Mechanisms of visible-light emission from electro-oxidized porous silicon

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High-porosity porous silicon, after electrochemical oxidation, is a stable and highly reproducible luminescent material with a luminescence quantum efficiency as high as 3% at room temperature. Luminescence decay rates as long as several hundreds of microseconds show that radiative and nonradiative processes both have low efficiencies even at room temperature. This shows that confinement of carriers inside nanometer-sized crystallites does not have a noticeable effect on indirect-band-gap selection rules but restricts strongly the different processes for nonradiative deexcitation. An analysis of the dependence of the nonradiative-decay rates on carrier confinement in terms of the tunneling of carriers through silicon oxide barriers surrounding the confined zone accounts well for our experimental results with an average barrier thickness of 5 nm. This tunneling model is also used to explain successfully the increase in quantum efficiency with the increase of the level of oxidation.

I. INTRODUCTION

The recent discovery of bright visible luminescence from porous silicon¹ has stimulated research for a better understanding of the basic mechanisms of light emission from silicon nanostructures and for a better control of the numerous parameters of porous silicon formation and further processing in order to give a high quantum efficiency of luminescence.

Rather simple considerations show that two conditions are required for efficient visible light emission from silicon structures: (i) a confinement of carriers into nanometer-sized silicon cells in order to get enough confinement to bring optical transitions in the visible range; (ii) an enhancement of the luminescence quantum efficiency, which can take its origin from an increase in the radiative recombination rate because of the breaking of momentum conservation or from a reduction of the nonradiative processes by a passivation of the confined zone surfaces.

Previous observations of visible light emission from various silicon structures confirm these trends. Dimaria et al.² have observed an electroluminescence in the visible range from SiO₂ layers containing tiny silicon precipitates; they proposed a quantum dot model to explain the shift of the emission in the visible range. More recently visible photoluminescence has also been obtained by Takagi et al.³ with silicon nanocrystallites embedded in SiO_2 ; though they found that all Si dangling bonds are initially compensated by hydrogen, luminescence at room temperature is obtained only after oxidation. Their observation of a blueshift during the thinning of Si particles by oxidation and the inverse relation between emission energy and the square of the crystallite size are seen as the evidence for confinement of the carriers in quantum dots. For structures related to porous silicon, Canham¹ showed that the confinement requirements can be obtained by chemical dissolution of porous samples. Related to chemical thinning of Si crystallites, a blueshift of the fluorescence was also observed. It is suggested that passivation is provided by hydrogenation during the dissolution, but spontaneous oxidation when samples are exposed to air could not be excluded as a perturbation to the passivation.

Previous work⁴ has shown that visible luminescence could be obtained from as-formed high-porosity samples without further chemical dissolution and that an enhanced emission is observed after anodic oxidation. This complementary process has the advantage of bestowing good mechanical properties on the porous layer. In addition it gives rise to a bright electroluminescence.⁵

The aim of this paper is to show that the use of wellcontrolled anodically oxidized porous silicon together with quantitative measurements of luminescence quantum efficiencies and lifetimes at various temperatures, and for various confinements, provides further confirmation of the quantum dot model. It also provides the basis for extending this model to include nonradiative decay by tunneling through oxide barriers.

II. ANODIC OXIDATION OF POROUS SILICON

While anodic oxidation of bulk silicon in water is a well-known electrochemical process,⁶ highly porous silicon, due to its large specific surface, has some particular features which are elaborated below.

A. Sample preparation

The results presented in this paper have been obtained on porous silicon layers of 65% porosity subsequently oxidized by electrochemical anodization. Porous films were formed on (100) p-type silicon substrates (1 Ω cm) in ethanoic electrolytes obtained by a mixture of seven volumes of hydrofluoric acid (HF) 50 wt % and three volumes of absolute ethanol. The anodic current density was 50 mA/cm², leading to the formation of layers with 65% porosity, as determined by gravimetric measurements.⁷ Samples of different thicknesses were obtained by varying the anodization time. Electrochemical oxidation of porous silicon layers was performed with the same experimental setup but with a different electrolyte solution composed of deionized water with 0.1*M* KNO₃ as the supporting electrolyte. It was carried out under galvanostatic conditions with current densities in the range 0.1–10 mA/cm².

The variation of the silicon potential during porous silicon anodization at constant current density is shown on Fig. 1. Two different regimes are observed independently of the layer thickness or of the anodic current density: Initially a slow increase in potential is observed, followed by a sharp rise when the exchanged charge exceeds a certain value Q_0 . The value of Q_0 , which increases with the layer thickness, is related to the end of the oxidation regime of the porous layer. However, this charge amount is always far below that which would be necessary to oxidize all the silicon atoms of the porous layer assuming a 100% current efficiency of SiO₂ formation and a fourelectron reaction. This can be explained by assuming that for a transferred charge equal to Q_0 there is a break in the electrical contact between bulk silicon and the partially oxidized porous silicon layer.

The oxygen profiles measured by Rutherford backscattering are mostly flat, with oxidized fractions between 40% and 60% in good agreement with those deduced from coulometry, showing that the current efficiency of SiO₂ formation is equal to 100% for exchanged charge amounts up to Q_0 . The explanation for this incomplete oxidation can be inferred from an examination of the layer microstructure. From TEM observations, porous layers formed in lightly *p*-type doped silicon can be described as a three-dimensional random array of intercommunicating empty spheres representing the pore network. Following this description, it is quite clear that the silicon walls between the pores do not have a constant thickness, but very likely have a large number of narrowings. Con-



FIG. 1. Typical potential variation as a function of time during anodic oxidation of a 70% porosity porous silicon layer in $1M \text{ KNO}_3$ aqueous solution at constant current density.

sequently, as anodic oxide growth is almost homogeneous, the narrowed regions are fully oxidized before complete oxidation of the thicker regions. At this stage, the unoxidized regions may become electrically disconnected from the substrate, and then remain unaffected on further polarization of the silicon substrate. Therefore, it can be concluded that the 40% silicon atoms which have not been oxidized during the anodic process form small crystallites randomly distributed within the oxidized porous layer. The crystallite size is at present unknown, but owing to the 65% porosity and the pore sizes of 1.5-2 nm of the porous layer, we estimate that they are much smaller than 10 nm.

B. Dependence of photoluminescence on the level of oxidation

Figure 2 shows different photoluminescence spectra of layers of identical initial porosity after different levels of oxidation. They have been normalized to the same vertical scale in order to emphasize the main spectral features: They have very similar shapes, and there is a noticeable blueshift similar to that observed by Takagi et al.³ Here, in addition, the accurately measured level of oxidation, which is directly connected to the porous silicon thinning, makes possible a test of the quantum dot hypothesis. If a simple quantum dot shape is assumed (cube or sphere of volume V), the carrier confinement energy E_c , which is the sum of electron and hole confinement energies, will be proportional to $V^{-2/3}$. The anodic oxidation up to Q_0 corresponds to a 50% uniform consumption of the porous layer, and the quantum dot volume will then have a dependence on Q proportional to $(1-0.5Q/Q_0)$. Consequently the carrier confinement energy $E_c(Q)$ will vary as

$$(1-0.5Q/Q_0)^{-2/3}$$
 (1)

Figure 2 gives a ratio $E_c(Q_0)/E(Q_0/4)=1.44$, while expression (1) gives 1.45. This good agreement needs to be confirmed on different samples with different porosities, for example, but it already gives confidence in a quantum



FIG. 2. Room-temperature photoluminescence spectra for two different anodic oxidation levels of a 65% porosity layer excited under the same conditions (note the scale change factor of 700).



FIG. 3. Variation of the room-temperature photoluminescence intensity (integrated over the solid line) as a function of the anodic oxidation level Q/Q_0 for a 65% porosity layer.

dot model, at least for the energy levels.

In addition to the blueshift effect, anodic oxidation strongly affects the photoluminescence intensity as shown on Fig. 3. Starting at a very low level, the photoluminescence intensity *increases* with Q and reaches a maximum for Q_0 . Such behavior contrasts with what is observed upon thermal oxidation, which on the contrary leads to a large *decrease* in the emitted intensity.⁹

The level of anodic oxidation thus appears as a critical parameter; its effect on spectral positions can be understood via the quantum size effect, but its action on the photoluminescence quantum efficiency is new and will be analyzed now.

III. QUANTITATIVE MEASUREMENTS OF PHOTOLUMINESCENCE

A. The quantum efficiency

The measurements were performed at room temperature on samples electro-oxidized up to Q_0 . Excitation of photoluminescence was provided by the 366-nm line of a mercury arc lamp. With this energy (3.4 eV), photons induce transitions well above the band gap and are then absorbed in less than the first micron of the porous layer preventing losses in the substrate. Quantitative measurement of the quantum efficiency η is obtained by comparing the porous silicon luminescence with that of a lightly doped ruby sample under the same conditions of excitation and detection. Since the spectral distribution of the two samples was different a careful calibration of the monochromator using the blackbody emission of a calibrated lamp was performed. Using the well-known quantum efficiency of the ruby⁸ and, after integration, of the emitted photons over the full porous silicon emission line, we deduced a quantum efficiency of 3%, which is much higher than for all but the most purified bulk silicon.

An external quantum efficiency η can be expressed as

$$\eta(E) = N(E) \{ W_r(E) / [W_r(E) + W_{nr}(E)] \},\$$

where $\eta(E)$ is the quantum efficiency for photons having

frequencies between E and E + dE, W_r and W_{nr} are the radiative and nonradiative rates, respectively, which can be frequency dependent. The term $W_r/(W_r + W_{nr})$ then expresses an internal efficiency that is only limited by the internal properties of each crystallite, while N(E) is the proportion of emitting crystallites.

It is important to know what is the determining factor that limits the 3% quantum efficiency. Fortunately the luminescence offers the possibility of a time-resolved detection after pulsed excitation, and this can be analyzed to give measurements of the sum of radiative and nonradiative rates.

B. Time-resolved measurements

Luminescence lifetimes were measured at various temperatures after excitation well above the band gap either by the third harmonic of a Q-switched Nd³⁺:YAG laser (wavelength 355 nm and pulse duration 10 ns) or by the 454-nm line of an argon laser chopped by an acousticoptic device. Excitation with different peak powers did not show any noticeable difference in luminescence decay shapes and durations. Although the decays are not exponential, they all have the same shape. More precisely they can be deduced one from the other by a simple time scaling. This allows quantitative analysis by defining an average lifetime

$$\tau = (1/I_{\text{max}}) \int I(t)dt , \qquad (2)$$

where I(t) is the luminescence intensity and I_{max} the signal at the time t = 0.

Figure 4 represents typical luminescence decays and luminescence spectra for two samples that differ by their anodic oxidation level. Clearly the luminescence decay is faster for the less oxidized sample, which is also the less efficient. The lifetimes and intensities are found to be nearly proportional.

The same conclusion can be obtained on a single sam-



FIG. 4. Examples of the dependence of the roomtemperature photoluminescence spectra and decay on oxidation level for a 65% porosity layer. The sample for the upper spectrum has the highest oxidation level.

ing does not permanently degrade the sample, as has been reported for nonanodically oxidized samples.⁹ Given that the lifetime is related to W_r and W_{nr} by $\tau = 1/(W_r + W_{nr})$ and that the luminescence intensity is

proportional to $W_r/(W_r + W_{nr})$, the experimental results lead us to conclude that at room temperature and above, the dominant mechanism for the relaxation is nonradiative so that $\tau = 1/W_{nr}$.

The luminescence spectrum with its broad distribution of photon energies, which represents the distribution of confinement energies, offers the interesting possibility of analyzing the dependence of the nonradiative decay as a function of the degree of confinement of the carriers. Figure 6 shows the luminescence decays at various wavelengths measured on a single sample. The main feature is a rapid shortening of decays with increasing frequency (i.e., confinement). A plot of decay rates versus energy of emitted photons is shown in Fig. 7 for samples having different levels of oxidation. Since, at room temperature, nonradiative deexcitation dominates for all frequencies, Fig. 7 illustrates more precisely the dependence of nonradiative recombination on the photon energy E. The law $W_{\rm nr} = A \exp(E/\beta)$ accounts well for the experimental results for nearly two decades of decay rates with a value of $\beta = 0.28$ eV. A systematic analysis of the dependence of A and β on the level of oxidation has not been performed, but it can be already seen from Fig. 7 that a small variation in the oxidation level does not induce a noticeable variation of the inverse slope β , rather it strongly affects the prefactor A. A is seen to increase when the level of oxidation decreases and a typical value for $A = 40 \text{ s}^{-1}$ is obtained for a sample oxidized up to Q_0 .

IV. A MODEL FOR NONRADIATIVE RECOMBINATION

Two interesting conclusions can be drawn from the fluorescence lifetime measurements.

(i) At room temperature, the long nonradiative life-



FIG. 5. The above-room-temperature dependence of photoluminescence and decay time for a 65% porosity layer oxidized up to Q_0 .



FIG. 6. Room-temperature photoluminescence decay signals detected at various wavelengths for a 65% porosity layer oxidized up to Q_0 . The rise times are experimental artifacts.

times measured together with the quantum efficiency of 3% yield a radiative lifetime of order 1 msec. This does not support the commonly made assumption concerning the breakdown of translational invariance in the porous silicon structure. If this were the case, radiative lifetimes would be much shorter, approaching that of a direct transition, that is to say in the range of nanoseconds to microseconds.

(ii) A second interesting result is the relatively low efficiency of nonradiative processes evidenced by the rather high quantum efficiency. Although standard silicon wafers have been used, the measured nonradiative rates are comparable with those obtained on highly pure bulk silicon with a highly passivated surface. We believe that this interesting behavior originates from the microstructure of porous silicon and mainly from the restricted volume available to the carriers. Crystallites of nanometer dimensions have indeed such small volumes and surface area $(10^{-19} \text{ cm}^3 \text{ and } 10^{-12} \text{ cm}^2$, respectively) that the probability of finding nonradiative centers inside or at the surface is very small even for silicon of modest purity. For example the *p*-type bulk silicon, used in experiments



FIG. 7. Dependence of photoluminescence decay rates on photon energy for three 65% porosity layers that differ by oxidation level increasing from the top curve to the bottom one. Measurements were made at room temperature.

reported here, has doping levels as low as 10^{16} cm⁻³, so even if all the dopants were nonradiative centers (which is unlikely) the proportion of quenched crystallite should be as low as 10^{-3} . Concerning the surface, it is well known that oxidation is an excellent surface passivator so a large proportion of dangling bonds should certainly be compensated. For these reasons, we propose that the mechanism for the remaining nonradiative decay comes from an escape of the carriers from the confined zone to more extended or less passivated regions where nonradiative recombination can occur.

The exponential dependence of nonradiative rates with confinement energy suggests two different possibilities: a temperature-activated process or an escape by tunneling through barriers surrounding the confined zone. The first process is ruled out because the β factor of 0.28 eV, which appears in the exponential law, is much larger than kT at room temperature.

Concerning the tunneling, we refer to the schematic potential representation shown in Fig. 8. This itself relates to a schematic view of the anodically oxidized porous silicon texture shown in Fig. 9. Both carriers, electrons and holes, can tunnel, but generally holes are more localized because the potential barriers are higher (this is well known for silicon oxide barriers¹⁰ and Fig. 8 represents such a case). So let us consider the tunneling of electrons through barriers whose thickness and height are a and V_0 , respectively. The well-known expression for the transparency of such a barrier is

$$T = \exp[-4\pi a \sqrt{m(V_0 - E_e)}/h] , \qquad (3)$$

where *m* is the effective mass of the electron inside the barrier material and E_e the electron confinement energy. In fact experiments give access to the luminescence energy instead of the electron confinement energy. They are related by $E = E_G + E_e + E_h$, where E_G is the bulk silicon energy gap and E_h the hole confinement energy. It is difficult to obtain an exact expression of the relation between E_e and E_h because it depends on the details of the geometry of the small crystallites in which the carriers are confined. For simple geometries like spheres or cubes, we will follow Dimaria *et al.*² and take $E_h = 2E_e$.

FIG. 8. Schematic energy-band representation of l = 0 levels formed in potential wells created by nanometer-sized silicon crystallite surrounded by SiO₂ walls. The vertical down arrow represents the optical transition, and the curved one symbolizes an escape of the electron by tunneling.



FIG. 9. Schematic representation of the oxidized porous silicon texture for a sample having roughly 70% initial porosity and electro-oxidized up to Q_0 .

Then using the relation $E = E_G + 3E_e$, expression (3) becomes

$$T = \exp[-4\pi a \sqrt{m(V_0 + E_G/3 - E/3)}/h] .$$
 (4)

Because the nonradiative rate is strongly dependent on the oxidation level we can suppose that the barrier material is SiO₂ for which a likely value of 3 eV can be chosen for V_0 .¹⁰ This is much greater than the confinement energy, so that Eq. (4) can then be approximated as

$$T = \alpha \exp(E/\beta) \tag{5}$$

with

$$\alpha = \exp\left[4\pi a \sqrt{m(V_0 + E_G/3)/h}\right]$$

α and

$$\beta = (3h/2\pi a)\sqrt{(V_0 + E_G/3)/m} \quad . \tag{6}$$

In fact it is not directly the transparency that is measured but the product of T and the nonradiative recombination outside the confined region. This last contribution is difficult to model because the exact nature of the nonradiative center is not known. For the following, we will focus on the non-temperature-dependent parameters.

Because this simple tunneling model provides good qualitative agreement with the experimental exponential law, it is interesting to determine the barrier thickness from the experimental value of β by setting $V_0=3$ eV, which corresponds to a SiO₂ barrier and an average effective electron mass of $m_e/2$. This leads to a value of a=5 nm, which is in the range of sizes that characterize the oxidized porous silicon structure. The result is not too strongly affected by the exact nature of the barrier be-

cause it depends on the square root of V_0 . This can explain the identical slope found for the plots of luminescence decay rate versus photon energy of differently oxidized porous samples as shown in Fig. 7. In contrast to β , the prefactor A, being proportional to α , is strongly affected by the variation of a and V_0 , since they appear in an exponential.

This remark can explain the particular shape of the luminescence decay signal and the fact that the shape is invariant though the time scales are different when the wavelength of observation is changed. Consider D(A) to be a distribution of the prefactor A, which is now considered as a random variable. D(A) originates from a distribution of barrier thicknesses and will be supposed not to be correlated with the crystallite size (and hence with confinement energy). The exact expression for D(A) is certainly difficult to establish, but it is not important for the following. The decay signal f(t,E) at a frequency E will then be a distribution weighted by D(A) of exponential decays

$$f(t,E) = \sum_{A} D(A) \exp(-W_{A}t) ,$$

where following the tunneling model, $W_A = A \exp(E/\beta)$.

It is then clear that the signals $f(t,E_1)$ and $f(t,E_2)$ observed at different frequencies E_1 and E_2 , respectively, have the same shape upon a scaling factor on the time because $f(t,E_1)=f(Kt,E_2)$ with $K=\exp[(E_1-E_2)/\beta]$. This interesting behavior can be useful as a new technique for the characterization of material such as porous silicon because it allows the extraction of the barrier distribution and its dependence with the electrochemical parameters.

At this point it is important to point out that the proposed explanation for the nonexponential luminescence decays, which originates from the nonradiativerecombination-rate distribution, contrasts with the usual one that is used for radiative recombination of carriers in bulk semiconductors. In this case the recombination rate, which depends on the electron-hole distance, is then dependent on time. The consequence is also a nonexponential decay signal but with a power dependence of the shape that has not been seen for porous silicon at room temperature.

V. CONCLUSION

Bright visible light emission from porous silicon after photoexcitation or electroexcitation is a very exciting phenomenon from a fundamental point of view and for its promise in applications. The anodic oxidation of well-controlled porous layers has been shown to be a quantitative passivation technique that allows for good control of the nonradiative losses. At room temperature and above, the measurement of the photoluminescence quantum efficiency and decay times show that nonradiative recombination dominates. The observation of an exponential dependence of the nonradiative rates with confinement energies, which increases with increasing confinements, is explained in terms of a model in which carriers escape from the crystallite where they were confined. A model of escape by tunneling through silicon oxide barriers accounts well for the experimental results. It provides another illustration of quantum size effects complementing the quantum size effect on energy levels. This model could also be useful to obtain a better control over of the numerous parameters that act on the luminescence properties of the electro-oxidized porous silicon.

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FIG. 9. Schematic representation of the oxidized porous silicon texture for a sample having roughly 70% initial porosity and electro-oxidized up to Q_0 .