Size effect in silicon quantum wires

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The quantum size effect in silicon quantum wires may lead to an observable and intense luminescence.

Silicon has been studied more thoroughly than any other semiconductor. A happy combination of physical and chemical properties has made silicon the basic material of microelectronics. However, silicon is an indirect-gap semiconductor, so the bulk material emits light only slightly. The bulk material is thus of no use for developing optoelectronic devices. For such devices it is necessary to use direct-gap semiconductors (GaAs, InP, etc.), but they are incompatible with silicon technology.

Canham *et al.*[1] recently demonstrated that so-called porous silicon (prepared by electrochemical etching from the ordinary bulk material) exhibits an intense luminescence in the visible region when excited with laser light. The photon energy is considerably larger than the indirect band gap, but it is much smaller than the direct gap at the Γ point [the latter is $E_g(\Gamma) = E(\Gamma_{15}) - E(\Gamma_{25}) = 3.42$ eV]. The frequency of an emitted photon is determined by the difference between the energy of an electron in the conduction band and that of a hole in the valence band. Direct radiative recombination of a hole at the top of the valence band and of an electron at a side minimum near the X point of the conduction band cannot occur in bulk silicon because of selection rules. If translational invariance is violated, as it is in microscopic crystals and quantum wires, this prohibition by the selection rules is no longer in force.

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The results of Ref. 1 on the observation of a luminescence have been verified by several groups, who have studied microscopic crystals of Si (Refs. 2 and 3) and Ge (Ref. 5). It was suggested in Refs. 1–5 that a quantum size effect is responsible for the luminescence. The emission is observed when the diameter of the microscopic crystals or the thickness of the quantum wire is in the interval 20–40 Å. The photon energy is in the interval 1.3–1.8 eV.

There have been several studies[6,7] of how the quantum size effect and the Coulomb interaction in microscopic crystals of III–V and II–VI direct-gap semiconductors influence the effective gap width. Since direct radiative transitions are possible even in the interior of semiconductors, the calculations reduce to finding corrections to the bulk gap. The effective-mass method works quite well for particles of size $d > 50$ Å. The Coulomb interaction is important only at $d > 50$ Å. At smaller sizes, the kinetic energy of the particles (which is proportional to $1/d^2$) is more important than the energy of their Coulomb interaction (which is proportional to $1/d$). The ratio of the first Bohr radius of the exciton to the diameter serves as a parameter. Since $a_B = 50$ Å is a typical value, the kinetic energy is large at $a_B/d \gg 1$ because of the quantum size effect, and the Coulomb interaction can be ignored. At smaller dimensions the change caused in the spectrum by the quantum size effect is described only poorly by the effective-mass method, and more-accurate calculations become necessary.[8]

In this letter we wish to show that the spectrum becomes a direct-gap spectrum in silicon-quantum wires of sufficiently small dimensions as a result of a 2D size effect, and there is an effective increase in the energy gap. As a result, luminescence in the visible region becomes possible.

There is another reason why the effective-mass method should not be used for Si particles of small dimensions. As we know, the conduction band is triply degenerate at the center of the Brillouin zone in bulk Si (we are ignoring the spin–orbit coupling, since it is so small here). The wave functions are transformed by the Γ_{15} representation, as the components x, y, z. The spectrum at the top of the valence band is also triply degenerate (the representation Γ_{25}; the wave functions transform as xy, xz, yz). We have a distance $E(\Gamma_{15}) - E(\Gamma_{25}) = 3.42$ eV. In contrast with the valence band, where all branches have the same curvature [$E(\Gamma_{25})$ is the point of the maximum], the different branches of the spectrum have curvatures of different sign near the Γ point in the conduction band. For a sufficiently small cluster, the motion of the bands with positive and negative mass in different directions along the energy scale may cause the conduction band at the Γ point to be comparable in energy to the side minimum. The result is the opening of a new channel for direct optical transitions at the Γ point. However, it can be seen from these arguments that for clusters of such small size it is no longer sufficient to consider only the effective-mass wave functions near the Γ and X points separately, since the scale of the mixing of wave functions with different values of k is, in order of magnitude, $|k|^2 \propto 1/d^2 \propto 2$ eV [the distance between $E(\Gamma_{15})$ and the side minimum]. The effective-mass method thus cannot deal with the effect in which we are interested here.

We have carried out calculations of the density of states and the spectrum for quantum wires of square cross section, oriented along the [001] direction. The calculations were carried out by the strong-coupling method in an sp^3s^* basis.[9] Figure 1

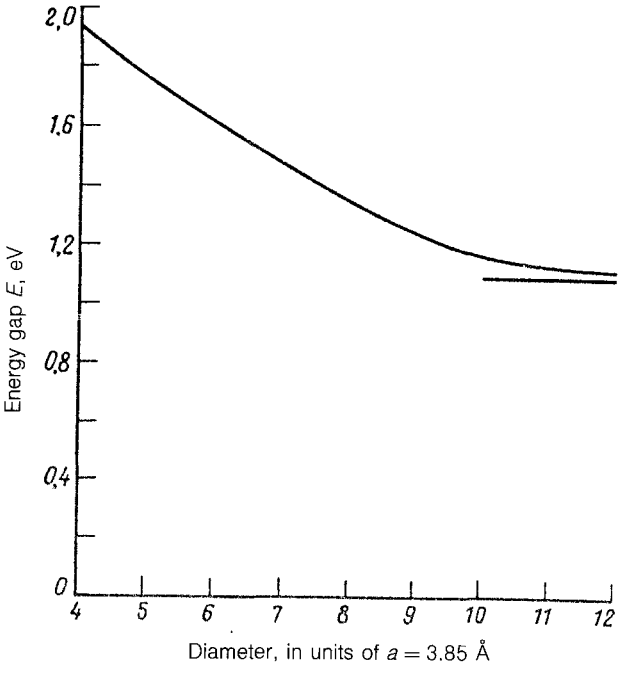

FIG. 1. Energy gap at the Γ point versus the wire diameter.

shows the size of the energy gap at the Γ point ($k_z = 0$, where k_z is the quasimomentum along the quantum wire) as a function of the cross-sectional size (specifically, as a function of the number of periods in the plane of the cross section with axes along [110] and [1$\bar{1}$0]; the period is $a_0 = 3.85$ Å). The vertical lines show the bulk value of E_g. Since we have no information on the atomic structure of the lateral surface of the wire (and since, furthermore, experiments indicate that the luminescence is associated with the interior of the wire[1] or microcluster[5]), dangling-bond states are excluded by the computer program. Calculations of the dispersion law in terms of k_z show that the smallest gap is reached at $k_z = 0$ (up to a cross section of 5×5).

Figure 2 shows the density of states of bulk Si and that of a quantum wire with a cross section of 5×5 (at the central atom in the cross section). We see from Fig. 2 that the effective increase in E_g stems primarily from the downward shift of the valence band along the energy scale, as a result of the quantum size effect. The edge of the conduction band is essentially unshifted by the quantum size effect, because the band moves in different direction at the Γ point and near the X point. A calculation of partial densities of states for various s and $p_{x,y,z}$ orbitals shows that the edge of the valence band is formed primarily from p orbitals, while the edge of the conduction band contains roughly equal proportions of the s state and the p orbitals. Direct optical transitions thus do occur in quantum wires. However, the size of the dipole matrix element for such transitions remains an open question. Clearly, the spectrum will

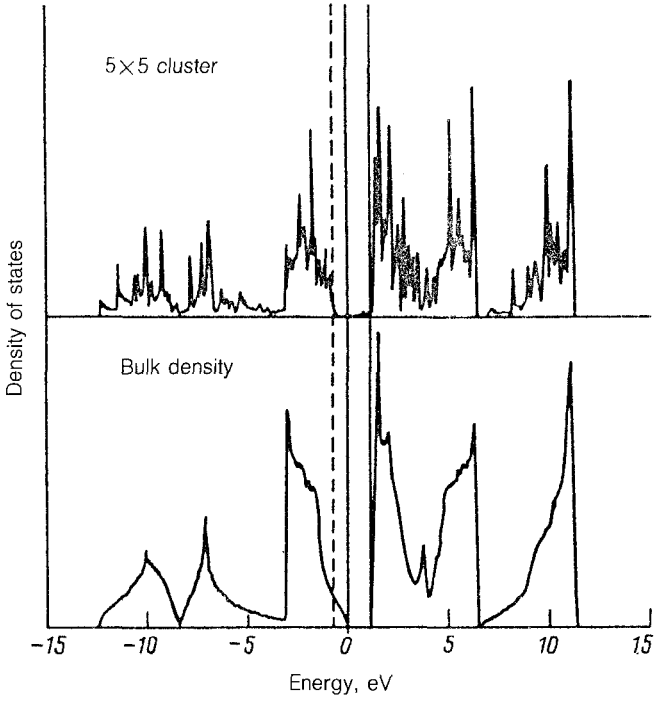

FIG. 2. Density of states in the interior of silicon and at the central atom in a wire with a 5×5 cross section.

approach the bulk spectrum with increasing cross section of the wire, and the intensity of direct transitions should vanish. Strictly speaking, when the wire has a sufficiently large cross section, the translational invariance is disrupted, and the side minima in the conduction band at a distance of 1.17 eV from the edge of the valence band along the (100) directions are projected to the Γ point ($k_z = 0$). This projected spectrum is a direct-gap spectrum (as in a calculation of the properties of a surface). Formally, we could project the spectrum for a bulk sample also, but this would be only a fictitious procedure, since transitions between the valence band and conduction band (the transition energy is 1.17 eV) at the Γ point have a vanishing intensity.

Calculating a dipole matrix element for a wire is a questionable procedure, since the atomic structure of the wire surface is not clear from experiments (surface states appear to be passivated). To estimate the particular wire thickness at which the dipole matrix element vanishes, it is convenient to carry out a calculation for a stack of a finite number of layers which are unbounded in the plane of the surface. The atomic and electronic structure of the [001] surface is known fairly well. Furthermore, in this case the side minimum near the X point projects to the Γ point ($k_{x,y} = 0$; the direct gap is 1.17 eV in this case). Figure 3 shows the results of a calculation of the dipole matrix element between a state at the edge of the valence band and the conduction band. Since the two surface bands are well separated from the bulk spectrum, it is a

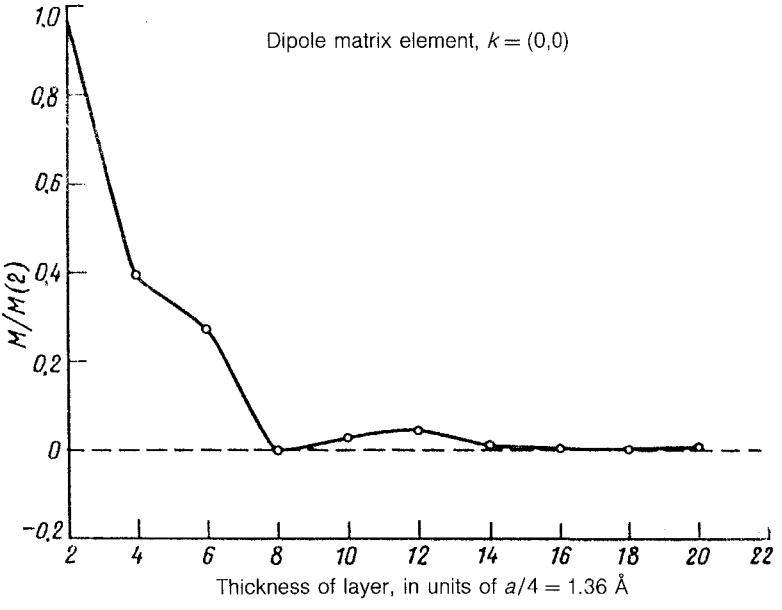

FIG. 3. Dipole matrix element between a state at the bottom of the conduction band and one at the top of the valence band versus the thickness of the layer.

straightforward matter to eliminate them from consideration; we are then left with transitions between the surface states. It follows from Fig. 3 that the dipole matrix element is nonzero for thicknesses of about 12 layers (15 Å) because of the quantum size effect in the direction across the layers. The energy gap reaches its bulk value over the same length scale. For a quantum wire, with quantization in two directions, the gap reverts to its bulk value at a cross-sectional size of 30 Å. The dipole matrix element should vanish over the same length scale.

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