SYNTHESIS AND CHARACTERIZATION OF PbSe NANOCRYSTALS USING

NON-CONVENTIONAL PROCESS MEDIA

THESIS

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CHAPTER 1

INTRODUCTION

Nanocrystals, sometimes called "quantum dots" are a rather recent discovery in the field of physics. They can range in size from 10nm to 500nm and display quantum confinement effects very well. Usually made from semiconductor material, they have been developed into infrared detectors because of their ability to create exciton pairs when illuminated with IR and NIR radiation. Since these crystals' behavior is based on quantum effects and not solid state behavior there is no band gap structure to consider when building devices with them. This means that the only minimum energy that must be considered is the energy between the lowest discrete energy levels of the potential well created by the structure. The focus of this thesis is to study the synthesis of colloidal PbSe nanocrystals and then characterize them to determine the size distribution that resulted from that synthesis. The synthesis is also done using two different chemicals than those that are commonly used in industry at the moment. In place of the precursor trioctylphosphine (TOP), tributylphosphine (TBP) was used, and instead of using TOP as the process medium for the reaction, a new solvent MCS 2811 from Solutia Inc. was used. These two changes helped reduce the cost of creating the particles by roughly 70%. PbSe is used because of recently published studies that show up to 700% quantum efficiency from PbSe nanocrystals when subjected to femtosecond laser pulses¹⁰. This

characteristic could prove very valuable in the application of these nanocrystals to a system where exciton creation is important, i.e. photovoltaics or photodetectors. Also, colloids are chosen over other methods of creation because of the ease of synthesis and cost of machinery necessary to produce them. Colloidal nanoparticles can be made fairly cheaply with basic chemistry supplies, where lithography and epitaxy require special machines that are very expensive. Also, characterization of colloids can be done in solution or on substrate making it possible to perform characterization with a wide variety of techniques.

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CHAPTER 2

THEORETICAL BACKGROUND

2.1 Quantum Reduction

The most complete way to introduce the idea of a nanoparticle is to begin with a larger material and move down to the smaller in steps, following the model of Schmidt in <u>Nanoparticles¹</u>. This process is known as quantum reduction. Nanocrystals are the third step in quantum reduction from a bulk material; the first and second are two dimension electron gas and one dimension electron gas (quantum wires), respectively.

2.1.1 Bulk Material

A bulk material is a material which is large enough in three dimensions that quantum confinement effects are negligible compared to the confinement provided by the crystal structure. The electrons are free to move in any of the three dimensions within the solid, as long as they have well behaved wave functions. We define "well behaved" to mean that the wave function for the electron is periodic in three dimensions, with a period the size of the bulk material. Mathematically this can be represented thusly:

$$\Psi(x, y, z) = A \exp(ik_x x) \exp(ik_y y) \exp(ik_z z)$$
(2.1)

"A" is simply a constant to denote the amplitude of the wave, x,y,z are the Cartesian coordinates, and $k_{x,y,z}$ are the wavenumbers in each respective direction. If we then use quantum mechanics and apply Schrödinger's Equation, the energy eigenvalues are:

$$E_{x_{t}} = \frac{\hbar^{2}k^{2}n^{2}}{8mx_{t}^{2}}$$
(2.2)

Here x_i is the width of the crystal in the ith direction, i=1, 2, 3 corresponding to the Cartesian coordinates x, y, z, m is the rest-mass of the electron, and n is an integer denoting the energy level in which the electron can be found. We can describe the bulk material in what is referred to as, " \vec{k} -space." \vec{K} -space is a set of coordinates that are designed to make it easier to plot and talk about the energy of electrons within a solid, by describing the energy as a function of the wave number k. Equation (2.2) implies that the "distance" between allowed energies that the electron can have in a \vec{k} -space

is
$$\Delta E \propto \Delta k^2 \propto \frac{1}{x_r^2}$$
. In order to complete the bulk material simplification, we allow x₁ to

become very large, so that even electrons near the edge of the material are not affected by the edge effects. Now we have $\Delta k^2 \sim 0$, which defines a quasi-continuous spectrum of possible energy values. By the Pauli Exclusion Principle, only one pair of electrons can occupy the same energy state at the same time. These electrons will have spin m= $\pm \frac{1}{2}$, and can occupy each of the states $(k_x, k_y, k_z) = (\pm n_x \Delta k, \pm n_y \Delta k, \pm n_z \Delta k)$ with $n_{x,y,z}$ being the principle quantum numbers, and therefore they are independent integers. If we made a graph of this in a \vec{k} -space it would look like a quasi-continuous spherical volume of radius equal to the highest occupied energy state. This is shown in Figure 2.1¹.



Figure 2.1

3dimensional representation of the k-states of a bulk material (free electron model) The radius of the sphere is a value called k_f . This is known as the Fermi level, or Fermi energy. The Fermi level is the highest energy state that is occupied by an electron when the material is in a totally unexcited (ground) state. This also means that there can be no thermal energy present; therefore k_f is defined at 0 K. In \vec{k} -space the density of states, D(k), is the number of states per a given interval of wavenumbers. This quantity is useful because it can be used to calculate the number of states and therefore the number of electrons with energies less than a certain k_{max} . The number of states between a given k and a Δk can be found by D(k) Δk . The total number of electrons N(k) can then be found by allowing Δk to shrink to a differential dk and integrating: N(k) = $\int_{k}^{k_{\text{max}}} D(k) dk$. We can't possibly know exactly how many electrons there are in a bulk material because there are so many, but knowing to within an order of magnitude is realistic, and can be quite useful. Therefore, we can approximate the number of electrons in the interval of $k+\Delta k$, by visualizing D(k) in a \vec{k} -space. If we want to know the number of states in $k+\Delta k$, we need to know the volume of the spherical shell which encloses them in \vec{k} space. The volume of a spherical shell is simply the surface area of the outer sphere,

times the thickness of the shell. Therefore: $V = 4\pi k^2 \Delta k$. In the limit as Δk gets very small, which we stipulated earlier; $D(k) = \frac{dN(k)}{dk} \propto k^2$. More often than this, scientists talk about the number of electrons with energies within the interval $E + \Delta E$. This can be found from the previous statement with a little tricky calculus. We know from equation (2.2) that $E(k) \propto k^2$ and therefore $k \propto \sqrt{E}$. It follows, then, that $\frac{dk}{dE} \propto \frac{1}{\sqrt{E}}$. It can then

be shown that:

$$D(E) = \frac{dN(E)}{dE} = \frac{dN(k)}{dk} \frac{dk}{dE} \propto E \frac{1}{\sqrt{E}} \propto \sqrt{E}$$
(2.3)

Figures 2.2¹ and 2.3¹ show E(k) versus k (equation 2.2) and D(E) versus E (equation 2.3) respectively.



Figure 2.2¹

Figure 2.3¹

E(k) versus k (figure 2.2), and D(E) versus E (figure 2.3) for a bulk material

2.1.2 Two Dimension Systems (2DEG)

The bulk material is the simplest case. The first step in quantum reduction involves taking a three dimensional bulk material and shrinking one dimension to the size of a few nanometers, so that the wavefunction of the electron is larger than the physical dimension of the material. This is called a two dimensional electron gas (2DEG), and it exhibits quantum confinement effects in the shrunken direction, but not in the other two. The electrons can flow freely in the two large dimensions, however, in the third dimension the electrons are bound as though in an infinite one dimension quantum well of the width of the material. For example, if we have the bulk solid above and shrink it in the x-direction to the point that d_x is less than the DeBroglie wavelength of the electron; the electrons are now confined to an infinite quantum well in the x-direction with

boundaries at $\frac{\pm d_x}{2}$. This is a well known problem from quantum mechanics, with well known solutions. Namely;

$$\Psi_x = \sqrt{\frac{2}{d_x}} \sin(n\pi \frac{x}{d_x}) \tag{2.4}$$

for the constricted direction, and

$$\Psi_{y,z} = A \exp(ik_y y) \exp(ik_z z)$$
(2.5)

in the other two directions, just as in the bulk material. If we operate on the x wave function with the energy operator, we get eigenvalues of

$$E = \frac{\hbar^2 k_x^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{8m d_x^2}$$
(2.6)

where m is the mass of the electron. The remaining two directions still maintain the quasi-continuous energy levels they had before. These can be visualized in \vec{k} -space as

planes in the y-z plane with spacing between them of Δk_x along the x-axis. The number of states within the quasi-continuous planes can be found by taking the area of the plane, as opposed to the volume of a sphere from the 3-D model. The number of states in a disk of radius k and thickness Δk , is then proportional to $k \Delta k$. Following the same derivation as the 3-D case:



E(k) versus k (figure 2.4¹), and D(E) versus E (figure 2.5¹) for a 2DEG

Figures 2.4¹ and 2.5¹ are graphical representations of E(k) versus k (eq. 2.6), and D(E) versus E (eq. 2.7), respectively, for the reduced direction. The other two dimensions are similar to Figure 2.2¹.

2.1.3 One Dimensional Systems (Quantum Wires)

The next step in reducing the bulk material is the one dimensional case, often called a quantum wire. This means that the electrons are free to move in a single dimension while the other two are restricted as though in a two dimensional infinite quantum well. This is also a fairly well known quantum problem with wave functions that look just like the previous case in the constricted dimensions (x,y):

$$\Psi_{x,y} = \frac{2}{\sqrt{d_x d_y}} \sin(\frac{n_x \pi x}{d_x}) \sin(\frac{n_y \pi y}{d_y})$$
(2.8)

$$E_{x,y} = \frac{\pi^2 \hbar^2}{8m} \left[\left(\frac{n_x}{d_x} \right)^2 + \left(\frac{n_y}{d_y} \right)^2 \right]$$
(2.9)

While the third dimension (z) maintains the same wave function and energy as before. The derivation of the density of states equations follow the same process as previously taken, and yield the following results:

Figure 2.6¹

Figure 2.7¹

E(k) versus k (figure 2.6¹), and D(E) versus E (figure 2.7¹) for a quantum wire Figures 2.6¹ and 2.7¹ show E(k) versus k, and D(E) versus E for the two quantum confined dimensions of the quantum wire. The third dimension follows the same energy distribution as shown in Figure 2.2¹ for the bulk solid. Since these quantum wires only transport charge freely in one dimension, they have been revolutionary to the micro-electronics industry. One of the more studied types of quantum wire to come about is the so-called "carbon nanotube." A nanotube is a chain of hexagonal carbon rings bound together to form a "long", very thin conducting tube. They have found applications as nano-scale wiring, as well as single electron emitters¹.

2.1.4 Zero Dimensional Systems (Quantum Dots)

The final step in quantum reduction from the bulk solid is the quantum dot or nanoparticle. This model has complete quantum confinement in all three dimensions. It can be thought of as an infinite spherical potential well of diameter d, which will yield a slightly more complicated wave equation in spherical coordinates:

$$\Psi_{l,m,n}(r,\theta,\phi) = \sum_{l,m,n} A_{l,m,n} J_l(x_{\ln}\frac{r}{d}) Y_l^m(\theta,\phi)$$
(2.11)

In this equation $A_{l,m,n}$ is an l, m, n dependent constant, $j_l(x_{\ln}\frac{r}{d})$ are the spherical Bessel functions, with x_{\ln} being the nth root of the lth order function (n being the principle quantum number, and l being the angular momentum quantum number). $Y_l^m(\theta, \phi)$ are the spherical harmonics (m being the spin quantum number). The energy eigenvalues can be found by operating on this equation with the energy operator. The results are:

$$E_{nl} = \frac{\hbar^2 k_{\rm ln}^2 n^2}{2M}$$
(2.12)

Where k_{ln} is x_{ln}/d , and M is electron mass. It is obvious from looking at this equation that the allowed energies states in the nanoparticle are discrete and widely separated. This is a very different situation from the bulk material, where the energy levels are nearly continuous.

Figure 2.9¹

E(k) versus k (figure 2.8¹), and D(E) versus E (figure 2.9¹) for a nanoparticle Again, Figures 2.8¹ and 2.9¹ show the E(k) and D(E) of the quantum dot structure. A quick comparison to Figure 2.2 will show the drastic difference between the continuous distribution of states, and the discrete case of the nanoparticle. Nanocrystals are currently being used in research and industry as photodetectors because of their atom-like absorption/emission spectra. If a photon with energy equal to the difference between two electron energy states is incident on a nanoparticle, then it can absorb that photon and excite one of its electrons. When that electron relaxes, it will emit a photon of a characteristic wavelength, determined by the energy difference between the initial and final levels. The interesting thing about these nanocrystals is that they can be easily tuned to absorb/emit certain wavelengths by changing the size of them during fabrication. There is another interesting case, though. If a photon of high enough energy is incident on the particle, it may lift an electron from a bound energy state a free state thereby creating an electron/hole pair (called an exciton). This can also be done by the creation of an Auger electron (this is explained in the TEM section). In both of these cases, there are new energies that must be thought about. Now that there are two separate charges present (the electron and the hole) the energies of each, and the Coulombic interactions of the two must be considered. To find the energy that binds these excitons we need to start from the band gap of the bulk material because that gives the energy needed to release an electron from the basic crystalline structure. However, we then add the Coulomb forces between the electron and hole, and then the excitation energies of both the electron and the hole. The Coulomb force may be sufficiently approximated to the first order in time-independent perturbation theory. The energy of the exciton created can be found using the hydrogenic Hamiltonian, wherein $m_{e(h)}$ is the effective mass of the electron(hole), ε is the dielectric constant of the bulk media, and $r_{e(h)}$ is the distance from the center of the sphere to the electron(hole):

$$\hat{H} = \frac{-\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\varepsilon(r_e - r_h)}$$
(2.13)

This operator is applied to the wave function of the electron/hole pair, which is simply the product of the electron wave function and the hole wave function. The energy eigenvalues returned would then be a sum of the energy eigenvalues for each individual wave function. The first two terms from the Hamiltonian will simply return the energy results from equation (2.12) with M now as the effective mass of the electron or hole. The third term, however, gets to be very complicated. This term describes the Coulomb interaction between the oppositely charged hole and electron as they become very close to one another. This factor can become very important when the two bodies begin to strongly interact i.e. orbiting one another. It has been shown³ that a good approximation can be made by finding the first excited energy of the exciton by applying the Hamiltonian to the product of the electron and hole wave functions.

$$E(\Psi) = \{\frac{-\hbar^2}{2m_e} \nabla_e^2 - \frac{\hbar^2}{2m_h} \nabla_h^2 - \frac{e^2}{\varepsilon(r_e - r_h)}\}(\Psi)$$
(2.14)

By applying this to the wave functions of the electron/hole pair, we can simplify it down to the relation:

$$E = \frac{\hbar^2 \pi^2}{2R^2} \left(\frac{1}{m_e} + \frac{1}{m_h}\right) - \frac{1.8e^2}{\varepsilon R}$$
(2.15)

In this relation R is the radius of the nanocrystals, $m_{e(h)}$ is the effective mass of the electron(hole), e is the elementary charge, and ε is the dielectric constant of the medium³. With regard to incident photons, the energy of the photonic wave packet in terms of c (speed of light), h (Planck's constant), and λ (wavelength of light) is given by:

$$E = \frac{hc}{\lambda} \tag{2.16}$$

Not all nanoparticles obey the above equations. These, equations are only valid as long as the assumption of spherical shape is valid, which should be the case for this research.

CHAPTER 3

CHARACTERIZATION TECHNIQUES

The techniques outlined in this chapter are the ideal techniques to be used when characterizing nanoparticles. It would be best if all of the techniques outlined in this chapter could be used to classify the particles, however this was not possible at the time of this thesis. The information is still included to show the variety of machinery that can be used, and present the reader with options outside of what was performed on the samples in question in this document.

3.1 Atomic Force Microscopy

Atomic force microscopy (AFM) is one method for determining the surface topography of a sample. It works off of a cantilever of known spring force constant, which scans the surface of the sample in a raster fashion using a very fine probe tip, as shown in the Figure 3.1 below. Note that the horizontal step and the vertical step sizes are equivalent.

Raster scanning pattern of AFM

The scan is either made by moving the tip over the sample, or by moving the sample under the tip, depending on the machine performing the scan. Regardless of which moves, sample or tip, the motion is made using four piezoelectric crystals bonded together and placed inside of a flexible tube. A potential is then applied to the crystals individually, causing them to flex and bend the tube, as seen in Figure 3.2^4 below. If only one of the $\pm x$,y directions is wanted, only that crystal is biased, but if $\pm z$ is wanted, both the $\pm x$ and $\pm y$ must be biased simultaneously.

Figure 3.2^4

Example of a piezoelectric tube for directional control of AFM

A piezoelectric material is one that will distort its crystal structure when placed under a potential difference. The amount of flex is in direct proportion to the applied potential, positive for expansion and negative for contraction. Lasers are used to determine the deflection of the cantilevers, thereby determining topography of the surface. A beam is reflected off of the back of the cantilever and into an array of two detectors. These detectors, A and B, are calibrated so that a beam that is centered between them gives no response, i.e. the output is based on a signal of A+B and A-B. If one signal is higher than the other, meaning the reflected beam is off center, a bias is applied to the piezocrystal tube to return the beam back to center, thereby always keeping the tip in contact with the sample. AFM can be done either inside or outside of vacuum, but if it is done outside of vacuum there must be software corrections for the likely presence of moisture and contaminants in the sample. There are three different types of modes in which an AFM can operate: constant contact, tapping, and non-contact. In constant contact mode the tip is always in contact with the surface, and surface imperfections will physically move the tip up and down. In contact mode, the selection of cantilever and tip is supremely important, because they will directly effect how well the surface is characterized. If the lever is too stiff, it will tear through the features and show nothing but a uniform surface. If a tip that is too large is used, it will not give enough detail of the surface, because the system can only resolve objects that rise less steeply than the sides of the tip. See Figure 3.3^4 for an illustration.

Figure 3.3⁴

Illustration of the importance of proper tip choice for contact AFM If the tip is too small, it may be damaged in the measurement process. The contact mode has the advantages of not being susceptible to interference from moisture because it will plow right through it, and also has very little noise. It does have the severe disadvantage of damaging the sample surface by leaving a small trench everywhere the tip contacts. Because of this aspect, this should not be the first measurement made on the surface. In tapping mode the cantilever will be oscillated at a predetermined frequency and amplitude ($\sim 20-100$ nm). As the tip oscillates over the sample, peaks will contact the tip and cause the frequency of oscillation to vary. These variations are measured and interpreted to see what the height of the peak is. Due to this, a stiffer cantilever must be used because it should not flex too much, since that may create false frequencies, which could be translated as surface anomalies. The final mode, non-contact, is the most difficult to perform and interpret. For this type of measurement, the tip is oscillated much like in tapping mode, however this oscillation is very small (~ 10 nm). The weak atomic interaction between the tip and the surface atoms, known as Van der Waals' forces, will cause a variation in the frequency that the system can measure. Just like in tapping mode, these variations are interpreted as topographical features. The difficulty presents itself when interpreting what data the system gives, because there is no difference between moisture on the surface and actual surface features. In order to

distinguish, another type of measurement must also be done. The AFM would be used for similar measurements as those of the TEM: size, shape, and distribution after application to some sort of substrate.

3.2 Electron Microscopy

This section will outline the background as well as the setup and procedure used for experimenting with the Transmission and Scanning Electron Microscopes.

3.2.1 Background

A Transmission Electron Microscope (TEM) operates in a similar manner to an optical microscope in that they bombard the sample with some controllable radiation through a series of lenses, pass the radiation through the sample, and collect it on the other side. A Scanning Electron Microscope (SEM), however, scans the sample surface with a beam and measures the backscattered electrons, but is not concerned with transmitting them completely through the sample. The main advantage to the either electron microscope is its ability to resolve a much smaller size regime than the optical scope. The resolution of an ordinary optical microscope is on the order of 3,000Å (the wavelength of visible light), while a TEM and SEM have resolution of ~ 2.5 Å. The electrons for the beam are created by some source, and then accelerated through a potential usually between 100 and 400 kV, for TEM and 10 to 30 kV for SEM. They are then focused using a series of condensing lenses, through an aperture and onto the sample. In TEM the electrons are transmitted through the sample and then passed through a series of objective lenses, and are finally incident on a phosphor screen, where it can be seen by the naked eye. In SEM the beam is not designed to penetrate the sample but is merely scanned across the surface. The incident primary electrons interact with the

low energy electrons in the surface atoms and may eject some of these from the surface, or deeper depending on the beam energy. These ejected secondary electrons are collected by secondary electron detectors and used to characterize the surface topography of the sample. The lenses used in this process are not ordinary optical lenses; they are electromagnetic lenses, which are circular variable magnets that focus the beam to different points. Just like normal lenses, these lenses have focal lengths, angles of divergence, aberration, etc. The condensing lenses usually consist of at least one focusing lens, followed by an aperture to further restrict the beam size by blocking out the high-angle electrons. The objective lenses simply magnify the image formed by the transmitted electrons, and guide it toward the phosphor screen. A schematic of a TEM can be seen in Figure 3.4 below.

Figure 3.4

Schematic of a typical electron microscope

Figure 3.5⁵

Examples of electron interactions in electron microscopy.

There are several interactions that can take place at the sample, and each can be measured to characterize a different physical aspect of the sample. These are shown in Figure 3.5⁵. Some scopes have other sensors added to them to pick up scattered x-rays, detect back-scattered electrons, Auger electrons, or secondary electrons. Backscattering occurs when an electron has a strong Coulombic interaction with the nucleus of an atom at a low angle of incidence (nearly normal to the surface), and is reflected nearly 180° back toward the source. The amount that this occurs is in direct proportion with the atomic number of the sample, because as the atomic number increases so does the size and charge of the nucleus. It makes logical sense then, that the electron would have a greater probability of interacting with the larger nuclei. With this type of microscopy, the brighter objects are the atoms of higher atomic number, whereas the darker areas have a lower one, allowing the researcher to easily see where the larger atoms are in their sample. Sometimes an electron will collide with another electron in the sample. This can happen either elastically, each giving a different type of data. If an electron undergoes

an elastic collision it loses very little of its energy, and therefore is still transmitted through the material and picked up on the other side by the phosphor screen. The elastic collisions usually occur with plasmons in the electron sea between the atoms on the sample. Some electrons have an inelastic collision in which much of there energy may be lost and they can be scattered in one of many directions. If the electron is left with enough energy, and is traveling in the proper direction to pass through the sample, then it will transmit and be picked up by the phosphor screen. Some of these lower energy electrons can be collected and analyzed by a method known as EELS, or electron energy loss spectroscopy. This method uses the amount of energy lost by the electrons to determine the composition of the material. The inelastic collisions can also create Kakuchi bands, which are very similar to a diffraction pattern. The width of these bands can be measured to show the spacing between atoms in the sample; the width of the bands being inversely proportional to the spacing. Inelastic collisions can also lead to xray emission, and Auger electron emission. These both occur in much the same fashion. For each, an electron must penetrate to the center of an atom and undergo an inelastic collision with a k-shell electron. This electron, called a secondary electron, will then be ejected from the sample leaving a hole in an inner electron orbital. These electrons are most often used to characterize samples in SEM. This hole is filled when a higher energy electron relaxes into that spot. The atom now has an excess of energy because the electron had to give some up to move down into the lower energy state. This energy can be emitted as an x-ray photon, or a different l-shell electron can be ejected, taking the energy away as kinetic energy. This ejected electron is called an Auger electron. The Auger electron, x-ray, and secondary electron, can all be used to determine the surface

contour, as well as the make up of the first few nanometers of the surface of the material. Each element has a unique Auger energy, so these electrons can easily be used to determine the makeup of the material. Since the secondary and Auger electrons will not have a very high kinetic energy, they must be ejected very near the surface (<10nm) or they will recombine within the sample, never reaching a detector. Therefore, they are only useful in determining the near-surface characteristics of the sample. Figure 3.6^5 is a graphic showing the depths at which the different interactions in Figure 3.5^5 occur.

Figure 3.6⁵

Depth of different electron interactions in electron microscopy.

If the sample has a crystalline structure, then the wave nature of the electron must be considered. If an electron passes fairly unscathed through the material, meaning that it had no actual collisions with other electrons, it may still have been diffracted by passing through the crystal structure. This diffraction would coincide with Bragg's Law, and the resulting diffraction pattern could be used to determine the lattice structure, spacing, etc. An electron microscope would be used to characterize size, distribution, and shape of the nanoparticles once they have been applied to a substrate, either by spin-on or other means.

3.2.2 Setup and Procedure

The equipment used for this thesis was a Jeol 6400 FESEM with XVision Plus imaging software, and EDAXX-ray analysis equipment attached. The first thing that must be done when operating this system is evacuation of the column and sample chamber to achieve proper vacuum. The column should have vacuum of $\sim 10^{-8}$ Torr. and the sample chamber should be $\sim 10^{-6}$ Torr. The sample is then mounted on a brass base by means of conductive carbon tape. If the sample is a semiconductor or insulator a contact to the upper surface by means of carbon or silver paint should be made. In the case of a Si wafer, carbon paint was used. If paint is used it must be permitted to fully dry to prevent degassing or evaporation in the chamber. If the paint evaporates then the chamber will become contaminated and cannot be used until it is fully cleaned. Once the sample is properly mounted it can then be placed in the loading chamber. The valve from the loading chamber to the specimen chamber must be closed before the loading chamber is opened! The brass base simply screws onto the threads of the sample loader and the door is closed. The red button at the side of the valve may then be pushed to evacuate the loading chamber and permit opening of the valve, so that the sample may be moved into the specimen chamber (or load-lock). Once the sample is in place, the loader is unscrewed from the base and removed from the sample chamber, the valve between the two chambers can be closed. Once the vacuum in the main chamber reaches the proper pressure again, the filament may be turned on. It is recommended that 10kV accelerating potential be used to start with and increased slowly to the working potential to extend the life of the filament. Once an appropriate working potential is achieved, image collection

may begin. If topographical imaging is required, an accelerating potential of 15-17kV will be sufficient. If higher than this is used, the electrons may have high enough energies to penetrate below the surface of the sample, and thereby compromising surface images. Higher energies can also damage sensitive structures such as nanocrystals, so caution should be used. Once the potential is chosen, a live image is shown on a small screen to the left of the main control monitor. This image will be used to focus the image, as well as adjust the brightness and contrast of the scope. The Jeol system has four different apertures that can be selected, ranging in size from 100µm to 20µm. The smaller the size of the aperture the smaller objects it can resolve, but the image formed may be of lower quality. For high magnification experiments, aperture 3 or 4 should be used. Focus, contrast, and brightness should be optimized before attempting to increase magnification, and should be continuously adjusted for the best possible picture as magnification is increased. It may also be necessary to adjust the probe current to obtain the optimum image. The probe current is what controls the size of the beam as it contacts the sample. Once good focus is obtained the use of the EDAX software can help fine tune the focus and is valuable for eliminating electrical noise. Several image scans can be made and added together to form a clearer image at higher magnification. Once an image is captured an x-ray spectrum can be taken to analyze the composition of the sample in question. A count value of at least 500 CPS and 20 DT% is recommended for best results in this scan. These values can be obtained by varying aperture, accelerating voltage, and probe current values. Once acceptable images and spectra are collected they can simply be saved to the computer's hard drive and transferred at the user's leisure. When characterization is completed the accelerating voltage must be reduced, in steps of

1kV, until 10kV and then the filament may be turned off. The stage should be returned to the home position by using the stage utility in the JEOL software. Specimen removal is performed in the reverse of the initial placement. If it has been several days since the specimen was placed, it may be a good idea to vent and re-evacuate the loading chamber to ensure the safety of the valve that closes off the specimen chamber. This valve may be damaged if it is opened in the presence of a large pressure gradient.

Photos of The JEOL SEM at Texas State University-San Marcos

3.3 Photoluminescence Spectroscopy

A main characterization technique used for nanocrystals is photoluminescence spectroscopy. Photoluminescence (PL) uses incident light of a known energy (wavelength) to excite a sample to emit photons of its characteristic wavelength. These emissions are collected and analyzed to determine the different transition energies of the material being examined. The main physical concept behind the technique of PL is that atoms can only absorb and emit specific energies due to the quantum confinement effects of the electron orbit about the nucleus. Therefore, when a photon is incident on an atom, if it has the proper amount of energy, an electron in a lower state may absorb it and be excited into the first, second, third etc. excited state. Depending on the stability of the state, the electron may remain at that energy for a finite, usually very short, time. After that time, however, the electron will relax back to a lower state. In order to conserve energy, the energy that the electron loses is emitted as a photon of wavelength characteristic for the amount of energy lost. The energy of the photon can be determined using equation (2.16) from above. This technique is so useful in characterizing nanoparticles because they exhibit the same quantization of energy as an atom, and the energy that the electrons absorb and emit can be used to directly calculate the size and/or shape of the crystals in the sample by equation (2.15).

Figure 3.8

Schematic of a simple photoluminescence spectrometer

Figure 3.8 shows a simple PL setup similar to the one that I built two semesters ago. The box surrounding the sample and lens combination is a light proof box, which helps to eliminate background light. The lens/filter shown is a system of lenses to gather and collimate the emitted radiation, while the filter was a cold mirror to reflect the undesired wavelengths. The monochromator uses diffraction gratings and parabolic mirrors to spread the collected light into a discrete spectrum. That spectrum is then sent via an optical fiber to a multi-channel analyzer where the intensity of the spectral peaks is plotted against the wavelength. Some types of photoluminescence experiments use microscopes with optical fibers to gather the light and transmit it to a detector. The most advanced types of PL systems can use the relative intensity of the peaks to determine the relative concentrations of the elements in the sample. Unfortunately the

Photoluminescence Spectrophotometers that were available at the time of experimentation were unable to detect in the IR range that was needed, therefore this technique could not be used to classify the particles in this research.

3.4 Fourier Transform Infrared Spectroscopy

This section will outline the concepts and use of Fourier Transform Infrared Spectroscopy (FTIR). FTIR is an optical characterization technique used to characterize many semiconductor materials, and optoelectronic materials.

3.4.1 Background

Fourier transform infrared spectroscopy (FTIR) is another optical method of characterizing samples. All FTIR systems employ some kind of interferometer, most often the Michelson interferometer (shown schematically in Figure 3.9). The Michelson interferometer is a device designed by Michelson in 1891 to create interference patterns that allow for determination of wavelengths of a source. The design is fairly simple in principle; a collimated beam is directed toward a beam splitter, which cuts the beam in half (ideally), and directs the beam toward two mirrors. One of these mirrors is stationary, while the other is mobile. The beams are then recombined and sent into a detector. The recombined beam will display interference effects based on the retardation of the system due to the pathlength difference between the beams. Retardation is given by the formula

$$2(d_{m}-d_{s})$$
 (3.1)

Where d_m is the distance from the mobile mirror to the beam splitter, and d_s is the distance to the stationary mirror from the splitter. When this retardation reaches a value of integral wavelengths of the source there is constructive interference, and when it falls

on half wavelengths there is destructive interference. If it is somewhere in between then Fourier transforms are used to determine the phase difference between the two beams. Figure 3.10 is an example of two waves interfering. The first two waves are cosine waveforms that have a 10% phase separation. This means that every ten cycles of one, and nine cycles of the other, they will be in phase again. The superposition of these two is the lower waveform, which is what would be picked up by a detector in an interferometer. Fourier analysis of waveforms converts the temporal functions that are presented to the detector and transform them into functions of frequency instead. A

Schematic of a simple Michelson interferometer

fourier analysis of this would permit the technician using the equipment to see what the frequencies responsible for the waveform are, and what percentage each is of the whole function. Adopting the notation of Griffiths, a Fourier transform for a polychromatic source is dependent on the retardation (δ) and the frequency (ν).

$$B(\nu) = 2 \int_{0}^{\infty} I(\delta) \cos(2\pi\nu\delta) d\delta$$
(3.2)

The transformed data will display as a spectrum of frequencies in the detected beam. The interferogram from Figure 3.10 would be transformed to graph like the spectrum represented by Figure 3.11. Notice that the two peaks are of equal amplitude, which means that the interferogram is equally caused by each of the two waves. This is the type of data expected from an FTIR, hence the name Fourier transform infrared spectroscopy.

Figure 3.10

Example of an interferogram involving two waves

Figure 3.11

Spectral interpretation of an Figure 3.10

The resolution in the interferometer is strictly dependent on the maximum retardation of the scan. As the retardation increases, so does the resolution possible. To help explain how this is possible we will take the case of figure 3.10. If we define the separation of these two waves as $\Delta v = v_1 - v_2$ cm⁻¹ then the two interfere purely destructively after $\frac{1}{2}$ $(\Delta v)^{-1}$ cm retardation, and regain constructive interference after $(\Delta v)^{-1}$ cm. If one wishes to resolve the doublet then the retardation must be at least $(\Delta v)^{-1}$ cm. It is therefore apparent that as the separation of the doublet decreases, the retardation must increase before the waves will once again regain phase. Therefore, the retardation and resolution are directly related. It may become necessary to correct for phase differences between the two signals in the interferometer due to electronic or mechanical errors. If, for example the first point sampled is not exactly at zero, but at a point $\pm \zeta$ from zero, then a correction factor of $\pm \zeta$ must be added into the equation's cosine term. Another common cause of phase lag is the use of an electronic filter, which often exhibits a frequency dependent lag which can be added in a similar fashion. The complication that ensues is that since each cosine of a sum may be represented as a combined identity of sines and cosines, new sine terms are added to the interferogram. This may be overcome by doing a bidirectional scan. Instead of only scanning to one side of a zero point, the scan runs to both sides. The main disadvantage to this method is that twice the distance must be scanned in order

to achieve the same resolution as the one sided scan. Another factor that will strongly influence the effectiveness of a scan is the sampling rate. If the sampling frequency is less then half of the wavelength of the incident beam, then there will be no problem. If, however, the rate is selected so that the points do not fall within half of a wavelength, then incorrect sinusoidal functions may be fit to the data. For example, the blue (dashed) wave in Figure 3.12 represents a received signal with the black spots being sampled points. If all the points are taken into account this is a properly sampled wave. If the sample frequency were halved, then the second wave (solid) in purple would give a better curve fit to the data collected than the actual signal. It is quite evident from this simple example that proper sampling frequency is crucial to data collection. Once a proper interferogram is obtained from the interferometer the signal can be sent to the sample.

Figure 3.12

Importance of proper sampling rate in FTIR.

The interferogram is sent to the sample, where it interacts as it will, and the result of this interaction is sent to a detector⁷. This spectrum is sent to a computer for analysis where it is Fourier transformed and displayed. There are many available measurement modes associated with FTIR. The first to be discussed is called Attenuated Total Reflectance (ATR). In ATR the penetration of the evanescent wave beyond the surface of a sample is measured and used to characterize the surface structure of the material. This is a

fascinating technique, from a physicist viewpoint. Mid-IR light is sent into a thin element, called an Internal Reflection Element (IRE), and is totally internally reflected down its length. This IRE is placed in direct contact with the sample to be characterized. The beam, upon reflection will still penetrate a small distance in to the sample material. This distance will be on the order of $1\mu m$. The effect that the sample has on these evanescent waves is what is measured by the detector. The data from this small penetration is used to determine bond structure and crystalline information about the sample because the absorption of the radiation is dependent on the vibrational modes of the bonds at the surface of the sample. Percent transmittance is an often employed technique which measures the attenuation of transmitted wavelengths as they pass through the sample. The incident interferogram is allowed to pass through the sample and the intensities of the reference and transmitted beam are then compared at each frequency from the interferometer. The percent transmittance is then calculated as a ratio of transmitted intensity to reference intensity, so that 100% transmittance will occur when the transmitted beam is unattenuated. Absorbance is measured using the same technique as transmittance; only interpolating the data is slightly different. Instead of giving a mere ratio of intensities, as in transmittance, the transmitted intensity is divided by the incident intensity and then turned into a log scale.

$A = -\log_{10}(T)$

Therefore, absorbance (A) is merely a log-scale permutation of the transmittance $(T)^8$.

3.4.2 Setup and Procedure

This system is a Thermo Electron Corporation Nicolet[™] 6700 FTIR, coupled with OMNIC data collection software, under the purview of Dr. David Donnelly

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at Texas State University-San Marcos. Silicon wafer and glass slide samples were characterized using transmission techniques to measure transmission spectra. Before all measurements a nitrogen purge was performed to clear the system of any water vapor and atmospheric contaminants that may interfere with data collection. At this point the system was aligned to maximize input signal and detector strength, and the system stability was checked with background comparisons to ensure precision in measurement. Data was taken as %transmittance with either 32 or 64 scans, at a resolution of 4 wavenumbers (cm⁻¹). Measurements taken were in the range of 2000 to 11000 cm⁻¹ using the XT-KBr beamsplitter with a DTGS detector and visible (white) light source.

Figure 3.13 Photos showing the Thermo Electron Corporation Nicolet[™] 6700 FTIR and Raman Systems

Figure 3.14 Schematic photo of Thermo Electron Corporation Nicolet[™] 6700 FTIR system

CHAPTER 4

SYNTHESIS OF SAMPLES

The creation of PbSe nanoparticles is dependent on the creation of stable precursors of lead and selenium, and combining them in an atmosphere of inert gases. This chapter will discuss the process of creating colloidal nanocrystals from lead and selenium.

4.1 General Synthesis Process

For PbSe nanoparticles the precursors conventionally used are trioctylphosphine selenide (TOPSe) and lead oleate. For this experimentation however, due to cost, tributylphosphine selenide (TBPSe) was used in place of TOPSe. TOPSe is created by mixing a 1M solution of trioctylphosphine (TOP) and Se powder in an Argon inflated glove bag, at approximately 95°C while magnetically stirring. An inert environment must be maintained because of the volatile nature of the TOP precursor, which oxidizes readily and therefore reacts violently to oxygen. The purity of the TOP ligand is critical to the reaction, because its bond strength will play a large role in the rate of formation of the nanoparticles. Because of this, only tech-grade or better tributylphosphine should be used. The lead oleate precursor solution is created by mixing lead acetate trihydrate with oleic acid in a 1:5 mixture (1 mol lead acetate.3H₂0:5 mol oleic acid) in an excess of an

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inert process medium (conventionally TOP), and stirring at a temperature of 100°C. The lead oleate precursor solution is then placed in an Ar inflated glove bag and brought to a temperature of 115°C. The TOPSe precursor is rapidly (<1s) injected using a syringe while the solution is magnetically stirred using a small stir bar. After injection, aliquots can be taken at intervals to monitor the progression of the reaction. These aliquots should be placed in a neutralizing medium, like isopropanol, to halt the reaction.

4.2 Growth Phases

The creation process of these nanoparticles occurs in three main phases: nucleation, growth, and ripening. Each is marked by specific behavior of the particles in solution and can be recognized based on data gathered from optical characterization.

4.2.1 Nucleation

The nucleation phase is the separation of reactants from their precursor molecules. The rate at which this occurs is highly temperature dependant, because as the temperature increases, the stability of the precursors decreases, but it is also strongly dependent on the concentrations of the solvents used in the precursors. The lead and selenium combine in a 1:1 ratio, but the different binding energies of the TOP and oleic acid ligands will alter the rate at which the lead and selenium will separate. As the temperature increases and the precursors become less and less stable, the lead and selenium will begin to spontaneously separate, releasing the reactants into the solution.

4.2.2 Growth

The growth phase is something of a misnomer, because it's actually the phase in which the lead and selenium combine initially, while the ripening phase is where the several particles will aggregate to "grow" the crystalline structure. The rate at which the growth phase takes place is dependant mostly on the strength of the TOP ligand. It surprisingly turns out that fast growth due to fresh TOP in the solution is not desirable, and actually makes for more difficult control of the size of the nanoparticles. This is due to too many TOP ligands bonding to the faces of the growing PbSe crystals, thereby stunting their growth. Once the ligands begin to adhere to the faces of the crystal, it will no longer grow in that direction. If the ligands in solution are too strong, or too numerous they will prematurely bond to the crystals, and halt growth at times that may not be desired. Conversely, if the ligands are too weak, or too sparse, they won't bond well enough and the separate crystals will aggregate and form a superstructure. If this happens, the sample will no longer display the quantum confinement effects that make these crystals so useful, making that solution virtually useless.

4.2.3 Ripening

The ripening phase is hard to distinguish completely from the growth phase, but it is marked by a distinct red shift in the emission/absorption spectra of the nanocrystals, due to their increasing size. This red shift can be monitored either during growth, which requires a very advanced real-time photoluminescence machine, or it can be seen in the aliquots that are taken during the process. Once the particles have reached the desired size, the reaction can be halted simply by removing the source of heat. Once the heat is removed, the Oleic Acid ligands will adhere to the faces of the crystals, growing an acid cap on the particle. This re-stabilizes the ligands, and stops the release of lead and selenium into the solution, thereby halting the reaction. An excess of methanol should then be added to the solution to dissolve any unbound solvent, unreacted precursors, and unbound coordinating molecules. Once complete, the solution can be centrifuged at a medium speed (~5000rpm) and the methanol decanted. The nanocrystals can then be dried in an inert environment, and dissolved in a hexane solution (often toluene). Storage should be done in a cool place, under an inert environment⁹. Application to a surface, i.e. Si wafer, can be performed by a simple spin-on coating from the hexane solution.

4.3 Synthesis Procedure

This section will outline the procedure that was performed specifically for the samples characterized in this paper. Where TOP or TOPSe is specified above, TBP and TBPSe were used for this research. For the two reactions performed, a 40mL quantity of TBPSe was created in a 100mL Erlenmeyer flask, following the procedure outlined in the previous section, and was stopped and stored in an Ar environment for the duration of this research. It was stored in this fashion to maintain stability, and to prevent oxidation of the precursor. This store was used as the selenium precursor for the both of the reactions in this research. As a dissolution medium for the lead acetate precursor a partially hydrogenated terphenyl process fluid, MCS 2811 from Solutia Inc was used. The lead precursor was mixed by combining 10mmol of oleic acid with 2mmol of lead acetate trihydrate in 40mL of MCS 2811, in a 50mL beaker, while magnetically stirred at a temperature of 95-105°C. Once dissolution was complete the lead oleate had a light yellow color while the TBPSe was clear. The lead precursor was then placed on a hot plate in an argon bag (pictured in Figure 4.3) and heated to 115-120°C. The selenium precursor was then injected using a glass syringe with a hypodermic needle. Upon injection the mixture turned from yellow to black in a matter of minutes. In the first reaction 1mL samples were taken, with a syringe, at 2, 5, 10, 20, 30, 60, 90, 120, 150, and 180 minutes to measure the reaction rate and size distributions. Aliquots were

injected into an excess of methanol to halt the reaction. In the second reaction aliquots were taken at 1, 2, 4, 6, 10, 15, 30, 45, 60, 90, 120, 150, and 180 minutes to get a better idea of the initial growth regime of the process. These samples were stored in an Ar bag until they were ready to be centrifuged. The samples were all centrifuged using a physician's centrifuge (pictured in Figure 4.2). Each sample was centrifuged and the methanol was decanted and replaced with toluene. Samples with longer reaction times were noted to have a black precipitate which, when washed with toluene, separated in solution. It was also observed that after being stored for several days the precipitate again separated from solution. This may have been due to aggregation of the crystals. After the first centrifugation each sample was washed with toluene and centrifuged again to remove any remaining methanol, or unreacted precursors. Once the second centrifugation was completed the samples were transferred into storage vials and labeled, and transported to the Department of Physics for characterization.

Figure 4.1 Fume hood used to perform reactions

Figure 4.2 Centrifuge used to

decant samples

Glove bag and hot plate used for sample preparation

Figure 4.3

CHAPTER 5

CHARACTERIZATION

5.1 Sample Preparation

In order to prepare the samples for characterization a spin coating process was performed using Si wafers. Initially 2" silicon wafers (100 face) were used. One half milliliter of solution was deposited on the surface of the wafer while it was spun at a speed of 300rpm for 30 seconds. The wafer was then initially annealed on a hot plate at a temperature of approximately 225°C for five minutes to evaporate the solvent. This initial anneal was then followed up with a 20 minute anneal on another hot plate at 250°C. It was determined that a second anneal was necessary after the first attempts at characterization with FTIR were unsuccessful. The reasoning behind this was that perhaps remaining solvent on the surface was attenuating incident radiation, or perhaps was preventing proper absorption by the nanocrystals on the surface. Also, glass slide samples were created by dropping the solution onto a glass slide and allowing them to dry at room temperature (22°C). After a consultation with a fellow student a new technique was attempted in which the sample solutions were heated on a hot plate at 75°C and agitated. This was proposed because the crystals may have aggregated in solution. If this was the case perhaps heat and kinetic energy may prove sufficient to break the weak bonds holding the separate crystals together.

5.2 Fourier Transform Infrared Spectroscopy

Initial data taken with Si wafer substrate were inconclusive. It was believed to be because the absorption made by the particles was not large enough to be detected through the substrate, so a different substrate was chosen. The solution was then swabbed onto a glass slide and allowed to dry before another test was performed. The initial data is shown in figures 5.2 and 5.3. Figure 5.1 is a typical background collected during experimentation. The jagged areas are interference due to water vapor in the system. Figure 5.2 shows a sample of a clean dry Si wafer, and Figure 5.3 is a wafer with the sample spun on the surface, and Figure 5.4 is the sample spectrum with the Si reference spectrum removed. This was done in Excel[™] by dividing the sample data by the Si data series. Since the transmitted intensity was only 4% or so of the incident intensity, it was believed that the wafer may have been blocking too much of the incident light to permit a proper reading of the transmittance of the particles, therefore a second set of runs was performed using a glass substrate instead of silicon. These results are shown in figures 5.4 through 5.7. Upon inspection, there was no discernable difference between these samples either, meaning that there was either no absorption or the equipment was improperly set up. In order to eliminate the latter possibility Dr. Donnelly was asked to review the system and no faults could be found. After these samples also returned negative results, the samples were heated and agitated and new tests were run after a new spin coating with the same parameters as the first. The data collected from this test was identical to the first set taken. This led to the conclusion that the particles either were not

there, or did not fall into the size range expected. If they were too large then they would not display quantum confinement effects and would not absorb and emit at all in the IR range. If they were too small then the absorption would occur in the far IR spectrum which was not measured in this experiment. The latter was not believed to be the case because the longer reaction time samples should have produced larger particles which would eventually reach large enough size to emit in the mid-near IR. This was not the case, even for the 180 minute samples.

Sample spun onto Silicon wafer.

Sample with Silicon reference removed

Figure 5.5

Reference spectrum taken with clean

Sample taken on Silicon after reheating

and agitating

glass slide

5.3 Electron Microscopy

After FTIR was inconclusive the samples were taken to the Scanning Electron Microscope outfitted with an EDAX[®] X-Ray analysis tool. First to be characterized was the 60 minute reaction specimen. This wafer revealed that aggregation had occurred at some point during the reaction process. Figure 5.8 shows this sample at 23,000 times magnification. Surface irregularities can be noted on the objects. Figure 5.9 shows the same area with magnification increased to 85.000 times. At this magnification it becomes clear that the larger object is comprised of many smaller, roughly spherical shaped objects, each of approximately 100-150nm in diameter. Further inspection of the other wafers revealed this to be the case for all of the samples. The 120 minute wafer contained both nanostructures as well as a number of single particles, each in the size range of 200-300nm. Testing proceeded on the 45, 30, 15, 10, and 4 minute wafers in a similar fashion to the first two. No samples from the first reaction were used because they were lost in an accident in the lab. The samples with moderate reaction times all displayed larger structures of aggregated particles, while the 10 and 4 minute wafers had no distinguishable particles. This was a noticeable shift from the 120 and 60 minute wafers which had distinguishable structures spread over the entire surface. Figure 5.10 shows a superstructure formed on the 120 minute wafer, the sizes of the particles there are around 200 nm. Figures 5.11 and 5.12 are representations of single particles also found on the 120 minute wafer, with sizes between 150 and 200 nm. The structure shown in Figure 5.13 is from the 45 minute wafer. The image is blurry due to electron buildup around the viewing area due to poor sample grounding. Figure 5.14 shows the particulate conglomerate on the surface of the 15 minute sample, composed of particles

of 75-80 nm. The 10 minute sample was analyzed, but all that was found were objects similar to Figure 5.15. It is believed that these objects were similar to the other conglomerates, except that they are composed of particles too small to resolve with the expertise available at the time of image capture. Figure 5.16 is a graph of particle size versus time. The graph appears to be fairly linear but the smaller slope at higher time would indicate an asymptotic behavior similar to those in publications¹¹. Those growth charts appearing in publications appear much more logarithmic than this one, however part of this may be contributed to differing bonding energies between TBP and TOP ligands used conventionally in industry. The reaction appears to have occurred in two phases, with the jump in the middle being the transition between the two. These two phases may represent the growth and nucleation phases of the reaction process as outlined previously.

Figure 5.8 60 minute sample at 23,000 magnification. Note the texture of the surfaces.

Figure 5.10

120 minute sample at 23,000 magnification. Again note the surface texture.

60 minute sample at 85,000 magnification. The circular objects are PbSe nanocrystals that have aggregated to form a superstructure.

Single nanocrystals found on 120 minute sample. Magnified 60,000 times. Approximately 175nm in size.

Figure 5.12 Single nanocrystals found on 120 minute wafer. Magnified 65,000 times. 150nm in size.

Nanostructure on 45 minute sample wafer. Magnified 20,000 times. Each crystal in this structure is only 100-120nm in diameter.

15 minute sample at 43,000 times magnification. The individual particles are 75 nm in diameter.

10 minute sample object at 23,000 times magnification. Object size is 500 nm.

Figure 5.16

Plot of particle size versus time.

CHAPTER 6

CONCLUSIONS

To conclude, the reactions appear to have proceeded as expected from publications; however some reaction and storage issues should be resolved in the future. FTIR data was inconclusive; however the reasons for this were discovered upon investigation with SEM. The growth procedure appears loosely similar to those in other publications, in that they appear to occur in stages, and have asymptotic behavior. It is easily seen however, that the growth does not appear to proceed in the logarithmic fashion seen in the rest of the community.

From the FTIR data it was obvious that the particles created from the reaction were not displaying any sort of quantum confinement because they were not absorbing or emitting in the energy ranges expected. After this technique failed to yield data that could be used to determine size distribution, it was believed that perhaps the particles did not form or, they formed superstructures that would destroy the potential well created by the size of the individual particles. The SEM data collected confirmed these suspicions. The formation of clusters allowed the electrons to flow in a more free fashion than in a nanoparticle, thereby making them unable to absorb and emit as in the 3-D confinement model. There are several possible explanations as to why this aggregation occurred.

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Initially this clumping was thought to be a result of Van der Waals forces between the particles, and so the samples were heated in order to break these weak bonds. This may have had a negative effect, because this heat may have been sufficient to actually cause the smaller particles to break apart and add to the size of the larger particles, as well as permit unreacted precursors to latch onto existing crystals, thereby increasing their size. Another possible explanation for this phenomenon is that perhaps TBP was not miscible in toluene, thereby making the particles prefer clumping to staying independent in solution. This would play a role because the particles may exist in a lower energy state when surrounded by other particles than when their entire surface area is exposed to the solvent. The protruding butyl groups from the surfaces of the molecules may form a potential between the particles and the surrounding solvent, thereby increasing the Gibbs free energy of this configuration. If an energy smaller than this exists between the particles and each other, then they will tend toward aggregation, simply to maintain the lowest energy possible. These same ideas may also be applied to the process medium. The butyl groups may react with the MCS 2811 in a similar fashion, thereby causing the aggregation to occur before it is ever transferred to the storage solute. This should be further investigated before future reactions are attempted. The fact that the particles separated from solution in storage may be indicative of the immiscibility of the TBP ligand with the toluene solvent. The reaction process on the whole seems to have proceeded as expected upon inspection of the sizes and shapes of particles, even if they are parts of a larger whole. The discrepancy in the growth rate as compared to others in the community may be due to the use of TBP as a precursor. The smaller size of the TBP molecule, as compared to TOP which is conventionally used in industry, may permit it to

more readily cap the molecules thereby stunting their growth. This would cause the particles to grow at a slower pace possibly accounting for the smaller slope of the initial growth phase. In the future it may be beneficial to try adding a surfactant to the reaction which will charge the capped particles thereby increasing the energy required to aggregate. If this occurs it would make clumping much less likely. Many surfactants exist, but those with carboxylic acid should prove the most effective ionizing the particles.

Future work on this project should include the creation of nanocrystals using TOP to act as a reference for the TBP synthesis, to ensure that proper procedure is being followed. Also, the miscibility of TBP with MCS 2811 should be researched and, if necessary, a more suitable process medium found. If a more suitable medium cannot be found, the addition of a carboxyl surfactant may solve the problem of aggregation in solution. The use of methanol instead of toluene, as a storage solvent, may also aid in prevention of the clumping effect, since methanol is more suited to the TBP molecule. If clumping is still a problem, the use of an ultrasonic stirrer, or the application of sheer forces to the molecules should be used instead of the application of heat. This will remove the possibility of causing the reaction of unreacted precursor that may be left in solution after centrifugation. An issue may exist surrounding the method of application to substrate. The parameters for spin-coating and heating the wafers were arbitrarily picked. There may prove to be optimum settings for rotation speed and temperature that give more uniform coverage. The rate at which the solvent evaporates may also contribute to the aggregation of the particles. If it rapidly evaporates, then the particles may be more likely to settle on top of one another, whereas if the evaporation occurs

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more slowly, this may give them the opportunity to separate from one another and settle independently on the surface of the substrate.

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