Studying Quantum Dots using Atomic Force Microscopy

Anand Dwivedi, ***Advisor:*** Dr. Kevin T. Riggs

[1] *Physics Department, Stetson University, Deland, FL 32723, USA*

Abstract. Quantum Dots are semiconductor nanocrystals whose diameter is in the range of 2-10 nm, corresponding to 10 to 50 atoms in diameter and a total of 100 to 100,000 atoms within the quantum dot volume. Many types of quantum dot emit light of specific frequencies if electricity or light is applied to them, and these frequencies can be precisely tuned by changing the dots' size, shape and material, giving rise to many applications. Because of their high tunable properties, quantum dots are of wide interest. It finds its applications in nanotechnology, medical imaging, transistors, solar cells, LED's, diode lasers, quantum computing, etc. With this project, we intend to further understand and study the properties of quantum dots by using atomic force microscopy.

1 Atomic Force Microscopy

Atomic Force Microscopy (AFM) is a kind of scanning probe microscopy that was designed to measure the local properties of a surface using a probe. The precursor to the AFM, the Scanning Tunneling Microscope (STM), was developed by Gerd Binning and Heinrich Rohrer in the early 1980's at IBM Research-Zurich, a development that earned them the Nobel Prize for Physics in 1986. Binning invented the atomic-force microscope in 1985 (Figure 1) to examine insulating surfaces. This microscope was made by gluing tiny shard of diamond onto one end of tiny strip of gold foil. A small hook was attached to the end of the tip that worked as the probe by pressing against the sample surface. The first commercially available atomic-force microscope was introduced in 1989.

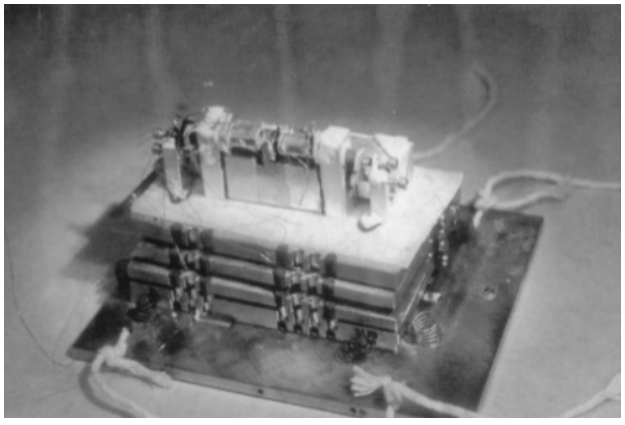

Figure 1. The first AFM invented by Gerd Binning in 1985.[1]

AFM's today use micro-machined Silicon cantilevers. AFM can be used on samples with minor preparation, over a large range of temperatures. High resolutions of the images produced by the AFM allow topographical imaging of samples such as DNA molecules. The AFM is also capable of techniques that provide information on other surface properties like friction, stiffness, elasticity, and so on.

1.1 Working Principles of AFM

The basic principles of AFM consist of three parts: surface sensing, detection method, and imaging. For surface sensing, the AFM uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, the close-range, attractive force between the surface and the tip cause the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over and causes the cantilever to deflect away from the surface. For the detection method, a laser beam is used to detect cantilever deflections towards or away from the surface. By reflecting an incident beam off the flat top of the cantilever, any cantilever deflection will cause slight changes in the direction of the reflected beam. A position-sensitive photo diode (PSPD) can be used to track these changes. Thus, if the AFM tip passes over a raised surface feature, the resulting cantilever deflection (and the subsequent change in the direction of reflected beam) is recorded by the PSPD. For imaging, an AFM images the topography of a sample surface by scanning the cantilever over a region of interest. The raised and lowered features on the sample surface influence the deflection of the cantilever, which is monitored by the PSPD. By using a feedback loop to control the height of the tip above the surface – thus maintaining constant laser position – the AFM can generate an accurate topographic map of the surface features.[2]

1.2 Topography

The AFM can use three different modes to map the surface: Contact mode, Non-contact mode, and Tapping mode. In contact mode, the AFM measures the repulsion between the tip of the probe and the sample. The force of the tip against the sample remains constant and the voltage required to keep the constant force indicates the height of the sample feature. Though this mode gives high resolution images of the sample surface and can be used to measure surface properties such as frictional forces, but it damages the sample as the tip of the probe remains in contact while mapping. In non-contact mode, the AFM measures the attractive forces between the tip of the probe and the sample. The Van der Waals forces between the tip and the sample are detected and this mode is used to analyze semiconductor surfaces. Though this mode gives lower image resolution than the contact mode, but no damage is caused to the sample as the tip doesn't the surface of the sample. In tapping mode, the tip of the AFM vertically oscillates on the sample surface at a frequency of 50,000 to 500,000 Hz. The amplitude of the oscillation is reduced as the probe comes in contact with the surface. This mode of measurement overcomes the problems associated with friction, adhesion or electrostatic forces, and is more effective for large scan sizes.

2 Quantum Dots

As we will be studying quantum dots using AFM, we need to understand quantum dots in further details. The extraordinary optical and electronic properties of nanocrystalline semiconductors were discovered in 1981 by Alexey Ekimov at the Vasilov State Optical Institute in St Petersburg, Russia, who first synthesized nanocrystals embedded in a glass matrix.[3] Four years later, Louis Brus, working at Bell Labs, synthesized the first colloidal semiconductor nanocrystallite solution. Mark Reed would go on to coin the phrase "quantum dots" in a 1988 paper, a much more linguistically palatable term than the "zero-dimensional semiconductor nanostructures".[4,5] However it was not until a seminal 1993 paper by Murray, Norris and Bawendi detailing a "hot-injection" synthesis for monodisperse colloidal nanocrystals[4] that researchers began to evaluate quantum dots for their potential commercial applications, not just as a curiosity.[6] Ekimov was a corecipient of the 2006 R.W. Wood Prize of the Optical Institute of America for "discovery of nanocrystal quantum dots and pioneering studies of their electrical and optical properties". Quantum dots display unique electronic properties, intermediate between those of bulk semiconductors and discrete molecules, that are partly the result of the unusually high surface-to-volume ratios for these particles. The most apparent result of this is fluorescence, wherein the nanocrystals can produce distinctive colors determined by the size of the particles.

Quantum dots obey the quantum mechanical principles of quantum confinement. Quantum confinement can be observed once the diameter of a material is of the same magnitude as the de Broglie wavelength of the electron wave function.

$$E_{confinement} = \frac{\hbar^2\pi^2}{2R^2}\left(\frac{1}{m_e} + \frac{1}{m_h}\right) = \frac{\hbar^2\pi^2}{2\mu R^2} \tag{1}$$

where m_e is the effective mass of the electron, m_h is the effective mass of the hole, μ is the reduced mass of the exciton system, and R is the radius of the quantum dot.

A particle behaves as if it were free when the confining dimension is large compared to the wavelength of the particle. During this state, the band gap remains at its original energy due to a continuous energy state. If the quantum dot radius is on the same order of magnitude as the exciton Bohr radius (Equation 2), it is said to be in the "weak confinement regime". However, as the confining dimension decreases and the radius of the quantum dot becomes smaller than the exciting Bohr radius ("strong confinement regime"), the energy spectrum becomes discrete. As a result, the band gap becomes size-dependent. This ultimately results in a blue shift in light emission as the size of the particles decreases (Figure 2). The confinement effects dominate in the "strong confinement regime", and the optical and electronic properties can be easily controlled.

$$a_b^* = a_b\epsilon_r\left(\frac{m}{\mu}\right) \tag{2}$$

where a_b^* is the Bohr exciton radius, a_b is the Bohr radius (0.529Å), and ϵ_r is the dielectric constant of the semiconductor, which varies as a function of size.

There is also an additional energy associated with the Coulombic attraction between the positive hole and the negative electron of the exciton(Equation 3)[4]

$$E_{exciton} = -\frac{1}{\epsilon_r^2}\frac{\mu}{m_e}R_y \tag{3}$$

where ϵ_r is the size-dependent dielectric constant of the semiconductor, and R_y is the Rydberg energy (approximately 13.6eV)

Thus, the total energy of a fluorescing photon can be modeled as the sum of the band gap of the quantum dot, the quantum confinement energy, and the bound exciton energy (Equation 4)[4]

$$E_{totoal} = E_{bandgap} + \frac{\hbar^2\pi^2}{2\mu R^2} - \frac{1}{\epsilon_r^2}\frac{\mu}{m_e}R_y \tag{4}$$

The discrete, quantized energy levels of quantum dots relate them more closely to atoms than bulk materials and have resulted in quantum dots being nicknamed 'artificial atoms'. Generally, as the size of the crystal decreases, the difference in energy between the highest valence band and the lowest conduction band increases. More energy is then needed to excite the dot, and concurrently, more energy is released when the crystal returns to its ground state, resulting in a color shift from red to blue in the emitted light. As a result of this phenomenon, quantum dots can emit any color of light from the same material simply by changing the dot size. Additionally, because of the high level

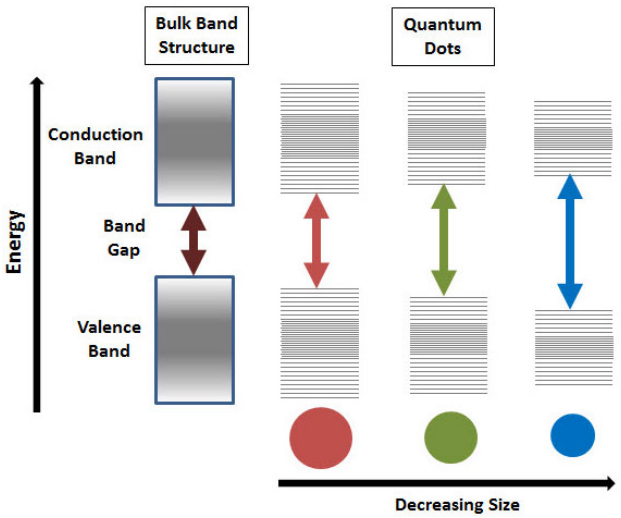

Figure 2. Splitting of energy levels in quantum dots due to the quantum confinement effect. Semiconductor band gap increases with decrease in size of the nanocrystal.[7]

of control possible over the size of the nanocrystals produced, quantum dots can be tuned during manufacturing to emit any color of light.

2.1 Types of Quantum Dots

Quantum dots can be classified into three different types based on their composition and structure: core-type quantum dots, core-shell quantum dots, and alloyed quantum dots.

2.1.1 Core-Type Quantum Dots

Quantum dots can be single component materials with uniform internal compositions, such as chalcogenides (selenides, sulfides or tellurides) of metals like cadmium, lead or zinc, example, CdTe or PbS. The photo- and electroluminescence properties of core-type nanocrystals can be fine-tuned by simply changing the crystallite size.

2.1.2 Core-Shell Quantum Dots

The luminescent properties of quantum dots arise from recombination of electron-hole pairs (exciton decay) through radiative pathways. However, the exciton decay can also occur through nonradiative methods, reducing the fluorescence quantum yield. One of the methods used to improve efficiency and brightness of semiconductor nanocrystals is growing shells of another higher band gap semiconducting material around them. These quantum dots with small regions of one material embedded in another with a wider band gap are known as core-shell quantum dots (CSQDs) or core-shell semiconducting nanocrystals (CSSNCs). For example, quantum dots with CdSe in the core and ZnS in the shell exhibit greater than 50% quantum yield (quantum yield of a radiation-induced process is the number of times a specific event occurs per photon absorbed by the system). Coating quantum dots with shells improves quantum yield by passivizing non-radiative recombination sites and also makes them more robust to processing conditions for various applications.During non-radiative recombination, an electron in the conduction band recombines with a hole in the valence band and the excess energy is emitted in the form of heat.[8] This method has been widely explored as a way to adjust the photophysical properties of quantum dots.

2.1.3 Alloyed Quantum Dots

The ability to tune optical and electronic properties by changing the crystallite size has become a hallmark of quantum dots. However, tuning the properties by changing the crystallite size could cause problems in many applications with size restrictions. Multicomponent quantum dots offer an alternative method to tune properties without changing crystallite size. Alloyed semiconductor quantum dots with both homogeneous and gradient internal structures allow tuning of the optical and electronic properties by merely changing the composition and internal structure without changing the crystallite size. For example, alloyed quantum dots of the compositions CdS_xSe_{1-x}/ZnS of 6nm diameter emits light of different wavelengths by just changing the composition.

Figure 3. Photoluminescence of alloyed CdS_xSe_{1-x}/ZnS quantum dots of 6nm diameter. The material emits different color of light by tuning the composition.[7]

Alloyed semiconductor quantum dots formed by alloying together two semiconductors with different band gap energies exhibited interesting properties distinct not only from the properties of their bulk counterparts but also from those of their parent semiconductors. Thus, alloyed nanocrystals possess novel and additional composition-tunable properties aside from the properties that emerge due to quantum confinement effects.

3 Brus Equation

The Brus equation (Eq.1) can be used to describe the emission energy of quantum dot semiconductor nanocrystals in terms of the band gap energy E_g, Planck's constant h, the radius of the quantum dot R, as well as the effective mass of the excited electron m_e^* and of the excited hole m_h^*, which are related to the curvature of the valence and conduction bands.

$$\Delta E(R) = E_g(R) + \frac{h^2}{8R^2}\left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) \quad (5)$$

The radius of the quantum dot affects the wavelength of the emitted light due to quantum confinement, and this equation describes the effect of changing the radius of the quantum dot on the wavelength λ of the emitted light ($\lambda = \frac{hc}{\Delta E}$, where c is the speed of light and ΔE is the emission energy).

Quantum dots have wide and exciting fields of applications. Quantum dots have started to make their entrance in the commercial marketplace. In 2013, the first quantum dot TVs were introduced, and they continue to be sold to this day despite their rather high pricing. Quantum dots play a huge role in medical imaging, as they are more resistant to degradation than other optical imaging probes. They have a wide broadband absorption spectrum while maintaining a distinct, static emission wavelength. Their use in making solar cells leads to high levels of efficiency. Researchers at the University of Toronto have built the first colloidal quantum dot solar cells certified to convert sunlight into electricity with greater than 10% power conversion efficiency.[9] Quantum dots also finds its applications in the fields of LED's and quantum computing. The precise topology of a quantum dot is also known to affect its electronic properties, but the exact nature of this relationship is not clear at this time, nor is a way known to control the topology of arbitrary quantum dot synthesis (Figure 4).

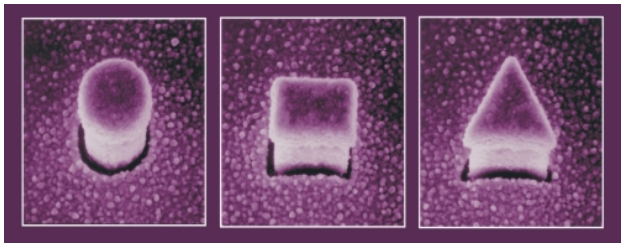

Figure 4. Differently-shaped quantum dots can be synthesized by various epitaxial means, though the precise electronic differences between differing topologies are not known at this time.[1]0

4 Project

In this project, we aim to buy some commercially available samples of quantum dots and use our Atomic Force Microscope to study those. Our first goal before purchasing new samples will be to study the AuNP (gold nanoparticles) solution available with Dr. Kevin Riggs. A similar study was done by Jaime R. Fields[11] under the supervision of Dr. Deborah B. Maxwell in the Chemistry Department at Stetson University. Jaime's project was titled "Fluorescent Gold Nanoparticles for Cellular Biomedical Applications" and had the purpose "to synthesize and characterize AuNP's with the goal of protein conjugation for potential application as a drug carrier system with cellular imaging capabilities." In this project, Jaime had used Physics Department's Atomic Force Microscope to study the solution of AuNP dispersed on a mica slide.

In our project, we will spend the first few weeks of the Fall 2017 semester to getting familiar with the working of the AFM and studying the available AuNP solution. Next, we would spend time getting familiar with more in-depth knowledge about quantum dots and their properties. Then we can purchase commercially available samples of quantum dots to study their properties and try to find new areas of applications. So far, most of the knowledge about quantum dots and AFM has been self-learned and independent. Some of the information about AFM also comes from other senior research projects that have used AFM. I have basic computer programming proficiency that comes from working on independent side-projects. I have done projects involving image analysis and machine learning and believe that these skills will prove helpful in this project. The future for the applications of quantum dots is massive and this project is yet another attempt to explore their properties and applications.

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