Effect of high-pressure water-vapor annealing on energy transfer in dye-impregnated porous silicon

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ABSTRACT

We have studied the effect of high-pressure water-vapor annealing (HWA) on the excitation energy transfer from Si nanocrystals to dye molecules in porous Si layers. Efficient photoluminescence, originating from both RhB molecules and Si nanocrystals, was observed. The behavior of the polarization memory of the photoluminescence showed the presence of energy transfer from the surface-passivated Si nanocrystals to RhB molecules. The fact that HWA, which is an effective method to stabilize and enhance the emission from Si nanocrystals in porous Si, does not suppress the energy transfer is an important result since it makes possible the realization of stable Si/dye-nanocomposite functional devices.

1. Introduction

The composite system based on an organic dye penetrated into a solid matrix is attracting wide interest because of its useful applications such as light concentrators in solar cells, optical waveguides, lasers, sensors and nonlinear optical components [1–4]. Embedding dye molecules in a rigid matrix leads to a better protection of the active molecule from the environmental attack and/or photofragmentation, resulting in an increase of the life of the material [5]. Different methods to trap organic molecules within a solid substrate have been developed, including direct soaking of the host material with dye solutions [6–8]. It has been shown that porous silicon (PS) can be impregnated with laser dyes by the latter method [9–11].

Analysis of the PL and its polarization memory (PM) has shown [12] that energy transfer can take place from Si nanocrystals to dye molecules in RhB-impregnated PS samples. PS is therefore a good host for potential functional devices. However, as-formed PS exhibits poor stability because its surface, mostly terminated by Si–H$_x$ bonds, is easily oxidized in air. This drawback seriously limits the practical use of PS.

Nevertheless, PS can be well stabilized using chemical modification with organic molecules [13]. Very good stabilization has been obtained by treating PS with high-pressure water-vapor annealing (HWA) [14,15]. HWA produces a very stable thin oxide layer of very good structural quality at the inner surface of PS. Using HWA, very stable and efficient photoluminescence (PL) has been obtained from PS [14,15]. Electroluminescence has also been stabilized [16].

HWA-treated PS is a promising candidate for the host material for stable and efficient Si/dye-nanocomposite systems. However, the barrier created by the passivating oxide thin layer may hinder or prevent energy transfer from Si nanocrystals to dye molecules.

In the present study, we have investigated the possibility of energy transfer in HWA-treated PS impregnated with RhB molecules. The PL spectra and PM of various samples have been investigated. Different experimental conditions and the effect of preliminary electrochemical oxidation [17] have been studied.

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2. Experimental

PS layers were formed by electrochemical anodization of (100)-oriented lightly doped p-type (resistivity: 1–4 Ω cm) Si wafers in an electrolyte solution composed of HF (40 wt%):C_2H_5OH:H_2O = 2:1:1 at a current density of 50 mA/cm^2 for 250 s. The PS samples were then subjected to HWA at a water-vapor pressure, temperature and time of 2.6 MPa, 3 h and 260 °C, respectively. After HWA, these samples were immersed in an ethanoic solution (5×10^{-4} M) of Rhodamine B (RhB) for 1 h.

For comparison, we prepared some additional PS samples under the same etching conditions, and immersed them in the solution of RhB for the same time before they are processed by HWA in order to examine the effect of HWA performed after dye molecules are incorporated.

Other PS samples were prepared under the same etching conditions to see the effect of electrochemical oxidation performed before HWA and dye impregnation. The electrochemical oxidation was carried out at a current density of 50 mA/cm^2 until the potential of the PS electrode rose sharply, in a solution of H_2SO_4 (1 M) [17]. Dye impregnation of these samples was performed after they were processed by HWA.

Fourier transform infrared (FTIR) spectra were recorded in the absorption mode using a Bruker IFS 66 v/s FTIR spectrometer with a resolution of 4 cm^{-1}. PL and PM spectra were measured using a fiber-optic spectrometer (Ocean Optics USB 2000). Either an argon laser (514.5 nm) or a diode laser (410 nm) was used for excitation. All the spectroscopic measurements were performed at room temperature.

The degree of PM is defined as $P = (I_\parallel - I_\perp)/(I_\parallel + I_\perp)$, where $I_\parallel$ and $I_\perp$ are the PL emission components polarized parallel and perpendicular to the polarization direction of the excitation light, respectively [18]. The excitation light was polarized along the direction of [001] crystallographic orientation. We did not find any dependencies of PM on the polarization direction of excitation light for the emission component originating from RhB molecules. For the PL component from Si nanocrystals, however, we observed some dependencies on the polarization direction that were similar to those reported before [19].

3. Results and discussion

3.1. Infrared absorption

The surface of our as-anodized PS layers is hydrogen-terminated [15,17]. The effect of HWA on the structure of PS has been studied using FTIR spectroscopy in previous works [15,17]. A FTIR spectrum of a HWA-treated PS layer is shown in Fig. 1. The main result is that HWA induces a thin oxide layer at the surface of PS, as shown by a large absorption peak (at about 1080 cm^{-1}) due to vibrations of Si–O–Si bridges. The original SiH bonds located at the surface of PS before HWA have almost completely disappeared, as shown by very weak absorption by SiH bending (~950 cm^{-1}) and stretching (~2050–2300 cm^{-1}) modes. This result confirms that most of the surface is covered by a thin oxide layer.

Fig. 1 also displays the FTIR spectrum of a HWA-treated PS sample after impregnation with RhB molecules. The absorption bands at 1400, 1533 and 1642 cm^{-1}, which are characteristics of the stretching mode vibrations of the −CH$_2$, C–H and C=C species of the RhB molecule, respectively, confirm the incorporation of RhB molecules inside the surface-passivated PS layer. The good incorporation was expected since the same experimental procedure worked well with as-formed PS [12].
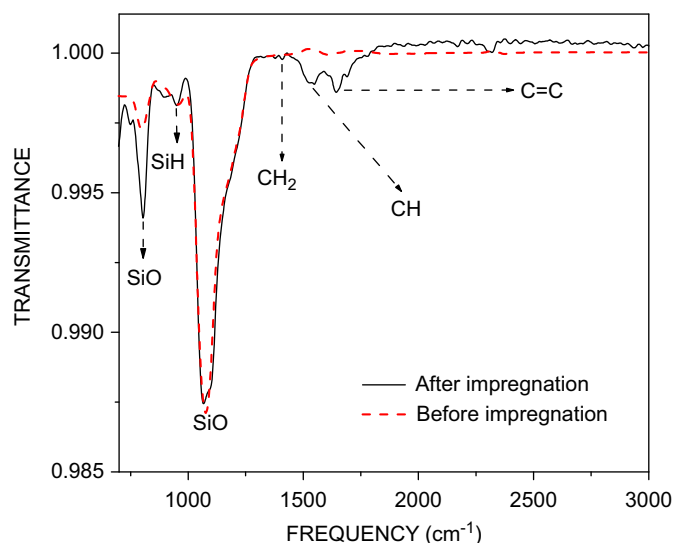

Fig. 1. FTIR spectra of a HWA-treated PS sample before and after impregnation with RhB molecules.
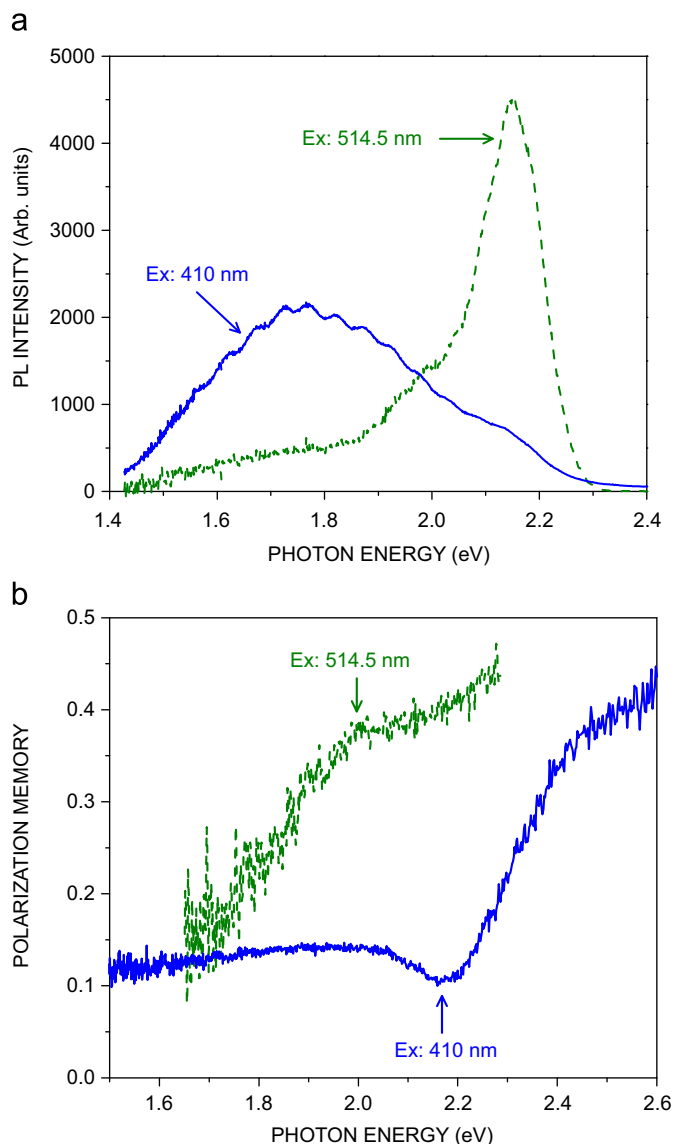
3.2. Effect of HWA before dye impregnation

Fig. 2(a) shows PL spectra obtained from a PS sample impregnated with RhB molecules after HWA. The contributions of both RhB molecules and Si nanocrystals, on the emission, can be observed. Each spectrum is composed of a broad band at ~1.8 eV originating from Si nanocrystals and a narrow band at ~2.1 eV representing the emission by RhB molecules. The latter emission becomes prominent under the excitation at 514.5 nm (2.41 eV) because this wavelength coincides well with the absorption spectrum of RhB molecules. To the contrary, the absorption by RhB molecules is very weak at the excitation wavelength of 410 nm (3.02 eV). This means that the RhB-related emission band obtained under the excitation at 410 nm can hardly be attributed to a direct excitation of the dye molecules. Instead, most of the emitted photons in the 2.0–2.3 eV range may result from the process of energy transfer from Si nanocrystals to RhB molecules. In fact, the necessary conditions for energy transfer predicted by the Förster–Dexter theory are satisfied since the high-energy part of the emission lineshape of Si nanocrystals overlaps with the absorption lineshape of RhB.

Fig. 2(b) shows the PM obtained for the same sample as that whose PL spectra are shown in Fig. 2(a). Under the excitation at 514.5 nm (2.41 eV), the degree of PM for the emission of RhB molecules is very high (~0.4). This implies that most of RhB molecules are excited directly at this wavelength. However, the degree of PM at the same emission photon energy range decreases remarkably when the PS sample is excited at 410 nm (3.02 eV).

Emissions resulting from excitation energy transfer have small values of P because the memory of polarization is lost during the process of energy transfer. This phenomenon is amplified by the fact that the dye molecules in PS are thought to be orientated randomly inside the porous matrix, since the PS layer has a sponge-like network structure.

Consequently, the PM results strongly suggest that there exists a significant amount of energy transfer from HWA-treated Si nanocrystals to RhB molecules. The efficiency of this energy transfer is found to be comparable to those of RhB-impregnated PS samples prepared without HWA. Thus, HWA provides a useful means to fully take advantage of energy transfer
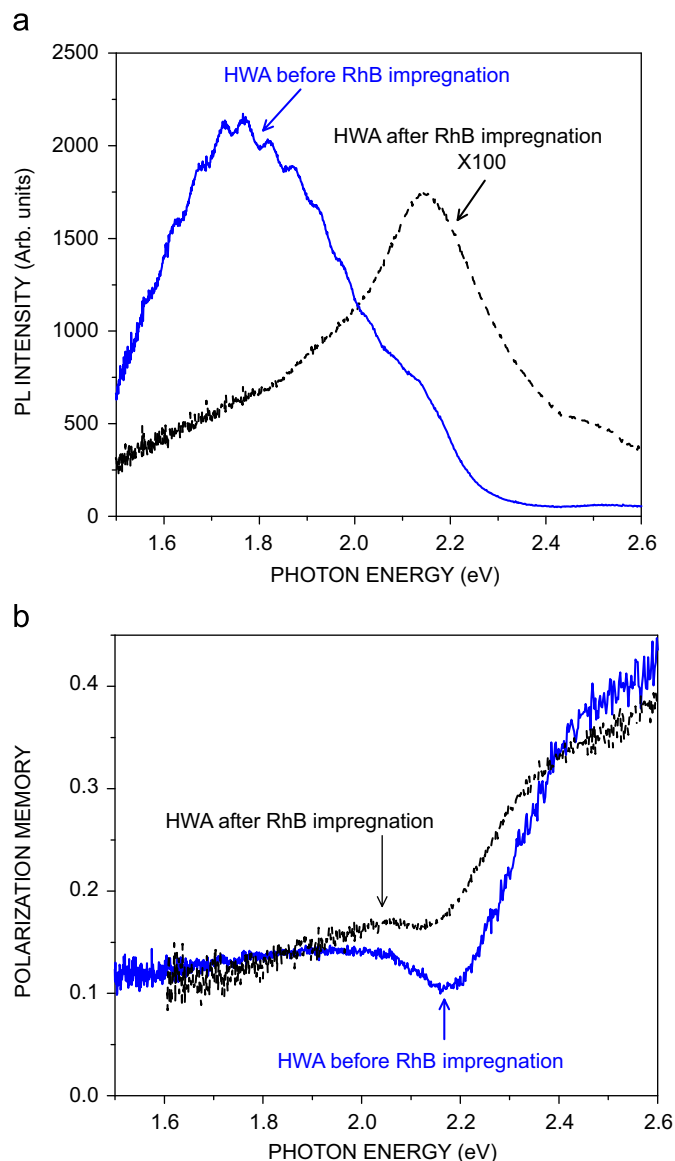
a

b

Fig. 2. PL (a) and PM (b) spectra obtained for excitation wavelengths of 514.5 and 410 nm for a PS sample treated by HWA before dye impregnation.

a

b

Fig. 3. PL (a) and PM (b) spectra excited at 410 nm for PS samples subjected to HWA *after* and *before* RhB-impregnation.

characteristics while getting stable and high-efficiency PL at the same time.

3.3. Effect of HWA after dye impregnation

Fig. 3 shows the PL and PM spectra for a PS sample subjected to HWA *after* impregnation of RhB molecules. For comparison, we also show corresponding spectra for the sample subjected to HWA *before* dye impregnation. As shown from the figure, the emission of the former sample is less efficient. In particular, the emission component originating from Si nanocrystals is very weak. This can be attributed to a significant amount of nonradiative recombination centers produced on the surface of Si nanocrystals as a result of the annealing process in the presence of dye molecules. These nonradiative centers should decrease the lifetime of photoexcited carriers, resulting in a decrease in the probability of energy transfer. Deactivation of the energy-transfer process is actually seen in the results of PM as shown in Fig. 3(b), since there appears only a small dip in the degree of PM at around 2.2 eV.
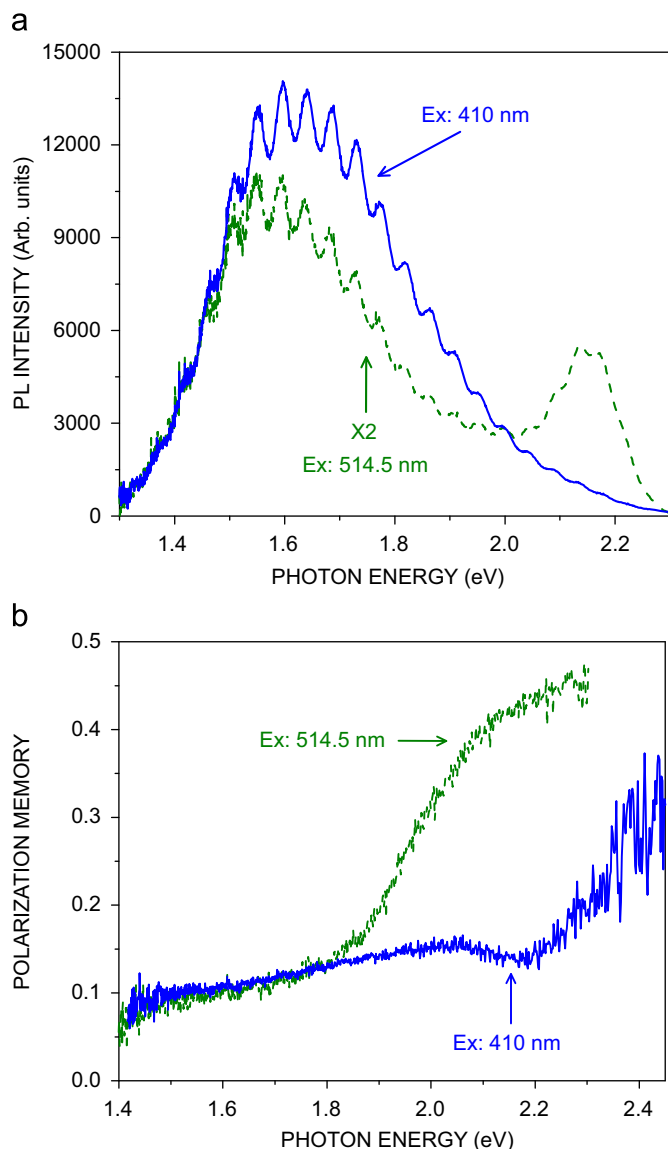
3.4. Effect of electrochemical oxidation before HWA and dye impregnation

Fig. 4(a) shows the PL spectra obtained for a PS sample which was subjected to electrochemical oxidation before it was treated by HWA and then by dye impregnation. The PL component originating from Si nanocrystals (peaked at ~1.6 eV) is slightly red-shifted compared to that of the samples which were not subjected to electrochemical oxidation (Fig. 2). Similar red-shift has been observed in PS samples without dye molecules [17].

The degree of PM in this sample is shown in Fig. 4(b). We can see that there is a dip at around 2.2 eV in the curve of the degree of PM for the excitation wavelength of 410 nm, demonstrating the presence of energy transfer in this sample. As shown in Fig. 5, the electrochemical oxidation step induces a smaller dip in PM at around 2.2 eV, and therefore tends to reduce the efficiency of the energy transfer. This result can be attributed to the fact that the average energy of photoexcited electron–hole pairs is lowered as indicated by the red-shift in the PL component of Si nanocrystals, reducing the overlap between the emission
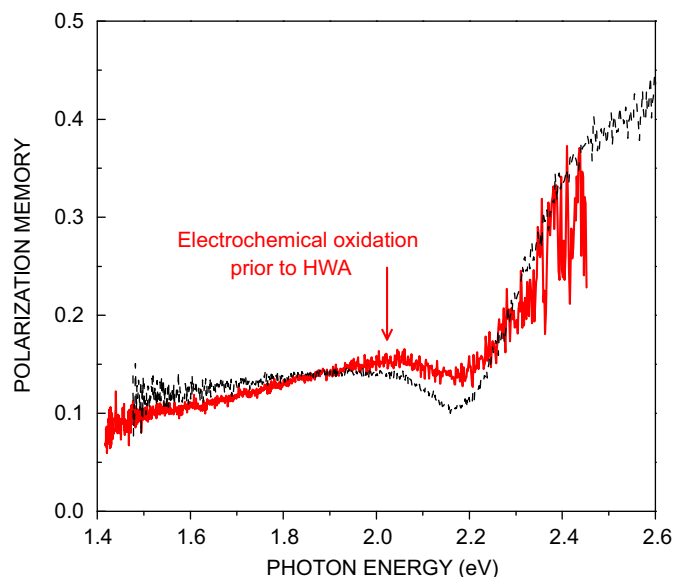
Fig. 5. Effect of electrochemical oxidation performed prior to HWA and dye-impregnation treatments on the degree of PM. The sample represented by the solid line has been electrochemically oxidized while the other one has not. The excitation wavelength was 410 nm.

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Fig. 4. PL (a) and PM (b) spectra for two excitation wavelengths of a PS sample electrochemically oxidized before HWA and dye-impregnation treatments.

spectrum of Si nanocrystals and the absorption spectrum of RhB molecules.

4. Conclusion

The effect of HWA, which is known to efficiently stabilize PS, on the energy transfer from Si nanocrystals to RhB molecules incorporated into PS has been studied. It is shown that the passivation provided by HWA do not suppress the energy transfer significantly. The energy transfer was found more efficient when HWA is performed before rather than after dye impregnation. Electrochemical oxidation performed before HWA results in a lower energy transfer efficiency due to reduced overlap of energy levels. HWA can be applied to PS/dye-molecule nanocomposites as an effective method to passivate the surfaces of Si nanocrystals without hampering the energy transfer characteristics.