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Application of Quantum Dots as Down Conversion Materials in white LED

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Abstract: The paper introduces the development history and light emitting method of White LED (WLEDs) and compares and analyzes the advantages and disadvantages of fluorescent powder and quantum dot as transition materials under WLEDs, specifies the development direction of quantum dot under WLEDs, states the layered structure and mixed structure of quantum dot and fluorescent powder, and the application and progress of quantum dot and quantum well Resonance energy transfer mechanism under WLEDs, and analyzes the development prospect of quantum dot as the transition materials in WLEDs.

Keywords: *Quantum Dot; Quantum Well; Layered Structure; Resonance Energy Transfer Mechanism; White LED*

I. INTRODUCTION

Since LED (Light emitting diode) came out 50 years ago, it has expressed huge potential in energy saving and life aspects. It has been hoped that it will become a new generation of solid lighting source[1]. As a solid-state lighting source, LED has the advantages of high light efficiency, small size and energy saving and environmental protection. In recent years, it has been widely used in the stage lighting, LCD display and advertising and other fields[2]. The market share is also expanding. It has become one of the most important research directions. WLED has not been achieved because of the failure to obtain high-efficiency blue LED. Until 1996, Japan Nichia Company has successfully developed WLED[1]. WLED has divided into No phosphor powder and Fluorescent powder in the mode of producing white light. The white light of WLED without Fluorescent powder is obtained from LED with three primary colors which gives out lights respectively. Different effects of white light may be obtained through adjusting the light emitting ratio of LED with three primary colors. WLED with fluorescent powder is light conversion device based on blue light or ultraviolet light, which is also called Fluorescence conversion WLED. Among these devices, the fluorescent powder produces the corresponding green light and red light, or blue light, green light and red light under the motivation of blue light or ultraviolet light, and obtains white light by mixing[2]. As the mainstream product on the Lighting market, Fluorescence conversion type WLED is characterized by simple and mature enclosing process, low cost, etc. while such problems as low luminescent efficiency, low luminous mass and emitting heat, etc[3,4,5]. In recent years, the researchers discovered that quantum dots play an important role in achieving luminous mass and improving luminescent efficiency depending on the advantages of high conversion efficiency, high stability and high rendering properties[6]. Therefore, using quantum dots as the transition materials under WLEDs replacing fluorescent powder (namely QDs-WLEDs) becomes an optimal selection of above problem.

II. THE APPLICATION OF QUANTUM DOTS IN THE WHITE LED

Quantum Dots (ODs) are also called “Artificial atom” or “Semiconductor nanocrystals” is the particles with the diameter of 1～100nm in Ⅱ－Ⅵ family or Ⅲ－Ⅴ family elements[7]. Because Semiconductor quantum dot is influenced by size effect and Dielectric confinement effect, the luminescent properties of quantum dots exhibit three characteristics: 1) Quantum dots can change the particle size and chemical composition, thus the light can cover all monochromatic light wavelength of the visible light wave; 2) Half width of monochromatic fluorescence spectrum emitted by quantum dots is only 40nm. With better monochromaticity, it is the most outstanding advantage compared to Fluorescence conversion type LED; 3) Fluorescence efficiency of quantum dots is very high. After covering a layer of inorganic materials, it may further improve the efficiency and protect the internal core and improve the stability[8]. Fig.1 shows the classical QD LED structure and QD luminescence diagram.

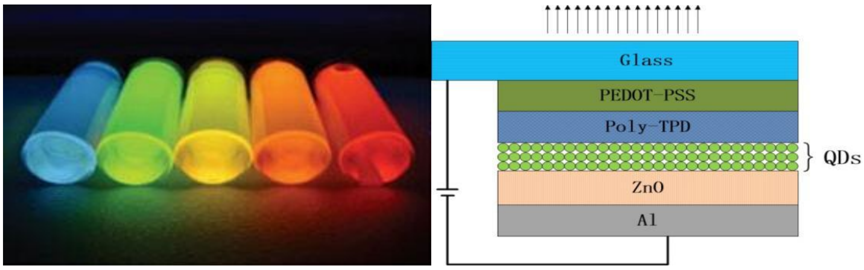

Figure 1 Schematic diagram of wavelength of OD light covering all visible wave and classical QD-LEDs

At present, three methods of OD-LED light are multi-color combination QLED, light conversion QLED, Quantum dots and quantum well resonance energy transfer QLED[3]. The principle of three methods to obtain white light is shown in Fig.2. Left) multi-color combination QLED; middle) light conversion QLED; right) Quantum dots and quantum well resonance energy transfer QLED.

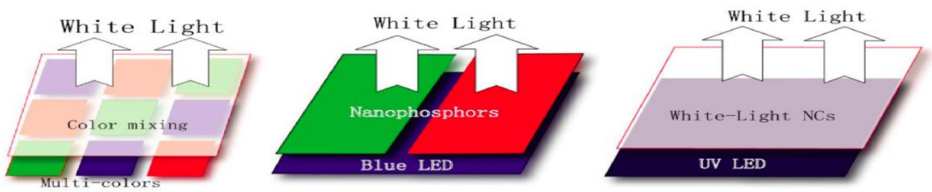

Figure 2 Schematic diagram of three methods obtaining white light Left) multi-color combination QLED; middle) light conversion QLED; right) Quantum dots and quantum well resonance energy transfer QLED

1. Multicolor combination QDs-WLEDs

The principle of multicolor combination QDs-WLEDs to obtain white light is: Three or more than three kinds of emission wavelength of quantum dots are set in a certain way as a white light emitting module[9]. Alivisat Research Group firstly prepared Emission induced luminescence QDs-WLEDs taking CdSe Quantum dots as light emitting bodies. The LEDs will be reconstructed via Coe, and the luminous efficiency is greatly improved. QDs-WLEDs may be prepared through mixing blue light (CdZnS alloy), green light (ZnSe/CdSe/ZnS core/shell/shell), red light (CdSe/ZnS core/shell) Colloidal nanocrystals. The color coordinates of WLEDs are (0.33, 0.41) and Ra value reaches 86[10]. However, some deficiencies still exist in WLED. For example, the complex preparation process makes it is difficult to keep the proportion of QDS. A small change will make the color coordinates a large offset. Because of small Stokes shift between quantum dot absorption peak and emission peak, the reabsorption of quantum dots makes the use of energy greatly reduced, and especially a large part of blue lights is absorbed by red and green QDs[11].

2. Light conversion QDs-WLEDs

The principle of light conversion QDs-WLEDs is: ODs of different luminous colors cause blue light/purple light via LED Chip electro luminescence, and give out yellow light, red light and green light. The white light is obtained taking use of RGB principle[12]. In 2003, Lauren Rohwer research group in Sandia National Laboratory of the United States firstly made the world's first Quantum dot solid white light emitting device and initiated the application of ODs as light transition materials into Light conversion composite WLED combining CdS and CdS QDS and Epoxy resin and silicone grease[13]. In 2005, Bowers of United States University of Derby coated super small size CdSe quantum dot and polyurethane into one 400nm commercial UV-LED[14]. After power-on, it may give out Yellowish white light under the motivation of LED. The chromaticity coordinate (0.32, 0.65) becomes the first QD WLEDs motivated by near ultraviolet LED. Chen et al. covered organic ligand on the surface of ZnSe quantum dot, thus obtaining a Broad spectrum combining intrinsic emission spectrum and Deep well emission spectrum and obtaining white light under the motivation of 385nm near ultraviolet LED chip. In 2007, Sapra and Nag also took use of similar principles and near ultraviolet LED chip to motivate core shell quantum dots in spectral broadening due to the trapping into deep well defect spectrum[3]. In 2009, Kim took use of yellow light CdS:Mn/ZnS Quantum dots and Yttrium Aluminum Garnet Phosphors to improve yttrium aluminum garnet WLED based om the blue light LED chip and improve the rendering index of LED to 85. In 2011, Han greatly improved the fluorescence property of red light CdSe/CdS/CdZn/ZnS/Resin composite through UV-exposure. Under the motivation of blue light LED chip and mixing with Yttrium aluminum garnet yellow phosphor, the white light with rendering index 91 and the colour temperature 4805K will be obtained[3]. Korean scholars Woo, J.Y. and others tested quantum dots and fluorescent powder of CdSe/CdS/CdZnS/ZnS core - Multiple shell structure and obtained the layered structure and mixed structure of Quantum dots and fluorescent powder. Upon comparison, the layered structure of Quantum dot fluorescent powder coating is higher than the mixed structure in Luminous intensity, light decay and heat loss efficiency, and the luminous intensity is improved by 40%. The rendering index was increased to 84.4 from 80.5[15]. Fig.3 shows the comparison of layered structure and mixed structure in luminous intensity. A) The layered structure of phosphor coated quantum dots is displayed. Under blue light source, comparing the structure with coated fluorescent powder, after coating QD layer on Phosphor layer, Red luminescence intensity is increased because the Blue light gives out the photons via fluorescent layer and reabsorption fluorescent layer. B) The hierarchical structure of phosphor coated on quantum dots is shown. Under blue light source, comparing with coated quantum dot layer and after coating Phosphor layer on Quantum dot layer, the green light intensity is obviously increased and the red light intensity is slightly reduced. C) The light intensity comparison of quantum dots and fluorescent powder on the mixed structure and the above two layered structures is displayed. It shows that the layered structure of coating QDs on fluorescent powder is higher the mixed structure in luminous intensity, light decay and heat loss efficiency. The comparison of three structures of WLED in rendering index, luminous efficiency and color temperature is shown in Table 1

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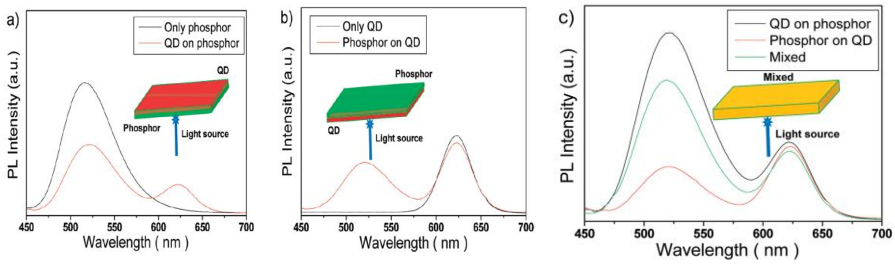

Figure 3 Contrast diagram of WLED of layered structure and mixed structure in luminous intensity

	CIE coordinate	Luminous efficiency(lm/W)	Color temperature（K）	Color rendering index	Chip temperature(° C)
QD on phosphor	(0.2889,0.3627)	71.6	8684	88.4	90.5
Phosphor on QD	(0.3651,0.2869)	58.5	4698	71.9	103.7
Mixed	(0.3178,0.3426)	63.5	6439	80.5	94.5

Table 1 Comparison of WLED parameters obtained from two layered structures (Quantum dots and fluorescent powder) and mixed structure

WLED obtained from the layered structure of coating QDS on fluorescent powder obtained better effect in improving color rendering index, color temperature and luminous efficiency. However, it is difficult to obtain WLED with high rendering index and luminous efficiency. Therefore, the scientific workers proposed a kind of new structure-Quantum dots and quantum well resonance energy transfer WLED[16].

3. Quantum dots and quantum well resonance energy transfer WLEDs

Recently the researchers have found a direct energy transfer channel exists between electro-hole pair and QDs in LED luminous zone, namely Fluorescence Resonance Energy Transfer (FRET), in order to transfer the energy in InGaN QW to QD directly, and motivate QD light[17]. The energy transfer process is shown in Fig.4. Some excitons produced to QW directly transfers the energy to nearby QS through the Non-radiative energy transfer process not through radiation recombination, in order to motivate QD light. The research proves that direct non radiative energy transfer path is formed by Interaction between dipoles, namely Ultrafast band relaxation occurred in QW-QDs coupling process and QDs[18]. In essence, the energy transfer process is different from the luminescence–excitation–luminescence process of ordinary fluorescent powder. In the multiple processes, each process will produce certain efficiency loss, thus it configures the final luminous efficiency. The direct energy transfer process between electro –hole in QDs and LED QW reduces the energy transfer steps, breaks the limitations of conventional fluorescent powder to luminous efficiency and greatly improves the energy transfer efficiency and luminous efficiency[19].

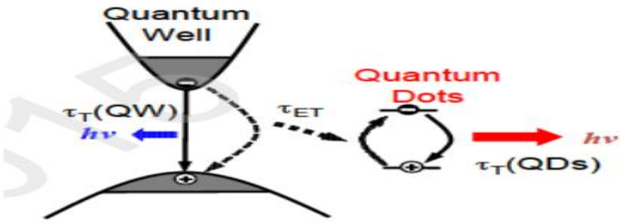

Figure 4 Schematic diagram of energy transfer process in QDs-QW structure

As shown in Fig.5, it is the schematic diagram of QDs-QW device structure. A) Nano hole array penetrates QW layer until n-GaN layer, and QDs are filled in nano hole; b) QDs in nano hole array contact QW surface[20].

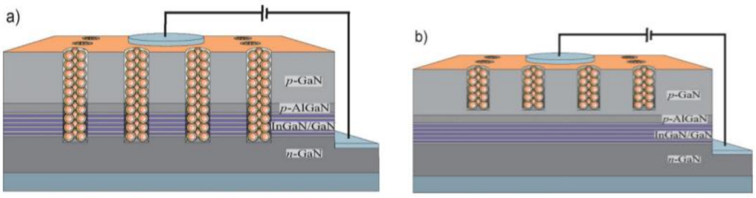

Figure 5 Schematic diagram of Quantum well quantum dot device structure

In 2015, Liu Bin research team of Nanjing University discussed a topic and researched Nitride semiconductor photovoltaic and energy conversion efficiency. In the research, InGaN/GaN Multiple quantum well optical electrode used UV curable lithography and top-down etching technology. IPCE is improved to 42% (wavelength is 400nm) from 16% (plane structure). What's more important, motivation–0.6v low voltage indicates the possible self-excitation[21]. In addition, Silicon dioxide / silicon nitride medium distribution Prague reflector further improved IPCE to 60%. Fig.6 shows the schematic diagram of device structure and quantum dot filling.

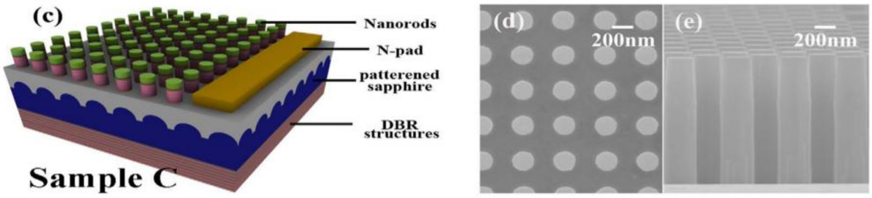

Figure 6 Schematic diagram of device structure and quantum dot filling

In 2016, Liu Bin research team designed a kind of Nitride nanocrystal light-emitting diode (h-LED) and took use of purple light/blue light InGaN/GaN Multiple quantum wells and various wavelength luminescent nanocrystal media. It was completed under FRET theory[22]. Apply nano pressing technology to penetrate nano hole array in InGaN/GaN multiple quantum well. Such a device structure can significantly reduce the exciton decay lifetime and the energy conversion efficiency may reach 80%. The research shows that in Förster equation, Exciton coupling distance mixed structure is less than Förster radium. It may improve the energy transfer efficiency of non-radiation. The research obtained WLED indicator of optimizing the device. The rendering index of h-LED of Three element mixed complementary colors may reach 82[23]. Different color temperature emitted by white light increases to 6636K from 2629K. It covers the warm white, nature white and cold white and obtains better luminous effect. Fig.7 shows the schematic diagram of device structure, nanopore array and quantum dot filling.

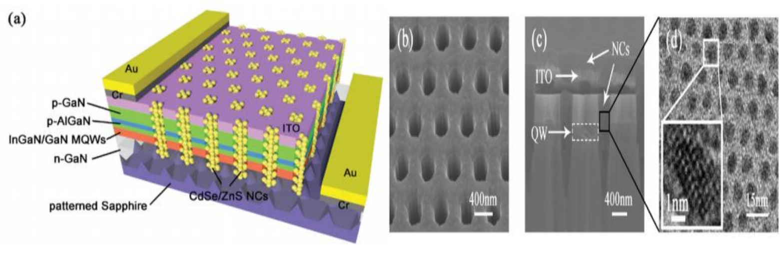

Figure 7 Schematic diagram of device structure, nanopore array and quantum dot filling

In fact, because Etching causes damage to the quantum well layer, it leads to that the quantum efficiency of quantum dots and quantum well resonant energy transfer white LED has not reached the theoretical height. The continuous improvement in device structure and process method may improve the quantum efficiency of WLED to a new level[24].

III. CONCLUSION

Making a comprehensive survey of LED development history, to overcome the disadvantages of surface coated fluorescent powder WLEDs (such as poor consistency, low self-absorption and evenness of different substrates of fluorescent powder, inconsistent service life of fluorescent powder and LED, low rendering index, high temperature changes), the Scientific research workers designed and prepared WLEDs of layered structure and mixed structure between Quantum dots and fluorescent powder, and obtained that the layered structure of Quantum dot fluorescent powder coating is higher than the mixed structure in luminous intensity, color rendering index, light decay and heat loss efficiency and the quality of light of light source is improved. In the experiment and application of WLEDs of layered structure and mixed structure of Quantum dots and fluorescent powder, although the process is simple and the cost is low, the quantum efficiency is unsatisfactory, and it is different to develop. Therefore, the scientific research workers designed Quantum dots and quantum well resonance energy transfer LED. Resonance energy transfer LED opened a new world for us with the novel design ideas and creative thinking mode. However, because Etching causes damage to the quantum well layer, it leads to that the quantum efficiency of quantum dots and quantum well resonant energy transfer white LED has not reached the theoretical height. We believe that through the device structure and process of continuous improvement, the quantum efficiency of white LED luminous intensity, color index and other performance parameters can be enhanced to a new level, in order to save more energy and benefit the mankind.

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