Calculations on Electronic States in QDs with Saturated Shapes

Wei Cheng

Key laboratory in University for Radiation Beam Technology and Materials Modification, Institute of Low Energy Nuclear Physics, Beijing Normal University, Beijing 100875, P. R. China

Shang-Fen Ren

Department of Physics, Illinois State University, Normal, Illinois 61790-4560

(November 13, 2018)

Abstract

Electronic States of Si and Ge QDs of 5 to 3127 atoms with saturated shapes in a size range of 0.57 to 4.92 nm for Si and 0.60 to 5.13 nm for Ge are calculated by using an empirical tight binding model combined with the irreducible representations of the group theory. The results are compared with those of Si and Ge quantum dots with spherical shape. The effects of the shapes on electronic states in QDs are discussed.

31.15.-p, 02.20.-a, 73.20.-r, 81.05.Cy
I. INTRODUCTION

Semiconductor quantum dots (QDs) have attracted much research attention in recent years because of their importance in the fundamental understanding of physics and potential applications \[1\]. One of the most important properties of semiconductor QDs is the change of the electronic band structure of QDs when the size of the QDs changes \[2–6\]. The blue shifts of the bandgap of semiconductor QDs has been demonstrated by numerous experimental observations \[1\], and there exist many successful theoretical investigations on this and other related important physical properties. Among theoretical models, the effective mass approach (EMA) which predicted the increase of the band gap as the size of the QDs decreases \[2–4\], which is simple to understand and provides qualitatively correct description of the increase of the band gaps. The electronic structures of semiconductor QDs has also been investigated by microscopic models \[2–12\], including an empirical tight-binding approach combined with the irreducible representations of the group theory \[8\] that has obtained many interesting results. One of the most important results is the existence of a critical size in spherical semiconductor QDs \[7\]. In above models, the shape of the QDs treated is taken as spherical. More shapes and structure of Si and Ge QDs are proposed \[1,13\], i.e., a complicated structure for Si_{10}, and between Si_{20} and Si_{30} alters from being elongated to spherical \[14\]. In this work, we have calculated the electronic states of QDs with saturated shapes at different sizes. Our results are compared with those of the spherical shape, and the effects of the shapes of QDs on electronic states in QDs are discussed.

This paper is organized as the following: first, we will describe the saturated shape of the QDs and briefly describe our theoretical approach, then we will show our results and have discussions.
II. SATURATED QDS AND THEORETICAL APPROACH

The semiconductor materials we discuss in the work, Si and Ge, have diamond structures. In QDs, this structure remains. The saturated shapes of semiconductor QDs discussed in this work are built up in the following way: first we start from a center atom with its four nearest neighboring atoms. This is a saturated QDs with the minimum size. Then we add all the next neighbors to the four surface atoms to form the next saturated QD, which has 17 atoms in total. Then we add all the next neighbors to the twelve surface atoms to form the next saturated QD again, which now has 41 atoms. The larger saturated QDs are built up by repeating this procedure. The number of Si (Ge) atoms we calculated here are 5, 17, 41, 83, 147, 239, 363, 525, 729, 981, 1285, 1647, 2071, 2563, and 3127. In Fig. 1, we show the shapes of the saturated QDs with 363, 1647, and 3127 atoms. The shape is a truncated cube. For large QD the four small and four large triangles will have nearly the same size, and six rectangles will be six squares. There are a few features of the saturated shape of QDs that we want to mention. First, when the number of atoms in QDs is equal or less than 17, the structure of the saturated QDs is exactly the same as the spherical QDs. So our calculated results should agree with the existing results of spherical QDs. At the beginning of this work, we did check it, and they agree exactly. Second, the saturated shape is not spherical, so the distances from surface atoms to the center of the QDs are not the same. We have defined the radius $r$ of the QDs in the following way: $Nm = \rho \left( \frac{4}{3} \pi r^3 \right)$, when $N$ is the total number of atoms in the QD, $m$ is the mass of a $\text{^{70}Ge}$ atom, $\rho$ is the density of the bulk material, and $r$ is an equivalent radius of the spherical QDs with the same number of atoms. Third, one important feature of the saturated shape is that even though it looks like more complicated, it keeps the same $T_d$ symmetry of the bulk material. Because of this, the irreducible representations of the group theory applied in the spherical QDs can also be applied in QDs with saturated shape. This makes the comparison with the results more convenient.

We employed the same empirical tight-binding approach and parameters as the calcu-
lations on spherical QDs [5–8]. This empirical tight-binding model reproduces the correct bandgap of bulk Si and Ge in the limit of infinite clusters by construction [13], and its simplicity makes the calculation for very large QDs feasible. We also made the following assumptions following the calculations of spherical QDs: first, we take the hydrogen saturated approximation, i.e., the dangling bonds of Si and Ge atoms at the surface of the QDs are terminated with hydrogen atoms; second, atoms in QDs take the diamond lattice sites. The hydrogen saturated dangling bonds at the surface of the QDs are assumed to have the same length as the nature H-Si or H-Ge bond length ($d_{H-Si} = 0.148\text{nm}$, and $d_{H-Ge} = 0.153\text{nm}$).

Then the electronic structures are evaluated by using the empirical Hamiltonian [13], that produces the accurate valence bands and good conduction bands near the fundamental band gap for bulk Si and Ge. We have considered five basis orbitals per Si or Ge atom for the Hamiltonian: $s$, $p_x$, $p_y$, $p_z$, and an excited $s^*$ state. In this Hamiltonian, only on-site and nearest neighbor interaction matrix elements are considered as non-zero. Each hydrogen atom has only one single $s$ orbital. Since the hydrogen free atom energy level (-13.6 eV) is close to the $s$-state energy level of Si (-13.55 eV), the on-site $s$ energy level of hydrogen is taken to be the same as that of Si. The nearest neighbor matrix elements $V_{H-Si}$ ($V_{H-Ge}$ between H and Si (Ge) are taken to be the same as Si-Si (Ge-Ge), but scaled inversely as the square of the bond length $d$ according to Harrison’s rule [16]. The QDs we have calculated ranging from five Si (Ge) atoms with twelve surface hydrogens to 3127 Si (Ge) atoms with 1188 hydrogens. Without group theory the dimension of the largest Hamiltonian matrix for the saturated QD of 3127 atoms is $16823=3127 \times 5+1188$. Such large matrices are difficult to be diagonalized directly, so the projection operators of the irreducible representations of the group theory [5–8] are employed to reduce the computational intensity. By employing the group theory, for example, the above matrix of size of 16823 can be reduced to five matrices in five different representations of $A_1$, $A_2$, $E$, $T_1$, and $T_2$, with the sizes of 849, 568, 1397, 1962, and 2242 respectively. Therefore, the original problem is reduced to a problem that can be easily handled by most reasonable computers. Furthermore, the employment of the group theory proves to have played a much more important role than expected. Not
only it allows the investigation of electronic states in QDs with a much larger size, but also it allows the investigation of electronic states in QDs with different symmetries. This group theory formalism has been also used in calculations of phonon modes in semiconductor QDs. These investigations lead to many interesting physics that otherwise can not be revealed [5–8,17–21].

III. RESULTS AND DISCUSSION

With this model, we have calculated the electronic states in saturated Si and Ge semiconductor QDs. Our results for Si saturated QDs are plotted in Fig. 2 (a) and (b) for Si. Fig. 2 (a) shows the calculated lowest unoccupied energy levels for saturated Si QDs ranging from 5 to 3127 Si atoms. Two levels are shown for each of the five different irreducible representations. Fig. 2 (b) shows the calculated highest occupied energy levels for the same sets of Si QDs, and also two levels are shown for each of the five different irreducible representations.

Our results show that when the QDs have only 5 or 17 Si (Ge) atoms, the results are exactly the same as those of spherical QDs (the corresponding results for Si spherical QDs are in Fig. 2 of reference [6], and those of Ge spherical QDs are in Fig. 2 of reference [5]). This is in this size range the saturated QDs and the spherical QDs have exactly the same structures. When the size of QDs increases, the shape of saturated QDs are different from the spherical QDs, so the electronic structures of the saturated QDs have obvious differences from those of spherical QDs.

A. Lowest unoccupied states of Si saturated QDs

From Fig. 2 (a) we see that all of the lowest unoccupied levels go up monotonically as the QDs decreases, while the very lowest three are always one from A_1, E, and T_2 each for QDs larger than 2.0 nm in diameter. These levels are well separated from all other energy levels above them but very close to each other. This is the same as the spherical QDs [3], and can be explained as that these three states are directly developed from the conduction minimum
in the bulk. When the QDs size is big, the coupling between different conduction minimum can be neglected, and all these three lowest unoccupied states have almost the same energy. As the size of QDs decrease, the coupling between different states increases, the originally almost indistinguishable energy levels of $A_1$, $E$, and $T_2$ develop to three separated ones. The other character similar to spherical QDs is as the QD size greater than 2.0 nm the two lowest $T_1$ modes have nearly the same energy.

**B. Highest occupied states of Si saturated QDs**

Fig. 2 (b) shows the highest occupied levels of above Si saturated QDs. We see that all the occupied levels go down monotonically as the size of the QDs decreases. On this figure, the highest occupied level is always a $T_2$ level, and the next one is always a $T_1$ level. Different from those of spherical Si QDs (Fig. 2 (b) of Reference [6]) where there are two crossovers of the $T_1$ and $T_2$ states, the first is the highest occupied state changes from a $T_2$ state to a $T_1$ state in the size range between 1.08 and 1.41nm, then the highest occupied state changes from a $T_1$ state to a $T_2$ state in the size range of 2.03 to 4.91nm. In our figure, the highest occupied state is always a $T_2$ state, and there is no crossover of $T_2$ and $T_1$ states in the size range we calculated here. This is because in the saturated QDs there are more hydrogen atoms, the interaction of hydrogen can increase the $T_2$ energy levels.

**C. Lowest unoccupied states of Ge saturated QDs**

Fig. 3 (a) shows the lowest unoccupied levels of Ge saturated QDs that go up monotonically as the QDs decreases. The very lowest two are always from $A_1$ and $T_2$ each for QDs larger than 1.5 nm in diameter. These levels are well separated from all other energy levels above them but very close to each other. This is the same as the spherical QDs (Fig. 2 (a) of Reference [5]), and can be explained as that these two states are directly developed from the conduction minimum in the bulk, which is at L point in the Brillouin Zone. When the QDs size is big, the coupling between different conduction minimum can be neglected, and these
two lowest unoccupied states have almost the same energy. As the size of QDs decreases, the coupling between different states increases, the originally almost indistinguishable energy levels of $A_1$ and $T_2$ develop to two separated ones. The other character similar to spherical QDs is as the QD size greater than 3.5 nm the two lowest $T_1$ modes have nearly the same energy.

D. Highest occupied states of Ge saturated QDs

Fig. 3 (b) shows the lowest unoccupied levels of above Ge saturated QDs. All the occupied levels go down monotonically as the QDs decreases. On this figure, the highest occupied level is a $T_1$ level when the size of QDs is large, and the next one is a $T_2$ level. On the other hand, when the size of QDs is small, the highest unoccupied level is a $T_2$ level, and the next one is a $T_1$ level. We see obviously that there is a crossover of the $T_1$ and $T_2$ states at the size of 3 nm in diameter. This is different from those of spherical Ge QDs (Fig. 3 (b) of Reference [5]), where the crossover is at 2 nm and the $T_1$ level is always a highest one in the same size range. Since we know that in bulk material, the highest unoccupied level is a $T_2$ level, we can image that there is another crossover of $T_1$ and $T_2$ at a larger QD size.

E. More about the Crossover of Highest Occupied $T_2$ and $T_1$ States

We see from above that the highest occupied levels for both Si and Ge saturated QDs are different from those of corresponding spherical QDs. The symmetry of the highest occupied levels is important, because there could exist a critical size in these semiconductor QDs that when the size of QDs decreases pass the size, the originally direct semiconductor becomes indirect and the originally indirect semiconductor becomes less indirect [7]. Our results show that when the shape of QDs is different, the crossover of the $T_2$ and $T_1$, if they exist, will happen at different size range. Therefore, if the crossover of the $T_2$ and $T_1$ states is desired, the selection of the shapes might help.
IV. SUMMARY

In summary, we have calculated electronic states in Si and Ge QDs of 5 to 3127 atoms with saturated shape in a size range of 0.6nm to 51.33nm in diameter. The calculated results are compared with those of corresponding QDs in spherical shape, and similarities and differences are discussed in detail. Our results show that the influence of the shape of QDs on the electronic states is important, and it may play an important role in the band gap property of semiconductor QDs.

ACKNOWLEDGMENTS

This research is supported by the National Science Foundation (INT0001313), and WC is also supported by the National Natural Science Foundation of China under Grant No. 10075008, Visiting Scholar Foundation of Key Lab in University, Research Fund for the Doctoral Program of Higher Education under Grant No. 20010027005, and Excellent Young Teacher Foundation of the Education Ministry of China. We thank Professor Shang-Yuan Ren for helpful discussions.
REFERENCES

[1] A. D. Yoffe, Adv. Phys. 42, 173 (1993); A. D. Yoffe, Adv. Phys. 50, 1 (2001).

[2] Y. Wang and N. Herron, J. Phys. Chem. 95, 525 (1991).

[3] L. E. Brus, Appl. Phys. A53, 465 (1991).

[4] A. P. Alivisatos, Science 271, 933 (1996).

[5] S. Y. Ren, Solid State Comm. 102, 479 (1997).

[6] S. Y. Ren, Phys. Rev. B 55, 4665 (1997).

[7] S. Y. Ren, Jpn. J. Appl. Phys. 36, 3941 (1997).

[8] S. Y. Ren and J. D. Dow, Phys. Rev. B 45, 6492 (1992).

[9] R. Kumar, Y. Kitoh, K. Shigematsu, and K. Hara, Jpn. J. Appl. Phys. 33, 909 (1994).

[10] M. V. Ramakrishna and R. A. Friesner, Phys. Rev. Lett. 67, 429 (1991).

[11] J. Pan and M. V. Ramakrishna, Phys. Rev. B 50, 15431 (1994).

[12] A. Bahel and M. V. Ramakrishna, Phys. Rev. B 51, 13849 (1995).

[13] K. M. Ho, A. A. Shvartsburg, B. C. Pan, Z. Y. Lu, C. Z. Wang, J. G. Wacker, J. L. Fye, and M. F. Jarrold, Nature 392, 582 (1998).

[14] D. C. Parent and S.L. Anderson, Chem.Rev. 92,1541 (1992).

[15] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids 44, 365 (1983).

[16] W. A. Harrison, Electronic Structures and the Properties of Solids, San Francisco, 1980.

[17] S. F. Ren, Z. Q. Gu and D. Y. Lu, Solid State Comm. 113, 273 (2000).

[18] S. F. Ren, D. Y. Lu, and G. Qin, Phys. Rev. B 63, 195315 (2001).

[19] G. Qin and S. F. Ren, J. Appl. Phys. 89 (11), 6037 (2001).
[20] G. Qin and S. F. Ren, Solid State Comm. 121, 171 (2002).

[21] W. Cheng and S. F. Ren, Phys. Rev. B 65, 205305 (2002).
FIGURES

FIG. 1. Schematic illustration of saturated shape which is a truncated cube with six rectangles, four small, and four large triangles (a). Surface atoms in saturated QD viewed from one side of the cube for 363 (b), 1647 (c) and 3127 (d) atom QDs. (e) and (f) are the 3127 atom QD viewed in two different directions. It can be shown that for large QD the four small and four large triangles will have nearly the same size, and six rectangles will be six squares.

FIG. 2. (a) The two lowest unoccupied energy levels for each of the five irreducible representations as functions of the saturated Si QDs size. Note that the A₁, E, and T₂ lowest unoccupied states are the very lowest three states and are almost well separated from other levels above. (b) The two highest occupied energy levels for each one of the five irreducible representations as functions of the size of above saturated Si QDs. Note that the T₂ and T₁ highest occupied states are almost always the very highest two levels and well separated from other levels below.

FIG. 3. (a) The two lowest unoccupied energy levels for each of the five irreducible representations as functions of the saturated Ge QDs size. Note that the A₁ and T₂ lowest unoccupied states are the very lowest two states and are almost well separated from other levels above. (b) The two highest occupied energy levels for each one of the five irreducible representations as functions of the size of above saturated Ge QDs. Note that the T₂ and T₁ highest occupied states are always the very highest two levels and well separated from other levels below, and there is a crossover of the T₂ and T₁ states at the size of about 2 nm in diameter.
