# BLUE AND GREEN LIGHT EMISSION FROM SILICON NANOCRYSTALS EMBEDDED IN SILICON DIOXIDE MATRICES

**Pham Thanh Huy, Vu Van Thu, Nguyen Duc Chien**

*International Training Institute for Materials Science (ITIMS), Hanoi University of Technology*

**Nguyen Tri Tuan**

*Department of Natural Science, University of CanTho, CanTho, Vietnam*

**Abstract.** In this paper we report on light emission from silicon nanostructures prepared by rf co-sputtering in argon of pure silicon and silicon dioxide. The concentration of excess silicon was varied in the range 0.5% to 1.8%. Specimens were subjected to thermal anneal up to 1100°C in a nitrogen atmosphere. Stable blue and green luminescence was observed from samples with a typical thickness of 400 nm when excited by 365 nm ultraviolet light, with an intensity strong enough to be visible to the naked eye. In the as-deposited samples and after anneal at temperatures below 600°C, the luminescence observed around 440 nm is ascribed to structural defects in the $SiO_2$ film. For anneal above 600°C the emissions at wavelengths 445 and 537 nm may be due to excitons bound at structural defects in an interfacial layer between a silicon nanoparticle with crystalline core and surrounding amorphous $SiO_2$.

## 1. Introduction

In recent years extensive studies have been devoted to the physics and engineering of nanostructures embedded in crystalline solids. Such studies were stimulated strongly by the novel aspects of electron quantum confinement. In addition, small particles have a large surface-to-volume ratio which as well affects their properties. Based on new fundamental parameters, such as for the electron band structure, new phenomena may be observed. As an example, the enlargement of the valence-to-conduction-band gap in semiconductors and the fact that transitions between them can become vertical in k space has resulted in new optical properties, hitherto not existent, and of eminent importance for a material like silicon. The realization of silicon-based structures which emit light in the visible range, from the near infrared corresponding to the bulk silicon band gap at 1.1 μm to within the near ultraviolet, has an enormous potential for optoelectronic applications. As such structures can be realized with techniques compatible with microelectronics processing the interest from engineering side is huge.

A number of techniques has been applied for the production of nanostructures. This has started with the method of anodic oxidation pioneered by Canham to produce porous silicon, emitting luminescent red light[1]. However, porous silicon is mechanically fragile and due to absorption of gasses and impurities not stable.

Alternative methods have therefore been explored. Silicon nanoparticles were produced by direct breakdown of silane ($SiH_4$) molecules in an intense laser beam[2,3]. Crystalline silicon particles collected on a substrate were subsequently oxidized. Straightforward implantation of silicon ions into silicon dioxide layers has also been used for controlled creation of silicon-rich non-stoichiometric glassy layers [4,5,6,7]. Methods of plasma-enhanced chemical vapor deposition were used as well, also allowing the doping of layers by impurities as nitrogen and hydrogen[8,9]. Another effective method is the co-sputtering of silicon dioxide and pure silicon [10,11,12]. In all cases the option of thermal anneal of produced structures, typically in a range of temperatures up to 1200°C, is employed beneficially.

Results obtained in the various studies differ vastly, even within an equal technique of preparation. A multitude of light emission wavelengths has been reported. Effects of temperature of annealing also show little similarities. Apparently, the results depend sensitively on details of production parameters. Control over the parameters and their tolerances to obtain a desired result still largely has to be established. The present paper aims at making a contribution to this task. The technique of co-sputtering of Si and $SiO_2$ has been used and characterizations were made by photoluminescence (PL). The effect of thermal anneal at various temperatures and of silicon concentration is reported.

## 2. Sample preparation and spectrometer

Samples were fabricated by rf magnetron co-sputtering of silicon and silicon dioxide. On an $SiO_2$ target (99.99% purity) with a diameter of 3 inches several small chips of silicon, each with area of 5 $mm^2$, were placed. The silicon source material is n type, doped with P to the resistivity of 5-10 Ohm.cm. The number of silicon chips, from 2 to 17, is used for control of the concentration of Si in the produced $SiO_2$:Si films. The silicon chips are arranged in such a way that best uniformity is obtained in the sputtered films. Before sputtering the chamber was first evacuated down to $3x10^{-7}$ Torr. Subsequently the deposition was performed by sputtering the whole target assembly under an argon pressure of $10^{-1}$ or $10^{-2}$ Torr. Films were deposited on thermally oxidized silicon substrates with a 3 inch diameter. By varying the duration of sputtering time films with thickness in the range 30 to 800 nm were produced. Thermal annealing treatments were given to the samples in a temperature range of 300 to 1200 °C and for durations of time from 30 minutes to 2 hours.

Photoluminescence intensity was measured using SPEX Fluorog-3 model 322. PL was excited by illumination at a wavelength of 365 nm (3.40 eV) from a 450-W xenon short arc focussed to a spot diameter on the sample of 0.6 to 1.5 mm. Emitted light was dispersed by a double 1200-groove/mm gratings monochromator (excitation 330-nm blaze 200–700 nm range, emission 500-nm blaze 300–1000 nm range), and detected with photomultiplier tube. Samples were kept at room temperature during PL measurements.

## 3. Results and discussion

Immediately after deposition already a bright luminescence, visible to the naked eye, is observed from the $SiO_2$:Si film. Fig. 1 shows the emission of a 400 nm thick layer with a silicon concentration of 1.3%, produced by sputtering from 12 silicon chips in the target. There is a maximum in the emission at 440 nm (2.82 eV). The brightness of the blue emission is shown to be comparable to the red light emission of a porous silicon sample with the maximum at 690 nm (1.80 eV), measured in the same set-up. For a similar study of co-sputtered as-deposited samples no such emission was reported [10].

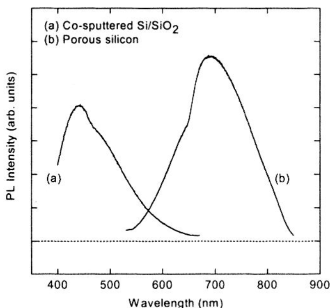


*Fig. 1.* Photoluminescence spectrum of (a) an as-deposited $SiO_2$:Si film, thickness 400 nm, Si concentration 1.3%, compared to (b) porous silicon. Samples at room temperature. UV light excitation at 365 nm.

The thermal stability of the luminescence was probed by annealing the samples at increasing temperatures. It was found that anneal at 600 °C for 1 hour completely removes the light emission. Upon further anneal treatment at higher temperatures luminescence reappears. A clear emission is again obtained by anneal at 800°C. The spectrum shown in Fig. 2 for a sample with 1.3% silicon concentration exhibits two bands with maxima at 445 nm (2.79 eV) and 537 nm (2.31 eV), respectively. Increase of anneal temperature to 1000°C enhances the 445 nm emission considerably, but has no effect on the 537 nm band. A further increase of anneal temperature to 1100°C almost completely removes all luminescence. Only a weak emission of the 445 nm band slightly shifted towards a lower wavelength at 436 nm is left.

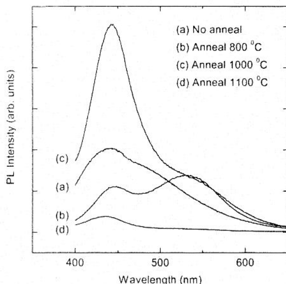


Fig. 2. Photoluminescence of $Si/SiO_2$ co-sputtered films. Shown is the spectrum of an as-deposited $SiO_2$:Si film, and after anneal in nitrogen atmosphere at 800, 1000 and 1100 °C. Films with Si concentration of 1.3% and thickness of 400 nm. All spectra excited by 365 nm UV light and observed at room temperature.

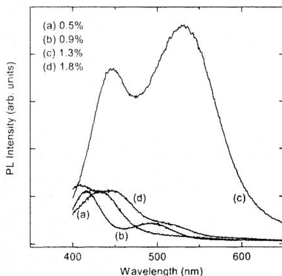


*Fig. 3.* Dependence of the photoluminescence spectra on silicon concentration in the $SiO_2$:Si co-sputtered films. All samples thermally annealed at 800 °C for 1 hour in nitrogen atmosphere. Film thickness 400 nm. Luminescence excited by UV light of 365 nm wavelength.

Results of luminescence were found to depend also strongly on the concentration of the excess silicon in the $SiO_2$ layers. Spectra for co-sputtered silicon concentrations of 0.5, 0.9, 1.3 and 1.8% are shown in Fig. 3. All samples had the thickness of 400 nm and were annealed for 1 hour at 800 °C. The intensity increases when the concentration rises from 0.5 to 1.3 %, but non-linearly, and falls rapidly for the higher concentration of 1.8%. Also the number of peaks in the spectra, probably related to luminescent centers or mechanisms, changes from one for the lowest concentration, via two for the intermediate concentrations to three for the most non-stoichiometric composition.

Additional experiments were performed in which the film thickness was varied and others in which the time dependence of center growth or loss was recorded in an isochronal anneal sequence. As such experiments were less systematic yet, they will not be reported here.

Visible luminescence has been reported to be emitted from UV excited plain $SiO_2$ layers [13]. In spite of that observation it is generally assumed and confirmed that some silicon-related nanostructures are required for the efficient light emission process. In order to verify this assumption for the present kind of experiments sputtered films were prepared without the simultaneous co-sputtering of silicon. The result as presented in Fig. 4 demonstrates the strongly reduced optical activity of such a film. Also an oxide grown thermally does not show any appreciable light emission. Figure 4 presents the comparison for as-grown films. A similar result is obtained after an anneal at 800 °C for 1 hour. It supports the conclusion that light emission requires the presence of some kind of silicon-related defect or nanostructure.

It was found in the experiments that after a thermal anneal at 600 °C all optical activity was absent. This observation indicates a natural division between a mechanism active at low temperatures and another one following the higher-temperature treatment. In the low temperature regime there has been no opportunity yet for the as-deposited silicon atoms in the film to form clusters. Isolated silicon atoms are expected to be present. The related film will show a similarity to films as produced by ion implantation. The non-stoichiometric excess of silicon atoms will lead by necessity to vacancies on oxygen sites. The E' center is a well known example of such a defect. E' centers can be monitored in electron paramagnetic resonance by the associated spectrum with isotropic g factor $g = 2.0023$. Following ion implantation the disappearance of the EPR signal of E' centers in parallel with diminishing luminescence was found to occur at 600 °C thermal anneal [7,8,9,10,11,12,13,14]. In analogy to this result the luminescence activity in as-deposited co-sputtered samples is ascribed to a small structural defect. This defect is not necessarily the E' center as the luminescence observed after ion implantation occurs at a different wavelength. Defect-related luminescence does not shift in wavelength upon annealing, in agreement with the observations made.

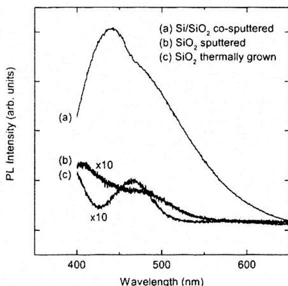


*Fig. 4.* A comparison of the photoluminescence spectra and intensities of (a) $Si/SiO_2$ co-sputtered film, (b) $SiO_2$ sputtered film, and (c) thermally grown silicon dioxide film. All films have thickness 400 nm. Note amplification of signal by factor 10 for the latter two cases.

Upon thermal anneal at the higher temperatures above 600 °C the silicon atoms tend to aggregate into clusters with crystalline core. The process has been observed in many studies by transmission electron microscopy [2,3,6,8,13]. These silicon nanoparticles with the core existing of silicon only are embedded in the silicon dioxide matrix. There will exist an interfacial region with an intermediate chemical composition $SiO_x$, with $0 < x < 2$, typically SiO. The bandgap in this interface layer is smaller than that of the silicon core which is increased above the bulk silicon value of 1.18 eV by quantum confinement. The gap in the insulator silicon dioxide is near 8 eV. Excitons created by the excitation light will be trapped in the interface layer binding themselves there to structural defects [2]. Observed luminescence is due to the electron-hole recombination of these bound excitons. The energy will depend on the trapping defect. In the present experiment the observed emissions are at 445 and 537 nm. In the initial stages of high-temperature anneal the luminescence intensity will increase as the result of the gradual formation of more silicon nanoparticles. Most efficient for luminescence are the smaller-sized nanoparticles. At further thermal anneal at higher temperatures the increased size of nanoparticles will lead to decrease of luminescence as actually is observed in the experiment. As the emitted energy will be determined by the structural defects the wavelength does not change with annealing status, in agreement with observations

in this and similar experiments, in contrast to its intensity. The prevailing explanation for luminescence of porous silicon is the phenomenon of quantum confinement. For this process a dependence of emission wavelength on nanoparticle size is expected. Theory predicts an energy of 2.0 eV for core diameters of 4 nm, decreasing to 1.3 eV for the 10 nm core size [2]. As such shifts were not observed for the co-sputtered samples, quantum confinement is not proposed as the effective luminescence mechanism.

**Acknowledgement.** The authors wish to thank Prof. Dr. C.A.J.Ammerlaan for his valuable comments on the manuscript and helpful discussions, N. V. Toan for preparation of $SiO_2$:Si films, and Ass. Prof. Dr L. H. Ha for kind assistance in the measurements. The work is supported by Vietnamese State Research Program on Natural Science, grant No. KHCB 42.01.03.

**Reference**

1. L. T. Canham, *Appl. Phys. Lett.* **57**, 1046.
2. Y. Kanemitsu, T. Ogawa, K. Shiraishi, and K. Takeda, *Phys. Rev.* B **48**(1993), 4883.
3. T. Kawaguchi and S. Miyazima, *Jpn. J. Appl. Phys.* **32**(1993), L215.
4. T. Shimizu-Iwayama, K. Fujita, S. Nakao, K. Saitoh, T. Fujita, and N. Itoh, *J. Appl. Phys.*, **75**(1994), 7779.
5. P. Mutti, G. Ghislotti, S. Bertoni, L. Bonoldi, G. F. Cerofolini, L. Meda, E. Grilli, and M. Guzzi, *Appl. Phys. Lett.* **66**(1995), 851.
6. J. G. Zhu, C. W. White, J. D. Budai, S. P. Withrow, and Y. Chen, *Mat. Res. Soc. Symp. Proc.* **358**(1995), 175.
7. J.-Y. Zhang, X.-M. Bao, N.-S. Li, and H.-Z. Song, *J. Appl. Phys.* **83**(1998), 3609.
8. Keunjoo Kim, M. S. Suh, T. S. Kim. C. J. Youn, E. K. Suh, Y. J. Shin, K. B. Lee, H. J. Lee, M. H. An, H. J. Lee, and H. Ryu, *Appl. Phys. Lett.* **69**(1996), 3908.
9. A. J. Kenyon, P. F. Trwoga, C. W. Pitt, and G. Rehm, *J. Appl. Phys.* **79**(1996), 9291.
10. Qi Zhang, S. C. Bayliss, and D. A. Hutt, *Appl. Phys. Lett.* **66**(1995), 1977.
11. [11]S. Hayashi, T. Nagareda, Y. Kanzawa, and K. Yamamoto, *Jpn. J. Appl. Phys.* **32**(1993), 3840.
12. Y. Osaka, K. Tsunetomo, F. Toyomura, H. Myoren, and K. Kohno, *Jpn. J. Appl. Phys.* **31**(1992), L365.
13. W. C. Choi, M. S. Lee, E. K. Kim, C. K. Kim, S. K. Min, C. Y. Park, and J. Y. Lee, *Appl. Phys. Lett.* **69**(1996), 3402.
14. H. Z. Song, X. M. Bao, N. S. Li, and X. L. Wu, *Appl. Phys. Lett.* **72**(1998), 356.