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Electron-paramagnetic resonance and photoluminescence study of Si nanocrystals-photosensitizers of singlet oxygen molecules

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Abstract

Si nanocrystals formed by electrochemical porosifying of c-Si wafers are investigated by means of the electron-paramagnetic resonance (EPR) and photoluminescence (PL) techniques. The PL spectra and transients give evidence of the photosensitization of singlet oxygen molecules by the energy transfer from excitons confined in Si nanocrystals to oxygen molecules adsorbed on the nanocrystal surfaces. The EPR experiments show that the singlet oxygen generation is accompanied by a slowing down of the spin-spin relaxation time of Si dangling bonds on the nanocrystal surfaces. This effect is explained by the transition of a large part of the adsorbed O_2 molecules in their ground (triplet) states to the excited (singlet) ones. The EPR data allow us to estimate the concentration of the photosensitized singlet oxygen molecules to be on the order of 10^{18} cm^{-3}.

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Keywords: Microwave; Nanocrystals; Photoinduced effects

1. Introduction

Singlet oxygen ($^1O_2$) is a highly reactive form of the excited molecular oxygen [1], which has a broad range of applications in ecology, photochemistry and biomedicine, e.g. photodynamic therapy of cancer [2]. While $^1O_2$ is not effectively generated by the direct optical excitation of O_2 (this process is forbidden by the selection rules on spin and parity), it can be obtained in chemical or biochemical reactions or under electrical discharge [1]. Another way of $^1O_2$ production is the photosensitization process, where a molecule-donor, being effectively optically excited, can transfer its energy and spin to a molecule of O_2 in the ground (triplet) state followed by the transition to the excited (singlet) one [1]. Recently it has been found that Si nanocrystals (nc-Si) could be used to photosensitize the $^1O_2$ generation [2]. Highly developed surface of nc-Si and long radiative lifetimes of excitons confined in nc-Si result in a high efficiency of the $^1O_2$ photosensitization, which can be explained by the energy transfer from the excitons to O_2 molecules adsorbed on the nanocrystal surfaces [3]. On the one hand, the quenching strength of the exciton photoluminescence (PL) of nc-Si can be used as a measure of the $^1O_2$ generation efficiency [3–5]. On the other hand, up to now no data is available about the concentration of $^1O_2$ molecules photosensitized with nc-Si because it cannot be quantitatively determined by the PL method. At the same time, the electron-paramagnetic resonance (EPR) technique is a powerful tool to detect Si dangling bonds (DBs) on nc-Si surfaces. Also, EPR can be employed to probe the interaction between DBs and adsorbed O_2 molecules in their paramagnetic (triplet) state. Thus, the measurements of the spin relaxation time of Si DBs during photogeneration of $^1O_2$ can be used to evaluate the $^1O_2$ concentration.

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In this paper, we demonstrate the possibility of the EPR method to determine the concentration of the $^1O_2$ molecules photosensitized with nc-Si in porous Si powder.

2. Experimental details

Samples were prepared by electrochemical etching of (1 0 0)-oriented boron-doped bulk Si wafers with a resistivity of 10–20 Ωcm in a solution of hydrofluoric acid [3–5]. The current density and etching time were 50 mA/cm^2 and 1 h, respectively. Then the prepared free-standing porous Si layers were dried in air for several hours and then they were milled to get powder, which consists of nc-Si. The powder was kept in a vacuum chamber in oil-free vacuum with residual pressure of 10^{-5} Torr. The oxygen admission into the chamber was controlled by using a microvalve. In our experiments the oxygen pressure (P_{ox}) does not exceed 760 Torr.

PL was excited by a pulsed nitrogen laser ($\lambda = 337$ nm, $\tau = 10$ ns) and was measured by using a monochromator equipped with a photomultiplier. PL spectra were corrected for spectral response of the registration system. EPR spectra were detected by a Bruker ELEXSYS-500 X-band EPR spectrometer (sensitivity 10^{10} spin/G). For the precise determination of g-values of the EPR signals the Mn^{++} etalon was employed. Illumination of the sample during selected EPR experiments was performed by a 100 W mercury lamp.

3. Results and discussion

Fig. 1 shows PL spectra of a sample in vacuum and just after oxygen admission. The PL intensity in vacuum is 2–3 times higher that in oxygen. It should be noted that the fast pumping of the oxygen returns back the PL intensity (I_{PL}). However the prolonged illumination of the sample in O_2 atmosphere results in irreversible PL degradation due to the photooxidation process as reported in Ref. [5]. The reversible quenching of I_{PL} is well explained by the energy transfer from excitons confined in nc-Si to molecular oxygen nearby, i.e. the $^1O_2$ photosensitization. As one can see from the inset of Fig. 1 the PL quenching is most efficient at wavelength $\lambda_{PL} = 760$ nm (1.63 eV), which corresponds to the transition energy from the ground (triplet, $^3\Sigma$) state to the upper excited (singlet, $^1\Sigma$) state of molecular oxygen [1,3]. We note that the absolute value of the reversible quenching of I_{PL} in O_2 atmosphere is several times larger than it was reported earlier [3–5]. This fact indicates that the samples prepared are efficient photosensitizers of $^1O_2$.

Additional evidence of the efficient energy transfer from the excitons to O_2 is obtained by using time-resolved PL measurements. Fig. 2 shows typical PL transients of the exciton PL at $\lambda_{PL} = 760$ nm. The strong reversible decrease of the PL decay time for the sample in O_2 atmosphere in comparison to that in vacuum demonstrates a high efficiency of the $^1O_2$ generation. The ratio between the PL decay times for the sample in vacuum and in O_2 atmosphere is close to the PL quenching strength shown in Fig. 1. It is worth noting that the PL quenching level as well as the PL decay time shortening are dependent on O_2 pressure. The inset of Fig. 2 shows the ratio of the PL decay times vs P_{ox}. This dependence can be well described by the Langmuir approach for molecular adsorption in agreement with the steady-state PL measurements reported earlier [4].

Typical EPR spectra of the samples measured at a high level of the microwave power are shown in Fig. 3. The EPR signal is characterized by the effective g-factor of 2.0055 ± 0.0005 and the line width of 12 ± 0.5 G. The corresponding paramagnetic defects are usually attributed to so-called P_b-like centers, which are Si DBs at Si/SiO_2 inter-

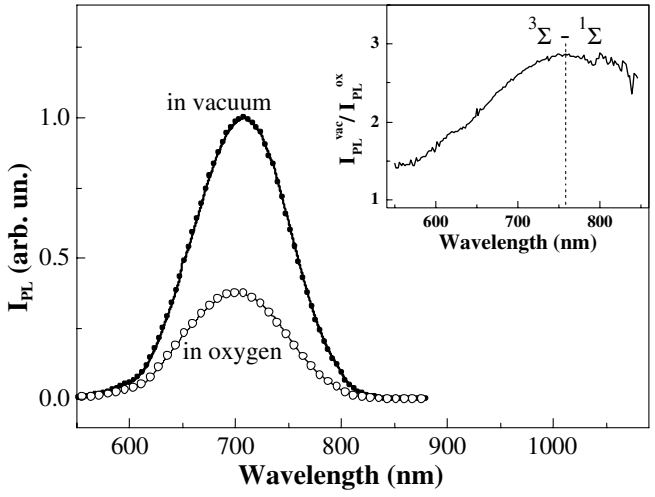

Fig. 1. PL spectra of nc-Si powder in oxygen atmosphere ($P_{ox} = 700$ Torr) and in vacuum. Inset shows spectral dependence of the PL quenching strength.

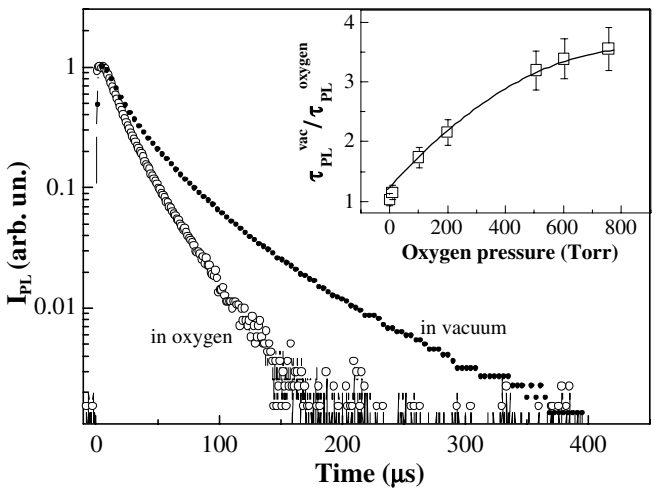

Fig. 2. Transients of the exciton PL at 760 nm measured for of nc-Si powder in oxygen atmosphere ($P_{ox} = 700$ Torr) or in vacuum. Inset shows ratio of the PL decay times in vacuum and in oxygen vs P_{ox}.