QUANTUM DOTS, ADVANTAGES AND DRAWBACKS FOR LIGHTING APPLICATIONS

David Schmidmayr, Johann Zehetner

Research Centre for Microtechnology, Vorarlberg University of Applied Sciences, Hochschulstrasse 1, 6850 Dornbirn, Austria

E-mail: david.schmidmayr@fhv.at, johann.zehetner@fhv.at

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Abstract

At present 19% of the world-wide consumed electricity is used for lighting purposes. Compared e.g. to the well-known incandescent light bulb a modern warm white LED with a similar light quality has a 25 times higher lifetime and operates approximately ten times more efficient. One major component limiting the efficiency is the color conversion material (phosphor). Due to broad emission bandwidths of traditional phosphors energy is wasted. In order to further improve efficiency new robust fluorescent materials which allow selective, narrow band conversion are needed. In this paper we investigate the potential of quantum dots and show that they are able to increase both luminous flux and spectral coverage at the same time. Furthermore we evaluate the optical properties of quantum dot samples under thermal stress and aerial oxygen influence. Photoluminescence intensity degradation as well as a shift of the emission peak wavelength still pose a problem.

1. Introduction

Amongst modern solid state lighting (SSL) sources used for general lighting applications the most common ones basically consist of two components, namely a light emitting diode (LED) and a fluorescent color conversion layer (phosphor layer). The diode emits blue light which is to some extent converted and preferably results in a combined spectrum completely covering solely the visible range.Conventional fluorescent materials (e.g. silicates, aluminates and nitrides) used for this purpose are available only with limited emission peak wavelengths andemit in a wide band of the spectrum therefore aggravating selective color enrichment.Especially in the red wavelength area where the sensitivity of the human eye dramatically decreases the broad emission peak of conventional materials causes losses because significant parts of the radiative energy simply cannot be seen. Hencewith respect to the human eye sensitivity curve an improved white-perception (correlated color temperature - CCT) as well as a high color rendition (CRI) result in a reduced luminous efficiency (“efficacy" in lm/W)[1].Quantum dots (QDs)[2,3]on the other hand exhibit a comparably narrow emission band where the peak wavelength is determined by the size of the QD.This enables the implementation of adjustable emission spectra tailored to the eye sensitivity curve resulting in improved color rendition and efficacy.Ongoingadvancements in QD quantum efficiency as well as manufacturing processes which are capable of synthesizing large amounts of QDsmake them interesting as possible new color conversion materials. In order to evaluate their potential for general lighting applications we built and measuredan experimental white-light-LED where QDs are used in combination with conventional phosphors.Furthermore we focused on the

influence of temperature and aerial oxygen on the optical properties of QD in order to evaluate if they can compete with the robustness of our standard phosphors.

2. Materials and Methods

2.1 Experimental white-light-LED comprising quantum dots

Similar to commercially available white-light-LEDs the experimental setup comprises a single blue chip-on-boardLED (455 nm peak wavelength) without primary opticsas excitation source. The LED is thermally connected to a heat sink and powered by a constant currentof 650 mA (forward voltage V_f=3,5 V). As color conversion materials we used traditional phosphors (yellow YAG80911, orange BR-102C) and QDs with an emission peak wavelength of 620nm. Instead of a globe-top containing the color conversion material mixed together we prepared individual discs of each single material. This gave us the possibility to build up a stackable architecture where we could easily vary the white light impression by alternating the single discs. We placed this stack on top of the excitation LED. Each single disc contained a specific conversion material sealed between two glass plates with epoxy resin. All measurements were carried out with an integrating sphere (model: Gigahertz OptikISD-50HF-V; 500mm diameter; X4 BTS Light Analyzer).

2.2 Influence of temperature and aerial oxygen on quantum dot samples

To investigate the influence of thermal stress the QD samples were heat treated.Spectral measurements were carried out simultaneously to the heating and cooling cycle with an Ocean Optics USB4000 spectrometer. For these measurements we built a special furnace with openings for the spectrometer and excitation source (blue LED) on opposite side. In a second measurement procedurewe used a standard laboratory furnace where the QD samples were not exposed to light during heating. They wereplaced in the cold oven, heated up to a given temperatureand not removed until the oven has cooled down. These treatments were repeated with the same samples at stepwise increasing temperatures and dwell times increasing from 30 minutes to 10 hours (load accumulation).By opening the samples the influence of aerial oxygen on the optical properties of the QD material with respect to the sealed ones were investigated. For all spectral measurements the sampleswereplaced between the excitation source and the optical fiber (Ocean Optics R400-7-VIS-NIR)of the spectrometer.

3. Results and Discussion

Building up our stack starting with a single yellow phosphor disc resulted in a cold white emission of 9800K, a luminous flux of 81lm and a color rendering index R_a=83,5. Adding a second orange disc lowered the CCT to 4860K, reduced the luminous flux to 77lm and improved R_a to 87. By substituting the orange phosphor disc with a QD discthe efficacy and color rendering ability wereboth improved. The CCT was further lowered to a more pleasant level of 3870K. Luminous flux and R_a improved to 78lm and 89,3 respectively.This demonstratesthe abilityof QDs to improve both efficiency and light quality. Energy losses due to the broad emission band of the traditional phosphor ranging into the hardly visible far red area (see figure 1) were minimized.

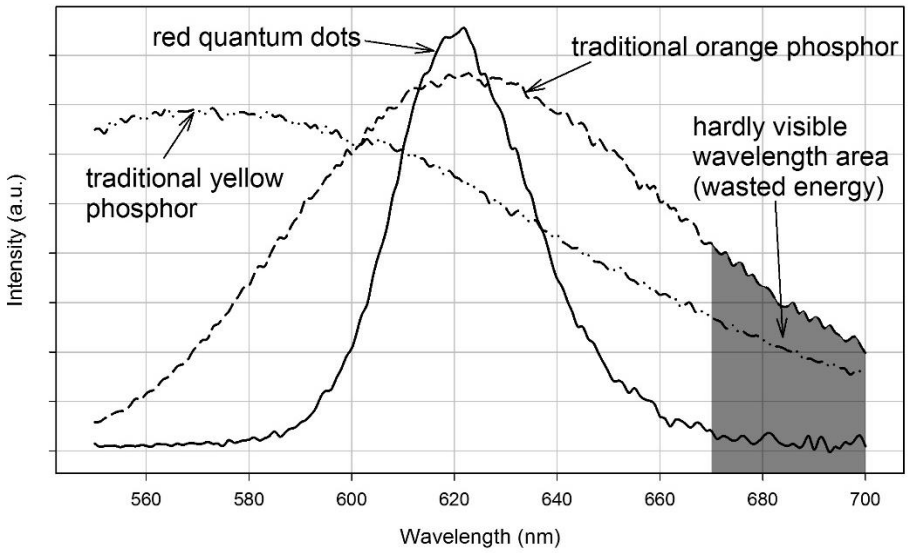

Fig.1: *Emission spectra overlay of traditional yellow/orange phosphors and red QDs.*

When exposed to increased temperature and/or aerial oxygen a change in the optical properties of the QD samples could be measured. We could observe four different phenomena: a reversible, temperature dependent red-shift and a permanent blue-shift after long-time heat treatment at a constant temperature of 120°C for both opened and closed samples. The third observation was an intensity degradation above 130°C for closed samples and 80°C for open samples exposed to air. Finally a partially reversible and temperature dependent intensity degradation was monitored. First indicators for this behavior were observed when the samples were measured simultaneously to the heating and cooling procedure. With increasing temperature the intensity decreased and the peak wavelength shifted from 617nm at 20°C to 634 nm at 180°C. During the cooling down periodthe intensity increased again but did not return exactly to its original value. Also the peak wavelength shifted back and finally settled at a slightly lower wavelength than the initial one. Both intensity degradation and blue shift accumulated with each cycle until they reached a stable value. Detailed measurements where the samples were periodically heated, cooled and measured showed distinct values for degradation and wavelength shift. The temperature cycles started at 50°C and were continued in 10°C steps up to 210°C. Dwell times for these treatments with the sealed samples were 1 hour and 10 hours respectively. Figure 2 shows an inflection point for the intensity degradation at 160°C. The 10h sample shown in figure 3 had the inflection point for degradation at 130°C.

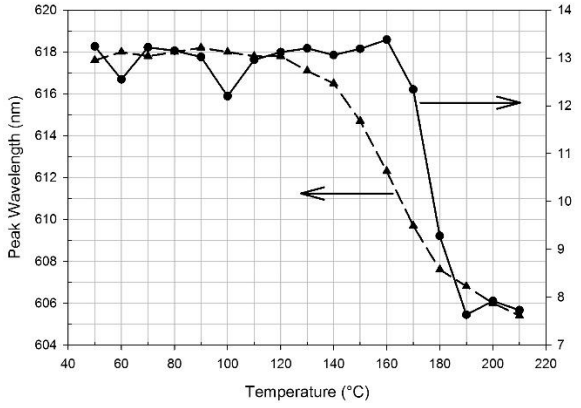

Fig. 2: *QD sample with 1h dwell time.*

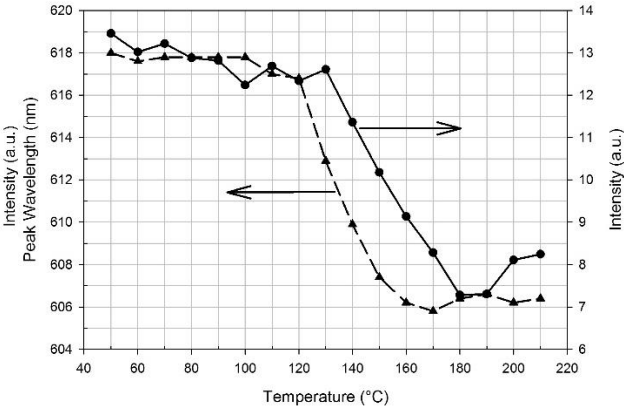

Fig. 3: *QD sample with 10h dwell time.*

The degradation shows a cross link between time and temperature dependence. The observed decrease can yet not be assigned solely to damaged quantum dots as they are embedded in a matrix and covered by a sealant. Depending on the temperature behavior of these two materials the overall optical properties of the sample could change. Darkeningof the resin for example would reduce the amount of excitation light impinging onto the dots and also absorb emitted light resulting in reduced photoluminescence (PL) intensity. Diffusion of oxygen or formation of chemical decomposition substances in the hot resin matrix could also cause degradation or color shift. In order to investigate the influence of oxygen we opened a QD sample disc before heat treatment.

The opened sample (quantum dot layer was exposed to air from all sides) was heated for 30 minutes again in 10°C steps starting from 50°C. Significant intensity losses were measured compared to a sealed sample undergoing four treatments at 180°C for also 30 minutes (see figure 4).

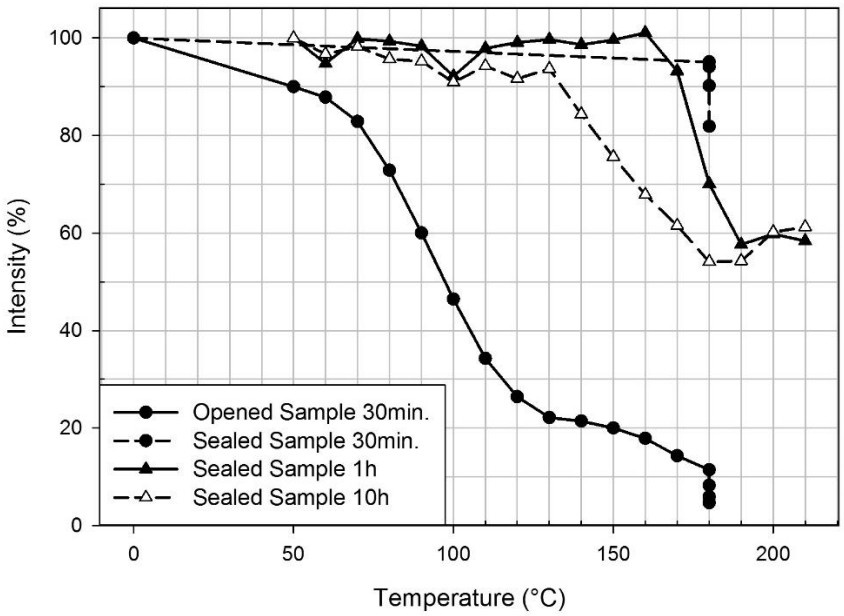

Fig.4: *Intensity decline of opened and sealed samples.*

While the opened sample was damaged already at 80°C the sealed samples degraded to approx. 60% of their initial PL intensity at 210°C. Different oxygen diffusion conditions show correlating intensity degradation at equal exposure times. The additional information from the 1h and 10hsamples with equal diffusion conditions leads to the conclusion that the PL deterioration is caused by two factors, namely the time of heat exposure and the presence of air. This shows that the dominant reason for degradation is oxidation. If we take in account the results from closed and opened samples we conclude that the diffusion speed of oxygen determines dominantly the degradation time at a given temperature. At a given diffusion rate samples with higher QD concentrations should have a longer lifetime with respect to samples with a lower concentration. This assumption could be verified by the measurement results of samples with three different concentrations. Possible chemical decomposition products e.g. hydrogen cyanide could have much easier evaporated from opened samples than from closed ones. In case the shift is related to these byproducts the opened sample should have shown less blue shift or it should have started at higher temperatures. However, we found that the trigger temperature for a blue shift is 120°C for opened and closed samples.

In contrast to the intensity degradation the peak wavelength shift of the heat treated samples showed no time but temperature dependency. In figures 2 and 3 can be seen that the permanent blue shift always occurs at temperatures >120°C. This also includes exposed QD

samplesand therefore discards oxygen and possible oxidation causing a reduction of the active diameter of the QDs as the reason of the shift. Similar to the PL intensity drop, different QD concentrations exhibit different wavelength shifts where the highest concentration showed the least shift.It is known that electronic coupling of quantum dots influences their optical properties [4,5]. The formation of closely packed quantum dot arrays (artificial molecules) during the sample preparation can cause an emission wavelength shift towards the red. It is supposable that these artificial molecules undergo a structural partitioning when they are heated. The previously generated quantum dot arrays are split up again which results in a shift towards shorter wavelengths. The measured shift differences within the concentrations can be attributed to the number of dots and array layers contributing to an artificial molecule. With higher concentrations the decomposition of the structure does not result in such spatially separated smaller fragments as it would with lower concentrations. Hence the blue-shift is not that distinct.

4. Conclusion

In an experimental setup of a white-light-LED it was demonstrated that QDs in principle are able to efficiently convert the blue excitation light and confine the fluorescent contents to the visible wavelength area. This way the color rendering ability as well as the luminous flux can be improved. The light source therefore emits brighter light with a better light quality. On the other hand the QDs showed complex degradation behavior which is very different from that of conventional phosphors. Aging of such a mixed phosphor/QD conversion material on a long time scale will show a noticeable change in the spectral properties of the light source. These drawbacks are strongly determined by the processing method and the used matrix material. In order to compete with traditional phosphors further research concerning the chemical interaction of the QDs with their environment has to be conducted.

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