

EarlyView publication on wileyonlinelibrary.com (issue and page numbers not yet assigned; ONLINE LIBRARY citable using Digital Object Identifier – DOI)

Phys. Status Solidi A, 1-7 (2012) / DOI 10.1002/pssa.201100815



## Excitation effects and luminescence stability in porous SiO<sub>2</sub>:C layers

Andriy Vasin<sup>\*,1</sup>, Andriy Rusavsky<sup>1</sup>, Alexei Nazarov<sup>1</sup>, Vladimir Lysenko<sup>1</sup>, Galyna Rudko<sup>1</sup>, Yurii Piryatinski<sup>2</sup>, Ivan Blonsky<sup>2</sup>, Jarno Salonen<sup>3</sup>, Ermei Makila<sup>3</sup>, and Sergii Starik<sup>4</sup>

<sup>1</sup>Lashkaryov Institute of Semiconductor Physics, pr. Nauki 41, 03028 Kiev, Ukraine

<sup>2</sup>Institute of Physics, pr. Nauki 46, 03028 Kiev, Ukraine

<sup>3</sup>Department of Physics, University of Turku, 20014 Turku, Finland

<sup>4</sup>Bakul Institute of Superhard Materials, Avtzavodskaya 2, 04074 Kiev, Ukraine

Received 27 December 2011, revised 14 February 2012, accepted 15 February 2012 Published online 6 April 2012

Keywords carbon incorporated silicon oxide, white luminescence

\* Corresponding author: e-mail andriv.vasin@gmail.com, Phone: +38 044 5256395, Fax: +38 044 5256177

White-light emitting porous SiO<sub>2</sub>:C layers on silicon wafers have been fabricated by oxidation of carbonized porous silicon. The study was focused mainly on the identification of the mechanism of light emission and photo-induced degradation. The effect of carbonization temperature and exposure to intense ultraviolet irradiation on the photoluminescence (PL) properties was studied by steady state and time-resolved PL measurements. Two types of photo-induced degradation

phenomena were observed: reversible and irreversible. The irreversible degradation is suggested to be associated with photo-induced chemical interaction of light emitting material with atmospheric oxygen. It is demonstrated that irreversible degradation can be reduced by encapsulation of the lightemitting material. The structural configuration of light-emitting centers and mechanism of reversible degradation are discussed.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

**1** Introduction Light emitting materials are of great importance in modern optoelectronics, lighting, and light indication technologies. In the field of lighting applications, the development of white-light emitting materials with high luminous efficiency and good color properties attracts a great interest. At present such materials (phosphors) are used in luminescent lamps and light emitting diodes for converting of ultraviolet (UV) irradiation into visible white light. Currently, all commercially available white light emitting phosphors contain heavy metals including transition and rare-earth metals. Hence, the development of new white light emitting materials free of expensive and toxic heavy metals is an important task.

During last decade, two alternatives to the phosphors based on metal activators were suggested and studied: (1) organic materials and (2) semiconductor nanoparticles. Despite the optimistic progress in the efficiency of organic white-light sources, the stability and long-term reliability issues of organic materials are still to be solved. On the other hand, semiconductor quantum dots (ODs) have attracted interest due to their high luminescence efficiency and sizetunable band-gap characteristics [1]. However, QDs exhibit relatively narrow emission band, so the color-rendering index (CRI) of these white light sources is low.

The general approach to obtaining white color with high CRI is a combination of materials with complementary spectral characteristics. However, single material phosphor converting blue-and/or-UV into white light with high CRI is more desirable because application of multicolor phosphors reduces the light emission efficiency. Moreover, the emission spectrum of such multicomponent phosphors usually changes with operation time due to different degradation properties of different phosphor components.

Recently, a new class of white-light emitting Si:O:C composite materials free of heavy metals was found. The material can be synthesized in form of sol-gel-derived SiOC thin films [2], a-SiO(x)C(y):H thin films deposited by thermal chemical vapor deposition (CVD) [3], a-SiO(x)-C(y): H thin films synthesized by low temperature oxidation of carbon-rich a-Si(x)C(y):H thin films [4], porous layers por-SiO<sub>2</sub>:C on silicon wafer [5, 6], or mesoporous nanopowders [7]. Emission spectrum of these materials covers the whole visible range and is very similar to that of the scattered sun radiation (natural day light).



In our previous work, it was demonstrated that photoluminescence (PL) band of por-SiO<sub>2</sub>:C layers is composed of at least two bands, namely the blue band with maximum intensity at about 400 nm and white-green band with maximum at about 500–540 nm [6]. It was shown that the white-green band is related to the presence of carbon whereas the blue shoulder most likely originates from defects in the surrounding SiO<sub>2</sub> matrix [8]. Present report is a logical continuation of the previous studies to understand light emission mechanisms in carbon-incorporated silicon oxide.

**2** Experiment Porous silicon precursors (por-Si) were fabricated by anodizing p<sup>+</sup>-type Si(100) wafers (0.015–0.025  $\Omega$  cm) in a hydrogen fluoride (40%):ethanol mixture 1:1. The por-Si samples were carbonized in N<sub>2</sub> (1.5 l min<sup>-1</sup>)/C<sub>2</sub>H<sub>2</sub> (1 l min<sup>-1</sup>) flow at 850, 950, and 1050 °C resulting in the formation of carbonized porous silicon (por-Si:C). The next sample preparation step was the thermal treatment at atmospheric pressure in moisturized argon (Ar/H<sub>2</sub>O) flow at 600 °C for 2 h resulting in the formation of light emitting carbon-incorporated porous silicon oxide (por-SiO<sub>2</sub>) layer. Hereafter, we have labeled the samples fabricated at different carbonization temperatures as PS850, PS950, and PS1050, respectively (see Table 1).

PL measurements were carried out using nitrogen laser  $(\lambda_e = 337.1 \text{ nm}, \text{ pulse duration } t_e = 9 \text{ ns}, \text{ pulse repetition}$ frequency  $f = 80 \,\text{Hz}$ ) for excitation. Time-resolved PL measurements were performed using stroboscopic registration system allowing PL registration with given delay times (hereafter "pulse regime"). We used the delay time about 0.7 ns and strobe window 0.1 ns for measuring PL spectra in the "pulse regime". The spectral slit width for measuring PL spectra was 0.2–0.4 nm. Obviously, contribution of light emission centers with longer radiative decay in PL spectrum is reduced when measuring in "pulseregime". It means that if the spectrum is composed of several components originating from recombination centers with different decay times it is possible to evaluate the relative contribution of these centers by comparing spectra measured in steady-state and "pulse regime".

Interatomic bonding structure of the layers was examined by Raman scattering (RS, excitation by 514 nm Ar laser radiation) and Fourier-transform infrared reflection spectroscopy (FTIR).

## 3 Results and discussion

**3.1 Raman scattering and FTIR** RS spectra of ascarbonized samples are presented in Fig. 1. Carbonization at

 Table 1
 Labeling of the samples.

carbonization temperature (°C)	por-Si:C	por-SiO <sub>2</sub> :C
850	PS850	PSO850
950	PS950	PSO950
1050	PS1050	PSO1050



Figure 1 Raman scattering spectra of por-Si:C layers: PS850; PS950, and PS1050.

850 °C resulted in the appearance of very weak carbon related RS band in the range of  $1000-1800 \,\mathrm{cm}^{-1}$  (bottom spectrum in Fig. 1). This band originates from sp<sup>2</sup>-coordinated carbon clusters. Intensity of carbon-related RS band increased strongly with increasing of carbonization temperature up to 950 and 1050 °C (Fig. 1, upper spectra). In these cases, RS band is composed by well-defined D-and G-bands inherent to graphite-like carbon structures. Integrated intensities of RS bands in PS950 and PS1050 are almost equal but the values of full width at half maximum of D- and G-bands are smaller in PS1050 indicating more ordered graphite-like structure in carbon clusters.

Samples of PS850 series were annealed in pure argon, humid argon, or dry oxygen flow for 30 min after carbonization. Integrated intensity of carbon RS band increased by several times after the annealing in pure and humid argon while no carbon related RS band was detected after the annealing in oxygen (Fig. 2). The main conclusion derived from these observations is that large fraction of carbon material in the porous layer after carbonization procedure exists in Raman inactive form.



**Figure 2** Intensities of RS bands in the samples of PS850 series: as-fabricated and thermally treated in dry argon, wet argon or dry oxygen at 600 °C for 30 min.

Presumably, carbon is incorporated in the form of few atoms clusters that cannot be "seen" by RS.

During the thermal treatment in dry or humid argon migration and coalescence of carbon precipitates take place resulting in formation of large sp<sup>2</sup>-coordinated clusters detectable by RS spectroscopy. Annealing in oxygen results in oxidation of carbon and its escape in the form of volatile mono- and/or carbon oxide.

Unfortunately, identification of carbon clusters in light emitting PSO series by RS spectra cannot be done because Raman signal (at 514 nm excitation) is masked by strong luminescence background in visible spectral range.

*FTIR*: due to the high conductivity of the Si substrate, the transmission FTIR measurements were not possible. Therefore, we used the reflection measurements. Despite strong interference features modulating FTIR spectra some useful information can be derived. First, no C–H bonds were detected in as-carbonized series (Fig. 3, spectrum 1). It means that during the carbonization procedure, carbon is deposited inside porous layer in an unhydrogenated form. Second, weak but well detectable Si–C related band is observed at  $800 \,\mathrm{cm}^{-1}$  accompanied by Si–O band at  $1060 \,\mathrm{cm}^{-1}$  (Fig. 3, spectra 2, 3, 4). The intensity of Si–C related band increases with increasing of carbonization temperature.

The presence of thin SiC surface layer allows to explain why carbon related RS band observed after short annealing in wet argon is significantly stronger than that measured after the annealing in dry argon (see middle bars in Fig. 2). Water vapor does not oxidize carbon at such temperature therefore it is reasonable to suggest that carbon atoms that are released after oxidation of SiC surface layer afterwards participate in the formation of carbon clusters that are active in Raman scattering.

Si–C band disappeared after oxidation and strong Si–O related bands appeared at  $826\,\mathrm{cm}^{-1}$  (symmetrical stretch-



**Figure 3** (online color at: www.pss-a.com) FTIR reflection spectra of por-Si (1), PS850 (2), PS950 (3), and PS1050 (4). Spectra are shifted in vertical direction for better visualization.



**Figure 4** (online color at: www.pss-a.com) FTIR reflection spectra of PSO850(1), PSO950(2), and PSO1050(3). The spectra are shifted in vertical direction. Inset illustrates  $C-H_n$  related bands.

ing),  $1110 \text{ cm}^{-1}$  (asymmetrical stretching TO mode) and  $1277 \text{ cm}^{-1}$  (asymmetrical stretching LO mode) [9].

Formation of C–H<sub>n</sub> bonds is identified by IR band at  $2800-3000 \text{ cm}^{-1}$  (see Fig. 4).

3.2 Interference of PL inside por-SiO<sub>2</sub>:C layer PL spectra of por-SiO<sub>2</sub>:C is very broad and covers the spectral range from near UV to near IR (350 to 800 nm). The spectra of the layers with the thickness of about 1–4  $\mu$ m often exhibit pronounced regular features. The number and width of these features vary from sample to sample-making analysis and interpretation of the spectra complicated. Distance between peaks is smaller in red spectral region in comparison with that in blue region. These observations allowed us to suggest that these peaks originate from the interference inside por-SiO<sub>2</sub>:C layer. To check this idea, the sample with well-defined regular features in PL spectrum was selected, and the spectra were measured at different angles between optical axis of the monochromator and surface plane of the sample (Fig. 5). One can clearly see that positions of the peaks are shifted with the change of the angle and the peak shift is larger in the long wave spectral region. This observation unambiguously identifies regular features as the interference effects.

Similar interference effect was observed in PL spectra of a-SiOC:H films [4] justifying the general character of such artifact for measurements of broad visible PL band in thin layers. The effect of interference on PL spectra is very complicated and depends on the excitation wavelength, spectral dependence of absorption and refraction coefficients of the layer in UV–VIS range, geometry of optical system, distribution of the density of light-emitting sites in depth etc. We would like to emphasize that the analysis of the spectral properties of broad PL generated in thin layers should be performed very carefully to avoid possible misinterpretations.

3





**Figure 5** Typical PL spectrum measured at different angle between optic axis of monochromator and surface plane of the sample:  $(1)20^{\circ}$ ;  $(2) 30^{\circ}$ ;  $(3) 50^{\circ}$ .

**3.3 Correlation of carbonization temperature and spectral properties of PL** As it was demonstrated in Ref. [6] the broad PL spectrum of por-SiO<sub>2</sub>:C layers is composed of two bands: (1) the broad band with maximum PL intensity at 500–540 nm, and (2) relatively narrow blue shoulder, with maximum intensity at about 400 nm. It was suggested that the broad band is associated with carbonized surface, while the blue shoulder is presumably originating from point defects in porous silicon oxide matrix [8]. In the present study, we carried out more detailed study of correlations between carbonization temperature and relative contribution of these two bands.

PL spectra of the samples PSO850, PSO950, and PSO1050 measured in steady state and "pulse regimes" are presented in Fig. 6a and b, respectively. It is clearly seen that relative contribution of the blue shoulder in steady state spectra is increasing with decreasing of carbonization temperature (Fig. 6a) so that color of the PL changes from orange in PSO1050 to white in PSO850. In "pulse regime" measurements, the blue shoulder was strongly reduced indicating the decay time of the blue band is significantly longer than that of the carbon-related band. Elimination of the blue shoulder by applying "pulse regime" demonstrates that carbon-related band is shifted gradually to shorter wavelength with the decrease of the carbonization temperature (Fig. 6b).

**3.4 Photo induced PL degradation** Another aim of the present research is examination of PL stability in por-SiO<sub>2</sub>:C material under intense UV radiation. UV radiation of Xe lamp was used as a UV source. We observed that the exposure of the samples to UV radiation of Xe lamp for 20 min resulted in the decrease of PL intensity by about 50% (Fig. 7a).



**Figure 6** PL spectra of the samples carbonized at different temperatures and measured in steady state (a) and "pulse" (b) regimes: (1) PSO850; (2) PSO950; (3) PSO1050.



**Figure 7** PL spectra of uncoated (a) and a-SiC coated (b) por-SiO<sub>2</sub>:C samples before (spectrum 1) and after (spectrum 2) 20 min exposure to Xe-lamp.

As it was shown in Ref.[8], annealing in oxygen atmosphere at the temperature as low as 600 °C for 30 min leads to strong reduction of carbon related PL band. Such quenching correlated with drastic decrease of carbon content in por-SiO<sub>2</sub>:C layer. This observation gives a reasonable suggestion that emitting sites are associated with carbon that is removed from porous layer by atmospheric oxygen. It is logical to suppose that rapid and strong photo-induced degradation results from photo-induced oxidation of carbon by atmospheric oxygen. To check this idea, some samples have been coated with 100 nm thick amorphous SiC thin film deposited by magnetron sputtering to protect light emitting layer from direct contact with air. SiC film is thick enough to reduce the effect of atmospheric oxygen and, on the other hand, it is sufficiently thin to avoid strong absorption of UV excitation and visible emission light. The substrate temperature during deposition process was as low as 200 °C to avoid structural changes in por-SiO<sub>2</sub>:C.

Such encapsulation by SiC reduced the degradation effect significantly (Fig. 7b). Some residual degradation can be attributed to incomplete protection due to the presence of micro defects in a-SiC film as well as to the diffusion of oxygen molecules through nanovoids in amorphous SiC network. This observation is the additional evidence of carbon-related origin of the broad PL band. However, the structure of carbon-related light-emitting sites is still an open question.

**3.5 Reversible degradation** To analyze photoinduced PL degradation under intense UV radiation in more details we have performed the study of time dependent PL evolution under cyclic Xe lamp radiation (on/off cycles). PL amplitude at 500 nm emission wavelength was measured as a function of time (Fig. 8a). One can see that the degradation rate in unprotected material is faster. In addition to gradual PL quenching step-like features can be seen at the moments of Xe lamp switching on/off. After Xe lamp was switched on, the intensity immediately dropped step-like for several percent followed by continuous monotonic reduction. After the lamp was switched off, the PL amplitude raised step-like.

At first sight the drop of the light emission intensity with increasing of the intensity of excitation radiation looks quite surprising. Additional UV radiation of Xe lamp obviously results in the increase of *total* emission intensity (well seen by eye) but in "pulse regime" the light detection system is synchronized with laser pulses so that only *pulsed PL* is detected. It means that intensity of *pulsed component of PL* decreased. It can be attributed to reduction of quantum efficiency of the PL under intense UV radiation and this reduction is reversible.

Typical evolution of PL amplitude within a single "on/ off" cycle in SiC coated sample is illustrated in Fig. 8b. One can see that under laser radiation PL intensity is almost constant, but when Xe lamp was switched on the emission intensity droped fast. Continuous exponential reduction of PL intensity during the "on" cycle can now be attributed to irreversible degradation associated with photo-stimulated 5



Figure 8 (a) Evolution of PL amplitude at 500 nm under continuous  $N_2$  laser and cyclic on/off Xe-lamp irradiation; (b) typical PL evolution within single cycle of Xe-lamp irradiation.

interaction of carbon with atmospheric oxygen. Height of the step in "on" and "off" edge is approximately the same indicating full recovery of PL efficiency.

**3.6 Discussion of local structure in por-SiO<sub>2</sub>:C** Let us focus now on the discussion of possible origin of carbon-related emission band in por-SiO<sub>2</sub>:C layers. We will analyze possible structural configuration that could be responsible for the broadband light emission in carbon incorporated silicon oxide. Hereafter we will confine our discussion to carbon related structural configurations.

During the carbonization treatment of porous silicon precursor acetylene molecules interact with hydrogenterminated silicon surface resulting in the formation of the  $SiC_n$  surface layer:

$$Si: Si - H_n + C_2H_2 \rightarrow Si: Si - C_m + H_2^{\uparrow}$$

The presence of Si–C layer in por-Si:C is proved by the presence of corresponding band at about 800 cm<sup>-1</sup> in FTIR spectra (see Fig. 3). Depending on carbonization time and temperature the carbonized (or carbidized) surface of pore walls could consist of (i) monolayer of carbon covalently bonded to silicon, (ii) carbon-rich SiC<sub>n</sub> surface layer containing few Si–C surface layers with attached multi-



atomic carbon clusters or (iii)  $SiC_n$  layer covered by continuous amorphous carbon layer a-C.

During the wet oxidation treatment, water molecules react with silicon but do not oxidize carbon material. As a result, porous silicon oxide layer is formed and surfacebonding reconstruction of carbonized surface occurs. Appearance of C–H<sub>n</sub> stretching band at 2800–3000 cm<sup>-1</sup> in FTIR spectra indicates formation of C–H<sub>n</sub> bonds after oxidation step (Fig. 4). It means that some of hydrogen atoms released after water molecule decomposition reacts with carbon dangling bonds.

There are two possible bonding "bridges" between silicon oxide matrix and carbonized surface:

$$Si: Si - C_n + H_2O \rightarrow SiO_x: Si - O - C_n - H_m$$

$$Si: Si - C_n + H_2O \rightarrow SiO_x: Si - C_n - H_m$$

In Ref. [8], the traces of Si–C bonds in por-SiO<sub>2</sub>:C were observed by EELS spectroscopy. But in the present study FTIR spectra of por-SiO<sub>2</sub>:C do not contain any detectable signs of Si–C.

Oxidation of porous silicon leads to a strong increase of the volume of the material and to the decrease of the volume of pores. Some very small pores can even totally collapse. Under these circumstances the interaction of carbon clusters with silicon oxide matrix increases. Some of the clusters can be trapped and encapsulated in nanovoids.

Briefly summarizing, we suggest that three carbonrelated structural configurations that possibly exist in porous SiO<sub>2</sub>:C layer can be responsible for carbon-related light emission band: carbon clusters, Si–O–C and Si–C bonds.

**3.7 Overview** SiO(x):C(y) compounds that exhibited broad visible PL can be divided into three general groups: (1) carbon implanted silicon oxide layers; (2) silicon oxycarbide thin films and (3) nanostructured composites.

(1) In Ref. [10, 11], it was suggested that PL of carbon implanted silicon oxide in blue-yellow range can be associated with the formation of carbon-related clusters in form of graphitic or SiC clusters. However in Refs. [12, 13], light emitting SiO<sub>2</sub>:C layers were fabricated by similar ion implantation method but no Si–C related bands in FTIR spectra were detected that makes SiC formation an unlikely assumption. They also argued that Si–C formation is energetically unfavorable.

(2) Broad visible light emission band was observed in hydrogenated and non-hydrogenated SiO(x)C(y) layers: thin films deposited by thermal CVD technique [3], atmospheric pressure microplasma jet [14], sol–gel-derived layers [2] or magnetron sputtering [15].

Amorphous hydrogenated oxycarbide thin films a-SiCO:H are intensively investigated as a material for low-k barrier dielectric for Cu-based multilevel interconnection in ultralarge-scale integrated circuits. Despite huge number of reports on optical, electrical, and chemical properties of this material there are only few publications reporting strong white PL. This may be an indication that effective luminescence is not inherent to hydrogenated silicon oxycarbide.

Structure of an "ideal" a-SiCO:H material is represented by amorphous  $SiO_x$  network terminated by  $-CH_3$  or -OHgroups with possible substitution of Si–O–Si bridges by  $-CH_2$ - crosslinking [16]. Such "ideal" structure contains no "defects" like homonuclear Si–Si and C–C bonds or Si–O–C bridges, but real materials contain variety of structural "defects". It is logical to suggest that the reported light emission of silicon oxycarbide films results from structural fluctuations associated with the "defects".

The authors of Ref. [3] have found correlation of PL intensity and position of the 437 cm<sup>-1</sup> IR absorption band in a-SiO(x)C(y):H films deposited by CVD method. This band is associated with bending (rocking) vibrations of Si–O–Si bridges, and in thermally grown dense silicon oxide layers this band is located at 457 cm<sup>-1</sup> [10]. Small shift of this band in CVD a-SiO(x)C(y):H films was ascribed to the presence of Si–O–C bonds. Based on the correlation of the IR band intensity and PL intensity, it was concluded that light emission originates from localized electron states associated with Si–O–C bonds. Unfortunately, no clear proof of this interpretation has been presented. In fact, shift of the vibration frequency can be caused by several factors, such as mechanical stresses, local Si–O–Si bonding distortions etc.

In Ref. [14], white luminescence of a-SiOC:H films deposited by atmospheric pressure microplasma jet was ascribed to neutral oxygen vacancy (NOV) defects in SiO<sub>x</sub> matrix. This interpretation was based on the PL intensity and hysteresis of C–V characteristics associated with trapped positive space charges. Authors assumed that all positive charges in a-SiOC:H/Si heterostructure are trapped by bulk NOV defects. They excluded from consideration a large number of other bulk and interface defects that are also able to trap positive charge and, thus, to contribute to C–V hysteresis.

Strong white light emission observed in sol-gel-derived SiOC layers [2] was ascribed to the combination of emission bands associated with Si, SiC, and C related precipitates. To support their interpretation the authors referred to Ref. [11] but no detailed argumentation has been presented.

Broadband light emission was observed in carbon incorporated silicon oxide thin films deposited by RFmagnetron sputtering [15]. Maximum intensity of PL band was observed to be shifted from about 2.1 to 2.3 eV with decreasing of carbon incorporation. It was suggested that PL is originating from carbon clusters.

(3) Here, we will discuss another possible origin of light emission in SiOC compound, i.e., radiative recombination in carbon nanoparticles. In fact, the first report on luminescent properties of individual carbon nanoparticles was published in 2006 [17]. Thereafter, chemists have discovered and

or

developed several methods of fabrication of light emitting nanoparticles, so called "carbon nanodots" (reviewed in Ref. [18]). It was shown that carbon particles with a size of several nanometers after an appropriate surface passivation become highly luminescent in broad visible spectral range. Unfortunately physical mechanism of light emission has not been studied properly. Nevertheless, the most important conclusion of the studies is that amorphous carbon nanoparticles can effectively emit visible light. It is also important to note that light emitting carbon dots usually contain very large amount of oxygen (tens of at. %)

If the carbon-related PL band in por-SiO<sub>2</sub>:C is associated with the presence of carbon clusters in porous layer, we would be able to explain the shift of the band depending on carbonization temperature and also the reversible and irreversible photo-induced degradation of PL.

First, in carbon-related molecular-like clusters the gap between HOMO and LOMO of  $\pi$ -orbitals decreases with increasing of the number of atoms. Obviously, with increasing of carbonization temperature the average number of atoms in carbon clusters inside porous layer increases; leading to decrease in the energy of radiative transitions.

Secondly, on the basis of the carbon cluster hypothesis, it is quite easy to explain irreversible photo-induced degradation by photo-induced oxidation of carbon material in porous layer.

Thirdly, one of the reasonable explanations of reversible photo-induced PL quenching/recovery under cyclic UV exposure is the mechanism of fluorescence intermittency (or "blinking"), phenomenon, which is well known in light emitting semiconductor nanoparticles [19]. Under irradiation by energetic photons, some of nanoparticles can be charged by electron jumping from core state to neighboring energy state at the interface or in the surrounding wide band gap matrix. In the charged state, the non-radiative Auger recombination becomes the dominating recombination path making the nanocrystal "dark" until neutrality will be recovered. Obviously, the higher relative fraction of charged particles the lower is the integral PL intensity. It has been demonstrated that such charging of QDs by trapped electrons is a dominant process limiting the efficiency of light-emitting devices based on organic materials and colloidal QDs [20]. From this point of view, step-like PL quenching and recovery can be assigned to charging and discharging of fraction of light emitting sites when photon flux is switching-on and -off.

**3.8 Summary** Pulse laser excitation effects and photoinduced degradation of PL of porous SiO<sub>2</sub>:C layers fabricated by successive carbonization and oxidation of porous silicon were studied. It was found that carbon-related emission band was shifted toward longer wavelengths when the carbonization temperature was increase. Two types of photo-induced degradation phenomena were observed: reversible and irreversible. Irreversible degradation is suggested to be associated with photo-induced chemical reaction of light emitting material (presumably carbon) with atmospheric oxygen. It is demonstrated that irreversible degradation can be reduced by encapsulation that prevents contact of the material with air. Reversible degradation is still under discussion and need additional work will be required to understand the phenomenon. But, on the basis of our results, we suggest that it is due to fluorescence intermittency effects.

**Acknowledgements** This study was supported by Science and Technology Center of Ukraine, project No. 5513.

## References

- [1] M. Shim and P. Guyot-Sionnest, Nature 407, 981 (2000).
- [2] A. Karakuscu, R. Guider, L. Pavesi, and G. D. Soraru, J. Am. Ceram. Soc. **92**, 2969 (2009).
- [3] S. Gallis, V. Nikas, H. Suhag, M. Huang, and A. E. Kaloyeros, Appl. Phys. Lett. **97**, 081905 (2010).
- [4] A. V. Vasin, Y. Ishikawa, S. P. Kolesnik, A. A. Konchits, V. S. Lysenko, A. N. Nazarov, and G. Yu. Rudko, Solid State Sci. 11, 1833 (2009).
- [5] A. V. Vasin, Y. Ishikawa, N. Shibata, J. Salonen, and V. P. Lehto, Jpn. J. Appl. Phys. **19**, L465 (2007).
- [6] Y. Ishikawa, A. V. Vasin, J. Salonen, S. Muto, V. S. Lysenko, A. N. Nazarov, N. Shibata, and V.-P. Lehto, J. Appl. Phys. 104, 083522 (2008).
- [7] Y. Ishii, A. Matsumura, Y. Ishikawa, and Sh. Kawasaki, Jpn. J. Appl. Phys. 50, 01AF06 (2011).
- [8] A. V. Vasin, Sh. Muto, Yu. Ishikawa, J. Salonen, A. N. Nazarov, V. S. Lysenko, and P. Okholin, Thin Solid Films 519, 4008 (2011).
- [9] C. T. Kirk, Phys. Rev. B 38, 1255 (1988).
- [10] L. Rebohle, T. Gebel, H. Fröb, H. Reuther, and W. Skorupa, Appl. Surf. Sci. 184, 156 (2001).
- [11] A. Perez-Rodrigues, O. Gonzales-Varona, B. Garrido, P. Pellegrino, J. R. Moprante, C. Bonafos, M. Carrada, and A. Claverie, J. Appl. Phys. 94, 254 (2003).
- [12] J. Zhao, D. S. Mao, Z. X. Lin, B. Y. Jiang, Y. H. Yu, X. H. Liu, H. Z. Wang, and G. Q. Yang, Appl. Phys. Lett. 73, 1838 (1998).
- [13] Y. H. Yu, S. P. Wong, and I. H. Wilson, Phys. Status Solidi A 168, 531 (1998).
- [14] Y. Ding and H. Shirai, J. Appl. Phys. 105, 043515 (2009).
- [15] S. Hayashi, M. Kataoka, and K. Yamamoto, Jpn. J. Appl. Phys. Part 2 32, L274, (1993).
- [16] K. Maex, M. R. Baklanov, D. Shamiryan, F. Iakopi, S. H. Brongersma, and Z. S. Yanovitskaya, J. Appl. Phys. 93, 8793 (2003).
- [17] Y. P. Sun, B. Zhou, Y. Lin, W. Wang, K. A. S. Fernando, P. Pathak, M. J. Meziani, B. A. Harruff, X. Wang, H. F. Wang, P. J. G. Luo, H. Yang, M. E. Kose, B. L. Chen, L. M. Veca, and S. Y. Xie, J. Am. Chem. Soc. **128**, 7756 (2006).
- [18] Sh. N. Baker and G. A. Baker, Angew. Chem. Int. Ed. 49, 6726 (2010).
- [19] M. Nirmal, B. O. Dabbousi, M. G. Bawendi, J. J. Macklin, J. K. Trautman, T. D. Harris, and L. E. Brus, Nature **383**, 802 (1996).
- [20] P. O. Anikeeva, C. F. Madigan, J. E. Halpert, M. G. Bawendi, and V. Bulović, Phys. Rev. B 78, 085434 (2008).