

## Strong and tunable white photoluminescence from carbon incorporated nanostructured silica

A.V. Vasin, A. V. Rusavsky, V.A.Tyortyh, A.N. Nazarov, V.S. Lysenko

Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine, Kyiv, Ukraine  
Institute of Surface Chemistry, NAS of Ukraine, Kyiv, Ukraine  
andriyvasin@gmail.com

Carbon incorporated silicon oxide nano-composite ( $\text{SiO}_2\text{:C}$ ) is one of new promising light-emitting materials. Unfortunately, origin of light emitting in these materials has not yet been identified. The main "candidates" suggested as light emitting centers were (1) point defects in  $\text{SiO}_2$  network (oxygen deficiency centers), (2) Si-O-C or Si-C isolated bonds, and (3) C or SiC nano-clusters. We believe that most reasonable hypothesis is light emission by carbon nanoclusters. Recently it was demonstrated that carbon nano-clusters with passivated surface exhibit strong visible photoluminescence (PL) with emission photon energy depending on the size of the cluster [reviewed in Ref.1 and Ref.2].

In present report we analyze structure and light emission properties of two types of  $\text{SiO}_2\text{:C}$  materials: porous  $\text{SiO}_2\text{:C}$  layers on Si wafers and  $\text{SiO}_2\text{:C}$  powders. Carbon incorporated porous silicon oxide layers (por- $\text{SiO}_2\text{:C}$ ) were fabricated by successive procedure of thermal treatment of porous silicon in flow of acetylene (in temperature range of 850-1150 °C) followed by oxidation in flow of wet nitrogen or wet argon in temperature range of 850-1050 °C [3-5]. The other type of nanostructured  $\text{SiO}_2\text{:C}$  composite was fabricated by successive chemical modification of nano-silica powder (specific surface area of 300  $\text{m}^2/\text{g}$ , particle size about 10 nm) by hydrocarbons or hydrocarbosiloxanes followed by calcinations at temperature up to 700 °C in inert ambient (pure nitrogen flow or vacuum). Correlations of fabrication conditions, local bonding structure and light emission properties have been studied. The main goal of the work was to check our hypothesis on carbon cluster origin of photoluminescence in nanostructured  $\text{SiO}_2\text{:C}$  materials

**Porous  $\text{SiO}_2\text{:C}$  layers.** It has been demonstrated that broad band light emission of por- $\text{SiO}_2\text{:C}$  is composed by two bands: (1) broad band centered at about 500-600 nm and (2) blue shoulder with maximum intensity at about 440 nm. The 500-600 nm band vanished completely after annealing in oxygen that was accompanied by strong reduction of carbon content in the layer, so that we assign this band to presence of carbon (carbon related band). Moreover, we have found spectral shift of carbon related PL band from orange to green spectral region with decrease of carbonization temperature (Figure 1). This shift is well explained by size-dependent PL shift observed in carbon nano-dots [1-2].

**$\text{SiO}_2\text{:C}$  powders.** General idea of the material synthesis procedure was to attach hydrocarbon radicals to surface of fumed silica nano-particles ( $\text{SiO}_2\text{:OH}$  nanopowder) by chemical treatment (formation of  $\text{SiO}_2\text{:C}_n\text{H}_m$  precursor nano-powder) with subsequent annealing in inert atmosphere (formation of  $\text{SiO}_2\text{:C}$  composite powder). The series of the materials with predominant Si-O- $\text{C}_n\text{H}_m$  and Si- $\text{C}_n\text{H}_m$  bonding configuration between silica nanoparticles and hydrocarbon radicals as well as the series of materials  $\text{SiO}_2\text{:C}_n\text{H}_m$  with the n in range of 1-9 have been fabricated and studied.

It was demonstrated that light-emission properties of  $\text{SiO}_2\text{:C}$  are not dependent on type of "bridging" bonds in the  $\text{SiO}_2\text{:C}_n\text{H}_m$  precursor while it was very sensitive to amount of carbon and annealing temperature/duration. The less carbon incorporation in the powder the larger temperature it needs for PL activation. Vice-versa, the more carbon in the powder the easier it goes black due to graphitization of carbon. PL efficiency is suggested to be determined by two competitive processes: nucleation of light emitting small carbon clusters and growth of large graphite-like precipitates that do not emit light. Light emitting powders were usually of light-gray or light-brown color.

The other important observation was the red spectral shift of PL maximum intensity with increase of annealing temperature (Figure 2) and/or number of carbon atoms in attached hydrocarbon radicals. Such spectral shifts of PL band is quite similar to that observed in porous  $\text{SiO}_2\text{:C}$  (Figure 1). This shift cannot be explained in terms of local defects or isolated bonds, however, it is in good agreement with the effect of the size of carbon cluster (the smaller cluster size the larger gap between HOMO and LUMO electron states).

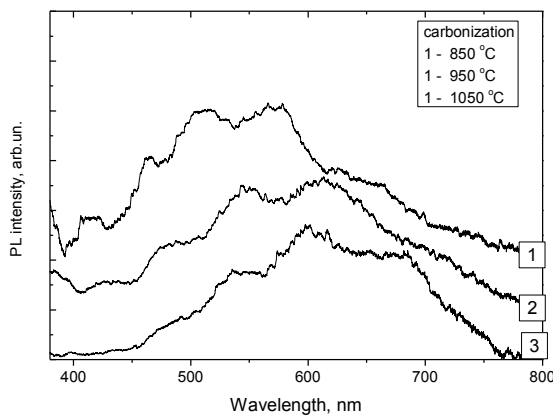
PL decay time in  $\text{SiO}_2\text{:C}$  (both porous layers and powders) was measured to be less than 10 ns. Short decay time is also hardly compatible with point defects hypothesis. Defect related light emission in silicon oxide in visible spectral range is associated with radiative recombination from triplet state to ground state ( $T_1 \rightarrow S_0$ ) [6]. Such recombination (i.e. "phosphorescence") is natively slow process with characteristic decay time of micro- and milliseconds.

In summary, it is demonstrated that light emission in  $\text{SiO}_2\text{:C}$  is originated most likely from carbon nano-precipitates. We have not observed carbon clusters directly in light-emitting material but all experimental data are shown to be self consistent in frame of the "carbon cluster hypothesis".

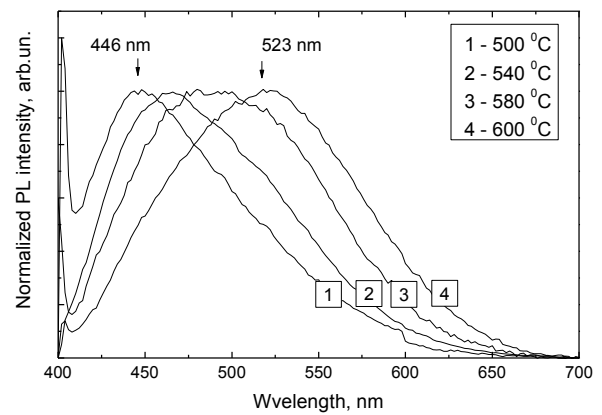
Size dependent spectral properties of SiO<sub>2</sub>:C makes possible “color engineering” of white light. Figure 3 illustrates that PL spectrum of SiO<sub>2</sub>:C can be almost ideally tuned to natural day light. Excellent spectral properties of white light emission along with lack of expensive heavy metal dopants make SiO<sub>2</sub>:C material extremely attractive as luminophor for artificial lighting applications.

## References

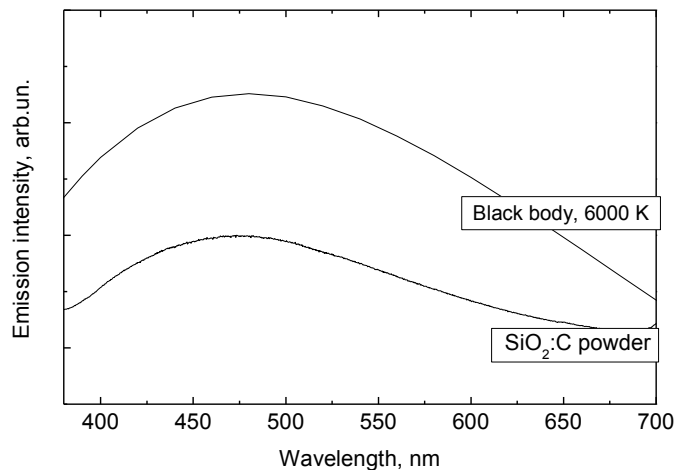
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**Figure 1.** Time resolved PL spectra of por-SiO<sub>2</sub>:C layers synthesized using carbonization temperature 850 °C (spectrum 1), 950 °C (spectrum 2) and 1050 °C (spectrum 3). Excitation by 337 nm.



**Figure 2.** PL spectra of SiO<sub>2</sub>:C powder synthesized using annealing temperature 500 °C (spectrum 1), 540 °C (spectrum 2), 580 °C (spectrum 3), and 600 °C (spectrum 4). Excitation by 370 nm.



**Figure 3.** Spectral distribution of light emission of black body at 6000 K (roughly corresponds to spectral distribution of Sun radiation) and representative SiO<sub>2</sub>:C powder (360 nm excitation).