Quantum-Dot Light-Emitting Diode (LED)

EE453 Project Report submitted by Ta Rae Kim (kimt3@unlv.nevada.edu), Fall 2008

Introduction

In nanotechnology, nanoparticles are classified by their size (in the range of 1 nm to 100 nm) and properties. Nanocrystals are described as having at least one dimension of less than or equal to100 nm and single-crystalline. Quantum dots, also known as nanocrystals, are a non-traditional type of semiconductor with limitless applications as an enabling material across many industries [1]. The quantum dots, which can also be called artificial atoms, are nanometer-scale "boxes" that selectively hold or release electrons. These semiconductors range in size from 2 nm to 10 nm in diameter, which consist of 10 to 50 atoms. From a few hundred to a few hundred-thousand atoms, quantum dots (QDs) bridge the gap between single atoms and solid state, and because of this, they exhibit a combination of atomic and solid-state properties. The emission wavelength, or the color emitted, of quantum dots depends on the size, and using simple chemistry with semiconductor nanocrystals, the color can be precisely controlled. Light-emitting diodes (LEDs) have been created and produced in various colors from quantum dots.

Project Description

Because the emission wavelength can produce a color by simply changing the size of the quantum dot, they are ideal in making quantum-dot light-emitting devices. The results, due to the small size of nanocrystal quantum dots, are that a new quantum phenomena yielding extraordinary bonuses. Material properties change dramatically because quantum effects arise from the confinement of electrons and "holes" in the material (a hole is the absence of an electron; the hole behaves as though it were a positively charged particle) [2]. By altering the size, other properties of the material, such as the nonlinear optical and electrical properties are affected by the change in the size. This makes the quantum dots unique in comparison to as if they were in bulk form of the material. Compared to the quantum dots and when in bulk form, the energy levels are in close proximity to one another. This makes the bulk energy levels to be considered continuous, which means the difference in energy is insignificant or almost nonexistent. If a dot is excited, the smaller the dot, the higher the energy and intensity of its emitted light; hence, these very small, semiconducting quantum dots are gateways to an enormous array of possible applications and new technologies [2]. Particular energy levels are unable to reached by electrons; these areas are called the band gaps or energy gaps.

According to the Los Alamos Science,

"One of the defining features of a semiconductor is the energy gap separating the conduction and valence energy bands. The color of light emitted by the semiconductor material is determined by the width of the gap. In semiconductors of macroscopic sizes—bulk semiconductors—the gap width is a fixed parameter determined by the material's identity. The situation changes, however, in the case of nanoscale semiconductor particles with sizes smaller than about 10 nanometers. This size range corresponds to the regime of quantum confinement, for which the spatial extent of the electronic wave function is comparable with the dot size. As a result of these "geometrical" constraints, electrons "feel" the presence of the particle boundaries and respond to changes in particle size by adjusting their energy. This phenomenon is known as the quantum-size effect, and it plays a very important role in quantum dots. In the first approximation, the quantum-size effect can be described by a simple "quantum box" model [4], in which the electron motion is restricted in all three dimensions by impenetrable walls. For a

spherical quantum dot with radius a, this model predicts that a size-dependent contribution to the energy gap is simply proportional to $\frac{1}{a^2}$, implying that the gap increases as the quantum dot size decreases. In addition, quantum confinement leads to a collapse of the continuous energy bands of a bulk material into discrete, atomic-like energy levels. The discrete structure of energy states leads to a discrete absorption spectrum of ODs, which is in contrast to the continuous absorption spectrum of a bulk semiconductor. The NQDs discussed earlier are small quantum dots that are made by organometallic chemical methods and are composed of a semiconductor core capped with a layer of organic molecules (Murray et al. 1993). The organic capping prevents uncontrolled growth and agglomeration of the nanoparticles. It also allows NQDs to be chemically manipulated as if they were large molecules, with solubility and chemical reactivity determined by the identity of the organic molecules. The capping also provides "electronic" passivation of NQDs; that is, it terminates dangling bonds that remain on the semiconductor's surface. As discussed below, the unterminated dangling bonds can affect the NQD's emission efficiency because they lead to a loss mechanism wherein electrons are rapidly trapped at the surface before they have a chance to emit a photon. Using colloidal chemical syntheses, one can prepare NQDs with nearly atomic precision; their diameters range from nanometers to tens of nanometers and size dispersions as narrow as 5 percent. Because of the quantum-size effect, this ability to tune the NQD size translates into a means of controlling various NQD properties, such as emission and absorption wavelengths. The emission of cadmium-selenium (CdSe) NQDs, for example, can be tuned from deep red to blue by a reduction in the dot radius from 5 nanometers to 0.7 nanometers" [3].

For example in Figure 1, there is a fixed energy gap, E_g , which separates the continuous conduction and valence energy bands for a bulk semiconductor such as cadmium selenium (CdSe). Normally, all states up to the edge of the valence band are occupied by electrons, whereas the conduction band states are empty. The figure also displays the quantum dot being characterized by discrete atomic-like states with energies determined by the radius *a*. Using atomic-like notations, the quantum dot states that are well-separated can be labeled with 1S, 1P, and 1D. The "quantum box" model can be used to obtain the expression for the size-dependence separation between the lowest electron and hole QD states [see Equation (1) and Equation (2)]. The continuous absorption spectrum of a bulk semiconductor, in black, compared with a discrete absorption spectrum of a quantum dot— the bars of color—as seen in Figure 2.



Figure 1

$$E_{G,quantum\,dot} = E_{G,0} + \frac{\hbar^2 \pi^2 n^2}{2m_r a^2}$$
 Equation (1)

$$m_r = \frac{m_e m_h}{m_e + m_h}$$
, $m_e is the effective electron mass Equation (2) $m_h is the effective hole mass$$

mm





Quantum dots are produced using several methods, such as through chemical and non-chemical means. Through chemical means, an organometallic method is used for the fabrication of highly monodisperse cadmium selenide nanocrystal quantum dots [see Figure 3]. Nucleation and subsequent growth of NQDs occurs after a quick injection of metal and chalcogenide precursors into the hot, strongly coordinating solvent such as a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) in the case shown. After a fixed period, removing the heat source stops the reaction. As a result, NQDs of a particular size form. The colloidal NQDs obtained by the method illustrated in Figure 4 consist of an inorganic CdSe core capped with a layer of TOPO/TOP molecules. In Figure 5, the solutions of cadmium selenide nanocrystal quantum dots of various radii emit different colors due to the quantum size effect under ultraviolet light. Orange is emitted for an energy gap of approximately 2 eV is for a dot of radius 2.4 nm; blue is emitted for a dot with a radius of 0.9 nm has a gap of approximately 2.7 eV. As observed, the light becomes redder as the radius of the dot increases. The wavelength becomes shorter in the direction of blue, when the radius of the dot decreases.



Figure 3—Injection of MeCd and Se in TOP into TOPO

Figure 4—CdSe Core



Figure 5—CdSe Solutions of Different Radii

In 2002, MIT researchers have combined organic materials with high-performing inorganic nanocrystals to create a hybrid optoelectronic structure—a quantum dot-organic light-emitting device (QD-OLED) that may one day replace liquid crystal displays (LCDs) as the flat-panel display of choice for consumer electronics [5]. A collaborative effort between Moungi G. Bawendi, professor of chemistry, and Vladimir Bulovic, assistant professor of electrical engineering and computer science, resulted in this work. Dr. Bawendi also researched the electronic and optical properties of semiconductor nanocrystal quantum dots to apply in areas ranging from biology to optical devices. "Unlike traditional LCDs, which must be lit from behind, quantum dots generate their own light. Depending on their size, the dots can be 'tuned' to emit any color in the rainbow. And the colors of light they produce are much more saturated than that of other sources." [5]

The QD-LEDs come in a wide range of colors, such as advertised on Evident Technologies' website, as one of their products. Coming in LEDs of sizes 3 mm and 5 mm, the available colors are plum, cobalt, aqua, lime, lemon, gold, tangerine, peach, persimmon, cranberry, pink, candlelight, pearl, and ice [see Table 1].

Products	Size	3 mm	5 mm
	Package Type	Round	
	Viewing Angle	30	15
Emission Color	Plum		
	Cobalt		
	Aqua	-	
	Lime	-	

Table 1—Standard Series Single Color Through-hole LEDs

Emission Color	Lemon		
	Gold		
	Tangerine		
	Peach	()	
	Cranberry		
	Pink		
	Candlelight		
	Pearl		
	Ice		

In a different approach to creating white light several researchers at the Department of Energy's (DOE) Sandia National Laboratories have developed the first solid-state white light-emitting device using quantum dots [6]. In development of the first solid-state white light-emitting device using quantum dots, Lauren Rohwer was the principal investigator of a research team for it. Any color is obtainable using quantum dots presently. "Quantum dots represent a new approach. The nanometer-size quantum dots are synthesized in a solvent containing soap-like molecules, called surfactants, as stabilizers. The small size of the quantum dots — much smaller than the wavelength of visible light — eliminates all light scattering and the associated optical losses. Optical backscattering losses using larger conventional phosphors reduce the package efficiency by as much as 50 percent." [6]

Most recently at the Los Alamos National Laboratories, multi-color light-emitting diodes have been developed on the basis of colloidal quantum dots encapsulated in a gallium nitride (GaN) semiconductor. Solid-state lighting offers the advantages of reduced operating expenses, lower energy consumption and more reliable performance [7].

References

[1] Evident Technologies, Inc., "Quantum Dots Explained," *Evident Technologies, Inc.*, 2008. [Online]. Available: http://www.evidenttech.com/quantum-dots-explained.html. [Accessed: Dec. 1, 2008].

[2] H. Lee, "Mighty Small Dots," *Science and Technology Review*, July 2000. [Online]. Available: https://www.llnl.gov/str/Lee.html. [Accessed: Dec. 1, 2008].

[3] V. I. Klimov, "Nanocrystal Quantum Dots: From fundamental photophysics to multicolor lasing," *Los Alamos Science*, no. 28, 2003. [Online]. Available: http://quantumdot.lanl.gov/pages/Publications/Klimov_LAscience.pdf. [Accessed: Dec. 1, 2008].

[4] Al. L. Efros, A.L. Efros, A. L. Efros, "Pioneering Effort I," in Sov. Phys. Semicond, vol. 16, pp. 772, 1982.

[5] "Quantum-dot LED may be screen of choice for future electronics," *MIT News Office*, Dec. 12, 2008. [Online]. Available: http://web.mit.edu/newsoffice/2002/dot.html. [Accessed: Dec. 1, 2008].

[6] "Sandia researchers use quantum dots as a new approach to solid-state lighting," Sandia National Laboratories, July 14, 2003. [Online]. Available: http://www.sandia.gov/news-center/news-releases/2003/elect-semi-sensors/quantum.html. [Accessed: Dec. 1, 2008].

[7] T. Hanson, "Scientists develop novel multi-color light-emitting diodes," Los Alamos National Laboratories (LANL), May 17, 2005. [Online]. Available: http://www.lanl.gov/news/index.php?fuseaction=home.story&story_id=6597. [Accessed: Dec. 1, 2008]