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Photodegradation of porous silicon induced by photogenerated singlet oxygen molecules

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We report on the mechanism of photodegradation of porous silicon luminescence in ambient containing molecular oxygen. Energy transfer from excitons confined in silicon nanocrystallites to molecular oxygen results in the generation of highly chemically reactive singlet oxygen molecules. The subsequent interaction of singlet oxygen molecules with the hydrogenated surface of silicon nanocrystals results in its photooxidation and the creation of additional nonradiative defects, i.e., the luminescence fatigue effect. © *2004 American Institute of Physics*. [DOI: 10.1063/1.1804241]

Excitons confined in silicon nanocrystals have a very long radiative lifetime due to their indirect nature and competition between radiative and various nonradiative processes results in a relatively low quantum yield of silicon nanocrystal assemblies. After the discovery of the photoluminescence (PL) from porous silicon[1] (Si) it has been recognized that the ultimate limitation is an issue of stability. Almost all groups involved in the study of as-prepared hydrogen-passivated porous Si layers at normal ambient conditions have encountered a significant reduction in the quantum yield: depending on the optical excitation level and exposure time, the initial quantum yield can be reduced by orders of magnitude.[2] Tischler *et al.*[3] found that the photodegradation is present only in oxygen ambient and is a result of photooxidation of the porous Si surface, which introduces an additional nonradiative recombination channel: Si dangling bonds. In contrast, light emission from naturally oxidized porous Si layers or Si nanocrystals embedded in a wide band-gap matrix[4,5] is more efficient and was found to be quite stable.[2] Recently, several alternative approaches for the photostabilization of porous Si via its surface modification have been suggested.[6,7] However, no distinct microscopic mechanism of the porous Si photodegradation and photooxidation has yet been proposed.

The electronic energy transfer from excitons confined in Si nanocrystals to adsorbed oxygen molecules was found to be very efficient at cryogenic temperatures.[8] Spectroscopic experiments clarified the details of the energy transfer mechanism. The energy transfer is mediated by a resonant direct electron exchange mechanism and results in the efficient generation of a chemically reactive species: singlet oxygen molecules.[9] It this Letter we demonstrate that PL photodegradation of H-terminated porous Si layers in oxygen ambients at room temperature is dependent on their PL quantum yield and is directly governed by the interaction of photosensitized singlet oxygen molecules with the surface of Si nanocrystals. For low quantum yield H-terminated and high quantum yield O-terminated surfaces, this effect is absent due to a strongly reduced single oxygen generation rate. Thus, the photodegradation mechanism is very similar to that of light-emitting polymers[10] or dye molecules.

Experiments were carried out using various porous Si layers having a different PL quantum yield. The porous Si layers were prepared by standard electrochemical etching[1] of (100)-oriented, boron-doped bulk Si substrates with a typical resistivity of 5 Ω cm. The etching current density was 30 mA/cm^2. To obtain samples with a high quantum yield, porous Si layers remained in the etching solution for one additional hour.[1] Thermal oxidation of Si nanocrystal surfaces was performed at 200 °C in oxygen ambient for 10 h. PL was excited by the 488-nm line of an Ar$^+$ laser and detected by a single monochromator equipped with a Si charge-coupled device. The samples were mounted in a He flow cryostat with temperatures between 5 and 300 K. The chemical composition of Si nanocrystal surfaces was analyzed by a Bohmem DA-3 FTIR spectrometer. All optical measurements were performed at room temperature.

Figure 1 shows the PL spectra of H-terminated samples having a high (sample A) and a low (sample B) quantum yield measured in vacuum (open circles). The featureless emission bands located in the near-infrared and visible region reflect the wide band-gap distribution of the Si nanocrystal assembly. The injection of molecular oxygen results in a partial PL quenching which depends on the oxygen ambient pressure and is stronger for samples having higher quantum yield. The prompt removal of oxygen molecules leads to a complete recovering of the initial emission properties of porous Si. The strength of PL quenching (defined as the PL intensity measured in vacuum divided by the PL intensity measured in oxygen ambient) at 1 bar for sample A is shown in the inset of Fig. 1 (open circles). The spectral dependence of the PL quenching strength does not depend on the PL band position and is most efficient at ~1.63 eV, which coincides with the excitation energy of the $^3\Sigma \rightarrow {}^1\Sigma$ transition in oxygen molecules.[11] Thus, excitons having energies in the vicinity of the $^3\Sigma \rightarrow {}^1\Sigma$ transition contribute most efficiently to the singlet oxygen generation. The inte-

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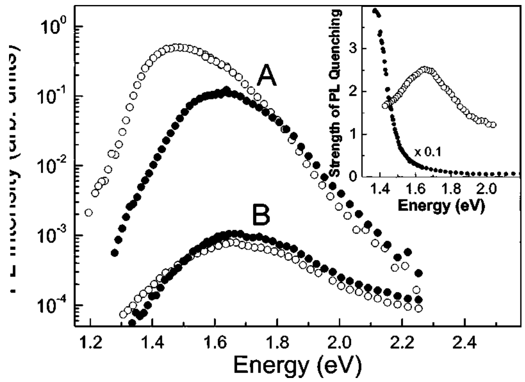

FIG. 1. Open circles: PL spectra of porous Si samples having a high (A) and a low (B) quantum yield in vacuum (10^{-5}mbar). Solid circles: PL spectra of porous Si samples having high (A) and low (B) quantum yield in vacuum after photodegradation in oxygen ambient at 1 bar. $T = 300$ K. $E_{ex.} = 2.54$ eV, $I_{ex.} = 100$ mW/cm^2, irradiation time is 1 h. Note the logarithmic scale of the plot. Inset: Spectral dependence of the strength of PL quenching for sample A induced by oxygen ambient (open circles) and that due to photodegradation (divided by factor of 10, solid circles).

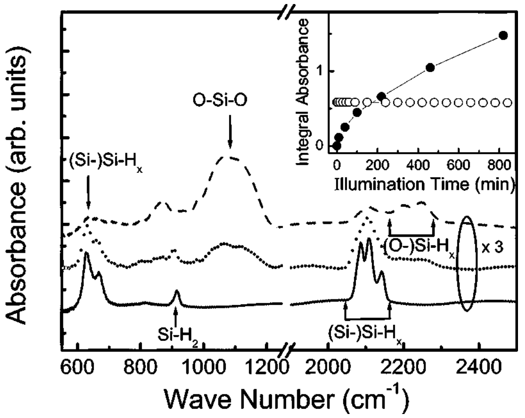

FIG. 2. IR absorbance of porous Si. Solid curve: H-terminated layer. Dotted curve: Sample B after illumination in oxygen ambient at 1 bar. $T = 300$ K. $I_{ex.} = 100$ mW/cm^2. $E_{ex.} = 2.54$ eV; irradiation time is 1 h. Dashed curve: Sample A after irradiation at the same conditions. Arrows label surface vibration bonds. Inset: Integral absorbance due to O–Si–O bonds (solid circles) and due to (Si)Si-H$_x$ and (O-)Si-H$_x$ stretching bond (between 2050 and 2300 cm^{-1}, open circles) vibrations.

gral level of PL quenching allows us to estimate the generation rate of singlet oxygen in porous Si layers. For sample A for 1 bar oxygen pressure, room temperature, and 1 W/cm^2 PL excitation intensity it is $\sim 10^{19}$ $^1O_2$/cm^3 sec. Because the singlet oxygen generation rate scales with the PL quantum yield, it is 3 orders of magnitude smaller for sample B. Efficiently emitting oxidized PSi layers are not able to generate singlet oxygen[8] and their PL quantum yield is not affected by the oxygen ambient.

A large difference in the singlet oxygen generation rate results in a distinct photodegradation behavior, depending on the PL quantum yield of the porous Si layers and their surface termination. While all H-terminated samples illuminated in vacuum possess completely stable PL, in oxygen ambient the PL intensity of efficiently luminescing samples exhibits fast photodegradation for large Si nanocrystals emitting at the low-energy part of the PL spectrum (Fig. 1, sample A, solid circles). Again, we define the strength of the persistent PL quenching as the ratio between initial PL intensity and that after photodegradation, both being measured in vacuum (inset of Fig. 1, solid circles). The behavior of porous Si layers having low quantum yield is completely different. Their PL intensity above 1.5 eV slightly rises with illumination time and only at low emission energies a small PL photodegradation is detected (Fig. 1, sample B, solid circles). We note that the quantum yield of oxidized samples is constant over time.

These observations indicate that the PL degradation efficiency directly correlates with the singlet oxygen generation rate and scales with the surface area of nanocrystals. Singlet oxygen molecules are known to have high chemical reactivity and can oxidize the surface of silicon nanocrystals. To confirm this conjecture we performed photooxidation experiments with samples having a different quantum yield and, therefore, a different singlet oxygen generation rate. Figure 2 shows the IR absorption spectra of porous Si layers in the spectral range of the Si-H$_x$($x = 1, 2, 3$) and the O-Si-O vibration bands.[12] While as-prepared layers exhibit only Si-H$_x$ surface bonds, the illumination in the oxygen ambient results in the oxidation of the nanocrystal surfaces. The oxidation is always more efficient for samples with high quantum yield. A complete rearrangement of the Si-H$_x$ stretching bond configuration shows that oxygen atoms backbonded to surface silicon atoms are introduced during illumination (Fig. 2, dashed line). The additional manifestation of oxidation can be seen as an efficient suppression of the S-H$_x$ wagging mode at ~ 650 cm^{-1} as well as the Si-H$_2$ scissor mode at ~ 912 cm^{-1}.[12] This effect is almost absent for the samples with a small quantum yield and the only noticable signature of oxidation appears due to strongly absorbing O-Si-O stretching bonds (Fig. 2, dotted line).

The time evolution of the Si-O bond concentration during illumination in oxygen ambient at 1 bar is shown in the inset of Fig. 2 (closed circles). On the initial stage of oxidation the decrease in the number of sites available for oxidation can be neglected. Instead, the sublinear rate of oxidation is governed by a reduced singlet oxygen generation rate due to photodegradation: again there is a clear anticorrelation between the oxidation rate and the PL quantum yield. The integral absorbance governed by the surface (O-)Si-H$_x$ and (Si-)Si-H$_x$ bond vibrations[12] does not change during photooxidation and evidences a constant number of surface H atoms (inset of Fig. 2, open circles).

In order to get oxygen backbonded a Si–Si bond should first be broken. The excitation energies of the $^1\Sigma$ and $^1\Delta$ singlet oxygen states being 1.63 and 0.98 eV, respectively,[11] are smaller than the Si-Si bond enthalpy (1.8 eV).[13] Therefore, the energy stored in a singlet oxygen molecule is not enough to break Si–Si bonds and to incorporate backbonded oxygen. Thus, the process of photooxidation similar to thermal oxidation is expected to be strongly temperature dependent. Figure 3 shows the IR absorption spectra of porous Si layers photooxidized at the same experimental conditions but at different temperatures. The rate of photooxidation varies significantly with temperature, indicating the presence of an additional energy barrier for the photooxidation reaction. Unfortunately, temperature-dependent measurements do not allow us to determine this value because the quantum yield of H-terminated samples and its temporal evolution, as well as the number of adsorbed oxygen molecules, are temperature dependent. We note that at 5 K, despite the highest singlet oxygen generation rate,[8] oxidation is completely absent at

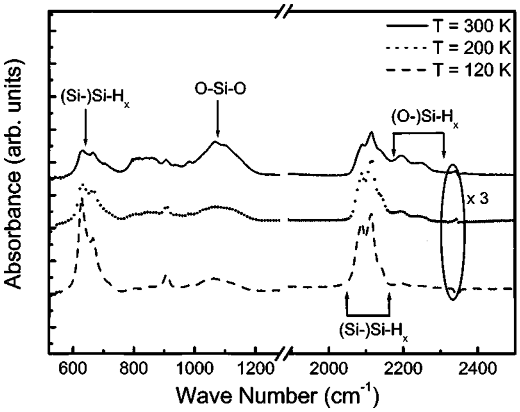

FIG. 3. IR absorbance of porous Si layers. Sample A after irradiation at different temperatures in oxygen ambient at 1 bar. $I_{ex.} = 100$ mW/cm^2. $E_{ex.} = 2.54$ eV; irradiation time is 1 h.

any photoexcitation levels (up to 10 W/cm^2) and any irradiation time (up to 10 h).

Oxidation mediated by singlet oxygen drastically modifies the emission properties of porous Si. Contrary to natural oxidation, which usually improves the quantum yield of porous Si layers due to passivation of dangling bonds,[14] the interaction of singlet oxygen with Si nanocrystals creates new dangling bonds.[3] Since singlet oxygen is generated in the gas phase it can interact with any nanocrystal assembling porous Si layers. The probability of interaction scales with the surface area of particular nanocrystals and the strongest degradation level is found as expected for the largest nanocrystals (see Fig. 1). A small increase of the PL intensity at higher energies is a direct result of photooxidation: the band gap of the oxidized nanocrystals shifts towards higher values due to quantum confinement.[14]

To conclude, we demonstrate that the efficient photodegradation of H-terminated porous Si layers is mediated by photosensitized singlet oxygen molecules. This effect is very similar to that known for light-emitting polymers or dye molecules. Therefore, H-terminated porous Si light-emitting devices will self-destruct during operation if fabricated without special attention to the elimination of molecular oxygen contamination. An alternative way of emission stabilization is the intentional oxidation of the surface of silicon nanocrystals which prevents the singlet oxygen formation.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] P. M. Fauchet, J. Lumin. **80**, 53 (1999).
[3] M. A. Tischler, R. T. Collins, J. H. Stathis, and J. C. Tsang, Appl. Phys. Lett. **60**, 639 (1992).
[4] M. Zacharias, J. Heitmann, R. Scholz, U. Kahler, M. Schmidt, and J. Bläsing, Appl. Phys. Lett. **80**, 661 (2002).
[5] M. Fujii, A. Mimura, S. Hayashi, and K. Yamamoto, Appl. Phys. Lett. **75**, 184 (1999)
[6] J. M. Buriak and M. J. Allen, J. Am. Chem. Soc. **120**, 1339 (1998).
[7] C. H. Chen and Y. F. Chen, Appl. Phys. Lett. **75**, 2560 (1999).
[8] D. Kovalev, E. Gross, N. Künzner, F. Koch, V. Yu. Timoshenko, and M. Fujii, Phys. Rev. Lett. **89**, 137401 (2002)
[9] E. Gross, D. Kovalev, N. Künzner, J. Diener, F. Koch, V. Yu. Timoshenko, and M. Fujii, Phys. Rev. B **68**, 115405 (2003).
[10] T. Zyung and J. J. Kim, Appl. Phys. Lett. **67**, 3420 (1995).
[11] P. H. Krupenie, J. Phys. Chem. Ref. Data **1**, 423 (1972).
[12] W. Theiss, Surf. Sci. Rep. **29**, 91 (1997).
[13] *CRC Handbook of Chemistry and Physics*, 78th ed., edited by D. R. Linde (CRC, New York, 1997).
[14] L. T. Canham, in *Optical Properties of Low Dimensional Silicon Structures*, edited by D. C. Bensahel, L. T. Canham, and S. Ossicini, NATO Advanced Study Institute Series, Vol. 244 (1993), p. 81.