# Interrelated Ultraviolet and Long-lived Blue luminescence bands of Oxidized Nanocrystalline Porous Silicon

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## Abstract

The origin and mechanism of the blue and UV luminescence of oxidized porous silicon are discussed. An interrelation between a long-lived blue phosphorescence band and a fast UV band exhibiting very specific excitation characteristics is shown. The results are important for the development of shortwavelengths silicon-based photonic applications.

## 1. Introduction

Silicon is the choice material in microelectronics. It also offers good photonic properties (e.g. waveguiding, photodetection), except for its light emission [1]. Bulk silicon can emit only infrared light (bandgap of about 1.1 eV) and with very low efficiency (due to indirect bandgap). However, nanosilicon can exhibit size-tunable visible light emission as a result of quantum confinement [2]. Efficiencies of photoluminescence (PL) over 20% have been reported in various types of nanosilicon systems, particularly for the red light emission [3-6]. Recently, we have obtained efficient blue PL from partially or heavily oxidized nanocrystalline porous silicon (OPSi) [7-9]. This blue emission includes an intrinsic blue phosphorescence band which exhibits a lifetime of several seconds at low temperature [8,9]. We have correlated this luminescence band to oxide related molecular species [8,9].

In this paper, we report a detailed study of the luminescence of OPSi. A specific UV band newly observed in OPSi was evidenced. This band was found linked to the blue phosphorescence band. The effect of chemical modifications of OPSi surface was also investigated. Commercial porous glass was also studied as a reference, in order to study the role of silicon nanocrystals in the luminescence emission of OPSi.

# 2. Experimental section

The substrates used were (100)-oriented, B-doped ptype (4  $\Omega$ cm) silicon wafers. Porous silicon layers were formed by anodization in an ethanoic HF solution. OPSi was obtained by thermal oxidation of porous silicon layers in O<sub>2</sub> atmosphere at 900 °C for 30 min followed by high-pressure water vapor annealing (at 260 °C for 3 h) as previously reported [3,4].

## 3. Results and discussion

Figure 1 shows the PL of OPSi at 17 K for 3 different excitation wavelengths. Three spectral regions can be identified: a blue band peaked at ~ 425 nm, a broad UV band (UV Band1) ranging from ~ 300 nm to ~375 nm, and another rather narrow UV band (UV Band2) showing 2 peaks at 275 and 290 nm. From the figure, it is clear that the PL exhibits a dramatic dependence on excitation wavelengths. When using the excitation at 240 nm or 250 nm, the blue band and UV Band1 were most intense, though these two bands were slightly less intense for the 250 nm excitation. UV band2 was not excited at all. Increasing the excitation wavelength to 270 nm led to a significant reduction in intensity of both the blue band and UV Band1, whereas UV Band2 was efficiently excited. Thus, a kind of anticorrelation exists between the blue band and UV band2 via their excitation mechanisms.

We propose the diagram shown in Figure 2 to explain the excitation mechanism of BPh and UV Band2. The blue band actually consists of one long-lived phosphorescent one (PPh) peaked at ~ 2.7 eV (460 nm) and another fast one peaked at ~ 3.0 eV (413 nm) [8,9]. The emission line  $T \rightarrow S_0$  relates to the long-lived BPh emission.  $S \rightarrow S_0$  relates to the fast component in the blue band. We have shown previously that BPh could be excited directly (Mode 2 in Fig. 2) for excitation energies below ~ 4.2 eV, though with a low efficiency and a redshifted emission spectrum [8,9]. The present study shows that for excitation energies above  $\sim 5 \text{ eV}$  (240 nm), the BPh is efficiently excited, likely via an intersystem crossing mechanism (Mode 1 in Fig. 2), whereas for a narrow range of excitation energies around ~ 4.6 eV (270 nm), UV Band 2 is preferentially excited, with a twopeak emission at 4.5 eV ( $S_1 \rightarrow S_0$ ) and 4.28 eV ( $S_2 \rightarrow S_0$ ).

Both UV Band1 and UV Band2 decayed very rapidly, typically in the nanosecond range. In sharp contrast, as previously reported [8,9], the blue band decayed very slowly, for temperature ranging from 10 to about 200 K and was termed blue phosphorescence (BPh).

The origin of the emission of BPh and UV Band2 was investigated. In particular, silicon nanocrystals potentially still present in OPSi could participate in the emission and/or excitation of BPh. We have studied the luminescence of commercial porous glass, which does not contain any silicon nanocrystals, and found that it was also exhibiting a long-lived blue phosphorescence similar to BPh. Therefore, we can conclude that silicon nanocrystals are not involved in the emission mechanism of BPh. However, silicon nanocrystals may still play a role in the excitation of BPh by a sensitizing effect. This hypothesis is supported by the fact that the BPh intensity is higher in silicon-rich OPSi than in porous glass.

The absence of carbon in our porous glass samples also rules out the possibility of carbonyl or carbon substitutional defect for silicon in the Si-O-Si network as a possible origin of the BPh.

The role of OH groups at the surface has been investigated. A treatment based on the soaking of OPSi in ethanol in order to increase the amount of surface OH groups was used. The biggest effect of the treatment was a dramatically enhancement of the intensity of UV Band2 whereas that of BPh was slightly reduced, as shown in Fig. 3. Structural characterization (infrared spectroscopy) correlates the luminescence evolution to an increase in OH groups at the OPSi surface. The effect of OH groups on the various luminescence bands of OPSi is currently under detailed investigation.

## 4. Conclusion

The blue phosphorescence band that we have previously reported in OPSi [8,9] was shown to be closely related to a newly observed and characterized UV band. The new results presented here, including the comparison with the light emission of porous glass, suggest that the phosphorescence originates from the oxide or oxide surface and not from silicon nanocrystals or any foreign species (such as organic molecules). The OH groups at the OPSi surface were shown to have a significant influence on the UV band. Further work is under way to fully clarify the emission origin and to optimize it for promising application, such as bioimaging or tagging, and display purposes.

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Figure 1: PL of OPSi at 17 K, for three different excitation wavelengths, as indicated.



Figure 2: Energy diagram showing two possibilities for the excitation of the phosphorescence: direct (mode 2) or via an intersystem crossing (mode 1; excitation above ~ 5 eV (240 nm)). Different relaxation processes are also shown: BPh ( $T \rightarrow S_0$ ), fast blue band ( $S \rightarrow S_0$ ). Emission  $S_1 \rightarrow S_0$  and  $S_2 \rightarrow S_0$  are observed only for excitation at ~ 4.6 eV (270 nm).

Figure 3: PL of OPSi at 300 K excited at 266 nm before



and after ethanol treatment.

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