

Short communication

Photoluminescence response of gas sensor based on CH_x/porous silicon—Effect of annealing treatment

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Abstract

The most spectacular feature of porous silicon (PS) is its ability of emitting very intense visible light at room temperature and to use this light emission as a sensor signal. In this paper, we report the sensitivity of porous silicon photoluminescence (PL) to carbon dioxide and propane gases. A hydrocarbon film has been applied to PS surface to enhance its luminescence since a complete surface passivation is important to suppress or reduce non-radiative recombination centres. The operation sensor effect is based on the variation of the photoluminescence of the CH_x/PS region due to the interaction with gaseous substances. Presence of carbon dioxide reduces the PL intensity while propane provokes an opposite behaviour. The PL quenching phenomenon leads itself to interesting optical sensor applications. The annealing effect on the photoluminescence of a p-type CH_x/PS has been investigated. The orange light disappears and an intense blue light is obtained. Moreover, the effect of this treatment on the PL response of porous silicon in presence of CO₂ and propane gases has also been studied.

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1. Introduction

The discovery of room temperature visible photoluminescence (PL) from porous silicon (PS) has attracted considerable attention [1]. Due to its large internal surface and high chemical reactivity with the environment, PS has stimulated great interest on sensing applications [2,3]. Properties such as PL and electrical conductivity change when molecules are adsorbed to the PS surface [4,5]. When an oxidizing or reducing gas interacts with the nanostructure surface, the local charge transfer induces electric dipoles, which can either give a positive or negative contribution to the confining potential. These potential height variations may significantly change the quantum wire electronic structure to a point where a clear signature is detectable in the optical and transport properties [6].

Stabilization of PS photoluminescent properties in the actual device is an important step towards the fabrication of devices for

characterization in reactive environments. As a matter of fact, the nature of visible photoluminescence of PS has not been established yet, as the efficiency and wavelength range of the emitted light can be affected by the physical and electronic structures of PS surface [7–9]. However, the most basic questions concerning the origin of the PL of porous silicon films still remain not completely understood.

Strong PL emission is generally in the red-green region and blue light emitting porous silicon materials are difficult to prepare. Some approaches, such as high-temperature annealing, boiling water treatment and carbon plasma implantation have been attempted. Their objective is the same, reducing the size of the silicon nanocrystal to further enlarge the band gap and a blue light emission could result [10–12].

In this work, porous silicon coated with a hydrocarbon groups (CH_x) was annealed at different temperatures, where the C will react with Si to produce SiC [13] and an intense blue light is emitted from the thermally carbonised PS surface after annealing at 600 °C.

Luminescence properties of modified PS samples towards carbon dioxide and propane gases before and after the annealing treatment were investigated.

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2. Experimental procedure

One centimetre square PS samples have been prepared by electrochemical anodization from (1 0 0) oriented, $1\ \Omega\ \text{cm}$ p-type, $450\ \mu\text{m}$ thick FZ-silicon wafers. The etching solution was prepared by the addition of methanol to 25% of an aqueous solution of HF. Etching was carried out as a three electrode anodic procedure at a current density of $15\ \text{mA}/\text{cm}^2$ for 30 min. After etching, the samples were rinsed in methanol and allowed to dry under nitrogen. The samples were then stored in a dessicator until use. Before CH_x deposition, the silicon samples were dipped in a mixture of 1 M hydrofluoric acid and 2 M ammonium fluoride solution for 1 min. Then, porous silicon samples were coated with hydrocarbon groups (CH_x) by RF (13.56 MHz) plasma decomposition of methane gas [14,15]. The deposition rate was about $60\ \text{\AA}/\text{min}$. The samples were divided into two groups: the first group, without annealing, was analysed in the flow of different gases. The second group was first annealed at different temperatures from 200 to $600\ ^\circ\text{C}$ for 30 min under nitrogen atmosphere and then exposed to a flow of the gas.

PL spectra were recorded at room temperature using an UV light (325 nm) from a Xenon lamp as the excitation source from a Perkin-Elmer LS-50B luminescence spectrometer. All spectra were corrected for wavelength dependent detection efficiency using the correction curve delivered by spectrometer supplier. Sensitivity: signal to noise is 500:1 rms, excitation and emission band pass: 10 nm.

The sample holder was contained in a chamber, equipped with a quartz window, where a mixture of 100 ppm of CO_2 or CH_4 in air from certified bottles can be introduced monitoring pressure and flux. Knowing the volume of the chamber and by control of the volumetric flow of the gas through the mass flow controllers and pressure of gas, we determined the mass concentration then we carried out conversion into ppm.

Fourier transform infrared spectroscopy (FTIR) was used to characterize samples before and after the annealing treatments. All FTIR spectra were recorded at $4\ \text{cm}^{-1}$ resolution in the $400\text{--}4000\ \text{cm}^{-1}$ range with a Nicolet Nexus spectrometer in transmission mode.

3. Results and discussion

The photoluminescence spectra of the porous silicon in as-prepared samples (a), coated with a CH_x layer (b) and after annealing at $200\ ^\circ\text{C}$ (c), $400\ ^\circ\text{C}$ (d) and $600\ ^\circ\text{C}$ (e) are presented in Fig. 1.

As seen from this figure, the as-prepared PS sample shows a broad asymmetric PL band with an apparent maximum at 670 nm. The band intensity increases when the samples were coated with a CH_x layer of $240\ \text{\AA}$ thickness. And the orange light is intense enough to observe with the naked eye with a maximum PL peak intensity located at 623 nm. In a previous work [16], we have shown that an efficient visible PL was obtained from a hydrocarbon layer coated PS. Using FTIR analysis, we deduced that the contribution of a higher carbon content in the PS layer in the form of methyl groups bonded to the silicon, as shown in Fig. 2, was probably the origin of the PL enhance-

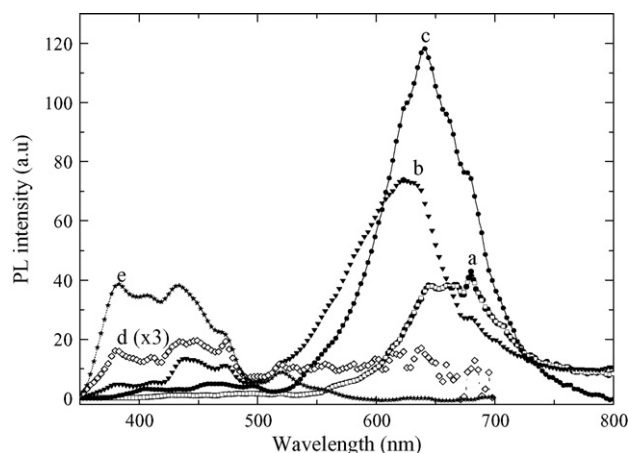


Fig. 1. Room temperature PL spectra of as-prepared samples (a), coated with a CH_x layer (b) and after annealing at $200\ ^\circ\text{C}$ (c), $400\ ^\circ\text{C}$ (d) and $600\ ^\circ\text{C}$ (e).

ment. This could arise from exciton-like electron–hole pairs with a strong Coulomb interaction and the confinement of photo-generated electron hole pairs inside π -bonded ‘grains’ in the polymer-like carbon films. However, the origin of luminescence of PS still remains unclear and this seems to prevent us from establishing a definitive explanation for the origin of the PL. Fig. 2 compares the FTIR spectra from an as-prepared PS sample and a CH_x coated PS sample. In the $2100\text{--}2300\ \text{cm}^{-1}$ region, peaks related to $\text{O}_y\text{--SiH}_x$ stretching vibrations appear (O_2SiH at $2190\ \text{cm}^{-1}$, O_3SiH at $2248\ \text{cm}^{-1}$) for the as-prepared PS sample. An intense band located in the $1000\text{--}1100\ \text{cm}^{-1}$ region attributed to Si--O--Si and Si--O_x stretching vibrations indicates an oxidation of the surface. This could be attributed to the Si--H bond oxidation in the etching solution and to exposure to ambient conditions. After CH_x deposition, strong absorption peaks associated with CH_x species are found in the stretching region $2850\text{--}2980\ \text{cm}^{-1}$ and in the bending region $1300\text{--}1500\ \text{cm}^{-1}$ [17]. In addition, another vibration band is clearly observed around $1000\text{--}1290\ \text{cm}^{-1}$ which is attributed to the Si--CH_3 symmetric bending at $1240\ \text{cm}^{-1}$ (as a shoulder) and the stretching vibration of SiO_x bond confound to the Si--O--C vibration [18].

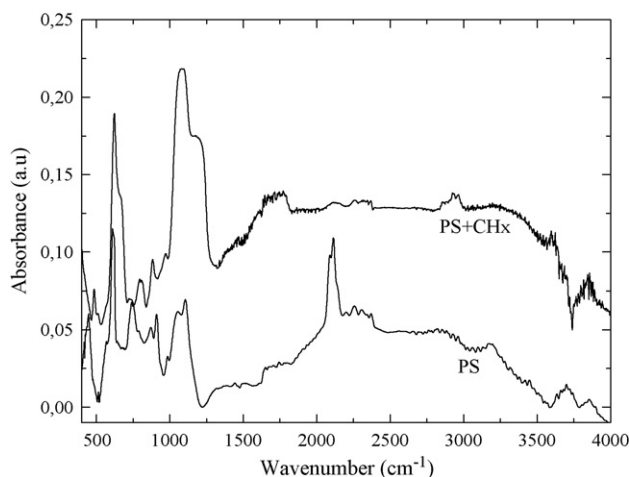


Fig. 2. Infrared absorption spectra of porous silicon before and after the CH_x deposition.

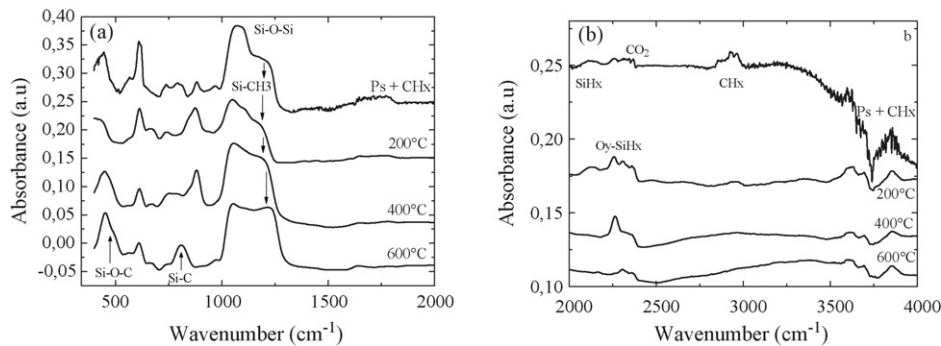


Fig. 3. FTIR spectra for samples annealed at 200, 400 and 600 °C compared to the PS coated with CH_x without annealing.

After annealing at 200 °C, the PL intensity increases substantially and shows a red shift of about 16 nm, as illustrated in Fig. 1. But following annealing at 400 °C, the PL intensity decreases. When increasing temperatures to 600 °C, a remarkable PL enhancement in the blue region was observed. The well-known red emission is now totally absent, the original peaks at 670 and 623 nm have been quenched. The PL arising from PS is generally located in the red and/or infrared spectral region and the blue band cannot be observed [19]. From our PL spectra, the orange light does not reappear even after high-temperature annealing (>600 °C, not shown here). Hence, the quenching of orange light and resurgence of blue light are probably due to the reduction of the size of the nanocrystallites in PS according to the quantum-confinement effects. Therefore, to identify the blue PL origin, luminescence is usually related to the change of the surface composition of the samples annealed at different temperatures.

In the FTIR spectra depicted in Fig. 3(a and b), peaks at 870, 1040–1160, 2080–2190, 2250, 2850–2960, represent Si–H₂ scissor, Si–O–Si stretching, Si–H stretching, O–Si–H stretching and CH_x stretching respectively. After annealing at different temperatures, the peak intensity at 2100 cm^{−1} associated with Si–H_x bond stretching is reduced. Traces of SiH_x have almost completely disappeared in the sample treated at 600 °C. Compared with the FTIR spectrum of the untreated CH_x–PS sample, the peaks associated with CH_x species (stretch 2800–3000 cm^{−1} and bend 1300–1500 cm^{−1}) have broadened significantly and decreased in intensity after annealing at 400 °C. After annealing at 600 °C, the blue PL has some characteristic infrared vibrations with new peaks at 488, 800 and 1240 cm^{−1} in the FTIR spectrum and most of the hydrogen is desorbed from the surface. In this sample, a sharp peak at 488 cm^{−1} is observed which indicates the Si–O–C vibration. The 800 cm^{−1} peak represents stretching vibration of Si–C bonds, while the band at 1240 cm^{−1} which indicates the symmetric bending mode of the CH₃ attached to silicon, has a large intensity and becomes larger for samples treated at 600 °C [20].

These results suggest that the increase in the blue band intensity is likely due to the formation of these substances. In the other hand, the fact that no significant change occurs at SiO_x peaks after annealing treatment indicates that the silicon oxide is not the major source of luminescence and is a very small contributor to the total luminescence from the sample.

Other groups have previously studied the PL originating from SiC-related materials [21]. The PL peaks from porous SiC reported by some researchers were located in a range of 2.4–2.7 eV [22]. Some results showed an intense blue light emission (454 nm) from carbon plasma-implanted porous silicon. It was attributed to SiC nanoparticles or SiC-related luminescence centres [12].

Biteen et al. attributed the blue shift of the silicon nanocrystal photoluminescence to the reduction of the size of the nanocrystallites in PS by an oxidizing anneal [23].

However, a model was proposed to explain the origin of the PL of porous silicon when the surface region is covered by a Si dioxide layer [24]. Zhao et al. proposed that the electron–hole pairs produced in a nanoscale Si unit recombine to emit visible light through various luminescence centres, which are located at the Si/SiO₂ interface. In addition, the luminescence centres are located on the surface of nanoscale Si units when the surface region is not covered by SiO₂. By introducing appropriate luminescence centres into PS, the blue emission can be obtained and its intensity increases with increasing temperature. Considering these previous studies, we tentatively assign the blue PL of our samples to substances, created after 600 °C, which are the silicon carbides with oxygen or hydrogen.

The first group of PS samples coated with a CH_x layer was exposed to propane then to CO₂ gases. The magnitude of PL quenching was recorded by measurements of photoluminescence intensity in time when a controlled amount of each gas was introduced into and subsequently removed from the system with air as a carrier gas. As seen in Fig. 4, the PL quenching with increasing time of exposure to CO₂, propane and air was measured by the I/I_0 ratio, where I_0 and I represent the integrated intensities of the PL band before and after gas injection. As a control experiment, the intensity of PL of the CH_x/PS sample was found to be completely stable for several tens of minutes under a flow of air. A necessary condition in the development of a sensor device with luminescent properties is that the sensor has to work normally in air in order to detect any other gas. The PL intensity increases when the sample is exposed to propane. The percentage of PL intensity increase after 5 min of exposure to 100 ppm of analyte is 26%. After removal of the gas from the system, the photoluminescence returns totally within 5–7 min to the initial intensity level, as shown in Fig. 5. We observe a reversible PL quenching behaviour. Measurements suggest a direct role

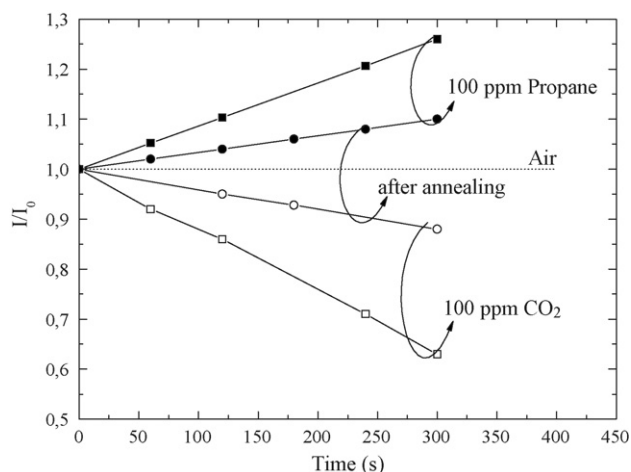


Fig. 4. Variation of I/I_0 for CH_x/PS samples with and without annealing treatment as a function of the time of exposure to CO_2 and propane gas.

of propane in surface passivation which reduces the number of non-radiative surface defects, as also reported by different authors [25]. The transport of excitons in a nanocrystal network is strongly suppressed as a result of the presence of potential barriers. Thus, excitons mainly recombine within the nanocrystal, in which they are created, i.e., recombination has a geminate character [26]. Therefore, the main reason for the enhancement of the emission from PS under propane results specifically from the non-radiative recombination channels being “disabled” [27].

However, sample exposed to CO_2 gas shows a decrease in PL intensity with a slight blue-shift by about 10 nm. Several authors have performed the experiment on a modified PS surface and they observed a shift of the fringe pattern which was attributed to the change in the refractive index of the medium [28]. The results confirmed the optical model invoked by Kim et al. which indicates that the PL in PS is emitted mostly from the upper surface of the layer [29]. Therefore, any change in the properties of the porous layer surface such as porosity, the refractive index due to the ambient conditions, should have an effect on the photoluminescence. During 5 min of exposure, the PL intensity

was allowed to stabilize and the percentage of quenching was 37%. After removal of CO_2 gas, 85% of the original PL intensity was recovered within more than 30 min, the full recovery of the PL intensity was much slower but after about 1 day the photoluminescence returned to the initial intensity level.

Another possibility of the quenching mechanism is believed to have been due to the formation of CO^- ions when the surface was exposed to CO_2 , according to the reaction: $\text{CO}_2 \rightarrow \text{h}^+ + \text{CO}^- + 1/2\text{O}_2$. The absorption of CO_2 modifies the concentration of holes at CH_x/PS surface. The injection of a hole into the porous silicon valence band was believed to have caused a non-radiative decay of the exciton responsible for the extent of the porous silicon photoluminescence [30]. Previous works have shown that the intensity of PL depends on the presence of surface adsorbates as reported by Harper and Sailor [31]. They found that molecules capable of acting as energy or charge acceptors can quench the PL of porous Si. Sailor and Lee [32] have suggested that surface species could couple into the porous silicon excited states as well as acting as non-radiative recombination centres. As a consequence, the interaction deeply affects material band structure and the assembly molecule-nanostructure results in a new material which changes its properties. The authors have shown that when PS is in the presence of O_2 , PL quenches proportionally to oxygen concentration and the results follows a dynamic Stern-Volmer model. Quenching was attributed to electron transfer from the luminescent chromophore in porous Si to an O_2 molecule weakly chemisorbed to a surface defect. CO_2 is an oxidizing gas which will probably induce variations near the surface comparable to O_2 gas.

The second group of samples annealed at 600°C was also exposed to the gases. In Fig. 4 PL intensities variations are reported and compared to light emission in air. An enhancement of PL intensity is recorded with propane and the opposite behaviour is observed for the carbon dioxide. The gases have the same effect on the PL variation as in the case of the orange red emission. However, it has been found that the rate of quenching vary across the photoluminescence spectrum and that the extent of quenching should be the greatest at longer wavelength, showing a decrease to 37% of the initial PL intensity in the orange region in the previous case, compared to 12% recorded in the blue region. In addition, the recovery rate was faster and the recovery time of 50% of the porous silicon photoluminescence after quenching was in approximately few seconds.

This was consistent with reported work on oxygen quenching of PS photoluminescence [33], where the authors have shown that the red-emitters were quenched faster than the blue-emitters and the extent of quenching was greatest at long wavelengths.

A variety of photoluminescence quenching mechanisms have been shown by several authors to be accessible to porous silicon. The mechanisms can be separated into four basic categories: the first, interfacial charge transfer which can occur when a molecular electron donor or acceptor comes in contact with an excited silicon nanocrystallite [34], secondly interfacial energy transfer which, likewise can occur if the molecular quencher has accessible singlet or triplet energy levels [35]. Introduction of non-radiative surface traps by a chemical reaction at the porous Si surface that generates mid-gap defects [2] is the

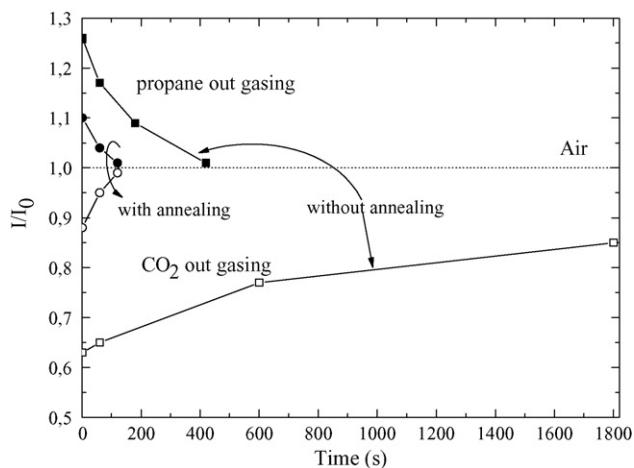


Fig. 5. Recovery behaviour of CH_x/PS samples with and without annealing after exposure to a flow of air.

third possibility, and the fourth, dielectric constant effect of the medium surrounding the porous Si which modifies the efficiency of geminate recombination [36]. This large number of quenching pathways accessible to porous Si allows the development of a variety of chemically specific sensors. However, quenching by the dielectric medium mechanism can occur with any adsorbate, although the most probable mechanism of quenching is attributed to the interfacial charge transfer. The CO₂ molecule is an electronegative species and electron transfer from photo-excited PS film to CO₂ is highly favourable. When the gas molecules achieve the PS surface, their molecular orbital (acceptor states) mix to donor excited states localized at the Si/CH_x surface promoting the electron transfer reaction and consequently the PL quenching.

4. Conclusion

We have presented a simple and efficient way to fabricate a blue light-emitting device from a thermally carbonised PS surface. The intense blue emission may be related to the carbon derivatized surface bounds species. Sensitive, direct detection of CO₂ and propane has been achieved by means of photoluminescence-quenching of modified porous Si. The effect of these gases on the porous silicon photoluminescence has been found to be reversible. The rate of quenching has been shown to vary from the red region to the blue region. The extent of quenching was greatest at long wavelengths. Whereas, the recovery rate was faster in the short wavelength region. The possible mechanism of quenching could be attributed to reversible electron transfer of quantum-sized nanocrystallites in the porous Si matrix. Such effects are very interesting for gas sensor applications especially taking into account that they have been recorded at room temperature.

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