

Photoluminescence properties of porous silicon nanocomposites

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Abstract

Different porous silicon (PS) layers were impregnated with rhodamine 6G (Rh) solution in order to form Rh/PS nanocomposites. The effect of the porous matrix (fresh, oxidised, type p⁺) on the propriety of photoluminescence (PL) has been investigated. It was found that the luminescence of this nanocomposite is provided by an energy transfer from PS nanocrystallites to rhodamine and from interaction of dye molecules with the chemical species on the Si surface. An antistokes PL has been observed using a He–Ne laser excitation. The dependence of its intensity via power excitation suggests a process of two-step two-photon absorption as origin of this PL. Nanocomposite formed by PS and ZnO has been also investigated. We show that this transparent oxide does not degrade the skeleton of PS and does not inhibit PL. The PL band shifts to high energy and the intensity becomes stable providing the passivation of the dangling bonds on the Si-surface by ZnO. © 2001 Elsevier Science S.A. All rights reserved.

1. Introduction

In recent years, many efforts have been devoted to the elaboration of nanocomposites based porous silicon (PS). The objective could be the stabilisation of light emission of PS, or the formation of new luminescing properties, or to improve the electroluminescence efficiency, or also the realisation of particular sensing properties. The amount of matter which is introduced into the pores, can vary to a very large extent. Canham [1] is the first who has tried the impregnation into the pores of different laser dyes. Ethanolic solutions of coumarin, xanthene and oxazine dyes were used. Different emissions from blue to red were produced depending on the dye type. Létant et al. [2] have impregnated PS in rhodamine 700. They show from diffuse reflectance a good dispersion of dye molecules in the porous matrix. Impregnation of transparent materials have been also studied by several authors [3–5]. The incorporation of conductive and transparent materials into the pores seems to be an attractive approach to realise efficient electroluminescence devices. Different materials have been tried like SnO₂, CdS and ZnS. The results are well encouraging.

In this work, we have studied the luminescence properties of two nanocomposites based PS/Rh and PS/ZnO.

2. Experimentation

Boron — doped silicon substrates of around 10 Ωcm were electrochemically etched in HF/C₂H₅OH/H₂O solution in order to obtain PS layers having 70% porosity with different thickness. For substrates type p⁺, the porosity and the thickness are fixed to 80% and 4 μm, respectively. Oxidation of PS was performed by ageing in the ambient.

The samples were impregnated for different times in a solution of rhodamine 6G and than dried at a temperature of 60°C. We note that the molecule of rhodamine 6G has a length smaller than 1 nm which makes its impregnation into the pores (3 nm for PS (p) and 10 nm for PS (p⁺)) possible.

ZnO was deposited by the spray technique on PS samples (1 μm thickness) which heated up to 420°C (crystallisation temperature of ZnO) by increasing the temperature with a slope of 5° min⁻¹.

The PL measurements were performed with a triple monochromator using the ray 514.5 nm of an Ar⁺ laser or the ray 632.8 nm of He–Ne laser as excitation sources.

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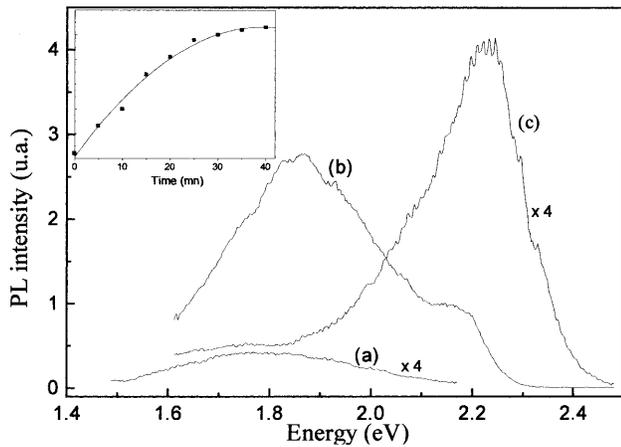


Fig. 1. PL spectra of PS layer (a) dye in solution (b) and Rh/PS after drying (c) The inset shows the evolution of the PL intensity versus impregnation time.

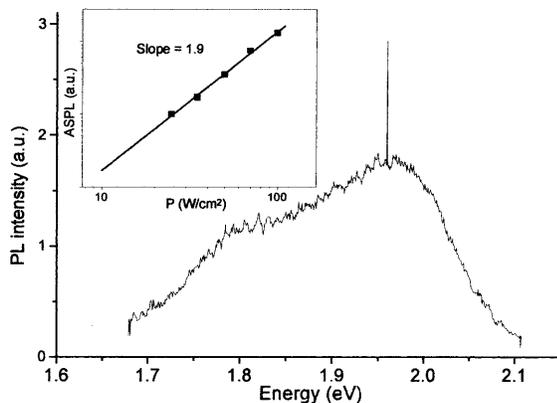


Fig. 2. PL spectrum of Rh/PS(p) for $E_{exc} = 1.959$ eV. In the inset we show the ASPL intensity as function of the excitation density.

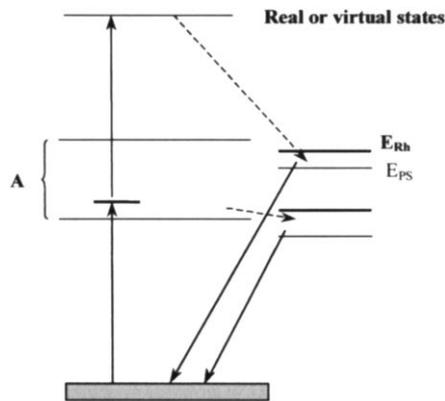


Fig. 3. Energy level diagram for Rh/PS corresponding to $E_{exc} = 1.96$ eV. E_{RH} and E_{PS} correspond respectively to emission energies of Rh and PS. A is the absorption band of PS and Rh.

3. Results and discussion

In Fig. 1, we present PL spectra of PS layer (a), dye in solution (b) and Rh/PS after drying (c). The nanocomposite Rh/PS luminesces out of the spectral range of PS emission (blueshift to lower wavelength) and its PL is more efficient than that of the PS layer. This indicates that the PL of the nanocomposite Rh/PS does not originate only from PS.

In the inset of Fig. 1, we observe a strong increase in the luminescence with time impregnation and then saturation. This may characterise the emergence of dye molecules into the pores up to saturation. Some authors [2] have shown through time resolved luminescence and reflectivity measurements a total infiltration of dye molecules into the pores.

It is well known that the luminescence of a dye depends strongly on its concentration in solution. The PL intensity becomes weaker when the molecules become too concentrated and eventually can be totally quenched. This means that more the dye molecules are dispersed, more the luminescence is efficient. This can explain the origin of the strong luminescence of the nanocomposite Rh/PS since the molecules penetrate into the pores and are sufficiently dispersed in the porous matrix. Each process could be produced by excitation transfer from nanocrystallites to dye molecules. In fact, the conditions of excitation transfer are satisfied for PS and rhodamine 6G: the rhodamine absorbs in the range 500–700 nm, which recovers with the range of PS emission. The excitation line (458 nm) is selected to excite only PS. The dye molecules do not absorb for this ray.

We have used also the He–Ne laser line (632.8 nm) in order to excite the dye only (at this wavelength, the PS absorption can be neglected). The intensity becomes weaker compared to that observed for the line 458 nm and the maximum of luminescence is pointed below the excitation energy (Fig. 2). The total PL band (stokes and antistokes) seems to be continue at the value of the excitation energy and can be decomposed in two others bands centred at 1.97 and 1.83 eV. The maximum intensity of the ASPL band (I_{ASPL}) is plotted versus the power P of laser excitation (inset in Fig. 2). The dependence of I_{ASPL} on P in the range 50–100 Wcm^{-2} is in the form $I_{ASPL} \propto P^{1.9}$ showing clearly a non linear effect. The origin of this ASPL could be a process of two photons absorption via real or virtual states as observed by Chine and al [8]. An energy level diagram of Rh/PS is proposed in Fig. 3.

The effect of the porous matrix in the luminescence of the nanocomposite Rh/PS has been studied. We have compared the PL spectra for two PS samples type p and type- p^+ impregnated for the same time in the dye solution (this time corresponds to PL saturation).

Fig. 4 shows a more efficient emission for Rh/PS(p) than for Rh/PS(p^+) due probably to a good dispersion

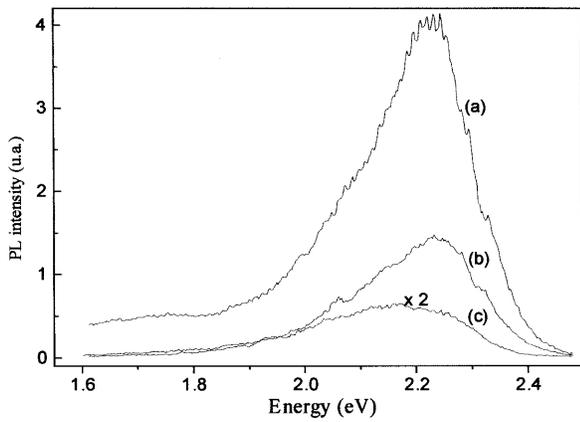


Fig. 4. PL spectra of the nanocomposites (a) Rh/PS(oxidised) (b) Rh/PS (fresh) and (c) Rh/PS(-p⁺).

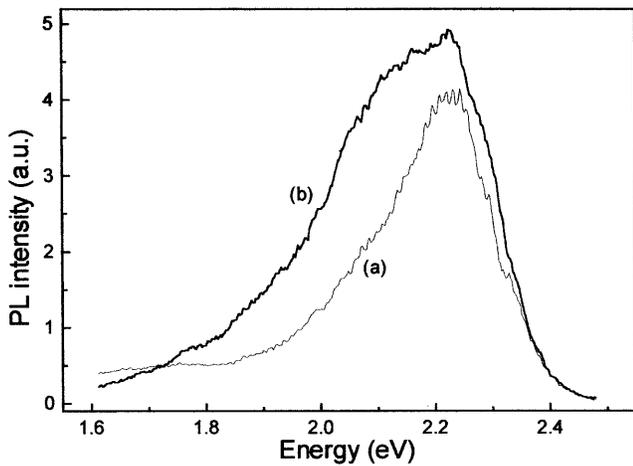


Fig. 5. PL spectra of as formed (a) and aged (b) Rh/PS(p) nanocomposite. The FWHM are 0.23 and 0.325 eV, respectively.

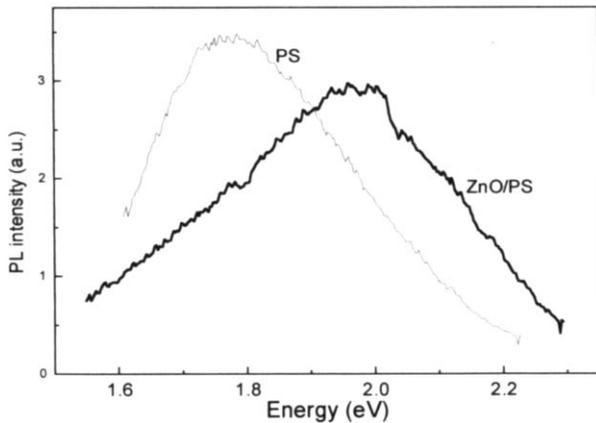


Fig. 6. PL spectra of PS layer and ZnO/PS nanocomposite.

of dye molecules in the matrix type p where the specific surface area is three times greater than for PS type p⁺ [6]. It can be attributed also to the important concentration of the donors (Si nanocrystallites) in the type p

compared to the type p⁺, which assures more energy transfer to dye molecules in the first matrix. Fig. 4 shows also a more efficient PL for nanocomposite based oxidised PS (p) than that based fresh PS(p). This is due to the fact that there are more dye molecules in the oxidised PS layer than in fresh ones as reported recently by Setzu et al. [7]. One may attribute this difference to the adsorption of dye molecules by the oxide and the chemical compound on the Si surface. We think also that water molecules in the oxidised layer play a key role to assure a more important dispersion of dye molecules. The contribution of the interaction between dye molecules and the Si surface on the PL intensity for the two nanocomposites cannot be neglected. The chemical compounds in the Si surface are, as suggested by the IR results, essentially Si–OH in oxidised PS and Si–H in fresh PS. For cationic dyes, the molecules interact with the ‘O’ site, but for anionic dyes, the interaction is preferentially with the ‘H’ sites. These interactions seem to be as ion–dipole type. Therefore, the more efficient emission for Rh/PS (oxidised) is justified since rhodamine 6G is known to be cationic. This raises the possibility of a charge transfer type interaction between Si surface and dye.

An evidence of charge transfer type interaction comes from the evolution of the PL spectrum within time. The PL intensity increases slightly and the FWHM increases from 0.22 to 0.325 eV in a period of 4 months (Fig. 5). These changes are verified for all the PL spectra corresponding to the different studied porous matrix. One can imagine that water molecules penetrate into the nanocomposites, which favours the dispersion of dye molecules and their interaction with the ‘O’ sites.

4. Nanocomposite ZnO/PS

As a transparent conducting oxide (TCO), ZnO ($E_g = 3.2$ eV) presents resistivity values about 10^{-4} Ωcm when doped with indium [9,10], a corresponding transmission coefficient above 80% in the visible range and a high dielectric constant. The viscosity of the starting spray solution (nearly that of water) as well as its low pH (around 1) makes it a good candidate to try to in situ TCO material directly into the pores of PS. We present in this part, the first optical approach with undoped material.

Since the impregnation is effectuated at the crystallisation temperature of ZnO (420°C), polycondensation and densification may have occurred and cassiterite material must have been formed. Fig. 6 shows a slight decrease of the PL intensity while the amount of Si–H bonds are reduced considerably and the oxidation remains negligible. Also, the modification of the effective dielectric constant has a direct effect on the electrons–

holes interaction, which is closely correlated with photon emission. It seems that these effects are compensated by the passivation of the dangling bonds on the surface of Si nanocrystallites, which can explain the PL stability even after a long period of ZnO deposition and provide that this solid phase does not degrade the skeleton of PS and does not inhibit PL. The deposited material provides a good coverage of the crystallite surface and may act as an efficient electric barrier. Then ZnO may play the role of SiO₂ as an energetic barrier preventing the escape of photogenerated carriers outside the confined crystallites. An other reason for this efficiency change could be the formation of a new interface consisting of some complex species when ZnO is deposited on the porous layer since the PS is characterised by its high reactive surface.

Together with the stabilisation of the PL intensity, the spectrum is shifted towards the blue. This phenomenon can be related to three effects: an increase of the energy barriers surrounding the crystallites, a tensile strength due to ZnO deposition on the crystallite walls and a change in the dielectric constant.

5. Conclusion

We have elaborated nanocomposites based PS and

rhodamine 6G by simple impregnation. New luminescence properties was shown. This luminescence could occur by energy transfer from silicon nanocrystallites to dye molecules and by ion–dipole interaction between Si surface and dye.

The PL study of undoped ZnO/PS nanocomposite shows a preliminary positive results which open the way towards solid state electrodes for electroluminescence application of PS with indium doped ZnO as a transparent n-type degenerated semiconductor electrode.

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