Ultraviolet and long-lived Blue Luminescence of oxidized Porous Silicon

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Bulk silicon exhibits an indirect bandgap of about 1.1 eV. As a result, the luminescence efficiency of its band-to-band recombination process is very low. However, because of quantum confinement, relatively efficient visible light emission can be obtained from nanocrystalline silicon layers, such as porous silicon (PSi).

The efficiency, stability and emission wavelengths of PSi are drastically affected not only by the size but also by the surface chemistry of the nanocrystals. Recently, we have significantly improved both the luminescence stability and efficiency (23% ext. quantum efficiency) of PSi by growing a relaxed and good quality oxide shell around the nanocrystals. The red photoluminescence (PL) (1, 2) and electroluminescence (3) of PSi was very much stabilized.

In practice, it is very difficult to achieve and stabilize blue emission from Si nanocrystals because of (i) the poor mechanical stability of very small nanocrystals in PSi, and (ii) the influence of surface impurities which tends to cancel the size effect(4). Nevertheless, recently, we could obtain efficient blue PL from partially oxidized PSi (5). This blue emission includes an intrinsic blue phosphorescence band which exhibits a lifetime of several seconds at low temperature (6). This phenomenon is unique for a silicon-based system and could have dramatic implications in short-wavelength photonics. This emission band exhibits a fine structure likely having a vibrational origin (7). Furthermore, we have demonstrated energy transfer from the phosphorescence to guest organic light-emitting molecules (8).

The long-lived emission remains unchanged up to about 200 K and then is progressively quenched due to a temperature activated process. The study of its excitation processes led to the proposition of the diagram shown in Figure 1. The emission lines $T \rightarrow S_0$ (phosphorescence emission) and $S \rightarrow S_0$ have been observed (6, 7).

Very recently, we were able to observe also luminescence associated to $S_1 \rightarrow S_0$ radiative transitions using resonant excitation. This UV emission band can be very strong and has some degree of correlation with the blue emission band, supporting our excitation mechanism of the blue band.

In this paper, we review our recent progresses on the understanding of the origin and mechanism of the blue phosphorescence of oxidized PSi. Furthermore, some properties of the UV emission band ($S_1 \rightarrow S_0$) will be presented. The effect of exposure to various liquids on the luminescence properties of all bands (red, blue and UV) will also be discussed.

The exposure to ethanol (soaking in liquid ethanol for 30 min followed by drying under nitrogen gas) is particularly interesting, as shown in Fig. 2. The blue band was partially quenched, whereas the UV band was dramatically enhanced by the exposure to ethanol. Ethanol may react with silicon dioxide via the hydroxyl

groups. Indeed, structural characterization correlates the luminescence evolution to surface chemistry evolution. Thus, this study could shed new light on the mechanism of the blue phosphorescence and on the role of the surface in its mechanism.
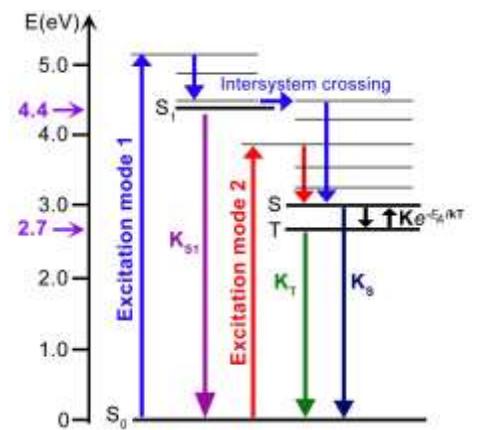
Figure 1: *Energy diagram showing the two possibilities for the excitation of the phosphorescence: direct (mode 2) or via an intersystem crossing (mode 1). Different relaxation processes are also shown. Emission ($S_1 \rightarrow S_0$) is observed only for resonant excitation.*
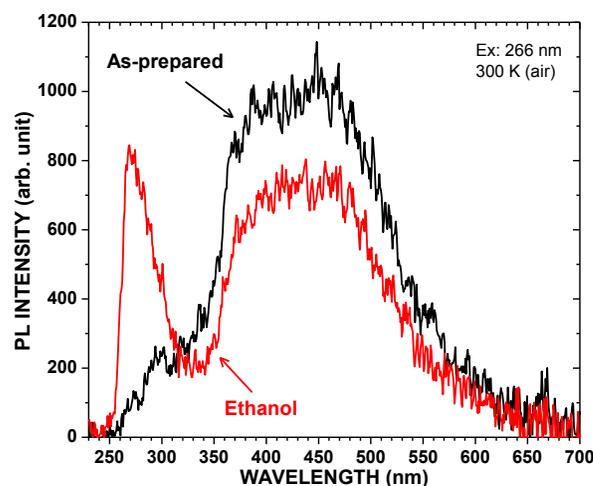
Figure 2: *Photoluminescence at 300 K of an oxidized PSi layer excited at 266 nm, as-prepared and after a treatment consisting in soaking in ethanol for 30 min and then drying under N_2 flow. The peak at about 270 nm is related to resonantly excited $S_1 \rightarrow S_0$ transitions in the diagram of Fig. 1.*

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