RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 52, NUMBER 20 15 NOVEMBER 1995-II

Enhanced optical properties in porous silicon microcavities

Vittorio Pellegrini and Alessandro Tredicucci
Scuola Normale Superiore and Istituto Nazionale per la Fisica della Materia, Piazza Dei Cavalieri 7, I-56126 Pisa, Italy

Claudio Mazzoleni and Lorenzo Pavesi
Istituto Nazionale di Fisica Moleculare and Dipartimento di Fisica, Università di Trento, Via Sommarive 14, I-38050 Povo (TN), Italy
(Received 13 July 1995)

We report the experimental investigation of the optical properties of porous silicon embedded in a planar microcavity structure in which both the active layer and the two Bragg reflectors are fabricated by electrochemical processing of a p-type porous silicon wafer. By tuning the cavity resonance energy around the maximum of the porous silicon emission we have observed photoluminescence linewidths as narrow as 18–25 meV and an intensity enhancement of more than one order of magnitude. The experimental results are clarified by theoretical calculations performed with the standard transfer-matrix approach in the framework of a porous silicon quantum-box model.

The recent observation of photoluminescence[1] (PL) and electroluminescence[2,3] emission from porous silicon (PS) samples has prompted great interest in view of possible applications of PS-based devices in optoelectronics. In addition, several models have been proposed in order to clarify the mechanism governing the PL emission.[4,5] Among them, the quantum confinement of excitons in silicon nanocrystals (dots or wires) seems to successfully explain many different experimental results. Examples are the observation of well-defined phonon structures,[6,7] the PS transport properties,[8] the PL decay times,[9,10] and the dependence of the PL peak energies on the size of the silicon dots or wires.[11]

In view of device applications, attention is currently focused on the enhancement of the optical and electro-optical properties of PS samples.[12–15] However, despite these strong efforts, no significant and definitive improvements have been obtained; critical issues are still the very broad spectral and angular emissions and aging effects.

In the field of III-V semiconductors, the use of cavity systems is a well-established tool to alter and control the spontaneous emission in both quantum-well embedded systems and three-dimensional bulk ones.[16–18] Semiconductor microcavities allow the analysis of the fundamental properties of photon-exciton coupling[19,20] and have consequences for the performance of nonlinear optical devices[21] and laser devices since they decrease the radiative emission lifetime and lead to strong unidirectionality of the emitted light. The aim of the present work is to extend these studies to the PS field. To this end we propose a system based on a PS microcavity structure (PSM) in which both the active layer and the two Bragg reflectors are produced by an anodization process on a p-type silicon wafer. The refractive index of PS is determined by its porosity, which depends only on the current density of the electrochemical process once the other etching parameters are kept fixed. An accurate measurement of PS porosity can be performed through gravimetric techniques. In this way, by controlling the current density one can control the index of refraction of PS layers; the anodization time determines the layer width.

The use of multilayered structures formed by PS at different porosity has already been suggested and successfully applied, and good optical quality Bragg reflectors and Fabry-Pérot interferences filters have been fabricated.[22–24]

Here we analyze the optical response of two PSM's consisting of a λ or $\lambda/2$ PS active layer of 75% porosity [index of refraction $n = 1.27$ (Ref. 25) at 760 nm], where λ is the wavelength measured in the material, enclosed between two distributed Bragg reflectors. Every sample was obtained from a B-doped Si wafer with a resistivity of 0.01 Ω cm. Each Bragg reflector was composed of six pairs of alternating PS $\lambda/4$ layers with porosities of 62% ($n=1.50$ at 760 nm) and 45% ($n = 2.24$ at 760 nm), respectively. The details of sample preparation have been given elsewhere.[3,24] We remark that the fabrication time is of the order of 1 h and that the computer-controlled parameters of the anodization process yield well-reproducible PSM optical features.

We have tuned the cavity mode to the photon energy corresponding approximately to the maximum emission of the PS active layer by simply choosing the appropriate value for λ. This yields 598-nm and 299-nm layer widths for the λ and $\lambda/2$ PS active layers, respectively, and 126 nm and 84 nm for the Bragg-reflector widths.

PL measurements were performed using the 458-nm line of an Argon-ion laser focused at approximately 45° from the z axis, perpendicular to the surface of the sample, with an incident intensity of about 10 W/cm^2. The PL light was detected along the z axis and dispersed with a 1-m double monochromator equipped with a GaAs phototube and a lock-in amplifier. Reflectivity measurements were performed using a 100-W xenon lamp source. The samples were analyzed between 10 K and room temperature using a closed-cycle cryostat.

Figure 1 shows the room-temperature reflectivity spectrum of the λ PSM (upper panel) and its PL spectrum (lower panel, solid line). For comparison we have also plotted in the lower panel the PL spectrum of a λ-thick PS layer without reflectors (dotted line). We observe strong changes in the spectral response: first, a dramatic reduction of the full width at half maximum (FWHM) of the PL emission from 320

 © 1995 The American Physical Society

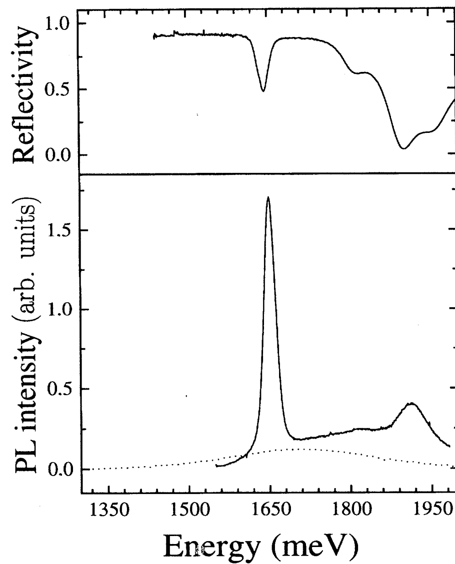

FIG. 1. Room-temperature reflectivity spectrum of a λ porous silicon microcavity (upper panel) and photoluminescence (PL) spectra of a porous silicon layer (lower panel) without any reflectors (dotted line) and of a λ porous silicon microcavity (solid line). The first edge of the Bragg reflectors stop band is not visible in the reflectivity spectrum due to the low efficiency of the detection system in this energy range. Excitation laser light intensity is ≈10 W/cm^2. PL is detected along the axis perpendicular to the surface of the sample.

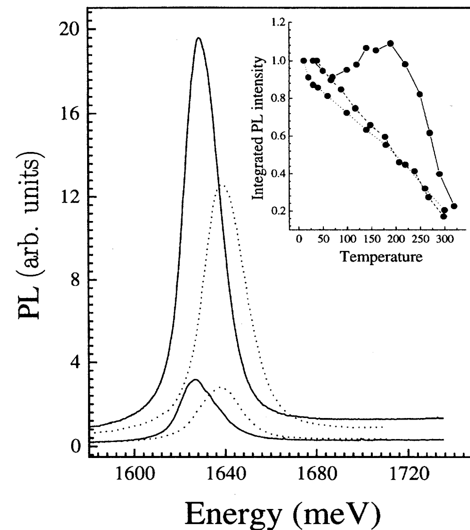

FIG. 2. Photoluminescence spectra of the λ (solid lines) and λ/2 (dotted lines) porous silicon microcavities at 30 K and at room temperature (the stronger emissions correspond to 30 K). The inset shows the temperature dependence of the photoluminescence integrated emission of the λ (dashed line) and λ/2 (dotted line) microcavities and of a reference PS λ-thick sample (solid line) normalized to the corresponding lowest temperature photoluminescence integrated spectra.

meV to 22 meV (the latter energy width being entirely determined by the quality of the cavity). Second, the PL peak emission intensity is increased by a factor of ≈16 in the microcavity sample. These two features are a consequence of the enhancement of the spontaneous emission originating from the states resonant with the optical mode of the Fabry-Pérot resonator and of the inhibited radiative decay of all other states. A second peak around 1920 meV is detected and corresponds to the edge of the Bragg reflectors stop band. At this energy the reflectivity of the whole structure becomes particularly low and a fairly strong PL emission from the λ PS layer and from the two reflectors can be detected.

In Fig. 2 we report the PL emission spectra at 30 K and at room temperature for both the λ (solid lines) and λ/2 (dotted lines) microcavities. The inset shows the temperature dependence of the normalized integrated emission intensity of both microcavities and, as reference, that corresponding to the PS λ-thick layer. We have observed a small shift (a few meV) of the PL peak towards lower energies as the temperature increases, probably owing to variations in the refractive indices and layer thicknesses. No significant dependendence of the FWHM on temperature can be revealed, confirming that the linewidth is determined only by the resonator finesse. The different PL peak energies of the λ and λ/2 microcavities can be ascribed to small deviations of the resonators' effective thickness from the nominal values, following small discrepancies in the porosity and thickness calibration. The stronger emission of the λ PSM is related to the larger active thickness although the normalized integrated emissions of the two microcavities become equal upon increasing the temperature as the hopping-mediated and thermally activated nonradiative processes more than compensate the thicker active layer of the λ cavity.

Microcavity effects are also revealed by the temperature dependence of the integrated PL (inset of Fig. 2). A different behavior is observed. In the λ-thick reference sample, as in usual PS samples,[26] the integrated PL emission behavior is explained with the help of concurrent measurements of the PL lifetime and is thought to be the result of two opposing processes: the thermally activated promotion of excitons from the low-energy dipole-prohibited exciton triplet state to the high-energy dipole-allowed exciton singlet state,[27] which increases the PL intensity and dominates at low temperatures, and the thermally activated nonradiative recombination, which decreases the PL intensity and dominates at high temperatures. These trends are strongly modified by the presence of the cavity. A detailed explanation would require the measurements of the temperature dependence of the luminescence time constants, which we plan to perform in the near future. Here we suggest that the major effect of the microcavity is to shorten significantly the singlet radiative lifetime so that recombinations from the singlet state predominate also at low temperature. This effect could be enhanced by a reduction of the phonon-scattering rates determined by the different densities of state for the dressed excitons, which is now governed by the coupled exciton-photon mode dispersion.[28]

To clarify the optical behavior of the PSM we have calculated reflectivity and absorption spectra using a transfer-matrix approach[29] and assuming a quantum-box model and exciton confinement in a Si-nanocrystal inside the PS layer. The first step is the computation of the first-order susceptibility given by

$$\chi(\omega)=\int_0^\infty P(\omega_o)\bar{\chi}(\omega,\omega_o)d\omega_o, \quad (1)$$

where $P(\omega_o)$ is the distribution of oscillators (excitons) as a function of frequency. The susceptibility of a single exciton $\bar{\chi}(\omega,\omega_o)$ is given by

$$\bar{\chi}(\omega,\omega_o)=\frac{f\omega_o^2}{\omega_o^2-\omega^2-i\Gamma\omega}, \quad (2)$$

where f is the oscillator strength and Γ the thermal broadening factor that is assumed to depend linearly on temperature.

We consider a Gaussian size distribution for the Si nanocrystals centered at d_c = 34.6 Å having a width σ_d = 1.3 Å. The emission energy E_i is related to the corresponding size d_i through the power-law relation $E_i=E_c(d_c/d_i)^n$ with $n\approx 1.4$,[30] where E_c is the transition energy corresponding to a Si nanocrystal of size d_c. Within these assumptions $P(\omega_o)$ is given by

$$P(\omega_o)\propto\frac{1}{\sigma_d}\frac{1}{\omega_o^{1+1/n}}\exp\left\{-\left[(d_c^2/2\sigma_d^2)\left(\left(\frac{\omega_c}{\omega_o}\right)^{1/n}-1\right]^2\right\}. \quad (3)$$

It is centered in ω_c = $E_c/\hbar$ and has a FWHM of 320 meV, as deduced from the PL emission spectrum. The PS dielectric constant is then computed as $\epsilon=\epsilon_b+4\pi\chi(\omega)$, where ϵ_b is the background dielectric constant of the layer.

The transfer matrix M for the whole PSM is obtained by multiplying together the transfer matrices m of every single layer. For the jth layer we have

$$m_j=\begin{bmatrix}\cos\left(\frac{\omega}{c}n_jl_j\right) & -\frac{i}{n_j}\sin\left(\frac{\omega}{c}n_jl_j\right)\\ -in_j\sin\left(\frac{\omega}{c}n_jl_j\right) & \cos\left(\frac{\omega}{c}n_jl_j\right)\end{bmatrix}, \quad (4)$$

where $n_j=\sqrt{\epsilon}$, l_j is the width of the jth layer, and c is the velocity of light.

From this we have calculated the reflectivity R = $|r|^2$ and the transmittivity T = $n_{\rm sub}|t|^2$, where $n_{\rm sub}$ is the index of refraction of the p-type silicon substrate and r and t can be calculated using[29]

$$r=\frac{M_{12}+n_{\rm sub}M_{22}-M_{11}-n_{\rm sub}M_{12}}{M_{21}+n_{\rm sub}M_{22}+M_{11}+n_{\rm sub}M_{12}},$$

$$t=\frac{2}{M_{11}+n_{\rm sub}M_{12}+M_{21}+n_{\rm sub}M_{22}}. \quad (5)$$

The absorption A is then calculated in the usual way as $A=1-R-T$.

The results are displayed in Fig. 3. The theoretical spectra exhibit the same behavior as the experimental ones (Fig. 1), not only for what concerns the reflectivity spectra, but also by comparing the calculated absorption spectrum and the experimental PL spectrum. This result was expected in view of the nearly symmetric line shapes of the PS luminescence spectra at low and room temperature. It is an indicator that the thermal contribution to the occupation of the high-energy states is not as important as in other semiconductor systems.[31] A broadening factor Γ for excitons belonging to each single Si nanocrystal is included in the linear susceptibility to take into account phenomenologically scattering and dephasing processes.

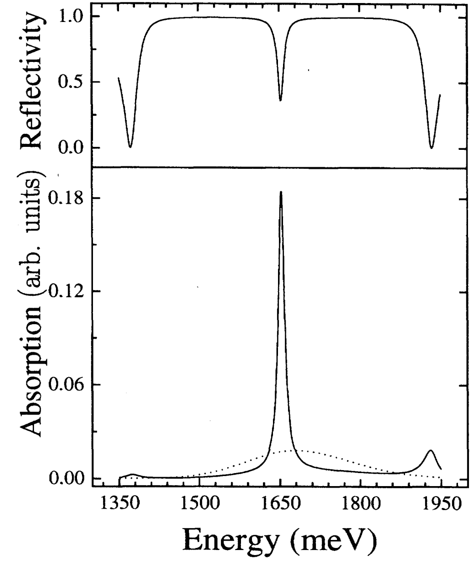

FIG. 3. Calculated reflectivity spectrum (upper panel) and absorption spectrum (lower panel) for a λ porous silicon microcavity. Also shown are the calculated absorption spectrum (dotted line) for a λ porous silicon layer without any reflectors. The best matching with the experimental results (Fig. 1) has been obtained with a broadening factor Γ=30 meV and with an oscillator strength $4\pi f=1\times10^{-4}$.

We have not performed a detailed line-shape fitting procedure and the calculated spectra of Fig. 3 have been obtained with Γ = 30 meV and $4\pi f$ = 1×10^{-4}. The Γ value is not critical and reasonable deviations from the reported values do not lead to strong modifications of the calculated spectra. The assumed value has been chosen of the order of the thermal energy. For the f value we have found that stronger oscillator strengths result in a saturation of the absorption at the cavity resonance, yielding a calculated reflectance spectrum which deviates more from the experimental one, whereas even an order of magnitude lower values do not result in appreciable changes.

In conclusion, we have shown a PS-based structure, namely, a PS microcavity, which strongly modifies the optical properties of the PS. The effect of narrowing and enhancement of the porous silicon emission band was experimentally demonstrated in both a λ and a $\lambda/2$ microcavity. Temperature dependence of the integrated emission intensity has been reported and discussed. Finally, we have performed a theoretical calculation based on the transfer-matrix approach and assuming exciton confinement in Si nanocrystals.

The experimental results for both the reflectivity and the emission spectra have been well reproduced. The PSM represents an exciting subject of investigation also in the field of nonlinear optical properties. Further investigations are in progress in order to analyze the modifications of the decay time in PSM photoluminescence and electroluminescence.

We wish to acknowledge the helpful collaboration of S. Puccini, M. Börger, and F. Fuso. The authors are also indebted to F. Beltram for stimulating discussions and for a critical reading of the manuscript. This work was partially supported by the Italian National Council (CNR) in the framework of the L.E.S. program.

[1] L.T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] P. Steiner, F. Kozlowski, and W. Lang, Appl. Phys. Lett. **63**, 2700 (1993).
[3] L. Pavesi, M. Ceschini, G. Mariotto, E. Zanghellini, O. Bisi, M. Anderle, L. Calliari, and M. Fedrizzi, J. Appl. Phys. **75**, 1118 (1994).
[4] L. Tsybeskov and P.M. Fauchet, Appl. Phys. Lett. **64**, 1983 (1994).
[5] S. Schuppler, S.L. Friedman, M.A. Marcus, D.L. Adler, Y.H. Xie, F.M. Ross, T.D. Harris, W.L. Brown, Y.J. Chabal, L.E. Brus, and P.H. Citrin, Phys. Rev. Lett. **72**, 2648 (1994).
[6] P.D.J. Calcott, J.J. Nash, L.T. Canham, M.J. Kane, and T. Brumhead, J. Phys. Condens. Matter **5**, L91 (1993).
[7] T. Suemoto, K. Tanaka, A. Nakajima, and T. Itakura, Phys. Rev. Lett. **70**, 3659 (1993).
[8] M. Ben-Chorin, F. Möller, and F. Koch, Phys. Rev. B **49**, 2981 (1994).
[9] L. Pavesi and M. Ceschini, Phys. Rev. B **48**, 17 625 (1993).
[10] T. Suemoto, K. Tanaka, and A. Nakajima, Phys. Rev. B **49**, 11 005 (1994).
[11] F. Buda, J. Kohanoff, and M. Parrinello, Phys. Rev. Lett. **69**, 1272 (1992).
[12] V. Pellegrini, F. Fuso, G. Lorenzi, M. Allegrini, A. Diligenti, A. Nannini, and G. Pennelli, Appl. Phys. Lett. **67**, 1084 (1995).
[13] L.T. Canham, A.G. Cullis, C. Pickering, O.D. Dosser, T.I. Cox, and T.P. Lynch, Nature (London) **368**, 133 (1994).
[14] M. Ben-Chorin, A. Kux, and I. Schechter, Appl. Phys. Lett. **64**, 481 (1994).
[15] H. Koyama, T. Nakagawa, T. Ozaky, and N. Koshida, Appl. Phys. Lett. **65**, 1656 (1994).
[16] F. De Martini, G. Innocenti, G.R. Jacobovitz, and P. Mataloni, Phys. Rev. Lett. **59**, 2955 (1987).
[17] H. Yokoyama, K. Nishi, T. Anan, H. Yamada, S.D. Brorson, and E.P. Ippen, Appl. Phys. Lett. **57**, 2814 (1992).
[18] A. Tredicucci, Y. Chen, V. Pellegrini, and C. Deparis, Appl. Phys. Lett. **66**, 2388 (1995).
[19] C. Weisbuch, M. Nishioka, A. Ishikawa, and Y. Arakawa, Phys. Rev. Lett. **69**, 3314 (1992).
[20] Y. Chen, A. Tredicucci, and F. Bassani, Phys. Rev. B **52**, 1800 (1995).
[21] T. Rivera, F.R. Ladan, A. Izraël, R. Azoulay, R. Kuszelewicz, and J.L. Oudar, Appl. Phys. Lett. **64**, 869 (1994).
[22] M.G. Berger, C. Dieker, M. Thonissen, L. Vescan, H. Luth, H. Munder, W. Theiss, M. Wernke, and P. Grosse, J. Phys. D **27**, 1333 (1994).
[23] G. Vincent, Appl. Phys. Lett. **64**, 2367 (1994).
[24] C. Mazzoleni and L. Pavesi (unpublished).
[25] The refractive index was determined by the interference fringe spacing measured through independent reflectance measurements on thick PS layers. More details are given in Ref. 24.
[26] J.C. Vial, A. Bsiesy, F. Gaspard, R. Herino, M. Ligeon, F. Muller, R. Romestain, and R.M Macfarlane, Phys. Rev. B **45**, 14 171 (1992).
[27] P.D.J. Calcott, K.J. Nash, L.T. Canham, M.J. Kane, and D. Brumhead, J. Lumin. **57**, 257 (1993).
[28] S. Pau, G. Björk, J. Jacobson, H. Cao, and Y. Yamamoto, Phys. Rev. A **51**, 7090 (1995).
[29] M. Born and E. Wolf, *Principle of Optics* (Pergamon, Oxford, 1980), p. 60.
[30] C. Delerue, M. Lannoo, and G. Allan, J. Lumin. **57**, 249 (1993).
[31] M. Gurioli, A. Vinattieri, J. Martinez-Pastor, and M. Colocci, Phys. Rev. B **50**, 11 817 (1994).