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Quantum confinement effects in Ge nanocrystals

A.Miranda, A.E.Ramos, L.Nino de Rivera, M.Cruz-Irisson*

Seccion de Estudios de Posgrado e Investigacion, ESIME-Culhuacan,
Instituto Politecnico Nacional, Av. Santa Ana 1000,
C.P. 04430 Mexico, D.F., Mexico
*Instituto de Investigaciones en Materiales, UNAM,
Mexico, D.F., 04510, Mexico

The exciton Bohr radius of bulk Ge is larger than that of Si, hence resulting more prominent quantum size effects. In this work, the electron structure of Ge nanocrystals is studied by means a sp^3s^* tight binding approximation. Comparing the theoretical calculations with experimental data, we conclude that, similar to the case of silicon, the blue-green photoluminescence of Ge nanocrystals probably comes from surface and the size dependent photoluminescence in the near infrared probably involves a deep trap in the gap of the nanocrystals.

Германий в объемной структуре имеет больший радиус экситона Бора, чем кремний, поэтому в нем сильнее выражены квантово-размерные эффекты. В работе электронная структура нанокристаллов германия исследована с применением приближения тесной связи sp^3s^*. Сопоставляя теоретические расчеты с экспериментальными данными, авторы пришли к выводу, что, как и в случае кремния, сине-зеленая фотолюминесценция нанокристаллов германия возникает, вероятно, на поверхности и процесс размерно-зависимой фотолюминесценции в ближней инфракрасной области протекает с участием глубоких ловушек в запрещенной зоне нанокристаллов.

Nanowires are one-dimensional nanostructures with electrical carriers confined in the other two (perpendicular) directions. They exhibit interesting physical properties differing considerably from those of quantum dots and the bulk. Of particular importance in technology are semiconductor nanowires that could be applied in many fields such as optoelectronics, photovoltaic cells, and especially in device miniaturization [1]. Recently, the discovery of efficient photoluminescence (PL) from Si [2] and Ge nanocrystals [3, 4] at room temperature has stimulated considerable efforts in understanding optical properties of nanocrystals of indirect-gap IV group semiconductors. In semiconductor nanocrystals (or zero-dimensional quantum dots), the band gap increases with decreasing nanocrystal diameter, and electron states become discrete with a high oscillator strength. Quantum confinement effects play an essential part in optical absorption and luminescence processes in nanocrystals. Quantum confinement theory leads to an expectation that this visible PL is made possible by band gap widening due to quantized levels and significant modulation of the usual electronic band structure in the band gaps, such as the change from an indirect gap to a direct gap, so that the emission efficiency may be enhanced at room temperature. To study details of the visible PL, we have to characterize the nanosystem size and find a way to control the average size and distribution as much as possible.

The tight-binding (TB) theory was originally proposed as an *ab initio* technique for calculating the electron properties of crystals from atomic wave functions. However,

the first-principle calculations based on a linear combination of atomic orbitals are computationally very demanding, and the TB approximation met with relatively little success until Slater and Koster suggested that it can be used as an interpolation scheme, in which the Hamiltonian matrix elements are fitted to experimental data or to band structures computed by other methods. This made it possible to describe atomic level physics in a basis of minimal size, leading to wide ranging applications in many areas of condensed matter physics. With modern computer capabilities, first principles electron structure calculations are now commonplace and *ab initio* TB theories are emerging. Yet even today, the empirical theory predominates because it is simple and physically intuitive.

One of the most effective means to convert an indirect optical transition into a direct one is to form a supercell structure. In this case, the size of the Brillouin zone is reduced and the conduction band bottom is folded onto the Γ point, resulting in a direct-gap material [5]. On the other hand, in nanostructures such as an isolated quantum dot, the periodicity is absent due to a superstructure and the above picture of zone folding is not applicable straightforwardly. In these structures, the electronic states become completely discrete as in atoms and molecules and the optical matrix element between a pair of discrete states must be evaluated to identify whether that transition is optically allowed or not. This is the most regular picture. However, in a relatively large nanostructure, we can employ approximately the zone folding picture. If the envelope function of carriers confined in a nanostructure has a sufficiently large Fourier component at the wave vector corresponding to the indirect-gap transition, that Fourier component plays the same role as phonons in the bulk material and the direct optical transitions become allowed.

On the other hand, the importance of the localized levels at the surface of nanostructures in the PL was emphasized by several authors [6, 7]. Because the mechanism of PL from nanostructures of indirect gap materials is controversial and not well understood, it is important to clarify theoretically the intrinsic electron properties of these quantum-confined structures. The comparison of the theoretical results with experimental data will shed a new light on the PL mechanism. Thus, the purpose of this work is to provide a theoretical description of the quantum confinement effects on the electron properties of Ge nanocrystals and to compare it with experimental results. In what follows, we describe the supercell structure and the Hamiltonian used in our model and calculation scheme. Then our numerical results are presented and compared with experimental data, along with some discussions. Finally, we will give our main conclusions.

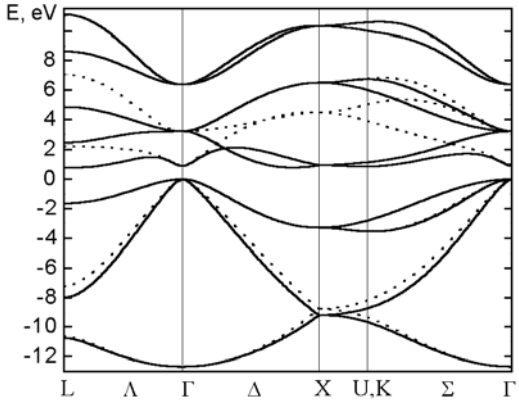

Fig. 1. Energy band structure of bulk Ge calculated under the tight-binding approach, using an orthogonal sp^3 (dashed line) and sp^3s^* (solid line) basis set.

In this study, we employ a semiempirical TB approximation of the energy band structure that, by construction, reproduces the correct band gap of bulk Ge in the limit of infinite supercell size. As we are interested in describing the band structure modifications around the gap, the minimum basis capable of describing an indirect band gap along the L direction is the sp^3s^* basis. We have used the parameters of Vogl, Hjalmarson, and Dow [8], which reproduce an 0.75 eV gap in bulk crystalline germanium. One point of this method is that is possible to investigate the properties of large supercells while avoiding the computation difficulties involved in the first-principle method.

As a starting point, we briefly repeat the discussion about the orbital s^* and the tight-binding approach following the line in [8]. Theories involving less than eight bands cannot describe the chemistry of localized states in covalently bonded semiconductors: the sp^3 bonding of diamond structures demands a basis set of al least four orbitals for each of the two atoms in the unit cell, namely, one s and three p orbitals per atom. Attempts to fit the conduction bands of Ge with this basis set and TB approach have generally failed. The nearest-neighbor sp^3

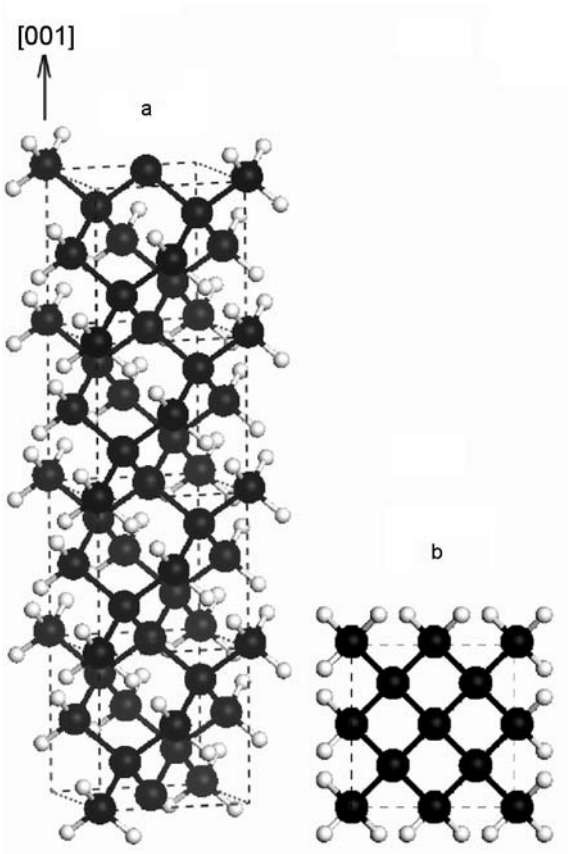

Fig. 2.(a) Example of quantum wire, hydrogen-passivated 8-atom unit cell, and (b) cross-sectional viewed from the top.

model fails to produce an indirect gap for Ge (Fig. 1, dashed line) because it omits essential physics: the excited atomic states, such as the s^* state of atomic Ge, couple with the anti-bonding p-like conduction states of Ge near the L points of the Brillouin zone, and press these states down in energy. Vogl and co-workers [8] overcame this deficiency by including an excited s-state, s^*, on each atom, giving an sp^3s^* basis and a ten-band theory (Fig. 1, solid line). The excited s^* state repels the lower, unoccupied energy levels of the neighboring atom, and, in particular, presses the indirect relative conduction band minima down in energy.

We employ a model of crystalline Ge wire along the direction [001] (z axis) [9]. The structure of the narrowest wire being considered is illustrated in Fig. 2(a), where three 8-atom supercells are represented, each one is a cube of side $a = 5.65$ Å with translational symmetry in the z direction. The cross section of this nanowire is shown in Fig. 2(b); a 72-atom supercell is built by joining nine such cubes in the X-Y plane,

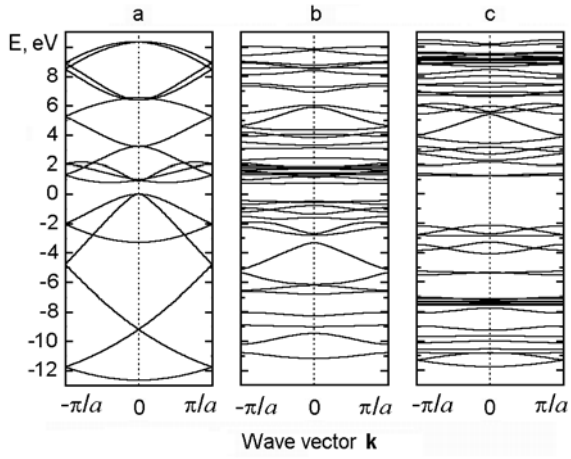

Fig. 3. Band structures for the 8-atom supercell, corresponding to Fig. 2. (a) Crystalline case (bulk), (b) Ge nanowire without saturation, (c) Saturated with hydrogen atoms.

resulting in a structure with parameters $a_x = a_y = 3a$ and $a_z = a$, the width of this nanocrystal is $d = 1.69$ nm. For a 392-atom supercell, the parameters are $a_x = a_y = 7a$ and $a_z = a$.

We suppose that the nanostructures have the same lattice structure and the same interatomic distance as the bulk silicon and that all the dangling bonds are saturated with hydrogen atoms. For simplicity sake, we suppose that there are no hydrogen-hydrogen interactions. The hydrogen atoms are used to simulate the bonds at the surface of the wire and sweep surface states out of the fundamental gap. We assume that the H-saturated dangling bonds on the wire surface have the natural H–Ge bond length. We are aware that we are simplifying enormously the surface description, ignoring other possible saturators and surface reconstruction [10–12]. This description is of course insufficient to study PL phenomena.

The on-site energy of the H and the Ge–H orbital interaction parameters are taken to be $E_H = 0.205$ eV, $ss\sigma_{Ge-H} = -3.618$ eV, and $sp\sigma_{Ge-H} = 4.081$ eV, respectively, which are obtained by fitting the energy levels of GeH_4 calculated in Local Density Approximation [13].

Once the Hamiltonian and the geometry are decided, it is possible to calculate the electron band structure of Ge nanocrystals by diagonalizing the TB Hamiltonian directly. The dimension of the TB Hamilonian matrix is $5\times N_{Ge} + N_H$, where N_{Ge} and N_H are numbers of Ge and H atoms in the nanowire supercell, respectively. This diagonalizing has to be done for each wave

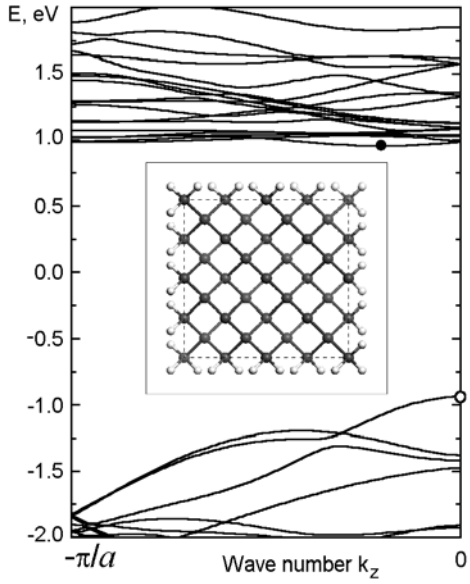

Fig. 4. Electron structure near the band-gap region for a 32-atom supercell (inset) Ge wire.

vector, **k**, within the irreducible first Brillouin zone. Obviously, the supercell size is limited by the computing capabilities.

We start by considering a narrowest wire, 8-atom supercell (Fig. 1) as the first step to study the quantum confinement effects on the electron band structure. Figures 3(a), 3(b), and 3(c) show the band structure when the structure is crystalline, when the dangling bonds are not passivated, and when these dangling bonds are saturated with hydrogen atoms, respectively. The Fig. 3(a) illustrates the concept of zone folding rests with an increase in the coupling of the conduction band minima of the zone boundary with the valence band maxima at zone center. The vertical transitions are now referred to as a quasi-direct. Note that the band gap is broadened as we have a columnar wire, and that the dangling-bond states are removed from the gap when those are saturated with hydrogen atoms. The observed gap broadening is in agreement with the quantum confinement scheme. Another important characteristic is that the dispersion curves are very flat for the nanocrystal case. We are calculated quantum wire band structures for seven wire widths.

Fig. 4 shows the calculated electron structures near the band-gap region for a 32-atoms supercell Ge nanocrystal. The atomic structure of this Ge wire is also plotted in the inset. The hydrogen atoms are shown by gray (small) circles, while black (bigger) circles represent the Ge

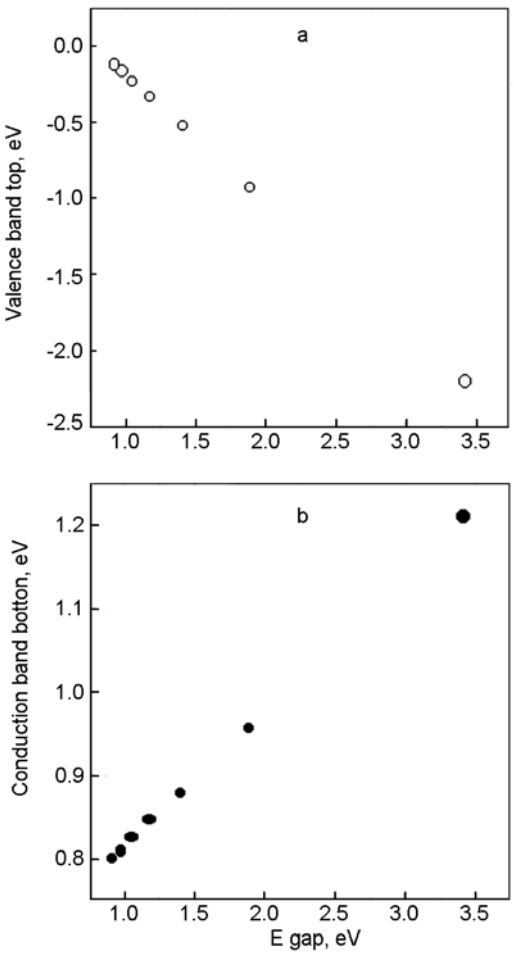

Fig. 5. Conduction band bottom and valence band top vs band gap for seven wire widths.

atoms. One of the most important features is that the conduction-band minimum (solid circle) is shifted towards the center of the Brillouin zone (open circle). The electron states associated with Ge–H bonds are located far away from the band gap region and do not affect directly the optical properties of the Ge nanocrystals. However, hydrogen termination contributes indirectly to effective light emission from Ge wire by removing the nonradiative Ge dangling-bond states in the band gap. Note that another important point is to consider the splitting of the otherwise degenerate states at the top of the valence band for all cases. This difference could be important in the luminescence process; for instance, the splitting of the states at the boundaries could infer a double peak in the FL spectrum. The electron structures for other Ge wires have almost the same characteristics as those of the 32-atom wire.

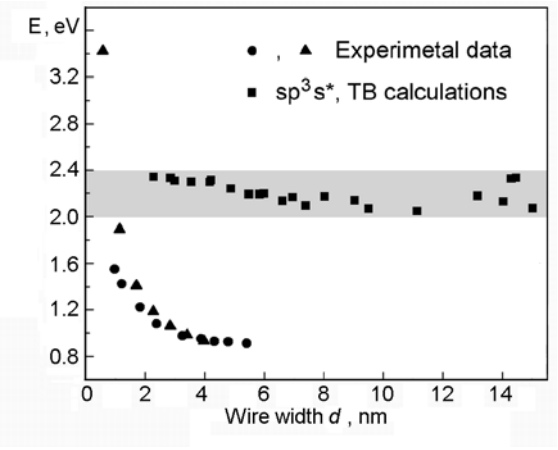

Fig. 6. Comparison of the experimental photoluminescence energies (•, ■) for Ge nanocrystals with our sp^3s^* TB calculations (Δ). The experimental data are taken from [14], and references therein.

Dispersion curves for all of the wire structures were calculated, and the energies of the valence band top and conduction band bottom were determined. In most of the dispersion curves, the valence band maximum occurs at the Γ point, and the conduction band minimum occurs elsewhere, although several cases were identified where the conduction band minima are near the Γ point. Thus, the one-dimensional periodic structure of germanium has an indirect dispersion curve.

Results for the band gap energy of Ge nanowires with respect to the width size, d, are plotted in Fig. 6. Comparison of the experimental photoluminescence energies (•,■) [14] with our sp^3s^* TB calculations are presented. Despite the fact that our model is a very simple approximation of the Ge nanowires, we can observe a good agreement with experimental data (•) only within the interval from 1.5 to 4.5 nm, in the near infrared. In general, the red and near infrared PL observed is considered to originate from recombination of electron-hole pairs between the widened band gap of Ge nanocrystals in accordance with quantum size effects. In all the cases, the PL maxima between 2–2.4 eV (region shaded in Fig. 6, blue-green PL emission) are quite independently of the nanocrystal size (2–15 nm). These results cannot be explained by a simple quantum confinement effects. Similarly to the case of silicon, there are two PL bands. a blue one probably due to SiO_2 defects and a infrared one below the gap of the nanocrystals due to the trapping of a carrier on a surface defect.

To conclude, we have studied the quantum confinement effects on the electron properties of germanium nanocrystals. Comparison to experimental data indicates that defects are probably involved in the two photoluminescence bands observed in the blue-green and near infrared regions. We have shown that the electronic structure of surface-hydrogenated Ge nanocrystals, from small to large supercells with bulk properties, can be calculated with a single TB model. Despite the fact that our model is a very simple, this gives a good agreement with experimental data in the near infrared, according with the quantum confinement model.

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References

1. X.Duan, Y.Huang, Y.Cui et al., *Nature*, **409**, 66 (2001).
2. L.T.Canham, *Appl. Phys. Lett.*, **56**, 2349 (1990).
3. Y.Maeda, N.Tsukamoto, Y.Yazawa et al., *Appl. Phys. Lett.*, **59**, 3168 (1991).
4. Y.Kanemitsu, H.Uto, Y.Mazumoto et al., *Appl. Phys. Lett.*, **61**, 2187 (1992).
5. S.S.Iyer, Y.H.Xie, *Science*, **260**, 40 (1993).
6. M.V.Wolkin, *Phys. Rev. Lett.*, **82**, 197 (1999).
7. S.Louhibi, N.Sekkal, N.Benkhettou, N.E.Chabane-Sari, *Superlattices and Microstructures*, **37**, 115 (2005).
8. P.Vogl, H.P.Hjalmarson, J.D.Dow, *J. Phys. Chem. Solids*, **44**, 365 (1983).
9. D.Guzman, U.Corona, M.Cruz, *J. Luminescence.*, **102**, 487 (2003).
10. J.Koga, *J. Non-Cryst. Solids*, **293–295**, 630 (2001).
11. J.Koga, K.Nishio, F.Yonezawa, T.Yamaguchi, *Phys. E*, **15**, 182 (2002).
12. H.-Ch.Weissker, J.Furthmuller, F.Bechstedt, *Surf. Sci.*, **566–568**, 961 (2004).
13. DMOL User Guide, Molecular Simulation, San Diego (1996).
14. S.Takeoka, M.Fujii, S.Hayashi, K.Yamamoto, *Phys. Rev. B*, **58**, 7921 (1998), and references therein.

Ефекти квантового обмеження у нанокристалах Ge

А.Міранда, А.Е.Рамос, Л.Ніньо де Рівера, М.Крус-Іріссон

Германій в об'ємній структурі має більший радіус екситона Бора, ніж кремній, тому в ньому сильніше виражені квантово-розмірні ефекти. У роботі досліджено електронну структуру нанокристалів германію з застосуванням наближення тісного зв'язку sp^3s^*. Зіставивши теоретичні розрахунки з експериментальними даними, автори дійшли висновку, що, як і у випадку кремнію, синьо-зелена фотолюмінесценція нанокристалів германію виникає, імовірно, на поверхні та процес розмірно-залежної фотолюмінесценції у ближній інфрачервоній області протікає за участю глибоких пасток у забороненій зоні нанокристалів.