Quantitative evaluation of boron-induced disorder in multilayers containing silicon nanocrystals in an oxide matrix designed for photovoltaic applications

G. Zatryb,1 A. Podhorodecki,1,7 X. J. Hao,2 J. Misiewicz,1 Y. S. Shen,3 and M. A. Green2

1Institute of Physics, Wroclaw University of Technology, Wybrzeze Wyspianskiego 27, 50-370 Wroclaw, Poland
2ARC Photovoltaics Centre of Excellence, University of New South Wales, Sydney, New South Wales 2052, Australia
3School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales 2052, Australia
*artur.p.podhorodecki@pwr.wroc.pl

Abstract: The effect of doping by boron on optical properties of multilayers containing Si-NCs were studied by means of photoluminescence (PL), time-resolved PL, photoluminescence excitation (PLE), transmission and reflection measurements. It was found that PL decay is strongly non-single exponential and can be described by means of Laplace transform of log-normal decay rates distribution. It was also proposed that changes observed in the distribution central moments reflect the disorder induced by boron-doping.

©2010 Optical Society of America

OCIS codes: (300.6500) Spectroscopy, time-resolved; (160.4236) Nanomaterials; (310.4165) Multilayer design.

References and links

1. Introduction

One of the especially promising examples of silicon nanocrystals (Si-NCs) in an oxide matrix applications is 3rd generation tandem solar cells [1] in which several layers containing Si-NCs with different bandgaps are stacked on top of each other. The multilayer design of the structures, alternating layers of silicon rich oxide (SRO)/SiO$_2$, allows controlling the Si-NCs size more precisely [2]. Moreover, due to quantum-confinement effect, Si-NCs band gap can be tuned to different sun light wavelengths separately in each stacked layers resulting in selective photon absorption and therefore theoretically higher cell efficiency.

In order to produce Si-NCs-based solar cell, it is also necessary to design a p-n junction that works in the multilayer system. One of the solutions is a p-i-n junction, in which the multilayer system is used as active region for enhanced photon absorption placed between p and n regions. Another way to dissociate photo-generated electron-hole pairs is p-(i)-n junction produced in nanoscale by doping Si-NCs itself in the multilayer system. As a first attempt to realize this kind of novel structures, it is necessary to investigate effects of doping of Si-NCs produced in the multilayer architecture. This is essential in order to identify the suitable structure for future device production.

There are also several questions about the impurity doping in low-dimensional structures like Si-NCs. For example, important questions arise as to whether the dopants will continue to play a role similar to that in bulk semiconductors. It is also unclear at present whether the doping of Si-NCs provides the generation of free charge carriers or not. Moreover, the possibility of incorporating impurities into very small Si-NCs remains an important issue. Therefore, any new experimental results that can contribute to answering these questions are valuable.

What is more, doping by different impurities may lead to significant changes of the optical properties of Si-NCs [3]. For instance, due to the disorder introduced to the system by foreign atoms, the carriers relaxation kinetic may be influenced. The effect of disorder may be described in some cases by Kohlrausch stretched-exponential function [4]. However, this kind of solution is not always valid. This work describes another method for quantitative description of non-single exponential behavior of carriers dynamics in the multilayer system containing Si-NCs in an oxide matrix.

2. Experimental details

For the purposes of this work, Si, SiO$_2$ and boron were co-sputtered to create a uniform alternating boron-doped SRO/SiO$_2$ multilayers. The boron was chosen as the most commonly used impurity for p-type Si. Each film consisted of 15 SRO/SiO$_2$ bi-layers. We investigated samples with two different O/Si ratios in the SRO layer. Two kinds of structures with the same O/Si ratio were deposited: undoped (reference) samples and samples doped with boron. The films were deposited by magnetron co-sputtering technique described in more details elsewhere [5]. To form Si-NCs, all samples were annealed 1h at 1100 °C in a nitrogen atmosphere.

The absorption properties were investigated by means of transmission and absorption measurements (with mixed xenon and halogen light sources). Time-resolved photoluminescence spectra were investigated by means of stroboscopic technique with pulsed xenon lamp used as an excitation source and photomultiplier tube used for detection. Structural properties were examined by means of X-ray photoelectron spectroscopy (XPS), glancing incidence X-ray diffraction (GIXRD) and transmission electron microscopy (TEM).

3. Results and discussion

The chemical composition of SRO was determined by XPS. The estimated O/Si ratio of SRO is around 1.0 and 1.3. Boron concentration in doped SRO films, was estimated to be around 0.7 at.%. The Si-NCs crystallization was confirmed by GIXRD (not shown here, it will be detailed elsewhere). The shape of the diffraction patterns with various boron concentration
were almost same for all samples, which suggests that boron concentration had no obvious effects on the crystallization of Si-NCs.

The formation of Si-NCs was also proved by TEM shown in Fig. 1 for the undoped Si-NCs/SiO$_2$ multilayer film with O/Si ratio of SRO around 1.0. Clear multilayer structure is present. Thickness of the Si-NCs and SiO$_2$ layer are 4 and 6 nm, respectively. The inset of Fig. 1 shows a TEM image of the same sample with visible lattice fringes corresponding to individual Si-NC. The average Si-NC size is around 4 nm.

Figure 2 shows PL, absorption and PLE spectra. The broad emission band centered at around 1.5 eV can be observed for all samples. As expected [6], the PL intensity drops strongly after boron doping for samples with O/Si = 1.0 as well as O/Si = 1.3. Additional PL investigations (not shown here, it will be detailed elsewhere) demonstrated that PL peak does not shift with changing Si-NCs size. Various authors have shown [7,8] that defect states localized on the nanocrystal surface may suppress the quantum confinement effect on the emission spectra. Therefore we relate the observed PL to emission centers at the interface between Si-NCs and SiO$_2$ matrix (surface states). In this scenario, carriers are excited inside
the Si-NCs core and then relax nonradiatively to the 1.5 eV emitting state related to the nanocrystal surface.

The presence of defect states was also confirmed by reflection (R) and transmission (T) measurements that were used to calculate absorption spectra according to the following formula $\alpha = -(1/d)\ln(T/(1-R)^2)$, where $d$ stands for sample thickness. First of all, long tails below the absorption edge are clearly visible for all investigated samples in absorption spectrum reaching almost 1.5 eV. What is more, in the case of O/Si = 1.0 samples absorption edge red-shifts after boron doping from 2.6 eV to 2.5 eV. This effect may be related to introduction of new defect states to the matrix after doping. It is worth mentioning that in O/Si = 1.3 samples this red-shift is not clearly present. We relate this effect to lower tendency for creating Si-B bonds in samples with higher oxygen content [5]. In this way introduction of impurity to the nanocrystal surrounding should exert stronger influence on the absorption spectra in case of O/Si = 1.0 samples. This explanation is also confirmed by the fact that the defect-related band is a bit stronger for lower oxygen content samples.

The absorption spectra reflect both matrix and Si-NCs properties at the same time. Contrary to this, PLE experiment probes only a particular emitting object. However, in the investigated case the 1.5 eV state is populated indirectly, i.e. excited carriers absorbed in the Si-NCs core relax nonradiatively to this emitting state related to the Si-NCs surface, and therefore PLE recorded at 1.5 eV reflects the absorption properties of Si-NCs. This PLE is shown in the inset to Fig. 2. Beside intensities, it can be seen that the shape of PLE remains the same for all samples. This proves that boron-doping does not influence Si-NCs as such, but rather their environment. It should be also noted here that in the investigated case the shape of PLE spectra measured for emission band centered at 1.5 eV does not depend on the detection energy.

![Photoluminescence decays for samples with (a) O/Si = 1 and (b) O/Si = 1.3. In both plots undoped and doped by boron samples are shown. The decay profiles were measured for emission band at 1.5 eV. Excitation wavelength was set to 350 nm.](image)

Fig. 3. Photoluminescence decays for samples with (a) O/Si = 1 and (b) O/Si = 1.3. In both plots undoped and doped by boron samples are shown. The decay profiles were measured for emission band at 1.5 eV. Excitation wavelength was set to 350 nm.

The kinetic of the carriers relaxation inside Si-NCs may be described by time-dependence of the fraction of the excited emitters $n(t)/n(0)$. Time-resolved PL measurements provide important information about relaxation behavior because PL decay is a negative time
derivative of the \( n(t)/n(0) \) function. Thus, to investigate the influence of defect states formation on carriers relaxation kinetic, we have measured PL decays at 1.5 eV. As a result, strongly non-single exponential decay curves were obtained, which is shown in Fig. 3. To analyze this kind of behavior for Si-NCs, Kohlrausch stretched-exponential function is frequently used. This kind of approach assumes recombination rates distribution [9] and is therefore applicable for systems characterized by strong disorder where we deal with many defect states or emitter size distribution. However, in the investigated case the stretched-exponential function did not satisfactorily fit the data. Thus, to model the obtained non-single exponential PL decays, we applied equation of the following form [10]:

\[
PL(t) = \int_{0}^{\infty} g(k) \exp(-kt) dk
\]  

This equation is the Laplace transform of non-negative function \( g(k) \). In most cases (e.g. in the absence of rise-time), the function \( g(k) \) can be understood as a distribution of decay rate constants (strictly, a probability density function). The condition \( PL(0) = 1 \) yields correct normalization of \( g(k) \).

Based on fit quality, we have found that for all investigated samples the best results were obtained with log-normal decay rates distribution:

\[
g(k) = A \exp \left[- \frac{(\ln k - \ln k_{mf})^2}{\gamma} \right]
\]  

where \( A \) is the normalization constant, \( \gamma \) is related to the width of the distribution and \( k_{mf} \) is the most frequent rate constant. While fit quality does not prove that the particular distribution is unique, it does provide important physical information about ensemble of emission centers and their environment.

First of all, we found that the most frequent life-time constant (defined as \( \tau_{mf} = 1/k_{mf} \)) decreases from 197 \( \mu \)s to 170 \( \mu \)s and from 196 \( \mu \)s to 186 \( \mu \)s after doping by boron for O/Si = 1.0 and O/Si = 1.3, respectively. Secondly, as shown in Fig. 4, the distributions of decay rates are very broad with long tails directed towards shorter lifetimes, which demonstrates the
strongly non-single exponential character of the decay curves. The width of the distribution at 1/e significantly increases after boron-doping from 6.53 ms$^{-1}$ to 13.67 ms$^{-1}$ and from 4.63 ms$^{-1}$ to 8.07 ms$^{-1}$ for samples with O/Si = 1.0 and O/Si = 1.3, respectively. Moreover, skewness (the third distribution central moment), which indicates distribution asymmetry, increases from 1.44 ms$^{-1}$ to 2.90 ms$^{-1}$ and from 0.98 ms$^{-1}$ to 1.71 ms$^{-1}$ for samples with O/Si = 1.0 and O/Si = 1.3, respectively. This means that after doping by boron, the tails in the distribution have significantly increased their length. It should be also noted that the increase of distribution width and skewness was more explicit in the case of samples with lower oxygen content. Above we demonstrated a similar effect of O/Si ratio on absorption spectra and therefore the explanation of this effect should be the same.

To explain all the observed features, it should be first mentioned that the obtained distributions provide information about both the radiative and nonradiative relaxation rates [11]. However, very low quantum efficiency of Si-NCs emission suggests that nonradiative processes should be predominant. This allows us to relate changes observed in decay rate distributions to introduction of more defect states to the matrix containing Si-NCs after doping samples by boron. In this way, some new nonradiative recombination sites appear, which results in the most frequent life-time shortening and PL intensity drop after boron-doping. Since boron addition introduces more defect states to the matrix, which then act as new possible recombination paths for the excited carriers, the distribution width and skewness significantly increases after doping, resulting in strongly non-single exponential decay curves. It is noteworthy that this kind of interpretation is similar as in the case of stretched-exponential function, where the shape of decay rates distribution [8] also reflects the disorder in the system.

4. Conclusions

To sum up, we have shown that photoluminescence decay of Si-NCs in SRO/SiO$_2$ multilayers doped by boron atoms is strongly non-single exponential and can be described by means of decay rates distribution. It has been also demonstrated that in the investigated case the broad decay rates distribution was defects-related. Doping the multilayers with boron atoms resulted in significant broadening of decay rates distributions and shortening of the most frequent life-time constant. This is most probably due to the introduction of some new nonradiative recombination sites in the Si-NCs environment, which favor faster decay of the fraction of excited carriers.

Moreover, it has been proposed how the disorder in the multilayer system containing Si-NCs in an oxide matrix may be evaluated quantitatively by means of distribution central moments. It has been also shown that log-normal rates distribution may be applied in cases when Kohlrausch response function cannot be used.

Acknowledgments

The authors (G. Z. and A. P.) acknowledge financial support from fellowship co-financed by European Union within European Social Fund. The authors (X. H. and M. G.) acknowledge the Photovoltaics Centre of Excellence supported by the Australian Research Council.