technique, for the purpose of this research are described below.

**Ge NCs or Si\textsubscript{1-x}Ge\textsubscript{x} NCs in SiO\textsubscript{2}**

Ge NCs embedded in a SiO\textsubscript{2} matrix are prepared by co-sputtering Ge and SiO\textsubscript{2} targets under an Ar gas pressure of 3 mTorr. The background pressure is kept at 3×10\textsuperscript{-7} Pa. In order to change the deposition rate of Ge sputtered layers, the power on the DC or rf gun is changed. For Si\textsubscript{1-x}Ge\textsubscript{x} NCs along with Ge and SiO\textsubscript{2} targets, a Si target is added and different sample thicknesses and material ratios are prepared by changing the powers on the guns containing the targets. The deposited layers are subsequently annealed in a tube furnace purged with N\textsubscript{2} gas at temperatures in the range of 800-1200 °C for 30-60 mins. Different sizes of NCs are formed by varying the annealing time and temperature.
**Er³⁺ and Si NCs in SiO₂**

For these samples the same procedure is used as described before. The difference is the inclusion of Er₂O₃ tablets on top of the Si target during sputtering. By changing the number of Er tablets, concentration of Er³⁺ ions is varied in the \([\text{Er}^{3+}] = 0.5 \times 10^{19} - 2 \times 10^{20} \text{ cm}^{-3}\) range. These samples are annealed in N₂ gas at temperatures ranging from 1100 °C to 1200 °C for 30 mins.

**Figure 2.1: Schematic of a magnetron sputtering unit.** The plasma is confined to an area where the magnetic field is strong. Keeping the plasma close to the target causes faster deposition rates, greater Ar⁺ ions refill and less substrate damage from stray particles.

**2.2 Plasma enhanced chemical vapor deposition**

The plasma enhanced chemical vapor deposition technique (PECVD) is a process used to deposit thin solid films on a substrate. PECVD uses electrical energy to generate a plasma in which the energy is transferred into a gas mixture and this mixture transforms into reactive radicals, ions, neutral atoms and highly excited species. These atomic and molecular fragments interact with the substrate and depending on the nature of these interactions, either etching or deposition occurs at the substrate. Some of the desirable properties of PECVD films are good adhesion, low defect (pinhole) density, good step coverage, and uniformity.
**Ge-rich SiGe NCs**

For depositing SiO$_x$ onto a substrate precursor gasses such as N$_2$O and silane (SiH$_4$) together with N$_2$ are led into the reaction chamber. By applying rf power across the top electrode (the shower-head) and the lower electrode (the substrate) reactive plasma was created. To deposit Ge-rich SiO$_x$ films germane (GeH$_4$) was added to the precursors N$_2$O, SiH$_4$ and N$_2$. After creating a plasma the following reaction took place:

$$\text{SiH}_4/\text{GeH}_4(\text{gas}) + 4\text{N}_2\text{O} (\text{gas}) \rightarrow \text{SiO}_2/\text{GeO}_2(\text{solid}) + 2\text{H}_2\text{O} (\text{gas}) + 4\text{N}_2(\text{gas}), \quad (2.1)$$

It is expected from equation 2.1 that the ratio between SiH$_4$/GeH$_4$ and N$_2$O is to be 1:4. However the dissociation of N$_2$O at lower rf powers is insufficient, causing lack of oxygen. This is compensated by having an excess of N$_2$O. Sub-stoichiometric SiO$_x$ and GeO$_x$ could be obtained by changing the N$_2$O content. By changing the ratios between SiH$_4$ and GeH$_4$, the amount of Ge in the deposited film is varied. However, the ratio between the precursors is only a rough indication for the final result since the dissociation energy for GeH$_4$ is smaller than that of the SiH$_4$. After the deposition process the samples are annealed at different temperatures ranging from 800 to 1200 °C in N$_2$ atmosphere for the formation of NCs. Figure 2.2 shows a schematic of the PECVD unit.

![Figure 2.2: Schematic overview of the parallel plate PECVD reactor. The sample is placed on the lower electrode. The gas inlet is via the powered showerhead top electrode.](image-url)
2.3 Photoluminescence
PL measurements performed in this work are either done at room temperature or at cryogenic temperatures. For low temperature measurements the samples are placed on a cold finger of either a closed cycle cryostat or a continuous-flow He cryostat (Oxford Instruments), accessing the 1.5 to 300 K temperature range. Different excitation sources are used together with different detection systems for different excitation and emission wavelength ranges.

2.3.1 Excitation sources

Nanosecond excitation
In order to generate coherent light pulses of a nanosecond duration, a Nd:YAG-pumped optical parametric oscillator (OPO) operating in Q-switched mode is used. The Q-switching unit (Pockells cell) provides high photon fluxes in a pulsed regime. As the Nd:YAG is initially pumped, population inversion is induced in the laser medium. When the maximum population inversion is reached the Pockells cell opens and the built-up energy in the gain medium is quickly released, and this generates a short intense light pulse at the fundamental lasing wavelength of 1064 nm. A third harmonic (355 nm) of the fundamental laser wavelength is then generated and by passing it through an OPO spectrally broad excitation range of $\lambda_{\text{exc}} = 210-2480$ nm is achieved. The conversion of 355 nm light is based on a second-order nonlinear effect in a beta-barium-borate (BBO) crystal. The pump photon splits up into smaller quanta of ‘signal’ and ‘idler’. This requires both conservation of energy and angular momentum, or phase-matching. The angle of incidence of the pump laser with respect to the optical axis of the BBO crystal determines the phase-matching conditions and thus the frequencies of the signal and idler. Since the signal and idler beams are orthogonally polarized, they can be separated using a Glan-Thompson prism and can be used directly as the excitation source. Two different systems are used for measurements presented in this work: one with a pulse duration of $\Delta t = 5$ ns and repetition rate $f = 20$ Hz, and the other with $\Delta t = 10$ ns and $f = 100$ Hz.

Femtosecond excitation
A tunable Ti:Sapphire laser with $f = 80$ MHz and $\Delta t = 140$ fs and $\lambda_{\text{exc}} = 690-1040$ nm is used to investigate the ultrafast dynamics. Prior to down-conversion, the repetition rate of 80 MHz is lowered to 4 MHz with the help of a pulse picker.

Continuous wave excitation
For continuous excitation, a Millennia IIs laser system with a fixed wavelength of $\lambda_{\text{exc}} = 532$ nm and a FluoroLog spectrofluorometer equipped with 450 W Xe-lamp and monochromator covering the $\lambda_{\text{exc}} = 200-700$ nm range are used.
2.3.2 Detection systems

Different detection systems are used for different emission wavelength ranges. A Ge detector and a charge-coupled device (CCD) are used to measure time-integrated PL signals whereas a photomultiplier tube (PMT) is used for the TR-PL signal. The emission signal is collected using a lens system and guided into the spectrometer (Triax 320, Solar M266, M20, Carl Zeiss or Jobin-Yvon THR-1000). These spectrometers are equipped with different gratings, each optimized for specific wavelength range. For detection of light, different detectors are used depending on the expected range of emission wavelength. For the detection of IR emission, a liquid-nitrogen cooled Ge detector (Edinburgh Instruments, $\lambda_{\text{det}} = 700-1700$ nm) with a DSP lock-in amplifier (Signal Recovery SR7265) or oscilloscope and similarly cooled PMT (Hamamatsu R5509-73, $\lambda_{\text{det}} = 300-1700$ nm, temporal resolution $\tau_{\text{res}} \geq 3$ ns) are used. In the visible range a PMT (Hamamatsu R91100, $\lambda_{\text{det}} = 185-900$ nm, $\tau_{\text{res}} \geq 1$ ns or a Hamamatsu R3809u-52, $\lambda_{\text{det}} = 160-650$ nm, $\tau_{\text{res}} \geq 25$ ps) and one stage thermoelectric-cooled CCD (Hamamatsu S10141-1108S, $\lambda_{\text{det}} = 200-1100$ nm) are utilized. In photon counting mode, the data acquisition for the PMT is done using a Fast Comtec P7887 data acquisition card. A photodiode (Thorlab) provided the start-stop signal by detecting the excitation pulse. Figure 2.3 shows the schematic for the experimental setup used to measure the time-integrated and TR-PL signals.

![Figure 2.3: Schematic of the PL-recording setup. The PL signal is recorded using a double lens system together with a fiber coupled spectrometer. Based on the emission wavelength range and type of measurement a CCD or a PMT is used for signal detection.](image-url)
2.4 Absorption

2.4.1 Linear absorption

A Perkin Elmer Lambda 950 ultraviolet (UV)-visible-near-IR spectrometer is used to measure the linear absorption of the samples. A tungsten-halogen and deuterium lamps in combination with a PMT and a Peltier-cooled PbS detector provide a detection range of $\lambda_{\text{det}} = 175-3300$ nm. For all the measurements done with this setup, the substrate material is measured prior to the sample, which then serves as a reference. The reference signal is subtracted from the sample signal to get the real absorption by the sample. An integrating sphere is incorporated in the setup to account for scattering effects.

2.4.2 Transient induced absorption

Transient induced absorption (TIA) spectroscopy is a powerful set of techniques for probing and characterizing the electronic and structural properties of short-lived states (transient states). In this method, the system is excited with a pump pulse prior to the absorption of a probe pulse. The pump pulse generates excited states which are then probed with the secondary pulse while undergoing different relaxation and recombination processes. A Ti:Sapphire amplifier system generates ultra-short pulses ($\Delta t = 130$ fs, $f = 1$ kHz). In order to obtain a continuous tunability from the UV to mid-IR spectral range, the pulse passes through the optical parametric amplifier (OPA) system converting it to the desired wavelength. Before the beam passes through the OPA system, it is separated by means of a beam splitter and the second split-off beam is used as a probe pulse to monitor the excited sample. With the help of a water cell or CaF$_2$ film, a mono-wavelength probe pulse is converted into a white or IR continuum, respectively. Due to some nonlinear phenomena arising from the optical Kerr effect and self-focusing of the laser pulses in transparent condense media, the pulse is stretched spectrally and temporally to ~ 200 fs. This effect leads to a wavelength-dependent arrival time of the probe at the sample and is referred to as ‘chirp’, where a wavelength-dependent refractive index of the sample material can enhance the temporal stretching of the pulse. This effect needs to be corrected for in order to recover the true time characteristics. The pump and probe pulses are gradually delayed with respect to each other using an optical delay stage to monitor the changes in the excited sample. Figure 2.4 shows the schematic of the TIA spectroscopy setup.

In TIA, we probe the absorption of the system after bringing it into an excited state by the pump pulse and compare it to the absorption of the ground state (without the pump pulse). The absorption follows the Beer-Lambert law, where the sample is irradiated with an intensity $I_o$ and the signal $I$ is detected as:
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\[ I = I_0 \exp(-\alpha L), \] \hspace{1cm} (2.2)

where \( \alpha \) is the absorption coefficient and \( L \) is the sample thickness. The product of the two is called the absorbance or the optical density (OD). This parameter obviously depends on the wavelength of the probing light and the delay time at which the spectrum is taken. The TIA can then be defined as the difference in optical density in the excited state compared to the ground state and is obtained as:

\[ \Delta \text{OD} (\lambda, t) = \log_{10} \frac{I_{\text{off}}(\lambda)}{I_{\text{on}}(\lambda, t)}, \] \hspace{1cm} (2.3)

With \( I_{\text{off}} \) (\( I_{\text{on}} \)) the transmitted probe fluence with pump laser off (on).

Figure 2.4: Schematic overview of the transient induced absorption configuration with multi-colour probing. The pump and probe pulses are generated by a Ti:Sapphire laser (\( \lambda_{\text{exc}} = 800 \text{ nm}, \Delta t = 130 \text{ fs} \) and \( f = 1 \text{ kHz} \)).

In this study TIA spectroscopy is performed on different samples using different wavelength ranges of pump and probe pulses. For white light probing, 370-750 nm wavelength range and for IR probing, 900-1700 nm wavelength range is used. The maximum time delay between pump and probe pulses is \( \sim 3.5 \text{ ns} \). The pump pulse is modulated by a chopper and detection is done with a multi-channel CCD (Ocean Optics) for white light and an InGaAs array (Control Development NIR-256L-1) for IR probing.
2.5 Photoluminescence quantum yield

The external QY (EQY) of PL is determined as the ratio between the number of emitted and absorbed photons by a system. The measurements of the EQY are performed using an integrating sphere, under excitation by a 150 W xenon lamp (Hamamatsu L2273) coupled to a double pass monochromator (Solar MSA-130). In order to calculate the number of absorbed photons, the excitation spectra are recorded at different energies using a monochromator (Solar M266) coupled to a CCD (Hamamatsu S10141-1108S, 200-1100 nm) by placing the reference (quartz substrate) and investigated samples in the integrating sphere. From the difference between spectra of the investigated and the reference (quartz) sample the absorption in the investigated sample is obtained. Depending on the emission wavelength range from the investigated sample, the emission signal is recorded either with the same CCD used for absorption measurements or a Ge detector (Edinburgh Instruments, 900-1700 nm) together with a lock-in amplifier (Signal Recovery SR 7265) and scope. Figure 2.5 shows the schematic of the experimental setup used to measure the EQY. All the measurements are corrected for the spectral response of the detection systems that are used.

![Experimental Setup](image_url)

**Figure 2.4: Schematic overview of the experimental setup used to measure the EQY of PL. Two different detection systems are used depending on the emission wavelength range of the investigated samples: for visible emission signal a CCD and for IR signal a Ge detector.**

2.5.1 Scaling different detection systems

For the samples, absorbing in the visible range of excitation and emitting in IR, the absorption and emission signals are recorded using two different detection
systems. Therefore, it is important to scale their efficiencies. A CCD ($\lambda_{\text{det}} = 200$-
1100 nm) is used to record the excitation spectra whereas IR emission is
recorded using a Ge detector ($\lambda_{\text{det}} = 900$-1700 nm). For scaling purpose, firstly
the correction curves are determined for both systems using tungsten-halogen
and deuterium lamps. To overlap the detection range of the two detectors, a Si
NCs dispersed in ethanol sample with emission range of $\lambda_{\text{em}} = 700$-1100 nm is
used. After measuring the PL spectra of this sample with both detectors, the
spectra are first corrected for spectral sensitivity by making use of the correction
curves and then properly scaled. This scaling factor is then used to correct all the
calculations done for the determination of EQY of IR emitting samples. Another
important thing is that the EQY calculated for IR emission is a relative
measurement, since the integrated PL signal, recorded by the lock-in amplifier or
scope, is used instead of the actual number of emitted photons. To convert this
number to an absolute number of photons, we measure the EQY of the same
sample mentioned above making use of two methods i.e: relative (two detection
system) and absolute (single detection system). Here we get another scaling
factor and this scaling factor is then used to convert the relative EQY to the
absolute value.