Mechanism of porous-silicon luminescence

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(Received 16 May 1997)

We discuss the discrete spectrum induced by bulges on threadlike mesoscopic objects, using two models, a continuous hard-wall waveguide and a discrete tight-binding model with two sorts of atomic orbitals. We show that elongated bulges induce numerous quasibound states. In the discrete model we also evaluate the probability of transition between the localized states and extended ones of the ''valence'' band. We suggest this as a mechanism governing the porous-silicon luminescence. In addition, the model reproduces the dominance of nonradiative transitions, blueshift for finer textures, and luminiscence suppression at low temperatures. [S0163-1829(97)03336-5]

The effect of luminescence of porous silicons has attracted a lot of attention recently.[1] There are various attempts to explain it, but none of them can be regarded as fully convincing at present. It is clear that the porous material texture plays the decisive role, because first the effect is absent in the bulk, and second, a refinement of the structure is known to cause a blue shift of the emitted light. In this paper we intend to discuss one possible quantum mechanical mechanism which employs transitions between the valence band and a large family of localized states below the conductance band; we put emphasis on describing the geometric conditions under which such families may exist.

It has been suggested that quasibound states in small crystallites may play important role.[2] It is natural to expect that the interior of the porous medium resembles a sort of a calcite cave containing not only loose-end material ''drops'' but also other structures; our main hypothesis is that *a significant portion of them are threadlike objects of a varying cross section*. Under this assumption we may employ recent results on electron bound states in quantum wires which are bent, protruded, or coupled laterally to another wire.[3–6] The mechanism behind the existence of these bound states is an effective attractive potential induced by the geometric modification of the tube. Our key observation is that if the deformation extends over a long interval (relative to the tube cross section), the wave guide can support numerous bound states and the discrete spectrum has typical one-dimensional features: most eigenvalues are found at the bottom of the spectrum, i.e., away from the continuum. Hence if the variation of the tube cross section produces protrusions which are rather long than wide, such a tube has many more quasibound states than other conceivable structures, so the corresponding radiative transitions are responsible for the most part of the emitted light.

Below we shall illustrate this feature on a tube with a single elongated bulge. On the other hand, any model of porous-silicon luminiscence has to be able to reproduce the other experimentally established properties, notably the dominance of the nonradiative transition mode as well as the frequency and temperature dependence of the effect. For this purpose the free-particle quantum waveguide model is oversimplified, because its continuous spectrum consists of a single band. This motivates us to treat the essentially same situation in the tight-binding setting, considering chains of ''atoms'' to which other chains of finite length are laterally attached. If the atomic orbitals are of two different sorts, the spectrum of an infinite chain can consist of distinguished bands which would play the role of the valence and conductance band, respectively.

Adding a finite chain will cause appearance of bound states whose distance from the band edges is controlled by the coupling strength between the two chains. Truncating the discrete ''tube,'' we are able to find the spectrum and the corresponding eigenfunctions numerically. This will allow us to estimate the rate of transition between the quasibound states below the conductance band and extended states in the valence band. This quantity can be compared to the probability of nonradiative transitions due to a tunneling escape of an electron localized in a bulge to a neighboring bulge or to the bulk from which the treadlike structure spreads.

Let us describe briefly the two models; more details will be given in a forthcoming paper.[7] In the continuous model we consider a tube with hard walls which has a constant cross section except for a finite part where it is protruded.[8] The bulge produces bound states no matter how small it is,[5] but of course, the number of such states and the distribution of the corresponding energy levels depend substantially on the geometry. For instance, a hard-wall planar strip of a unit

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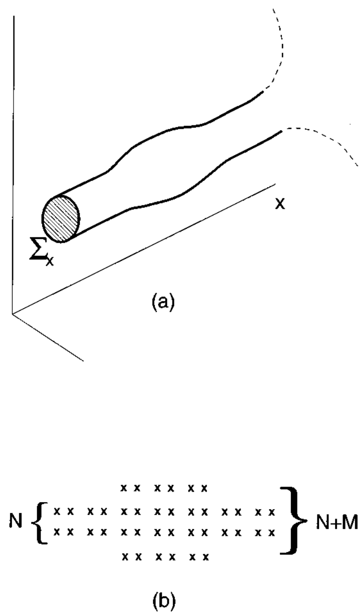

FIG. 1. The models. (a) A tubular guide with a bulge. The bound states of an infinite tube change to quasibound when we couple it to the bulk. (b) The tight-binding model.

width with a stub of the same width and length ℓ considered in Ref. 9 has just one bound state $\lambda(\ell)$ such that $\lambda(\ell)=\pi^2-\pi^4\ell^2+\mathcal{O}(\ell^4)$ for small ℓ and $\lim_{\ell\to\infty}\lambda(\ell)\leqslant 0.93\pi^2$, cf. Refs. 4,10, making the protrusion two-sided, we have still one bound state with the eigenvalue which cannot be lower than $0.66\pi^2$.

On the other hand, elongated bulges produce numerous bound states. As a simple example, consider a boxlike protrusion on a straight planar strip, so the width is $1+\eta$ on an interval of a length L and 1 otherwise. By a bracketing argument[11] the discrete energy levels are squeezed between the eigenvalues of the Laplacian on the rectangle $[0,L]\times[0,1+\eta]$ with the Dirichlet condition on the ''parallel'' boundary and Dirichlet or Neumann, respectively, on the ''perpendicular'' one, that is,

$$\left(\frac{\pi j}{1+\eta}\right)^2+\left(\frac{\pi(n-1)}{L}\right)^2\leqslant\lambda_{j,n}\leqslant\left(\frac{\pi j}{1+\eta}\right)^2+\left(\frac{\pi n}{L}\right)^2 \quad (1)$$

for $n=1,2,\ldots$. The discrete spectrum consists of those $\lambda_{j,n}$ which are below π^2, the bottom of the continuous spectrum; it is clear that with the lowest transverse mode, $j=1$, such states exist for any $\eta>0$ as long as L is large enough. Moreover, in the case $L\gg 1$ there are numerous bound states, with most eigenvalues being concentrated in the vicinity of $\pi^2(1+\eta)^{-2}$, or the higher thresholds $(\pi j)^2(1+\eta)^{-2}$, provided the latter are below the bottom of the continuous spectrum. These conclusions extend easily to a tube with a steplike bulge in three dimensions.

The fact that elongated bulges produce many bound states is not restricted to the above simple example; on the other hand, the eigenvalue distribution depends substantially on the protrusion shape. To get a better understanding, consider a tube whose cross section Σ_x is constant for $|x|>\frac{1}{2}L$ and varies smoothly in the interval $[-\frac{1}{2}L,\frac{1}{2}L]$ [see Fig. 1(a)]. For a fixed x let $\nu_1(x)<\nu_2(x)\leqslant\nu_3(x)\leqslant\cdots$ denote the eigenvalues of the Laplacian with the Dirichlet condition in $L^2(\Sigma_x)$; the corresponding eigenfunctions are $\chi_j(x,y)$, $j=1,2,\ldots$; y being the transverse variable(s). The ''full'' wave function may be then written in the form $\psi(x,y)=\Sigma_j a_j(x)\psi_j(x,y)$ with the normalization $\int_{-L/2}^{L/2}\Sigma_j|a_j(x)|^2dx=1$.

The protrusion-induced discrete spectrum is essentially determined again by the spectrum of the bubble alone; one can employ the bracketing argument closing the bulge at $x=\pm\frac{1}{2}L$ by the Dirichlet and Neumann ''lid,'' respectively. If we assume now that the bulge is *long* and its cross section *changes only slowly* with respect to x the longitudinal derivatives of χ_j may be neglected and we arrive at a Born-Oppenheimer-type approximation: the stationary Schrödinger equation decouples into a family of equations for the slow motion

$$-a_j''(x)+\nu_j(x)a_j(x)=Ea_j(x), \quad (2)$$

where the transverse eigenvalues play role of the potentials. At the same time, if the bulge is long the eigenvalues $E_{j,n}$ of the jth equation are determined approximately by the semiclassical quantization condition

$$\int_{M_j(E)}\sqrt{E-\nu_j(x)}\,dx=n\pi+\mu_j, \quad (3)$$

where $M_j(E):=\{x:\nu_j(x)\leqslant E\}$ is the classically allowed region; the explicit value of the Maslov factor μ_j is not important as long as we are interested in the distance $\delta E_{j,n}=E_{j,n+1}-E_{j,n}$ between the adjacent energy levels which determines the density of states $\rho(E)$. Expanding the square root and neglecting the difference between $M_j(E_{j,n})$ and $M_j(E_{j,n+1})$, we find that the latter approaches in the limit $L\to\infty$ the form

$$\rho(E)=\frac{1}{2\pi}\sum_j\int_{M_j(E)}\frac{dx}{\sqrt{E-\nu_j(x)}}; \quad (4)$$

recall that we are interested only in the behavior of this function below $\nu_1(L/2)$, the bottom of the continuous spectrum, where just one or several lowest transverse modes can have $M_j(E)\neq\emptyset$.

Returning to our example of a boxlike bulge on a unit-width strip, we find that for large L the jth mode contribution to the discrete-spectrum density is

$$\rho_j(E)=\left(\frac{L}{2\pi}\right)\left[E-\left(\frac{\pi j}{1+\eta}\right)^2\right]^{-1/2}, \quad (5)$$

with a singularity at $E_j^{\min}:=(\pi j/1+\eta)^2$.

Other shapes may change the form of the distribution; it is more concentrated close to the bottom of the discrete spectrum the closer is the bulge to the cylindrical shape. For instance, consider the strip of the width $d(x/L)$, where $d(\xi):=(1+\eta)(1-b\xi^2)^{1/2}$ and b is chosen in such a way that $d(\pm 1/2)=1$. The jth term on the right-hand side (RHS) of Eq. (4) is then expressed as

$$\rho_j(E)=\frac{L(1+\eta)}{2\pi\sqrt{\eta(2+\eta)}}E\left(\sqrt{\frac{E-E_j^{\min}}{E}}\right), \quad (6)$$

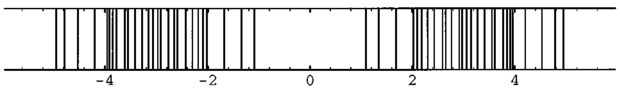

FIG. 2. The spectrum of the tight-binding model.

where $E_j^{\min}$ is the same as above and E is the full elliptic integral of the second kind;[12] it has still a peak at $E=E_j^{\min}$ but less pronounced.

Let us now pass to description of the tight-binding model. We employ the simplest possible choice for the atomic geometry as well as for the interactions between orbitals. We consider N parallel chains of atoms forming a strip in the plane to which we add M finite-length chains which constitute a bulge [Fig. 1(b)]. To mimick the band structure of the semiconductor spectrum, one can choose interactions between orbitals (side-diagonal elements of the tight-binding Hamiltonian) switching between two values **a** and **b** in the horizontal direction; vertically one can choose the same structure or simply a single coupling constant c.

If one has an infinite horizontal strip of width N with no bulge the corresponding spectrum can be obtained summing the spectrum of one horizontal infinite chain [i.e., the pair of intervals $(-\mathbf{a}-\mathbf{b},\mathbf{b}-\mathbf{a})$ and $(\mathbf{a}-\mathbf{b},\mathbf{a}+\mathbf{b})$] and the discrete spectrum corresponding to a vertical line of N atoms; the latter is of course contained in the mentioned intervals if the structure is the same in both directions. The resulting spectrum still exhibit gaps if **a** and **b** are chosen appropriately; in general they become narrower with increasing N.

The spectrum of an infinite strip of width N with a finite number of bulges of width M has a continuous part identical with that of the ''unperturbed'' strip and eigenvalues outside of it. The latter are nevertheless contained in the spectrum of a strip of width $N+M$. Figure 2 shows the eigenvalue plot obtained numerically for a chain ($N=1$) of 40 ''atoms'' and a bulge of 14 ''atoms,'' $a=3$, $b=1$ (in the vertical direction $b=1$). We can distinguish the eigenvalues in the intervals $(-4,-2)$ and (2,4) corresponding to the extended states of the ''valence'' and ''conduction'' bands, and those outside corresponding to states localized mainly on the bulges with an exponential decay outside. In case of several bulges it may occur that an eigenstate is supported by more than one of them; this happens typically if the system has a symmetry. Notice that the extended states are not Bloch states due to the lack of translational invariance.

The knowledge of the eigenfunctions makes it possible to compute the radiative transition probability between the excited bound states living in the bulges and the valence-band extended states which is given in general by the Fermi golden rule

$$W_r(\omega)=\frac{2}{3}\,\frac{e^2}{4\pi\epsilon_0\hbar c}\,\frac{\omega^3}{c^2}\,\frac{1}{V}\sum_{i,f}\;\delta(E_i-E_f-\hbar\omega)\times\left|\int_\Lambda(\vec{e}.\vec{r})\,\psi_i(\vec{r})\,\psi_f^*(\vec{r})\,d^3x\right|^2. \quad (7)$$

We have evaluated the matrix element in question. It is nonzero but not large; the value is typically at least 2–3 orders of magnitude below the upper bound given by the potential step between the bulge ends.

Inserting the values of the constants into Eq. (7), the above observation tells us that the transition probability does not exceed $10^8\ \mathrm{s}^{-1}$; it increases, but not more than one order of magnitude, when ω runs through the visible spectrum. The last named property conforms with the experimentally observed shorter lifetime at the blue edge of the spectrum.[1]

It is further known[1] that $W_r(\omega)$ exhibits a dramatic decrease below the room temperature. To explain this effect one has to take into account that the final-state probability is determined by the Fermi distribution, and therefore the matrix element in Eq. (7) should be multiplied by $P_{\beta,\mu}:=1-(e^{\beta(E_F-\mu)}+1)^{-1}$. Assuming that the chemical potential takes value in the middle of the gap between the two bands, the above factor is of order of e^{-40} at room temperature and the decrement is inversely proportional to T; the suppression is larger at the blue edge of the spectrum.

Other properties of this model also conform with experience for the effect under consideration. Long bulges support many excited states which is necessary to create a macroscopic luminosity output. At the same time, a simple scaling argument shows that the distance between the bound states and the valence band increases as the lateral size of the tubes and bulges become smaller; hence a finer material texture results in a blueshift.

Experimental data show a low emmision efficiency of photoluminiscence measured at room temperature. This strongly suggests that the radiative recombination W_r is dominated by the nonradiative probability W_{nr} which involves the escape of the confined carriers (electrons, holes) from a bulge into a more extended/less passivated neighborhood where a nonradiative recombination can occur. Hence the emitted intensity $I(\omega)\sim W_r(\omega)\tau(\omega)$, where the lifetime $\tau(\omega)=[W_r(\omega)+W_{nr}(\omega)]^{-1}$. Independent measurements[1] of $I(\omega)$ and $\tau(\omega)$ show that $W_{nr}\gg W_r$ and $W_{nr}(\omega)=Ae^{\alpha\hbar\omega}$. In the framework of both our model a decay process related to W_{nr} occurs if the bulged tube is connected to a wider part of the structure (bulk). The tunneling probability can be estimated in the second model from the eigenfunction decay[13]

$$W_{nr}(\omega)=\mathrm{Im}(E_i-E_f)/\hbar=\frac{1}{\sqrt{2m_e}}\,\sqrt{\mathrm{Re}(E_i-E_f)}\,|\psi_{\mathrm{Re}E_i}(L)|^2, \quad (8)$$

where L is the tunneling distance. For typical light photon energies we get $W_{nr}\sim10^5e^{-\gamma(E)L}$, where $\gamma(E)$ is a function of the distance between the eigenvalue and the bottom of the ''conduction'' band. We get $W_{nr}\gg W_r$ at the room temperature as long as $L\lesssim50$ a.u.; for a cooler material and bluer light the dominance is preserved at longer distances.

It is certainly not easy to decide which mechanism is responsible for the porous-silicon luminiscence as long as we know little about the actual texture, and it is fully conceivable that the effect comes from conspiracy of different physical processes. On the other hand, it seems to be straightforward to check experimentally whether the states discussed in this paper may contribute, since quantum wires with bulges of appropriate shape can be fabricated. One could, *a fortiori*, taylor in this way luminiscent systems emitting light of prescribed properties. Moreover, since the mechanism producing bound states in infinite tubes are similar, the same can be done for quantum wires with numerous bends, or pairs of wires coupled laterally through a long ''window.''

In conclusion, we have presented a mechanism which could be responsible for the porous-silicon luminiscence illustrating it on two models. Despite the simplifications, they yield the basic features, i.e., the existence of numerous quasibound states away of the continuum, the dominance of nonradiative transitions, and the spectral shift associated with refining the texture.

Enlightening discussions with F. Arnaud d'Avitaya, I. Berbeziet, J. Derrien, and L. Vervoort are gratefully acknowledged. P.E. thanks Centre de Physique Théorique, CNRS, where this was work was done for the hospitality extended to him. The research has been partially supported by Grant No. AS CR 148409.

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