Quantum confinement of edge states in Si crystallites

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A theoretical investigation exploring the major physics on the quantum confinement of Si crystallites related to the many band structure, multiple conduction band minima and degenerate valence band maximum of bulk silicon is presented, it shows the overlaps in the k space between the highest occupied states and the lowest unoccupied states in Si crystallites become more significant when the diameter is $\leqslant 15$ Å. The highest occupied T_1 states, rather than the highest occupied T_2 states, could play a more important role for optical transitions in nano Si crystallites. [S0163-1829(96)02043-7]

I. INTRODUCTION

The quantum confinement of Si crystallites is a problem with great practical and theoretical significance. Practically, it is directly related to the potential applications of luminescence in nano Si crystallites and porous Si.[1,2] Theoretically, although the ordinary quantum confinement of a simple particle in a potential well is well understood and treated in almost any standard quantum mechanics textbook, however, for a more complicated system such as Si crystallites, the electron motion is subject to its complex band structure, the quantum confinement effect contains more physics and is understandably even more interesting. Although there are many theoretical investigations on the quantum confinement of Si crystallites,[3–6] we do not see that any of them explores the physics characteristic of the all major points of the Si band structure, like its six conduction band minima (CBM), degenerate valence band maximum (VBM), and many energy bands. Here we present such an investigation, it provides a basic physics picture on the edge state development covering the entire range from the bulk silicon to nano Si crystallites.

We consider spherical hydrogenated Si clusters having the symmetry of the T_d group. In the limit of cluster of infinite size, the six lowest unoccupied states (LUS's) are made of the six CBM of the bulk Si transforming according to three irreducible representations A_1, E, and T_2 under the operations of the point group T_d. They are

$$|A_1,\mathrm{LUS}\rangle=\frac{1}{\sqrt{6}}(|\Delta_1,\mathbf{k}_{0,x}\rangle+|\Delta_1,-\mathbf{k}_{0,x}\rangle+|\Delta_1,\mathbf{k}_{0,y}\rangle+|\Delta_1,-\mathbf{k}_{0,y}\rangle+|\Delta_1,\mathbf{k}_{0,z}\rangle+|\Delta_1,-\mathbf{k}_{0,z}\rangle), \quad (1)$$

$$|E_1,\mathrm{LUS}\rangle=\frac{1}{\sqrt{3}}(|\Delta_1,\mathbf{k}_{0,x}\rangle+|\Delta_1,-\mathbf{k}_{0,x}\rangle)-\frac{1}{\sqrt{12}}(|\Delta_1,\mathbf{k}_{0,y}\rangle+|\Delta_1,-\mathbf{k}_{0,y}\rangle+|\Delta_1,\mathbf{k}_{0,z}\rangle+|\Delta_1,-\mathbf{k}_{0,z}\rangle), \quad (2)$$

$$|T_{2,x},\mathrm{LUS}\rangle=\frac{1}{\sqrt{2}}(|\Delta_1,\mathbf{k}_{0,x}\rangle-|\Delta_1,-\mathbf{k}_{0,x}\rangle), \quad (3)$$

and their partner states. Here $\mathbf{k}_{0,x}=(k_0,0,0)$, k_0 is the location of CBM on the Δ axis, and Δ_1 means the lowest conduction band in one of the Δ directions.

Correspondingly, in the limit of infinite cluster the three highest occupied states (HOS's) transforming according to the T_2 irreducible representations of the point group T_d are made of the three $\Gamma_{25'}$ states of the bulk Si,

$$|T_{2,x},\mathrm{HOS}\rangle=|\Gamma_{25',x}\rangle, \quad (4)$$

and its partner states. The problem that we are interested in here is how the LUS's and HOS's develop under the quantum confinement, as the size of the cluster decreases.

II. FORMALISM

We employ an empirical tight-binding formalism to investigate the electronic structure of hydrogenated Si clusters of different size, as in our previous work.[6] This tight-binding formalism[7] reproduces the electronic structure of bulk Si rather well in the limit of infinite cluster size: It gives the correct band gap (by construction), good valence bands, and a fairly good indirect lowest conduction band. The calculated CBM are located at $2\pi/a(0.73,0,0)$ and its symmetrical points (Fig. 1). We calculated all eigenenergies and wave functions of different symmetry using this tight-binding Hamiltonian for spherical hydrogenated Si clusters of eight

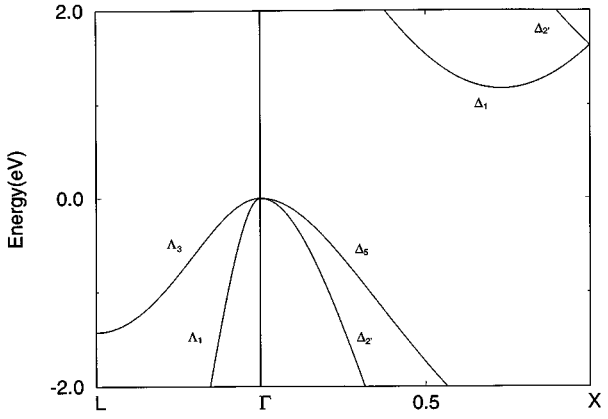

FIG. 1. The band structure of Si near the gap, calculated by the tight-binding Hamiltonian of Ref. [7].

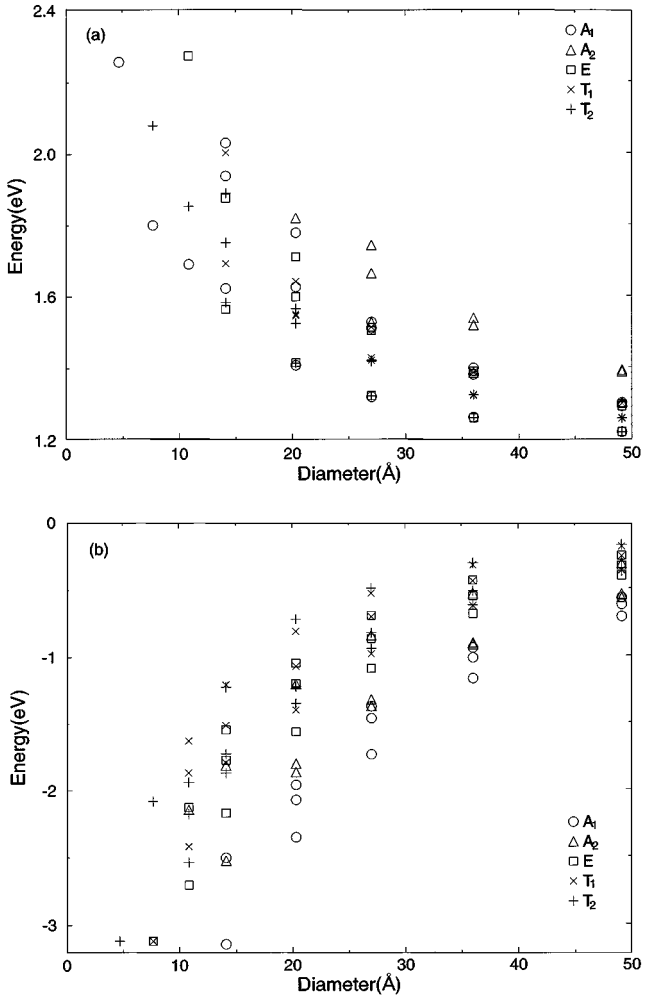

FIG. 2. (a) The three lowest unoccupied energy levels for each one of the five irreducible representations as functions of the cluster size: note that the A_1, E, and T_2 LUS are the very lowest three levels and are almost always well separated from other levels above. (b) The three highest occupied energy levels for each one of the five irreducible representations as functions of the cluster size: note that the T_2 and T_1 HOS are almost always the very highest two levels and well separated from other levels below.

different sizes, their diameters are 49.14, 36.0, 27.0, 20.31, 14.10, 10.81, 7.68, and 4.70 separately Å and the corresponding numbers of Si atoms in the clusters are 3109, 1235, 525, 239, 87, 35, 17, and 5 separately.[6] The three lowest unoccupied energy levels and three highest occupied energy levels for each one of the five irreducible representations as functions of the cluster diameter are shown in Figs. 2(a) and 2(b).

In order to have a clear understanding on the physics about how the specific band structure of Si affects the quantum confinement of Si crystallites, we calculated the wave function distributions in Bloch space (WDBS) of some edge states in the clusters. This quantity is defined as

$$P_{n,\mathbf{k}}^{\alpha,j}=C_{\alpha,j}|\langle n,\mathbf{k}|\alpha,j\rangle|^2. \tag{5}$$

Here $|n,\mathbf{k}\rangle$ indicates the Bloch states and α is the index for symmetry and j is the index for the energy level position for the states in the clusters. In Figs. 3(a)–3(c), we show the WDBS for $\alpha=A_1$, E_1 or $T_{2,x}$, $j=$LUS and $\alpha=T_{2,x}$ or $T_{1,1}$ and $j=$HOS for the clusters of diameter 49.14, 14.10, and 4.70 Å. We take the coefficients $C_{\alpha,j}$ to be 6, 3, and 2, respectively, for the A_1, E_1, and $T_{2,x}$ LUS and 1 for the $T_{2,x}$ and $T_{1,1}$ HOS, considering the proportionality coefficients in Eqs. (1), (2), (3), and (4).

III. QUANTUM CONFINEMENT OF LOWEST UNOCCUPIED STATES

From Fig. 2(a), we see that all of these lowest unoccupied energy levels go up monotonically as the cluster size decreases, while the very lowest three are always one from A_1, E, and T_2 each,[8] and at least for the clusters of diameters >20 Å, they are well separated from all other energy levels above them, but very close to one another. From Fig. 3(a), corresponding to the cluster of diameter $D=49.14$ Å, we see that the three LUS's show almost mutually indistinguishable strong peaks near $\mathbf{k}_0$, obviously these three states are directly developed from the CBM [Eqs. (1), (2), and (3)] in the bulk. In fact, the quantum confinement of the LUS's for clusters of $D>49.14$ Å can be considered as each conduction band minimum changing independently: the spread of the peaks caused by the quantum confinement is narrow for $D>49.14$ Å and therefore the intervalley couplings between different CBM can be neglected and all these three LUS's have almost the same energy (in our calculation they are 1.2206 eV for A_1, 1.2212 eV for E, and 1.2208 eV for T_2 for the cluster $D=49.14$ Å). As the cluster size decreases, the peaks corresponding to different symmetry decrease in amplitude, spread more in width Δk and separate from each other. At the same time, the intervalley couplings increase and the originally almost indistinguishable energy levels of A_1, E, and T_2 develop to three separated ones [Fig. 2(a) and Fig. 3].

We see the WDBS of LUS's from only the lowest conduction band Δ_1 in Fig. 3(a), the largest cluster calculated. As the cluster size further decreases, except that the peaks become weaker and broader, the WDBS from other bands, the conduction band $\Delta_{2'}$ first and then other bands, also emerge and become stronger step by step, as can be seen in Fig. 3(b) and then Fig. 3(c). For small clusters, even the WDBS from energy bands with the curvature of different sign (like the valence band $\Delta_{2'}$ to A_1 LUS, etc.) can be significant. Finally, for the smallest cluster, the WDBS from almost all bands come out and become flatter [Fig. 3(c)], corresponding to highly localized states in the real space.

Therefore a theory which could predict the energy gap of small Si crystallites correctly must contain the following three major physics points: (i) The effect of state spread in k space—the ''average effective mass'' becomes heavier due to the nonparabolicity of the bulk band structure as the cluster size decreases. (ii) The intervalley couplings. It can be proven that not including the intervalley couplings always makes the gap larger. (iii) The effect of state spread in other bands—even the bands with a curvature of a different sign can have a significant contribution in small crystallites. The standard effective mass approach does not contain any one of them and therefore always overestimates the gap[2,4] for small crystallites.

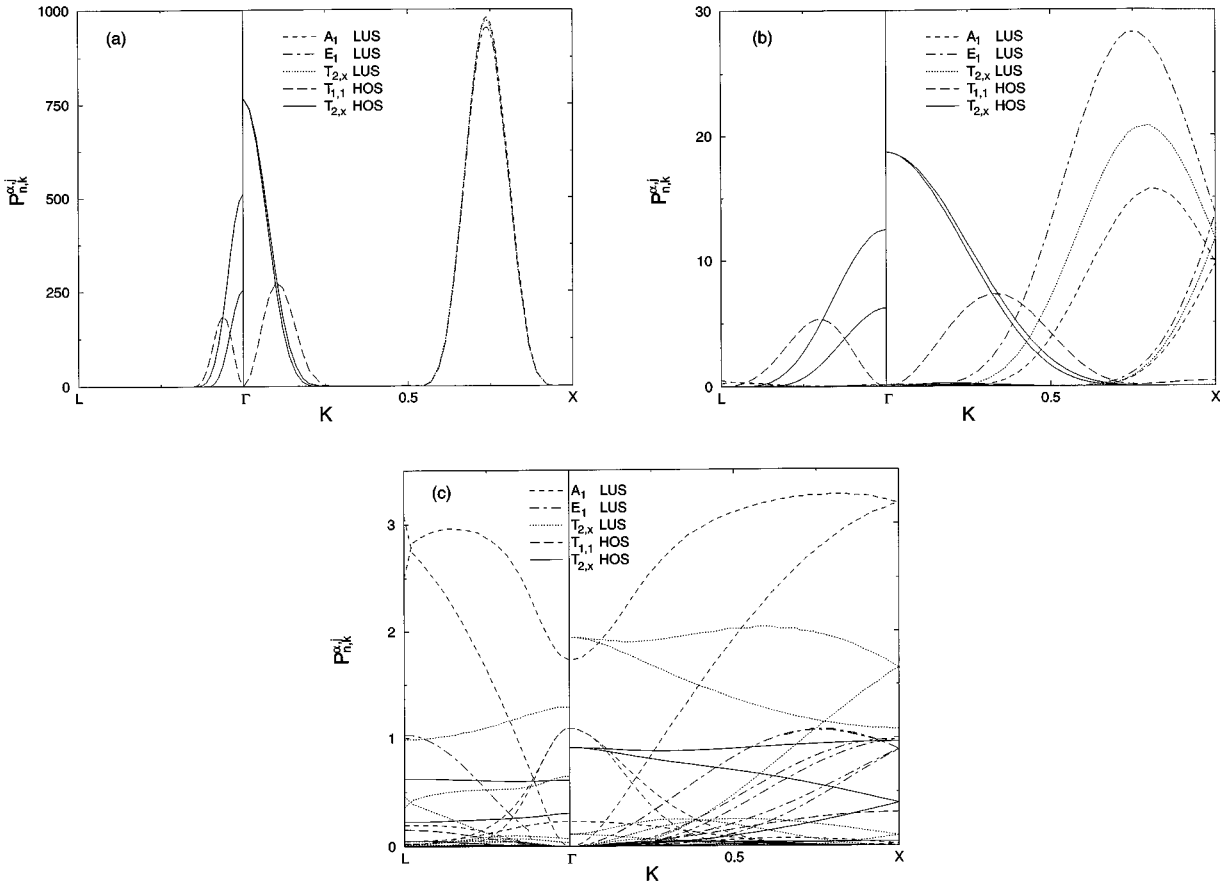

FIG. 3. $P^{\alpha,j}_{n,\mathbf{k}}$ of the A_1, E_1, and $T_{2,x}$ LUS for $\mathbf{k}$ in the [1,1,1] and [1,0,0] directions and of the $T_{2,x}$, $T_{1,1}$ HOS for $\mathbf{k}$ in the [1,1,1] and [0,1,0] directions, and of the $T_{2,x}$ HOS for the $\mathbf{k}$ in the [1,0,0] direction, all in the unit of $1/N$ (N is the number of unit cells in the bulk). The two solid lines for the $T_{2,x}$ HOS in the Γ-L region correspond the contributions from the Λ_3 (upper) and the Λ_1 (lower), but the two solid lines for the $T_{2,x}$ HOS in the Γ-X region correspond the contributions from the Δ_5 for $\mathbf{k}$ in the [0,1,0] direction (upper) and from the $\Delta_{2'}$ for $\mathbf{k}$ in the [1,0,0] direction (lower). The $T_{1,1}$ only has contributions from double degenerate bands Λ_3 and Δ_5, so it only shows one long dashed line in (a) and (b). (a) Hydrogenated Si cluster of diameter 49.14 Å: note that the three peaks for A_1, E_1, and $T_{2,x}$ LUS are all composed of components of Δ_1 and are almost indistinguishably located near $\mathbf{k}_0$, well separated from the HOS located near Γ. (b) Hydrogenated Si cluster of diameter 14.10 Å: note that all peaks are much lower and broader, the conduction band $\Delta_{2'}$ contributions can be clearly seen for three LUS; the overlaps between the LUS and HOS are significant; (c) Hydrogenated Si cluster of diameter 4.70 Å: note that the WDBS are flatter (vs k) and have stronger contributions from other bands, corresponding to the states being highly localized states in the real space.

IV. QUANTUM CONFINEMENT OF HIGHEST OCCUPIED STATES

The quantum confinement of the HOS is even more interesting. Obviously the T_2 HOS has a peak at Γ, the VBM; it behaves very similarly to the A_1, E, and T_2 LUS thus this peak weakens and broadens and its corresponding energy level goes down as the cluster size decreases [Fig. 2(b) and Fig. 3]. All of these behaviors seem easy to understand. But from Fig. 2(b), we see that there is also a T_1 HOS level, well separated from the energy levels below but so close to the T $_2$ HOS level, as if they come together from the HOS of the bulk, like the case of A_1, E, and T_2 LUS. The T_1 HOS level could be even above the T_2 HOS level for some smaller clusters. The WDBS of this T_1 HOS is very different from the other LUS's and HOS's discussed before: it has a zero rather than a peak at Γ, the location of the VBM (Fig. 3). We know that in bulk Si we only have T_2 symmetry for the HOS [Eq. (4)]. Where does this very differently behaved T_1 HOS level come from and what is its significance? We will see in the following that this is a direct consequence of the VBM degeneracy of bulk Si. Before further discussing this, we point out that there are some general orthogonality relationships between the states in the spherical clusters $|\alpha,j\rangle$ and the states in the bulk $|n,\mathbf{k}\rangle$. Especially, we have for the $T_{1,1}$ state of the clusters,

$$\langle \Delta_{2'},\mathbf{k}_\Delta | T_{1,1},j\rangle = 0, \tag{6}$$

$$\langle \Lambda_1,\mathbf{k}_\Lambda | T_{1,1},j\rangle = 0, \tag{7}$$

and

$$\langle \Gamma_{25'} | T_{1,1},j\rangle = 0. \tag{8}$$

Here $\mathbf{k}_\Delta$ means $\mathbf{k}$ in the [1,0,0] or its symmetrical directions, $\mathbf{k}_\Lambda$ means $\mathbf{k}$ in the [1,1,1] or its symmetrical directions.

For $T_{2,x}$ states of the clusters,

$$\langle \Delta_5,\mathbf{k}_{\Delta x} | T_{2,x},j\rangle = 0, \tag{9}$$

$$\langle \Delta_{2'},\mathbf{k}_{\Delta(y,z)} | T_{2,x},j\rangle = 0, \tag{10}$$

and

$$\langle \Lambda_{3,2}, \mathbf{k}_\Lambda | T_{2,x}, j \rangle = 0. \tag{11}$$

Here $\mathbf{k}_{\Delta(y,z)}$ lables $\mathbf{k}$ in either the [0,1,0] or the [0,0,1] direction.

For A_1 states of the clusters,

$$\langle \Delta_5, \mathbf{k}_\Delta | A_1, j \rangle = 0, \tag{12}$$

and

$$\langle \Lambda_3, \mathbf{k}_\Lambda | A_1, j \rangle = 0. \tag{13}$$

All of these general orthogonality relationships were obtained by pure symmetry considerations, and therefore are model independent. So the conclusions based on these orthogonality relationships are also model independent. These orthogonality relations provide very powerful tools for understanding the physical behaviors of electronic states in fully semiconductor quantum dots, nanocrystallites, and clusters.

Referring to Fig. 1, we can consider that the Δ_5 and Λ_3 correspond to a heavier hole mass and $\Delta_{2'}$ and Λ_1 correspond to a lighter hole mass, near the degenerate VBM. The T_1 HOS is affected only by the heavier hole bands in the Δ and Λ directions [Eqs. (6) and (7)], this makes its quantum confinement energy change the least. So, although in the infinite cluster limit there are many states just below the $\Gamma_{25'}$, as the cluster size decreases, the T_1 HOS is the state whose energy level goes down the least and therefore the state closest to the T_2 HOS. On the other hand, the $T_{2,x}$ HOS is composed of the lighter hole band $\Delta_{2'}$ for $\mathbf{k}$ in the [1,0,0] direction but heavier hole band Δ_5 for $\mathbf{k}$ in the [0,1,0] and [0,0,1] directions, and is also affected by both heavier hole Λ_3 and lighter hole Λ_1 bands in the [1,1,1] and its symmetrical directions. Therefore, its quantum confinement energy variation is often stronger than that of the T_1 HOS. These two effects make the T_1 HOS level and T_2 HOS level very close to one another. The general analysis presented here could be applied to almost any cubic semiconductor, therefore, the very highest occupied state in a spherical nanocrystallite of almost any cubic semiconductor should be either the T_1 HOS or the T_2 HOS. However, whether the T_1 HOS could be above the T_2 HOS or not—and if it could, in what size range of the crystallites—is a matter depending on the specific band structure, mainly the valence band structure, of the bulk.[9] On the contrary, the A_1 HOS level is only affected by the lighter hole bands in the Δ and Λ directions [Eqs. (12) and (13)] and therefore always changes the most as the crystallite size decreases, as can be seen clearly from the Fig. 2(b).

It is also interesting to notice that the T_1 HOS, not like the T_2 HOS, is orthogonal to the $\Gamma_{25'}$ states of the bulk [Eq. (8)]. This orthogonality relation pushes the WDBS of the T_1 HOS away from Γ at the center of the k space, and therefore closer to the LUS, as clearly seen from Fig. 3. Obviously the overlap with LUS of this T_1 HOS is larger than the one of the T_2 HOS. In fact, this larger overlap with the LUS of the T_1 HOS over the T_2 HOS could be even further enhanced by the lower peaks of the T_1 HOS than the T_2 HOS. The dipole transitions between the T_1 HOS and the E LUS and T_2 LUS are permitted, so that the T_1 HOS could play a more important role for optical transitions in Si nanocrystallites than the T_2 HOS, especially for clusters of diameter $\geqslant 10$ Å. However, so far many previous calculations concerning the optical transitions in spherical Si nanocrystallites only considered the T_2 HOS—a practice probably carried on from the similar calculations in the bulk. Now we know this is not good enough—a small energy change might mean that completely different symmetrical states are involved.

From the WDBS calculations of clusters of different sizes, we found that the overlap in k space between the LUS and HOS is noticeable for the cluster of diameter 20.31 Å and becomes more significant for clusters of diameters 14.10 Å and smaller. If combined with the fact that the T_1 HOS is above the T_2 HOS for the clusters of diameter of 14.10 and 10.85 Å, we could expect that in that size range the optical transitions in the clusters might be much stronger. It may be noticed that very recent experiments[2] determined the luminescence structure in porous Si, with the wavelength peak in the visible range, is particles whose short range character is crystalline and whose dimensions are typically <15 Å.

V. SUMMARY

In summary, we have shown clearly how the band structure of Si, like its multiple conduction band minima, the degenerate valence band maximum, and the many band structure, specifically affects the quantum confinement of the edge states in Si clusters. In particular, we have pointed out that independent of any special model, the T_1 valence states always have the weakest quantum confinement effect and the A_1 valence states always have the strongest quantum confinement effect. We have also given the wave-function distributions in the Brillouin zone for some of the most important edge states in the hydrogenated Si clusters of several different sizes, which could play a rather significant role in understanding the physics process in Si nanocrystallites.

We have also pointed out that the T_1 highest occupied state, could play a more important role in the optical transitions in Si nanocrystallites than the T_2 HOS developed directly from the VBM of bulk Si.

It may be noteworthy that some major conclusions obtained here *are not* only restricted to the fully symmetrical crystallites. In a small asymmetry, three states will come from basically the linear combinations of the triple degenerate T_1 HOS states, according to the perturbation theory. Then these three states will also have the major properties of the T_1 HOS, like these states have the weakest quantum confinement effect and overlap more with the LUS than the T_2-like states, etc. Of course, how small an asymmetry can be is the subject of further investigations.

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[8] The authors of Ref. 5 obtained similar results but did not address the issues from the viewpoint we are discussing here.
[9] The T_1 HOS could be above T_2 HOS in the spherical crystallites of some cubic semiconductors in a much larger size range. For example, by our calculation the T_1 HOS is above T_2 HOS for the Ge crystallites of diameter from 11 Å to 51 Å, the largest crystallite calculated.