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1996 J. Phys.: Condens. Matter 8 6235

(http://iopscience.iop.org/0953-8984/8/34/013)

J. Phys.: Condens. Matter **8** (1996) 6235–6249. Printed in the UK

Eigenstates in irregular quantum wells: application to porous silicon

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Received 29 February 1996, in final form 17 May 1996

Abstract. We discuss the effects of geometrical irregularities on the properties of quantum states in irregular wells. This may apply to small crystallites, quantum dots or wires. We show that geometrical irregularity may play an essential role in the electro-optical properties of porous silicon. The fundamental state is found to be essentially confined in the inner free volume of the irregular structure. The consequence is a screening of the fundamental wave-function from the surface. This leads to an enhancement of the quantum confinement effect hence an increase of the effective band gap and modifications in the density of states in the near band gap region. The screening also lowers the coupling with surface states, a fact which may contribute to explaining the large luminescence yield found in this material. We show that geometrical irregularities may have a surprising passivation effect for the fundamental state. In the same way the acoustic phonons have a qualitative tendency to be localized near the surface, so that the electron–phonon coupling could be also decreased, for the fundamental energy state, by the existence of geometrical irregularity.

1. Introduction

Quantum states in wells constitute one of the fundamental ingredients in the understanding of the properties of solids. In the lack of analytical results, we have no knowledge of the specific effects of the shape of crystals on their quantum properties. This lack is compensated by the fact that most of the properties of solids, for instance the density of states, are indeed independent of the shape for large crystals. If, however, we consider small systems, in the nanometre range, this approximation may not be valid. This is the question that we discuss here for a specific example. This work was motivated by the existence of the remarkable electro-optical properties of porous silicon, a system in which strong geometrical irregularity may exist.

Since the paper of Canham [1] in 1990 the fact that porous silicon emits intense visible light has excited considerable interest. There essentially exist three explanations for the mechanism of visible photon emission: a quantum confinement effect due to the very small scale of the porosity, a possible emission by microscopic local molecular groups or luminescence from states in the band gap of possible amorphous structures. Many recent experiments and discussions leave the physical nature of the luminescence open to question. On the other hand the mesoscale geometry of this porous material is far from being precisely described and possibly will never be. It has been suggested [2, 3] that geometrical irregularity may play an important role in the properties of this material. This

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0953-8984/96/346235+15$19.50

paper is devoted to discussing the possible effects that small-scale irregularity (of the order of 1 nm) would have on the opto-electronic properties. The effective band gap and the density of states near the band gap are strongly perturbed by geometrical irregularity [4]. A number of experimental facts such as the weakness of non-radiative processes and the influence of the medium surrounding the porous structure itself can also be possibly linked to the roughness of the structure. In particular we show that small-scale irregularity has a surprising passivation effect on the surface.

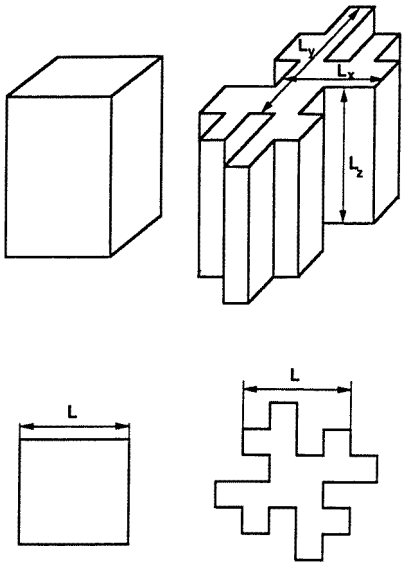

Figure 1. The two geometries that we compare: on the left a square wire and on the right the irregular structure that we discuss. It is a cylinder of height L_z with an irregular base. If $L_z \gg L_x, L_y$, it pictures an irregular wire. We will also discuss the case of $L_x = L_y = L_z = L$ which corresponds to an irregular crystallite or quantum dot. The geometry of the base, an irregular 'prefractal', is shown at the bottom. The area of this irregular base is the same as that of the square from which it is issued. Hence, classically, the density of states for these two systems should be the same independent of their shape. Figures 4 and 5 show that this is far from being true.

The reason why geometrical irregularity was not considered before in order to understand the properties of porous silicon is that knowledge on quantum states in irregular wells was not available until recently. The present work is the extension to semiconductor physics of the results which have been found in the study of the fractal drum described in [2] and [5]. The present work is devoted to describing what may be the possible links between the properties and structure of porous silicon and the known properties of irregular or fractal resonators with eigenmodes named 'fractinos'. We do not consider here that porous silicon is indeed a mass fractal as in [6]. We restrict the discussion of the possible effects of a simple geometrical irregularity of the prefractal type shown in figure 1. We will show that there exists a strong increase in the quantum confinement effect due to the irregularity. This indicates that irregular silicon crystallites or wires might display a strongly increased blue shift in the luminescence. Qualitatively speaking this tells us that, from the point of view of electrons or holes, irregular solids appear to be smaller than their actual size.

One of the main results of this study is that, at small energy, the density of states in

a solid depends strongly on the shape of the solid. This differs from the usual statement in solid state physics that the density of states depends on the volume only, a statement which is only true in the asymptotic (small-wavelength) limit. It is not true for those states of small energies which participate in the transport and electro-optical properties of small semiconductor clusters. Up to now, little has been done to take care of the shape dependence of the properties of small quantum structures.

In this work we aim to describe the overall qualitative effects of the irregularity for a specific example. We consider what we call a Sommerfeld regular or irregular wire or crystallite as pictured in figure 1. It is a cylinder of height L_z, the base having the shape shown in the figure. It is considered here as an empty box with infinite potential walls. Because we wish to discuss the effect of the irregularity alone we will compare irregular wires (or crystallites) with regular wires (or crystallites) having the same volume [5]. Clearly this geometry is very particular and cannot be considered as a precise model for the material. However, upon understanding the nature of the physical effects behind the numbers that we obtain, we will be able to draw a few conclusions concerning the effects of geometrical irregularity in general.

2. Electronic states in irregular geometry

In this first approach we forget the crystalline structure of silicon and look only for the envelope wave-functions in the framework of the effective mass theory. First-principles pseudo-potential calculations [7, 8] for regular wires have indicated that quantum confinement transforms the wires from indirect gap to direct gap and that effective mass approximation is not a bad approximation [9, 10]. We then take care of silicon electronic properties by using appropriate effective masses [11]. The envelope functions are solutions of the Schrödinger wave equation in the volume of the irregular solid with boundary condition close to the so-called Dirichlet condition: $\Psi = 0$. This would be the correct boundary condition for an infinite work function. (On the contrary the boundary conditions for the lattice vibrations are free and this induces a very different behaviour for the spatial dependence of the lattice vibrational amplitude.)

To indicate how we transpose the results obtained for the fractal drum to our problem we recall that the solutions of the Schrödinger equation, $i\hbar\partial\Psi/\partial t = (-\hbar^2/2m)\Delta\Psi$, in such an empty box have the same form of time evolution and the same eigenstates as the Helmholtz scalar wave equation $\Delta\Psi - (1/c^2)\partial^2\Psi/\partial t^2 = 0$, if we use the same boundary condition $\Psi = 0$. (Here c is the wave velocity). In turn, in [2] and [5] we have used the analogy between the Helmholtz equation and the diffusion equation, $\Delta\Psi - (1/D)\partial\Psi/\partial t = 0$, where D is a diffusion coefficient, with the same boundary condition $\Psi = 0$. Note that this last equation is formally identical to the Schrödinger equation under the change of D by $(i\hbar/2m)$. These three problems have similar eigenvalue equations which in our case are written

$$(-\hbar^2/2m)\Delta\Psi_N = E_N\Psi_N. \tag{1}$$

In the particular geometry that we consider in figure 1 there exists only a geometrical irregularity in the horizontal x, y-plane. In consequence the general solution splits into a product of a function of z multiplied by a function of x and y

$$\Psi_N(x, y, z) = (2/L_z)^{1/2}\Psi_n(x, y)\sin(k_z z) \tag{2}$$

with $k_z = n_z\pi/L$ with $n_z = 1; 2; \ldots$ Note that we use here the condition $\Psi = 0$ on the boundary instead of periodic boundary conditions. The difference is very small for long

wires but it is of great significance in the case of the quantum dot. The function $\Psi_n(x, y)$ is a solution of the planar eigenvalue equation

$$(-\bar{h}^2/2m)\Delta\Psi_n = E_n\Psi_n \qquad E_N = E_n + (\bar{h}^2k_z^2/2m). \tag{3}$$

In our work on the fractal drum we have obtained about 300 eigenvalues for the corresponding planar eigenvalue equation $\Delta\Psi = (-\omega^2/c^2)\Psi$. The computation was based on the exact analogy between the Helmholtz and diffusion equations. In this calculation there remain errors which are due to the space discretization of the problem and errors which are due to numerical truncations. As discussed in detail in [5], these errors are negligibly small in the part of the energy spectrum that we consider here. The numerical values which are given in [5] are the values of Ω^2 where Ω is a reduced eigenfrequency defined by $\Omega = \omega/\omega_0$ where $\omega_0 = 2\pi c/L$ is the fundamental frequency of the square drum with a side L. The computation has been performed with a 128×128 grid for the square and with an equivalent number of points for the irregular case of figure 1. The number of points on the smaller linear segment of the perimeter is then equal to 31. The reader can find numerical values for the 20 lowest eigenstates in [5] or can write to the first author for more numerical values.

In the corresponding square well with side L the eigenfunctions are of the form $(2/L)\sin(k_x x)\sin(k_y y)$ with $k_x = n_x\pi/L$ ($n_x = 1; 2; \ldots...$) and $k_y = n_y\pi/L$ ($n_y = 1; 2; \ldots...$). The eigenvalues for the square well are

$$E = E_{cf}(n_x^2 + n_y^2)/2 \qquad n_x, n_y = 1, 2, 3, \ldots$$
$$E_{cf} = (\pi^2/L^2)(\bar{h}^2/m). \tag{4}$$

With this notation the energy E_{cf} is the confinement energy in an infinite square wire with side L. In the following discussion we use the correspondence $E/E_{cf} = \Omega^2$ to transpose our numerical results into eigenvalues for the irregular well. To keep in mind an order of magnitude related to porous silicon we take as an example $L = 4$ nm and $E_{cf} = \approx 47$ meV. Instead of the free-electron mass one should use, as discussed in [7], for the conduction band an effective mass given by $3m^{*-1} = (m_l^{-1} + 2m_t^{-1})$ with $m_l = 0.98m$ and $m_t = 0.19m$ that is $m^* = 0.26m$. The scale of confinement energy for conduction electrons in the infinite square wire is then $E = E_{cf}(m/m^*) \approx 0.180$ eV. In a first approximation for the valence band we deal separately with the heavy and the light holes. The confinement energy is of the order of $E_{cf,hh} \approx 0.1$ eV for heavy holes (with $m_{hh} = 0.49m$) and of $E_{cf,lh} \approx 0.29$ eV for light holes (with $m_{lh} = 0.16m$). Giving this scale of energies and considering that we are interested in the near-band-gap energies we can restrict the discussion to the very few lower-energy states. The values of E/E_{cf} for the fundamental and the first six excited states are listed in table 1.

Table 1. Eigenvalues of the lowest seven eigenstates of the irregular well (in units of the confinement energy for a square well or irregular wire with infinite length). The first and fifth excited states are doubly degenerate due to the symmetry that exists in our example.

	Fund.	1st	2nd	3rd	4th	5th	6th
E/E_{cf}	3.31	6.26	6.26	6.56	6.93	8.75	8.75

One sees from these values that due to the above irregularity there exists an upshift of the bottom of the conduction band of the order of $0.18 \times 3.3 = 0.59$ eV and a downshift of 0.3 eV for the (heavy-hole) valence band. This effect is large and cannot be neglected. Within the

same volume, the band gap in the regular wire is $0.18+(E_g = 1.12)+0.1 = 1.40$ eV while in the irregular wire it is of the order of 2 eV.

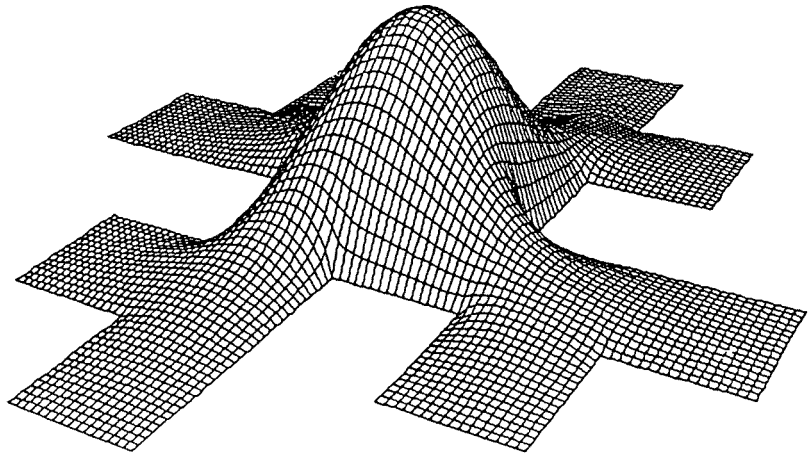

Figure 2. The wave-function of the fundamental state of the irregular quantum well. The strong decrease of the wave-function amplitude in the protrusions is indicative of an efficient screening by the irregularity. In a very crude approximation the state is confined in the inner square of the prefractal shown in figure 1. In this approximation the electron does not see the total surface of the crystallite.

The waveform of the fundamental is shown in figure 2. The fundamental state exhibits no nodeline, as predicted by general theorems, and it is centred in the larger region of the wire or dot. One observes in the figure that the amplitude decays strongly from the centre towards the edges of the crystallite. There exists then a 'screening' of the waveform by the irregularity. This screening effect is general, whatever the particular form of the irregularity. It is illustrated in figure 3, which presents maps of the amplitude of the fundamental state for different contour geometries. In all these cases, the fundamental state is seen to be confined in the interior of the grain, in the 'internal free volume', which is smaller than the physical size of the system. This is why its energy is markedly increased. The general origin of this effect is the known impossibility for a structure with a given size to propagate a wave of half-wavelength larger than its size. This is valid in 2D as well as in 3D. An extensive quantitative discussion of this effect has been given in [5]. It is based on the formal analogy between the diffusion and wave equation.

A conspicuous consequence of the screening effect is that the wave-function of the fundamental state is very small on the surfaces of the protuberances (see figures 2 and 3). This indicates a smaller coupling with surface states and weaker surface recombination as discussed later.

To compute the near-gap density of states, relation (3) is applied and the states are reordered according to their energy in order to obtain the differential density of states. The results are shown in figure 4 for an irregular cylinder of height $L_z = 100$ nm (an irregular wire) and in figure 5 for an irregular cylinder of height $L_z = 4$ nm (an irregular quantum dot). The zero of energy has been taken at the bottom of the conduction band of a large silicon crystal. We have not taken care of the light-hole contribution which would contribute moderately below an energy $-[E_g + (3.3 \times 0.29)] \approx -2.1$ eV. The large density of states for the near-gap energies in the case of the wire is reminiscent of the divergence of the

Figure 3. The wave-function of the fundamental state of irregular quantum wells of various shapes. As the fundamental state has no nodelines, the amplitudes are always positive. The heights of the amplitudes are represented by different grey levels, the black region representing the maximum values and the white regions nearly zero amplitudes. Screening by the irregularity is always observed, in the same way as in figure 2. This illustrates the generality of the screening effect, and its insensitivity to the peculiar shape of the irregular contour.

differential density of states in a 1D system: for these energies the states are the product of the fundamental state for the irregular quantum well and an ordinary 1D sine function (2). The strong increase in the density of states around 1 eV for the irregular wire is due to the fact that, as seen in table 1, there is a group of four excited states which are close in energy. It is clear from the comparison between the regular and irregular density of states that if geometrical roughness exists in the porous silicon filaments it will play an essential role in the optical properties of the material. Besides the density of states, other specific properties may be related to the effect of the irregular geometry. They will be considered later.

3. Are porous silicon wires smooth or irregular?

If one asks the reason for irregularity, one should first ask whether there are serious reasons to believe in regularity. The etching process has no reason to produce smooth surfaces. IR spectroscopy of single-crystal surfaces after HF treatment has established that HF-treated surfaces are microscopically rough [12].

But do we know more about the geometry? Small-angle x-ray scattering of porous silicon layers [13] has indicated roughness on the 1 nm scale, the range that we use in our examples. Geometrical features down to the 1 nm scale are mentioned in atomic force microscopy and STM studies of porous silicon [14, 15]. In the high-resolution STM pictures of Dumas *et al* [16] geometrical features of 2–5 nm are typically observed and exhibit details even smaller than 1 nm.

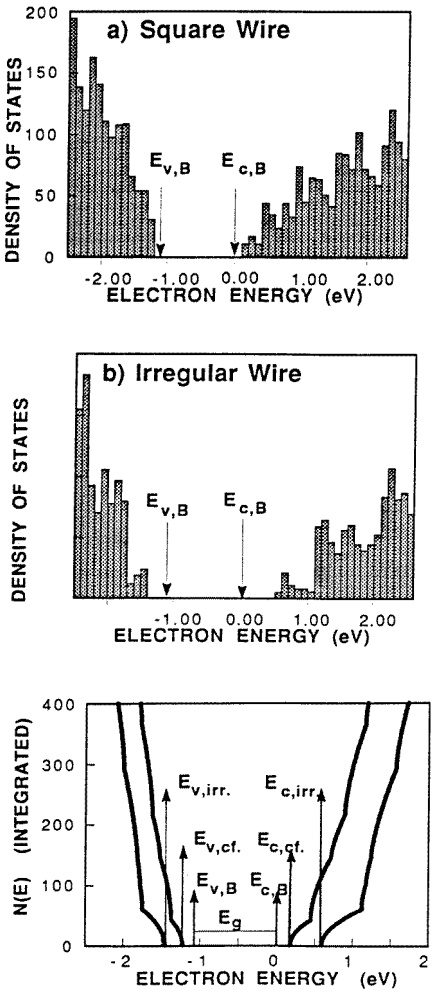

Figure 4. A comparison between the density of states in a square wire and in an irregular wire of silicon having the same volume $L_x L_y L_z = 4 \times 4 \times 100$ nm^3. Only the near band-gap region is shown. (a), (b) The differential density of states (within a width of 0.1 eV). The zero of the energy scale $E_{c,B}$ has been chosen at the bottom of the conduction band of a large silicon crystal. The band edges for a large single crystal are indicated as $E_{c,B}$ and $E_{c,V}$. The integrated density of states is shown at the bottom. This last panel exemplifies the respective role of regular and irregular confinement, showing a strong blue shift due to irregularity only.

Specific surface areas up to 900 m^2 cm^{-3} have been mentioned [17]. For example for a porosity of $P \approx 70\%$, the measured surface area is of the order of $S \approx 600$ m^2 cm^{-3}. If one considers a simple model of porous silicon made of irregular wires as discussed here, each wire has a volume $v = L_x L_y L_z = L_x^2 L_z$ and a total surface area $s = 8 L_x L_z$. If there are n such wires per cubic centimetre, the porosity and specific surface areas are related by $P = (1 - nv)$ and $S = ns$, hence

$$P = 1 - S(v/s). \tag{5}$$

Using the measured values for P and S one finds from (5) a ratio $v/s = 0.5$ nm.

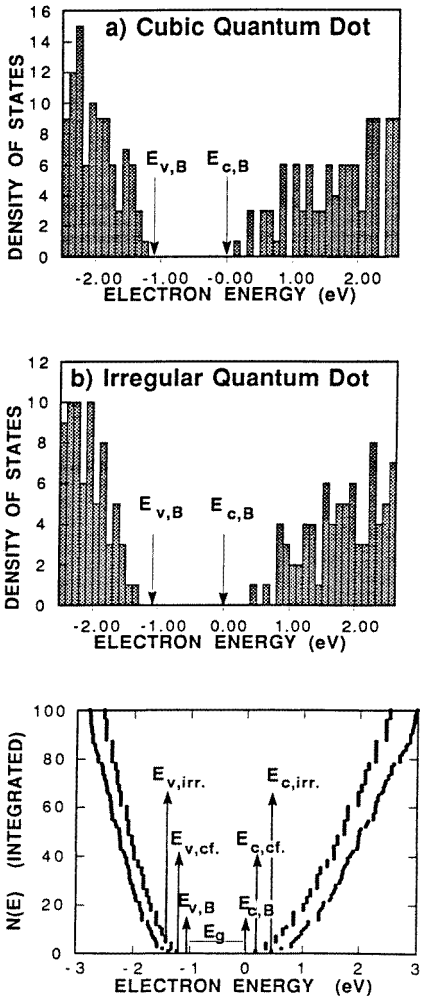

Figure 5. A comparison between the density of states in a cubic quantum dot and in an irregular quantum dot of silicon having the same volume $L_x L_y L_z = 4 \times 4 \times 4$ nm^3. Only the near-band-gap region is shown. (a), (b) The differential density of states (within a width of 0.1 eV). The zero of the energy scale $E_{c,B}$ has been chosen at the bottom of the conduction band of a large silicon crystal. The band edges for a large single crystal are indicated as $E_{c,B}$ and $E_{c,V}$. The integrated density of states is shown at the bottom. This last panel exemplifies the respective role of regular and irregular confinement showing a strong blue shift due to irregularity only.

In our geometry the volume to surface ratio v/s is equal to $L^2 L_z/8LL_z = L/8$, and the corresponding value for L is then $L = 4$ nm. This is precisely the size that we have considered. Of course other geometrical models could be compatible with these experimental measurements but the measured values do not exclude the kind of roughness that we consider and indicate that the numbers that we use have an acceptable order of magnitude. Then, much experimental evidence establishes that irregularity actually exists at the characteristic scale considered in our model.

4. Surface recombination in irregular systems

We now give a semi-quantitative discussion of the coupling of a surface state (surface recombination centre) with the fundamental electronic state. In a crude approximation we consider that the surface recombination probability is proportional to the square of the matrix element between the fundamental electronic state and a surface state. This surface quantum state is described by a wave-function φ_s centred at some point on the surface of the crystallite. This wave-function is supposed to be localized within a short distance from the surface of the system. In a first approximation we consider that the matrix element $|\langle\Psi, \varphi_s\rangle|$ of the interaction of interest is proportional to the absolute value $|\Psi(\Delta)|$ of the fundamental wave-function at a small distance Δ (of the order of 0.1 nm) from the boundary. As seen in figure 2, the waveform of the fundamental state is essentially confined in the inner 'free' volume of the irregular structure. In our case, this free volume is a square of side $L/2$.

To discuss how the luminescence yield may be modified by geometrical irregularity, one should discuss surface recombination for the same confinement energy in square or irregular wires. For this reason we compare surface recombination for a square wire of side $L/2$ and for our irregular wire with similar confinement energies as indicated schematically in figure 6. Note that from (4) for a given confinement energy E_{cf} the side of the corresponding square wire is $L_{sq}^2 = (\hbar\pi)^2/mE_{cf}$. The side of the square generator which gives the same confinement energy is $L_{ir}^2 = 3.3(\hbar\pi)^2/mE_{cf}$ as we know from table 1 that the effect of irregularity is to increase the confinement energy by a factor of order 3.3. Another way to express the same result is that the fundamental state is confined in a square of radius $L/3.3^{1/2}$, a length of the same order as $L/2$.

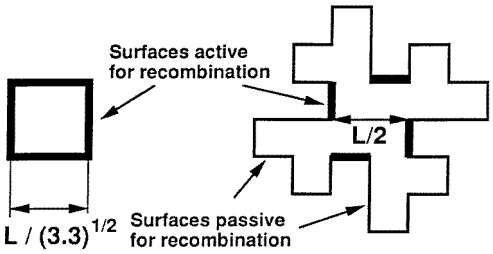

Figure 6. A schematic representation of the surface passivation effect for the fundamental state. For sizes which give rise to the same luminescence energy the very structure of the electron density in figure 2 indicates that a large fraction of the surface is weakly coupled with the fundamental state and that consequently the surface recombination probability may be smaller if the zones which are possibly active have no surface recombination centres.

There are regions of the surface, as indicated schematically in the figure, which may not contribute to surface recombination for electrons or holes in the fundamental state because the electron density is screened. These regions behave as if they were passivated by the irregularity. In the square wire the entire surface may contribute to surface recombination whereas, in the irregular structure, which has a larger surface, the fraction of the active surface is of the order of one-eighth of the total surface.

In order to compare the surface recombination in the two situations we have computed the average of the square of the matrix element $|\langle\Psi, \varphi_s\rangle|$ that we take proportional to the average $|\Psi(\Delta)|_{av}^2$ of the square of the value of the wave-function at a distance Δ from the surface. We find numerically for the same confinement energies that the ratio

$|\Psi(\Delta)|^2_{av,square}/|\Psi(\Delta)|^2_{av,irregular}$ is approximately equal to three. There are then three situations:

(i) If the surface recombination centres are a given *fraction* of the surface sites, the surface overall recombination efficiency will be the product of the average square of the matrix element and the surface area. In this situation we find that the surface recombination efficiency is slightly higher (25%) for the irregular case although the surface is four times as large.

(ii) In contrast if the *number* of surface recombination centres is the same in both systems, the surface efficiency will be smaller by a factor of the order of three in the irregular case. This situation may occur if the number of surface recombination centres is not proportional to the surface area but is limited by some other phenomenon. For instance this would be the case when transition element impurities, known to be very efficient recombination centres on silicon surfaces, are present in the etching solution as remaining impurities and have been deposited on the surface.

(iii) Furthermore, if the number of recombination centres per crystallite is small enough, it may even happen that they are situated on that part of the irregular surface where the wave-function is very small. In this last case these wires or dots will have a very low surface recombination rate. The system will behave in a very inhomogeneous manner with some of the wires or dots presenting a very weak surface recombination. The fact that the wave-function of the fundamental state is contained in the inner volume will be also true if there exists irregularity in the third dimension. Consequently, the passivation effect could even be greater than what we have discussed.

Note that this passivation effect will be reduced for the excited states which are shown in figure 7. For these first excited states, the electron density occupies the protuberances and these excited states will be more strongly coupled to the surface.

Irregularity of the geometry can contribute to localization of the electronic states. Localization may exist for lowest-energy states if there exist narrow ‘paths’ or ‘necks’ in the structure. As discussed in [5], irregularity favours localization but does not systematically lead to localization. Note, however, that the particular geometry that we have considered possesses a C_4 symmetry. With the same overall structure but without symmetry, for example if the four protrusions in figure 1 were different, each of the first four excited states would be localized in each of the protrusions. An example of a localized state is shown in figure 8. In this case it is easy to see that the coupling to the surface will be increased by a localization occurring near the surface.

The boundary conditions for the lattice vibrations are free and this could induce an opposite behaviour for the spatial dependence of the lattice vibrational amplitude, which could be large at the surface. Note that even a smooth, but small, crystalline cluster presents a large surface to bulk ratio as compared to crystals of macroscopic size. Were the cluster to possess irregular and even more fractal geometry, this surface to bulk ratio would even be larger. Take the case of a cubic silicon cluster of 3 nm side: the ratio of the numbers of surface to bulk atoms is of the order of one. This means that half the phonon density of states represents the ‘surface’ phonon density of states. In our preliminary results for the behaviour of the vibrations of a fractal drum with free (Neumann) boundary conditions we have found that this is indeed the case [18]. We find that the eigenmodes for acoustical vibrations are significantly ‘confined’ in a part of the drum. This is illustrated in figure 9, which shows an example of a particular acoustical mode in an irregular crystallite. All these properties could modify the electron–phonon coupling. Although the *average* phonon density is uniform over the structure, the fundamental electronic state will be only weakly

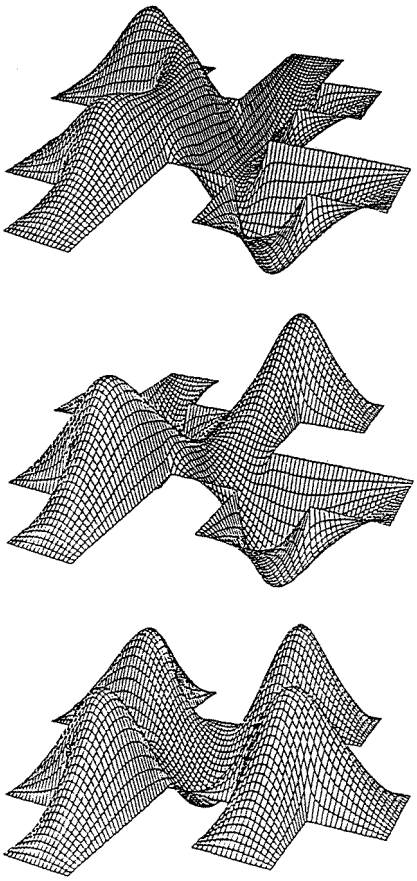

Figure 7. Wave-functions of the first excited states of the irregular quantum well: from top to bottom, the first (doubly degenerate) and third and fourth excited states. The electron density in these states is large near the surface and these states will be strongly coupled to surface states.

coupled to the high-energy phonons because they have a short wavelength. Only those phonons which have a smooth spatial dependence will be relevant to couple the lower-energy states. For these reasons it is quite feasible that the dynamics of thermalization of carriers are slower in irregular structures.

In the same way it is possible that (radiative and non-radiative) recombination processes involving phonons in porous silicon would be slowed down as compared to ordinary bulk material. Here again, this decrease should be especially pronounced for the lower-energy states, which stay remote from the surface. Since these states are the most plausibly involved in the recombination pathway, the lifetimes (radiative and non-radiative) should be further increased by this effect, as compared to standard confinement theories.

5. Other specific experimental effects of geometrical irregularity

We now discuss what other types of experimental evidence may be related to the same facts. Amisola *et al* [15] have mentioned that their measurements of the surface density

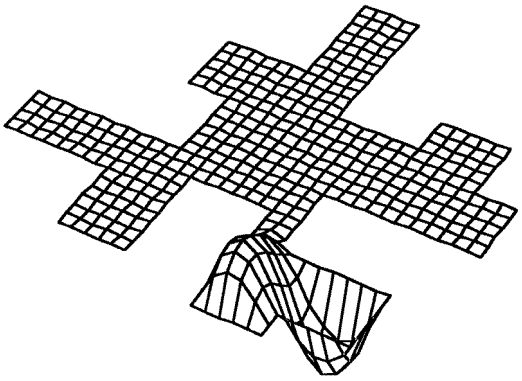

Figure 8. If the geometry presents no symmetry a localized excited state of the form indicated in the picture can exist.

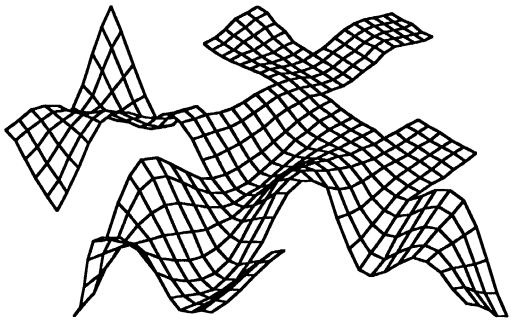

Figure 9. A particular acoustical phonon mode in an irregular structure.

of states do not show a peak corresponding to the 1.8 eV photoluminescence peak energy. This is directly compatible with the fact that those states which are responsible for intense luminescence are in fact 'far' from the surface as observed for screened states.

Recently, Dubin *et al* [19] have observed that the electronic states occupied by excited photo-carriers are delocalized when porous silicon is in etching solution and localized when porous silicon is in dry ambient. Correspondingly, the strong red photoluminescence is only observed in dry ambient. This effect was interpreted by Chazalviel *et al* as the consequence of the change in the dielectric constant of the surrounding medium [20]. Besides this effect, which may actually exist, one could also use the fact that there is a lowering of the work function due to the existence of an external medium. This lowering may result in a coupling of the electron states with the external medium, a coupling which should be especially strong for the excited states and for an irregular geometry. The electron states, which may be localized for dry porous silicon, can become delocalized in a wet environment. The photocarriers may then be transferred to remote parts of the structure, and recombine non-radiatively. In contrast, in a dry environment, the residence time of an electron in a given crystallite may be long enough that electrons and holes can cascade preferably to a local lowest-energy state, hence yielding the intense red luminescence. In this picture the strong IR absorption mentioned by Dubin *et al* could be the direct absorption between the

local lowest-energy state and the excited states of the irregular structure.

In our framework, it is also of interest to discuss the experiment of Dumas *et al* [16, 21]. These authors have used STM in vacuum together with low-energy scanning cathodoluminescence microscopy. This method was highly promising in the sense that there was hope to detect directly the size of the emitting elements. These authors have observed that the STM topography and the photon map of the same region of the sample are different. We believe that geometrical irregularity can give a hint to understand this fact.

To illustrate how the quantum behaviour in protrusions can perturb common expectation about STM we compare qualitatively an STM image of a crystal with one protrusion for a metallic and a silicon surface with the same geometry, as shown in figure 10. If the object to be imaged is a metal then the Fermi electrons which give rise to the tunnel current have a quantum wavelength of order 0.1 nm. They occupy evenly a protrusion of 1 nm and the STM image gives a faithful representation of the topography. If however the material is a semiconductor, the quantum state corresponding to the fundamental state does not penetrate a protrusion of 1 nm. In consequence, at low applied potentials, the tunnel current will hardly change when the scanning tip approaches the protrusion instead of being increased as in the case of a metal. For higher potentials, since STM probes the local density of states, the current map may exhibit either a protrusion or a dip. Such perturbations are expected to occur in a wide potential range, and only at high values of tip potential (much larger than the confinement energy) can one hope for topographic information to be recovered. On the other hand, even in the simplest model of luminescence, a given current injection will give different luminescence depending upon whether the current is injected in regions with high or low luminescence efficiency. These facts should be taken into account in order to understand the differences between STM pictures and photon maps obtained in cathodoluminescence spectroscopy.

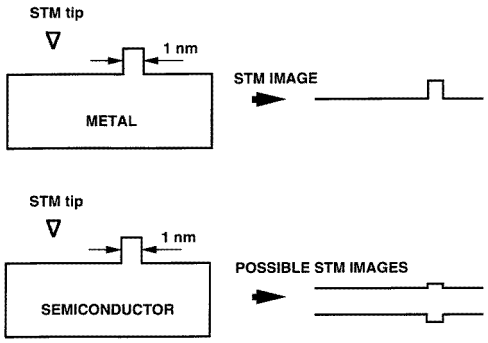

Figure 10. How STM can give a different image in the case of an irregular metallic structure and in the case of a semiconducting structure with the same geometry. In this case the STM imaging may be altered by the screening of the fundamental state in the protrusion.

6. Conclusions

In summary we have discussed, in a particular case, the specific properties of wave-functions in irregular quantum wells. We have shown that a semiconductor irregular wire or quantum dot appears spectroscopically smaller than its physical size. This effect is due to an increase

in the confinement effect due to the screening of the wave-function by the geometrical irregularities. In their fundamental state electrons and holes are expected to be weakly coupled to the surface. The picture that we have developed is simpler than the quantum sponge model of porous silicon proposed by Sawada *et al* [22].

The screening effect of the fundamental wave-function is a general effect. It is not related to the particular geometry that we have used. Note that excitonic effects would still increase the shielding from surface states. The shielding effect may then help to understand the high yield of luminescence.

Of course, our results cannot be used directly to understand quantitatively the properties of a given sample in which the geometry is unknown but this is the situation of porous silicon geometry. The ideas that we have presented are simple and general and are based on a single main hypothesis: geometrical irregularity. The screening, leading to increased confinement and smaller coupling to the surface, is a direct consequence of the very general property that there exists a cut-off wavelength in wave-guides. The simple concept of geometrical irregularity helps us to understand in simple language some of the principal properties of porous silicon.

Acknowledgments

This work was supported by DRET under contract 93-2525A. One of us (SR) has benefited from the EEC 'Human Capital and Mobility' program. The computation was performed at the Institut du Développement et des Ressources en Informatique Scientifique (IDRIS) in Orsay. Useful discussions with F Ozanam are gratefully acknowledged.

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