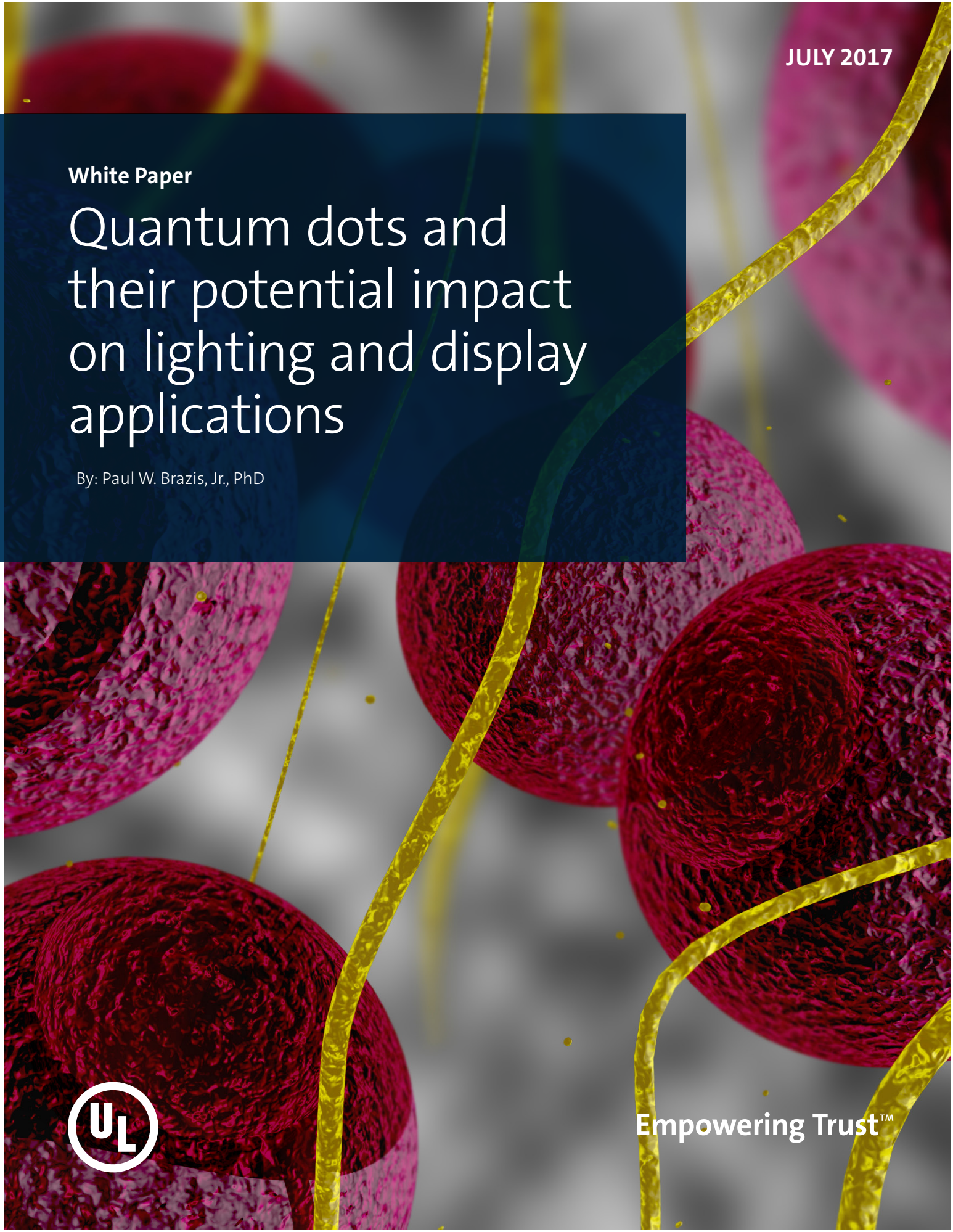

JULY 2017

White Paper

Quantum dots and their potential impact on lighting and display applications

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Empowering Trust™

Executive summary

References to "quantum dots," which are defined as semiconductor structures that have all dimensions sufficiently small to enable quantum confinement in all three dimensions, can be traced back to at least 1988.[1] The electronic structure of quantum dots gives them unique semiconductor and optical properties that are tunable as a function of their physical size and composition. A key property of quantum dots is that the optical emission spectra can be tuned by changing their diameter. For example, quantum dots made from cadmium selenide (CdSe) can be adjusted to fluoresce from blue to red by increasing the particle size. This property suggests the potential for higher performance and more efficient light emitting diodes (LEDs), displays, and lasers. Quantum dots have also been proposed for the construction of improved transistors and for quantum computing and medical imaging applications.

One key issue hindering widespread adoption of quantum dots, at least from some sources, is that some compounds contain cadmium. The Restriction of Hazardous Substances (RoHS) directive restricts cadmium in consumer devices, though a temporary exception had been approved by the European Union for quantum dots. However, this exemption is expiring and a renewal is currently under debate with the outcome remaining uncertain.

Quantum dots appear to be sufficiently mature for certain lighting and display applications and have been proven viable for display backplane applications. Several manufacturers of tablets, mobile devices, and televisions already offer products with quantum dot-containing displays. Such manufacturers include Amazon, Samsung, LG, and Sony. Though more advanced uses are possible, it is likely they will continue to be utilized mainly for red/green emitting layers for generating white light. It is not clear how much growth will be seen for the technology, especially if intellectual property issues are limited through the expiration of the RoHS cadmium exemption. It is therefore expected that quantum dots will remain a niche technology for high-end displays and will be primarily used for this application in the near future. Lighting may eventually adopt the use of quantum dots, though it is not clear whether the improved color gamut is a sufficient counterweight to increased materials costs, as LED lighting is currently very price sensitive. More novel applications are in the research phase and likely will not be commercialized for several years.

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Background and Introduction

References to "quantum dots," which are defined as semiconductor structures that have all dimensions sufficiently small to enable quantum confinement in all three dimensions, can be traced back to at least 1988.[1] This is related to structures where quantum confinement is attained in one dimension (quantum wells) and in two dimensions (quantum wires). Such structures allow for certain electronic and optical behavior to be leveraged through quantum effects that arise due to the physical size and composition of quantum dots. Initially, quantum dots were fabricated through the use of electron beam lithography, chemical vapor deposition (CVD), or some similar materials deposition technique that allows for atomic-scale control of the deposited layers. Since the early 2000s, "quantum dots" became better known as standalone semiconducting spheres fabricated in solution using colloidal or plasma synthesis.

The electronic structure of quantum dots gives them unique semiconductor and optical properties that are tunable as a function of their physical size and composition. These structures tend to exhibit properties that are intermediate between bulk semiconductor materials and single molecules. A typical property of quantum dots is that the optical emission spectra can be tuned by changing their diameter. For example, quantum dots made from cadmium selenide (CdSe) can be adjusted to fluoresce from blue to red by increasing the particle size (Figure 1). This property suggests the potential for higher performance and more efficient light emitting diodes (LEDs), displays, and lasers. Quantum dots have also been proposed for the construction of improved transistors and for quantum computing and medical imaging applications.

This report explains the physics behind quantum dot operation and what technical advantages the technology has in lighting and display applications. Cost and environmental health and safety are also explored as fabrication costs have been relatively high compared to other alternatives, and there is concern that most quantum dots conducive to manufacturing applications consist of semiconducting compounds that include cadmium. The inclusion of cadmium makes adoption more difficult in light of global RoHS regulations and other environmental laws, though temporary exemptions are in place. Due to this, cadmium-free alternatives are also discussed and evaluated on their feasibility and readiness for large-scale use in manufacturing.

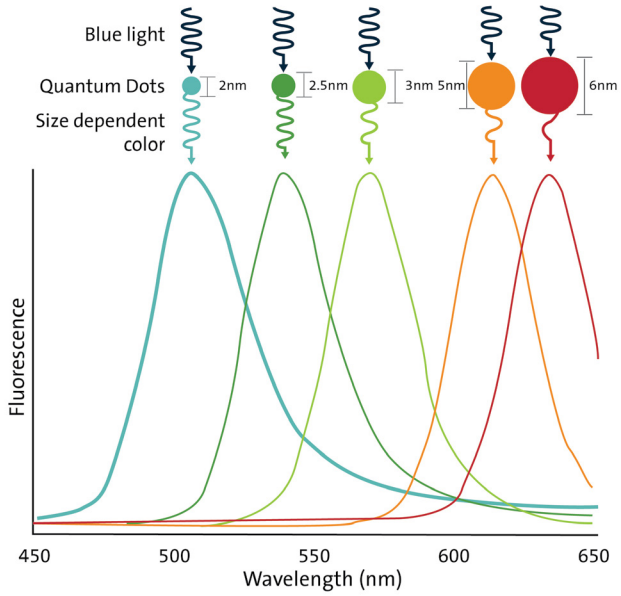

Figure 1. Example of size-dependent fluorescence spectra for quantum dots supplied by Nanosys Inc. (from Nanosys website, http://www.nanosysinc.com/what-we-do/quantum-dots/)

Physical Theory

The novel behavior of a quantum dot is attributable to quantum confinement of a charged particle (for example, an electron). This confinement is due to the particle being trapped within a potential well, where the particle is located in a region with low potential and surrounded in one or more dimensions by barriers with high potential. In the three-dimensional world, confinement can be in one, two, or all three dimensions, describing the conditions of a quantum well, a quantum wire, and a quantum dot, respectively. An explanation of quantum confinement is useful in explaining the ability of a quantum dot to have size-dependent properties, as this phenomenon is what is typically exploited.

Since the description of the physics of quantum dots relies heavily on quantum physics and some concepts of semiconductor physics, a brief introduction to some of the key concepts of quantum physics used in this discussion is necessary for those unfamiliar with the subject. The description here is not intended to be a comprehensive discussion of the topic and is only included to facilitate the understanding of the subject for quantum dot behavior. References are given to help the reader explore certain concepts introduced here in greater depth.

Introduction: Wave-Particle Duality

Quantum physics was first developed early in the 20th Century to explain experimental observations that could not be readily interpreted by classical (i.e.,, Newtonian) means.[1] A key concept of quantum theory is the wave-particle duality of electrons, photons, phonons, and other quantized particles and quasiparticles. As an example, light is often perceived as a wave, proven through experiments involving diffraction, interference, and dispersion, and the perceived color of light is due to its frequency.[2] Light also exhibits behavior that is characteristic of a particle, such as being able to have definite and finite measurable position and momentum. Another artifact of the particle-like nature of light is Albert Einstein's postulation that electromagnetic waves (such as light) can only exist as discrete "wave-packets," or "light quanta," now referred to as "photons."[2] This was based on Max Planck's earlier work that suggested that energy carried by electromagnetic waves can only be released in "packets" of energy.[3] These concepts relate the energy of a single photon to its frequency through the Planck-Einstein relation, where *h* is defined as the Planck constant:

$$E = h\nu$$

This concept of wave-particle duality carried over to electrons as well, where electrons are considered to have particle-like properties such as mass[4] ($m_0 = 9.109 \cdot 10^{-31}$ kg) and charge ($q = 1.602 \cdot 10^{-19}$ C), but also wave-like properties. This wave-particle duality was first introduced by de Broglie[5] and then given a mathematical form by Schrödinger.[6] The Schrödinger equation can be thought of as a quantum mechanical analogue of Newton's laws for classical mechanics and allows the ability to describe the wavelike behavior of particles. A time-independent form of the Schrödinger equation can be expressed as follows:

$$E\Psi(\mathbf{r}) = \hat{H}\Psi(\mathbf{r})$$

More details of this equation and its application are given later in this report. Here, the Schrödinger equation is treated as a first principle and is not derived, as is now common practice in modern applications of quantum mechanics. Should the reader be interested in the derivation, several approaches to this proof can be found in the literature, including Schrödinger's own 1925 paper.[7]

The exact position and momentum of a particle cannot be simultaneously known per the Heisenberg uncertainty principle.[7] The Schrödinger equation, however, results in a "wavefunction" that predicts the probability distributions for these particles. Such wavefunctions are a fundamental postulate of quantum mechanics and are used here to derive a mathematical description of the wavefunctions within a quantum dot. This facilitates explaining the unique properties of a quantum dot and its use in electronic and optical applications.

An additional concept that is often used in semiconductor quantum physics is the Brillouin zone and the use of "reciprocal k-space." For this report it is not important for the reader to be familiar with these concepts, but it is mentioned in the discussion of direct and indirect semiconductors. The k-space concept is used to relate the energy of an electron to its momentum. Since the wave vector **k** is inversely proportional to the wavelength, it has units of inverse length and therefore constructs utilizing k-space are often referred to as "reciprocal space." For the purposes of this report, the reader only needs to recall that these concepts allow for the construction of band structures for materials, and in turn allow for determination of the band gap for a semiconductor and whether it is a direct or indirect semiconductor, among other useful physical properties. Should the reader be interested in a more in-depth discussion of band structure and reciprocal space, many introductory solid state physics works cover the subject.[2,8]

[1] R. Hummel, "Electronic Properties of Materials, Second Edition,"Berlin: Springer-Verlag, 1993. This book gives a comprehensive introduction to the application of quantum theory for understanding electrical properties of materials, including an introduction to electron theory as it applies to electronics, optics, and magnetics.

[2] A. Einstein, "Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt," *Annalen der Physik*. 17 (6): 132–148 (1905).

[3] M. Planck, "Über das Gesetz der Energieverteilung im Normalspectrum," *Annalen der Physik,* 4 (3): 553–563 (1901).

[4] More accurately, this is the *invariant* mass of an electron, which is the mass in the rest frame of the electron. This clarification is important in reference to particle physics. This is in contrast to relativistic mass which is dependent on the velocity of observer.

[5] L. de Broglie, "Recherches sur la Théorie des Quanta," *Annales de Physique,* 10e série, 3 (22): (Janvier-Février 1925).

[6] E. Schrödinger, "An Undulatory Theory of the Mechanics of Atoms and Molecules," *The Physical Review,* 28 (6), December 1926

[7] W. Heisenberg, "Über den anschaulichen Inhalt der quantentheoretischen Kinematik und Mechanik", *Zeitschrift für Physik,* 43 (3–4): 172–198, (1927).

Band Theory in Semiconductors

Since quantum dots are most useful for their semiconducting properties, particularly their interaction with photons (i.e., light), some basic concepts of semiconductor band theory are needed to understand the physics of quantum dots. This section introduces the concept of discrete energy bands in semiconductors and how this is related to the "electron shell" concepts that are taught in introductory chemistry courses. Also introduced is the concept of a semiconductor band gap, a key property of semiconducting materials that has a direct influence on how semiconductors interact with light energy. As with earlier sections, the focus here is to introduce the reader to these concepts to facilitate understanding of quantum dot behavior, and one is directed to other literature sources should more detail be desired.

Light absorption and emission in semiconductors is explained through the transition of an electron from one energy state to another: absorption of a photon (quantized light energy) results in the electron transitioning to a higher energy state; during light emission, the electron transitions to a lower energy state and releases the energy as a photon. These energy levels are attributed to the series of energy levels the electrons within each atom occupy, where the levels with the lowest energy are filled first before higher energy states become occupied. A schematic of these energy levels is shown in Figure 2, with each circle representing a pair of electrons. As an example, helium with two electrons fills the 1*s* layer completely, carbon with six electrons first fills the 1*s* and 2*s* layers, with its remaining two electrons located in the 2*p* layer. This valence shell is therefore defined as the 1*s* level (or "K shell") for helium and 2*s*2*p* ("L shell") for carbon, as this is the layer that defines the atom's valence. For carbon, the valence is +4 because four electrons occupy the valence band. The inertness of helium is attributed to the fact that its valence shell is completely filled.

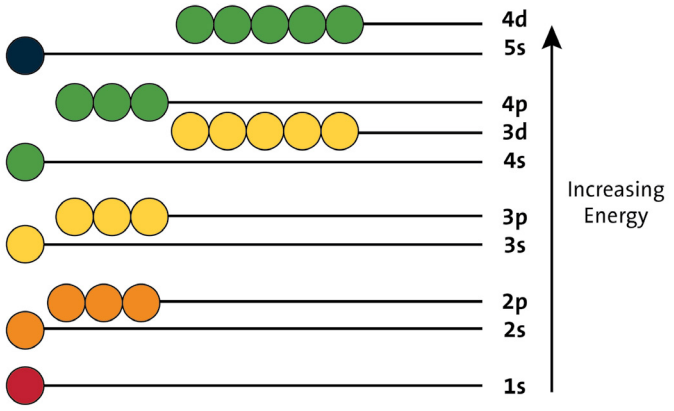

Figure 2. *Representation of the energy levels of electrons in an atom.*

When large numbers of atoms come together to form a solid, each of these discrete energy levels begin to interact and blend together to form continuous bands of energy (Figure 3). As atoms come together, each atom's energy bands are shifted slightly due to the interaction from surrounding atoms. As the number of atoms grows larger, the difference between the individual levels becomes very small and essentially forms continuous bands of energy levels the electrons may occupy.

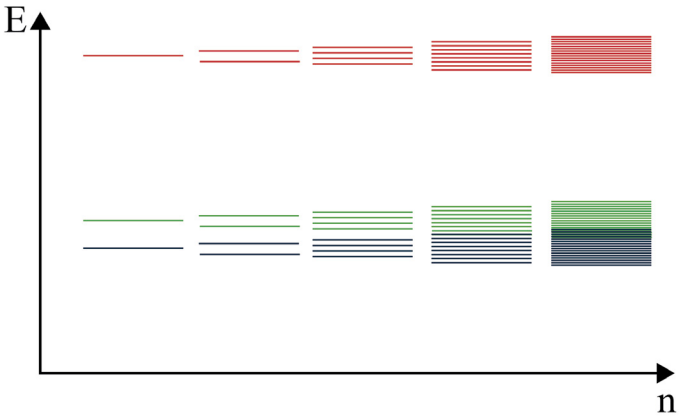

Figure 3. *Illustration of how the band structures of individual atoms come together and form bands. As the number of atoms increase, the energy levels at each atomic orbital blend together to form continuous bands of energy states.*

[8] C. Wolfe, N. Holonyak, and G. Stillman, "Physical Properties of Semiconductors," Englewood Cliffs, NJ: Prentice-Hall, 1989.

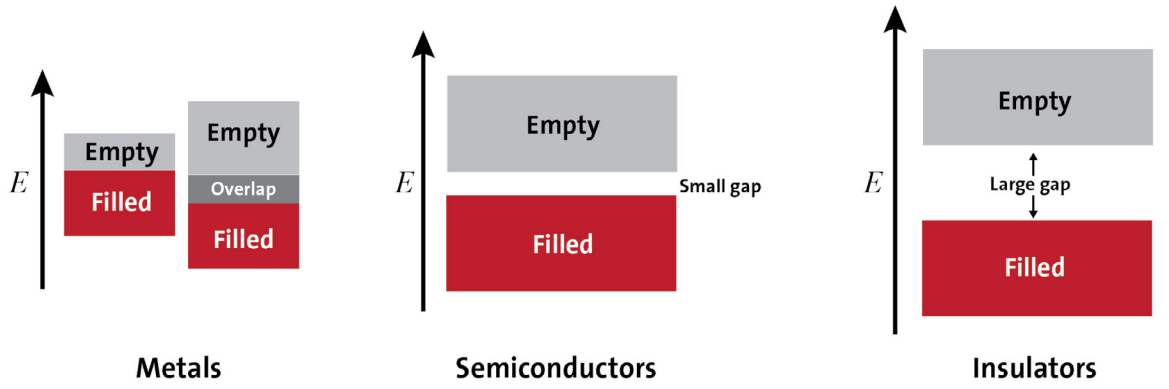

Figure 4. Graphical representation of the band structure of metals, semiconductors, and insulators.

These bands of energy levels can be found to overlap one another or gaps may form, with the gaps being energy levels that cannot be occupied by electrons. In metals, the valence band (formed by the merging of each atom's valence shells) will overlap with the next higher band (the lowest unoccupied shell of each atom, collectively called the conduction band). With semiconductors and insulators, there will be an energy gap between the valence band and conduction band (Figure 4). There is no well-defined gap size that differentiates semiconductors and insulators, and individual materials may be considered semiconductors or insulators depending on the context of their specific use.

This "forbidden" energy gap between the valence and conduction band is referred to as the bandgap of the material, measured in units of energy, usually electron volts (eV). Typically, the valence band is nearly full of electrons, which prevents mobility of the electrons and disallows the flow of electric current. For current to flow through a semiconducting material, electrons need to transition to the conduction band, creating an electron-hole pair (where the "hole" is a theoretical positively charged particle which is essentially the absence of an electron, created when the electron transitioned to the conduction band). Since this conduction band is at a higher energy than the valence band, an electron needs to gain energy at least equivalent to that of the bandgap to transition to the higher-energy state. Less energy will not allow a transition, as the electron is not allowed to have an energy within the bandgap energy range. This energy may originate from a number of sources, which include thermal, photonic, and electromagnetic radiation. In most real-world instances there is a fraction of electrons in the conduction band, as any temperature above absolute zero will provide sufficient energy to transition some electrons into the conduction band (only at absolute zero is it possible to have all electrons in the valence band). Increasing the temperature of a material causes more electrons to transition to the conduction band due to the increased thermal energy: this is the mechanism explaining why the electrical conductivity of semiconductors increases with increasing temperature.

Optical Absorption and Emission in Semiconductors

As was mentioned, all semiconductors transition electrons between the valence band and the conduction band through the absorption and emission of energy, which can be from a variety of sources. An electron loses energy and transitions back to the valence band, which is often referred to as electron-hole pair recombination, as the electron eliminates the charge carrier vacancy in the valence band, effectively "recombining" the hole with the electron. This transition can release thermal or photonic energy, or both. The semiconductor — direct bandgap or indirect bandgap — determines the type of energy. The type of semiconductor is defined by whether the maximum-energy state of the valence band and the minimum-energy state of the conduction band have the same crystal momentum (i.e., same "k-vector" in the Brillouin zone: see earlier discussion of reciprocal space for additional details). In most instances, only direct bandgap semiconductors (for practical purposes) are capable of emitting photonic energy. Direct bandgap materials (such as gallium arsenide and indium arsenide) require only a change in energy, not momentum, of the particle; indirect bandgap materials (such as silicon and germanium) require a

change in both the energy and momentum of an electron (Figure 5). Since photons cannot carry crystal momentum, a second process is required to balance the difference in momentum. One such process is the absorption or emission of a phonon, a quasiparticle derived from the collective vibrations of atoms in a solid (in a way, this can be thought of as analogous to thermal energy). As this two-step process is far slower and less efficient, light absorption and emission are not significant properties of indirect bandgap semiconductors.

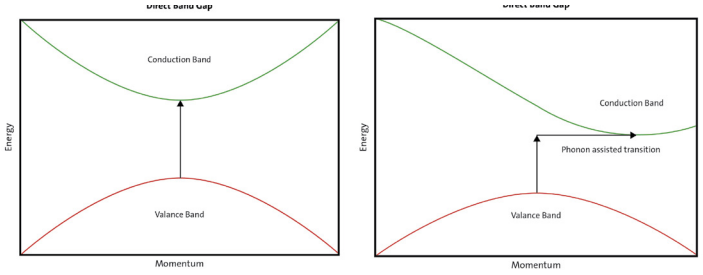

Figure 5. Examples of (Left) direct and (Right) indirect bandgap materials, showing the change in momentum required for transitions to the conduction band in indirect semiconducting materials.

Assuming a direct bandgap semiconductor, the absorption of photons is dependent on their energy. Photons with energy below that of the semiconductor bandgap will not be absorbed and will tend to pass through or reflect off the material. As a result, insulating materials tend to be clear or white and relatively conductive materials tend to be gray or black. For photons with energy above the bandgap energy, the absorption coefficient, α, is related to light frequency by the following equation, where h is the Planck constant and ν is the light frequency:

$$\alpha \approx A^* \sqrt{h\nu - E_g}$$

This is valid only when the photon energy ($h\nu$) is greater than the semiconductor bandgap (E_g). The constant A^* is dependent on material properties such as the index of refraction, permittivity, and lattice properties. From the formula it can be seen that absorption increases roughly parabolically with light energy. This equation shows that for a material to absorb photons, the photon energy needs to be greater than that of the bandgap energy.

The energy of photons emitted when electrons lose energy in a direct bandgap semiconductor is primarily dictated by the bandgap energy. For an electron to transition to the valence band from the conduction band and recombine with a hole, it must release energy equivalent to the bandgap energy E_g. This energy is therefore released in a photon with the same energy. This dictates the frequency of the light emitted, related to energy using the Planck-Einstein relation:

$$E = h\nu$$

Here, energy is typically expressed in units of electron volts and ν in Hertz.[9]

Particle-In-a-Box and Quantized Energy Levels

A simplified example of quantum confinement is the "particle-in-a-box" model, which assumes a one-dimensional potential well with zero potential surrounded by barriers with infinite potential (Figure 6). In this model, the *x*-axis denotes the position of the particle in the one-dimensional space, and the y-axis denotes its potential energy. Since the barriers have infinite potential, the particle is not able to attain sufficient energy to exit the well (for real-world systems, the potential barriers are finite and particles therefore can exit the box under some conditions).

The potential energy of the box is defined by the following equation, where a is the length of the box:

$$V(x) = \begin{cases} 0, & 0 \le x \le a \\ \infty, & \text{otherwise} \end{cases}$$

The position and energy of the particle are derived from its wavefunction. This wavefunction for the particle within the box is found by solving the Schrödinger equation for the system. Starting with the time-independent Schrödinger equation with the general form:

$$E\Psi(\mathbf{r}) = \hat{H}\Psi(\mathbf{r})$$

where E is the energy of the particle, Ψ (the Greek letter psi) is the wave function of the quantum system, $\mathbf{r}$ is the position vector, and $\hat{H}$ is the Hamiltonian operator (which characterizes the total energy of any given wave function and takes different forms depending on the situation).Squaring the term $\Psi(\mathbf{r})$ reveals the probability of locating the particle at a certain position within the box at a given energy level. The most typical form for

[9] In this application, the value of Planck's constant is $4.135668 \cdot 10^{-15}$ eV•s.

a single, non-relativistic particle in an electric field is defined by the following equation:

$$E\Psi(\mathbf{r}) = \left[\frac{-\hbar^2}{2m}\nabla^2 + V(\mathbf{r})\right]\Psi(\mathbf{r})$$

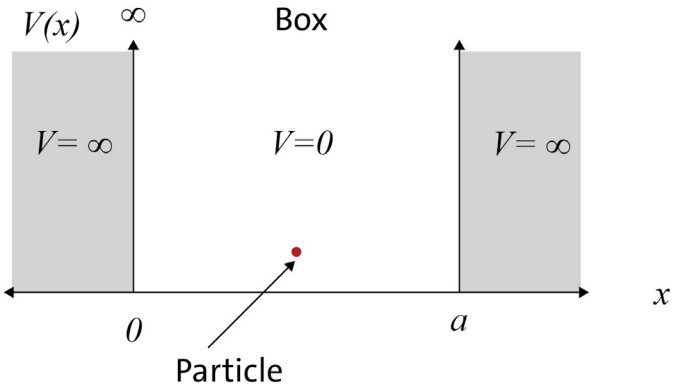

Figure 6. Schematic for the particle-in-a-box model for quantum confinement.

where *m* is the effective mass of the particle and *ħ* is the Planck constant divided by 2π. For the one-dimensional system being analyzed here (i.e., position defined for the *x*-axis only), the equation reduces to the following:

$$E\Psi(x) = \left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)\right]\Psi(x)$$

Since *V(x)* is defined as being zero inside the box:

$$E\Psi(x) = \frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

Inside the box, no forces act on the particle, meaning part of the wavefunction inside oscillates through space and time with the same form as a free particle. The above differential equation has the following general solution, where *A, B,* and *k* are constants:

$$\Psi(x) = A\sin(kx) + B\cos(kx)$$

The boundary conditions now need to be applied to find the solution for the system. Since the potential at the barriers is infinite, there is a zero probability of finding the particle at these boundaries. Therefore:

$$\Psi(0) = \Psi(a) = 0$$

Since the sine *at x* = 0 is zero and the cosine is 1, the constant *B* must equal zero to fulfill the boundary condition. Therefore, the solution reduces to:

$$\Psi(x) = A\sin(kx)$$

To solve for *k,* the wavefunction is differentiated with respect to *x*:

$$\frac{d\Psi}{dx} = kA\cos(kx)$$

$$\frac{d^2\Psi}{dx^2} = -k^2A\sin(kx)$$

$$\frac{d^2\Psi}{dx^2} = -k^2\Psi(x)$$

Taking the form of the Schrödinger equation above and rearranging the terms gives the following:

$$E\Psi(x) = \frac{-\hbar^2}{2m}\frac{d^2\Psi}{dx^2}$$

$$\frac{d^2\Psi}{dx^2} = -\frac{2m}{\hbar^2}E\Psi(x)$$

Comparing the solution above to this form of the Schrödinger equation gives a value for *k:*

$$-k^2 = -\frac{2m}{\hbar^2}E$$

$$k = \sqrt{\frac{2mE}{\hbar^2}} = \sqrt{\frac{2mE}{h^2/4\pi^2}} = \sqrt{\frac{8\pi^2mE}{h^2}}$$

Plugging this value for *k* into the solution now gives:

$$\Psi(x) = A\sin\left(\sqrt{\frac{8\pi^2mE}{h^2}}x\right)$$

To solve for *A*, the boundary condition at *x = a* is applied again:

$$\Psi(a) = 0 = A\sin\left(\sqrt{\frac{8\pi^2mE}{h^2}}a\right)$$

This is only true when the argument inside the sine function is a multiple of pi, where *n* is any positive integer:

$$\sqrt{\frac{8\pi^2 mE}{h^2}}a = n\pi$$

Plugging this back into the equation gives the following:

$$\Psi(x) = A\sin\left(\frac{n\pi}{a}x\right)$$

The value of *A* is found by normalizing the wavefunction using the fact that the probability of finding the particle in the box is equal to 1. As noted earlier, the probability is found by using the square of the wavefunction:

$$\int_0^a \Psi^2(x)\,dx = 1$$

$$\int_0^a A^2\sin^2\left(\frac{n\pi}{a}x\right)dx = 1$$

Solving for *A* gives:

$$A = \sqrt{\frac{2}{a}}$$

This gives the normalized wavefunction as the following:

$$\Psi(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

Returning to the following equation, the allowed energy levels can be solved. Solving for the energy *E:*

$$\sqrt{\frac{8\pi^2 mE}{h^2}}a = n\pi$$

$$8\pi^2 mEa^2 = h^2n^2\pi^2$$

$$E_n = \frac{h^2n^2}{8ma^2} = \frac{\hbar^2\pi^2n^2}{2ma^2}$$

As *n* can be any nonzero integer, the allowed energy states are quantized. The particle cannot be at rest because it always has some kinetic energy, meaning *n* cannot be zero. This is also required per the Heisenberg uncertainty principle because, if the particle had zero energy, we would have knowledge of both its position in space and time, which is not allowed.[8] Solving for each value of *n,* a series of wavefunctions can be calculated (Figure 7). Figure 7 also shows the probability densities from these wavefunctions, which is equivalent to the square of the wavefunction.

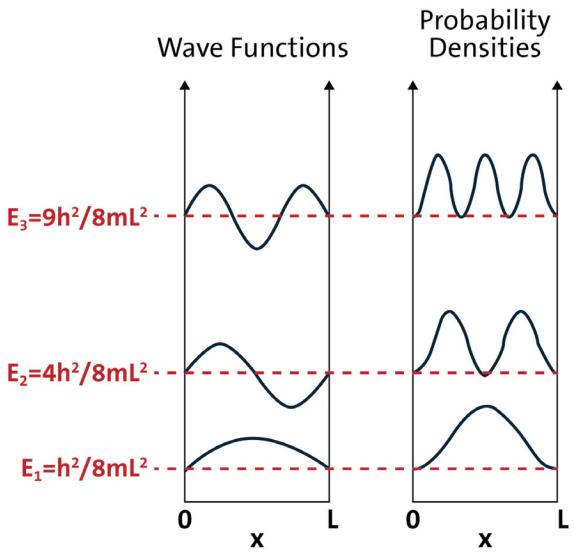

Figure 7. Wavefunctions and probability densities for the particle-in-a-box model.

Quantum Dot Behavior

To understand the physical behavior of a quantum dot, the concepts of a bulk semiconductor bandgap and quantum confinement (the above "particle-in-a-box" model) are brought together. When a semiconducting crystal is sufficiently large (for example, 1 µm or larger), quantum confinement is not a significant effect and the semiconductor bandgap dominates behavior. As the crystal becomes smaller (i.e., nanometer sized), the quantum confinement model becomes more significant. This transition is typically delineated when the crystal becomes smaller than twice the exciton Bohr radius of the material, where a_b is the Bohr radius (0.053 nm), m is the mass, μ is the reduced mass and ε_r is the relative permittivity:

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

Values for the exciton Bohr radius for semiconductors typically used for quantum dots generally range from 5.6 nm for CdS to 40.0 nm for PbS.[10]

The effective bandgap of the quantum dot material is determined by adding the bulk semiconductor bandgap to the quantum confinement energy, where E_g is the bulk semiconductor bandgap and the mass from the particle-in-a-box model is replaced with the reduced mass:

$$E_{QD} = E_g + \frac{\hbar^2 \pi^2 n^2}{2\mu a^2} - R_y^*$$

Here, a is the radius of the quantum dot. The additional term R_y^* incorporates an additional effect from the bound exciton energy, which is a Coulomb attraction between the negatively charged electron and the positively charged hole, where q is the electron charge ($1.602 \cdot 10^{-19}$ C) and ε_0 is the permittivity of free space ($8.854 \cdot 10^{-14}$ F/cm):

$$R_y^* = \frac{1.8q^2}{4\pi\epsilon_r\epsilon_0 a}$$

The equation for the quantum dot bandgap shows that the gap energy is dependent on the physical size of the quantum dot; as the quantum dot radius falls below the exciton Bohr radius, the quantum confinement energy becomes larger and dominates over the bulk semiconductor bandgap. As the crystal size grows very large (i.e., a becomes large), the additional terms approach zero and the value approaches that of the bulk semiconductor bandgap (Figure 8). This shows that tuning of the effective bandgap of the quantum dot can be achieved

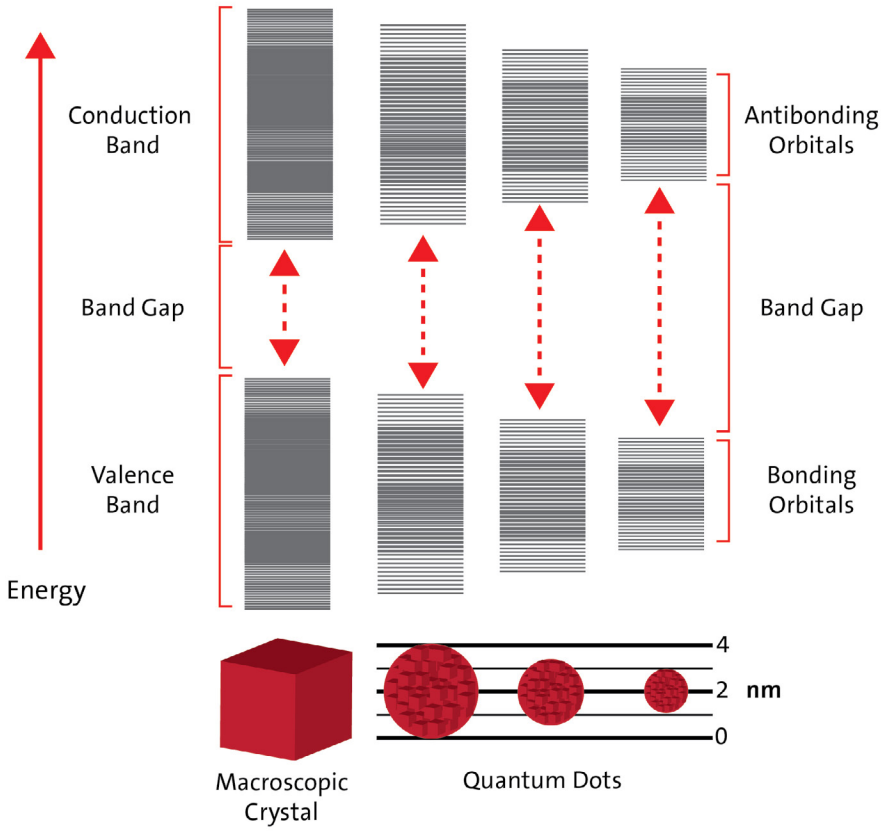

Figure 8. Illustration of the change in energy levels as a function of crystal size. The quantum dot materials show the individual energy levels which can be calculated using the particle-in-a-box model. As the crystal grows large it approaches the bulk semiconductor state with energy bands separated by the bandgap energy, E_g.

through a combination of selecting a particular semiconducting material and controlling the physical size of the quantum dot. The change in bandgap for several semiconductor materials commonly used for quantum dots is shown in Figure 9. Further, how this bandgap energy maps to the wavelength of light emitted is shown in Figure 10.

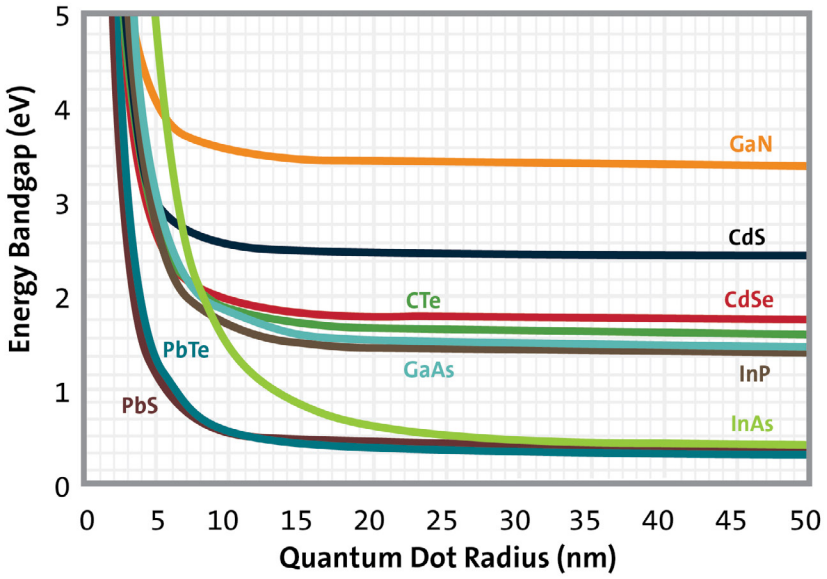

Figure 9. *Quantum dot bandgap energy as a function of crystal radius and semiconducting material.*

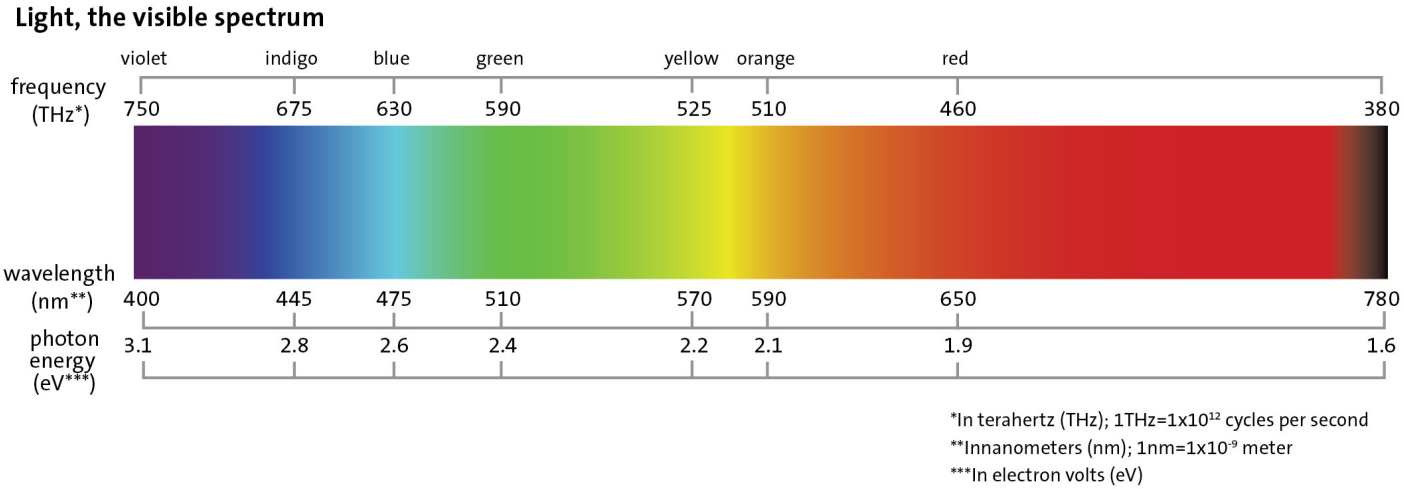

Figure 10. *Wavelength and frequency of visible light, shown with corresponding bandgap energies.*

Applications of Quantum Dots

A variety of applications have been proposed for quantum dots, from lighting and photovoltaic applications to use in quantum computing and biological applications. In this report, focus is placed on applications involving lighting and related technologies (such as displays).

Lighting applications for quantum dots typically leverage the narrow and tunable emission bandwidth of the materials. This allows for relatively monochromatic light emission with pure and saturated color. The quantum dots could replace or supplement phosphors used in white LEDs, or the color filters in displays, particularly for increasing red emission. It is also possible that quantum dots could be added to colored LEDs to tune or otherwise refine the emitted color spectrum. However, in that particular application some energy efficiency may be lost since the applied photonic energy would have to be higher than the desired emitted energy to allow the quantum dots to absorb photons to be emitted at the desired wavelength.

Quantum Dots Used for LED Lighting

The use of white LED lighting to replace incandescent and fluorescent lighting has been increasing in popularity as production costs have dropped and volumes have increased. White LEDs for lighting have the advantages of superior energy efficiency and greater service lifetimes relative to alternative lighting technologies. LEDs also have the advantage of having a tunable emission spectrum, allowing for lighting to be tuned to resemble daylight or to closely match light from incandescent bulbs.

Such tuning of LEDs can be achieved in a number of ways, including the use of a trio of red, green, and blue (RGB) LEDs that allow for a wide range of colors by changing the relative emission of each color. This, however, is not the preferred method for the generation of white light for LED lighting. Instead, a blue LED (normally made from InGaN) is typically paired with a yellow-emitting phosphor (such as cerium-doped yttrium aluminum garnet, or Ce:YAG). The combination of the blue light from the LED with the emitted yellow light from the phosphor is perceived as white light (Figure 11). This approach is less complex and therefore typically lower cost than an approach based on the grouping of RGB LEDs.

The use of quantum dots as a replacement for the phosphor layer has been reported in academic literature, though it does not appear to have been commercialized. *Xin et al*[11][12] reported an inorganic-organic hybrid blue LED/quantum dot light source that uses silicon quantum dots. Fabrication appears to be a hybrid between solution processing at least some layers (quantum dots are often deposited out of a carrier solution), with pre-patterned indium tin oxide (ITO) substrates. In a 2009 article,[13] QD Vision was cited as pursuing lighting with better color performance relative to LED lighting at the time. However, the company's current website focuses on quantum dots for displays and does not mention the use of quantum dots for lighting applications.[14]

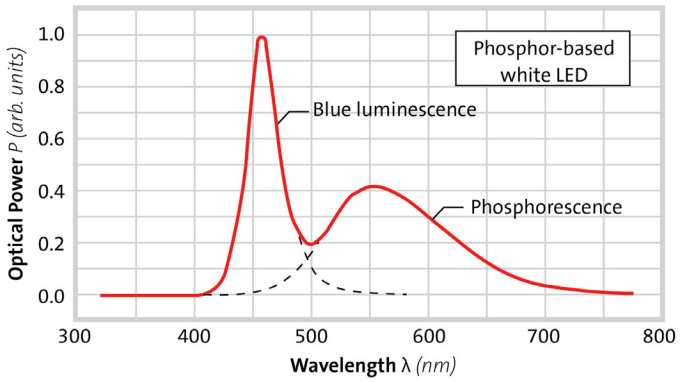

Figure 11. *Example spectrum for a cool white LED, showing blue luminescence from the LED and yellow emission from the phosphor layer (Nichia Corporation).*

Review of the literature shows that the majority of reports of using quantum dots for white lighting applications were

[10] K. Jasim, "Quantum Dots Solar Cells," excerpt from "Solar Cells – New Approaches and Reviews," L. Kosyachenko (ed.), Intech Publishing, 2015. (http://www.intechopen.com/books/solar-cells-new-approaches-and-reviews)

[11] Y. Xin, K. Nishio, and K. Saitow, "White-blue electroluminescence from a Si quantum dot hybrid light-emitting diode," Applied Physics Letters, **106,** 201102 (2015).

[12] D. Johnson, "Quantum Dots Enable Next Generation of LED Lighting Systems", IEEE Spectrum, June 2015, (http://spectrum.ieee.org/nanoclast/semiconductors/optoelectronics/quantum-dots-enable-next-generation-of-led-lighting-systems).

[13] N. Savage, "Quantum Dots Enhance LED Lighting," *IEEE Spectrum,* December 2009, (http://spectrum.ieee.org/semiconductors/optoelectronics/quantum-dots-enhance-led-lighting).

[14] As of October 2016. See QD Vision, Inc., website: http://coloriq.com/.

published prior to 2010. Most of these citations were sourced from academic teams or small start-ups; few reports of commercialized LED products were found by the author. A prototype commercial product was announced by QD Vision in 2009, but does not appear to have been commercialized further.[15] The lack of announcements past 2010 suggests that the use of quantum dots for white lighting applications has lost interest in favor of other applications. This may be a result of the rapid growth of Ce:YAG phosphor white LED lighting since 2010 with a corresponding drop in unit cost.

Quantum Dots in Display Technologies

In contrast to lighting applications, the literature regarding display technologies suggests that, at the time of this report (mid-2017), there is an active interest in the use of quantum dots for displays and early efforts to commercialize the technology into consumer products. Some displays utilizing quantum dots are found to be commercially available.

Conventional LCD displays use color filters to generate red, green, and blue light. These are backlit with a white light source, originally a series of fluorescent tubes, but in more recent years this has been replaced with arrays of white LEDs. This white light is then passed through color filters to create the desired color pixel. Since much of the light spectrum is absorbed by the filter, energy efficiency is not optimized. The original vision of a "quantum dot display" is the use of quantum dots instead of these filters, which promises greater energy efficiency and better control over the color spectrum. It is therefore anticipated that such a quantum dot display will give better color rendering while delivering better energy efficiency. Fabrication of such displays has been reported, but appears to be at a laboratory scale.[16] In current production displays that cite use of quantum dots, however, the dots tend to be used as part of the backlight as a replacement for a yellow-emitting phosphor.

"Quantum dot displays" are already available to consumers in both large and small formats. Prior to the launch of the Apple iPhone 6 series of devices, there were reports that the display would use quantum dots.[17] This, however, was not the case, with Apple citing the "toxic" nature of cadmium-containing materials.[18] However, Apple is reportedly continuing their investigation of quantum dots and may use them in a future product (after their anticipated 2017 release of an OLED display).[19] Amazon has already entered the market with a quantum dot-containing display with their Kindle Fire HDX.[20] The display, which exhibits a blue glow at the edges, is manufactured by LG and utilizes quantum dots sourced from Nanosys (Figure 12).[21] Quantum dots are used on a single sheet as part of the backplane light: quantum dots that emit in the red and green wavelengths are deposited in a sheet and paired with a blue LED backlight. This approach promises a more true white light and, therefore, better color gamut (Figure 13).[22]

Large-format displays are also being found to have quantum dots utilized in their fabrication. Sony, LG, and Samsung have all released quantum dot televisions, with Samsung diverting

[15] "Lamp That Integrates Quantum Dot Technology to Be Demonstrated at Lightfair 2009; Breakthrough Technology Combines Warm, Rich Color with LED Efficiency, Providing 2700K, 90+ CRI at 65 Lumens Per Watt," *QD Vision Press Release,* 5 May 2009 (http://www.qdvision.com/release-05052009).

[16] L. Kim, P. Anikeeva, S. Coe-Sullivan, J. Steckel, M. Bawendi, and V. Bulović, "Contact Printing of Quantum Dot Light-Emitting Devices," *Nano Letters,* 8 (12), pp. 4513-4517, 2008.

[17] C. Smith, "The iPhone 6's killer feature tipped to be the display... but not because its size," *BGR.com,* 24 February 2014 (http://bgr.com/2014/02/24/iphone-6-specs-quantum-dot-display/).

[18] J. Horowitz, "Apple passes on "toxic" Quantum Dot displays, reaffirms Mac as "different on purpose" from iPad," *9to5Mac.com,* 13 October 2015 (https://9to5mac.com/2015/10/13/imac-input-design-lab-tidbits/).

[19] J. Purcher, "Apple Advances Work on Quantum Dot Displays for Future Macs, iOS Devices & Possible TV," *Patently Apple,* 28 July 2016 (http://www.patentlyapple.com/patently-apple/2016/07/apple-advances-work-on-quantum-dot-displays-for-future-macs-ios-devices-possible-tv.html).

[20] A. Vandervell, "Quantum Dots Explained: What are quantum dots and why are they so awesome?" *Trusted Reviews,* 7 January 2016 (http://www.trustedreviews.com/opinions/quantum-dots-explained-what-they-are-and-why-they-re-awesome).

[21] J. Inofuentes, "The Kindle Fire HDX display bleeds blue—and that's OK," *Ars Technica,* 26 October 2013 (http://arstechnica.com/gadgets/2013/10/the-kindle-fire-hdx-display-bleeds-blue-and-thats-ok/).

[22] W. Fenlon, "Kindle Fire HDX 7 and Nexus 7 Handily Beat Retina iPad Mini in Display Shoot-Out," *Tested.com,* 19 November 2013 (http://www.tested.com/tech/tablets/459137-kindle-fire-hdx-7-and-nexus-7-handily-beat-retina-ipad-mini-display-shoot-out/).

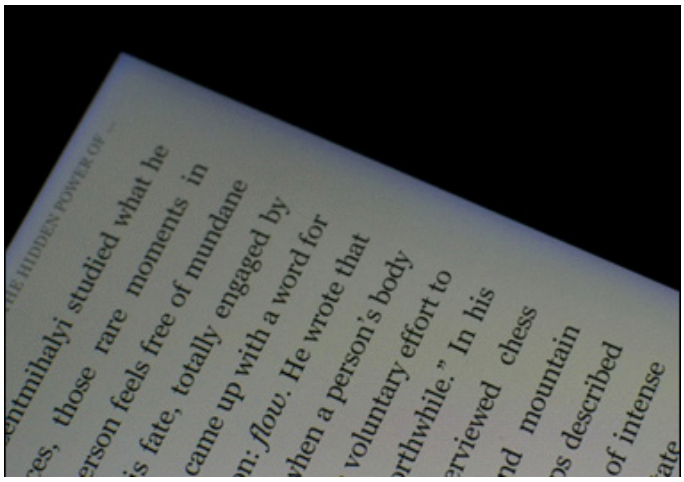

Figure 12. Detail of Kindle Fire HDX display showing blue glow at edges of display.[22]

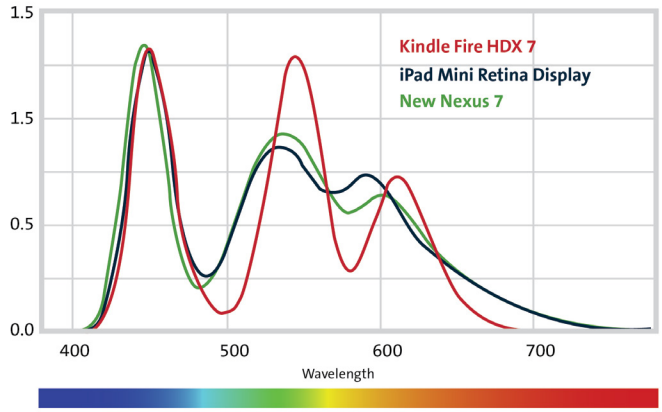

Figure 13. Emission spectra for quantum dot-containing Kindle Fire HDX 7 backlight compared to two displays that utilize more traditional yellow phosphor layers.[23]

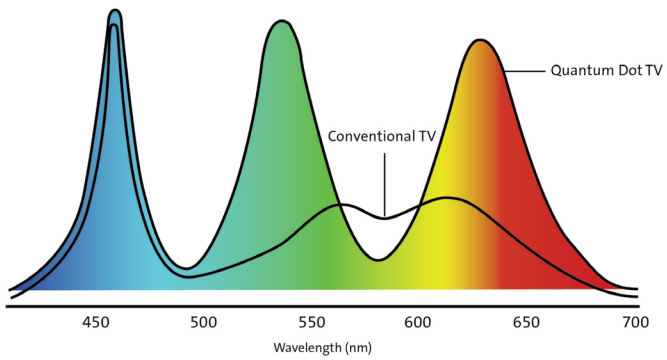

Figure 14. Comparison of quantum dot television backplane spectrum to conventional television (LED) output. From Samsung website.[23]

attention from further development of OLED televisions in favor of quantum dots.[21] As with the smaller format displays, the cited advantages are better color reproduction and greater efficiency. The approach is also similar, where the phosphor layer is constructed using red- and green-emitting quantum dots paired with a blue-emitting LED (Figure 14).

Other Applications

Quantum dots are also used in applications beyond lighting and displays. One such application is in photovoltaic power generation, where quantum dots are intended to replace bulk materials. As half of solar radiation is in the infrared, solution-processable quantum dots (typically lead selenide, PbSe; lead sulfide, PbS; and indium arsenide, InAs) may be useful in extracting this energy. This use of quantum dots is not yet ready for commercialization, as the efficiencies are not as high as more established technologies with laboratory-scale demonstrations having been as high as 4 to 5 percent efficiency.[25] At the time of this report, most reports of quantum dot-containing solar cells are in the academic literature and appear to still be a subject of academic research.

Medical applications for quantum dots are also being explored. Nanoco Technologies is exploring the use of cadmium-free quantum dots as a replacement for traditional dyes in cancer detection and surgery.[26] The cited advantages of quantum dots for this application are that the quantum dots migrate relatively slowly and are able to function for many hours. Light emission can be tailored to any frequency desired by the surgeon, including in the infrared which can be seen through other tissue. Such experiments are being conducted on mice and other simulations of tumor surgery on animals. It is also hoped that quantum dots could be utilized in photodynamic therapy, where the quantum dots are absorbed into a tumor and designed to absorb light energy more readily than the surroundings. This causes localized heating of the quantum dots, therefore destroying the tumors without surgery.

Materials Considerations

Quantum dots can be fabricated with a number of semiconducting materials, as long as their size can be adequately controlled and the semiconductor is direct bandgap, as was

[23] Samsung blog: "Why Are Quantum Dot Displays So Good?" (http://www.samsung.com/global/tv/blog/why-are-quantum-dot-displays-so-good.html).

described earlier in this report. As was shown in Figure 9, several binary semiconductors are capable of covering the full visible light spectrum as the particle radius is changed; however, some of these materials show a rapid shift in bandgap energy with relatively small changes in radius. This shift poses a potential issue with manufacturability as a narrow range of particle diameters would need to be maintained during fabrication to obtain a desired color response. Considering this, it would therefore be preferable to select a material where the bandgap changes relatively slowly as radius changes, but within a range conducive to the growth process and one that allows sufficient control of the variation in particle size. As Figure 9 suggests, CdSe and CdTe appear to be optimal materials with respect to bandgap variation and particle size. It is found that in most applications, semiconductors containing cadmium (Cd) are preferred due to their optical performance and tunability.

However, as previously discussed, the use of cadmium poses a concern due to the toxicity of the metal, and cadmium is one of the original ten substances included in the RoHS directive. This directive limits cadmium to 0.01% or 100 ppm by weight to any homogenous material in a product. This therefore potentially limits the ability to use cadmium-containing semiconductors for commercial quantum dot usage. Regardless, QD Vision, Inc. and their commercial partner, 3M Optical Systems Division, applied for, and were granted, exemptions for cadmium quantum dots used in LED light down-conversion and for LCD light control films and components.[27] The exemption is allowed only for displays and not for general lighting applications. This exemption was granted by the European Commission expiring on 1 July 2014, with the limit being less than 10 µg of cadmium per square millimeter of light-emitting area.

A renewal of this exemption has been pursued by QD Vision and 3M, requesting an extension to 2017 for displays and 2018 for light control films. This extension is supported by the Öko Institute, who prepared and submitted a report to the European Commission, which also recommended the extension.[28] This was in response to the European Parliament rejecting the extension in 2015.[29] The objection to extending the exemption is due to the fact that cadmium-free quantum dots, usually indium phosphide (InP), have been introduced onto the market. One developer of these cadmium-free quantum dots, Nanoco Group, mentioned earlier, is disputing the findings of the Öko Institute report, citing that InP displays have been shown to have as good or better energy efficiency and performance of cadmium-containing quantum dots and therefore the exemption is not necessary. The Öko report, however, suggests that cadmium-based quantum dots continue to have superior performance. Samsung's commercialized quantum dot displays are given as an example of a successful implementation of cadmium-free quantum dots, which use InP materials.[28,30]

As of the writing of this report, no further information beyond June 2016 was found, therefore it is unclear at this time whether the RoHS exemption will be extended or allowed to lapse. Reviewing Figure 9 shows that InP is capable of covering the full light spectrum, though the range of particle sizes may need to be controlled with greater precision relative to CdSe. This may be one reason CdSe is preferred, as it gives more tolerance on particle size for a given application. However, since the status of the cadmium exemption for displays is currently in question, and no such exemption exists for general lighting applications, cadmium-free quantum dots will likely be preferred (or necessary) in the future for all products.

[24] E. Sargent, "Infrared Quantum Dots," *Advanced Materials,* 17, no. 5, 2005. (http://nathan.instras.com/ResearchProposalDB/doc-188.pdf)

[25] R. Ahmed, "Quantum dots: The pros and cons in PV," *PV Magazine,* February 2013 (http://www.pv-magazine.com/archive/articles/beitrag/quantum-dots--the-pros-and-cons-in-pv-_100010173/572/).

[26] I. Naasani, "The Cancer Surgeon's Latest Tool: Quantum Dots," *IEEE Spectrum*, October 2016 (http://spectrum.ieee.org/biomedical/imaging/the-cancer-surgeons-latest-tool-quantum-dots).

[27] C. Gensch, Y. Baron, and M. Blepp, Assistance to the Commission on Technological Socio-Economic and Cost-Benefit Assessment Related to Exemptions from the Substance Restrictions in Electrical and Electronic Equipment: Pack 10 Final Report," Öko-Institut e.V., Institute for Applied Ecology Report, 17 May 2016 (http://rohs.exemptions.oeko.info/fileadmin/user_upload/reports/20160602_Final_Report_RoHS_Pack_10_Cd_QDs.pdf).

[28] "Row breaks out over cadmium quantum dot TVs," Optics.org, 7 October 2015 (http://optics.org/news/6/9/57).

[29] "EU report sends mixed message on cadmium quantum dots," Optics.org, 6 June 2016 (http://optics.org/news/7/6/8).

Conclusions

Quantum dots are nanoscale semiconducting materials that have differing optical properties based on their physical size. This is due to quantum mechanical effects, where the effective semiconductor bandgap of the material increases as size decreases. This enables a quantum dot to absorb and emit photons (i.e., light) within a narrow spectral range according to the particle size selected during fabrication. Quantum dots can be suspended in liquid media, allowing for the material to be coated through a variety of low-cost techniques, such as spin coating, spray, dip coating, or other large-area methods.

The primary advantage of quantum dots is the ability to tune light emission to a specific wavelength and the ability to use a single semiconducting material to emit different wavelengths by using particles of different sizes. This has shown particular advantage in generating red and green light when paired with a blue LED light source, enabling generation of white light output. This approach is reportedly able to give improved color gamut compared to yellow Ce:YAG phosphors (also paired with blue LEDs for white light generation). The use of quantum dots also promises improved energy efficiency over the use of color filters. These filters absorb most light while emitting the desired color, but quantum dots re-emit most of the incoming light energy, with some loss depending on the incident light and other optical factors. Other applications for quantum dots are also suggested, including for photovoltaics and medical applications. Such applications appear to be experimental only and are not yet at a commercial scale.

Though the use of quantum dots has been mentioned for both white LED lighting use and for displays, commercial use seems to focus on quantum dots in displays. Several manufacturers of tablets, mobile devices, and televisions already offer products with quantum dot-containing displays. Such manufacturers include Amazon, Samsung, LG, and Sony. Prices are comparable to other backplane technologies, though quantum dot displays tend to be at a higher price point (which may be due to the use of quantum dots, the fact that most quantum dot televisions are top-of-the-line 4K displays, or both). The use of quantum dots for LED lighting applications had been cited in the past, but does not appear to be the focus for quantum dot materials manufacturers. It is possible that current Ce:YAG materials are “good enough,” or that the downward pricing pressure on LED lighting manufacturers has limited their ability to utilize more novel red/green emitting materials. Early white LED lighting tended to be perceived as too bluish and harsh to the eye, though more recent “warm white” LEDs seem to have reduced this issue.

One key issue that is mitigating widespread adoption of quantum dots, at least from some sources, is that some compounds contain cadmium. The RoHS mandate restricts cadmium in consumer devices, though a temporary exception had been approved by the European Union for quantum dots. However, this exemption is expiring and a renewal is currently under debate with the outcome remaining uncertain. This uncertainty is due to the commercial availability of quantum dots that do not contain cadmium (e.g,. Samsung quantum dot displays use cadmium-free materials). The push to continue the cadmium exemption is likely due to intellectual property issues, though manufacturing conditions may also be a factor. For example, the cadmium-containing materials CdSe and CdTe appear to require a looser tolerance on the particle size distribution relative to InP, a cadmium-free material. However, considering that cadmium-free options exist and are commercialized, it is likely that the cadmium exemption will eventually expire even if it is extended into 2018.

Regarding environmental concerns, the presence or absence of cadmium or other heavy metals may be of interest. As quantum dots are particles on the nanoscale, there is a potential that they may be eventually subjected to future regulation, though at the time of writing no specific limitations are known. Quantum dots tend to be suspended in some sort of matrix and can be considered similar to paints or other sorts of composite coatings. There are no known end-of-life issues that would be unique to quantum dot-containing products, and disposal regulations are not likely to differ significantly from other lighting and display products.

Quantum dots appear to be a technology sufficiently mature for certain lighting and display applications and have already proven viable for display backplane applications. Though more advanced uses are possible, it is likely that they will continue to be utilized mainly for red/green emitting layers for generating white light. It is not clear how much growth will be seen for the technology, especially if intellectual property issues are limited through the expiration of the RoHS cadmium exemption. It is therefore expected that quantum dots will remain a niche

technology for high-end displays and will be primarily used for this application into the near future. Lighting may eventually adopt the use of quantum dots, though it is not clear whether the improved color gamut is a sufficient counterweight to increased materials costs, as LED lighting is currently very price sensitive. Interest in using quantum dots in lighting applications was stronger prior to 2010 than it seems to be now. More novel applications are in the research phase and likely will not be commercialized for several years. These new applications are likely to encounter resistance of adoption due to pricing (for photovoltaic applications) and regulatory (for medical applications) pressures. Ultimately, these pressures are likely to slow penetration of quantum dots into additional applications.

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