Spin coating of Silver Nanoparticles and Silicon quantum dots for enhanced down conversion efficiency

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Abstract
The commercial efficiency of a c-Si solar cell is ~18% although the thermodynamic limit is ~95%. This indicates a good scope for improvements. The major loss mechanism in a solar cell is spectral mismatch which is contributed to by non-absorption of low energy photons and thermalization of high energy photons. In this thesis, it is sought to reduce the loss that occurs through thermalization of high energy photons. For this purpose, the concept of down conversion is used.

Silicon being relevant to the semiconductor industry, being abundant in nature and having been proved to exhibit down conversion in the form of spherical particles in the nm size range through space separated quantum cutting is opted. However, the down conversion efficiency of these is low owing to their indirect bandgap which leads to higher absorption within the material than enhancement in the number of photons through down conversion. In order to reduce the absorption within the material, it is sought to enhance the rate of radiative decay through the use of plasmonics exhibited by metal nanoparticles. Silver nanoparticles are used for our purpose as they exhibit resonance in the visible region of the spectrum and have the lowest absorption among different plasmonic materials.

The silicon nanoparticles (quantum dots) powders are fabricated through the expanding thermal plasma chemical vapor deposition route while the silver nanoparticles fabricated through wet chemical synthesis are purchased from the market as powders. The silver nanoparticles are also deposited as metal island films in-house. Optimal deposition parameters for the deposition of quantum dots are arrived upon by depositing samples using different parameters and analyzing the results. A configuration for the down conversion layer is arrived upon based on simulations and analysis of design. The powders are then dispersed in ethanol for the purpose of spin coating. The dispersions are then spin coated on glass substrates. The quantum dot dispersion is also spin coated onto the metal island film substrate as per the chosen configuration. The silver nanoparticle samples are analyzed for plasmonic behavior, quantum dots for their absorption characteristics and the combination for enhancement in transmission through down conversion from their reflection and transmission spectra. To confirm the interaction between the silver nanoparticles and quantum dots, the enhancement in the photoluminescence spectra is checked.

From the results, it is observed that there is agglomeration in the spin coated silver nanoparticles resulting in a loss of plasmonic behavior. The quantum dots are also agglomerated due to which an enhancement in the transmission spectra was not observed. However, the interaction between the quantum dots and the silver nanoparticles could be observed through the enhanced photoluminescence of the quantum dots. The enhancement is found to vary from 9 folds to about 50 folds which are high compared to similar results in the literature. Keeping in mind that this down conversion layer has not yet been optimized, even higher enhancements may be possible. This indicates the potential for the combination of silicon quantum dots and silver nanoparticles for application in solar cell down conversion layers.
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5.1 Conclusions

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1. Introduction

We as a civilization have achieved great marvels in various engineering disciplines such as civil, chemistry, mechanical, materials, electronics, power etc. These were achieved through extraordinary advancements within, along with coordination and support between various fields. But, one indisputable fact remains that all these achievements rely heavily on energy in one form or the other like the transportation sector and industrial sector using electricity/petroleum products for their functioning. The continued advancements in various fields indisputably require energy for sustenance, augmenting the use of per capita energy consumption as a mark of economic development.

Due to rising population [1.1] and the economic advancements in developing countries like India and China[1.2, 1.4], the world energy consumption is on the rise which is predicted to be of the order of 0.7 to 1.4% per annum in the period between 2008 till 2035 depending on the scenario chosen [1.2, 1.3]. We have somehow been able to make ends meet with the help of various energy sources currently available especially fossil fuels [1.2, 1.5] but, all these are limited in nature and are not replenishable. With such high energy consumption and a corresponding decrease in the available resources, one can foresee with much clarity the impending energy crisis unless suitable alternates are found in due time which can be utilized economically. Though the time available before such a crisis exposes itself is debated upon, the global economy has nevertheless decided to take action and one of the means envisioned is to go for renewable sources of energy.

Renewable sources of energy also reduce the carbon dioxide footprint due to lower amounts of emission per unit of energy produced thereby alleviating the problem of climate change associated with the use of fossil fuels as energy sources [1.6].

Adopting solar energy amongst the other alternates to fossil fuels poses various advantages. In terms of availability, solar energy is the source of energy available in plenty as is exhibited by the amount of energy received by earth as solar radiation. The Sun emits a large amount of energy $(3.839 \times 10^{26} \text{ W})$. The earth is perceived to receive $\sim 174$ peta watts (peta = $10^{15}$ units) of incoming solar radiation at the outer atmosphere out of which nearly 30% is reflected back into space. Since the earth’s surface is almost spherical, the amount of light received per unit area on the surface depends on the latitude (due to variations in the Azimuth angle, the angle at which the rays hit the earth’s surface). This is further diminished by various climatic factors like presence of clouds and the absorption by the atmospheric gases. The net solar radiation thus hitting the earth’s surface over a unit area summed over one hour is referred to as solar insolation or radiation (it is typically expressed in KWh/m$^2$). The energy received by the earth is still considerably high compared to the overall energy consumed by us. It is estimated that the amount of energy received by a desert in south-western United States that measures 161 km on one side (which amounts to 0.3% of land area of the United States) when converted to electricity using a device with 10% efficiency could theoretically meet the energy demand of the United States [1.7]. Since sunlight is available everywhere (though in different concentrations as mentioned), decentralised production of power, avoidance of politics and price manipulation (as is seen related to crude oil) are other attractive points. The cost of production of electricity from solar cells is also going down (by a factor of 100
compared to 1950 and halved in the last decade \[1.8\]) as depicted by the learning curve giving a major incentive to look upon solar for future energy needs.

The solar radiation thus received can be converted to electricity by either solar thermal route using concentrated solar power plants or the photovoltaic (PV) route where the radiation is directly converted to DC electricity using modules. PV devices use the photovoltaic effect (discovered by Becquerel in 1839 \[1.9\]) to convert solar radiation to electricity. The incident photons are absorbed in an absorber layer forming an electron - hole pair (also referred to as exciton when it is coupled together by coulomb attraction) which is then separated using electric fields (by forming a diode in c-Si cells) via semi-permeable membranes allowing the flow of either the electron or the hole which are then collected at the electronic conductors.

### 1.1 Current limitations of solar cells

The output from the solar cell is limited by various loss mechanisms involved which are as follows –

1. Loss due to non-absorption of long wavelengths – Photons with energy less than the band gap energy of the solar cell will not be able to generate an electron-hole pair and hence, longer wavelengths are not absorbed.

2. Loss due to thermalization of the excess energy of photons – The photons with energy higher than the band gap energy leads to the creation of “hot” electron-hole pair which then decays to the lowest energy state shedding off the excess energy through thermalization of the material.

3. Loss due to reflection – The reflection from the top surface of the solar cell based on its optical properties leads to non-availability of those photons for conversion.

4. Loss by incomplete absorption due to the finite thickness – The absorption coefficient of the solar cell varies with the wavelength, decreasing with increasing wavelength. Hence, the photons with energy close to the bandgap require higher path length within the material in order to get absorbed for conversion. Due to finite thickness of the cell, part of the long wavelength radiation escapes from the cell leading to non-availability of these photons for conversion.

5. Loss due to recombination – The electron hole pair thus produced is unstable and recombines to either yield a photon back or heat up the material and has a defined decay time within which it needs to be collected at the electrodes. The presence of defects within the material also aids recombination which then doesn’t contribute to the power output of the cell.

6. Loss by metal electrode coverage, shading losses – In front contact solar cells, the top surface has metal electrode coverage for the collection of the charge carriers which in turn blocks the incoming radiation.

7. Loss due to voltage factor – The \(V_{oc}\) of the solar cell is lower than the band gap energy due to fundamental recombination which in turn depends on the electronic quality of the material and the doping concentration hence, leading to lower conversion efficiency.

8. Loss due to fill factor – Due to the presence of series and shunt resistances in the solar cell, the fill factor which is the ratio of the power delivered to the maximum power deliverable is lower, further reducing the efficiency of the cell.
For a c-Si solar cell having a commercial efficiency of 15%, the losses are as shown in figure 1.1.

![Figure 1.1 Losses in a commercial c-Si solar cell with 15% efficiency][1]

**Figure 1.1** Losses in a commercial c-Si solar cell with 15% efficiency [1.10]
Spectral mismatch (1&2); reflection & transmission (3, 4&6); fundamental recombination (5&7); excess recombination, resistance etc. (8)

### 1.2 Techniques for efficiency enhancement

In order to achieve competitive cost/kWh for solar electricity generation (also referred to as solar power generation), the conversion efficiencies of the devices need to be increased. The theoretical limit calculated by Shockley and Queisser for solar cells with band gap energy of 1.1 eV is about 30% [1.11]. The Carnot efficiency however is 95% indicating a huge potential for improvements. Advanced concepts are used to produce such high performance cells often referred to as third generation solar cells. The concepts include use of tandem cells with decreasing band gap from source to back reflector; generation of multiple electron hole pair by impact ionisation or photon cutting using down conversion layers; use of hot carrier cells to prevent thermalization losses; multiband cells or up conversion layers to use the low energy photons for the generation of charge carriers; thermophotovoltaic devices etc. [1.12]

Among the various losses in the solar cell, the bulk of it is due to spectral mismatch (non-absorption and thermalization as seen in figure 1.1) contributing to more than 50% loss of energy from the incident radiation (AM1.5 spectrum). The excess energy available in high energy photons could theoretically be used to generate two or more low energy photons by the process of down conversion (DC) thereby reducing the thermalization losses. Similarly, low energy photons can be coupled together to form a high energy photon utilising the sub-bandgap photons by the process of up conversion (UC), thereby reducing the non-absorption losses. For a c-Si solar cell whose band gap is 1.08 eV, the amount of excess energy in the solar spectrum is 37% and the low energy photons contribute to 14% of the spectrum. The reduction in non-absorption and thermalization losses leading to the enhanced usage of solar spectrum with DC and UC layers for c-Si are as depicted in figure 1.2.
1.2.1 Down Conversion with Si Quantum Dots

By using the quantum cutting process, a high energy photon can be split into two or more photons of lower energy. This is referred to as down conversion and it would enable us to use the blue region of the light more efficiently as has been shown in figure 1.2. Silicon being an abundant material in nature and its relevance to the semiconductor industry has been tried out for the process of down conversion. The space separated quantum cutting of high energy photons by silicon nanocrystals (also referred to as quantum dots) was demonstrated by Timmerman et al [1.15]. Beyond the threshold value (twice the energy of band gap), the probability of evolution of two photons from one incident photon increases thereby increasing the quantum efficiency (Quantum efficiency here is the ratio of photons emitted to that of photons incident on the material, in this case by the erbium ions [1.15]). This increase in quantum efficiency as demonstrated by Timmerman et al. can be clearly seen from figure 1.3.

The quantum cutting observed is achieved through Auger process of interband relaxation. Figure 1.4a shows the excitation of erbium ions through auger interband relaxation which were used to confirm the mechanism as erbium ions are not excited by the incident laser beam and hence, the luminescence observed from the erbium ions is purely from the excitation of the Silicon quantum dots. Figure 1.4b illustrates how the down conversion process would occur in silicon quantum dot network [1.15]. It can be seen that an efficient down conversion process requires interaction between two neighbouring quantum dots. Hence, for the down conversion layers, inter particle distance plays a crucial role as they must be within each other’s energy transfer range in order for this phenomena (auger process of interband relaxation) to occur efficiently.
The possible physical mechanisms by which this process of Auger interband relaxation occurs are hypothesised as –

1. Impact ionization by hot carriers generated by the absorption of high energy photons.
2. Coherent superposition of single and multiexciton states caused by the strong Coulomb interaction between the carriers confined in the nanocrystal.
3. Multiexciton formation through a virtual state.

The details of these mechanisms are beyond the scope of this project. Details of these can be referred to from the work of Timmerman et al [1.15].

The efficacy with which the incident solar radiation is utilised by means of a DC layer depends on the energy of the photon emitted by these quantum dots as this in turn determines the threshold beyond which down conversion would be observed. The energy of the emitted photon or the emission wavelength of the quantum dots is determined by its band gap energy. The bandgap energy of bulk silicon is 1.1 eV but as we venture into the nanoscale, the bandgap can be tuned with the help of quantum confinement effect. As the size of the particles decreases, there is a blue shift in the emission wavelength indicating an increase in bandgap [1.25, 1.26]. Needless to say, the
The emission wavelength of the quantum dot must be such that it can contribute to charge generation in the solar cell through the photoelectric effect i.e. the photon emitted by the QD has equal or higher energy than the bandgap energy of the solar cell. The increase in bandgap energy of the quantum dots can be clearly seen in figure 1.5.

![Figure 1.5 Quantum dots illuminated by UV light. The change in bandgap energies with size can be clearly seen from their colour (emission wavelength) [1.27].](image)

Hence, by adopting a down conversion layer, the number of photons incident on the solar cell can be theoretically enhanced, thereby increasing its efficiency. However, there are practical limitations as to the degree to which the spectrum can be efficiently used based on this concept. The efficiency of the auger process of interband relaxation is dependent on interparticle (QD) interaction and hence involves losses in energy transfer between particles. The particles once excited to the higher energy state can relax back through either radiative decay wherein it involves the emission of photon or through non-radiative decay wherein the energy is lost as heat. The probability of radiative decay is lower in indirect bandgap materials like silicon resulting in absorption of the incident photons within the material. These losses overcompensate for the gain from down conversion leading to lower quantum efficiency (the ratio of emitted photons to incident photons) of such a down conversion layer. It has been observed that the probability of radiative decay can be improved by the use of surface plasmon resonance (SPR) phenomena observed in metal nanoparticles which will be detailed in the coming sections.

### 1.2.2 Light concentration with Plasmonic Metal Nanoparticles

The electron cloud in the conduction band of metal nanoparticles in the presence of an oscillating electric field (light waves for example) tends to oscillate with it coherently as is exhibited in figure 1.6. These charge density oscillations confined to the metal nanoparticle are referred to as localised surface plasmons (LSPs). The frequency at which these LSPs oscillate is determined by the density of electrons, the effective electron mass, shape and size of the charge distribution [1.28]. This in turn is determined by the type of material, its size, size distribution, shape and the nature of the medium in which the particle exists [1.29].
Resonance occurs when the frequency of the incident light is the same as the frequency of oscillation of the LSPs which results in strong light scattering and enhancement of local electromagnetic fields. This is referred to as surface plasmon resonance (SPR) which among the various possible uses can be used to concentrate light in the vicinity of the nanoparticles where an enhancement of local electromagnetic fields is observed. Atwater et al. [1.13] summarize several results obtained by the use of this enhanced electromagnetic field for enhancement of absorption in the solar cell. Santbergen et al. [1.31] studied the effect of concentration of light using these silver nanoparticles at various locations in the solar cell. They find a loss in the output of the cell due to parasitic absorption of the photo-generated current in these nanoparticles. This can be avoided by using these particles outside the path of photo-generated current in the cell. This in turn can be done by using them to concentrate light on a down conversion layer made of silicon quantum dots which would be external to the solar cell. Thus, it is external to the path of photo-generated current while it enhances the probability of radiative decay in the quantum dots. As a result, the number of photons capable of generating an electron–hole pair incident on the absorber layer increases thereby increasing the efficiency of the cell.

It must be noted that not all metal nanoparticles exhibit surface plasmon resonance since the imaginary part of the refractive index is high (except noble metals and some alkali metals) leading to suppression of the excited state. Only noble metals have the surface plasmon resonance peak in the visible range. Silver has the lowest absorption and highest resonance among all metals with plasmon resonance at visible frequencies and hence is our prime focus [1.22].

1.2.3 Coherent Plasmon-exciton interaction for enhanced photoluminescence

The increase in performance of the quantum dots by using the plasmonic effect observed in metal nanoparticles has been coveted and is a hot topic in research for various applications including solar cells. An increase in photoluminescence when the quantum dots are placed near the plasmonic nanoparticles has been reported [1.16, 1.19, 1.20, 1.21, 1.32 and 1.34 - 1.41]. This is due to the interaction between the exciton and plasmon which depends on the distance between the metal nanoparticles and the quantum dot. The efficacy of the process is inversely proportional to $d^6$ decreasing with increase in the distance $d$ [1.16]. Nola et al. [1.21] studied the interactions between the metal nanoparticles and silicon quantum dots using Monte-Carlo method and attributes the increase in the photoluminescence observed in the combination to near field interactions. If the quantum dots are placed in the near-field region of the metal nanoparticle plasmonic field, an increase in photoluminescence is observed. The interaction is stronger when the exciton energy and the plasmon resonance energy are equal due to efficient coupling of plasmon and exciton [1.16]. The coupling causes an increase in the rate of radiative decay in the quantum dot [1.22] which can be
tuned by adjusting the mutual orientation between the quantum dot and the metal nanoparticle (in case of cylinder/rod like shapes) and the dipole polarizability of the metal nanoparticle [1.16]. The enhancement observed in the PL spectrum varies from a little over 1 to 60 folds depending on the type of QD and how it is placed in the vicinity of the metal nanoparticle [1.34 - 1.41].

The plasmon resonance energy (Ag NPs) is determined by the size, shape of the nanoparticle and the surrounding medium while the exciton energy (QDs) is determined by the bandgap which depends on the material and its size [1.17, 1.18]. The interaction among the metal nanoparticles causes a shift in the resonance peak observed. The degree of shift depends on the inter-particle separation and is considerably low above a separation of 0.75*D where D is the diameter of the metal nanoparticle [1.42]. It is preferable to place the QDs as close to the metal nanoparticle as possible as the efficacy of enhancement in radiative emission decreases with distance. But, as the particles get much closer, quenching of the radiated photon is observed due to resonance energy transfer between the quantum dot and the nanoparticle and tunnelling of excitons from very close quantum dots to the metal nanoparticle [1.19]. Quenching would result in an increased absorption of photons in the metal nanoparticles which is not desirable as it would decrease the number of photons available for conversion in the solar cell. It is estimated that the photoluminescence peak is obtained at an optimised distance of 10 nm between the quantum dot and the metal nanoparticle [1.19, 1.20].

The absorption of near bandgap photons for c-Si is low as is illustrated in figure 1.7. In order to realise better output from the solar cell, the resonance wavelength of the silver nanoparticle, silicon quantum dot combination must be chosen not at the bandgap of the absorber layer but rather at a little lower wavelength so that the down converted photons are efficiently absorbed. But, this would reduce the number of photons that can be down converted as the threshold for down conversion is pushed to lower wavelengths. An optimal value would need to be chosen based on the properties of the absorber layer of the solar cell. A resonance wavelength lower than the bandgap of the solar cell also ensures that the lifetime of the electron-hole pair in the absorber layer are not negatively influenced by the metal nanoparticles (if any).

Figure 1.7 Absorption coefficient of silicon. Lower absorption is observed in higher wavelengths [1.33].
1.3 Project objective

In this project, we aim to utilise the enhanced luminescence of the quantum dots present in the near-field of metal nanoparticles in a down conversion layer thereby achieving a higher down conversion efficiency. For making the down conversion layer, we choose cheap manufacturing methods wherein the Si QDs are manufactured through the plasma enhanced chemical vapour deposition (PECVD) technique using the cascade-ETP setup available in-house and the silver nanoparticles through wet chemical synthesis which is a well established technique on the industrial scale and suitable for solar cell application as elucidated by the work of Christopherson et al. [1.23, 1.24].

As part of the objective of the project, spin coating has been chosen to be studied as the means of fabricating the down conversion layer. Si QDs are obtained as dry powders through the PECVD route while silver nanoparticles are either obtained as dispersion or as a dry powder. For spin coating of these, the powders need to be made into dispersion. Considering these, the following studies will be done within the scope of this project –

1. The optimal parameters for obtaining Si QDs through the PECVD route will be studied
2. Silver nanoparticles manufactured through the chemical synthesis route, will either be manufactured in-house or procured from the market
3. Spin coating of these will be studied and an appropriate procedure be developed for the same
4. The effect of quenching will be studied by deposition of a passive layer in between the Si QDs and the silver nanoparticles
5. The down conversion layer thus fabricated through spin coating will be studied for its photoluminescence

The outline of this report is as follows. In chapter 2, the possible enhancement in the performance of the solar cell will be discussed along with the configuration of the DC layer. Chapter 3 will discuss the experimental setup used and the various procedures involved within the thesis. The results along with its discussion will be presented in chapter 4 and finally in chapter 5 the conclusions are presented.
2. Theory

In this chapter, the enhancement in efficiency limit will be discussed in section 2.1 followed by the analysis of how the final configuration of the down conversion layer was achieved in section 2.2.

2.1 Efficiency enhancement with Down Converter

As entailed in the introduction, the down conversion of high energy photons using silicon quantum dots is our focus. Schottky-Queisser developed a model depicting the maximum limit that could be achieved in a solar cell of a given bandgap taking into account the trade-off between non-absorption/transmission losses and thermalization losses (figure 2.1).

![Figure 2.1 The detailed balance efficiency limit as a function of the band gap of a solar cell illuminated by different incident spectra: Black body radiator at 6000K (blue dots); sampled black body radiator (blue dashes); AM0 (black solid line); AM1.5 (red dash-dot) [2.1].](image)

In order to understand the benefit of using down conversion in solar cells, a model similar to the Schottky-Queisser model [2.9] was developed. The efficiency of the cell is calculated using,

\[
\eta = \frac{P_m}{P_m} = \frac{J_{mp} V_{mp}}{P_m} = \frac{J_{sc} V_{oc} FF}{P_m}
\]

Here, \(J_{sc}\) is assumed to be contributed by the number of photons entering the cell (\(m^2s^{-1}\)) and is calculated as

\[
J_{sc} = (Number\ of\ photons\ incident) \times \left(\frac{Photon\ energy}{Bandgap\ energy}\right) \times (charge\ of\ electron)
\]

The number of photons is calculated from the AM1.5 data obtained from the reference solar spectral irradiance (ASTM G-173) provided by National Renewable Energy Laboratory shown in figure 2.2. \(P_m\) is in Wm\(^{-2}\) and hence, number of photons is also kept in \(m^2s^{-1}\).

\([Photon\ energy/Bandgap\ energy]\) refers to the integer part of the fraction which gives the number of photons after down conversion. Fill Factor (FF) is calculated using,
\[ FF = \frac{v_{oc} - \ln(v_{oc} + 0.72)}{v_{oc} + 1} \]
\[ v_{oc} = \frac{V_{oc}}{(kT/q)} \]

which is a good approximation for the ideal value of FF for \( v_{oc} > 10 \) where, \( v_{oc} \) is the normalised voltage.

![Figure 2.2 ASTM G-173 reference spectra [2.3].](image)

\( V_{oc} \) in turn is calculated using the relation between \( V_{oc} \) and bandgap as seen in figure 2.3. The relation is extrapolated for bandgap energies below 0.3 eV.

![Figure 2.3 Relation between Voc and bandgap energy [2.2].](image)

From the spectrum, the number of photons (\( m^{-2} s^{-1} \text{nm}^{-1} \)) at different energy levels is calculated (figure 2.4). To calculate the upper efficiency limit obtainable with the down conversion process, photons with \( n \) times (or above) the bandgap energy are assumed to split into \( n \) photons (where \( n \) is an integer) having the energy same as the bandgap of the solar cell. It can be visualised that the
efficiency of the solar cell using a down converter increases as the band gap energy of the solar cell (and down converter) reduces since the number of photons available for down conversion becomes higher. Also, the thermalization loss is reduced to its minimal. This is because the number of photons carrying excess energy as they are above the band gap but below twice the bandgap (for down conversion to happen) is reduced.

The result of the simulation is shown in figure 2.5. Theoretically, a solar cell with negligible bandgap (~0 eV) with an ideal down converter under given assumptions would yield an efficiency limit approaching 100%. However, such a trend is only partially observed in the simulation results. This is because of $V_{OC}$ being lower than the bandgap. And a peak is observed at 0.73 eV with an efficiency limit of 46%.

It is clear that in order to use a down converter to obtain reasonable increase in efficiencies, one need to look at solar cell absorber materials with lower bandgap. In the AM1.5 spectrum, the number of photons available above 4 eV is negligible. Hence, there is hardly any scope for efficiency enhancement using down-conversion for bandgap energies above 2 eV. Due to limitations on $V_{OC}$ for
a given bandgap energy, this limit reduces further to 1.92 eV. The overall maximum efficiency limit moves from 33.44% at 1.13 eV to 46.17% at 0.73 eV. The conversion efficiency for a-Si with bandgap of 1.77 eV increases from 27.5% to 28.5% while that for c-Si with bandgap of 1.1 eV, it increases from 33% to 42.8%. Hence, it can be seen that a down conversion layer is more suitable for c-Si solar cell with a 30% increase in efficiency limit rather than a-Si solar cell with a 4% increase in efficiency limit. This helps in anticipating the possible target solar cell (c-Si) which is relevant during the designing the down converter layer as will be discussed in the following section.

2.2 Down converter layer design

The down converter would ideally consist of three components –

1. Silicon quantum dots
2. Spacer layer
3. Silver nanoparticles

2.2.1 Silicon quantum dots

As has been mentioned in section 1.2.1, the efficacy of Auger inter-band relaxation for down conversion process depends on the inter-particle distance and hence, a uniform and dense layer of quantum dots is preferred. As regards to the thickness of the silicon quantum dot layer, it depends on two factors –

1. The number of quantum dots which fall in the near field of the metal nanoparticles. This in turn determines the absorption of photons within the layer and hence its spectral conversion efficiency
2. The degree of light transmitted through the layer

Lower the thickness, a larger fraction of quantum dots will be in the near-field of the metal nanoparticles but, the conversion efficiency will be lower owing to more photons being transmitted before down conversion occurs. On the contrary, if a high thickness is opted, the quantum dots at the end farther from the metal nanoparticles will not have the positive influence of the plasmons leading to lower radiative decay. This would imply higher absorption since radiative decay is required for reemission of absorbed photons. Hence, an optimal thickness needs to be found. As a first step to understand this, the extent of near field surrounding the metal nanoparticles has been calculated.

![Figure 2.6 Extent of Near and Far field](image-url)
Near field is roughly defined as the region from the surface of the source of radiation up to a
distance measuring one wavelength (figure 2.6). This is further divided into two sub-regions -
reactive and radiative near field [2.4]. Since the wavelength of the photon depends on the refractive
index of the medium, the surroundings of the emitter (source of radiation) plays a crucial role in
determining the extent of near field. But, this definition holds true only when the photon has been
emitted by the source. In our case, we deal with plasmon polaritons which are photons bound to the
electron cloud in the plasmonic material. Based on the final configuration chosen in section 2.2.2,
studying the effect of surface plasmon polaritons for near field calculations is preferred. In case of
plasmons, the term near field is not applicable as these are no longer waves and are bound to the
surface of the particle. Instead, the decay length/propagation length of the polaritons inside the
dielectric medium is used.

The intensity of the polaritons in the dielectric medium decays exponentially and the distance at
which the intensity reaches 1/e of its intensity at the surface is termed as the decay length. This is
given by, 1/k_{2,z} where,

\[ k_{2,z} = \frac{\omega}{c} \sqrt{\frac{\varepsilon_2^2}{\varepsilon_1' + \varepsilon_2} \left[ 1 - i \frac{\varepsilon_1''}{2(\varepsilon_1' + \varepsilon_2)} \right]} \]

\( \varepsilon_1 = \varepsilon_1' + i\varepsilon_1'' = \text{dielectric function of metal nanoparticle} \)

\( \varepsilon_2 = \varepsilon_2' + i\varepsilon_2'' = \text{dielectric function of the surrounding medium} \)

\( \omega = \text{frequency of the incident light} \)

\( c = \text{velocity of light} \)

The calculation assumes that the refractive index of the dielectric medium is real i.e. \( \varepsilon_2'' \) is zero [2.5].
The permittivity of silver is obtained from the Matlab code provided by Meierbachtol [2.6] and the
permittivity of silicon (QD layer) is obtained from the refractive index of silicon provided by Palik
[2.7]. For the permittivity of silicon, the effect of porosity is taken into account by assuming the QDs
to be perfectly spherical and monodisperse. Assuming such a condition, the maximum packing
density that can be achieved is 74% (lattice packing fraction model is considered with max 74% for
hexagonal closed packing (hcp) and face centred cubic (fcc) stacking) yielding a porosity of 26% and
an intermediate value of 50% (for simple cubic stacking). The dielectric property of the mixture (QDs
and air porosity) is obtained by weighted average between that of air and silicon. The propagation
length (decay length) thus calculated for the two situations is as shown in figure 2.7.

This propagation length is used to calculate the thickness of the QD layer that would ideally suit the
down converter layer. It must be noted that the propagation length calculated with 26% porosity is
an extremely conservative value for spherical particles since it assumes it is a perfectly closely
packed structure. A thin layer of QDs would tend to be translucent and hence, an optimal value for
the thickness of the QD layer should be found by optimising the transparency and enhancement of
conversion efficiency due to the influence of the silver nanoparticles.
The resonance wavelength of the silver nanoparticles would be chosen close to the bandgap of the material which makes up the absorber layer in the solar cell. Hence, for c-Si solar cells, the resonance wavelength would be chosen a little lower than 1100 nm and for a-Si solar cell, a little lower than 700 nm depending on the absorption coefficients (refer section 1.2.3). At 1100 nm resonance for a closely packed structure (hcp/fcc), the propagation length is ~130 nm and that for a loosely packed structure (simple cubic) is ~210 nm. The thickness of the QD layer also depends on the fraction of quantum dots in the near-field of the nanoparticles. This is explained in section 2.2.3.

2.2.2 Spacer layer configuration
As mentioned in section 1.2.3, enhanced rate of radiative decay has been observed in quantum dots which are in the near field of the metallic nanoparticles. Also, quenching of the excited electrons in the quantum dot is observed when the dots are less than 10 nm away from the metal nanoparticles. In order to prevent this, the quantum dots must be separated from the metal particles through a passive spacer layer. The thickness of this layer must ideally be 10 nm based on the literature. A layer with lesser thickness would result in quenching while a thicker layer would reduce the number of quantum dots in the near-field of the metal nanoparticles and the intensity of the plasmons (i.e. the intensity of the enhanced electromagnetic field) effective on the surface of the quantum dots.
With regard to the method of coating the spacer layer, two configurations are possible (figure 2.8) –

1. Coat the metal nanoparticles completely with the spacer layer
2. Make a flat separator layer with metal nanoparticles on one side and quantum dots on the other

![Figure 2.9 The emission of down converted photons from the down converter layer in case of configuration 1. The picture on the left shows the incident blue photons and that on the right shows the emitted down converted photons. Only part of the emitted photons reaches the solar cell. (Not to scale)](image)

![Figure 2.10 The emission of down converted photons from the DC layer in case of configuration 2. (Not to scale)](image)

It has been mentioned that spin coating would be used as the means for fabricating the down conversion layer. In case of configuration 1, controlling the distribution of silicon quantum dots along the surface of the metal nanoparticle would be difficult even though the relative concentrations of the two are maintained in the dispersion. The surface coverage of the silver nanoparticles and its uniformity in distribution on the substrate would be a difficult task. Also, the configuration is most likely to be disrupted during spin coating. Also, the photons emitted by the quantum dots after down conversion would propagate in all directions and hence, those emitted from the dots at the outer end relative to the solar cell would be lost as re-radiation into atmosphere (figure 2.9). Also, to achieve the chosen configuration with two different dispersions employing spin coating would be difficult. Hence, configuration 1 poses disadvantages in general and especially for the method chosen for this thesis.

Most of these disadvantages can be overcome with the use of configuration 2 wherein a nascent surface of the silver nanoparticles is maintained and ease in spin coating of individual layers through separate dispersions is observed. However if two different dispersions were made, the layer (Ag NP/Si QD) which is deposited first would be affected during the deposition of the second layer.
The photons emitted by the silicon quantum dots are emitted in random directions as is the case in configuration 1 as well. However, the photons emitted do not directly go into the atmosphere and instead interact with the silver nanoparticles (figure 2.10). This can be converted to a surface plasmon in the silver nanoparticles which would be redirected back to the silicon quantum dot layer through the Auger process of interband transfer thereby creating a loop for the emitted photon to be preferentially emitted towards the absorber layer in the solar cell. Hence, the re-radiation back to the atmosphere is reduced and is considerably lower than in configuration 1. Considering these aspects, configuration 2 is chosen as the optimal configuration for the given conditions in the current thesis.

2.2.3 Silver nanoparticles

The silver nanoparticles are a key component for enhancing the performance of the quantum dots as has been detailed in section 1.2. Based on the configuration chosen, the light incident on the solar cell first interacts with the silver nanoparticle layer. In case of plasmonic materials, the absorption cross-section of the particles may be different from the geometrical cross-section of the particle depending on its resonance characteristics and the wavelength of the incident light. An example is shown in figure 2.11 where \( C_{\text{ext}} \) is the cross-section experienced by the incident photons which is much larger compared to the actual cross section of the particle. The photons interact with the electron cloud in the metal particle to form plasmons (section 1.2.2) which travel across the surface of the particle. These plasmons have a specific decay time after which they radiate back as photons while part of the plasmons get absorbed into the material. The radiated photons which fall on the same side as the source of light form the reflected photons. It can be visualised that if the surface coverage of nanoparticles is increased, the amount of reflection increases as well. Moreover, the nanoparticles can interact with each other the effect of which is explained in section 1.2.3. Hence, with regard to reflection and a probable loss due to interaction between the nanoparticles demands a lower surface coverage.

Figure 2.11 The absorption cross-section of a plasmonic nanoparticle [2.10].
On the other hand, the surface coverage also influences the amount of quantum dots which fall into the near-field of these nanoparticles. In order to understand the effect of surface coverage on the number of quantum dots in near-field of the particles, calculations were made as is detailed below.

For ease of calculation, the spacer layer is neglected and, the metal nanoparticles are assumed to be perfect spheres and deposited as a grid like array with a constant spacing of \( d \) between their centres. The radius of the particles is assumed as \( R \) and \( 2x \) the distance between the two spheres giving,

\[
d = 2x + 2R
\]

The dashed lines in figure 2.12 & 2.13 represent the limit of near-field for the respective nanoparticles. Based on the work by Nola [2.8], this is taken as \( 3R \). But, the nature of the nanoparticles is different for Nola’s work and the current work. Hence, in order to see the variation with change in the extent of propagation length, two values are chosen namely \( 3R \) and \( 2R \) yielding,
$t = 2R$ or $3R$

Assuming a uniform distribution of the nanoparticles, we can think of a cuboid of dimension $(2R+2x)(2R+2x)$ (square shown in figure 2.12) along the plane of the particles and $t$ along the depth (figure 2.13). This cuboid is repetitive along the plane of the nanoparticles and hence, the calculation of near-field made in this unit is assumed representative for the whole structure (figure 2.14). By varying the value of $x$, we can change the surface coverage of the silver nanoparticles and calculate how it influences the volume fraction of QDs that falls in the near-field of these nanoparticles. In order to calculate this, we need to find the contribution of the following in the control volume (cuboid) –

1. Volume falling in the near field within the control volume ($V_N$)
2. Common volume between the near-fields of two neighbouring nanoparticles ($V_{2C}$)
3. Common volume between the near-fields of four nanoparticles occupying the four corners ($V_{4C}$)

The volumes $V_N$ and $V_{2C}$ are quite simple to calculate, but $V_{4C}$ is a little complex and hence, it is simplified into a cube. The volume fraction falling in the near-field is then given by,

$$V.f = (V_N - V_{2C} + V_{4C})/V$$

Where, $V$ is the volume of cuboid (control volume). The error resulting out of this simplification is not too serious and doesn’t affect the original purpose of providing an insight hence is neglected.

![Figure 2.15 Variation of volume fraction of quantum dots in near-field of the metal nanoparticles with coverage factor.](image)

This calculation is done in Matlab (appendix B) for two values of $t$ namely $2R$ and $3R$ and the result is shown in figure 2.15. As was expected, the volume fraction of quantum dots in the near-field of the nanoparticles reduce as the surface coverage reduces. But, it is interesting to note that the drop in the fraction of QDs (%) in the near-field is drastic below a certain coverage factor. Hence, depending on the optical properties of the particle, the wavelength of incident light and the absorption properties of the solar cell, a suitable surface coverage can be chosen. It is also noted that there is a
slight drop in the volume fraction in case of \( t = 3R \). This is due to the simplification that was made prior in the calculation of \( V_{AC} \).

Mieplot (software for Mie scattering simulations) simulations were done to identify the suitable size of the Ag NPs. The range of sizes for these nanoparticles defined by the radius \( R \) is simulated through Mieplot assuming the complex refractive index of silver and a medium with a fixed refractive index of 1.77. The refractive index of the medium is chosen at 1.77 assuming 50% porosity for the QD layer and, it falls in the intermediate region of SiO\(_2\) and AZO which are the possible candidates for the spacer layer. A variation in the refractive index at 1.77±0.2 yields a shift in the peak (resonance wavelength) by about 50 – 75 nm. In order to keep the resonance wavelength close to the emission wavelength of QDs which in turn depends on the bandgap of the solar cell, the size range is varied accordingly during the simulations. The result of mieplot simulations is shown in figure 2.16 and 2.17. It is seen that the size of the nanoparticles needs to be of the order of 100-200 nm in diameter for c-Si solar cell.

It must be noted that Mieplot assumes a single nanoparticle for calculations. Since the inter-particle separation plays a role as has been mentioned in section 1.2.3, resonance shift needs to be considered as well if \( x > 0.75 \times D \). This corresponds to a surface coverage of 25.65% and above.
3. Experimental setup & procedure

Having decided on the structure of the down converter, the next step is to fabricate the individual components and test them. In the following sections, the three major components to be manufactured and the procedure developed for their fabrication will be discussed.

3.1 Physical components

The fabrication of the individual components required in the down conversion layer namely the quantum dots, the silver nanoparticles and the spacer layer will be discussed in this sub-section.

3.1.1 Silicon Quantum Dots

As has been mentioned in section 1.3 the fabrication route for the silicon quantum dots has been decided as the ETP-CVD (Expanding Thermal Plasma - Chemical Vapor Deposition) technique, the setup for which is available in-house. The setup known as CASCADE (Cascaded Arc Solar Cell Apparatus Delft Eindhoven) is as shown in figure 3.1.

In ETP-CVD, the incoming Ar plasma is used to break the silane gas (introduced through the pores in injection circle) into silicon ions or radicals which then agglomerate into larger particles before reaching the substrate. Since the plasma expands from the source nozzle till the substrate, it is referred to as expanding thermal plasma. The advantage is that high deposition rates can be achieved with this technique and deposition rates of up to 10 nm/sec has been achieved for μ-crystalline silicon solar cells [3.5]. The cost of production of these layers would reduce by a considerable extent owing to such high deposition rates. This reduction in processing cost can be realized in the fabrication of quantum dots as well. As is mentioned in section 2.2.2, the down conversion layer tends to keep the photons within the solar cell. Also, the refractive indices of the layer are such that it gradually increases from the spacer layer to the QDs to the absorber layer. Hence, it can be thought of to have the ability to replace the anti-reflection coating used normally in
solar cells. This along with the low cost of these layers aided by such techniques, the cost/kWh of solar cells can be brought considerably down.

Depending on the process parameters, the material deposited on the substrate can vary between amorphous silicon to μ-crystalline silicon. The set of parameters which are required to form quantum dots are intermediary to that of amorphous and crystalline. Hence, the quantum dots usually contain some amount of amorphous tissue on its surface. The amorphous tissue protects the quantum dot from oxidation. However, for the purpose of down conversion it poses a negative consequence since it reduces the probability of Auger interband relaxation (refer section 1.2.1). The play of parameters is such that as the amorphous tissues decrease, the size of the quantum dots increases. Hence, optimal parameters with minimal amorphous tissues for given quantum dot size is necessary. The optimal parameters for deposition of silicon quantum dots on a substrate with the original setup have been developed in-house previously. In order to be of use in solar cells, quantum dots need to be in the size range of a little over 1 nm to about 10 nm in size since the band gap lies in the relevant part of the solar spectrum (UV till NIR) of light in those size ranges. The Stokes shift, emission wavelength and the size of a QD is related based on these formulae

\[
 d = 2\pi \frac{B}{\Delta\omega}
\]

\[
 Eg = 1.136 + \frac{9.75}{d^2}
\]

Where \( d \) is the diameter of the silicon QD, \( \Delta\omega \) is the Stokes shift’s deviation from that of c-Si, \( B \) is a constant 2.24 nm\(^2\)/cm and \( Eg \) the band gap energy of the QD. In case of c-Si solar cells, the QD needs to have an emission wavelength close to 1100 nm. However as has been discussed in section 1.2.3, it is advisable to have the emission wavelength a little lower. For an emission wavelength of 1000 nm, the QD needs to be of ~9.6 nm in size which corresponds to a Stokes shift of ~519.5 cm\(^{-1}\) in the Raman spectrum. Similarly for a-Si solar cells, QDs of dimension 3.8 nm which have an emission wavelength of ~690 nm and exhibit a Stokes shift of ~514.5 cm\(^{-1}\) are required. It was found during the course of development of the optimal parameters in the original setup that there was a considerable amount of larger particles (> 10 nm) being formed. This was attributed to recirculation of the particles. Recirculation is the re-introduction of the particles which escape the main plasma stream and are reintroduced back to the source of the plasma stream. This happens due to pressure differences which causes the generation of a vortex in the extraneous part of the plasma within the chamber (similar to the red circle shown in figure 3.1 right). As a result, these particles interact with the fresh silicon ions or radicals generated in the plasma and grow larger. In order to curtail the effect of recirculation, it was decided to introduce a copper tube in the ETP head (figure 3.1 right). It was observed that this setup proved to reduce the quantity of large particles (> 10 nm) being formed. This was attributed to recirculation of the particles. Recirculation is the re-introduction of the particles which escape the main plasma stream and are reintroduced back to the source of the plasma stream. This happens due to pressure differences which causes the generation of a vortex in the extraneous part of the plasma within the chamber (similar to the red circle shown in figure 3.1 right). As a result, these particles interact with the fresh silicon ions or radicals generated in the plasma and grow larger. In order to curtail the effect of recirculation, it was decided to introduce a copper tube in the ETP head (figure 3.1 right). It was observed that this setup proved to reduce the quantity of large particles [30]. The CASCADE setup with copper tube installed will be referred to as the modified setup henceforth. Also, the substrate was placed at a raised level close to the injection circle to reduce the degree of agglomeration. Since this changes the condition within the chamber, it was decided to find out if the standard deposition conditions of 1 mbar chamber pressure, 230 sccm (standard cubic centimeter) silane flow and 30 A current was valid for the modified setup or if new optimal parameters had to be found as a part of this thesis work.
The major parameters that affect the size distribution of the silicon quantum dots at a set argon flow are the plasma current, chamber pressure and the silane flow. The current decides the plasma intensity i.e. the amount of ions or electrons generated per unit area (cross-section) of plasma; current along with pressure decides the plasma velocity; and the silane flow at a set argon flow decides the ratio of silicon particles (ions/radicals) to argon ions or electrons in the plasma. The combination of all three affects the degree of interaction between the silicon particles before it reaches the substrate which in turn decides the size of the particles as the particles grow through agglomeration. Various combinations of these parameters were chosen as shown in table 3.1.

<table>
<thead>
<tr>
<th>Current (A)</th>
<th>Pressure (mbar)</th>
<th>Silane flow (sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>0.7</td>
<td>200</td>
</tr>
<tr>
<td>30</td>
<td>1.0</td>
<td>230</td>
</tr>
<tr>
<td>40</td>
<td>1.3</td>
<td>300</td>
</tr>
</tbody>
</table>

Table 3-1 Deposition parameters for Si QD deposition through ETP-CVD.

It was observed during the previous work [30] that pressures below 0.7 mbar yielded a large fraction of amorphous silicon while the pressure control in the equipment above 1.3 mbar during the deposition period of 60 seconds is quite difficult. Hence, three values of 0.7, 1.0 and 1.3 mbar were chosen. The minimum current setting in the equipment is 20 A while currents above 40 A lead to overheating of the substrate disrupting the study as high temperature would lead to agglomeration of the deposited particles. Hence, three values of 20, 30 and 40 A were chosen. It was observed that for the set argon flow of 710 sccm, silane flows below 200 sccm yielded a large fraction of amorphous material. Best results for the original setup were observed at silane flow of 230 sccm, plasma current of 30 A and 1 mbar chamber pressure. In order to not deviate much from the original optimal flow value, the third flow rate was chosen as 300 sccm. The samples thus generated were examined for their sizes using stokes shift in Raman spectrum (refer section 3.3.1).

3.1.2 Silver nanoparticles

As mentioned in section 1.3, wet chemical synthesis was chosen as the method for fabrication of silver nanoparticles based on the work by Christopherson et al [1.23, 1.24]. In wet chemical synthesis, nanoparticles are generated by reducing a salt of silver to form silver ions using a suitable reducing agent. The reduced ions then agglomerate in the solution to form nanoparticles over time. In order to cap the degree of agglomeration, capping agents are added which adhere to the surface of the nanoparticle preventing further interaction with neighboring silver ions/particles. The size of the nanoparticles is thus determined by the concentration of these capping agents in the solution in comparison to the silver ions. The means to develop this technique as part of the thesis and for future use within the PVMD group for solar cells was explored with the help of chemical faculty of TU Delft where this technique was already in use for fabrication of silver nanoparticles. But, procedures were available only for smaller nanoparticles with sizes of a couple of nanometers. Silver nanoparticles in these size ranges are not preferable as they are strongly absorbing and have very low resonance wavelengths. The silicon quantum dots fabricated yield a photoluminescence spectrum peaking at about 700-800 nm [1.30]. As mentioned in section 1.2.3, the resonance wavelength of the silver nanoparticles needs to be close to the emission wavelength of the quantum dots. From simulations using Mieplot (section 2.2.3), it was observed that, for this purpose and under the surrounding conditions of the silver nanoparticles based on the DC structure chosen, the silver nanoparticles need to be of size close to 150 nm.
Table 3-2 Comparison of various market options in terms of cost requirements.

The fabrication of particles of such sizes was not possible with the current knowhow. Hence as an alternative, the purchase of silver nanoparticles of such sizes from the market was investigated. Based on the findings (table 3-2), it was seen that the purchase of silver nanoparticles as powders fabricated through wet chemical synthesis and dried were the most economic option. Hence, nanoparticles were procured from Skyspring Nanomaterials, Inc (refer appendix C). Since powder was procured and the chosen method of investigation was spin coating, the powders needed to be made into dispersion.

![Figure 3.2 Provac setup in CR10000, DIMES, TU Delft.](image)
Since the procurement of nanoparticles from the market takes time, an alternate technique for fabrication of nanoparticles was also examined to check the effectiveness of the silver nanoparticle silicon quantum dot combination. This would also serve the purpose of comparison of results. The technique chosen was PVD (physical vapor deposition) using the Provac setup (figure 3.2) followed by annealing in vacuum using the amigo setup (figure 3.3) available within the DIMES facility. This thin film deposition followed by annealing to obtain a metal island film was developed in-house by Tan et al. [3.1].

In order to obtain particles of desired size, two depositions were made in Provac with a target film thickness of 10 nm and 12 nm. These were then annealed under vacuum at 400°C. An example of the metal island obtained through this technique is shown in figure 3.4.

3.1.3 Spacer layer
As has been mentioned in section 2.2.2, the spacer layer has a serious role to play in the performance of the down conversion layer. A spacer of 10 nm is ideally what is preferred in the final structure. Silicon dioxide was considered for this purpose as it is transparent in the required wavelengths and is also electrically non-conducting. Within the DIMES facility, the possibility of depositing SiO₂ was considered using the Provac deposition chamber mentioned before. A test deposit was made to calibrate the instrument but it was found that the deposition was highly non-
uniform. A substrate of 10 cm diameter with a target deposition of 100 nm yielded a variation of 50 nm from one end to the other. Considering the high deviation in deposition thickness, and that the accuracy of deposition deteriorates with lower target thicknesses, an alternate to the use of Provac for SiO₂ deposition was considered. The use of CHA evaporator was sought for this purpose but the trial deposits proved to be challenging as the deposited material turned granular. The trials in the setups took considerable time (due to administrative reasons) and there wasn’t enough time to incorporate the spacer layer in the spin coated samples. Hence, it was decided to check the effect of silver nanoparticles on the quantum dots without the spacer layer as there is a high probability that this combination will also give a good indication of the coupling between the silver nanoparticles and the silicon quantum dots.

3.2 Spin coating
As has been mentioned in section 1.3, spin coating has been chosen as the method for fabrication of the down converter layer due to its low cost, equipment’s simplicity and ease of integration into a continuous process. The QD layer is spin coated instead of depositing directly using the CASCADE since a thickness of ~100 nm to around 200 nm is preferred (based on results of section 2.2.1 and 2.2.3) which is difficult to achieve in the CASCADE owing to its high deposition rate. Spin coating is a process wherein the material to be coated is spread/coated onto the surface of the substrate using the centrifugal reaction arising from the spinning action of the surface. The different stages during spin coating are as shown in figure 3.5. The droplet initially placed at the centre spreads and thins out with the excess falling off and a thin layer remains on the substrate. The degree of reduction in thickness of the layer depends on the viscosity of the liquid and the spin parameters.

Figure 3.5 Spin coating. [3.2]

In order to use this technique, the material to be coated must be able to flow in the given condition uniformly. Considering the fact that both the silicon quantum dots from the ETP-CVD and purchased silver nanoparticles from the market are in powder form, these need to be made into dispersion before spin coating can be done.

In order to disperse the particles in a solvent, different solvents available within the DIMES facility like IPA, acetone, ethanol, ethylene glycol were considered. To be able to choose a suitable solvent, the viscosity and boiling point of the solvents were considered apart from the compatibility for dispersing the nanoparticle/quantum dot. Viscosity plays a role as it determines the ease of flow of
the dispersion during spin coating. A low viscosity would result in an extremely thin layer of the dispersion during spin coating. This in turn would lead to lower deposition thicknesses requiring larger number of depositions to achieve a required deposition thickness. This issue is worsened considering that the subsequent depositions also disturb the initial depositions deteriorating its quality. The reduction in thickness during spin coating also implies a larger wastage of the dispersion. In order to limit wastage during spinning, the amount of liquid poured should be reduced. However, if the amount of liquid is too low, the flow of the liquid during spin coating would be non-uniform leading to a starburst pattern (figure 3.6)

![Figure 3.6 Spin coated quantum dot solar cells showing the typical starburst pattern in the QD layer. [3.7](image)](image)

Hence, a high viscosity liquid is preferable. But, this leads to a higher boiling point and hence lower evaporation rate leading to agglomeration of the particles in the droplets that evaporate last as was shown by Christopherson et al. [1.23, 1.24]. The properties of these solvents are shown in table 3-2. An optimum was found in ethanol with a reasonable viscosity and low enough boiling point to suit our purpose.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Viscosity (mPa@20°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>1.14</td>
<td>78.37</td>
</tr>
<tr>
<td>IPA</td>
<td>2.30</td>
<td>82.50</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.31</td>
<td>56.00 – 57.00</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>16.10</td>
<td>197.30</td>
</tr>
</tbody>
</table>

Table 3-3 Viscosity and boiling point of solvents available within the DIMES facility.

### 3.2.1 Preparing the dispersion
Having decided on the solvent, the next step is to dissolve the particles fabricated/purchased into dispersion. The quantum dots were deposited onto a glass substrate in the standard conditions mentioned before and for a time period which would yield the desired weight output of quantum dots based on the deposition rate measurements done (section 4.1.1). This is then introduced into a beaker containing the solvent of desired volume which in turn is placed inside the ultrasonic bath. The bath is allowed to run for about 30 minutes after which, the substrate containing the quantum dot is dried and weighed again. The concentration of the dispersion made is thus found and used for deciding the number of depositions required to achieve the desired deposition thickness.
Similarly, the silver nanoparticles are weighed and added to a pre-measured quantity of solvent. This is then subjected to ultrasonic vibration for 120 minutes to make the dispersion uniform.

3.2.2 Spin coating parameters
The Polos spinner used for spin coating purposes can handle samples of up to 8 inches diameter and is provided with a vacuum chuck to hold the substrate/sample well. With a programmable digital process controller having capability of storing up to 50 programs and speed variations from 1 to 10000 rpm, it provides a good means of carrying out the spin coating process required. The various parameters which can be modified in the given spin coater are the spin speed (rpm) as mentioned, acceleration (rpm/sec) and spinning time. The programmable process controller allows the possibility to program a series of steps in between to automate the whole coating cycle (if any). The pouring of the dispersion is done manually with a pipette. Since this is done manually, it is also possible to adjust the way in which the dispersion is poured and the quantity of the dispersion per spin cycle. It was observed that 1 ml dispersion was drained through 25 drops implying that 1 drop corresponds to approximately 0.04 ml. Hence, the volume of dispersion added per cycle can be done in steps of 0.04 ml. It was a standard practice to use 1000 rpm/s as the standard acceleration for coating of photoresists. This was kept as such and the spin speed was varied along with the introduction of increasing the spin speed through two or three steps. The volume of dispersion added was also modified and the different samples were analyzed.

3.3 Test equipments
In order to characterize the samples fabricated, several test equipments were employed which are as elucidated below.

3.3.1 Raman spectroscopy
The Renishaw inVia Raman microscope is equipped with two laser sources of 514 nm (green laser) and 628 nm (red laser) and can measure Raman shifts from 250 cm\(^{-1}\) to 3000 cm\(^{-1}\). Information such as crystalline fraction and crystal orientation can also be obtained using this setup.
In this thesis, the Raman spectroscope was used for three purposes. First was the normal use for analyzing the Stokes shift (also referred to as Raman shift), second the analysis of anti-Stokes shift and third photoluminescence measurement. Stokes shift is the difference in the wavelengths of absorption and emission spectrum band maxima of a given electronic transition. An electron in the material upon excitation by light goes to a higher energy state and relaxes back possibly by the emission of a photon. The energy of the incident light and the light emitted is different and the shift in the band peak is characteristic of the material under investigation and hence, a Stokes shift gives information about the material at hand. For crystalline silicon, a shift of about 521 cm\(^{-1}\) is observed. Stokes shift refers to the shift that involves a loss in energy by the photons to the lattice. It is also possible that the emitted photon gains some energy from the lattice. This is referred to as anti-Stokes shift. This is more pronounced when the material is at a high temperature. This property is used to find the temperature of the sample using the anti-stokes shift [3.3].

As has been mentioned in section 1.2.1, the size of the quantum dots affects their emission wavelength due to a change in their electronic levels. This also affects the Stokes shift observed which is observed to be below 521 cm\(^{-1}\) at about 510-520 cm\(^{-1}\). The smaller the particle, the lower the Stokes shift [3.6]. This is used to find the approximate size of the particles which is used to characterize the samples produced through the ETP-CVD route. The anti-Stokes peak shift is used to determine the temperature levels developed in the sample during measurements which in turn is used to choose probing parameters that do not cause much heating in the sample. This is especially important in the present case as an increase in temperature might cause agglomeration of the particles which in turn would affect the reading. By expanding the detection range, it is also possible to measure photoluminescence using the Raman spectrometer. As mentioned in section 1.2.3, the presence of silver nanoparticles enhances the PL spectra of the QDs. The enhancement observed in the down conversion layer can be studied through PL measurements.

Apart from these, the spectrometer was also used to measure the size of the particles on the substrate in the vertical direction (thickness). The spectrometer requires that the laser beam be focused on the surface of the sample for which, a vertical adjustment is provided on the substrate platform. The adjustment was done through a stepper motor and each incremental step corresponded to 100 nm change in the vertical direction resulting in a ±50 nm (approximately) accuracy of the measurement in vertical direction.

1.3.2 Perkin Elmer Lambda (IS)
The Perkin Elmer 950 (Lambda) is a spectrophotometer used to measure transmission and reflection which, with the help of the TIS accessory can be used for measuring the diffuse transmission/reflection as well. It has an incident beam wavelength range from 250 nm to 2500 nm. With the help of the ARTA module, angular distribution function can be measured from 10° to 350°. Information such as thickness, wavelength dependant complex refractive index, bandgap (Klazes/Tauc), angular distribution function (ADF) and haze parameters can be obtained from the sample using this device.

For the spin coated sample, the integrating sphere in the Perkin Elmer setup is used to calculate the reflection and transmission spectrum. The sample beam whose wavelength varies from the minimal to the maximal values set at given steps as defined by the user is illuminated on the sample and the reflection and transmission data are calculated from the number of photons detected in the detector as compared to the number of photons emitted by the source.
It is expected that the effect of the silver nanoparticles on the quantum dots would be visible in the absorption spectra as determined from the transmission and reflection spectra using this setup. In case the conversion layer works well, it is also expected that the transmission spectra might be enhanced more than that of the substrate which would prove as a means of affirming the occurrence of down conversion.

3.3.3 Horiba PL measurement
The Fluorolog 3 is a spectrophotometer provided by Horiba Jobin Yvon used to measure the photoluminescence (PL) spectrum. The source is a 450 W continuous wave lamp and the instrument has monochromators on both the emission side and the excitation allowing variation of excitation wavelength on the sample and its corresponding PL spectrum over a range of wavelengths.
The Horiba setup is used to measure the photoluminescence of the samples generated using spin coating. It is possible to measure the PL spectrum for a varied illumination wavelength using this device. The PL spectrum can be used to determine the emission wavelengths of the quantum dots generated and to check if the silver nanoparticles enhance the emission of these quantum dots from the enhancement in the PL intensity.

3.3.4 Sartorius RC210P weighing balance
In order to measure the weight of the samples when required, Sartorius RC210P weigh scale was used. It has the capacity to weigh samples of up to 10g with an accuracy of ±0.01 mg.
4. Results & Discussions

Using the equipments and procedures detailed in the previous chapter, the individual components of the DC layer were fabricated and tested. The results of each step will be presented and discussed in this chapter. In section 4.1 the fabrication of the quantum dots in powder form is characterized. Section 4.2 explains how these quantum dots are brought into dispersion and combined with silver nanoparticles by means of spin coating. Finally the fabricated quantum dot films are characterized by reflection/transmission measurements (section 4.3) and by photoluminescence measurements (section 4.4).

4.1 Silicon Quantum Dots fabrication

As explained in section 3.1.1 the silicon quantum dots are fabricated in the CASCADE system using remote plasma. The first step, described in section 4.1.1, is to determine the absolute deposition rate for different deposition conditions, i.e. the quantity of material deposited per unit time and per unit area. After that, section 4.1.2 will focus on the composition of the deposited material in an attempt to maximize the deposition of quantum dots in the suitable size range of <10 nm (see section 3.1.1).

4.1.1 Rate of deposition of quantum dots in CASCADE

The depositions were done in three different flows of silane (SiH₄) 230, 420 and 600 sccm and three deposition times of 60, 240 and 480 seconds with other parameters kept in standard conditions mentioned in section 3.1.1. Depositions were done at three different times since the plasma takes a little time to stabilize varying from a couple of seconds to a couple of 10s of seconds depending on the deposition parameters and the machine condition. Also, this gives an idea of variation of the rate of deposition over time. Since a raised platform is used, the option of using the shutter to eliminate the initial fluctuations is not feasible. The substrates were weighed before and after the deposition using a weighing balance (section 3.3.4) and the rate of deposition was calculated from the weight and deposition time. The average of five readings was taken for each sample before and after deposition and the standard deviation noted. The areas of the substrates were measured using vernier calipers and the deposition rate per unit area calculated. The measurements are shown in appendix D and result is shown in figure 4.1.

It is seen that for 230 sccm deposition conditions, the deposition rate doesn’t vary much with time indicating uniform plasma and deposition conditions over time. In case of 420 sccm depositions, a rising trend is observed while in case of 600 sccm deposition, a decreasing trend is observed. The cause for the variation in rate of deposition for higher flows was not investigated in detail. However, it is speculated that the decreasing trend in the 600sccm flow could be related to a possible limitation in deposition on substrate beyond certain thicknesses owing to the loose nature of the silicon quantum dots (eroded top layer at centre right in figure 4.3) which yield to the plasma pressure leading to erosion of the top layer on par with the deposition rate.
However, the overall rate of deposition increases with increase in silane flow as was expected shown in figure 4.2. The deposition on the substrate was also found to be quite non-uniform as can be seen in figure 4.3 with little deposition at the centre (the central circular zone at the top in figure 4.3) and streaks of enhanced deposition zones (four lines/bands seen emanating from the arc centre on the right and bottom in figure 4.3). These streaks/bands seem to coincide with the pores in the injection circle (section 3.1.1) and consequently perhaps are the path taken by the reduced silane gas. It was later noted during the removal of the ETP header (figure 3.1) that there was a partial meltdown of the injection circle used and clogging of some of the pores. This would have affected the flow pattern of silane in the plasma. This could explain the lower quantities of deposition found on the left side of the substrate compared to its right in figure 4.3. Hence, the position at which the sample is kept affects the readings and the position as such is a little difficult to handle since the platform used for mounting the substrates is not rigid. The visual inspection of the eroded zones shown in figure 4.3 along with comparison to the substrates with low amount of deposits (230 sccm, 60s for
example) indicate that the growth mechanism of the deposit varies at different stages with a reasonably dense layer being formed at the beginning and a more porous layer forming at later stages increasing the possibility of erosion mentioned before. This is less prominent visually in the 230 sccm samples probably leading to the comparatively more stable deposition rates observed.

![Figure 4.3 Si QD on glass substrate. The sample shown is of 600 sccm, 480 seconds deposit mentioned in the table.](image)

It can be seen that the deposition rate is stable for 230 sccm flow and varies for higher flows. The weight of the QDs deposited in the 230 sccm flow is easier to predict compared to that in higher flows. Hence, 230 sccm flow is preferable for future depositions with the weight of the QDs in mind.

### 4.1.2 CASCADE deposition parameters for Si QDs

As was mentioned in section 3.1.1, a set of deposition parameters were chosen to find the optimal parameters for deposition of quantum dots (refer table 3-1). The optimal set of parameters was defined as the one which would yield the highest fraction of QDs with size of 10 nm or less (see section 3.1.1). The series of samples were fabricated using these parameter sets and were analyzed using the Raman spectroscope to determine the size of the particles by observing the Stokes shift. However, it is observed from literature [4.1] that the QDs get heated under laser and the Stokes peak might get distorted if agglomeration of the particles were to occur during measurement. To check this, the anti-Stokes peak for four samples were determined and analyzed using the procedure provided by Leonid et al. [4.1]. From the anti-Stokes shift the temperature of the QDs can be estimated. The result of the temperatures thus observed is plotted in figure 4.4. It is seen that at 0.2 mW laser intensity which corresponds to 1% of max intensity (20mW) has hardly any heating effect while heating is observed at higher laser intensities. Jason et al. [4.2] indicate that sintering starts to show in silicon nanoparticles (5 nm) at temperatures above 550°C. The degree of heating upon exposure to laser also depends upon the particle size. It must also be noted that better signal is obtained from the Raman spectrometer with higher intensities. As a compromise, the laser is set at 1% (0.2 mW) which has a low heating effect under test conditions and the exposure characteristics decided accordingly to obtain a good signal.
At 1% laser intensity for which there is little temperature effect, the samples were analyzed for Stokes shift to determine the size of the quantum dots generated. As has been mentioned in section 3.1.1, the quantum dots are not completely crystalline and have amorphous tissues on their surface. Hence, along with Stokes shift which gives an idea of the particle size, the analysis of the crystalline fraction developed by Swaaij et al. [4.3] was also used (detailed in appendix E). In this method, the Raman spectrum is split into crystalline and amorphous contributions by subtracting a scaled Raman spectrum of a-Si film. The area under the curve of the two contributions is then used to determine the crystalline fraction. During measurement on a random sample at multiple spots, it was noted that a streak (green circles in figure 4.5) in general gave a uniform Stokes shift and that the crystalline fraction decreased from centre to the edge (left to right for green circles in figure 4.5). Based on this, the samples were analyzed at multiple spots (red circles in figure 4.5) and on an average, 10 measurements were taken in each sample (~10cm*5cm) to have a reasonable sample size. The probability of finding a quantum dot of given size (Stokes shift) was calculated as the ratio of the number of occurrences of a certain Stokes shift to the total number of measurements taken. For example, if there were 10 measurements taken in a sample of which 8 resulted in a Stokes shift of 516 cm$^{-1}$, the probability of achieving a Stokes shift of 516 cm$^{-1}$ is 80%.

The probability thus obtained is multiplied with the crystalline fraction of the individual spots to get the fraction of crystalline QDs obtainable under the given deposition condition (figure 4.6). This will be referred to as the overall probability of obtaining QDs henceforth. The overall probability of obtaining QDs (of size <10 nm; Stokes shift ≤ 519.5 cm$^{-1}$) would be the sum of the individual probabilities and for the case mentioned above would be ~36%. Since separation of QDs based on size is not done as part of this thesis, the overall sum is considered for comparison of deposition conditions. The comparison of probability of QDs and crystalline fraction is done by taking the averages of the probability of QDs and the crystalline fraction for QDs of different sizes (Stokes shift ≤ 519.5). For example, the crystalline fraction of the deposition condition shown in figure 4.6 would be calculated as the weighted average of crystalline fraction of individual QD sizes (stokes shift) i.e. average of 44%, 27%, 47%, 26%, 65% which yields a value of 41.8%. This weighted average is used for comparing two deposition conditions.

![Figure 4.4 The measured sample temperature using anti-Stokes peak against the incident laser intensity.](image)
Figure 4.5 Spots analyzed using the Raman spectroscope for one of the samples.

Figure 4.6 Histogram illustrating the method used for calculation of overall probability for different Stokes shifts.

The overall probability is required to get a grasp of the various QDs that could form in the given conditions on the substrate and to choose the best possible parameters for deposition. It has been mentioned that the location of the substrate within the chamber affects the result obtained. The lesser the contribution of the central arc (the grey region in figure 4.5), the higher is the amount of QDs found on the substrate. Also as mentioned before, the contribution of the amorphous tissues becomes higher as we move away from the beginning of the streaks. Hence, the ideal zone for QD collection would be a circular band with its inner radius covering the center of the plasma while the outer radius would depend on the deposition parameters. Since the substrate holder was a raised platform (section 3.1.1), a temporary stand made from aluminum sheets it was difficult to control of position of the substrate. Hence, a strictly position controlled sample was difficult to obtain.

To assert the importance of finding the overall probability, consider the results for one of the deposition conditions (40 A) shown in figure 4.7b. Based on the probability of QDs (figure 4.7b1), the 1 mbar, 300sccm (point 1) is the most favorable deposition condition closely followed by 1 mbar, 230 sccm (point 2), 0.7mbar, 300sccm (point 3) and 1.3 mbar, 300 sccm (point 4). The crystalline...
fraction (figure 4.7b2) indicates though that the conditions 1 mbar, 200 sccm (point 1) and 1.3 mbar, 200 sccm (point 2) are more favorable than the 1 mbar, 300 sccm (point 3) condition. The probability graph by itself would lead us to conclude that the 1 mbar, 300 sccm (point 1) condition is to be opted since the chances of forming the QDs are very high. However, this also includes the amorphous tissues. The crystalline fraction by itself would lead us to choose 1 mbar, 200 sccm (point 1) and 1.3 mbar, 200 sccm (point 2) condition since it has the least amorphous Si in the measured regions. However, it gives no idea about the degree of formation of QDs at different regions within the substrate. Only by combining the two, we get an overall picture of the formation of QDs in the given deposition condition. In the chosen example, the conditions 1 mbar, 200 sccm (point 1) and 0.7 mbar, 230 sccm (point 4) which were favorable due to the higher crystalline fraction lose ground due to the low probability of QD formation. The overall probability indicates that among the 40 A deposition conditions, a chamber pressure of 1.3 mbar and silane flow of 200 sccm (point 1) is the most favorable followed by 0.7 mbar, 300 sccm (point 2) and 1 mbar, 230 sccm (point 3) in that order.

The comparison of chamber pressure vs. silane flow plots at 30A and 40A conditions is shown in figure 4.7. For 1 and 1.3 mbar pressures, it is seen that the probability of forming a QD (figures A1 and B1) is dominant at 230 sccm flow (points 1 & 2) at 30 A which shifts towards the 300 sccm flow (points 1 & 3) for 40 A current. The trend could probably be thought of as an indicator of dependency on the ratio of plasma ions to silane molecules injected into the stream. Higher the current, higher the ions or electrons in the plasma and to maintain the ratio, the silane flow has to be increased. No clear trend is observed in 0.7 mbar region. The crystalline fraction (figures A2 & B2) on the other hand follows a reverse trend with higher crystalline fraction observed with conditions involving lower ratios of plasma ions to silane molecules i.e. at lower silane flows. The rate of formation of silicon based particles (radicals/ions) which then lead to the formation of the QD could be used to explain this. Higher the rate of generation of silicon based radicals, the time required to arrange the silicon atoms into a proper crystal lattice reduces and hence a lower crystalline fraction. Again, a clear trend is not observed in the 0.7 mbar region. The overall probability (figures A3 and B3) indicates that the 40 A, 1.3 mbar, 200 sccm (figure B3, point 1) condition has the best condition for generation of QDs with 51% while that of 30 A, 1 mbar, 230 sccm condition is 23% (figure A3, point 1). In the 40 A overall probability graph (figure A3), it is seen that there is a certain band which has a higher probability of formation of QDs indicated by the counter diagonal (top left through bottom right marked by the points 1, 3 and 2). It must be noted that the troughs observed in between are a result of the linear interpolation used (refer appendix G) which makes these regions affected by the data points from all sides. This diagonal indicates a role of inter-particle interaction playing a role in the formation of QDs. Higher the pressure, greater is the inter-particle interaction between the silicon radicals/ions. Similarly, higher the silane flow, higher is the probability of formation of these radicals which indicates a higher inter-particle interaction. Now, since the band is formed along the counter diagonal, the probability of formation of QDs can be thought of as being higher in a narrow region of inter-particle interaction probability. In the 30 A plot (figure A3) however, similar trend is observed along the main diagonal which disagrees with the interpretation made for the 40 A condition. In the 30 A condition, the overall probability is comparatively higher at higher pressures than at lower pressures. A higher pressure indicates a higher probability of inter-particle interaction and hence, the plots give an interpretation that higher interaction probabilities are favorable for the formation of QDs.
Having discussed the depositions at 30 A and 40 A, the 20 A condition remains. Under 20 A conditions however, samples with silane flow of 300 sccm alone were made assuming it would result in the formation of predominantly amorphous depositions in case of 200 or 230 sccm flows. The results of these deposits are made as P vs I plot at 300 sccm flow and are shown in figure 4.8. As can be seen from the probability graph (figure i), the probability trend observed in case of 40 A is similar to that of 20 A condition as well. It is speculated that the band formation observed in the 40 A condition could also be observed in the 20 A condition indicating a narrow band of inter-particle interaction probabilities being more favorable for the formation of QDs. The plot of crystalline fraction in the 20 A (figure ii) region shows a decreasing trend with increasing pressure. This could probably be explained by the probability of inter-particle interaction mentioned before. As the pressure decreases, the probability of interaction decreases indicating that there is comparatively more time for crystallization of the particle formed. However, similar trend is not observed in the 30
A and 40 A regions. An increasing trend is observed with an increase in current in the 1 mbar and 1.3 mbar region and to an extent in the 0.7 mbar region as well. The probable explanation to this is that a higher current is required for the dissociation of silane at 300 sccm flow. The overall probability in this case is in favor of higher current and lower pressures.

![Figure 4.8](image)

**Figure 4.8** The results for deposition under 300 sccm silane flow. i) Probability of obtaining a QD within the sample ii) crystalline fraction of the QDs obtained and iii) the overall probability of obtaining a QD under the given conditions of deposition.

Considering the use of CASCADE for future development of QDs targeting c-Si or a-Si-H solar cells, deposition conditions which yield the maximum fraction of 9.6 nm QDs (for c-Si) and 3.8 nm (for a-Si-H) are to be identified. From the measurement results (appendix F), it is observed that the QDs exhibiting a Stokes shift of 514.5 cm\(^{-1}\) (3.8 nm QD) shift is not common. The only set of parameters where such QDs are observed is 20 A plasma current, 1 mbar chamber pressure and 300 sccm silane flow. The overall probability observed is a mere 3.19% with a probability of 28.57% and a crystalline fraction of 11.15%. This indicates that the formation of smaller QDs might be a little difficult to achieve. However, there is also an exception to this statement within the sample space measured. The parameters 30 A, 0.7 mbar chamber pressure and 200 sccm silane flow yield a considerable quantity of QDs exhibiting 510 cm\(^{-1}\) and 510.5 cm\(^{-1}\) stokes shift. This relates to a QD of size ~2.9 nm with an emission wavelength of ~550 nm. The probabilities for 510 cm\(^{-1}\) and 510.5 cm\(^{-1}\) stokes shifts are 66.67% and 16.67% with a crystalline fraction of 19.35% and 43.76% resulting in an overall probability of 12.9% and 7.29% respectively. As can be seen, in comparison to the general result observed in the formation of QDs (Appendix F) this is a considerable value.

The QDs exhibiting a Stokes shift of 519.5 cm\(^{-1}\) (9.6 nm) on the other hand are more common and the results are plotted as before in figure 4.9. It is seen that both probability of formation (figures A1 & B1) is favorable at higher current of 40 A, higher silane flow of 300 sccm and lower pressure conditions of 0.7 mbar (point 1). Crystalline fraction (figures A2 & B2) is favored at 200 sccm, 1 mbar (point 1) and 300 sccm, 1 mbar (point 2) for both the current conditions. The overall probability of
forming QDs (figures A3 & B3) is higher at higher silane flows for 30 A condition. At 40 A condition, 300 sccm and 0.7 mbar (point 1) has a pretty high overall probability with ~35%. Based on the previous hypotheses, the condition favorable for the formation of these QDs is with high concentration of silicon based radicals and a comparatively lower interaction parameter. Incidentally, the standard condition of deposition used in the previous setup (without copper tube) performs not too well for the formation of these QDs in the modified setup (with copper tube). Although the fraction of QDs formed in these conditions are low, there is also a trend observed wherein higher silane flows are found to be favorable for the formation of these QDs. The crystalline fraction in the 30 A condition however is quite low possibly due to insufficient ions in the plasma to cause sufficient dissociation of the injected silane.

Figure 4.9 Probability of forming QDs with 519.5 cm$^{-1}$ stokes shift under 30A (top left) and 40A (top right) plasma current; Crystalline fraction of QDs formed under 30A (mid left) and 40A (mid right) plasma current; Overall probability of formation of QDs under 30A (lower left) and 40A (lower right) plasma current.

Note: Scales are different for the top, mid and bottom graphs.

Assuming that the issue with the injection ring did not affect the results, the ideal deposition condition is 40 A current, 200 sccm silane flow, and 1.3 mbar chamber pressure. Note that for
practical reasons in the remaining part of this report 30 A current, 230 sccm silane flow and 1 mbar chamber pressure is used instead of the ideal ones. Although not ideal, these conditions also result in a reasonable QD production of ~23%.

4.2 Spin Coating
After the deposition of QDs, the next step is to bring these into dispersion and spin coat them onto a substrate along with silver nanoparticles to form the DC layer. Section 4.2.1 describes the procedure to make a dispersion of the QDs followed by section 4.2.2 which describes the procedure to make a dispersion of Ag NPs. After that, section 4.2.3 focuses on the development of a procedure for spin coating to achieve a uniform distribution of QDs over silver nanoparticles.

4.2.1 Dispersion of QDs
The objective of this section is to make a dispersion of QDs. Before the procedure for dispersing the QDs is developed, calculations are made for the concentration of the dispersion. The deposition rate at the deposition conditions in CASCADe has been found to be about 0.7 mg/s. The substrates to be used for spin coating are 10*10 cm$^2$ corning glass and the calculations for the amount of quantum dots required for spin coating a QD layer with a target thickness of ~100 nm is as elucidated below –

\[
\text{Volume} = 100cm^2 \times 100 \times 10^{-7} \text{ cm} = 10^{-3} \text{ cm}^3
\]

\[
\text{Density of c-Si} = 2.65 \text{ g/cm}^3
\]

Assuming a porosity (refer section 2.2.1) of 90% post spin coating, the required weight of quantum dots on the substrate for spin coating is 0.265 mg. Further assuming that 50% of the quantum dots are lost as spin off, the weight required per sample comes out to 0.53 mg/sample.

Since the particles are nascent (devoid of coatings), there is a chance of agglomeration of these particles in the dispersion. A high concentration would result in achieving the target thickness within one spin cycle. However, it increases the risk of agglomeration as the probability of inter-particle interaction increases. A low concentration on the other hand reduces the chance of agglomeration. However, a low concentration would result in the requirement of higher volumes of the dispersion to achieve that target thickness which would increase the number of cycles required for spin coating. As mentioned in section 3.2, this might be deleterious as subsequent spin coating cycles might affect the deposition achieved in the previous spin cycle. A moderate concentration of the dispersion needs to be chosen so as to reduce the risk of agglomeration as well as prevent the requirement for multitudes of spin cycles to achieve the target layer thickness. Dispersions with 1 mg/mL have been noted in literature [4.4, 4.5] wherein one is with a surface coating. The dispersion to be prepared in our case was targeted at 0.4 mg/mL which requires about 1.5 mL of the dispersion for the above mentioned assumptions to achieve the target thickness. The dispersion in such quantities is assumed to be appropriate for spreading through the substrate during spin coating. As a result, a deposition time of 120 seconds was chosen in the CASCADe setup for a solvent of 200 mL. The substrate with QDs was then weighed and introduced in a jar containing 200 mL of the solvent. The system was then subjected to treatment in ultrasonic bath to aid the removal of the QDs from the substrate into the dispersion. The dispersion was then made as mentioned in section 3.2.1. After the removal of the substrate, the dispersion was transferred to a container and the substrate measured for its weight after drying. It was noted visually that some of the QDs remained on the substrate. Weight measurements showed that the weight of the QDs introduced in the dispersion was only 30 mg.
Later, another deposition was made to make a dispersion of the QDs in ethylene glycol for which a 920 sec deposition time was used. It was noted that post exposure to ultrasonic bath, the amount of QD remnant on the substrate was substantial. This is evident from the brown regions in the substrate shown in figure 4.10 which represent thicker QD layers. The results of both depositions are shown in table 4-1. From the table it can be seen that the net quantity of QDs that got transferred into the dispersion is lower than that of the 120 sec deposit. It is believed that the QDs formed initially tend to agglomerate under the influence of temperature of the plasma. Since we can see a similar behaviour in the 120 sec deposition as well, it is possible that there is an “agglomeration front” that is formed progressing through the deposited layer upon exposure to the temperatures of the plasma. This would mean that a higher deposition time will not be suitable for the deposition of large number of QDs especially with the 9.6 nm particles (suitable for c-Si solar cells) which require higher current as higher current mean higher temperatures.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time</th>
<th>Weight after deposition</th>
<th>Weight after dispersion</th>
<th>Weight of QD in dispersion</th>
<th>Solvent volume</th>
<th>Final concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>120 sec</td>
<td>8.777 g</td>
<td>8.747 mg</td>
<td>30 mg</td>
<td>200 ml</td>
<td>0.15 mg/ml</td>
</tr>
<tr>
<td>2</td>
<td>920 sec</td>
<td>9.341 g</td>
<td>9.321 mg</td>
<td>20 mg</td>
<td>200 ml</td>
<td>0.10 mg/ml</td>
</tr>
</tbody>
</table>

Table 4-1 Concentrations of QDs dispersion made through CASCADE.

Figure 4.10 Substrates used for making QD dispersions post ultrasonic bath. The substrate used for making dispersion in ethylene glycol (left) shows a higher degree of remnant QD on the substrate compared to that for a dispersion in ethanol (right).

The dispersion has been prepared. However, the concentration of the dispersion being lower than our calculations, a higher quantity of ~3.5 ml would be required during the spin coating process.

4.2.2 Dispersion of Ag NPs

The next step to achieving the DC layer is making the dispersion of Ag NPs. As mentioned in section 3.1.2, Ag NP powders were purchased from Skyspring Nanomaterials, Inc. These will be made into a dispersion as well in order to spin coat them on to the substrate. A surface coverage of 20% was targeted for the spin coated sample. The concentration of the dispersion required was calculated thus –

Area of substrate = 5*5 cm² = 25*10⁻⁴ m²

Projected area of a 100 nm particle = π*(50*10⁻⁹)² = 25*10⁻¹⁶ m²
Number of particles/sample = \( \frac{25 \times 10^{-4} \times 20\%}{25 \times 10^{-16}} = \frac{2 \times 10^{11}}{\pi} \) particles

Using the density of silver (10.5 g cm\(^{-3}\)), the weight of silver required for one sample is obtained as 0.35 mg. Assuming a 50% wastage during spin coating, yields a concentration requirement of 0.7 mg/ml. 70 mg of the powder was weighed and poured in 100 mL the solvent which was then subjected to treatment in ultrasonic bath for 120 min. The dispersion of Ag NPs thus prepared is then used for spin coating.

### 4.2.3 Spin coating parameters

The objective of this section is to develop a set of parameters for the spin coating of the QDs and Ag NPs. In order to arrive at the spin coating parameters, a few trials were conducted. For the deposition of Si QDs it was mentioned that 3.5 ml of the dispersion would be required. As a first step, 3 ml of the dispersion was used since this was the measurable capacity of the pipette available. The dispersion was first poured on the substrate and then the spinning process was started. It was observed that as soon as the dispersion was poured inside, it spread over the surface rapidly and a part of the dispersion dripped over the extremities of the substrate. Literature [4.7] recommends the use of 300 rpm for 5 sec for initial spreading of the liquid followed by spinning at 1500 rpm. Since the dispersion had already spread in the spin coater, the initial spreading part was skipped and the spinning was done at 1500 rpm. It was observed that most of the liquid dripped over the extremities of the substrate. The substrate upon removal and visual inspection proved to be completely transparent. Assuming that the layer thickness was too low to be visually perceptible, the sample was then viewed under a microscope at 1000x magnification. There was hardly anything visible in the microscope as well. For the sake of confirmation, the sample was tested under the Raman spectroscope as well which yielded nothing but noise despite increasing the laser intensity and measuring at different points on the substrate. Scanning through the surface of the substrate, few particulates were observed which upon testing gave amorphous peaks with very low intensity. It was concluded that there was no deposition found on the substrate. The probable cause for this was surmised as a very high reduction in thickness of the dispersion under the given spin parameters coupled with a lower tendency to precipitate from the dispersion. Over the course of further trials, the speed of rotation was reduced from 1500 through 600, 300 and 150 rpm with only marginal deposits visible through the naked eye. Analysis in the Raman spectroscope proved the same. The reason for this was thought to be high reduction in thickness of the dispersion and either a possible repulsion of the particles from the glass surface leading to most of the particles ending up in the drain or a very low rate of precipitation of the particles from the dispersion. Drop casting of the dispersion was then performed and as expected, the surface distribution was extremely poor although a good quantity of deposition was observed. The use of high temperatures during spin coating was considered as a possible solution however the means to do so in situ were not available. Based on the results observed, two paths were considered for further working.

#### 4.2.3.1 Viscous solvent

In this path, it was considered to use ethylene glycol as a solvent as it has a very high viscosity (refer section 3.2) which would result in lower reduction in thickness of the dispersion during spinning. This would imply more particles available in the dispersion post spinning which would then result in the deposition of larger number of particles.
However, this is accompanied by the problem of agglomeration as noted by Christopherson et al. [1.23, 1.24] mentioned in section 3.2. Also, the boiling point of ethylene glycol being high (197.3°C) leads to a low evaporation rate resulting in the formation of pools of dispersion prior to complete evaporation. This was observed to cause formation of isles of deposition which resemble an agglomeration of the deposited particles. Christopherson et al. [1.23, 1.24] contributes this to agglomeration of the particles while in dispersion. However if the solubility of the QD is reasonably high in the solvent, the QDs would diffuse to the last pools of solvent available before they deposit onto the surface of the substrate. This principle is similar to the one used in zone refining process for purification of c-Si ingots applied in a reverse fashion. This results in a deposition with regions of very high concentrations and little/no deposition in the rest of the areas. To prevent this situation and to be able to proceed further, a modified version of high temperature spinning was considered since there is a chance that at high temperatures, the evaporation would be more uniform. The substrate after the spinning of the dispersion was kept in a high temperature platform (heater) to aid faster evaporation of the solvent. Heating prior to spinning was prevented to avoid damage to the chuck (plastic) on which the substrate is placed in the spinner. The temperatures were increased from 150°C to 300°C. The increase in temperature although reduced the degree of pooling/coalescence of the dispersion, did so only marginally and was not found useful for our purpose. The use of a viscous solvent was hence dropped.

4.2.3.2 Lower rate of application of dispersion

In this path, it was considered to limit the amount of dispersion poured during spinning to a very low value. By doing so, the precipitation of the particles onto the substrate is enhanced as the evaporation of the smaller unit of dispersion happens faster due to higher surface area to volume ratio. When the dispersion evaporates during the course of spinning, the particles cannot migrate to adjoining droplets through diffusion and hence are forced to deposit on the substrate. However by doing so, there is a chance that the dispersion poured later affects the deposition achieved from the droplets poured before as is also mentioned in section 3.2. Also, if the subsequent droplets are poured before the evaporation of the droplets poured before, it would reduce the precipitation of the particles (QDs or Ag NPs) from the previous drops. In order to be able to proceed, a trial was conducted to study the evaporation characteristics of the solvent during spinning. It was noted that a drop (~0.04 ml) of the dispersion evaporated in ~3 sec in 1500 rpm condition. Spinning was tried with varying speeds at one drop of the dispersion being dropped every 3 secs. The sample at 1500 rpm showed streaks of deposition moving radially outwards. The depositions were better visible a little away from the centre (of the substrate) and the streaks had a lower deposition at the centre (along its thickness) and higher deposition at the edges indicating that the QDs had been deposited along the way as the droplet moved outward during spinning. This confirms our speculation that the dispersed particles precipitate better when the solvent evaporates. Similarly depositions were tried at 600 rpm and 300 rpm. The lower the speed, higher the thickness of the streaks observed along with an increase in the meandering of the streak path. Also, the depositions ended before the end of the substrate in case of lower speeds. This could probably be explained as the result of coalescence of subsequent drops which coalesce and drip off the substrate. Since the droplets coagulate, the particulates are retained within the dispersion and hence lack of deposition close to the edges.
It was decided to proceed at 0.4 ml/cycle wherein one cycle included a spinning at 300 rpm for 5 sec to facilitate spreading of the dispersion over the substrate followed by a spinning at a higher speed of 1500 rpm. The samples of QDs upon visual inspection showed a circular central region with a lower but uniform deposition and an outer region with streaks as mentioned before. It must be noted however that the spin coated QD samples upon inspection through the microscope reveal extensive agglomeration of the particles. The central region exhibits lower agglomeration while the degree of agglomeration increases as we go to the extremities. Agglomeration of QDs possibly occurs in the fabrication stage itself due to the conditions present (refer section 4.2.1) and ultrasonication perhaps possesses not enough energy to separate the QDs. Hence, agglomeration would reduce the distance between nanoparticles thereby aiding the energy transfer between the particles. However, the aim is to enhance the radiative decay in QDs for which the Ag NPs need to be tuned to resonate at wavelengths close to the bandgap of the QDs. The QDs are not monodisperse. Hence, agglomerates with QDs of different sizes would make it impossible to tune the size of the Ag NPs. Or in other words, the Ag NPs would only enhance the radiative decay rate in part of the QDs which have the desired emission wavelength if they are available within the field of influence. Hence, agglomeration is not desirable.

In case of Ag NPs, higher spin speeds were tested and the target spin speed was increased to 2500 rpm. The depositions were observed to possess a uniform central distribution and outer regions with more disperse black patches similar to the ones observed by Christopherson et al. [1.23, 1.24]. The inspection of Ag NPs under a microscope proved difficult. SEM images indicate an extensive agglomeration of the particles as is shown in figure 4.11. It is expected that agglomeration would possibly disrupt the plasmonic effect observed thereby rending the nanoparticles useless.

![SEM image of spin coated Ag NPs exhibiting agglomeration of most of the particles.](image)

Figure 4.11 SEM image of spin coated Ag NPs exhibiting agglomeration of most of the particles.

The Ag NP samples were prepared after preparing the dispersion and subjecting it to ultrasonication for 120 minutes. The use of surfactant seems unavoidable to prevent agglomeration of these particles.
The spin coating parameters for QDs and Ag NPs have thus been identified as 0.4 ml/cycle of dispersion, initial spreading at 300 rpm for 5s followed by spinning at 1500 rpm for QDs and 2500 rpm for Ag NPs.

4.3 Reflection-Transmission (RT) measurements
The objective of this section is to measure the reflection and transmission spectra of the generated samples using the integrating sphere (see section 3.3.2). The sample side were measured in all cases.

The following types of samples were used:
A. Spin-coated QDs
B. Metal island film (see section 3.1.2)
C. Spin-coated Ag NPs
D. Metal island film with spin-coated QDs on top

In order to have a reasonably good base for comparison of data, the same Ag NP samples (sample type B) measured are in turn used for spin coating of QDs on top and then measured again (sample type D).

4.3.1 RT measurements of spin-coated QDs (sample type A)
In this section, the RT measurement of QDs spin coated on glass substrate is presented. This will serve as a reference for comparison of QDs in the presence of Ag NPs. Since the spin-coated QD samples are not entirely uniform (see section 4.2), the measurement was performed at different parts of the sample. It was noted that although there were minor variations observed, the standard deviations were negligible. The results of the above measurements are shown in figure 4.12 in the form of an error bar plot where, the error bars represent the standard deviation among the measurements. The centre of the sample was chosen as a standard area of measurement as it is very close to the average values.

![Reflection vs Wavelength Graph](image_url)
Figure 4.12 Reflection and transmission spectra of spin coated QDs (sample type A) measured at different locations and the standard deviation plotted as error bars.

The reflection and transmission spectra of QDs were then studied with an increasing volume of dispersion used during spin coating. The absorption in the QDs was calculated by using the formula,

\[
\%\text{Absorption in QDs} = 100\% - (\%\text{Transmission} + \%\text{Reflection} + \%\text{Absorption in glass})
\]

The results are shown in figure 4.13. It is seen that there is a decrease in the degree of transmission (figure 4.13a) as the amount of QD deposited increases. This is expected as QDs absorb light due to low radiative emission attributed to its indirect bandgap. The reflection spectrum (figure 4.13b) however shows a peculiar trend wherein, lower reflection is observed in the wavelength range of \(\sim325\text{ nm} - 450\text{ nm}\). The degree of lowering seems to be proportional to the concentration of the QDs on the substrate indicating that the phenomena observed is caused by QDs. Similarly, an increase in the reflectivity is observed in the remaining region with increase in the QD concentration. It must be noted that the fluctuations observed beyond 860 nm is due to a change of detector to one with lower sensitivity. The absorption spectrum (figure 4.13c) is looked into to see if selective absorption could explain the observed trend. Although there is higher absorption observed at the concerned wavelengths of 325 nm – 450 nm which also increases with increasing concentration of QDs, it does not correlate properly with the rest of the wavelength regions.
Figure 4.13 Reflection, Transmission and Absorption spectra of spin coated QDs (sample type A) with different amounts of deposition compared to glass.
To view the trend better, the difference between the reflection spectra of the QD samples with that of glass is plotted (figure 4.14). It is seen that the reflection from the QD surface is lower than that of glass in the 325 nm – 450 nm range peaking at ~375 nm followed by an increase in reflection peaking at ~640 nm. The decrease in the relative amount of reflection can be attributed to the absorption in the QDs but the trends in reflection below 325 nm and above 450 nm does not follow with the absorption spectra. Also, the rate of increase in the region above 375 nm does not correlate with the rate of decrease in the absorption spectra. Another phenomena leading to an increase in the reflection is suspected.

1. It is speculated that re-emission of absorbed photons could play a role. The re-emission increases the probability of photons being directed away from the glass interface which would be perceived as reflection. However, this would cause a more or less uniform increase.

2. It is also possible that scattering of light by the QDs plays a role. Since the light is scattered, the probability of photons hitting the glass interface at an angle above the critical angle is increased. However, since the QDs are a mixture of different sizes and due to the presence of high amounts of agglomerates, the trend would be less predictable and not have a clear peak as observed in the current results.

3. The effect of down conversion if present would present with a peak at a wavelength lower than 550 nm and a rapid change should have been observed after at about 550 nm. Such a trend is not observed in the present case.

At this juncture, a clear explanation for this phenomenon seems difficult.

![Figure 4.14 Difference in reflection between the QD samples and plain glass.](image)

From the measurements of QDs, we have seen that the transmission decreases with an increase in the number of QDs and the absorption increases with an increase in the number of QDs as would be expected. The reflection on the other hand exhibits a peculiar trend with a decreased reflection in the range 325 nm – 450 nm followed by an increase in reflection in the rest of the spectrum. The reason for such a trend is only speculated and not investigated further.
4.3.2 RT measurements of Ag NPs

In this section, the RT measurements of Ag NPs are presented. These measurements along with those of QDs and plain glass are used as a reference for the measurements of QDs in the presence of Ag NPs. Two types of Ag NPs have been used as part of this thesis namely the powder which is made into dispersion and spin coated and the metal island films. The metal island films (sample type B) will be discussed in section 4.3.2.1 followed by the spin coated Ag NPs (sample type C) in section 4.3.2.2.

4.3.2.1 RT measurements of metal island films (sample type B)

The RT spectrum of the metal island films was studied next and the results are as shown in figure 4.15. The transmission (figure 4.15a) and reflection (figure 4.15b) spectra show that there is resonance occurring in metal island films. The resonance occurs at approximately 490 nm with a higher order resonance at 360 nm (quadrupolar mode). This clearly indicates the plasmonic nature of these particles. As a result, there is also a considerable amount of absorption in the Ag NP layer.
Based on the resonance behaviour, it was tried to calculate the size of the Ag NPs using the Mieplot simulations using the refractive index of air and varying the size of the silver particles. It is observed that a similar behaviour is observed in particles with a size of ~160 nm. The silver layer deposited through PVD was 12 nm for this sample prior to formation of nanoparticles through annealing. Another sample with a 10 nm deposition thickness was also prepared which through a similar analysis is observed to correspond to 140 nm particles. This is close to the required size of 150 nm as mentioned in section 3.1.2.

4.3.2.2 RT measurements of spin coated Ag NPs (sample type C)

The RT spectrum of the spin coated QD was studied next and the results are as shown in figure 4.16. It is seen from the transmission and reflection spectra that there is no resonance behaviour in these samples as compared to the metal island films. The agglomeration observed in these particles (figure 4.11) is believed to be the reason for not observing the plasmonic behaviour. Hence, these spin coated Ag NPs will not be used and QDs will be spin coated only on the metal island films for further studies.
Figure 4.16 Reflection and transmission spectra of spin coated Ag NPs (sample type C).

4.3.3 RT measurements of QDs combined with Ag NPs

The combination of QDs and Ag NPs (metal island films) is then measured to see if the enhancement of the radiative emission in QDs is visible in the transmission spectrum of the DC layer. The comparison between QDs, Ag NPs, and QDs spin coated on Ag NPs and glass is shown in figure 4.17. It is seen that the transmission (figure 4.17a) through the combination is slightly lower than that in either individually. This indicates that the down conversion happening in the QDs is either negligible or not adequate enough to overcome the losses incurred in the individual layers (QD & Ag NP). The reflection spectrum (figure 4.17b) of the combination is almost the same as that of Ag NP alone. This is probably because Ag NPs dominate the reflection spectrum compared to QDs which deviate very little from the reflection spectrum of glass. It is also seen that when the silver particles are coated with QDs, the change in the resonance wavelength is negligible indicating that the QDs do not change the refractive index around the silver nanoparticles. This indicates that the QD layer formed is highly discontinuous and that the distribution of QDs is scarce. A uniform QD layer would have changed the refractive index surrounding the Ag NP layer which in turn would have red shifted the resonance peak. It is believed that the lack of enhancement in the transmission spectra due to down conversion coupled with the lack of red shift in the resonance wavelength of the Ag NPs is due to the scarce distribution of the QDs. The absorption spectra (figure 4.17c) show that the amount of absorption in the combination of QDs and Ag NPs is higher than that in plain Ag NPs. Further, the absorption in the QDs spin coated on the Ag NPs was compared (graph not presented) to the sum of absorptions observed in a similar QD layer and Ag NP layer. It was observed that the absorption in the combination is either marginally higher or lower than the sum of the individual absorptions affirming that there is not much of interaction happening between the QDs and the nanoparticles.
Figure 4.17 Transmission, Reflection and Absorption spectra of QD (1.5 mL) spin coated on Ag NP, Ag NP, QD and glass.
From the RT measurements, it has been observed that the spin coated Ag NPs agglomerate in the solution thereby losing their plasmonic behaviour. The metal island films exhibit plasmonic behaviour and are in the size of these particles is in the desired range of ~150 nm. The QDs exhibit a decrease in transmission and an increase in absorption with an increase in concentration of QDs as expected. However, the reflection spectrum had peculiar characteristics. Further investigation is required to comment on this behaviour which is not done within the scope of this thesis. The QD layer spin coated on the metal island films is discontinuous and hence, down conversion is not clearly seen in the spectrum.

4.4 PL Measurements
The objective of this section is to measure the enhancement in the PL spectra of QDs in the presence of Ag NPs. In order to do this, the PL of the QDs is measured and compared with that of QDs in the presence of Ag NPs. The spectrum of the bare substrate is also taken to affirm the obtained result.

As mentioned in section 3.3.1, the photoluminescence (PL) spectrum can be captured in both the Raman spectroscope and the Horiba PL setup. The PL measurements done in the Horiba PL setup is mentioned in section 4.4.1 followed by the PL measurements in the Raman setup in section 4.4.2.

4.4.1 Horiba PL measurements
The Raman spectroscope focuses the laser beam to a very narrow spot and hence, the readings obtained would be of a specific spot and might not represent the whole sample. This would make comparison of different spin coating parameters difficult. The Horiba setup on the other hand although is a dedicated setup for PL measurements, is found to exhibit poor reproducibility due to unknown reasons. Also, the measurement of QD samples has been found to be difficult prior owing to the rough surface of the QDs. This is because, the PL setup measures the spectral reflection and QDs have poor spectral reflectance. However, it provides an area measurement which is required to compare samples from different spin coating parameters. Due to this, measurements were tried in the Horiba setup. While preparing the instrument for initial measurements, it was noted that the spectral range for measurement depends on the excitation wavelength (λ_{exc}). The upper limit of the measured spectral range is practically limited to a value lower than 2*λ_{exc}. The limitation arises from the fact that second harmonics (higher order emissions) are emitted from the source which would mask the signal from the PL spectrum. Hence, down conversion cannot be observed as it presents itself in the wavelengths (λ_{exc}/n) where n is a positive integer greater than 1. Plain glass was first measured and it was noted that the glass exhibited a PL spectrum. The PL spectrum of the QDs was observed to be similar to the spectrum of plain glass. The results couldn’t be adequately compared due to lack of standard for normalising the spectra. Hence, the comparison of different samples could not be done.

4.4.2 Raman PL measurements
In order to measure the enhancement in the PL spectra, the Raman spectroscope was used to study the effect of silver nanoparticles on the QDs. The PL spectra of the bare substrate and Ag NPs on the substrate are presented first. This is then followed by that of QDs on Ag NPs and comparison of QDs on Ag NPS with that of QDs with similar features (dimensions/surface coverage).

The excitation beam (laser) used in the Raman spectrometer are of 514 nm and 628 nm wavelengths. Also, the detector could measure only up to 1000 nm. Hence, down conversion could not be observed here either. The laser intensity can change when the laser source is restarted. In order to
have comparable readings, the Stokes peak is taken as a standard to normalise the spectra. In those samples which didn’t have any (glass, Ag NP on glass etc.), the Stokes peak observed in the calibration (done using Si wafer) reading is used as a crude reference standard. The PL spectrum of glass (corning), wafer, Ag NP on glass and wafer were taken (figure 4.18, 4.19). The wafer showed no PL spectrum as expected. This is due to the emission wavelength of silicon being close to 1.08 eV or ~1150 nm which is beyond the measured range. The introduction of Ag NPs on the surface of the wafer introduces a low yet observable PL with multiple peaks between 550 nm and 750 nm apart from the peak at 542 nm. The peak at 542 nm also occurs in the plain wafer but is so weak that it is hardly visible in the graph.

![Figure 4.18 PL spectra of Si wafer (top) and Ag NP on Si wafer (bottom).](image)

The plain glass (figure 4.19a) exhibited photoluminescence although of low intensities (0.12 a.u. max @ 760 nm) with multiple peaks between 500 nm and 900 nm. Such peaks are mentioned in literature [4.8] and they are attributed to the oxides which make up the glass. The 530 nm peak is attributed to MgO [4.9] but, sources for PL at other wavelengths were not found in the literature.
The introduction of Ag NPs on the glass diminishes the PL observed in plain glass and introduces peaks similar to the ones observed when Ag NPs are deposited on the wafer surface indicating that these PL belong to the Ag NPs. The twin peaks at 554 nm and 560 nm correspond to Ag$_2$O and Ag$_2$S bonds \[4.1\] while the sources for PL at other wavelengths were not found in the literature. These could perhaps correspond to the resonance behaviour of the particles. The PL intensity observed in glass and Ag NPs on glass although can be used to understand the behaviour cannot be used for comparison purposes since they lack a reliable standard for comparison (normalised based on the Stokes peak of calibration measurement).

![Figure 4.19 PL spectra of glass (top) and Ag NP on glass (bottom).](image)

Having looked at the PL spectra of the substrate and Ag NPs deposited on the substrate, we now look at the PL spectra of QDs spin coated on metal island films. Using the measurement in vertical direction (section 3.3.1), it was noted that QD agglomerates of up to 5 µm were formed. Several of these were measured and similar QDs in the presence and absence of Ag NPs were compared. The spectrum of QDs which are agglomerated to a lower extent (low size of the agglomerate) are shown in figure 4.20. A dense distribution (higher coverage) of QD agglomerates is observed to emit a good PL spectrum (blue) compared to the scarcely distributed (low coverage) QD agglomerates (embedded picture in figure 4.20). This is possibly because the probability of Auger interband relaxation decreases with increase in inter-particle distance and that more QDs are present in the densely populated region.
The PL spectra of QD films (densely distributed thin layer of QDs) of ~100 nm thickness are shown in figure 4.21. It can be seen that the PL observed is lower than that observed in the densely distributed layer shown in figure 4.20. This is probably because QDs of various sizes are present and perhaps more favourable size distribution was present in the former.

A trend was observed in the PL spectrum as a function of size. As mentioned in section 2.2.1, an optimal thickness of the QD layer is required to get the maximal PL output. Assuming that the distribution of QD size within the agglomerate is similar in the different agglomerates, the trend is analysed. It is seen from the graph (figure 4.22 top) that the PL intensity decreases with increase in the size of the agglomerate. Hence, the optimal thickness is probably less than 2.2 µm. The PL intensity of QDs in the presence of Ag NPs on wafer shows that there is an increasing trend up to 900 nm (figure 4.22 mid) while a decreasing trend is observed above 900 nm (figure 4.22 bottom). The optimal thickness is perhaps between 0.5 µm and 1.9 µm.
Figure 4.22 PL spectra of QD agglomerates of different sizes in the presence of Ag NPs on glass (top) and wafer (mid, bottom); a typical agglomerate is shown in the embedded picture.
From the various PL measurements, QD agglomerates with similar size (thickness) and distribution were chosen with and without Ag NPs and the PL spectra compared as is shown in figure 4.23. As can be seen, there is a clear increase in PL intensity in the presence of QDs.

The degree to which the intensity is increased is measured as the PL enhancement factor calculated as the ratio of PL intensity of the QDs in the presence of Ag NPs to that in their absence. The result is plotted in figure 4.24.

It is seen that there is a considerable enhancement observed. Based on the observations from literature (section 1.2.3) an enhancement factor from a little more than 1 till 60 folds is observed. The 60 fold increase is observed when the QDs are placed at strategic points where the plasmon intensity is the highest. In our case, an increase of up to 50 fold is observed in case of a 100 nm film. It is worth pointing out that although such a high enhancement is observed; neither the silver nanoparticles nor the QD layer is the ideal layer as was desired. An increase of up to 25 fold is observed in case of particles similar to moderately dense QD distribution shown in figure 4.19 and
up to 9 fold increase is found in case of a 2.2 µm agglomerate. It must also be noted that for the measurement of PL in Raman spectroscopy, the photons emitted back in the direction of the incident beam (specular reflection) are collected and analysed in the spectrograph. Since the QDs make the surface rough, the specular reflection is low. This coupled with the surface of the QD agglomerates being non-flat, reduces the specular reflection further. Although a trend is clearly observed in the above graphs (for agglomerates), a lot of noise is also observed. Hence the absolute enhancement factors might deviate a little to the higher or the lower side. This introduces the possibility of observing higher PL intensities and enhancement factors provided the short comings of QD size, corresponding Ag NP size, introduction of spacer layer, and issue of agglomeration are tackled.

From the various PL measurements, it is observed that considerable PL enhancement is observed in the QDs in the presence of Ag NPs which is greater than most of the claims in literature. It is considered that the presence or absence of QDs of favourable sizes (2 - 5 nm) during measurements could affect the degree of enhancement observed. However, the enhancement is observed to be consistently on the higher side which indicates that the variation in the distribution of QDs in the measured regions if present is not much.

To summarize, the QDs were successfully fabricated in the CASCADE with factorable size ranges, made into a dispersion and spin coated on the substrates based on the procedures developed. The purchased Ag NP powder was also successfully made into a dispersion and spin coated on the substrate although agglomeration proved to be deleterious to its plasmonic properties. The metal island films proved to be useful in their stead to study the enhancement in photoluminescence of QDs and the QDs were successfully spin coated on them. However, the QD layer was discontinuous and scarcely distributes as a result of which, down conversion could not be observed in the RT spectrum.
5. Conclusions & Recommendations

5.1 Conclusions
The primary objective of this thesis was to fabricate a down conversion layer using cheap techniques and to observe if the increase in the photoluminescence of QDs in the presence of Ag NPs proves useful with regard to the efficiency of down conversion. It is observed that the DC layer can be made using these cheap techniques.

5.1.1 Silicon Quantum Dots
The optimal parameters for the deposition of Silicon QDs were to be found for the modified CASCADE setup and through the course of experimentation, it was observed that the standard deposition conditions used in the original setup were usable in the modified setup as well. However, deposition conditions which yielded higher QD fraction were also observed. These were in comparison to the standard conditions more favorable but due to the melting of the injection circle, the reliability of the results was slightly questionable. Also, it is preferable to have more data points to form a clearer picture of the effect of deposition parameters on the QD yield.

The QDs fabricated in the CASCADE setup were found to be agglomerated and of varied sizes. It is unknown to what degree subjecting the dispersion to ultrasonic treatment had any effect on agglomeration. For the application considered (DC layer), it is preferable to have a monodisperse QD dispersion with no agglomeration.

5.1.2 Silver Nanoparticles
Due to lack of sufficient know how on the fabrication procedure of Ag NPs via chemical synthesis route in house, they were purchased from the market. The nanoparticles when made into dispersion were observed to agglomerate quite fast. Subjecting the dispersion to ultrasonic vibration did not prove useful enough. As a result, the samples spin coated didn’t exhibit any resonance. However, the alternate route (PVD + Annealing) that was chosen for comparison of results proved useful in determining the influence of Ag NPs on the Si QDs.

5.1.3 Spin coating procedure
Although the spin coating of QDs proved challenging, a set of parameters was arrived upon for spin coating the QDs onto a substrate. However it must be noted that this set of parameters corresponded to a dispersion of agglomerate of QDs. In case of a dispersion containing individual QDs especially if agglomeration is prevented by the use of coatings, the parameters would change.

Similarly, set of parameters were arrived upon for the spin coating of Ag NPs but the same argument mentioned for QDs holds true for Ag NPs as well.

5.1.4 Effect of quenching
It was decided to study the effect of quenching by comparing samples with and without a passive separator layer between the Ag NPs and the QDs but, due to difficulties with equipment, this step could not be completed.

5.1.5 Effect of Ag NP on Si QD photoluminescence
The Ag NPs were found to be highly influential on the PL spectra of the QDs with an enhancement of up to 50 fold. It is noteworthy that this result has been achieved despite the QDs being of random
size which is supposed to decrease the enhancement observed. This indicates that further enhancement can be expected with monodisperse QDs. Also, the 60 fold improvement that was observed in the literature was achieved when the QDs were placed at specific locations between the Ag NPs where the electromagnetic intensity was maximal. Although such high gains are observed in the PL spectrum, it does not present itself as an increase in the transmission spectra of the DC layer due to the poor quality of the QD layer formed.

5.2 Recommendations
The prime concern with regard to the DC layer was the agglomeration of the Ag NPs and Si QDs. In case of Ag NP dispersion formed from powder, sufficient quantity of surfactants can be added to the solvent and once the powder is dispersed, the dispersion kept in an ultrasonic bath for uniform coating of the surfactant on the Ag NP surface. Popular surfactants for silver are sodium dodecyl sulfate (SDS), dioctyl sodium sulfosuccinate (AOT) and cetyltrimethylammonium bromide (CTAB). Based on the size of the Ag NPs and the concentration of the dispersion to be made, the amount of surfactant required can be calculated. A little excess surfactant will help prevent any agglomeration caused due to deviation between calculation and reality. Also, it is advisable to measure the dispersion stability to see if the dispersion is uniform enough during the spin coating process and if not, measures need be taken to make the dispersion stable. However, the dispersions made during the course of the thesis work were observed to yield to sedimentation only after a couple of weeks which indicates a good dispersion stability. Hence, the solvent chosen seems to be good enough for our purpose. The surface modification on the other hand might change the properties of the surface plasmon which needs to be confirmed before deciding on the final size of the nanoparticle.

The Ag NPs available in the market have either quite a varied size distribution in the required size range or are not economic. It is preferable to develop the knowhow for the technique in-house for better control on size. This is also beneficial in the aspect that the surfactants are spread over the surface of the NPs during the fabrication step itself.

With regard to the Si QDs, it was suspected that the agglomeration had already occurred when the QDs were deposited on the substrate in CASCADE. The inspection of the samples under the microscope (1000x magnification) post spin coating showed that there were particles of close to 100 nm as well (viewed as dots since 100 nm is the limit of resolution for 1000x magnification). Based on this and the agglomeration front talked about in section 4.2.1, it can be suggested that the agglomeration is soft at the outer edge (the latest deposition layer) and becomes harder towards the substrate. Soft agglomerate is one which breaks apart when subjected to shear stresses like in an ultrasonic bath [5.1]. It is possible that the agglomeration front can be deflected by placing the substrate farther away from the injection circle. If the substrate were to be placed on the stage directly, the use of the shutter will be possible and the fluctuations in the plasma during the initial stages can be eliminated. However, this increases the residence time of the particles allowing growth to higher sizes. This would require a repetition of the study for these conditions. By adopting this measure, it is possible that the QDs are only soft agglomerates in case of which, they can be dispersed better in the solvent through prolonged ultrasonic treatment [5.2]. However, ultrasonic treatment is only a temporary solution [5.3, 5.4] as the particles cluster together over time as the dispersion strength is low. In case clustering occurs before spin coating after treating the dispersion in an ultrasonic bath, surface modification can be sought. Gupta et al. [5.5] suggest a valuable method for the same but care must be taken while choosing the alkenes so as to not hinder with the
A auger process of interband relaxation which is dependent on inter-particle distance. Etching of particles with higher sizes produced in the CASCADE can also be thought of to get a more monodisperse QD distribution.

In CASCADE, deposition parameters which seemed to provide higher QD fraction were observed but were preferred over with the standard deposition parameters due to lower reliability. Depositions in these conditions need to be repeated with the new injection circle to confirm the results obtained. It is preferable to increase the number of data points from that of table 3-1 to understand better the role of parameters of deposition. It was mentioned in section 3.1.1 that the chamber pressure is observed to be difficult to control as the set pressure is increased. This difficulty arises due to an increase in the chamber pressure over time observed during the depositions in CASCADE. An increase was observed in all cases (0.7 mbar to 1.3 mbar) however the rise was lowest in 0.7 mbar and increased with increase in set pressure. The increase is of the form,

$$P(t) = P_f * (1 - e^{bt})$$

Where, $P(t)$ is the instantaneous pressure and $P_f$ is the set chamber pressure. The term $b$ which shall be named as delay factor is observed to be inversely proportional to $P_f$. As the $P_f$ increases, the time required for the system to stabilize at the set pressure increases. More insight into the plasma dynamics is necessary to make a reasonable comment on it. However, the value for $b$ can be derived through experiments and a counter measure to adjust the pressure by opening the valve to the root pump can be employed and investigations at further higher pressure could be performed. With regard to the current, placing the sample on the stage instead of the temporary stand would help reduce the heating of the substrate and also reduce the plasma pressure which is speculated to be responsible for the decreasing rate of deposition observed in case of 600 sccm silane flows.

It was difficult to incorporate the spacer layer during the course of the thesis. Since a deviation on either side has a considerable impact, a method to deposit the spacer layer with minimal tolerance needs to be found. After the improvements have been incorporated in the silver and silicon nanoparticles, the spacer layer needs to be incorporated and measurements done.

The reflection spectrum for the Ag NP + QD exhibited hardly any difference from that of the Ag NPs alone. The major reason for this is the poor QD layer that was achieved. However, to understand the degree of reflection that might be observed when the DC layer is incorporated on a solar cell, it might be helpful to incorporate the DC layer on a silicon wafer and do the measurements.

The reflection spectrum of QDs showed peculiar trend of deviation from that of glass. Further studies need to be done to understand this effect.

Based on the configuration chosen, it is possible to replace the ARC in a solar cell. A gradient in refractive index is observed from the outer edge to the solar cell in the DC layer. The spacer layer would have a refractive index of 1.5 (SiO2), the QD layer of approximately 1.7 (assuming 50% porosity), ~2 (AZO) for the conductive layer followed by ~3.5 for the C-Si layer. Optics suggests that a gradient when introduced reduces the reflection from the surface. For this purpose, anti reflective coating (ARC) like silicon nitride is deposited on top of solar cells. This reduces the overall reflection
from 39% to ~25%. The gradient provided by the DC layer without the silver particles reduces it further to 12% if only the refractive index is considered. However, the role of silicon and silver requires simulations to assess the change in efficiency due to the removal of ARC.
Bibliography


[1.5] BP Statistical Review of World Energy 2010

[1.6] Mitigation of climate change, Climate change 2007 http://books.google.nl/books?id=U_4ltxID60UC&printsec=frontcover#v=onepage&q&f=false


[2.10] Figure provided by R. Santbergen combines an image from Bohren and Huffmann (ISBN 978-0-471-29340-8) (black lines) and a MEEP simulation performed by S. Solntsev.


[3.7] Łukasz Brzozowski, Photovoltaics Research Program, Department of Electrical and Computer Engineering, University of Toronto


Appendix A

Simulation of Spectral Conversion efficiency limit

As an added effort, the effect of up conversion was also studied along with the combined effect of the two spectral converters on the efficiency limit of the solar cell. For the up converter, it was assumed that all photons with energy above half the bandgap energy of the solar cell would be up converted.

In case of down conversion, the increase in efficiency is expected to be higher as the bandgap energy decreases. On the other hand, the efficacy of an up converter layer is higher at higher bandgap energies. Since the AM spectrum has a Planck distribution and considering the assumption that photons with energy less than the bandgap and above half the bandgap energy are only being up converted, the number of photons available for up conversion increases and then decreases. Hence, a peak is expected where a balance is met. This is observed at a bandgap of 1.85eV with an efficiency limit of 48.88%. It can be seen clearly that in order to use an up converter to obtain reasonable increase in efficiencies, one needs to look at materials with reasonably high bandgap. Hence, a-Si solar cells are a better candidate for a UC layer exhibiting an increase in efficiency from 27.54% to 47.48% compared to the c-Si solar cells which exhibit a comparatively lower increase from 32.96% to 38.74%.
It is also worthwhile to look at the combined effect of both spectral conversion layers. In this case, a peak is observed at 1.46 eV with an efficiency limit of 50.38%. The effect of the combination increases the efficiency for c-Si from 32.96% to 48.58% and that of a-Si from 27.54% to 48.42%.

It must be noted that the simulation has been done assuming the emission wavelength of the conversion layer to be exactly same as that of the absorber layer in the solar cell. In case of indirect bandgap materials like silicon, the absorption of light at bandgap wavelengths is quite poor [1,2,3]. Hence, it would be beneficial to adjust the emission wavelength to higher values where an optimal balance between spectral utilisation and absorption efficiency of the absorber layer is met.

Matlab Code:

```matlab
c1c clear all
c=299792458; %velocity of light in vacuum%
h=6.62606876*10^-34; %planck's constant%
e=1.602176462*10^-19; %energy of electron%
Eg=[0.01:0.01:4.5]; %bandgap energy in eV%
am15=importdata('AM15.mat'); %AM1.5 data from file%
Voc=importdata('Bandgap_Voc.mat'); %max Voc for a given bandgap from file%
w=am15(:,1)*10^-9; %wavelength of photon incident in mtr%
am0=am15(:,2); %AM0 spectrum%
g=am15(:,3); %spectrum for global tilt%
dir=am15(:,4); %direct solar spectrum%
Eph=h*c./(w*e); %energy of photon in eV%
np0=am0./(Eph*e); %no of photons at AM0%
npg=g./(Eph*e); %no of photons at global tilt%
npd=dir./(Eph*e); %no of photons at direct sunlight%
Eem_DC=Eg; %[0.01:0.01:Eg];
Eem_UC=Eg; %[0.01:0.01:Eg];
T=300; %temperature of cell in K
voc=Voc.((1.38065803*10^-23*T)/(1.602176462+10^-19));
FF=(voc-log(voc+0.72))/(voc+1);
```
%normal solar cell%
np0_abs=zeros(length(g),length(Eg));
npg_abs=zeros(length(g),length(Eg));
npd_abs=zeros(length(g),length(Eg));
Econv0_en=zeros(length(g),length(Eg));
Econv0_p0=zeros(length(g),length(Eg));
Econv0_p15=zeros(length(g),length(Eg));
Econvg_en=zeros(length(g),length(Eg));
Econvg_p0=zeros(length(g),length(Eg));
Econvg_p15=zeros(length(g),length(Eg));
Econvd_en=zeros(length(g),length(Eg));
Econvd_p0=zeros(length(g),length(Eg));
Econvd_p15=zeros(length(g),length(Eg));
%calculation of absorbed no of photons and the corresponding energy converted in the solar cell%
for y=1:length(Eg)
  for x=1:length(w)
    if Eph(x,1)>=Eg(y);
      np0_abs(x,y)=np0(x,1);
      npg_abs(x,y)=npg(x,1);
      npd_abs(x,y)=npd(x,1);
    %energy conversion%
      Econv0_en(x,y)=np0_abs(x,y)*Eg(y)*e;
      Econv0_p0(x,y)=np0_abs(x,y)*Eg(y)*e*Voc(2,y)*FF(2,y);
      Econv0_p15(x,y)=np0_abs(x,y)*Eg(y)*e*Voc(3,y)*FF(3,y);
      Econvg_en(x,y)=npg_abs(x,y)*Eg(y)*e;
      Econvg_p0(x,y)=npg_abs(x,y)*Eg(y)*e*Voc(2,y)*FF(2,y);
      Econvg_p15(x,y)=npg_abs(x,y)*Eg(y)*e*Voc(3,y)*FF(3,y);
      Econvd_en(x,y)=npd_abs(x,y)*Eg(y)*e;
      Econvd_p0(x,y)=npd_abs(x,y)*Eg(y)*e*Voc(2,y)*FF(2,y);
      Econvd_p15(x,y)=npd_abs(x,y)*Eg(y)*e*Voc(3,y)*FF(3,y);
    else
      np0_abs(x,y)=0;
      npg_abs(x,y)=0;
      npd_abs(x,y)=0;
      %energy conversion%
      Econv0_en(x,y)=0;
      Econv0_p0(x,y)=0;
      Econv0_p15(x,y)=0;
      Econvg_en(x,y)=0;
      Econvg_p0(x,y)=0;
      Econvg_p15(x,y)=0;
      Econvd_en(x,y)=0;
      Econvd_p0(x,y)=0;
      Econvd_p15(x,y)=0;
    end
  end
end
Eff0_en=sum(Econv0_en)/sum(am0);
Eff0_p0=sum(Econv0_p0)/sum(am0);
Eff0_p15=sum(Econv0_p15)/sum(am0);
Effg_en=sum(Econvg_en)/sum(g);
Effg_p0=sum(Econvg_p0)/sum(g);
Effg_p15=sum(Econvg_p15)/sum(g);
Effd_en=sum(Econvd_en)/sum(dir);
Effd_p0=sum(Econvd_p0)/sum(dir);
Effd_p15=sum(Econvd_p15)/sum(dir);
%DC solar cell%
np0_abs_DC=zeros(length(g),length(Eg));
npg_abs_DC=zeros(length(g),length(Eg));
npd_abs_DC=zeros(length(g),length(Eg));
Econv0_DC_en=zeros(length(g),length(Eg));
Econv0_DC_p0=zeros(length(g),length(Eg));
Econv0_DC_p15=zeros(length(g),length(Eg));
Econvg_DC_en=zeros(length(g),length(Eg));
Econvg_DC_p0=zeros(length(g),length(Eg));
Econvg_DC_p15=zeros(length(g),length(Eg));
Econvd_DC_en=zeros(length(g),length(Eg));
Econvd_DC_p0=zeros(length(g),length(Eg));
Econvd_DC_p15=zeros(length(g),length(Eg));

%calculation of absorbed no of photons and the corresponding energy
converted in the solar cell%
for y=1:length(Eg)
    for x=1:length(w)
        if Eph(x,1)>=Eg(y);
            np0_abs_DC(x,y)=np0(x,1)*floor((Eph(x,1)./Eg(y))); 
            npg_abs_DC(x,y)=npg(x,1)*floor((Eph(x,1)./Eg(y)));
            npd_abs_DC(x,y)=npd(x,1)*floor((Eph(x,1)./Eg(y)));
        end
    end
end
Eff0_DC_en=sum(Econv0_DC_en)/sum(am0);
Eff0_DC_0=sum(Econv0_DC_p0)/sum(am0);
Eff0_DC_15=sum(Econv0_DC_p15)/sum(am0);
Effg_DC_en=sum(Econvg_DC_en)/sum(g);
Effg_DC_0=sum(Econvg_DC_p0)/sum(g);
Effg_DC_15=sum(Econvg_DC_p15)/sum(g);
Effd_DC_en=sum(Econvd_DC_en)/sum(dir);
Effd_DC_0=sum(Econvd_DC_p0)/sum(dir);
Effd_DC_15=sum(Econvd_DC_p15)/sum(dir);

%UC solar cell%
np0_abs_UC=zeros(length(g),length(Eg));
npg_abs_UC=zeros(length(g),length(Eg));
npd_abs_UC=zeros(length(g),length(Eg));
Econv0_UC_en=zeros(length(g),length(Eg));
Econv0_UC_p0=zeros(length(g),length(Eg));
Econv0_UC_p15=zeros(length(g),length(Eg));
Econvg_UC_en=zeros(length(g),length(Eg));
Econvg_UC_p0=zeros(length(g),length(Eg));
Econvg_UC_p15=zeros(length(g),length(Eg));
Econvd_UC_en=zeros(length(g),length(Eg));
Econvd_UC_p0=zeros(length(g),length(Eg));
Econvd_UC_p15=zeros(length(g),length(Eg));

%calculation of absorbed no of photons and the corresponding energy
converted in the solar cell
for y=1:length(Eg)
    for x=1:length(w)
        if Eph(x,1)>=Eg(y);
            np0_abs_UC(x,y)=np0(x,1);
            npg_abs_UC(x,y)=npg(x,1);
            npd_abs_UC(x,y)=npd(x,1);
        end
    end
    end
end

Eff0_UC_en=sum(Econv0_UC_en)/sum(am0);
Eff0_UC_p0=sum(Econv0_UC_p0)/sum(am0);
Eff0_UC_p15=sum(Econv0_UC_p15)/sum(am0);
Effg_UC_en=sum(Econvg_UC_en)/sum(g);
Effg_UC_0 = \frac{\text{sum}(E\text{convg}_UC_p0)}{\text{sum}(g)};
Effg_UC_15 = \frac{\text{sum}(E\text{convg}_UC_p15)}{\text{sum}(g)};
Effd_UC_en = \frac{\text{sum}(E\text{convd}_UC_en)}{\text{sum}(d)};
Effd_UC_0 = \frac{\text{sum}(E\text{convd}_UC_p0)}{\text{sum}(d)};
Effd_UC_15 = \frac{\text{sum}(E\text{convd}_UC_p15)}{\text{sum}(d)};

\%UCDC solar cell\%
np0_abs_UCDC = \text{zeros}(\text{length}(g), \text{length}(Eg));
npg_abs_UCDC = \text{zeros}(\text{length}(g), \text{length}(Eg));
npd_abs_UCDC = \text{zeros}(\text{length}(g), \text{length}(Eg));
Econv0_UCDC_en = \text{zeros}(\text{length}(g), \text{length}(Eg));
Econv0_UCDC_p0 = \text{zeros}(\text{length}(g), \text{length}(Eg));
Econv0_UCDC_p15 = \text{zeros}(\text{length}(g), \text{length}(Eg));
Econvg_UCDC_p0 = \text{zeros}(\text{length}(g), \text{length}(Eg));
Econvg_UCDC_p15 = \text{zeros}(\text{length}(g), \text{length}(Eg));

\%calculation of absorbed no of photons and the corresponding energy converted in the solar cell\%
for \(y=1: \text{length}(Eg)\)
    for \(x=1: \text{length}(w)\)
        if \(E\text{ph}(x,1) \geq Eg(y)\);
            np0_abs_UCDC(x,y) = np0(x,1) * \text{floor}(\frac{E\text{ph}(x,1)}{Eg(y)})
            npd_abs_UCDC(x,y) = npd(x,1) * \text{floor}(\frac{E\text{ph}(x,1)}{Eg(y)})
            Econv0_UCDC_en(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e;
            Econv0_UCDC_p0(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econv0_UCDC_p15(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
            Econvg_UCDC_en(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e;
            Econvg_UCDC_p0(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econvg_UCDC_p15(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
            Econvd_UCDC_en(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e;
            Econvd_UCDC_p0(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econvd_UCDC_p15(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
        elseif \(E\text{ph}(x,1) \geq \frac{Eg(y)}{2}\);
            np0_abs_UCDC(x,y) = np0(x,1) / \text{ceil}(\frac{Eg(y)}{E\text{ph}(x,1)})
            npd_abs_UCDC(x,y) = npd(x,1) / \text{ceil}(\frac{Eg(y)}{E\text{ph}(x,1)})
            Econv0_UCDC_en(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e;
            Econv0_UCDC_p0(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econv0_UCDC_p15(x,y) = np0_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
            Econvg_UCDC_en(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e;
            Econvg_UCDC_p0(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econvg_UCDC_p15(x,y) = npg_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
            Econvd_UCDC_en(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e;
            Econvd_UCDC_p0(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e * V(2,y) * FF(2,y);
            Econvd_UCDC_p15(x,y) = npd_abs_UCDC(x,y) * Eg(y) * e * V(3,y) * FF(3,y);
        else
            np0_abs_UCDC(x,y) = 0;
            npg_abs_UCDC(x,y) = 0;
            npd_abs_UCDC(x,y) = 0;
        end

end
%energy conversion%
Econv0_UCDC_en(x,y)=0;
Econv0_UCDC_p0(x,y)=0;
Econv0_UCDC_p15(x,y)=0;
Econvg_UCDC_en(x,y)=0;
Econvg_UCDC_p0(x,y)=0;
Econvg_UCDC_p15(x,y)=0;
Econvd_UCDC_en(x,y)=0;
Econvd_UCDC_p0(x,y)=0;
Econvd_UCDC_p15(x,y)=0;
end

Eff0_UCDC_en=sum(Econv0_UCDC_en)/sum(am0);
Eff0_UCDC_0=sum(Econv0_UCDC_p0)/sum(am0);
Eff0_UCDC_15=sum(Econv0_UCDC_p15)/sum(am0);
Efgg_UCDC_en=sum(Econvg_UCDC_en)/sum(g);
Efgg_UCDC_0=sum(Econvg_UCDC_p0)/sum(g);
Efgg_UCDC_15=sum(Econvg_UCDC_p15)/sum(g);
Effd_UCDC_en=sum(Econvd_UCDC_en)/sum(dir);
Effd_UCDC_0=sum(Econvd_UCDC_p0)/sum(dir);
Effd_UCDC_15=sum(Econvd_UCDC_p15)/sum(dir);

figure(1)
plot(Eg,Effg_15,Eg,Effg_DC_15,Eg,Effg_UC_15,Eg,Effg_UCDC_15)
legend('Normal Eff','DC Efficiency','UC Efficiency','UC+DC Efficiency')
set(gca,'xlim',[350 850],'ylim',[0 1.0])
title('Simulation of efficiency limit for different conversion layers','fontsize',18)
xlabel('Bandgap Energy [eV]','fontsize',14)
ylabel('Efficiency [%]','fontsize',14)
set(gca,'fontsize',14)
figure(2)
plot(Eg,Effg_15,Eg,Effg_DC_15)
legend('Normal Eff','DC Efficiency')
set(gca,'xlim',[350 850],'ylim',[0 1.0])
title('Simulation of efficiency limit for down conversion','fontsize',18)
xlabel('Bandgap Energy [eV]','fontsize',14)
ylabel('Efficiency [%]','fontsize',14)
set(gca,'fontsize',14)
figure(3)
plot(Eg,Effg_15,Eg,Effg_UC_15)
legend('Normal Eff','UC Efficiency')
set(gca,'xlim',[350 850],'ylim',[0 1.0])
title('Simulation of efficiency limit for down conversion','fontsize',18)
xlabel('Bandgap Energy [eV]','fontsize',14)
ylabel('Efficiency [%]','fontsize',14)
set(gca,'fontsize',14)
Appendix B

Calculation of effect of surface coverage

Note: In the matlab code for \( t = 3R \), the calculation is not proceeded below \( x = 0.06R \) as this leads to a situation where the limit of near-field exceeds the diagonally opposite edge of the control volume making the calculation extremely complex.

Matlab Code:

```matlab
clc
clear all
vf1=zeros(1,10000); % volume fraction for 3R SOI
vf2=zeros(1,10000); % volume fraction for 2R SOI
a=zeros(1,10000); % coverage factor
% volume fraction with 3R sphere of influence
for i=1:60
    vf1(1,i)=0;
a(1,i)=100*pi()/(4*(1+(i/1000))^2);
end
for i=61:500
    vf1(1,i)=100*(27*pi()-pi()*(7+(i/1000))*((2-(i/1000))^2)-pi()*(1-2+1000)^2)\(4*(i/1000)+6-\)
    (2*sqrt(2)*(1+i/1000))^2))/(18*((i+1)^2));
a(1,i)=100*pi()/(4*(1+(i/1000))^2);
end
for i=501:1121
    vf1(1,i)=100*(27*pi()-pi()*(7+(i/1000))*((2-(i/1000))^2)+(6-
    (2*sqrt(2)*(1+i/1000))^2))/(18*((i+1)^2));
a(1,i)=100*pi()/(4*(1+(i/1000))^2);
end
for i=1122:1999
    vf1(1,i)=100*(27*pi()-pi()*(7+(i/1000))*((2-(i/1000))^2))/
    (18*((i+1)^2));
a(1,i)=100*pi()/(4*(1+(i/1000))^2);
end
for i=2000:10000
    vf1(1,i)=2700*pi()/(18*((i+1)^2));
a(1,i)=100*pi()/(4*(1+(i/1000))^2);
end
% volume fraction with 2R sphere of influence
for j=1:414
    vf2(1,j)=100*(8*pi()-pi()*(5+(j/1000))*((1-(j/1000))^2)+
    (4-(2*sqrt(2)*(1+j/1000))^3))/(12*((j+1)^2));
a(1,j)=100*pi()/(4*(1+j/1000))^2);
end
for j=415:1000
    vf2(1,j)=100*(8*pi()-pi()*(5+(j/1000))^2)/
    (12*(1+(j/1000))^2));
a(1,j)=100*pi()/(4*(1+j/1000))^2);
end
for j=1001:10000
    vf2(1,j)=100*(8*pi())/(12*(1+j/1000)^2));
a(1,j)=100*pi()/(4*(1+j/1000))^2);
end
figure(1)
plot(a,vf1,a,vf2)
%plot(vf1)
legend('Volume fraction')
% set(gca,'xlim',[350 850],';ylim',[0 1.0])
```
title('Calculation of QD in DC layer within nearfield of AgNPs','fontsize',18)
xlabel('Coverage factor [%]','fontsize',14)
ylabel('QD% in nearfield [%]','fontsize',14)
set(gca,'fontsize',14)
figure(2)
plot(a,vs)
figure(3)
plot(a,vc)
figure(4)
plot(a,vs-vc)
Appendix C

Purchase of Silver nanoparticles

Based on market research, it was observed that two forms of product were available which were manufactured through the chosen technique namely nanoparticles in solution and powders. The various options available are illustrated in table C-2 and it can be clearly seen that powders prove to be quite economic.

| Company              | Quantity (ml|g) | concentration (mg/ml) | Cost ($) | Cost/Quantity ($/g) | Quantity required (ml|g) | Quantity to order (ml|g) | Final Cost ($) |
|----------------------|-----------|-----------------------|----------|---------------------|---------------------|------------------------|----------------|----------------|
| SS Nano 100nm        | 25        | -                     | 168      | 6.38                | 0.18                | 25                     | 168.0          |
| SS Nano 200-400nm    | 100       | -                     | 497      | 4.72                | 0.18                | 100                    | 497.0          |
| Cytodiagnostics      | 500       | 0.02                  | 499      | 39920               | 8750                | 9000                   | 8982.0         |
|                      | 100       | 0.02                  | 160      | 64000               | 8750                | 8800                   | 14080.0        |
| BBI                  | 100       | 0.11                  | 241.7    | 23019.05            | 1666.67             | 1700                   | 4108.9         |
| nanocomposix         | 500       | 0.02                  | 2500     | 42500               | 8750                | 9000                   | 9000.0         |
|                      | 100       | 0.02                  | 150      | 63750               | 8750                | 8800                   | 13200.0        |
| Seashell tech        | N/A       | N/A                   | N/A      | N/A                 | N/A                 | N/A                    | N/A            |
| sigma aldrich 100nm  | 25        | 0.02                  | 77.5     | 155000              | 8750                | 8750                   | 27125.0        |
| sigma aldrich 157nm  | 5         | 0.027                 | 142.5    | 1055555.56          | 6481                | 6485                   | 184822.5       |
| SiO2 coated AgNP 100 nm | 1   | 1                     | 400      | 340000              | 175                 | 175                    | 70000          |

Table C-1 Comparison of various market options in terms of cost requirements

<table>
<thead>
<tr>
<th>Item</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Corning glass</td>
<td></td>
</tr>
<tr>
<td>Area</td>
<td>100</td>
<td>cm²</td>
</tr>
<tr>
<td>Coverage</td>
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<td>%</td>
</tr>
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<td>particle radius</td>
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<td>nm</td>
</tr>
<tr>
<td>particle area</td>
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<td>cm²</td>
</tr>
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<td>Number of particles</td>
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<td>per sample</td>
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<tr>
<td>Weight of particle</td>
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<td>g/particle</td>
</tr>
<tr>
<td>Wastage during spin coating</td>
<td>50</td>
<td>%</td>
</tr>
<tr>
<td>Weight of particles</td>
<td>0.0035</td>
<td>g/sample</td>
</tr>
<tr>
<td>Number of samples</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Total Weight required</td>
<td>0.175</td>
<td>g</td>
</tr>
</tbody>
</table>

Table C-2 Estimate of nanoparticles required for the current work

An estimate of the amount of nanoparticles required was also done to estimate the cost of the material to be purchased. A substrate of 10*10 cm² was assumed (corning glass). Based on the calculations done (refer section 2.2.3), an optimal coverage of 25% was chosen and a nanoparticle of size 100nm diameter (refer section 3.1.2). Considering a 50% loss during spin coating of these particles and assuming 50 samples, it was estimated that ~175mg of nanoparticles was required. From table C-1, it can be concluded that the silver nanoparticle powder from Skyspring Nanomaterials, Inc satisfies our size requirements and is the most economical option.
Some of the details pertaining to the silver powder are provided below –

- **Product #:** 0115CY
- **Purity:** 99.95% (trace metals basis)
- **Appearance:** Dark Grey Powder
- **APS:** ~100 nm
- **SSA:** ~5 m²/g
- **Morphology:** spherical
- **Bulk density:** 0.50 - 0.60 g/cm³
- **True density:** 10.5 g/cm³

The SEM picture of the particles is shown in figure C-1. As can be seen the particles are not monodisperse and the size varies from ~40-100 nm.

![SEM picture of the product 0115CY](http://ssnano.com/inc/sdetail/silver_nanoparticles/236)
Appendix D

Rate of deposition of QDs in CASCADE

Deposition rate of Si QDs is determined by measuring the weight of the substrate before and after deposition in CASCADE. The rate is determined for a unit area to have comparable results.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Blank wt (g cm⁻²)</th>
<th>Depo Wt (g cm⁻²)</th>
<th>Diff (g cm⁻²)</th>
<th>Time (s)</th>
<th>Ave_Rate (mg cm⁻² s⁻¹)</th>
<th>Overall Ave_Rate (mg cm⁻² s⁻¹)</th>
<th>Std Dev</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiH₄ = 230 sccm</td>
<td>C2160 8.33529</td>
<td>8.67691</td>
<td>0.34162</td>
<td>480</td>
<td>0.71</td>
<td>0.72</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>C2161 8.36981</td>
<td>8.55023</td>
<td>0.18043</td>
<td>240</td>
<td>0.75</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C2162 8.31823</td>
<td>8.35985</td>
<td>0.04163</td>
<td>60</td>
<td>0.69</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₄ = 420 sccm</td>
<td>C2163 8.24933</td>
<td>8.31763</td>
<td>0.06831</td>
<td>60</td>
<td>1.14</td>
<td>1.25</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>C2164 8.44167</td>
<td>8.73966</td>
<td>0.29798</td>
<td>242</td>
<td>1.23</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C2165 8.76656</td>
<td>9.42399</td>
<td>0.65742</td>
<td>480</td>
<td>1.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiH₄ = 600 sccm</td>
<td>C2155 8.43364</td>
<td>9.05495</td>
<td>0.62131</td>
<td>480</td>
<td>1.29</td>
<td>1.51</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>C2156 8.24060</td>
<td>8.62150</td>
<td>0.38090</td>
<td>240</td>
<td>1.59</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C2157 8.56432</td>
<td>8.66355</td>
<td>0.09924</td>
<td>60</td>
<td>1.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table D-1 Deposition rate (per unit area) of silicon quantum dots in CASCADE
Appendix E

Calculation of crystalline fraction from Raman spectroscopy
As has been mentioned in section 3.1.1, the quantum dots have a fair amount of amorphous tissues surrounding it. The Raman analysis of these samples shows a peak at 480 cm\(^{-1}\) for the amorphous tissues and a peak in the range 510 - 521 cm\(^{-1}\) depending on the size of the quantum dot. A sample is shown in figures 1 through 3 for better understanding.

Figure E.1 Raman spectrum of QD sample. The blue line is the Raman spectrum. The red line is the amorphous signal filtered out and the green lines are the split of the amorphous signals into different modes.

Figure E.2 Raman spectrum of QD sample. The blue line is the Raman spectrum. The extra red line compared to figure 1 is the signal for the crystalline part of the sample filtered out from the Raman spectrum by subtracting the amorphous signal; and the extra green lines are the split of the crystalline signals into different modes.
E.3 Raman spectrum of a different QD sample with a higher amorphous contribution to the spectrum.

The blue line in the figure is the original Raman spectrum which is split into the amorphous and crystalline spectrum (red lines) which in turn are divided into different modes (green lines). It can be seen that some of the samples possess a considerably high amorphous fraction as seen in figure 3. The area under the spectrum is used in the calculation of the crystalline fraction using the formula

\[
\text{Crystalline Fraction} = \frac{A_{520}}{A_{520} + (0.8 \times A_{480})}
\]

Where, \(A_{520}\) is the area under the crystalline spectrum and \(A_{480}\) is the area under the amorphous spectrum. The crystalline fractions of the samples in the figure are 76% (figure 1&2) and 43% (figure 3).

Matlab Code:

```matlab
%number of gaussians to use
filename = '1C2170D-100s1\1';
filedot = strcat('D:\TUD\thesis\office\Raman measurement\New Folder\221112\04122012\', filename,'.txt');
idram = fopen(filedot,'r');
fileram = fscanf(idram,'%lf %lf',[2 inf]);
savecur = strcat('D:\TUD\thesis\office\Raman measurement\New Folder\221112\04122012\', filename,'.cr.dat');
savedat = strcat('D:\TUD\thesis\office\Raman measurement\New Folder\221112\04122012\', filename,'.dt.dat');
fidsavec = fopen(savecur,'w');
fidsaved = fopen(savedat,'w');
%fileram=sort(fileram0,2); %in ascending order
waven = fileram(1,:);
ramanexp = fileram(2,:);
```
filesize = size(waven);

% Define region where to fit the gaussians and the background
j=1;
for i=1:filesize(2)
    if (150 <= waven(i)) & (waven(i)<=470) | (waven(i)>=550 & waven(i)<=900);
        wavetofit(j) = waven(i);
        ramantofit(j) = ramansubstrat(i);
        j=j+1;
    end
end

% completed region of interest
jj=1;
for i=1:filesize(2)
    if (170 <= waven(i)) & (waven(i)<=750);
        waveregion(jj) = waven(i);
        ramanregion(jj) = ramanexp(i);
        jj=jj+1;
    end
end

%============================= %GAUSSIANS DEFINITION %background for amorphous and microcrystalline fitting
bgamorp=500;
    lbbgam = -500; ubbgam = 10000;
bgmicro=0;
    lbbgmi = -.005; ubbemi = 005;

% center of the gaussians
c0 = 330; %LA
    lbc0 = 300; ubc0 = 331;
y0 = 150; %LA
    lby0 = 0; uby0 = inf;
w0 = 100; %LA
    lbw0 = 50; ubw0 = 500;

%---------------------------
c1 = 440; %LO
    lbc1 = 439; ubc1 = 441;
y1 = 200; %LO
    lby1 = 0; uby1 = inf;
w1 = 100; %LO
    lbw1 = 0; ubw1 = 150;

%---------------------------
c2 = 480; %TO
    lbc2 = 479; ubc2 = 485;
y2 = 600; %TO
    lby2 = 0; uby2 = inf;
w2 = 50; %TO
    lbw2 = 0; ubw2 = 300;

%---------------------------
c3 = 502; %Intermedia component peak J.Appl. Phys Vol 87, pag 1882 (2000)
    lbc3 = 500; ubc3 = 510;
y3 = 1000; %Intermedia component peak J.Appl. Phys Vol 87, pag 1882 (2000)
    lby3 = 0; uby3 = inf;
w3 = 38; %Intermedia component peak J.Appl. Phys Vol 87, pag 1882 (2000)
lbw3 = 0; ubw3 = 100;

%---------------------------
c4 = 520;  %Crystalline TO
lbc4 = 510; ubc4 = 522;
y4 = 5500;  %Crystalline TO
lby4 = 0; uby4 = inf;
w4 = 14;  %Crystalline TO
lbw4 = 0; ubw4 = 20;

%---------------------------
c5 = 630;  %HYDRITES
lbc5 = 620; ubc5 = 660;
y5 = 150;  %HYDRITES
lby5 = 0; uby5 = inf;
w5 = 100;  %HYDRITES
lbw5 = 0; ubw5 = 100;

%---------------------------
c6 = 180;  %TA
lbc6 = 160; ubc6 = 200;
y6 = 150;  %TA
lby6 = 0; uby6 = 200;
w6 = 50;  %TA
lbw6 = 0; ubw6 = 100;

%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%%
warning off MATLAB:divideByZero

% FITTING 3 amorphous peaks
% initial values
% x0amorp = [   1     2   3   4   5   6   7   8   9   10  11  12  13
14  15  16
x0amorp = [bgamorp, c0, c1, c2, c5, c6, y0, y1, y2, y5, y6, w0, w1,
w2, w5, w6];
varx0amorp = ['bg'; 'c0'; 'c1'; 'c2'; 'c5'; 'c6'; 'y0'; 'y1'; 'y2'; 'y5'; 'y6';
'w0'; 'w1'; 'w2'; 'w5'];
% lower limit
lb = [lbbgam, lbc0, lbc1, lbc2, lbc5, lbc6, lby0, lby1, lby2, lby5,
lby6, lbw0, lbw1, lbw2, lbw5, lbw6];
% upper bond
ub = [ubbgam, ubc0, ubc1, ubc2, ubc5, ubc6, uby0, uby1, uby2, uby5,
uby6, ubw0, ubw1, ubw2, ubw5, ubw6];

options=optimset('Display','off','TolFun',1e-20);  % Termination
tolerance on the function value.
[xamorp, resnorm] =
lsqcurvefit(@fitraman5g,x0amorp,wavetofit,ramantofit,lb,ub,options);

% using the fitted parameters
 gaussianas = fitraman5g1(xamorp,waveregion);
 ramanfitted = gaussianas(1,:);
 gaus1 = gaussianas(2,:);
 gaus2 = gaussianas(3,:);
 gaus3 = gaussianas(4,:);
 gaus4 = gaussianas(5,:);
 gaus5 = gaussianas(6,:);

plot(waveregion,ramanregion,'b')

% plot(wavetofit,ramantofit,'b')
hold on
plot(waveregion, ramanfitted, 'r')
plot(waveregion, gaus1, 'g')
plot(waveregion, gaus2, 'g')
plot(waveregion, gaus3, 'g')
plot(waveregion, gaus4, 'g')
plot(waveregion, gaus5, 'g')

% Subtract fitted amorphous from sample
ramanmicro = ramanregion - gaussianas(1,:);
endprogram = [];
while isempty(endprogram) == 1
    % number of gaussians to use
    micropeaks = menu('Fitting microcrystalline peak', 'Enter gaussian parameters', 'Fit data', 'End program');
    switch micropeaks
    case (1) % Enter gaussian parameters
        peak500old = [lbc3, c3, ubc3; lby3, y3, uby3; lbw3, w3, ubw3]
        peak500 = input('Peak at 500 cm\(^{-1}\): ');
        if isempty(peak500) == 1
            peak500 = peak500old;
        else
            for ipeak = 1:3
                for jpeak = 1:3
                    if isempty(peak500(ipeak, jpeak)) == 1
                        peak500(ipeak, jpeak) = peak500old(ipeak, jpeak);
                    end
                end
            end
        end
        lbc3 = peak500(1,1); c3 = peak500(1,2); ubc3 = peak500(1,3); lby3 = peak500(2,1); y3 = peak500(2,2); uby3 = peak500(2,3); lbw3 = peak500(3,1); w3 = peak500(3,2); ubw3 = peak500(3,3);

        peak520old = [lbc4, c4, ubc4; lby4, y4, uby4; lbw4, w4, ubw4]
        peak520 = input('Peak at 520 cm\(^{-1}\): ');
        if isempty(peak520) == 1
            peak520 = peak520old;
        else
            for ipeak = 1:3
                for jpeak = 1:3
                    if isempty(peak520(ipeak, jpeak)) == 1
                        peak520(ipeak, jpeak) = peak520old(ipeak, jpeak);
                    end
                end
            end
        end
        lbc4 = peak520(1,1); c4 = peak520(1,2); ubc4 = peak520(1,3); lby4 = peak520(2,1); y4 = peak520(2,2); uby4 = peak520(2,3); lbw4 = peak520(3,1); w4 = peak520(3,2); ubw4 = peak520(3,3);

    case (2)
    % 2 crystalline peaks
    % region to fir microcrystalline
\text{jjj}=1; \text{filesizen} = \text{size(waveregion);}
for \text{i=1:filesizen}(2)
  \text{if} (440 <= \text{waveregion}(\text{i})) \& (\text{waveregion}(\text{i})<=560);
    \text{waveregionmicro(\text{jjj})} = \text{waveregion}(\text{i});
    \text{ramanregionmicro(\text{jjj})} = \text{ramanmicro(\text{i});}
    \text{jjj}=\text{jjj}+1;
end
end

\text{x0micro} = [\text{bgmicro, c3, c4, y3, y4, w3, w4}];
\text{varx0micro} = [\text{'bg'; 'c3'; 'c4' ;'A3'; 'A4'; 'w3'; 'w4'}];
%lower limit
\text{lbmicro} = [\text{lbbgmi, lbc3, lbc4, lby3, lby4, lbw3, lbw4}];
%upper bond
\text{ubmicro} = [\text{ubbgmi, ubc3, ubc4, uby3, uby4 ubw3, ubw4}];

\text{options=optimset('Display','off','TolFun',1e-20); } \%
\text{Termination tolerance on the function value.}
\text{[xmicro, resnorm] = lsqcurvefit(@fitraman2g,\text{x0micro},\text{waveregionmicro, ramanregionmicro, lbmicro, ubmicro, options});}

\text{c3=\text{xmicro}(2); c4=\text{xmicro}(3); y3=\text{xmicro}(4); y4=\text{xmicro}(5); w3=\text{xmicro}(6); w4=\text{xmicro}(7);}

%using the fitted parameters
\text{gaussianasmicro} = \text{fitraman2g1(xmicro, waveregionmicro)};
\text{gaussianasmicro} = \text{fitraman2g1(xmicro, waveregion)};
\text{ramanfittedmicro} = \text{gaussianasmicro(1,:)};
\text{gau31micro} = \text{gaussianasmicro(2,:)};
\text{gau32micro} = \text{gaussianasmicro(3,:)};

\text{plot(waveregion, ramanregion, 'b')}
\text{hold on}
\text{plot(waveregionmicro, ramanregionmicro, 'r')}
\text{plot(waveregion, ramanfitted, 'r')}
\text{plot(waveregion, gaus1, 'g')}
\text{plot(waveregion, gaus2, 'g')}
\text{plot(waveregion, gaus3, 'g')}
\text{plot(waveregion, gaus4, 'g')}
\text{plot(waveregion, gaus5, 'g')}
\text{plot(waveregion, ramanfittedmicro, 'g')}
\text{plot(waveregion, gau31micro, 'g')}
\text{plot(waveregion, gau32micro, 'g')}
\text{hold off}

\text{case (3)}
\text{end program = 1;}
end

%these matrix indicate if the variables are limited by the boundaries
\text{touchlb} = \text{xamorp} - \text{lb};
\text{touchub} = \text{ub} - \text{xamorp};
\text{touchboundaries} = [\text{xamorp', lb', touchlb', x0amorp', touchub', ub'}];
%===================================
%%FWHM for peak at 520 cm$^{-1}$

\begin{verbatim}
xwave = 440:.05:560;
g510 = y3*exp((-2*log(4)*((xwave-c3)/w3).^2);
g520 = y4*exp((-2*log(4)*((xwave-c4)/w4).^2);
gmicro = g510+g520;

[maxval,maxpos]=max(gmicro);
hm = maxval/2;

gmicroleft = abs(gmicro(1:maxpos) - hm);
gmicroright = abs(gmicro(maxpos:end) - hm);
[leftval,leftpos]=min(gmicroleft);
[rightval,rightpos]=min(gmicroright);

FWHM = xwave(maxpos+rightpos-1) - xwave(leftpos);
HWHMleft = xwave(maxpos) - xwave(leftpos);
HWHMright = xwave(maxpos+rightpos-1) - xwave(maxpos);
anchura = [xmicro(3), FWHM, HWHMleft, HWHMright,xamorp(14)*sqrt(log(4))];
\end{verbatim}

%===================================
%crystalline fraction

\begin{verbatim}
area480 = xamorp(14)*xamorp(9)*sqrt(pi/2);
area510 = xmicro(4)*xmicro(6)*sqrt(pi/2);
area520 = xmicro(5)*xmicro(7)*sqrt(pi/2);

%integration of microcrystalline area of sample
micropeakarea = (waveregionmicro(2)-waveregionmicro(1))*trapz(waveregionmicro,ramanregionmicro);

水晶分数 = 100 * ( micropeakarea ) / ( 0.8*area480 + micropeakarea )

水晶分数 = 100 * ( area510 + area520 ) / ( 0.8*area480 + area510 + area520 )

upper = 100 * ( area510+area520 ) / ( area480 + area510+area520 );

CF = [水晶分数 tint,水晶分数, upper];
hk = [area480, area510, area520];
\end{verbatim}

salidacss = [x(10), x(28), x(19)*x(28)*pi/2]; %for lorentzian
salidala = [xamorp(2), xamorp(12),
  xamorp(12)*xamorp(7)*sqrt(pi/2)]; %for gaussina
salidalo = [xamorp(3), xamorp(13), xamorp(13)*xamorp(8)*sqrt(pi/2)];
salidato = [xamorp(4), xamorp(14), xamorp(14)*xamorp(9)*sqrt(pi/2)];
salidah = [xamorp(5), xamorp(15), xamorp(15)*xamorp(10)*sqrt(pi/2)];
salidata = [xamorp(6), xamorp(16), xamorp(16)*xamorp(11)*sqrt(pi/2)];
salidaint = [xmicro(2), xmicro(6), xmicro(6)*xmicro(4)*sqrt(pi/2)];
salidatoc = [xmicro(3), xmicro(7), xmicro(7)*xmicro(5)*sqrt(pi/2)];
salidagaus = [waveregion; ramanregion; gaussianas; gaussianasmicro];
fprintf(fidsaved,'crystalline fraction (% integral of sample - of
gauss): %12.2f ; %12.2f ; %12.2f\n',CF);
fprintf(fidsaved,'TO(c-SI) posi: %12.4f   FWHM & half max (left &
right) for 520, FWHM for 480: %12.2f %12.2f %12.4f %12.4f \n',anchura);
fprintf(fidsaved,'LA (330): %12.2f %12.4f %12.4f \n',salidala);
fprintf(fidsaved,'LO (440):   %12.2f %12.4f %12.4f \n',salidalo);
fprintf(fidsaved,'TO amorp (480):     %12.2f %12.4f %12.4f
\n',salidato);
fprintf(fidsaved,'intermediate (510):    %12.2f %12.4f %12.4f
\n',salidaint);
fprintf(fidsaved,'TO crystalline (520):     %12.2f %12.4f %12.4f
\n',salidatoc);
fprintf(fidsaved,'H (640):     %12.2f %12.4f %12.4f \n',salidah);
fprintf(fidsaved,'LA (180):     %12.2f %12.4f %12.4f \n',salidala);
fprintf(fidsaved,'background:     %12.2f \n',xamorp(1));

fprintf(fidsavec,'wavenub (cm-1) Raman meas. amorp.Raman fit. g0am
glam  g2am g3am g4am cryst.Raman fit. g1cry  g2cry\n');
fprintf(fidsavec,'%7.3f %7.3f %7.3f %7.3f %7.3f %7.3f %7.3f %7.3f %7.3f %7.3f %7.3f
',salidagaus);

dat_range = 'G27:H31'; %values of Raman
empty=1; amorparea=xamorp(14)*sqrt(log(4));
dat_value = [crystalfract, upper; xmicro(3), empty; FWHM, empty; HWHMleft,
HWHMright; amorparea, empty];
%matlabtoexcel(filename,dat_range,dat_value)

close('all')
## Appendix F

### Probability of obtaining QDs in CASCADE

<table>
<thead>
<tr>
<th>Current</th>
<th>NH3 Flow/Pressure</th>
<th>Crystalline fraction of QDs under various deposition conditions</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.7</td>
<td>Table F.1 Crystalline fractions of various QDs formed in the CASCADE under different deposition conditions</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>300 Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>200 Total</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230 Total</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table F.1 Crystalline fractions of various QDs formed in the CASCADE under different deposition conditions
<table>
<thead>
<tr>
<th>Current</th>
<th>SiH₄ flow</th>
<th>Pressure</th>
<th>510</th>
<th>510.5</th>
<th>514.5</th>
<th>516</th>
<th>516.5</th>
<th>517</th>
<th>517.5</th>
<th>518</th>
<th>518.5</th>
<th>519</th>
<th>519.5</th>
<th>520</th>
<th>520.5</th>
<th>Grand Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>300</td>
<td>0.7</td>
<td>16.67%</td>
<td>16.67%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1</td>
<td>28.57%</td>
<td>14.29%</td>
<td>14.29%</td>
<td>28.57%</td>
<td>14.29%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>50.00%</td>
<td>16.67%</td>
<td>16.67%</td>
<td>16.67%</td>
<td>16.67%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>100.00%</td>
</tr>
<tr>
<td>20 Total</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</table>
Appendix G

Interpolation technique used in graphs

Due to the lower data points available in CASCADE parameter study, interpolation was used to provide a better graphical representation of the data. Interpolation was done using Matlab the program for which is provided below.

Matlab Code:

```matlab
clear all
clc

x=[20,30,40];
y=[0.7,1.0,1.3];
c=[0.00 0.00 3.42
0.00 9.91 3.81
0.14 15.90 0.00];
[x1, y1] = meshgrid(x,y);
[x2, y2] = meshgrid(linspace(x(1),x(end),100),linspace(y(1),y(end),100)); %100 data points in between
z1 = interp2(x1,y1,c,x2,y2);

figure(1)
contourf(x2,y2,z1,100)
shading flat
legend('Overall probability')
% set(gca,'xlim',[200 300],'ylim',[0.7 1.3])
title('Probability of QD formation under different deposition conditions','fontsize',22)
xlabel('Current [A]','fontsize',18)
ylabel('Chamber pressure [mbar]','fontsize',18)
set(gca,'fontsize',18)
```