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Strong Electron Correlations Determine the Stability and Properties of Er-doped Silicon Quantum Dots

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The electronic structure of the Goldberg silicon quantum dots with central symmetric hollows and their endohedral complexes with erbium was studied using DFT with and without the strong electron correlations, whose inclusion was found to determine the binding energy. Based on optimized DFT structures, we were able to explain the details of Er-doped nanocrystalline silicon made in experiment. The role of symmetry of the central hollows in quantum dots was elucidated, and the key features of the density of states are explained, providing information for the tuning and design of Er-doped silicon light emitters.

Keywords: DFT, Quantum Dots, Er/Si clusters, electronic structure, energetic stability, strong electron correlations.

Introduction

Er-doped silicon in different forms has been attracted much experimental interest because of its potential application as an efficient semiconductor light emitter [1-13]. From the technological point of view Er-doped nanocrystalline silicon (*nc*-Si) embedded into silica (*nc*-Si:Er/SiO_2, with effective *nc*-Si core sizes 1.5-5 nm) is a very promising material to produce light emitter devices [6-8, 13]. The photoluminescence (PL) of *nc*-Si:Er/SiO_2 (driven by the Er^{+3} $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions in the $[Xe]f^{11}$ configuration) is thought to proceed by the recombination of photogenerated carriers in *nc*-Si and the subsequent energy transfer to Er^{+3}. Also, complexes of transition metals (Hf, Ta, W, Re, Ir etc.) encapsulated in small Si_n clusters have been synthesized using an ion trap and calculated using *ab initio* and LDA methods [14, 15].

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The joint analysis of the spectroscopic experimental data [6-8, 13, 16-18] implies that each Er ion enters one *nc*-Si quantum dot of 1.5–5 nm size without forming Er-O chemical bonds with silica environment. The most probable interpretation of these facts is the penetration of erbium ions into *nc*-Si, covered ouside by silica, but the atomic structure is entirely unknown experimentally. In this work, we attempt to give answers to the following questions: a) what is the atomic structure of Er-doped quantum dots and b) are these systems stable and why?

Structural models and methods of calculations

The addition of several <111> silicon layers to the central hollow Si_m (m=20+k, k=0 ,4, 6, 8) cages produces the Goldberg quantum dots (GQD) [19, 20]. For example, the icosahedral dot $Si_{20}Si_{80}H_{60}$ with one <111> external layer has Si_{20} core [20]. Larger dots can be made by adding external silicon layers to the inner Si core [19]. The first members of the GQD family are energetically preferable among all possible silicon quantum dots with effective size up to 3-5 nm [19, 20].

The electronic structure of the endohedral complexes Er@GQD of erbium ions with the Goldberg quantum dots[19] $Si_{20}Si_{80}H_{60}$ (I_h), $Si_{24}Si_{96}H_{72}$ (D_{6d}), $Si_{26}Si_{26}Si_{104}H_{78}$ (D_{3h}) and $Si_{28}Si_{112}H_{84}$ (T_d), where the symmetry of the inner core is shown in parentheses, was calculated by VASP [21, 22] and GAUSSIAN [23] codes using LDA Vanderbilt Ultra-Soft pseudopotential projector augmented wave (PP PAW) [24, 25] and B3LYP [26, 27] methods with plane wave and Gaussian-type basis sets, respectively. For B3LYP calculations the 3-21G* basis set was used for all Si and H atoms. For Er the Stuttgart RSC 1997 basis set [28] with an effective core potential with $6s^24f^{12}$ valence electrons (SRSC97-ECP) was used. The reasons for using two methods (B3LYP and PP PAW) are a) to elucidate the role of the strong electron correlations, taken into account in PP PAW, and omitted in B3LYP, b) to study the partial density of Er 4f states, which can be defined in B3LYP, but not in PP PAW. To build total and partial density of states (TDOS and PDOS, respectively) the Gaussian broadening for the corresponding electronic occupation numbers was used with a smearing width of 0.1 eV.

The Vanderbilt Ultra-Soft pseudopotential with effective core potential for [Xe]$4f^{11}$ configuration was used for PP PAW calculations. Effectively the strong correlations effects in Er/Si systems [29, 30] were taken into account by excitation of one Er4f-electron from Er$4f^{12}$ shell to the valence Er5d-state [26, 27]. By considering the electrons from Er$6s^2$ shell, this method allows one to have the correct number of valence electrons [3] donated by erbium to the quantum dot. The Vanderbilt Ultra-Soft pseudopotentials also significantly reduce the maximal kinetic energy cutoff without loss of accuracy.

For electronic structure calculations in PP PAW method we used E_{cutoff} energy equal to 250 eV. Geometry optimizations were carried out until the forces acting on all atoms become lower than 0.001 eV/Å using $1*10^{-4}$ eV parameter to achieve the self-consistency during electronic structure calculations. For B3LYP/3-21G*/SRSC97-ECP, we used the $1*10^{-6}$ self-consistency threshold, and optimization was performed until the gradient became smaller than 10^{-4} hartee/bohr. Geometries were optimized for all degrees of freedom in C_1 symmetry. The B3LYP relative energies were calculated with taking into account the basis set superposition errors (counterpoise scheme).

Results and discussion

Both free Er atom and Er-doped quantum dots were computed in B3LYP for the lowest triplet state. Note that Er experimentally has the ground state of ^{3}H; it was found that for Er@

Table 1. Structure and stability of Er/Si clusters. The B3LYP/SRSC97-ECP data are presented for triplet states. ΔE_{BG} is an energy of band gap, E_a is adhesion energy (Er E_a is the same as the energy of formation of Eq@GQD), $R_{Er\text{-}Si}$ is Er-Si distance.

Object	Symmetry	size, mm	$\Delta E_{BG,}$ eV PPPAW(B3LYP)	Si E_a, (kcal/mol), PPPAW(B3LYP)	Er E_a, (kcal/mol), PPPAW(B3LYP)	$R_{Er\text{-}Si}$, Å (PP PAW)
$Si_{20}Si_{80}H_{60}$	I_h	1.3	2.041(3.428)	-87.1(-101.3)	-	-
$Si_{24}Si_{96}H_{72}$	D_{6d}	1.4	1.613(2.958)	-86.4(-100.7)	-	-
$Si_{26}Si_{104}H_{78}$	D_{3h}	1.6	1.672(3.012)	-86.3(-100.6)	-	-
$Si_{28}Si_{112}H_{84}$	T_d	1.5	1.760(3.125)	-86.3(-100.7)	-	-
$Er@Si_{20}Si_{80}H_{60}$	C_i	1.3	0.924(1.199)	-87.9(-101.1)	-76.4(22.1)	3.285-3.323
$Er@Si_{24}Si_{96}H_{72}$	D_{2d}	1.4	1.043(1.506)	-87.0(-100.7)	-67.6(-0.7)	3.461-3.930
$Er@Si_{26}Si_{104}H_{78}$	D_{3h}	1.6	1.224(1.843)	-86.8(-100.6)	-60.4(0.9)	3.543-4.435
$Er@Si_{28}Si_{112}H_{84}$	C_s	1.5	1.445(2.052)	-86.7(-100.7)	-49.1(-3.3)	3.980-4.148

GQD systems the triplet state has the lowest energy (Er^{3+} has the ground state of ^4I, which is coupled with the GQD state possessing three excessive electrons to form the triplet in Er@GQD). It was found that in B3LYP Er atom has the Mulliken charge of about +2, corresponding to Er^{+2}, whereas in PP PAW Er atom is in the Er^{+3} state.

All parent Goldberg-type silicon quantum dots display high energetic stability at both PP PAW and B3LYP/3-21G* levels of theory (Table 1). At the DFT level the GQDs of all studied symmetries have practically the same adhesion energy (E_a) of the silicon atoms (about -86 and -101 kcal/mol at the PP PAW and B3LYP/3-21G* levels, respectively). All parent GQDs reveal perfect symmetries determined by the central Si_{20+k} cores. The strong electronic correlations in the Er 4*f*-shell of all endohedral complexes lead to a distortion of the silicon cages with significant symmetry lowering (Table 1). The Er ion always occupies the center of mass of the clusters (Fig. 1). The silicon adhesive energies of the quantum dots at both levels of theory (PP PAW and B3LYP) are very little changed upon Er doping.

For all Er-doped quantum dots, the B3LYP predicts ether repulsive (22.1 kcal/mol) or small attractive Er (-3.3 kcal/mol) adhesive energies, see Table 1. Taking into account the SEC effects in the PP PAW method results in a large energetic stabilization of the Er ions inside the central cages: erbium adhesive energies, equal to the complex formation energies, vary from -76.4 to -49.1 kcal/mol. It is necessary to note that the energy difference of Er E_a ~100 kcal/mol (4.3 eV) between B3LYP and PP PAW methods is on the same order as the Habbard constant (6.2 eV) determined by the LDA+U method [29, 30]. It means that strong electron correlations determine the large binding energies of the erbium ions in the central hollows of Goldberg-type quantum dots by the donation of one additional electron into valence bands of the silicon clusters.

The total (TDOS) and partial (PDOS) Er4*f* density of states of the parent GQDs and Er@GQD complexes obtained at PP PAW and B3LYP levels of are presented in Fig. 2. The corresponding band gaps are given in Table 1. The TDOS of the valence bands of the parent GQDs obtained at different levels of theory display the close shapes. The PP PAW method, nevertheless, gives sharper peaks keeping the same or close energy positions with band gaps ~1.4 eV smaller the B3LYP ones. The GQD symmetry determines the shape and energy splitting of the TDOS peaks. The I_h $Si_{20}Si_{80}H_{60}$ cluster displays a sharp main peak at -7.157 eV and low-intensity maximum near Fermi level. Increasing the size of the central

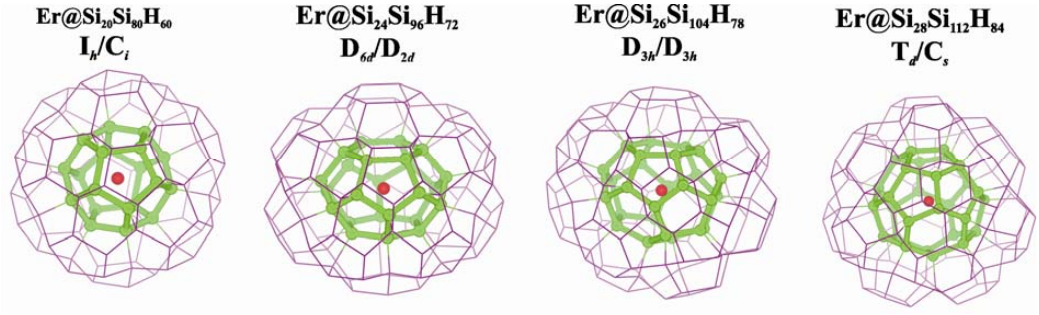

Fig. 1. Structures of Er-doped silicon quantum dots (optimized with PP PAW). Hydrogen atoms are hidden, the inner silicon core is shown as green sticks, the outer silicon atoms are purple; Er is red. The symmetry (point group) is shown for the inner core Si_{20}-Si_{28}, followed after a slash with the group for the whole system

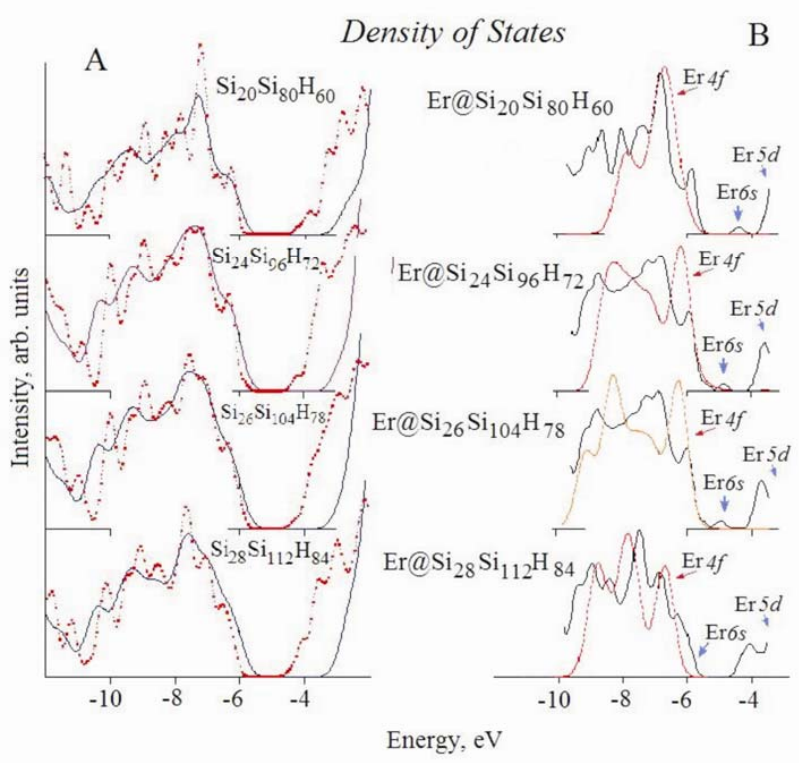

Fig. 2. a) TDOS of Goldberg quantum dots (GQD), obtained using PP PAW (red dashed lines) and B3LYP/3-21G*/SRSC-97-ECP levels of theory (black solid lines). b) TDOS (PP PAW) of the Er@QGD endohedral complexes (black solid lines) and PDOS of Er4*f* PDOS (B3LYP, red dashed lines), whose intensity was magnified by a factor of 20. The spectroscopic features due to the Er6*s* and Er5*d* states are shown by arrows

hollow (and, consequently, the Er-Si distances) and decreasing the symmetry up to D_{3h} results in a smearing of the main peak and its merging with the first low-intensity peak forming one wide DOS structure below the Fermi level (Fig. 2b). The insertion of Er into the central hollows creates the embedded levels inside the forbidden gaps. In both methods, the states are formed by mixing Si3*p*- and Er6*s* orbitals (Fig. 2b). The PP PAW method gives lower energetic positions of the Er6*s*-derived states compared to B3LYP.

Next, we discuss the differences between the four kinds of GQDs. Because Er atom always occupies the center, larger hollow cores (Si_{20}-Si_{28}) have a longer Er-Si distance, resulting in a lower stability (Table 1), as the electrostatic attraction between the -3 charge on the quantum dot and Er^{+3} is weaker for longer distances. The symmetry of the central hollow produces the ligand-like field splitting effect upon the electronic levels of Er, which is observed in Fig. 2b: PDOS of Er 4*f* states have more peaks (are more split) for the lower symmetry cores. Thus, GQDs with a lower symmetry are less stable, but should have a different wavelength of PL transitions, providing means for designing emitters with the desired properties.

Comparing the experimental facts (*nc*-Si:Er/SiO_2 species have a single Er per quantum dot and the very important fact of the absence of Er-O fingerprints in XRD structural data [13, 17, 18], as well as the existence of the caged and semi-caged small silicon clusters with transition metals inside[14]) with our theoretical results, we make the following conclusions: a) experimentally observed Er-doped Si light emitters are made from Goldberg quantum dots with an Er atom occupying their central hollow (the I_h variety like $Er@Si_{20}Si_{80}$ is the mostly likely candidate, embedded in experiment into silica instead of our model systems with hydrogen caps; also, a larger GQD may be formed in experiment), b) the stability is determined by the strong electron correlations responsible for creating the Er^{+3}... GQD^{-3} system, stabilized by the Coulomb attraction, and the photoluminiscence is due to the Er^{3+} transitions. The theoretical analysis in this work elucidating the properties of the experimentally made Er-doped light emitters creates basis for the design of new materials with desired optical and magnetic properties.

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Эффект сильных электронных корреляций, определяющий стабильность и свойства Er-легированных кремниевых квантовых точек

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С помощью теории функционала плотности (DFT) в работе проводилось изучение электронной структуры кремниевых квантовых точек Голдберговского типа с центральными симметрическими пустотами и их эндоэдральными комплексами с эрбием. После оптимизации структуры с помощью DFT-метода был проведен расчет экспериментальных свойств Er-допированного нанокристаллического кремния. Кроме того, исследования позволили объяснить роль симметрии центральных пустот в квантовых точках и провести интерпретацию особенностей в плотностях состояний.

Ключевые слова: теория функционала плотности (DFT), квантовые точки, Er/Si-кластеры, электронная структура, энергетическая стабильность, сильная электронная корреляция.