Luminescent germanium and group IV quantum dots: synthesis and surface passivation

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LUMINESCENT GERMANIUM AND GROUP IV QUANTUM DOTS

SYNTHESIS AND SURFACE PASSIVATION

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Abstract

The first conclusion from this research is the successful synthesis of multiple diameters germanium quantum dots from a non thermal plasma synthesis. An argon discharge is ignited and the hot electrons in the non thermal plasma are able to partially decompose the precursor gas, GeCl$_4$. In order to give the partially decomposed germanium-chloride molecules the time to bond together the chlorine is scavenged by hydrogen radicals. Hydrogen is injected separately into the reaction. This results in the formation of HCl. Particles crystallize due to the selective nanoparticle heating mechanism. This crystallization process only occurs if the power input into the plasma is high enough, usually above 25 W. The germanium quantum dots as-synthesized have a very high concentration of chlorine atoms at their surface, and some hydrogen atoms as well. The hydrogen concentration at the surface is found to be almost independent of the H$_2$:GeCl$_4$ ratio in the plasma. XRD spectra show three well defined diameters (4.8, 6.8, 10.2 nm) that are used to characterize optical properties of germanium quantum dots.

The second important result is the removal of all chloride surface states with grignard reagents. This is a chemical reaction where the chlorine atom is replaced with an alkyl chain. grignard reagents require only very mild temperatures (80 °C) to be effective. This allows a wide choice of solvents with relatively low boiling points to be used. The choice for diethyl ether in this thesis as a solvent is made out of practical considerations. Dodecylmagnesiumbromide (the used grignard reagent) is already in diethyl ether, so no drying of the particles after chemical treatment is necessary. FTIR spectra of the particles before and after chemical treatment show that all chlorine disappears after reaction with an excess amount of grignard reagent. The attachment of the alkyl chains is an important step for the stabilization of the quantum dots in solvents. After attachment of the alkyl chains the quantum dots are stable in diethyl ether, as well as non polar solvents of which decane (C$_{10}$H$_{22}$) has been tried.

The most important conclusions are made from the optical measurements of the germanium quantum dots. Weak luminescence is observed from three different sizes germanium quantum dots. The photoluminescence (PL) curves shift with the average diameter of the quantum dots, although they do not exactly match the theoretical behavior predicted by the Brus equation. There are multiple reasons for this small deviation from the theoretical behavior: an error in effective electron and hole masses, or a wrong dielectric constant due to the use of a polar solvent such as diethyl ether. The absorbance measurements are in correspondence with the observed PL. However, an absorption offset has been proven very difficult to determine because of the indirect band gap of germanium. This results in a very gradual decay of the absorption at high wavelengths. Comparison of the PL of germanium with other results in literature shows a good correspondence which makes it more feasible that indeed band gap emission from these crystals is observed. Another important reason that band gap emission has been observed is that the PL spectra did not show a shift with a changing excitation wavelength.

The last chapter is about SiGe alloys and the synthesis of pure tin. Alloys syn-
thesized from GeCl$_4$ and SiCl$_4$ result in crystalline quantum dots of about 15 nm diameter in every possible composition. No stability issues have been found although there is a 4% lattice mismatch between silicon and germanium crystals. The synthesis of pure tin is only briefly investigated. SnCl$_4$ in combination with argon and hydrogen in a plasma results in $\beta$-tin with some traces of $\alpha$-tin.
Preface

A large fraction of this thesis is scientifically relevant enough to be published in an academic journal. Very recently a paper has been submitted to the Journal of Physical Chemistry Letters with the title: Tunable band gap emission and surface passivation of germanium nanocrystals synthesized in the gas phase. Authors are L Wheeler, LM Levij, and UR Kortshagen. A reaction from our editor is pending at the moment.
# Contents

1 Introduction .......................................................... 9  
1.1 Renewable energy .................................................. 9  
1.2 Solar energy and photovoltaics ................................... 10  
1.3 Nanocrystals ........................................................ 10  
1.4 Multiple exciton generation ....................................... 11  
1.5 Germanium ........................................................... 13  
1.6 Photoluminescence .................................................. 14  
1.7 Contents of this thesis ............................................. 14  

2 Germanium synthesis .................................................. 15  
2.1 Abstract .............................................................. 15  
2.2 Theory ................................................................. 16  
2.2.1 Agglomeration .................................................... 16  
2.2.2 Charging ............................................................ 17  
2.2.3 Confinement ....................................................... 19  
2.2.4 Heating ............................................................. 19  
2.2.5 Germanium ........................................................ 20  
2.2.6 Surface model ..................................................... 20  
2.3 Experimental ........................................................ 21  
2.3.1 Reactor .............................................................. 21  
2.3.2 Electrodes .......................................................... 22  
2.3.3 Pump system ....................................................... 23  
2.3.4 Matching network ............................................... 24  
2.3.5 Recipes ............................................................. 25  
2.4 Analysis techniques .................................................. 25  
2.4.1 Raman ............................................................... 26  
2.4.2 XRD ................................................................. 26  
2.4.3 TEM ................................................................. 27  
2.4.4 FTIR ............................................................... 27  
2.4.5 Size analysis ...................................................... 28  
2.5 Results and discussion .............................................. 29  
2.5.1 Crystallinity ....................................................... 29  
2.5.2 Size ................................................................. 31  
2.6 Conclusion ........................................................... 37
## 3 Surface passivation

3.1 Abstract ........................................ 38
3.2 Theory ......................................... 39
   3.2.1 Particle synthesis ......................... 39
   3.2.2 Hydrogermylation ......................... 39
   3.2.3 Grignard chemistry ....................... 40
3.3 Experimental ................................. 41
3.4 Results and Discussion ...................... 42
   3.4.1 Chlorine ................................ 42
   3.4.2 Hydrogermylation ......................... 45
   3.4.3 Grignard chemistry ....................... 47
3.5 Conclusion .................................... 50
3.6 Outlook ...................................... 50

## 4 Optical properties

4.1 Abstract ...................................... 51
4.2 Theory ....................................... 52
   4.2.1 Crystal momentum ......................... 52
   4.2.2 Confinement .............................. 53
   4.2.3 Lifetime ................................ 53
   4.2.4 Brus equation ............................ 53
   4.2.5 Photoluminescence in semiconductor quantum dots .... 55
   4.2.6 Photoluminescence in germanium quantum dots .... 56
4.3 Experimental ................................. 56
   4.3.1 Absorbance ................................ 56
   4.3.2 Photoluminescence ......................... 57
4.4 Results and discussion ...................... 58
   4.4.1 Absorbance ................................ 58
   4.4.2 Photoluminescence ......................... 60
4.5 Conclusion .................................... 63
4.6 Outlook ...................................... 64

## 5 Alloy synthesis

5.1 Abstract ...................................... 65
5.2 Theory ....................................... 66
   5.2.1 Particle synthesis ......................... 66
   5.2.2 SiGe ..................................... 66
   5.2.3 Lattices ................................ 67
   5.2.4 Tin ..................................... 69
   5.2.5 Phase diagrams ............................ 69
5.3 Experimental ................................. 70
5.4 Results and discussion ...................... 71
   5.4.1 SiGe-alloys ............................... 71
   5.4.2 Tin ..................................... 75
5.5 Conclusion .................................... 76
5.6 Outlook ...................................... 77

## 6 Conclusion

6.1 Abstract ...................................... 78
7 Appendix

7.1 Nano crystal surface model .......................... 80
  7.1.1 Nanocrystal ................................... 80
  7.1.2 Gas flow ...................................... 81
  7.1.3 Result ...................................... 82
7.2 Residence time ................................. 82
7.3 Particle recipes ................................. 84
Chapter 1

Introduction

This chapter starts with the broad context of this research. The focus will be on solar energy and what role it could play in the future world energy supply. Afterwards, the focus will be on the process of multiple exciton generation (MEG). An explanation will be given for the potential solar energy application of germanium in combination with MEG.

1.1 Renewable energy

It is generally believed that fossil fuels like gas and oil will be depleted at some point in the future. A recent estimate [1] shows that there is oil for another 100 years at the moment. The accuracy of these long term estimates is always doubtful, and not without reason. Recent developments of shale gas in the United States show that there might be fossil fuels for many more centuries [2].

Even if there would be fossil fuels forever, and carbon dioxide emissions would cause no problems, there are more arguments to spend money on the research of renewable energies. The United States have recently launched their ‘Energy independent 2030’ strategy [3]. This plan involves the ambition of the United States to import no more fossil fuels by 2030 from foreign countries, except Canada. This might be a little over-ambitious, but it shows the intention to decrease the dependence on unstable countries like Venezuela and Saudi-Arabia. The US follows two main pathways to become energy independent. First, the production of oil and gas will be increased significantly. This is partially done by new methods like hydraulic fracturing. Secondly, the efficiency and capacity of renewable energy sources is increased.

There are a couple forms of renewable energy possible. Currently available are wind, solar and hydro-energy. Hydro-energy is currently a large contributor [4] of renewable energy but often limited by the landscape, such as the number of waterfalls in a country. Wind-energy is currently the second most installed renewable power generation method, but it is relatively expensive per kWh and it is difficult to reduce these costs. Another renewable energy in the future might be nuclear fusion. The first test reactor is currently planned in France, but nuclear fusion is probably not going to be a significant power source before
Solar energy is currently the third most installed renewable energy. The market is completely dominated by silicon solar cells. Germany is the world leader in installed solar power, and it currently generates about 3% (32 GW) [5] of its total electricity consumption via solar energy. The total installed solar energy capacity worldwide lies around 80 GW.

1.2 Solar energy and photovoltaics

The classical way people tend to think about solar energy is to use the heat coming from the sun to warm up water or a similar application. Most solar cells nowadays however, are photo voltaic devices. It is a method to directly convert solar radiation (photons) into electricity. This can be done with conventional polycrystalline silicon or amorphous silicon. Polycrystalline silicon refers to a range of materials in the transition region from amorphous to micro crystalline. Polycrystalline silicon is thus a material which consists of amorphous silicon with some crystals incorporated.

When referred to nanocrystals (NC) in this thesis, it means particles with a diameter around 20 nm or smaller, fully crystallized. This is very different from polycrystalline silicon.

The most significant economic difference between silicon wafer cells and amorphous silicon is the amount of material used. For silicon wafer cells the absorption layer has to be around 350 microns, where for amorphous silicon, this layer has to be only one micron. The reason for this is that amorphous silicon has a much higher absorption coefficient for wavelengths in the visible range. The absorption coefficient of nanocrystals depends on their surface functionalization, size, and material. It is expected that the layer thickness for a NC solar cell will be in the order of one micron because of the high absorption coefficient compared to bulk material in NC's. This means that material cost will decrease compared to silicon wafer cells.

1.3 Nanocrystals

Nanocrystals (NC) or quantum dots (QD) are based on the quantum mechanical principles of particles smaller than the Bohr exciton radius. Because of their small radius, energy levels within a nanocrystal become discrete. These energy levels are tunable with the size (diameter) of a nanocrystal. The discrete nature of the energy levels is similar to the discretized energy levels in atoms, this explains the reason for the nickname of quantum dots: ‘artificial atoms’. The band gap in these nanocrystals is defined by the diameter of the quantum dots.
Figure 1.1: A quantum dot band gap. There are two main effects that make up the band gap energy. One is the bulk band gap, the second effect is the confinement of holes and electrons. These confinement terms increase when the diameter of the NC is decreased

The ability to tune the band gap makes quantum dots interesting for solar cell applications. Quantum dots are usually synthesized with colloidal methods. One of the first demonstrations of this is shown in [6]. This method is different from the plasma synthesis that is used in this research, but it has some analogies that will be explained.

If a photon is absorbed by a quantum dot, an exciton (electron-hole pair) is confined inside the QD. The resulting effective band gap of the quantum dot will always be higher than the band gap of the bulk material, this is caused by the confinement effects as in figure 1.1. Besides the tunability of the band gap energy, there is another reason that makes QD’s very interesting: Multiple Exciton Generation (MEG). In 2005 the National Renewable Energy Laboratory showed [7] MEG in lead sulfide QD’s. In 2007 NREL also demonstrated MEG in silicon quantum dots [8].

1.4 Multiple exciton generation

Multiple Exciton Generation (MEG) has the promise to greatly increase the efficiency of solar cells. Conventional photovoltaic devices use one photon to create one exciton (electron-hole pair). The excess energy of the photon is mostly lost as heat. With MEG, one high energetic photon is used to induce multiple excitons. This is schematically shown in figure 1.2. The reason that this second exciton cannot be generated in a bulk semiconductor is that in bulk semiconductor the phonons are used to conserve crystal momentum. In a quantum dot however, on very small length scales, only angular momentum has to be conserved [9].
Figure 1.2: Left: Classical semiconductor with thermalization losses caused by phonon emission. Right: Multiple exciton generation

Figure 1.3: Losses of a solar cell made of silicon. The thermalization (heat) loss is especially high for high energetic photons with low wavelengths. Losses caused by extracting the charge carriers from the material will always exist. This graph is reprinted from [10]

Thermalization in figure 1.3 means heat loss. High energetic (blue) photons are not very efficiently used in a conventional solar cell, since the band gap of silicon only requires 1.12 eV, and these photons have an energy of around 3 eV. But it is known from [8] that the theoretical efficiency of a solar cell can be greatly improved with MEG [11]. This is shown in figure 1.4.
Figure 1.4: M1 is a conventional solar cell with one photon inducing one exciton. M2 generates two excitons for every photon with energies with at least twice the band gap, and Mmax represents the maximal efficiency. The band gaps of bulk silicon and germanium are also shown. A quantum dot can only have a band gap higher than the bulk band gap of the material it is made from. Note that the ideal band gap would lie around 0.85 eV. This graph is reprinted from [11].

Two conclusions can be made from figure 1.4: First, MEG is potentially a very interesting method to increase the efficiency of photovoltaic devices. The blue line (Mmax) might be difficult to achieve, but significant increases in efficiency are already possible at M2 and M3. The second conclusion is that the bulk band gap of silicon is too large to reach the optimum efficiency. A nanocrystal will never have a smaller band gap than the bulk material because of the quantum confinement. This means that silicon nanocrystals are not optimal in a MEG solar cell, since there are not so many high energetic photons in the solar spectrum. Germanium seems to have a better bulk band gap of 0.67 eV which can be shifted to higher energies due to quantum confinement.

1.5 Germanium

From the previous section it is clear that germanium might be a very interesting material to use in solar cells. Nowadays however, silicon is the most frequently used material for solar cells. One reason involves the cost of germanium compared to silicon. A kg of germanium costs about $1200 [12], whereas silicon costs about $32 per kg [13]. This huge cost difference is an important reason for the lag in development of germanium solar cells.

The cost difference might seem huge, but material expenses are obviously not the only costs to produce a solar cell. By using very thin layers, the material cost of silicon or germanium are only a very small percentage of the total production cost. The increase in efficiency by using germanium is more important in this scenario than the increase in material cost. Another advantage is the absorption coefficient of germanium compared to silicon. For most wavelengths,
the absorption coefficient of germanium is almost one order of magnitude higher than that of silicon [14]. This means that germanium layers can be made thinner than silicon, and still absorb the same amount of radiation.

Germanium has a bulk band gap of 0.67 eV. This is equivalent to a wavelength of 1851 nm. This low energy gap means that a lot of photons can be used to excite an electron-hole pair, but that thermalization losses will be very large for the high energetic photons. This problem can be solved with MEG, since the high energetic photons will induce multiple electron-hole pairs.

1.6 Photoluminescence

Germanium is thus a very interesting material for a solar cell if it can be synthesized in such a way that MEG occurs in the material. An important first step in this process would be to observe photoluminescence (PL) from germanium nanocrystals with a band gap of 0.8 ∼ 0.9 eV (maximum in figure 1.4). Obviously, photoluminescence is not the ultimate goal of a solar cell, since PL is an indication for radiative recombination of electrons and holes. PL from a material however, shows a high quality semiconductor with carriers having a long life time that are able to reach the radiative limit. In a device, these carriers could be extracted before they recombine and thus produce electricity.

1.7 Contents of this thesis

This thesis consists of four chapters. The first chapter will cover the synthesis of different sizes of germanium nanocrystals. In the theoretical section of this thesis the formation of nanoparticles with a plasma synthesis method will be explained. The second chapter focuses on the surface of germanium nanocrystals. The surface functionalization is important for further processing of the nanocrystals. Different chemical surface treatments will be discussed. The third chapter will discuss the optical properties of germanium nanocrystals, directly after synthesis, and functionalized with the methods of the second chapter. Both absorbance and photoluminescence are shown. The fourth and last chapter covers the synthesis of other Group IV materials. A SiGe alloy and the synthesis of pure tin is discussed.
Chapter 2

Germanium synthesis

2.1 Abstract

This chapter describes the synthesis and analysis of germanium nanocrystals. The particles are synthesized via a non thermal argon plasma which allows precise control of the nanocrystal size. Average reactor pressures are around 2 Torr. All germanium crystals are synthesized from GeCl$_4$. Crystal size, meaning average crystal diameter, can be varied between 4-25 nm. This is done by changing the residence times of crystals in the plasma. Particles can be made either amorphous or crystalline by varying the power input to the plasma. Higher powers are used to synthesize crystalline material. The lattice constant for germanium is 5.66 Å, though distances on the surface may be different. This is caused by the strain on the surface of the NC’s. Analysis of crystallinity is done with Raman spectroscopy, while all size analysis is done via X-ray diffraction and transmission electron microscopy (TEM).
2.2 Theory

This section describes theoretically the synthesis of germanium nanocrystals with a plasma. The analogy with silicon will be made, since this is the most frequently used material in plasma synthesis. In general, it is expected that germanium behaves in a similar way as silicon does, since both are group IV elements, and thus have an equal number of electrons in their outer shell. Germanium (72 AMU) is a heavier element than silicon (28 AMU). Another difference is the precursor gas. Most silicon plasma syntheses are done with silane (SiH$_4$), while the germanium NC’s are synthesized from germanium tetrachloride (GeCl$_4$). The difference involves the hydrogen. The overall reaction for the silane synthesis is:

$$SiH_4 \longrightarrow Si + 2H_2$$

For the germanium synthesis, the overall reaction is:

$$GeCl_4 + 2H_2 \longrightarrow Ge + 4HCl$$

The hydrogen in the germanium synthesis is necessary to scavenge the chlorine atoms, while in the silicon synthesis the hydrogen is just a residual product.

2.2.1 Agglomeration

When a hot electron collides with a chlorine atom, it will bounce that chlorine atom away. This means there are now a GeCl$_3$ molecule and a Cl atom in the plasma. The chlorine atom will immediataly re-attach to the GeCl$_3$ molecule unless it is scavenged by hydrogen atoms or radicals. Once the chlorine atom is gone, the GeCl$_3$ molecule will have time to find another GeCl$_3$. These two can bond together and form a Ge$_2$Cl$_6$ agglomerate. This is the start of a small particle, and it will continue to grow as long as the chlorine is sufficiently scavenged by hydrogen. The process is schematically shown in figure 2.1.
Figure 2.1: The formation of a small germanium cluster in four steps. The gases enter at the top of the figure, these gases are argon, hydrogen, and GeCl₄. In the second step, high energetic electrons decompose or excite molecular hydrogen and partially decompose GeCl₄. The chlorine atom, which is now floating around, is captured by a hydrogen radical to form HCl in the third step. When multiple GeCl₄ atoms are simultaneously decomposed they can bond together forming a small cluster, hence the Ge₂Cl₆ structure is formed. This process continues and in combination with the selective nanoparticle heating, caused by recombination of Ar⁺ at the surface of the particles, such a structure becomes a nanocrystal. The electrons and argon ions are not drawn in every step for clarity.

2.2.2 Charging

The charging of nanoparticles is very important for both confinement and heating in the plasma. In this subsection a distinction is made between small and large particles. Charging of large particles can be described by orbital motion limited theory, under the assumption that there is a collisionless sheath around
such a large particle. Large particles are at least 5 nm in diameter.

Small particles comprise of every particle from a couple of atoms, to particles up to about 5 nm in diameter. These small particles can only have a very small number of electrons at their surface, because Coulomb forces prevent multiple electrons to be situated near each other.

2.2.2.1 Large particles

Large particles will be approached by an electron and ion current which can be described by orbital motion limited theory. This is under the assumption of completely collisionless ion motion, only those ions are taken into account that have an angular momentum below a certain threshold, referenced to the particle. The electron current approaching a negatively charged particle is given by a thermal electron flux enhanced by a Boltzmann factor [15]:

$$I_e = \frac{1}{4} n_e S \sqrt{\frac{8k_B T_e}{\pi m_e}} \exp \left( - \frac{e|\Phi|}{k_B T_e} \right)$$

Here $I_e$ is the electron current, $n_e$ the electron density, $S$ the surface area of the particle, $\Phi$ the negative particle potential ($\Phi < 0$), $m_e$ the electron mass, $k_B$ the Boltzmann constant, $e$ the elemental charge, and $T_e$ the average electron temperature. Within the orbital motion limited theory the ion current ($I_i$) is given by:

$$I_i = \frac{1}{4} n_i S \sqrt{\frac{8k_B T_i}{\pi m_i}} \left( 1 + \frac{e|\Phi|}{k_B T_i} \right)$$

Here $n_i$ is the ion density, $T_i$ the ion temperature, and $m_i$ the ion mass. The ion and electron current explain the charging of a small group of agglomerated atoms with a sufficiently large diameter ($> 5$ nm). This small group is confined in the plasma and has time to grow further. The average charge on a particle ($Q$) with radius ($R_p$) at a certain point in time in the plasma is constant. This leads to the differential equation:

$$\frac{dQ}{dt} = I_i + I_e = 0$$

This means that ion and electron current exactly cancel each other in equilibrium. The result of this is a constant charge on the particle which can be derived in a similar method as in [15]. The result is a charge ($Q$) on the particle:

$$Q = 4\pi \varepsilon_0 R_p \Phi$$

The agglomerate of germanium atoms with chlorine on their surface easily attracts negatively charged electrons in the plasma to form negative ions. This charging is caused by a high electron mobility in non thermal plasmas [15]. These negatively charged clusters can be electro statically confined in the plasma, since the walls are grounded but the plasma potential is positive.
2.2.2.2 Small particles

Small particles (< 5 nm) can only carry a very small negative charge. Two charges of similar sign will simply repel each other because of the Coulomb force between them. It is often assumed that particles with very small diameters are neutral or even positively charged. These particles will thus have similar residence times as the neutral species in the plasma [16].

2.2.3 Confinement

Confinement of large species in non thermal plasmas works through electrostatics. Due to a high electron mobility, all large species will become negatively charged. The walls are grounded, however, since the plasma potential is positive, all walls repel negative charges. Repulsive Coulomb forces between two negatively charged objects cause particles to stay in the discharge for relatively long times. Residence times of particles in non thermal plasmas are usually in the order of 10 ∼ 200 ms [17].

At some point, the large particles do leave the plasma. This will be caused by the flow of gases and the resulting fluid drag on the particles. Still, residence times of charged particles are longer than that of neutral species.

2.2.4 Heating

From the previous subsections, it is now understood how molecules agglomerate to bigger particles, and how these particles are confined. This does not explain their crystallinity. Crystallization happens through selective heating of nanoparticles. Selective heating happens primarily through ion-electron recombination at the surface of a nanoparticle. In [18] it is shown that nanoparticle temperatures can exceed the gas temperature up to 600 K. This means that it is possible to reach temperatures at which these nanoparticles will crystallize.

A model in [19] shows selective heating of small nanoparticles (d < 10 nm). The temperature of the particle is given by:

\[
\frac{4}{3} \pi R_p^3 \rho C T_p \frac{dT_p}{dt} = G - S
\]  

(2.5)

Here \( R_p \) is the particle radius, \( C \) the specific heat, \( \rho \) the density of the material, and \( T_p \) the particle temperature. The particle temperature is affected by the heat release term \( G \), and the heat loss, \( S \). Heat losses include conduction and convection, but not radiation since it is insignificant in this temperature range [20].

Equation 2.5 uses electron-ion recombination for the surface recombination and a set of specific surface chemical reactions involving hydrogen atoms. Argon is the dominant ion which releases 15.6 eV to the particle in every recombination event. Additional energy comes from the acceleration of the ion argon in the sheath around the nanoparticle. This can add up to approximately 5 eV of extra energy. The result of this model is that small particles can easily reach temperatures up to 1000 K. This explains why it is possible to make crystalline material
with a non thermal plasma. A size dependent study for silicon nanoparticles in [21] shows that for 8 nm silicon nanoparticles the crystallization temperature lies at 1070 K.

2.2.5 Germanium

As mentioned in previous sections, all the heating and confinement theory is about the formation of silicon nanocrystals from SiH$_4$. The case for germanium is slightly different since hydrogen is not coming from the precursor gas, but is injected separately in the form of H$_2$. This will slightly change the plasma kinetics and chemistry, but it is assumed that both the heating and confinement mechanisms are similar for silicon and germanium nanocrystal synthesis. Higher powers are needed for GeCl$_4$ compared to SiH$_4$, because the Ge-Cl bond is stronger than the Si-H bond. In the germanium case, the energy needed to decompose the precursor gas is higher, so higher plasma powers are necessary. More power is also needed because the hydrogen has to be excited as well. H$_2$ needs to be excited or decomposed in order to be chemically active and thus scavenge the chlorine atoms coming from the GeCl$_4$.

2.2.6 Surface model

A germanium nanocrystal can be modelled as a simple sphere. From such a model, an approximation of the number of surface spots can be made.

![Diagram](image)

\[ A_{NC} = 4\pi R^2 \]
\[ V_{NC} = \frac{4}{3} \pi R^3 \]
\[ d_{crystal} = 0.56 \text{ nm} \]  

Where $A_{NC}$ is the surface, $V_{NC}$ is the volume of the sphere, $R_{NC}$ is the radius of the nanocrystal, and $d_{crystal}$ is the crystal length. The number of atoms per nanocrystal is simply calculated by putting spheres into the large nanocrystal:
\[
\frac{V_{NC}}{V_{Ge-atom}} = \frac{\frac{4}{3}\pi R_{NC}^3}{\frac{4}{3}\pi d_{Ge}^3}
\] (2.7)

The number of surface spots per nanocrystal can be calculated with the square surface with sides \(\sqrt{A_{NC}}\).

\[
\text{number of surface spots} = \left(\frac{\sqrt{A_{NC}}}{d_{crystal}}\right)^2
\] (2.8)

2.3 Experimental

Two main topics will be covered in this section, one is the plasma reactor where the particle synthesis happens, the other is a description of the analysis techniques that are used in this research. These include Raman spectroscopy, XRD, TEM, and FTIR.

2.3.1 Reactor

A flow-through non thermal plasma reactor, similar to the one described in [17], is used for the formation of germanium nanocrystals. A schematic overview of this setup is shown in figure 2.3.
Figure 2.3: The single plasma reactor setup. A glass tube, diameter one inch, with a length of 12 inch is used. The gases flow in from the top. Gases used for germanium nanocrystals are GeCl$_4$, Ar, and H$_2$. The distance between the top electrode and the top of the glass tube is important, this will determine the length of the plasma and thus the residence time of particles in the discharge. This distance is usually put at 5.5 cm. The particles are collected on a substrate (gold or glass) and can be transferred to an oxygen-free environment without exposure to air.

The gases (Ar, H$_2$, and GeCl$_4$) are regulated with standard pressure based MKS mass flow controllers (MFC). The GeCl$_4$ is in the liquid phase in an ampul and with a vapour pressure at room temperature of 76 Torr, flow rates up to 2.0 sccm can be achieved. For H$_2$ and Ar, flow rates between 0 and 100 sccm can be reached.

2.3.2 Electrodes

The electrodes are connected to the match box that are described in section 2.3.4. The electrodes are not directly in contact with the plasma but separated from it by the glass tube. This is shown in figure 2.4.
2.3.3 Pump system

A chemical vacuum pump (Welch) is used for this system. For each new experiment, a clean glass tube is installed. After the system is closed, it is pumped down for about one hour. After this, twenty minutes of argon (50 sccm) is pumped through the system to remove any remaining contaminations. Once the system is clean, the desired argon and hydrogen flows are set, and the plasma is ignited. The plasma runs for about ten minutes to clean the tube. Once these ten minutes are over, the GeCl₄ is switched on, and the actual deposition of material happens. This usually takes about ten minutes.

The glass substrate lies on a push rod. Once the experiment is done, the entire system is pressurized with argon slightly above 1 bar. The push rod is now pulled out of the reactor and immediately put into a transfer chamber to a nitrogen filled glove box. Since the push rod is slightly over pressurized, only argon leaks out and no air leaks in. In this way, the particles are not contaminated by
oxygen or water. This is especially important for FTIR analysis and chemical treatment. For TEM, XRD and Raman analysis, oxidation is not important. In these instances, particles are simply brought to the analysis machine while being exposed to air. Size and crystallization tend not to change through water and oxygen. Only surface bonds are sensitive to oxygen and water contaminations.

After the experiment, the reactor is pumped down to base pressure. The MFC which controls the GeCl$_4$ flow has to be purged with argon, since GeCl$_4$ can damage the MFC if it reacts with any oxygen or water that might very slowly leak into the system. After three or four purges, the system is pumped down and the vacuum pump is shut off.

2.3.4 Matching network

The capacitive discharge in this research is driven by an RF power source. If this power source would be connected directly to the electrodes, the power transfer would be very inefficient [22]. The frequency that is used in this plasma is always 13.56 MHz. To increase the power transfer to the plasma a matching network is used. Two different matching networks have been used for the synthesis of particles in this thesis. The first one is a so called Pi-network, it is schematically shown in figure 2.5.

![Figure 2.5: The Pi-network. This network consists of two variable capacitors and one fixed inductance. The load is the impedance of the plasma which has to be matched by the combination of capacitors and coils.](image)

The Pi-network has two variable capacitors and one fixed inductance. This type of network is able to match impedances below and above 50 Ω. The major disadvantage of the Pi-network is its sensitivity of matching due to the two variable components. Another downside is that for a certain range of loads, there are two possible settings which will give a match. The power which is lost in the components is relatively high compared to other networks which causes lots of RF noise around the reactor. In particular, the MFC’s can be affected by this type of radiation and should therefore be properly Faraday-shielded. Because of all the lost power, the input power from the power supply has to be around 100 W to synthesize crystalline germanium. The power input is measured at the power supply and is not the actual amount of power in the
plasma. If diffusion is assumed to be the main loss mechanism in the discharge, there is about 10 W of power in the discharge. This means that 90 % of the power is lost with a Pi-network.

The other matching network is an enhanced L-network. It is schematically shown in figure 2.6.

![Figure 2.6: The enhanced L network. The coil works as a transformer with a specific turns ratio. There is only one variable capacitor. The turns ratio determines the potential difference between the electrodes.](image)

There are a couple of advantages of this kind of matching network. It is more specific for the power and frequency range than the more general Pi-network. Input powers to get crystalline material lie around 30 W, much lower than for the Pi-network. This matchbox is developed during the year of this thesis and has been used for all samples later in the thesis. In this report it will be mentioned if the Pi-network is used, usually the enhanced L-network is used. All powers are read out directly from the power supply. This is a RFX 600 from Advanced Energy Productions.

### 2.3.5 Recipes

The gases used for the germanium synthesis are argon, hydrogen and germanium-tetrachloride. By varying the flow rates and thus changing the residence times in different experiments, different sizes of crystals can be synthesized. There is however one recipe, producing 6.8 nm germanium crystals, which has proven to be useful in a lot of experiments. These particles have been used to investigate all the surface chemistry. The conditions of multiple recipes are given in Appendix 7.3.

### 2.4 Analysis techniques

In this section some analysis techniques will be described. There will also be a brief part about the procedure in which these techniques are used.
2.4.1 Raman

Raman spectroscopy is a spectroscopic technique used to observe vibrational, rotational and other low frequency modes in a material. The technique is based on inelastic scattering, which is also called Raman scattering. In this particular setup a red laser with a wavelength of 635 nm is used to illuminate the sample of germanium quantum dots. In this case, the QD’s are deposited on a glass substrate. To measure the Raman spectrum a glass substrate with nanocrystals is put under the laser light, the beam is focused on the sample.

The main difficulty of Raman spectroscopy is to separate the weak emission from inelastic collisions from the intense Rayleigh scattered laser light. To achieve the rejection of the Rayleigh scattering a band-stop filter is used that precisely filters out the laser frequency.

Any crystalline material has a very specific lattice distance. This means that a fully crystalline material will show a very specific peak (vibrational mode) which is a result of this lattice distance. For germanium, this peak lies at 300 cm$^{-1}$. If the material is crystalline, a distinct crystal peak will appear. If the material is amorphous, a large broad hump around the crystal peak appears.

2.4.2 XRD

X-ray diffraction is a technique to measure the average grain size of crystalline material. The average particle diameter is determined from XRD patterns. An example of a couple of these patterns is shown in figure 2.11. Crystalline atoms cause a beam of X-rays to diffract into many specific directions. By measuring the angles and intensities of these beams the density of electrons can be calculated. From this electron density the mean positions of atoms in the crystal can be determined.

A sample of germanium QD’s on a glass substrate is mounted on a goniometer and gradually rotated while being illuminated with X-rays. This produces a diffraction pattern of regularly spaced spots. Images taken at different rotations can be converted into a model of the density of electrons using a Fourier transformation.

If the particle sizes get smaller, the peaks in the XRD spectrum tend to broaden. This is because of the Scherrer equation:

$$B = \frac{K \lambda}{L \cos(\theta)}$$  \hspace{1cm} (2.9)

Where $B$ is the mean size of the ordered crystallite domains, $\theta$ is the Bragg angle, $\lambda$ the radiation wavelength, and $L$ the line broadening after subtraction of the instrumental broadening. $K$ is a constant which depends on the peak shape. For spherical crystallites, $K$ is very close to unity. The XRD patterns of particles for multiple sizes is shown in figure 2.11. One obtains the average size of the particles from equation 2.9.

XRD analysis is operated in a relatively similar method as Raman spectroscopy.
The quantum dots are deposited on a glass substrate. The X-ray beam has to be focused on the sample, and this is done with the assistance of a laser. Once the X-ray beam is focused, one has to close the entire system. X-rays are very dangerous for your health so the entire system is closed and ensures that no X-rays ‘leak’ to the environment. After the XRD spectrum is measured, it has to be integrated over the entire sample. The system measures every grid point on the sample, but the only relevant data is the intensity per angle ($2\theta$). The integration over the entire sample is incorporated in the software of the XRD machine.

2.4.3 TEM

Transmission Electron Microscopy is a technique that uses an electron beam to illuminate a sample and produce a magnified image. Larger magnifications can be achieved with TEM compared to standard light microscopes. This is possible because the wavelength of electrons is about five orders of magnitude smaller than that of visible light.

Germanium QD’s for TEM analysis are deposited on special TEM grids. These are made out of copper and covered with a carbon layer. Deposition times on these grids are very short because the QD’s cannot be stacked too closely together. In that case one will only see a black area on a TEM image.

2.4.4 FTIR

FTIR stands for Fourier Transform Infrared Spectroscopy which is an example of absorption spectroscopy. The goal of any absorption spectroscopy measurement is to measure how well a sample absorbs light at each wavelength. Certain bonds in materials, Ge-Cl for instance, can be identified because they show this absorption at specific wave numbers.

FTIR is a technique where a beam with many frequencies illuminates a sample. It measures how much of that beam is absorbed by the sample. Next, the second beam contains different frequencies of light and the procedure is repeated. The light is directed into a Michelson interferometer. As the mirror in the interferometer moves, each wavelength is periodically blocked and transmitted. Different wavelengths are in this way modulated at different rates, so that the beam that comes out of the interferometer looks different at every point in time.

To combine all these spectra, a computer is required to turn the data, light absorption for each mirror position, into a comprehensible result. To convert the data into light absorption per wavenumber, a Fourier transform is used. A FTIR spectrum can be used to identify specific chemical bonds on the surface of a sample. To prepare the sample, it should not be exposed to air, since germanium oxidizes. This is why FTIR analysis is done in a glove box in an almost 100 % nitrogen environment.
2.4.5 Size analysis

Sizes of quantum dots can be measured with two separate techniques: TEM and XRD. TEM is slow and takes more time than XRD. However, TEM provides a very good overview of the QD’s, and the possibility to estimate a standard deviation of the mean diameter. XRD is faster and cheaper, but only provides an average crystallite size, calculated from equation 2.9. Most size measurements have been done with XRD, although thorough investigations have been done with TEM analysis.
2.5 Results and discussion

In this section the synthesis of germanium nanocrystals will be discussed. This will include Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) analysis. There are three main issues for the germanium synthesis, two will be treated in this chapter. Crystallinity and size distribution of the germanium nanoparticles will be covered in this chapter, while surface coverage will be the topic of the next chapter.

2.5.1 Crystallinity

The crystallinity of a material is very important for its properties. Gas temperatures of the non thermal discharge used in this research are estimated only slightly above room temperature, too low to crystallize group IV materials. At those temperatures, there is not enough thermal energy to induce crystallization. As described in the theoretical section of this chapter, individual particle temperatures can exceed this gas temperature with hundreds of Kelvins. At some point, there is enough energy to start a nucleation process.

Raman spectroscopy is a technique to observe vibrational, rotational and other low-frequency modes of a material. A sample is illuminated with a laser beam, and small changes in the laser frequency due to interaction with vibrational modes in the sample are measured that are characteristic to the material.

Fully crystalline samples are expected to have a very sharp and intense peak, this represents the specific distance between two atoms in a crystal. An amorphous sample on the other hand, is expected to have a very broad, less intense ‘hump’ situated around the crystalline peak. The crystalline germanium peak lies at 300 cm$^{-1}$ [23].
One of the first tests on germanium nanocrystals was done with the Pi-network matchbox and varying powers. This will be compared with the synthesis of crystalline material with an enhanced L-network in this section. The results for the Pi-network are shown in figure 2.7.

![Figure 2.7: The Raman spectrum of germanium samples for different powers. As shown, the limit for crystalline material is at 100 W. Below this power, only amorphous material is synthesized. The parameters were similar to the recipe of 6.8 nm diameter particles as in table 7.1.](image)

Figure 2.7 shows an expected behavior for the germanium nanocrystals. For a certain power, crystalline material is synthesized, and with increasing power (150 W) the crystal peak will get higher meaning that there is less amorphous material. The peak in the Raman spectrum is indeed at 300 cm$^{-1}$, so crystalline germanium is synthesized. A similar power series has also been made with the enhanced L-network in figure 2.8.

A similar experiment with a SiH$_4$ plasma requires 50 W of power for crystalline silicon, so less than the 100 W in figure 2.7. To decompose GeCl$_4$ more energy is necessary than for SiH$_4$. Furthermore, the H$_2$ has to be excited as well during the germanium synthesis. The combination of these two factors explains the higher powers for the synthesis of crystalline germanium compared to silicon.
Figure 2.8: The Raman spectrum of germanium samples for different powers. As shown, the limit for crystalline material lies around 25 W. Below this power, only amorphous material is synthesized. This is significantly lower than the synthesis with a Pi-network. This means that the power transfer is much more efficient with an enhanced L-network. Parameters were similar as in figure 2.7.

The previous analysis shows that with high enough powers in the plasma, crystalline germanium nanoparticles can be synthesized.

2.5.2 Size

There are multiple ways of changing the size distribution of nanocrystals. A convenient way of controlling the mean diameter of particles is with the average neutral species residence time. An example of a residence time calculation is shown in Appendix 7.3. However, residence times can be influenced by multiple parameters. Examples are: flow rates of argon, electrode position, and orifice diameter through its effect on the reactor pressure.
Figure 2.9: The particle diameter as a function of residence time in the plasma. These results are in correspondence with what has been found in [24]. Residence times have been calculated in a similar method as in [25]. The blue data point for very large particles (46 nm) is not measured in this research but is used from [26]. Sizes are measured through XRD. Flow rates are held constant while different reactor pressures were reached via multiple orifice diameters.

The neutral particle residence time affects the particle diameter, but this is not a parameter that is directly tunable. The total flow rate is inversely proportional to the particle diameter as in figure 2.10, and this is something which is controllable. Although residence times are the physical mechanism behind changes in size distributions, flow rates will allow the precise control of particle sizes in the plasma.
Figure 2.10: The particle diameter as a function of total flow rates. This is a combination of Ar, H₂ and GeCl₄. The flow rates of these gases are individually controllable. The pressure increases with higher flow rates and all other parameters (power, orifice diameter) are held constant. The ratio between different flow rates of each gas is also constant. Particle diameters are determined by XRD.

The mean diameters of nanocrystals in this thesis is usually determined from XRD patterns. An example of these patterns is shown in figure 2.11. Because of Bragg’s diffraction law, only certain Miller planes are visible. These Miller planes are indicated by the number above every peak.

The size, and also orientation, of these Germanium nanocrystals can also be investigated by TEM. Figure 2.12 shows a film of 6.8 nm germanium nanocrystals. These particles are only visible at the edge of the film, since the thick film is just visible as a black area.
Figure 2.11: XRD patterns for multiple particle sizes. Graphs are offset for clarity. Identification of different crystal planes are from [27]

Figure 2.12: A: TEM image of germanium nanocrystals with an average diameter of 6.8 nm. The resolution is too low to see lattice fringes in the crystals. The black area is made up of particles very closely stacked. The particles are best visible on the edges. B: inset of zoom of two individual particles where the (111) lattice orientation is clearly visible

The TEM image in figure 2.12 shows nanocrystals with an average diameter of 6.8 nm. The nanocrystals look like circles (spheres in 3D), which justifies the
assumption that a germanium nanocrystal can be modeled as an exact sphere as an approximation. This will be done in Appendix 7.1. For completeness, also the 10.2 nm particles are investigated with TEM, this is shown in figure 2.13.

![Figure 2.13: Transmission electron microscope image from a set of 10.2 nm germanium nanocrystals. The diffraction pattern (upper right corner) is an indication for the crystallinity of the material. These crystals are not in a thick layer as in the previous image, meaning the yield is lower. The large 'structure' is the TEM grid](image)

The 10.2 nm diameter particles are deposited in just a very short time on the grid. This makes it easier to investigate individual particles. Some statistics have been done on basis of these images to estimate a standard deviation for the average diameter. This has also been done for the 6.8 nm and 4.8 nm particles.

In the ideal case, all nanocrystals have exactly the same diameter. The ratio between standard deviation and mean ($\frac{\sigma}{\mu}$) in colloidal synthesis of germanium is about 0.3 in [27]. This article describes colloidal synthesis of germanium NC’s from GeI$_2$. Another article [28] describes a ratio of 0.25, where GeI$_4$ was the precursor for the Ge NC’s. The ratio for the plasma synthesis method used in this chapter never exceeds 0.15. This means that the distributions are sharper, which allows a more precise tunability of the properties of these crystals.
Figure 2.14: Simulated size distributions based on means and standard deviations determined from XRD and TEM analysis. The standard deviation tends to grow with particle size, but as a percentage, it stays roughly the same. All standard deviations lie between 10-15 % of the mean of the distribution. The bars represent actual counts from TEM images.
2.6 Conclusion

In this chapter, it is shown that it is possible to synthesize different sizes germanium nanocrystals with a plasma synthesis method. The ability to produce different sized germanium quantum dots will prove to be important for the next chapters. The size distributions of the germanium nanoparticles are narrow compared to colloidal synthesis methods of germanium. These narrow size distributions are useful since it allows precise control of the properties of the quantum dots.

The recipe described in this thesis which produces 6.8 nm diameter germanium nanocrystals will be used throughout the rest of this thesis, and modified when mixing it with other group IV materials such as silicon and tin. This recipe has been used as the standard because of the ease of the recipe, the narrow size distribution, and the favorable operating regime of the experimental setup.
Chapter 3

Surface passivation

3.1 Abstract

The focus in this chapter is on the surface of germanium nanocrystals. The surface of the germanium nanocrystals is important for further processing of the nanocrystals. The surface states should also be considered when optical properties are investigated. It is found that the crystals, synthesized from GeCl$_4$, do not have enough hydrogen at the surface to perform a successful conventional hydrogermylation. This has been solved by using a grignard reagent, dodecylmagnesiumbromide, CH$_3$(CH$_2$)$_{10}$CH$_2$MgBr. This grignard reagent is able to remove chlorine from the germanium particles and attach alkyl chains. This ensures the stability of the particles in a whole range of solvents like decane and diethyl ether.
3.2 Theory

The functionalization of the nanocrystal surface is a challenge that is more pronounced in plasma synthesis than in conventional colloidal synthesis methods. The nanoparticles in colloidal synthesis retain ligands from their synthesis and growth, and are already in solution. Further processing and surface chemistry is thus relatively easy. There are many examples of this such as [29] (PbS), [30] (Si), [28] (Ge), and [31] (Si). In a plasma synthesis however, the nanocrystals will be in powder form, agglomerated together, and not yet soluble because of the chlorine or hydrogen at their surface. The standard procedure with silicon particles to overcome this solubility problem is hydrosylation [32].

3.2.1 Particle synthesis

From a simple theoretical model, given in Appendix 7.1, it is concluded that there is insufficient atomic hydrogen to cover all surface sites of the germanium nanocrystals with hydrogen. Considering there is chlorine bonded to the Ge in GeCl₄, it is reasonable to expect that there would be Cl at the surface of the particles directly after synthesis. FTIR measurements show this to be the true in figure 3.3. Two possible ways of getting these particles in solution are proposed: The first option is to perform hydrogermylation on the particles. In hydrogermylation, it is expected that the ligand will react with hydrogen terminated surface sites, thus creating a steric barrier to stabilize the particle in solution. The hydrogermylation leaves the chlorine atoms on the NC surface.

The hydrogermylation requires a hydrogen terminated surface, however it will be shown, the surface of these Ge particles is terminated by chlorine. A second option is explored wherein a grignard reagent is used to attack the electrophilic germanium that is bonded to chloride and therefore graft the organic group of the reagent to the surface of the nanocrystal.

3.2.2 Hydrogermylation

Hydrogermylation is the attachment of unsaturated alkyl chains to hydrogen terminated germanium surface sites. The process is schematically shown in the center bottom part of figure 3.1. In this case, there is no need to remove any oxygen first, since the particles have not been exposed to air before this process.

\[ H - Ge + CH_2 = R \rightarrow H + Ge(111) - R \]

The hydrogen is replaced by a carbon atom, and the alkyl chain now creates a steric barrier against particles with other alkyl chains. This reaction needs to be thermally activated at 250°C. The solvent during this hydrogermylation process is decane (C₁₀H₂₂), while the ligand is 1-dodecyl (C₁₂H₂₄). There is a disadvantage of this method for particles only partially covered with hydrogen: The concentration of alkyl chains might be too small to actually stabilize these particles in solution. This will depend on the initial concentration of hydrogen at the surface of a NC.
3.2.3 Grignard chemistry

Grignard reagents are known to react with metal-halide bonds to replace the halide (Cl, F, Br) with an alkyl group, and so their use is explored to attach alkyl steric stabilizers to the surface of chlorine terminated germanium nanocrystals based on previous work on Ge single crystals. The first work on this has been done in [33] and the general stabilization of Ge(111) surfaces has been reviewed in [34]. The following figure shows the steps that are involved in the stabilization of Ge-(111) surfaces.

![Figure 3.1: This figure comes from [34]. Grignard chemistry is shown on the left part of this figure. Germanium surfaces start with oxygen bonds and are chlorinated with a mixture of Cl\textsubscript{2} and HCl gas. This is usually done with a N\textsubscript{2} background above atmospheric pressures. Once the surface is chlorine terminated the grignard-reagent (MgBr-group) is able to remove this chlorine atom. An alkyl chain is attached to the surface. The right part of this figure is an option to stabilize alkyl chains on a hydride covered germanium surface. The middle step in the bottom is hydrogermylation, while the right bottom procedure is similar to hydrogermylation but a Ge-S-C bond is created on the surface.]

Only a part of this scheme is followed for the Ge NC’s. The particles after reaction are already passivated with chlorine (although some hydrogen is present at the surface). So only the last step on the left of figure 3.1 has to be performed. The grignard reagent that is used to stabilize the NC’s is 1-dodecyl-magnesiumbromide, CH\textsubscript{3}(CH\textsubscript{2})\textsubscript{10}CH\textsubscript{2}MgBr. As a proof of concept also a very short grignard reagent has been used, which is called methyl-magnesiumbromide, CH\textsubscript{3}MgBr. These methyl groups are too small to actually stabilize the crystals in solution since they provide an insufficient steric barrier. They do show however, if the chlorine is replaced by carbon.
Germanium is sensitive to both water [35] and oxygen [36]. This means that all procedures must be done without contamination of air. The specific method will be discussed in the next section.

### 3.3 Experimental

All steps in the chemical procedure of the germanium nanocrystals should be done in water and oxygen poor-conditions. The nanocrystals are synthesized and transferred to a nitrogen glovebox without air exposure. The push-rod is pressurized with argon in the reactor so the pressure difference between glovebox and reactor will not blow the particles off the substrate when it is brought up to glove box pressure.

Once the particles are inside the glove box, the glass substrate (with the nanocrystals on top) is put into a 5 inch glass tube, which is sealed with a rubber stopper. This is where the chemistry starts. The tube is filled with diethyl ether so the glass substrate is fully submerged in the solvent. After this, the grignard reagent (1.0 M in diethyl ether) is injected. The reaction already starts happening at this point, indicated by the gas forming in the tube. The tube is now sealed and transferred from the glove-box to a fumehood. The particles are now sonicated, to ensure they are in solution. The sonicated solution is transferred to a reaction flask with a cannula. In this flask, the solution is heated to 80°C for about two hours.

The particles are transferred after the reaction into smaller, sealed vials to investigate their optical properties. With each of the transfer steps in this procedure there is a risk of contamination by water or oxygen. The particles are not exposed to air though solvents were not degassed before use.

The result of this procedure can be checked. If the solvent and the nanoparticles form a transparent solution, enough alkyl chains have been attached to the surface. The particles will not agglomerate in this case and they will not fall to the bottom of the tubes. If the solution is opaque however, and the particles tend to fall down to the bottom of the tube after some time (minutes), the reaction product has been contaminated by water, oxygen or some other kind of impurity.
3.4 Results and Discussion

This section will start with a FTIR spectrum showing there is chlorine at the surface of the as-synthesised germanium nanoparticles. This will be followed by a FTIR spectrum of a germanium sample which is hydrogermylated. The hydrogermylation sample still has chlorine at the surface. Afterwards there are samples which have been treated with grignard reagents.

3.4.1 Chlorine

The precursor gas in the synthesis of germanium nanocrystals is GeCl$_4$. The nanocrystals come out of the reactor in powder form as shown in figure 3.2.

If one tries and suspend this powder in a non-polar solvent, the particles will agglomerate and fall to the bottom quickly. This is because of the surface termination. A FTIR spectrum of the surface is shown in figure 3.3. This shows that the surface of these particles is covered with a mix of hydrogen and chlorine atoms. Because of the very sharp peak in the Raman spectrum it is unlikely that this chlorine and hydrogen is inside the nanocrystals, since this would cause lots of defects in the crystal lattice.

For all FTIR spectra in this chapter the germanium recipe of 6.8 nm in Appendix 7.3 is used. When GeCl$_4$ flow rates are varied, the H$_2$ and Ar flow are kept constant, although this results in slight variations in the pressure.
Figure 3.3: A FTIR spectrum with indications of Ge-Cl and Ge-H stretches and wags. It is difficult to draw any real conclusion in the region between 500 and 1000 cm\(^{-1}\) since it contains lots of wags and vibrations. A known hydrogen peak is visible at 575 cm\(^{-1}\) though. The Ge-Cl peak at 400 cm\(^{-1}\) is clearly visible, as are the distinctive hydrogen peaks and chlorine peaks around 2000 cm\(^{-1}\).

The conclusion from figure 3.3: There is a high concentration of chlorine at the surface of the germanium nanocrystals. Because of the very high degree of crystallinity of the material it is unlikely the chlorine is inside the crystalline material. There are two reasons why this chlorine is not desired at the surface. The first reason concerns problems with solubility in solvents and thus further processing. The second reason is that the chlorine on the surface might decrease the lifetime of photo-excited carriers and therefore decrease the photoluminescence to a level that is undetectable [36]. The expectation is that low flow rates of GeCl\(_4\) lead to relatively high hydrogen concentrations at the surface, since the H:Cl ratio is favorable for these kind of syntheses.

From figure 3.4 it is clear that changing the flow rates of the GeCl\(_4\) is not the solution for getting less chlorine at the surface of the nanocrystals. A calculation in Appendix 7.1 shows that there is simply not enough atomic hydrogen to cover all surface sites of a 6.8 nm germanium crystal at a 1.0 sccm flowrate of GeCl\(_4\).
In this model it is assumed that only atomic hydrogen can be used to cover the surface of the crystals and any molecular hydrogen will not contribute. Lower precursor flow rates (bottom two graphs in figure 3.4) do give more hydrogen at the surface, but there is a lot of chlorine in all these experiments.

Figure 3.4: Different flow rates of GeCl₄ with constant argon and hydrogen flow; increasing the ratio of hydrogen to germanium does not seem to affect the amount chlorine at the surface of the particles. The hydrogen peak seems to grow for lower GeCl₄ flows, but it is clear that not all chlorine is replaced in any of these samples indicated by the high peak at 400 cm⁻¹. Note that the pressure, and thus the particle size, varies slightly because there is no compensation of the change in GeCl₄-flow. Pressure varies between 1.9 and 2.1 Torr.
3.4.2 Hydrogermylation

Figure 3.4 shows that there is hydrogen at the surface of the NC’s, the problem however is that there is also chlorine. Since FTIR is not a quantitative analysis it might be possible that the particles can be hydrogermylated despite the chlorine [37]. Hydrogermylation is a process where the hydrogen atom at the surface of a germanium crystal is replaced with an unsaturated alkyl chain. If enough of these alkyl chains are attached to a nanocrystal, this will create steric barriers between the nanocrystals in solution, and thus make them soluble in a non polar solvent. The process of hydrogermylation is already explained in 3.2.2.

In figure 3.5, a FTIR spectrum of a succesful hydrogermylation reaction is shown. A succesful hydrogermylation reaction has been proven to be very difficult for the germanium nanocrystals, the particles tend to agglomerate after the reaction, which should not happen if a sufficient concentration of alkyl chains are attached to the surface. This confirms the FTIR spectra that there is much more chlorine than hydrogen at the surface (indicated by a higher chlorine than hydrogen stretch). A FTIR spectrum of a successful hydrogermylation reaction is shown in figure 3.5. This is the sample with a 0.2 sccm GeCl$_4$-flow from figure 3.4.
Figure 3.5: FTIR of a successful hydrogermylation of Ge NC’s. Successful means that all hydrogen is removed and replaced with carbon atoms. The particles still tend to agglomerate after some time (10 minutes) in a solvent. This means that there are not enough alkyl chains at the surface to create a sufficient barrier between the particles.

A schematic overview of the surface of these particles after hydrogermylation is given in figure 3.6. The surface will consist of a combination of Ge-Cl and Ge-C bonds. If there are enough alkyl chains, i.e. enough carbon atoms at the surface, the particles will be stable in solution. This stability has not been achieved for any of the samples due to high concentrations of chlorine atoms at the surface.
Figure 3.6: The surface after hydrogermylation. A combination of chlorine and carbon atoms are now covering the surface

The hydrogermylation method is not a good way to functionalize the surface of germanium nanocrystals synthesized from GeCl$_4$. This is caused by the large concentration of chlorine atoms. Performing a hydrogermylation and leaving the chlorine at the surface of the NC’s is not a sufficient method to solve this problem.

### 3.4.3 Grignard chemistry

As described in section 3.2.3, grignard reagents are capable of removing chlorine from the germanium particle surface. This is shown in figure 3.1, although the method varies slightly. The first step, where the chlorine removes the oxygen is not necessary in this case. The grignard reagent is a long alkyl chain (12 carbon atoms) with a MgBr-group at the end. To observe this in the FTIR spectra the C-H$_x$ stretches around 3000 cm$^{-1}$ will be visible.

The grignard reagent is put in contact with a germanium particle of 6.8 nm diameter and has been functionalized with a single carbon atom and with an alkyl chain of twelve carbon atoms. The Ge-Cl peak at 400 cm$^{-1}$ disappears because of the Grignard reaction and is replaced with a Ge-C wag at 510 cm$^{-1}$. For the long alkyl chains, there is also the Ge-C-C wag at 550 cm$^{-1}$ [38]. The intensity of the C-H$_x$ bonds increases for the longer alkyl chains. A reaction product of the grignard reaction is MgCl$_2$. This salt is insoluble in diethyl ether and is observed at the top of the syringe, used for the injection of the Grignard reagent.
Figure 3.7: Graphs are offset for clarity. FTIR spectra of un-functionalized particles (black), particles with CH$_3$ groups at the surface (red) and particles with (CH$_2$)$_{11}$CH$_3$ chains at the surface (blue). The C-H peak at 3000 cm$^{-1}$ is higher if the longer alkyl chains are attached. The reason that the Ge-C wag looks like two peaks for the CH$_3$(CH$_2$)$_{11}$ is that in this case there are Ge-C and Ge-C-C stretches, the latter one is not present at the CH$_3$MgBr.

A number of new, unidentified peaks (between 1000 and 1500 cm$^{-1}$) appear as a result of the grignard reaction. A spectrum of the solvent (diethyl ether) and the grignard reagent have been taken to see which of these peaks overlap. These spectra are shown in figure 3.8. There are many wags and vibrations that could appear in this region. The diethyl ether can interact with the grignard reagent in multiple ways since the solvent is C$_4$H$_{10}$O. The certainty that these peaks do not represent something completely different comes from the solubility of the nanoparticles in a solvent. This is proof of the attachment of the alkyl chains and the chlorine removal.
Figure 3.8: FTIR spectra of diethyl ether (black), the Grignard reagent (blue), and the functionalized particles (green). The peaks between 1000 and 1500 cm$^{-1}$ in the bottom spectrum are caused by the interaction between the alkyl chains and the diethyl ether.

All peaks in the region 800 - 1500 cm$^{-1}$ are indeed a result of the solvent and some excess reagent. A new problem arises however from figure 3.8. The double peak around 500 cm$^{-1}$ which was identified as a Ge-C stretch is also present in the pure reagent (dark blue line). The double peak is shifted about 20 cm$^{-1}$ but this is a very small shift considering the resolution of 2 cm$^{-1}$. Conclusions about the Ge-C and Ge-C-C stretch are thus difficult because the signal of the excess reagent could overlap the peak of the Ge-C stretches.

However, the attachment of alkyl chains (peaks around 3000 cm$^{-1}$) is very clear. This means that the most important conclusion of this chapter still holds, independent of the identification of the double peak around 500 cm$^{-1}$. The best indication that the grignard reaction has worked is the disappearance of the Ge-Cl stretch at 400 cm$^{-1}$ in figure 3.7.

The difference between the surfaces after hydrogermylation and grignard chemistry is shown in figure 3.9.
3.5 Conclusion

The most important conclusion from this chapter is the successful removal of chlorine from the germanium surfaces with a grignard reagent. This chemical reaction ensures the stability of the particles in non polar solvents and removes the Ge-Cl bonds that are possibly inducing non radiative recombination states. With this method, there are no concerns about the concentration of chlorine at the surface of the germanium particles, since it is removed.

3.6 Outlook

The experimental setup that is used for all the germanium experiments has the possibility to use different gases such as tin tetrachloride (SnCl$_4$) and silicon tetrachloride (SiCl$_4$). Together with germanium, several alloys can be synthesized, and this will be shown in the next chapter. Because all precursor gases are tetrachlorides, all syntheses from any combination of these gases will give material with chlorine at the surface. The removal of chlorine on silicon and tin surfaces works in a similar way as for germanium. This means that all surfaces of alloys synthesized with any kind of tetrachloride gas can be functionalized and thus stabilized in solution with the Grignard reagents.

The identification problem addressed in figures 3.7 and 3.8 concerning the double peak around 500 cm$^{-1}$ could be solved by washing the particles. When the particles are washed, any excess grignard reagent will disappear, this would give definitive proof whether the peaks represent indeed Ge-C and Ge-C-C stretches.
Chapter 4

Optical properties

4.1 Abstract

This chapter contains the spectra of weakly emitting germanium nanocrystals in the NIR (1000 - 1800 nm) regime. In general, photoluminescence (PL) coming from a semiconductor material is an indication for high crystallinity and high purity of the material. The ultimate objective for solar cell applications is charge carrier extraction, but this is more difficult to show because of the construction of an entire device around the specific semiconductor material. PL is thus a method to show the high quality of semiconductor material without all the particularities of building a device. Emission wavelengths from germanium quantum dots are found to be shifting with the size of the nanocrystals in accordance to the Brus equation. Absorption spectra are in correspondence with PL, although absorption offsets are difficult to determine because of the indirect band gap in germanium.
4.2 Theory

This section starts with an explanation of quantum confinement of holes and electrons in a quantum dot. After this, there is a short introduction of photoluminescent properties of some selected and frequently used quantum dots. Previous work done for germanium quantum dots is also included. In general, PL is an important measuring technique for the purity and crystallinity of semiconductors. Impurities in semiconductors are known to induce non radiative recombination paths, which could cause the PL intensity to drop significantly. Amorphous material usually also induces non radiative states, causing a drop in the PL intensity as well.

4.2.1 Crystal momentum

On very small length scales (∼ 20 nm) a very interesting effect happens. For an exciton in a conventional indirect semiconductor material, crystal momentum, or k-vector, has to be conserved. This means that any recombination of an exciton has to be assisted by a phonon in indirect semiconductors, which can reduce the probability of such a process with several orders of magnitude. The k-conservation becomes more relaxed for smaller QD diameters [39]. This can be explained with Heisenberg’s uncertainty relation causing spreading of the wave function in momentum space by the confinement in real space.

Figure 4.1: A: Direct transition from conduction to valence band. B: Indirect transition from conduction to valence band in bulk semiconductors. A phonon (lattice wave) is necessary in this case to assist in the transition to conserve crystal momentum. In indirect band gap QD’s, this phonon is no longer a requirement because the k-conservation requirement is relaxed.
4.2.2 Confinement

If the dimensions of a crystal fragment, i.e. NC, are smaller than the Bohr exciton radius, the exciton looses its nature of delocalized exciton and is confined in the material. The electron is confined to move around the hole in a 3-dimensional well. The dimensions of this well are the same as the dimensions of the NC. Because of this confinement, the energy levels become discrete. Confinement thus causes a quantization of the energy levels allowed for the hole and electron. This is schematically shown in figure 4.2.

![Figure 4.2: Splitting of energy levels in a quantum dot. The horizontal axis shows the diameter with a* the Bohr exciton radius, which is the upper boundary for quantum confinement](image)

4.2.3 Lifetime

Lifetime of excitons is a very important parameter for PL in semiconductors. Recent work [40] on single silicon quantum dots shows that the lifetime of excitons in this group IV material is in the order of 10 µs. This is much longer than the relaxation of the electron within the conduction band of a semiconductor and also much longer than most non radiative processes in semiconductors. If there exists a non radiative recombination path, the probability of the exciton to follow this path is very high. This last remark means that non radiative recombination paths will likely suppress the PL intensity to levels which are undetectable.

4.2.4 Brus equation

The Brus equation [41] describes the band gap energy of a semiconductor quantum dot. The band gap of a QD is a function of the bulk energy gap, $E_{\text{bulk}}$, the effective electron ($m_e^*$) and hole ($m_h^*$) mass, the dielectric constant ($\epsilon$), and the particle radius, $R_p$. The dielectric constant of germanium is found from [42]. The effective masses are taken from [43]. $\|r_e - r_h\|$ is the absolute value of the distance between electron and hole. The Brus equation considers the confinement of both holes and electrons, and the interaction between the hole and electron via a Coulomb interaction. The Hamiltonian to solve the band gap structure is given by:

\[ H = ... \]
In this equation the polarization terms have not been included. The result for the energy gap of a quantum dot NC:

\[
E_{NC} = E_{Bulk} + E_{Confinement} + E_{Coulomb}
\]

The simple relation above is possible since the correlation between electron and hole position is not strong. The major effect is additive. This means that confinement energies are independent for holes and electrons in a first order approximation \cite{41}. The confinement effect goes as \( R_p^{-2} \), which is stronger than the Coulomb interaction which goes as \( R_p^{-1} \). This means that a quantum dot energy gap is always larger than that of the bulk material. This is observed in many different materials. The different terms are schematically shown in figure 4.3.
Figure 4.4: The theoretical relation from the Brus equation between energy gap and particle diameter plotted for germanium

Note that in figure 4.4 the value of $\epsilon$ is estimated at 16. This is the value for bulk germanium. There are many debates on the exact value of the dielectric constant for QD's [44]. The value of the bulk material is assumed in this case. Since the Coulomb term is only about 1% of the total value of $E_{NC}$ in equation 4.2, the error as a consequence of this will only be minor.

Equation 4.2 will be used to plot the theoretical relation of the emission wavelengths in this chapter. The following elemental relation between wavelength and energy is used:

$$E = \frac{hc}{\lambda} \quad (4.3)$$

Here, $E$ is the energy in Joule, $h$ is Planck’s constant, $c$ is the speed of light, and $\lambda$ the wavelength.

4.2.5 Photoluminescence in semiconductor quantum dots

The shift of emission wavelength with the crystal diameter has been shown before in silicon quantum dots in [45]. Figure 4.5 shows silicon quantum dots with diameters in a range of 3 - 6 nm. All samples are illuminated with blue light, and the different colours of emission are a result of shifting band gap energies through different sizes of quantum dots. This effect is given in equation 4.2.

The emission is a result of quantum confinement in the silicon NC’s, except the blue emission. The blue emission was found to shift with excitation wavelength and is a result of surface oxidation-induced defects at the surface of the Si NC’s. Nonetheless, the other results are in close agreement with the Brus equation and are thus consistent with the theory. The same kind of effect will be shown for germanium NC’s in the next section. For germanium, expected emission wavelengths are not in the visible regime, but in the NIR, since the bulk band gap (0.67 eV) is much smaller than that of silicon (1.1 eV).
4.2.6 Photoluminescence in germanium quantum dots

The writer and others [46] are aware of only three instances of photoluminescence from germanium quantum dots approaching the bulk band gap and shifting with NC size: [27], [28], and [47]. These publications all describe NIR emission from Ge NC’s. Two of the three examples described above are Ge NC’s from colloidal synthesis. The largest diameter crystal for which photoluminescence has ever been observed is 5.3 nm. The photoluminescence from germanium in this research is different in the sense that it is the first time that photoluminescence is observed from particles synthesized in the gas phase.

Photoluminescence from germanium in the visible range (300 - 700 nm) has also been observed before [48]. However, this is attributed to defect states on the surface of the crystals, not due to quantum confinement in the QD’s.

4.3 Experimental

In this section two experimental setups will be discussed. First, the absorption measurement is discussed. Afterwards there is information about the setup in which photoluminescence is measured.

4.3.1 Absorbance

In an absorbance measurement, every wavelength moves through the sample, and a detector records which wavelengths are lost in the sample (absorbance) and which wavelengths are not (transmission). The background solvent that is used is again diethyl ether. Because of some features in the solvent that are measured, wavelengths above 1600 nm are not reliable. Wavelength below 400 nm are also unreliable because over 99 % of the light is absorbed in this region. This means that the transmitted signal is too low to actually trust any results in that region.

The result is that only wavelengths between 400 and 1600 nm are plotted in the next section.
4.3.2 Photoluminescence

Samples for PL measurements are diluted in diethyl ether. The nanocrystals (3 mg) are deposited on a glass substrate and afterwards exposed to an excess amount of grignard reagent and heated. The 3 mg of QD’s is diluted in approximately 24 mL of diethyl ether, meaning concentrations are about 0.12 mg/mL in diethyl ether. The choice of the solvent is primarily for practical reasons. The grignard reagent is already in diethyl ether, so no drying of the QD’s is necessary. This drying process is undesired because of the risk of air exposure of the crystals during this process. However, diethyl ether is a polar solvent, meaning that the dielectric constant is not exactly known in this case.

A Xenon lamp is used to excite the QD’s and this light is focused on an InGaAs detector (900 - 2000 nm). The Xenon lamp is used in combination with a monochromator which allows the use of excitation wavelengths between 400 and 900 nm. A chopper is used in combination with a lock-in amplifier to reduce the signal to noise ratio.

![Diagram of setup to measure PL](image)

Figure 4.6: Simplified schematic of setup to measure PL. White light is coming from the Xenon lamp and the monochromator filters one specific frequency. This light is transmitted through the sample (dashed line). The light coming from the sample (dashed-dotted line) is focused to an InGaAs detector.

Light from the monochromator is also focused to the detector, but because it has a very well defined wavelength, this light is filtered electronically. In this particular setup, higher order optical processes are found to be quite efficient, meaning that 2\(\lambda\) and 3\(\lambda\) are also detected. This means that choosing a useful excitation wavelength requires some effort, since the emission range from the QD’s should not overlap with integer multiples of the excitation wavelength.
4.4 Results and discussion

The results are split into two different sections. First, the absorbance measurements will be shown, afterwards the photoluminescence measurements are discussed.

4.4.1 Absorbance

The absorbance spectra for three different sizes germanium QD’s are shown in figure 4.7. The concentrations of all three solutions is approximately 0.12 mg/mL. Smaller nanocrystals are expected to absorb less light and this behavior is indeed observed.

![Absorbance Spectra](image)

Figure 4.7: The absorbance of different sizes germanium QD’s. This is a similar result as found in [46]. Larger diameter QD’s are expected to absorb more light, as in equation 4.4, this behavior is indeed shown.

The absorbance behavior is in very close agreement with results which have been found in [46]. Absolute absorption cross sections have not been determined from these spectra because they are of little interest in this research. The dependence of the absorbance as a function of diameter can be determined from equation 4.4 from [46]. This is valid because the absorbance is directly related to the absorption cross section via some constant factors. Light scattering is not taken into account in this case.
\[ \sigma_{abs} = 8\pi m_2 \left( \frac{r^3}{\lambda^3} \right) \text{Im} \left[ \frac{m_1^2 - m_2^2}{m_1^2 + 2m_2^2} \right] \] (4.4)

Here, \( \sigma_{abs} \) is the absolute absorption cross section, \( m_1 \) and \( m_2 \) are the complex refractive indices \((m = n - ik)\) of sphere and medium (diethyl ether), and \( \lambda \) is the wavelength in vacuum. Actually, \( \sigma_{abs} \) is an infinite series in \( \frac{2\pi r}{\lambda} \), but for \( r << \lambda \) only the first term is relevant. The \( \sim r^3 \) behavior is indeed found in figure 4.7.

The absorption offset is of great interest. This is the wavelength at which the nanocrystals start absorbing light. One would expect that this absorption offset is always at higher energies than the emitted light. To determine the absorption offset the curves of figure 4.7 have been plotted on a logarithmic scale in figure 4.8.

![Absorbance plot](image)

Figure 4.8: The absorbance of the different sizes germanium QD’s plotted on a logarithmic scale. This is a similar result as found in [46]. Wavelengths after 1600 nm are not plotted because there are some features in the solvent that cause noise in the absorbance signal.

The absorbance plotted on a logarithmic scale still does not give a clear absorption offset. There is a much sharper offset at the start of the absorption for direct band gap semiconductors. In figure 4.8, the E1 absorption edge is clearly identified, as in [46]. The absorption offset is not well defined in all
three samples. The reason for this is the indirect nature of the band gap of germanium.

### 4.4.2 Photoluminescence

The PL spectra have been taken of the same samples as the absorbance measurements. The PL spectra show Gaussian-like behavior in figure 4.9.

![Normalized photoluminescence spectra for three different sizes of germanium QD's](image)

Figure 4.9: Normalized photoluminescence spectra for three different sizes of germanium QD's. The maximum excitation wavelengths shift indeed with average QD diameter. Smaller diameters lead to shorter wavelengths and thus higher energies because the confinement effects of electron and hole become stronger when the quantum well has smaller dimensions.

All spectra in figure 4.9 have been normalized. The PL peaks are quite narrow compared to other PL peaks previously reported from germanium QD’s in the NIR regime, such as [27] and [28]. These two papers have PL peaks with a total width of around 800 nm, whereas the peaks in this research are not broader than 500 nm. The sharpness in the PL peaks could be a result of the different synthesis method of the QD’s. In both papers a colloidal synthesis method is used to produce the Ge NC’s. Because of the high crystallization temperatures of group IV materials like germanium, the solution in colloidal synthesizes has...
to be heated to relatively high temperatures. This causes all kind of undesired chemistry resulting in a wide size distribution of the particles and also non spherical particles. These could be reasons that the particles, synthesized with a non thermal plasma, show a more narrow PL peak.

Emission peaks do not tend to shift when a different excitation wavelength is used, they do shift however when the polarity of the background solvent is changed. This has been tried with the 6.8 nm QD’s. If the solvent is diethyl ether, the PL peak is around 1340 nm, while for the same crystals in decane, the PL peak is at 1410 nm. A change in polarity of the solvent results in a change of dielectric constant in equation 4.2. The shift in emission wavelength (quenching) with a changing polarity of the solvent is a known effect described in [49].

4.4.2.1 Chlorine

As mentioned in previous chapters, the particles synthesized from GeCl$_4$ are covered with chlorine atoms. These particles can be diluted in benzonitrile, something which has been done previously in [46]. No photoluminescence is observed from these ligand-less particles. This could mean that the Ge-Cl bond, or perhaps some Ge-Cl$_x$ bonds which are also present at the nanocrystals as-synthesized, induce some kind of non radiative recombination path for the excitons. This effect is known for chlorine on the fluorescence of polynuclear aromatic hydrocarbons [50].

4.4.2.2 Brus equation

The peaks of the spectra in figure 4.9 can be recalculated with equation 4.3 into energies. These energies can be compared to the theoretical result of the Brus equation which is shown in equation 4.2.
Figure 4.10: The Brus equation plotted with the peak emission energies of the PL spectra of figure 4.9. The blue datapoint represents Ge NC’s in decane, while all other data points (red) are Ge NC’s in diethyl ether. Because of the polarity of diethyl ether, and thus a change in dielectric constant, it is expected that the particles in decane are in closer agreement with the theoretical behavior, since the relative dielectric constant is probably closer to the bulk value of germanium which has been used in the Brus equation.

Peak emission energies do not give an exact match with the Brus equation. One reason for this is probably the background solvent, diethyl ether. This is a polar solvent meaning the dielectric constant is probably different from the bulk value of germanium in air. Another reason could be a small error in the effective masses of holes and electrons in equation 4.2. These values are taken from [43], but are calculated as the bulk value for germanium. Effective masses of holes and electron in quantum dots are assumed to have different values than their bulk counterparts [51].

Three instances of luminescent germanium quantum dots have been previously reported in literature. These are [27], [28], and [47]. Comparison of these peak emission energies with the data in this thesis has been performed with a similar method as in [52].
Figure 4.11: Comparison of new data points of germanium quantum dots with other examples in literature. [27] uses a colloidal synthesis method with GeI$_2$ as precursor. [28] uses a similar colloidal synthesis method with a combination of GeI$_2$ and GeI$_4$ as a precursor. In [47] the germanium QD’s are embedded in a SiO$_2$ matrix. The Brus equation is also plotted with a black line. The dashed black line represents the band gap energy of bulk germanium.

From figure 4.11 it is concluded that the data point of 4.8 nm diameter quantum dots is in exactly the same region as other researches on this topic. The quantum dots with diameters of 6.8 and 10.2 nm are very new in the sense that the author is not aware of any example in literature where PL has been observed from germanium quantum dots with a diameter larger than 5 nm. Another difference with this research compared to references [27], [28], and [47] is that all these three instances synthesized germanium quantum dots with liquid colloidal syntheses, a very different method than a plasma synthesis which is in the gas phase.

4.5 Conclusion

The most important conclusion from this chapter is the observed photoluminescence in the NIR regime from the germanium nanocrystals. This photolumines-
cence is the first reported PL from germanium nanocrystals synthesized from a gas phase process. The PL peaks are relatively narrow with an approximate width of 500 nm. This is partially caused by the relatively narrow size distribution, which is a direct result from the non thermal plasma synthesis.

The Brus equation predicts the theoretical band gap of germanium quantum dots. The peak emission wavelengths, converted to energies, are not in full agreement with this equation. One reason for this is the error in the dielectric constant. The value of the dielectric constant for bulk germanium is probably not applicable for germanium quantum dots. Another reason for deviations in this dielectric constant is the use of diethyl ether as a background solvent, instead of a non polar solvent like decane. A polar solvent will definitely cause changes in the relative dielectric constant. Other deviations from the Brus equation could be caused by small errors in the effective hole and electron masses in this equation.

The PL from the germanium QD’s is very weak, although photo luminescent quantum yields (PLQY) have not been determined. Still, the weak PL from the germanium is very good in terms of narrow PL peaks. Another important characteristic is the approach of the bulk band gap of germanium with the 10.2 nm diameter QD’s.

4.6 Outlook

The reported photoluminescence from germanium QD’s has great promise. An important next step would be to determine and improve the PLQY. As shown in the introduction, a promising effect for germanium QD’s would be MEG. If the efficiency of the germanium QD’s would be high enough (∼30 %), a very efficient germanium solar cell could be constructed.

The next generation solar cells are probably going to be some kind of quantum dot material. Germanium in combination with MEG could be a very good option because of its high absorption coefficient and low bulk band gap, meaning that a lot of IR radiation of the sun can be absorbed and converted into electricity without losing a lot of energy from the high energetic photons in the solar spectrum because they will induce multiple excitons.
Chapter 5

Alloy synthesis

5.1 Abstract

In this chapter the synthesis of group IV materials is discussed. The previous chapters are about synthesis and functionalization of pure germanium nanocrystals. To synthesize other group IV materials the precursors SiCl\textsubscript{4} and SnCl\textsubscript{4} are used. This results in crystalline alloys between silicon and germanium. For SiGe alloys, every atomic ratio is achievable and it is found that this ratio is closely correlated to the flow rates of the precursor gases. Deposition of pure tin results in a mixture of α and β tin. This will be explained in detail.
5.2 Theory

5.2.1 Particle synthesis

The theory about the formation of nanocrystals is discussed in section 2.2. It will not be repeated here. The concept of nanocrystal formation is the same: a discharge is ignited but instead of one (GeCl$_4$), there are now multiple precursor gases. It is thus assumed that charging, confinement and nanoparticle heating concepts work in a similar way for alloy synthesis as they do for pure germanium NC’s. This is very reasonable to assume since all precursor gases contain group IV elements with four chlorine atoms. The tetrachloride gases are GeCl$_4$, SiCl$_4$, and SnCl$_4$. A schematic overview of the formation of a small SiGe cluster is shown in figure 5.1. The resulting cluster is electro statically confined and has time to grow further.

5.2.2 SiGe

To synthesize silicon-germanium alloys the precursor gases are SiCl$_4$ and GeCl$_4$. There is only a very small lattice mismatch of 4 % between silicon and germanium. SiGe alloys have been investigated many times before, e.a. [53] and [54], but rarely synthesized with a plasma. The overall reaction of the formation of a SiGe alloy from these precursor gases will be:

\[ \text{GeCl}_4 + \text{SiCl}_4 + 4\text{H}_2 \rightarrow \text{Ge} + \text{Si} + 8\text{HCl} \]

The only SiGe alloy synthesis that has been done with a plasma method is with different precursor gases. An example is an experiment with silane (SiH$_4$) and germane (GeH$_4$) in [55]. There are two disadvantages of these gases compared to the tetrachlorides. The first has to do with safety. Germane is much more dangerous than GeCl$_4$. Another advantage is that, with the Grignard reagents from the previous chapter, chlorine terminated surfaces are relatively easy to functionalize. This explains why it is interesting to synthesize alloys from tetrachloride gases.
Figure 5.1: The formation of a small SiGe-cluster in four steps. In step one, all the gases enter the reactor. These are Ar, $\text{H}_2$, $\text{GeCl}_4$, and $\text{SiCl}_4$. In step two, the plasma will ionize argon atoms and thus create high energetic electrons. These electrons can partially decompose the $\text{H}_2$, $\text{GeCl}_4$, and $\text{SiCl}_4$. The hydrogen radicals scavenge the chlorine atoms and form HCl in step three. This gives the partially decomposed precursor gases time to form a bond with each other in step four. These small agglomerates are electro statically confined and thus have time to grow further. These nanoparticles can crystallize because of the selective nanoparticle heating described in section 2.2.4.

5.2.3 Lattices

Every crystal is arranged in a specific lattice. Germanium and silicon from a plasma synthesis are arranged in a so called diamond cubic structure of eight atoms. This structure automatically means that only certain planes in XRD
can be seen because of Bragg’s diffraction law.

Although silicon and germanium have the same crystal structure, it does not mean that an alloy between them is a perfect fit. Every element has its own lattice parameter. This is a specific distance between each unit cell. The unit cell of a diamond cubic structure is shown in figure 5.2.

Figure 5.2: This figure is from [56]. The unit cell of a diamond cubic lattice. Each unit cell has eight atoms. Silicon, germanium, and SiGe alloys have this structure.

The challenge with the synthesis of a SiGe alloy is to overcome the lattice mismatch. Every element has a specific lattice parameter. For silicon and germanium these distances are 5.430Å and 5.658Å respectively [56]. The mismatch between them is approximately 4%. The lattice mismatch will cause strain in the material. Because the lattice mismatch in the case of SiGe is relatively small, this is not a problem. The reason that these structures crystallize is the selective nanoparticle heating.
5.2.4 Tin

Tin is a very interesting group IV material. At room temperature, tin is a metal, this is so called $\beta$-tin. This is very different from an intrinsic semiconductor material such as germanium. Below 286 K, tin is an intrinsic zero band gap semiconductor, $\alpha$-tin. However, the phase transition from metal to semiconductor does not occur at 286 K, but is only seen around 250 K and lower, as in [57].

A plasma synthesis is a non-equilibrium method. This means that certain material configurations can be achieved that would not occur under ‘normal’ conditions. This is the reason for the hypothesis that it is possible to synthesize $\alpha$-tin with a plasma synthesis.

5.2.5 Phase diagrams

Besides the crystal structure there is the miscibility of different materials. Silicon and germanium are miscible over the entire range of possible compositions at temperatures below 1200 K [58]. The binary system of germanium and tin is more complicated [59]. For very small concentrations of tin, compositions below 400 K are fully miscible.

It is questionable whether the traditional phase diagrams are fully applicable in the experiments with a non thermal plasma. A plasma synthesis is a non equilibrium method, while phase diagrams usually assume local equilibria. A good example of this non equilibrium is the selective nanoparticle heating which causes the crystallization in the plasma synthesis method.
5.3 Experimental

The experimental setup to synthesize alloys is very similar to the one used to synthesize germanium nanocrystals. It is schematically shown in figure 5.3. The gases flow in from the top, but now there are multiple precursor gases, GeCl$_4$, SnCl$_4$, and SiCl$_4$. These precursor gases are mixed with H$_2$ and Ar.

The matchbox and power supply to drive the plasma are the same as in 2.3.4.
5.4 Results and discussion

This section will consist of two main parts. First, SiGe-alloys will be discussed. The second and final part will be about the synthesis of pure tin, with a focus on α and β tin.

5.4.1 SiGe-alloys

Synthesis of a Si$_x$Ge$_{1-x}$ alloy is done with a plasma synthesis method. A Raman spectrum of the resulting material is shown below.

![Raman spectrum of Si$_x$Ge$_{1-x}$ alloy](image)

Figure 5.4: The Raman spectrum of a Si$_x$Ge$_{1-x}$ alloy with an atomic Si concentration of 0.18. The three main peaks around 300, 400, and 500 cm$^{-1}$ are indicative for Ge-Ge, Si-Ge, and Si-Si bonds [60]

The Raman spectrum shows a small shift of the Ge-Ge peak. For a pure Ge sample, the peak lies at exactly 300 cm$^{-1}$, while in this case the Ge-Ge peak is at 285 cm$^{-1}$. This effect is well understood [61] and is caused by the strain in the material. This is also the reason that the Si-Si peak, normally at 520 cm$^{-1}$, is shifted just below 500 cm$^{-1}$.

An important conclusion from figure 5.4 is the successful synthesis of a Si$_x$Ge$_{1-x}$
alloy. Because of the pronounced Si-Ge peak, an alloy must have been synthesized. There is another method to investigate the alloy: The peaks of an XRD spectrum have very distinctive angles ($2\theta$) at which they appear. It is possible to show a shift in one of these peaks with increasing silicon ratio.

Figure 5.5: XRD measurement of different compositions of a Si$_x$Ge$_{1-x}$ alloy. The ratios are based on the flow rates of the precursor gases and not determined by EDX measurements. It is clear that all three peaks lie between the germanium and silicon (111) peaks. An increasing silicon flow leads to a shift further away from the lower germanium angle.

Figure 5.5 shows a shift towards the position of the silicon (111) peak with an increasing flow of SiCl$_4$. There is no binary peak at the germanium or silicon position, so no binary compound has been synthesized. A small shoulder in the red curve in figure 5.5 is present though. This shoulder could be an indication of some silicon dominated phase. The XRD spectrum is, in combination with the Raman spectrum in figure 5.4, an indication that a Si$_x$Ge$_{1-x}$ alloy has been synthesized.

To further investigate the size of these particles some TEM analysis has been done in figure 5.6.
The TEM image confirms the measurement from the Raman spectrum. It is possible to synthesize a crystalline $\text{Si}_x\text{Ge}_{1-x}$ alloy.

Another experiment is done to investigate different atomic ratios between Si and Ge. The expected atomic concentrations have been calculated based on the flow rates during the experiment, and have been measured by energy dispersive X-ray spectroscopy (EDX).

$$ Si - ratio = \frac{\text{SiCl}_4_{flow}}{\text{SiCl}_4_{flow} + \text{GeCl}_4_{flow}} $$ (5.1)
Figure 5.7: EDX measurements of $\text{Si}_x\text{Ge}_{1-x}$ alloy compared to the ratios expected by the flow rates. The black line is the ideal correlation, and this matches the experimental results (blue squares) very well.

Two conclusions can be made from figure 5.7: The first conclusion is that any ratio between silicon and germanium can be synthesized. This means that the strain, induced by the lattice mismatch, does not cause instabilities that can not be solved by the non-equilibrium plasma synthesis method. Secondly, the incorporation of Si and Ge in a crystal is closely correlated to the flow rates of their precursor gases. This means that both gases are decomposed with equal efficiency. The incorporation of both elements in a nanocrystal also seem to have a similar efficiency.
5.4.2 Tin

Pure tin is synthesized from SnCl\textsubscript{4}. The result of this is a tin film as shown in figure 5.8.

![Image of a tin film synthesized with a plasma synthesis method. This is clearly a metal as indicated by the reflection of the visible light.](image)

The most obvious conclusion from this tin film is that the result of the synthesis is a pure metal, so called white tin. The synthesis of this metal can be done much easier and is not the goal of this tin synthesis. The XRD spectrum of this tin is shown in the figure below.
Figure 5.9: XRD pattern from a tin sample. There is mostly $\beta$-tin present, but there are some traces of $\alpha$-tin as well. Reference lines are from [62].

The conclusion from this tin synthesis is that there are traces of gray tin, but the bulk of the synthesized material is white tin. Further investigation is needed to see if it is possible to stabilize gray tin. This could be possible in a germanium or silicon matrix [63].

5.5 Conclusion

The first conclusion from this chapter is that the plasma synthesis method allows for the precise control of a Si$_x$Ge$_{1-x}$ alloy. The full range of compositions is achieved. Both low concentrations of silicon in a germanium crystal and low concentrations of germanium in silicon crystals are achievable with this method. The ability to control both size and composition of these crystals shows great promise for further development of Si$_x$Ge$_{1-x}$ alloys with a non-thermal plasma approach. The chemistry developed in chapter three of this thesis could be useful to perform some kind of surface passivation on these alloys.

The synthesis of pure tin is the last option discussed in this chapter. The result of this is the synthesis of $\beta$-tin with some traces of $\alpha$-tin in the material. It is
not yet fully understood how this works.

5.6 Outlook

The potential applications of the synthesis of these group IV alloys are numerous. With a change in size and composition it is theoretically possible to show a very precise control of the band gap energy in all these NC’s. Photoluminescence of these alloys has not been investigated but the grignard reactions are found to work on multiple chlorine covered surfaces. This opens new paths to all kinds of group IV solar cells.

It is questionable whether the plasma synthesis can be scaled up to an industrial level. It definitely has higher yields than the method by which these materials are usually created, molecular beam epitaxy. The scalability would be an important step to create an industrial application from this method.
Chapter 6

Conclusion

In this chapter, the conclusions of this research are presented in a very short form. They are separated into four subsections, which correspond to the four chapters of this thesis. The abstract at the start of this thesis also provides a scope of this research.

1. The first conclusions are about the synthesis of germanium quantum dots from a non thermal argon plasma.

   (a) A successful synthesis of germanium quantum dots from a non thermal argon plasma is achieved

   (b) Hydrogen is necessary in the synthesis to scavenge the chlorine atoms from the GeCl$_4$

   (c) Crystallization of the quantum dots happens through recombination of argon ions at the surface of the particles

   (d) At least 30 W of power input to the plasma is necessary to synthesize crystalline germanium quantum dots

   (e) Sizes of 4.8, 6.8, and 10.2 nm in mean diameter have been successfully synthesized

2. The following conclusions are made from chapter three.

   (a) Germanium quantum dots synthesized from GeCl$_4$ have a very high concentration of chlorine at their surface

   (b) Achieving solubility in most solvents (e.g. hexane, diethyl ether) is impossible with chlorine terminated surface states

   (c) Chlorine at the surface of germanium quantum dots can be removed using a grignard reagent (CH$_3$(CH$_2$)$_{10}$CH$_2$MgBr)

   (d) Alkyl chains with a length of twelve carbon atoms provide sufficient steric barriers to prevent germanium quantum dots from agglomerating in solution
3. The conclusions about chapter four are made from the optical properties of germanium quantum dots after treatment with grignard reagents.

(a) Larger diameter germanium quantum dots absorb more light, as expected from theory
(b) An absorption offset is impossible to determine because of the indirect band gap of germanium
(c) Photoluminescence peaks shift with mean diameters of the germanium quantum dots
(d) The shift in band gap energy by varying the diameter of the quantum dots is in line with the Brus equation
(e) The 10.2 nm diameter particles’ band gap energy approaches the bulk band gap of germanium and has never been observed before in literature

4. The last group of conclusions are based on the chapter about group IV alloys.

(a) The lattice mismatch of 4 % between silicon and germanium is not a limitation for a successful synthesis of a Si$_x$Ge$_{1-x}$ alloy
(b) Every ratio ($x$) in a Si$_x$Ge$_{1-x}$ can be achieved, and the ratio in the material is extremely well correlated to the flow rates of the precursor gases
(c) During the synthesis of tin mainly β-tin is synthesized, however traces of α-tin in the XRD spectrum suggest some kind of binary phase

The most important result from this thesis is the photoluminescence from germanium quantum dots and the shifts in band gap energy for different sizes.
Chapter 7

Appendix

7.1 Nano crystal surface model

In this section it will be shown that there is insufficient atomic hydrogen in the plasma to cover all surface states of a 6.8 nm diameter germanium nanocrystal.

7.1.1 Nanocrystal

Figure 7.1: The nanocrystal is represented by an exact sphere. The surface is simplified to a square

\[
A_{NC} = 4\pi R_{NC}^2 \\
V_{NC} = \frac{4}{3} \pi R_{NC}^3 \\
d_{\text{crystal}} = 0.56 \text{ nm}
\]  

(7.1)

Where \( A_{NC} \) is the surface, \( V_{NC} \) is the volume of the sphere, \( R_{NC} \) is the radius of the nanocrystal, and \( d_{\text{crystal}} \) is the crystal length. The number of atoms per nanocrystal is simply calculated by putting spheres into the large nanocrystal:
The number of surface spots per nanocrystal can be calculated with the square surface with sides $\sqrt{A_{NC}}$.

\[
\left(\frac{\sqrt{A_{NC}}}{d_{\text{crystal}}}\right)^2
\]  

(7.3)

The molar mass of Germanium, $M_{Ge}$ is 72.64 g/mol. The mass of a germanium nanocrystal, $M_{NC}$, without its surface atoms is thus given by:

\[
M_{NC} = \frac{1}{N_A} \frac{V_{NC}}{V_{Ge-atom}} M_{Ge}
\]  

(7.4)

Where $N_A$ is the Avogadro number. The deposition is an estimate. It can be fairly accurately determined from experiments but it will rise with an increasing flow rate of the precursor gas. In this derivation it is $M_{dep}$.

\[
\#_{\text{crystals}} = \frac{M_{dep}}{M_{NC}}
\]  

(7.5)

Where $\#$ stands for ‘The number of’. The number of surface spots is given by the number of crystals multiplied by the number of surface spots per crystal:

\[
\#_{\text{ surfacespots}} = \left(\frac{\sqrt{A}}{d_{\text{crystal}}}\right)^2 \frac{M_{dep}}{M_{NC}}
\]  

(7.6)

From equation 7.6 the number of surface spots can be calculated. In the next subsection the amount of hydrogen atoms will be calculated and see if this exceeds the number of surface spots.

7.1.2 Gas flow

One sccm stands for one cubic centimeter per minute at standard pressure and temperature. This can be calculated in atoms per second by:

\[
1 \text{sccm} = \frac{N_A}{22.4} \left[\text{cm}^3 \text{mol}^{-1}\right] \frac{1}{10^3} \left[\text{cm}^3 \text{L}^{-1}\right] \frac{1}{60} \left[\text{sccm} \text{min}^{-1}\right]
\]  

(7.7)

This results in about $4.47 \times 10^{17}$ atoms s$^{-1}$.

The maximum deposition of germanium nanocrystals is thus the molar mass of Germanium, $M_{Ge}$, multiplied by the number of atoms per second, divided by the Avogadro number:

\[
Deposition_{\text{max}} = \frac{1 \text{sccm} \times M_{Ge}}{N_A} = 5.3 \times 10^{-5} \frac{g}{s}
\]  

(7.8)

The estimated deposition from a 1 sccm GeCl$_4$ flow is approximately 1 mg per minute, which is equal to:

\[
1 \text{mg minute} = 1.7 \times 10^{-5} \frac{g}{s}
\]  

(7.9)

This means that roughly 30% of the GeCl$_4$ atoms actually end up in a crystal. This is comparable to yields in [48].

81
7.1.3 Result

Based on the numbers and assumptions calculated in this appendix it is known that:

\[
\#_{\text{surfacespots}} = 9 \times 10^{16} \tag{7.10}
\]

Number of H atoms per second in 20 sccm flow under the assumption as in [15] there is a 0.1 % ionization degree of the hydrogen:

\[
0.1\% \times 20 \text{ sccm} \times 2 = 1.8 \times 10^{16} \text{ atoms} \tag{7.11}
\]

This means that there are almost five times more surface spots to fill, than hydrogen atoms to do it with. So if all the atomic hydrogen attaches to the crystals there is still a lot of chlorine on the surface. This model even underestimates the concentration of chlorine at the surface a little, since it does not take into account that there are Ge-atoms that can have Ge-H\(_2\) or even Ge-H\(_3\) bonds.

7.2 Residence time

The residence time in the discharge is calculated with a combination of flow rates and pressures. This appendix will cover one example of the calculation of a residence time.

\[
\tau = \frac{V}{q} \tag{7.12}
\]

Where \(V\) is the volume of the system, \(\tau\) the average residence time, and \(q\) the flow of the system.

One sccm of flow at STP has a much larger volume at 2 Torr.

\[
1 \text{ sccm} = 1 \frac{cm^3}{min} = 1 \frac{cm^3}{60 \left[\frac{s}{min}\right]} = 6.34 \times 10^{-6} m^3/s \tag{7.13}
\]

The volume of the entire vacuum system is difficult to determine exactly. But a rough estimate of the system with a one inch diameter tube:

\[
V \sim 50 \text{ cm}^3 \tag{7.14}
\]

To determine the residence time of neutral particles in the plasma the volume of the plasma has to be taken into account. The plasma is never in the entire volume of the tube. The plasma volume \(V_{\text{plasma}}\) is divided by the volume of the entire system \(V\). If this is incorporated in equation 7.12:

\[
\tau = \frac{V_{\text{plasma}}}{q} \tag{7.15}
\]

A numerical example with flows of 30 sccm of Ar, 20 sccm of H\(_2\), 1.0 sccm of GeCl\(_4\), and a one inch diameter tube results in:

\[
\tau \sim 60 \text{ ms} \tag{7.16}
\]
Note that the orifice, and thus the pressure is not directly included in this formula, except via the volume of 1 sccm flow in equation 7.13. This simple calculation does not take electro statical confinement into account because of the charging of the nanoparticles, but very small particles are assumed to be neutral.
### 7.3 Particle recipes

Table 7.1: Parameters for producing 4.8, 6.8, and 10.2 nm diameter germanium nanocrystals. Note that parameters above the blank row are directly adjustable, parameters below that row are results of the parameters above. Examples are residence times and pressure.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>unit</th>
<th>4.8 nm</th>
<th>6.8 nm</th>
<th>10.2 nm</th>
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</thead>
<tbody>
<tr>
<td>Argon flow</td>
<td>sccm</td>
<td>30</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>Hydrogen flow</td>
<td>sccm</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>GeCl$_4$ flow</td>
<td>sccm</td>
<td>1.0</td>
<td>1.0</td>
<td>1.5</td>
</tr>
<tr>
<td>Tube diameter</td>
<td>inch</td>
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<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Orifice diameter</td>
<td>mm</td>
<td>4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Plasma length</td>
<td>inch</td>
<td>3</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>RF input power</td>
<td>Watt</td>
<td>40</td>
<td>40</td>
<td>50</td>
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<tr>
<td>Deposition time</td>
<td>min</td>
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<td>3</td>
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<tr>
<td>Pressure</td>
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<td>2.020</td>
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<td>ms</td>
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<td>60 ± 10</td>
<td>105 ± 10</td>
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Table 7.2: Parameters for producing SiGe and Sn nanocrystals. Note that parameters above the white space are directly adjustable, parameters below that space are results of the parameters above. Examples are residence times and pressure.

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<th>Sn</th>
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<td>50</td>
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<tr>
<td>Hydrogen flow</td>
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<td>SiCl₄ flow</td>
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</tr>
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<tr>
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Bibliography


