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Evaluation of the doctoral thesis by Michael Greben

The doctoral thesis entitled "Advanced spectroscopic characterization of quantum dot ensembles" by Michael Greben contains a ~100 page summary and 10 appended papers. The papers have been published in various physics journals (one paper still in "submitted" status) such as Appl. Phys. Letters (2), J. of Appl. Phys. (3) and one each in AIP Advances, Rev. of Sci. Instrum. and finally the Beilstein J. of Nanotech. All of these are highly reputed journals with impact factors in the range 1.5 to 3.5. Michael Greben is first author on 6 of these papers, indicative of a substantial contribution to the research presented. He lists also ~10 conference and summer school contributions and in addition 8 other publications which do not form the basis for the thesis.

The theme of the thesis is experimental studies and analysis of quantum dots (QD), in particular "direct bandgap" PbS quantum dots (1 paper) and "indirect" type silicon quantum dots (9 papers). The techniques used are photoluminescence (PL) spectroscopy and time-resolved PL also complemented by photo-thermal deflection spectroscopy (PDS). In addition, quantum yield measurements have been performed using an in-house integrating sphere.

The analyzed samples have been fabricated in labs of collaborating groups and in one case obtained by purchasing PbS quantum dot solutions. For the Si QD experiments colloidal Si nanocrystal solutions were obtained by collaborating with the group of Xiadong Pi in China while samples with single or multi-layers of Si QDs embedded within an oxide matrix were fabricated by the group of Margit Zacharias at Freiburg university. Thus, M. Greben had limited control of the sample fabrication. On the other hand, the group were performing the major experimental analysis and the mathematical treatment of the data presented in the papers. It is not clear to me the exact contribution of M. Greben within the group but judging from his presentation in the summary my feeling is that he performed some part of the experiments but contributed mostly to the mathematical analysis and the physical interpretation of the experimental data.

The thesis is in general nicely written with many illustrative figures and makes an adequate summary of the appended papers (except for paper VIII which is not dealt with). The English is of good command with an easy flow, although I have made some small corrections which can be included. The theme of the thesis is well held together to result in a very focused study going into considerable depth of the selected subject! Thus, I think this is a very good piece of research work and well worth a doctorate title!

<i>Address</i>	<i>Visiting address</i>	<i>Telephone</i>	<i>E-mail/Web</i>
Material Physics, Appl. Phys. Science school, KTH Electrum 229, 164 40 Kista	Isafjordsgatan 22 Plan B4 Kista-Stockholm	Direct +46 8 790 4370 Cellular +46 706 959195	linnros@kth.se http://www.ict.kth.se



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In my analysis of the thesis I have read the summary thoroughly and my detailed comments to the text and the analysis will follow as an appendix to this general evaluation. Here are some main conclusions from the work:

The system of Si QD ensembles (contained in 8 of the 10 papers) that M. Greben has studied is generally very difficult to analyze since samples contain a size dispersion and also many other effects such as a fraction of dark nanocrystals, defects and the possible migration of excitons between nanocrystals. Thus, the system is inherently very complex and many different mechanisms for the PL decays need to be invoked. If special samples could have been fabricated to test only some of the mechanisms excluding others, the conclusions could have been stronger. Thus, in many cases I feel that data are fitted by some arbitrary mathematical function without any physical model behind. This is particularly true for the multi-layered structures fabricated in Freiburg where a size dispersion is present while the nanocrystal-to-nanocrystal distance varies within the layer as well as the distance between layers – a very difficult scenario! Another subject of criticism to the work is the varying absorption cross section with excitation fluence and temperature which is controversial with respect to the commonly accepted model of an excitation cross section only related to the oscillator strength. The question here is whether the data has been treated correctly or whether there can be an error in the estimation of the effective number of nanocrystals for different samples.

Important conclusions from the work are the high QY of colloidal Si samples, the methods for derivation of both internal quantum efficiency yield as well as the overall quantum yield and the two methods of measuring the absorption cross section. Also the mapping of the quantum yield for both single and multilayers combined with passivation studies that finally point to an “optimum size” of Si QDs. These conclusions are all nicely highlighted in the conclusions chapter.

Summarizing, I find the work of M. Greben presented in his doctoral thesis very well performed with an adequate in-depth analysis providing a significant step forward in the understanding of the PL mechanism in Si nanocrystals. This will contribute to the field and has already been communicated in the literature and at conferences. Indeed, M. Greben was also selected, among many other PhD students, for the E-MRS young scientist award in 2016.

Thus, I happily recommend Michael Greben for the title of doctor of philosophy and I really look forward to his dissertation on Mach 15 to discuss his work!


Jan Linnros, Prof.

Address

Material Physics, Appl. Phys.
Science school, KTH
Electrum 229, 164 40 Kista

Visiting address

Isafjordsgatan 22
Plan B4
Kista-Stockholm

Telephone

Direct +46 8 790 4370
Cellular +46 706 959195

E-mail/Web

linnros@kth.se
<http://www.ict.kth.se>

Appendix: Detailed comments to the thesis summary of Michael Greben

P15: Equation 3 and separation of time and spatial dependence only valid for steady state!

P16: Quantum confinement is not a priori associated with the exciton Bohr radius. Indeed, the QC shifted states exist even without exciton and confinement is the same for the case of only an extra electron or hole!

P19: Figure 2.4a shows an excited electron at non-resonant excitation. But cannot the hole left behind also be excited thus sharing the excess energy??

Sec 2.3.2: Free carrier absorption is usually in the infrared range and can be used to probe the instantaneous carrier concentration. Absorption goes as wavelength squared. Here it is not clear whether FCA is meant in the IR range or at the emission wavelength. At emission wavelength the process probability is very small and would be dominated by band-to-band absorption. For optical gain however this loss mechanism is clearly detrimental since the optical mode usually travels long distances.

P26 a) I suggest the following modification for obvious reasons: "... that is linked with the indirect (phonon participation) or quasi-direct (no phonon related – large Δk according to Heisenberg) excitonic radiative...."

P42 Why is a long excitation pulse needed? A short pulse would do the same just that the number of photons per area ensures <1 exciton per nanocrystal absorption.

Sec 4.2.1 I had some troubles understanding this section until I realized that it assumes a certain fixed excitation power as set by the cw PL. In a practical experiment the pump power is usually varied and then excitation pulse can be very short and there is no "optimum" pulse length. This assumption needs to be pointed out.

Sec 4.3 The method for ACS determination described here is of importance for samples where the PL lifetime varies with excitation. This is mostly not the case according to our experience.

Fig 5.6 What is absorption peak? QDs generally have an absorption edge and then absorption increases steadily towards the UV. Are you referring to some kind of exciton peak? Would be good to have an absorption spectrum here showing what you mean by absorption peak (include from paper V, fig 1a)!

Fig 5.7 (a) These very curved decays do not seem to be fit by a bi-exponential function! (b) Are fits bi-exponential as indicated in text above?

Sec 5.1.3.2 The discussion here where the homogenous line broadening is invoked to explain the dispersion in lifetime could easily have been checked by cooling the samples. Then HLB would be significantly reduced and also dispersion in lifetime!

Sec 5.2.2 There must be something wrong in the derivation of eqs. 43 and 46: The Auger recombination cannot lead to a decrease of the PL intensity at increasing excitation, it would saturate at the one exciton per nanocrystal value or possibly increase slightly if bi-exciton recombination is radiative. In paper VII eq 5 indeed a different formula is derived which describes Auger correctly.

P69 One mechanism which could explain the observed behavior is described as a shortening of the radiative lifetime due to heating. Generally the radiative lifetime is considered as

independent of temperature and the lifetime reduction for Si NC and porous Si is usually believed to be an increased non-radiative recombination for increasing T simply because the access to non-radiative channels increases.

Fig 5.17a Why do layers of different thickness have different ACS ? Is it just a scaling problem?

Sec 5.2.6 In the analysis of the internal quantum efficiency ON/OFF blinking, which is well documented for oxide passivated Si NCs, is not considered. In the OFF-state there are obviously no decays so the lifetimes extracted describe the time when it is in ON-state. Thus the IQE refers only to the ON-state while measured QY is also affected by blinking. This should be pointed out here in the text!

Sec 5.2.7 Equation 50 is just an interpretation of the data relying on very few data points and has no physical meaning. Why not instead use the Bosonian phonon statistics yielding a linear increase with T (if I remember correctly)? Thus the exponential decay would instead be a linear function of T and a residual cross section at T=0.

Fig 5.20 Absorption cross section – which wavelength does it refer to?

Sec 5.4 The optimum size is an important observation in this work. The mechanism behind the decreasing IQE and QY at higher energies, an unknown mechanism as stated here, may also be the reason why green and blue emission is so hard to observe for decreasing size of the Si QDs!

Brief comments on the papers

Paper I An absorption cross section which varies with excitation power seems mysterious but apparently needs to be invoked for SRON layers. These are, however, very complicated samples from a modelling perspective. Anyway, the derived absorption curve of Fig 2c where for high excitations the ACS is reduced by up to 2 orders of magnitude seems largely erroneous! Indeed, it is stated that the ACS values are derived from Eq 9 but, Eq 9 seems to have been derived from the more general formula Eq 7 by assuming N_2/N_1 goes to zero for the case of low to moderate excitation powers. That is of course not the case for 100 – 1000 W/cm² excitation! If the Auger term is not considered, the ACS of course is judged as being very low.

Paper II Interesting paper on colloidal Si QDs where it is shown that the internal quantum efficiency reaches up to 100 % at the emission peak. The QY of ~60 % is attributed to dark nanocrystals.

Paper III A paper on the analysis of PL decays demonstrating several different fitting possibilities all yielding similar lifetimes.

I may have more comments later.....

Jan Linnros, 2018-03-05