White light from annealed porous silicon: Broadband emission from violet to the near infrared

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ABSTRACT

We report white light emission under UV excitation from porous silicon (PS) samples annealed at different temperatures and surrounding atmospheres. The photoluminescence (PL) spectra show a broad emission from ultraviolet to near infrared. Annealed PS samples were studied by photoluminescence, FTIR and EPR spectroscopies. The PL spectra were found to include three main components centered at the violet, green and infrared. The FTIR experiments suggest the formation of a system composed by silicon nanocrystals embedded in a nonstoichiometric silicon oxide matrix (nc-Si/SiO$_x$). The EPR measurements reveal the existence of the well-know P_{b0} ($g \sim 2.007$) and P_{b1} ($g \sim 2.004$) centres, and of a signal at $g \sim 1.9997$. The combined PL, FTIR and EPR results suggest that violet and green emissions come from oxygen-excess defects in SiO$_x$ while the infrared emission is related to defects located at Si/SiO$_x$ interfaces.

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1. Introduction

In the last decade, light emission from porous silicon (PS) and similar systems such as silicon nanocrystals embedded in SiO$_x$ and silicon nanowires have been subject of extensive investigation. However, a full understanding on the processes and the mechanisms involved in the light emission from these materials have not been achieved and are still under debate [1]. Several models have been proposed to explain the visible photoluminescence (PL) from PS, the quantum confinement (QC) and the quantum confinement/luminescent centers (QCLC) models being the most widely invoked [2]. Depending on the size of silicon nanocrystals and the nature of oxygen species formed during oxidation, different processes may occur. Extensive discussions of the different models that describe the behaviour of the PL from PS and other types of nanostructured Si can be found in references [3–6]. White luminescence from materials and devices is a topic that has attracted great interest due to its relevance for potential applications in white light illumination devices. To our knowledge, white light emission from bare PS has been reported rarely. Tsai et al. [7] and Karacali et al. [8] reported the white PL in the 350–700 nm range

from p-type PS annealed at high temperature and from oxidized/carbonized PS, respectively. The purpose of this work is two-fold: (A) to show that white light emission from n-type PS that extends to a broader range into the near-IR ($\sim$900 nm) can be achieved by annealing samples in Ar+O$_2$, and (B) to elucidate, combining PL with electron paramagnetic resonance (EPR) and Fourier transform infrared (FTIR) spectroscopies, the physical origin of the components to the broad PL spectra observed.

2. Experimental section

The PS samples were obtained from anodization of n-type crystalline silicon. Fabrication details are described in a previous report [9]. The annealing processes were carried out in a quartz tube placed in a horizontal tubular furnace under constant Ar and O$_2$ flow rates. The as-prepared PS samples were placed at 19.5 and 23.5 cm from the centre of the furnace downstream. The furnace was heated to 1100 °C at a rate of 27 °C/min and then kept at 1100 °C for 20 min. The temperature at the PS substrates positions reached 950 and 840 °C, respectively. In order to study the role of the O$_2$ flow, two different O$_2$ flow rates were used (8 and 40 sccm, while the Ar flow rate was kept constant at 125 sccm). PL spectra were excited by illuminating the samples at ambient air with a He–Cd laser set at a wavelength of 325 nm with 15mW power over

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an area of 0.031 cm^2. All PL spectra were corrected for the detection system response. The FTIR transmission measurements were carried out in a Thermoscientific model 3000 spectrometer. The EPR experiments were performed in a Bruker EMX-Plus EPR Spectrometer in the X Band. The magnetic field was applied parallel to the ⟨1 0 0⟩ axis of the PS crystalline Si substrate.
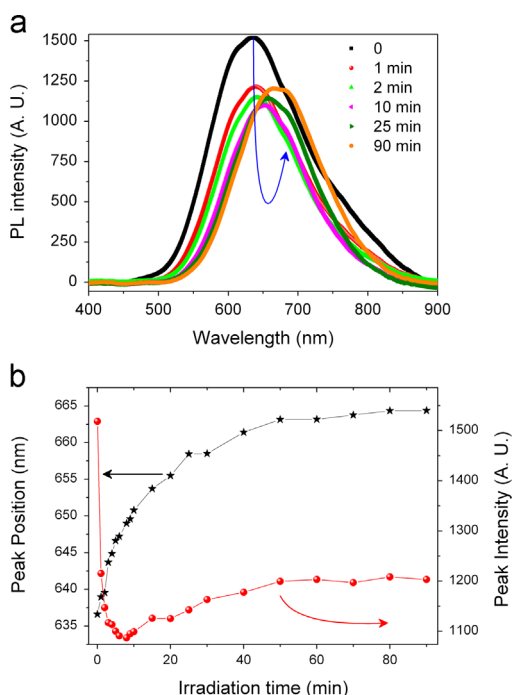

Fig. 1. (a) PL spectra from the as-anodized PS sample (curve arrow shows the evolution of PL peak) while being irradiated with 325 nm photons, (b) evolution of the PL peak intensity and position.

3. Results and discussion

Fig. 1(a) and (b) show the PL behavior for an as-anodized PS sample and its evolution while being irradiated with the HeCd laser excitation source. As shown, a peak at 637 nm is observed which is initially quenched, reaching a minimum intensity after 8 min, followed by an increase for larger irradiation times. Concomitantly, a monotonic redshift of the PL peak position is observed throughout the experiment. This behavior would be in disagreement with a simplistic interpretation of the QC model, which predicts a blueshift as a result of the reduction of the nanocrystalline size due to photo-oxidation process. Alternatively, the results shown in Fig. 1 may be explained by the QCLC model, which proposes that excitons are created in the nanocrystalline silicon and transported to the c-Si/SiO$_2$ interfaces to recombine radiatively in specific centers. Taking this into account, it is reasonable to suggest that the UV illumination leads to the creation of silicon dangling bonds (which act as efficient non-radiative recombination centers) by photoinduced hydrogen diffusion and effusion, as previously suggested [10] and, as a consequence, the quenching of PL intensity is observed for short times. This process is counterbalanced by the activation of previously H-passivated luminescent centers at the c-Si/SiO$_2$ interfaces emitting in the NIR that lead to both, the redshift and increasing PL intensity for longer times.

Fig. 2(a and b) shows the PL behavior of annealed PS at different conditions (varying temperature and O$_2$ flow rate) and their respective fit with 3 Gaussian components. After the annealing treatment, a broad white light emission from 350 to 900 nm was observed, which can be decomposed in NIR (∼760 nm–E∼1.65 eV), green (∼500 nm–E∼2.47 eV) and violet emissions (∼400 nm–E∼3.1 eV) for all samples. In Fig. 2(c), the relative intensities of these components are depicted. It is seen that PL intensities are greater for samples annealed with higher oxygen flow rate. In addition, the intensity of violet and infrared emissions are strongly affected (the former decreases and the latter increases) when the annealing temperature is increased from
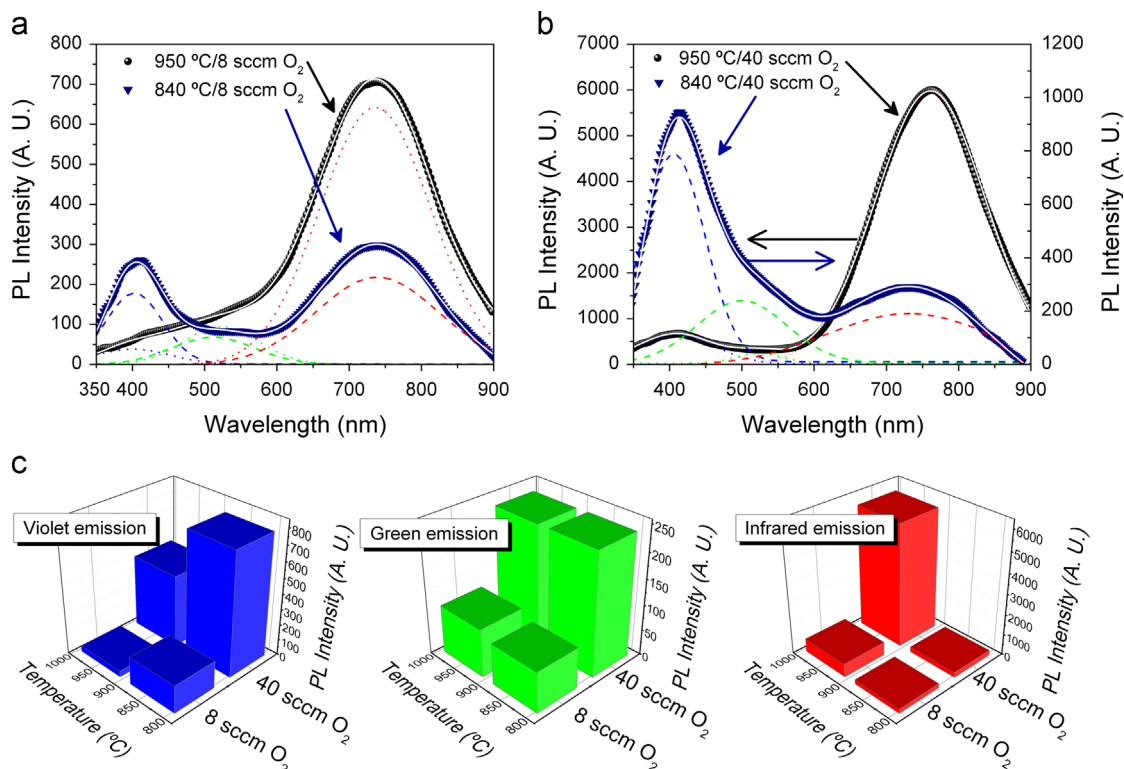

Fig. 2. (a and b) PL spectra from annealed PS at different conditions. (c) Relative intensity of PL components. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
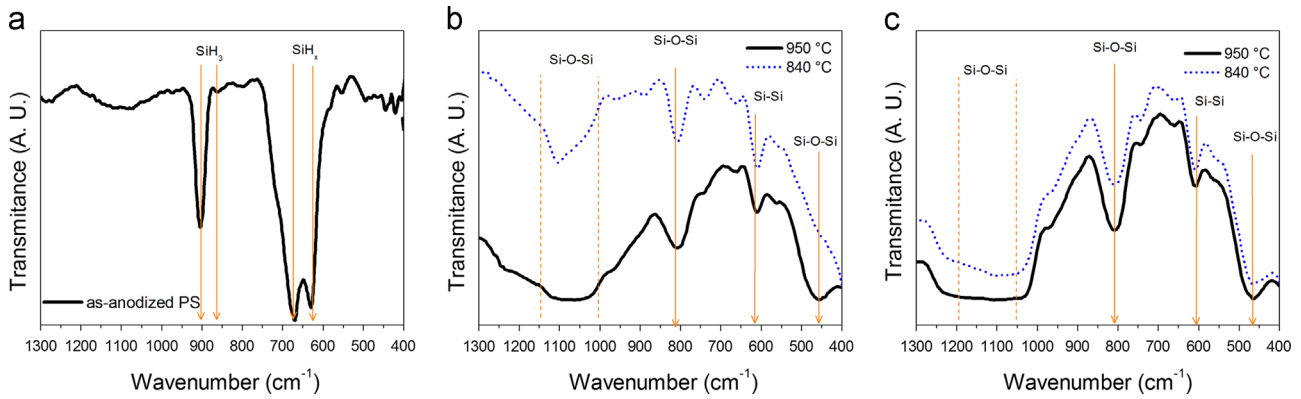
Fig. 3. FTIR transmittance spectra for (a) the as-anodized PS sample, and for annealed PS samples (O_2 flow rate of (b) 8 sccm and (c) 40 sccm).
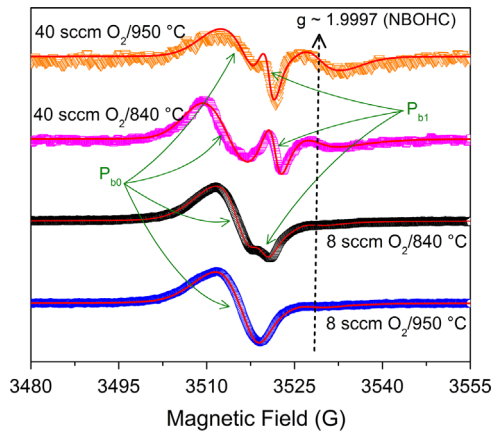

Fig. 4. EPR spectra for the annealed PS samples (symbols) and their respective simulations (solid lines).

840 to 950 °C, while the green emission intensity remains essentially unchanged. For annealing experiments carried in pure Ar (at both 840 to 950 °C), the PL was totally quenched in the 200–1100 nm region. This can be attributed to the complete driving out of H, which leaves behind efficient non-radiative centers (Si dangling bonds).

The results of FTIR experiments in the 400–1300 cm^{-1} range are shown in Fig. 3(a–c) ((a) as-anodized PS sample and (b–c) annealed PS). As observed, the bands due to Si–H vibration modes (907–862 and 670–630 cm^{-1}) predominate for as-anodized PS [11,12], while only a small band associated with Si–H (670–630 cm^{-1}) [12] remains for the annealed samples. Furthermore, Si–O–Si (stretching at $\sim 1100\ cm^{-1}$, bending at $\sim 800\ cm^{-1}$ and rocking at $\sim 470\ cm^{-1}$) modes [11] are clearly detected as well. The Si–O–Si broad band at $\sim 1100\ cm^{-1}$ implies the formation of silicon sub-oxide structures (SiO_x with $x < 2$) [11]. The band at 615 cm^{-1} may be attributed to Si–Si vibrational modes [13]. These features indicate that during the annealing, the PS samples were strongly oxidized and suggest the formation of silicon nanocrystals embedded in a SiO_x matrix [14].

The increasing intensity of the Si–O–Si modes observed in samples annealed with increasing oxygen flow rate, as observed in Fig. 3(b and c), can be correlated with the greater intensity of the violet emission for increased oxygen flow rate. Hence, it seems that the violet emission is related to radiative recombination in defects associated to excess O in SiO_2. According to Zhu et al., the origin of the violet emission (~ 3.2 eV) observed in a-SiO_x:H is related to the presence of the peroxy linkage defect (–Si–O–O–Si), which is a well-know oxygen-excess defect in SiO_x [15]. As for the green emission, although its intensity is not affected by temperature, it shows a similar trend to that exhibited by the violet component with increasing oxygen flow rate, so it is

reasonable to also associate this emission with oxygen-excess defects. As discussed previously, the photo-irradiation effects shown in Fig. 1 indicate that the NIR (~ 1.65 eV) emission in annealed PS samples is related to radiative defects at the c-Si/SiO_x interface or the SiO_x matrix. Prokes et al. have associated an emission at 1.72 eV from photo-annealed PS with the presence of NBOHC (non bridging oxygen hole center) defects [16]; although the NBOHC are responsible for emission at ~ 1.9 eV from SiO_x, the local strain and chemistry may modify the energy of the NBOHC defect state and consequently the corresponding PL emission energy in the 1.4–2.0 eV range [17].

In Fig. 4, the EPR spectra and their simulations are shown. Three main components in all spectra with g-factor values around 2.0069–2.0072, 2.0034–2.0042 and 1.9999–1.9997, respectively, are revealed. The intensity of the $g \sim 1.9997$ resonance is greater for samples annealed with higher oxygen flow rate. This paramagnetic centre could be attributed tentatively to a NBOHC defect, which has been identified in a-SiO_2 [18]. The other two components of the EPR spectra can be associated with the well known P_{b0} ($g \sim 2.007$) and P_{b1} ($g \sim 2.004$) centers [19].

In summary, broadband white light emission from annealed n-type PS in Ar+O_2 was obtained and studied. The annealing treatments of PS led to the formation of a SiO_x matrix embedding the Si nanocrystals. Three main PL components (violet, green and NIR) could be identified. Analysis of the PL and FTIR spectra for samples annealed under different O_2 flow rates shows that the violet and green emissions are originated from oxygen-excess defects in SiO_x, while the NIR emission is originated from defects located at c-Si/SiO_x interfaces, ascribed tentatively to NBOHC [11,12] in consistency with the observation of the $g \sim 1.9997$ resonance in the EPR spectra [13].

Acknowledgements

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