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Contributed Paper

The DFT Study of Electronic and Optical Properties of the Surface Functional SiGe, GeSn and GeSn Nanostructures

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ABSTRACT

The electronic and optical properties of Si, Ge, and Sn nanostructures are widely studied for various applications, including drug delivery, cell imaging, biosensing and biomedical. This work considers the effect on electronic and optical properties of SiGe, SiSn and GeSn nanostructures by varying the surface functional and the structure size. The considered structures are about spherical-shaped, with a zinc-blende crystal structure, and H, O+H, OH, and NH_2-capped. The optimized structures and their absorption energies are calculated by density functional theory (DFT) and time-dependent density functional theory TD-DFT techniques. In all calculations, the B3LYP and 6-31g basis are used for investigation of electronic and optical properties for SiGe nanostructures, while the LanL2DZ is used for SiSn and GeSn nanostructures. The results show that the optical gap depends not only on the size but also on the terminations on the nanostructure surface. This dependence allows for the possibility of electronic and optical gap engineering.

Keywords: optical properties, electronic circular dichroism (ECD), TD-DFT, surface functional SiGe, GeSn and GeSn, SiGe, GeSn and GeSn nanostructures

1. INTRODUCTION

The possibility of tunable photoluminescence from silicon and silicon-like (e.g. germanium) nanocrystals, as well as from porous silicon, p-Si, composed of Si nanocrystals, has stimulated intensive research on this type of materials over the last decade [1-3]. Most of the work has been done to correlate the optical and electronic characteristics to a diameter of these structures, mostly for "bandgap engineering" [2]. By varying their diameter, intense photoluminescence across the visible spectrum can be obtained. Because of the large blue shift of the observed radiation, relative to the bulk Si band-gap energy (1.2eV), indicates that the luminescence in the visible range is mainly due to the quantum confinement effects. However, the quantum dots involving siloxane derivates, polysilane, and hydrides on the surface of the structure have challenged this hypothesis

[3-5]. Since the structure size is small, the effect of quantum confinement leads to widening of the gap of Si quantum dots from the bulk value of 1.1 eV to 2-3 eV (for larger nanocrystals), or even to 6-7 eV for smaller nanocrystals [1-3]. For the small size of nanocrystals, this effect is less strong in Ge nanocrystals, compared to Si, because of the smaller bandgap of bulk Ge. Therefore, the possibilities of adjusting the optical gap (and the bandgap) are limited only by the proper size selection. Combining the advantages of Si and Ge, not only for optical property but also for electronic and mechanical properties, is an exciting opportunity, whose potential should be explored [6-7]. One way of adjusting the gap to a required value is via the size of nanocrystal. The other obvious way is the substitution of Si atoms by other atoms with similar properties (Ge, Sn) or by doping. Besides, different surface functionals significantly affect the photoluminescence of the quantum dot.

In this work, the pure silicon nanocrystals, or with Si partially the substituted by Ge or Sn atoms, are investigated for their optical and electronic properties. Additionally, electronic and optical properties of Ge nanocrystals, with Ge partially substituted by Sn, is also investigated. The surface functionals such as H, O+H, OH, and NH_2, that terminate the quantum dot structure are used to study the influence on the optical and electronic properties.

2. CALCULATIONS AND METHODS

The structural, optical and electronic properties of SiGe, SiSn and GeSn nanocrystals are studied by using the Gaussian 09 code [8]. These structures are arranged as zinc-blende crystals truncated at an appropriate radius. The shape of the structure is close to spherical. The sizes of nanocrystals considered here are from 4 to 15 Å. This corresponds to the number of Si, Ge and Sn atoms between 10 and 66. For the particular case of SiGe, GeSn and SiSn dot3, the dots are covered by H, O+H, OH group, and NH_2 with 10-64 H, O and N atoms (a total of about 130 atoms). With O+H covering the dot, there are two types of bonds that cap the dot, so both oxygen atoms and H atoms will be bonded with Si, Ge or Sn. The density functional theory (DFT) is used to optimize the quantum dot structure, and the time-dependent density functional theory (TD-DFT) is used to study the optical properties, i.e. UV-visible absorption of the nanocrystals.

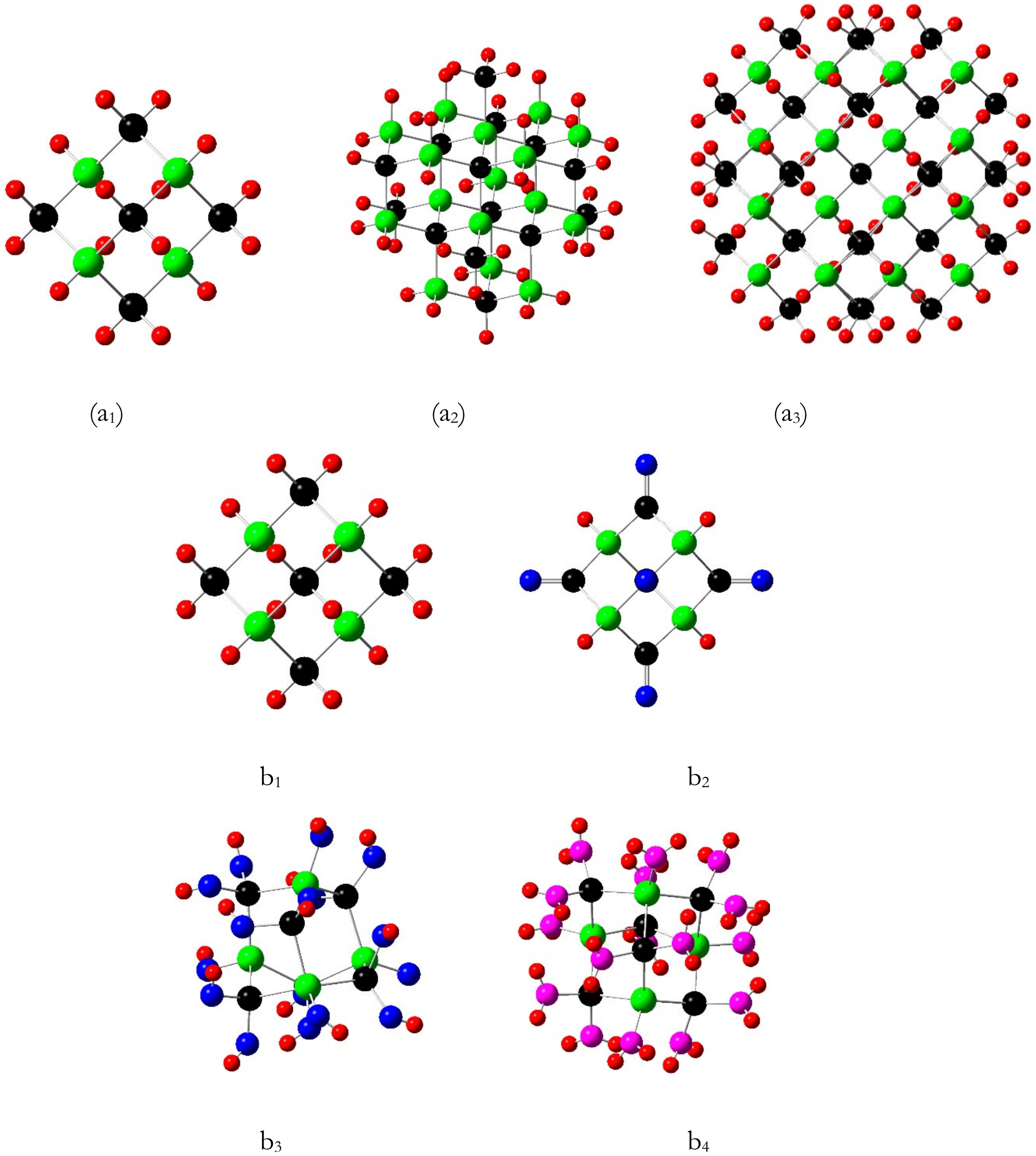
3. RESULTS AND DISCUSSION

The SiGe, SiSn and GeSn nanocrystals covered by H, O+H, OH, and NH_2 are constructed and used to study the structural and optical properties of these nanocrystals. The geometry optimization was performed using DFT/B3LYP for all dots, but the basis sets are different, the 6-31g is used only for the SiGe dots while the SiSn and GeSn dots are calculated by using the LanL2DZ basis sets which can take advantage of the effective core for heavy atoms (i.e. Sn). The bond length is calculated and compared with the reference. After a structure is optimized, the optical properties are investigated by TD-DFT with excited states.

3.1 Structural Properties

3.1.1 SiGe nanocrystals

Representative optimized structure of SiGe nanocrystals are shown in Figure 1 for various sizes and also for different surface functionals in the case of the smallest size dots. The number of atoms used to compose the SiGe nanocrystal, and the average diameter in each case, are given in Table 1. The bond lengths have been calculated by the optimization of the structure. The average Si-Ge, Si-H and Ge-H bond lengths are given in Table 2. The average Si-Ge bond length found in this work is 2.376-2.411 Å. In the largest SiGe nanocrystal, this is in agreement with the experimental value from Nishino et al (2.410Å) [9]. The bond between silicon and hydrogen, germanium and hydrogen were found to be about 1.503-1.505 Å and 1.538-1.544 Å, respectively. The Si-H bond length in this work is larger than that



(a$_1$) (a$_2$) (a$_3$)

b$_1$ b$_2$

b$_3$ b$_4$

Figure 1. The Optimized structures of SiGe nanocrystals. The black, green, red, blue and pink represent the Si, Ge, H, O and N atoms respectively. The a$_1$, a$_2$ and a$_3$ show the SiGe structures with different diameters: dot3, dot5, and dot7. The b$_1$, b$_2$, b$_3$, and b$_4$ show the SiGe structures with different surface functional: H, O+H, OH, and NH$_2$.

Table 1. The number of different atoms in each of SiGe structures considered, and the average diameter after optimization.

SiGe

	Surface functional	**Number of atoms**					**Diameter**
		Si	**Ge**	**H**	**O, N**	**All**	**Å**
dot3	**H**	6	4	16	-	26	7.444
	O	6	4	5	5	20	8.753
	OH	6	4	16	16	42	9.288
	NH	6	4	32	16	58	9.357
dot5	**H**	14	16	40	-	70	11.020
dot7	**H**	38	28	64	-	130	14.222

Table 2. The average bond lengths of Si-Ge, Si-H, Ge-H, Si-O, Ge-O, Si-N, Ge-N, O-H and N-H in each of SiGe nanocrystals considered.

		The bond length of SiGe							
Surface functional		**Si-Ge**	**exp**	**Si-H**	**exp**	**Ge-H**	**exp**		**exp**
H	**dot3**	2.397		1.505		1.544			
	dot5	2.376		1.504		1.538			
	dot7	2.411		1.503	1.481[10]	1.542	1.548[11]		
O+H		**Si-Ge**		**Si-H**		**Ge-H**		**Si-O**	
	dot3	2.418	2.410[9]			1.620		1.527	1.611[12]
OH		**Si-Ge**		**Si-O**		**Ge-O**		**O-H**	
	dot3	2.396		1.743	1.655[12]	1.834	1.810[13]	0.979	0.960[15]
NH_2		**Si-Ge**		**Si-N**		**Ge-N**		**N-H**	
	dot3	2.391		1.783	1.763[14]	1.875	1.850[17]	1.036	1.008[16]

from Z. Jing et al (1.481Å) [10]. In the case of Ge-H, the average bond length in our calculations is close to the bond length reported by E. Sheka (1.548Å) [11]. For various surface functionals, the bond lengths of Si-O, Ge-O O-H, and N-H are tracked in each case. The average bond length of Si-O is 1.527Å, lower than the value calculated by M. T. Dove (1.611 Å) [12]. The calculated average Ge-O bond length in this work is about 1.834, larger than that found by G.V. Gibbs et al (1.810) in [13]. The Si-N bond is 1.783Å, a bit larger than that found by Shetty S. et al (1.763) [14].The bond length between hydrogen and oxygen atoms in H_2O is 0.96Å [15], a bit smaller than the average bond length in this work (0.976Å). The N-H bond length in this calculation (1.036Å) is larger than that in NH_3 molecule (1.008Å) [16]. The Ge-N bond length found here is 1.875 Å comparable to Kim M Baiines (1.850 Å) [17]. Overall, from the above data, the average values for all bond lengths found in this calculation are near but slightly larger than those from the literature, probably related to the small size of the structures.

3.1.2 GeSn nanocrystals

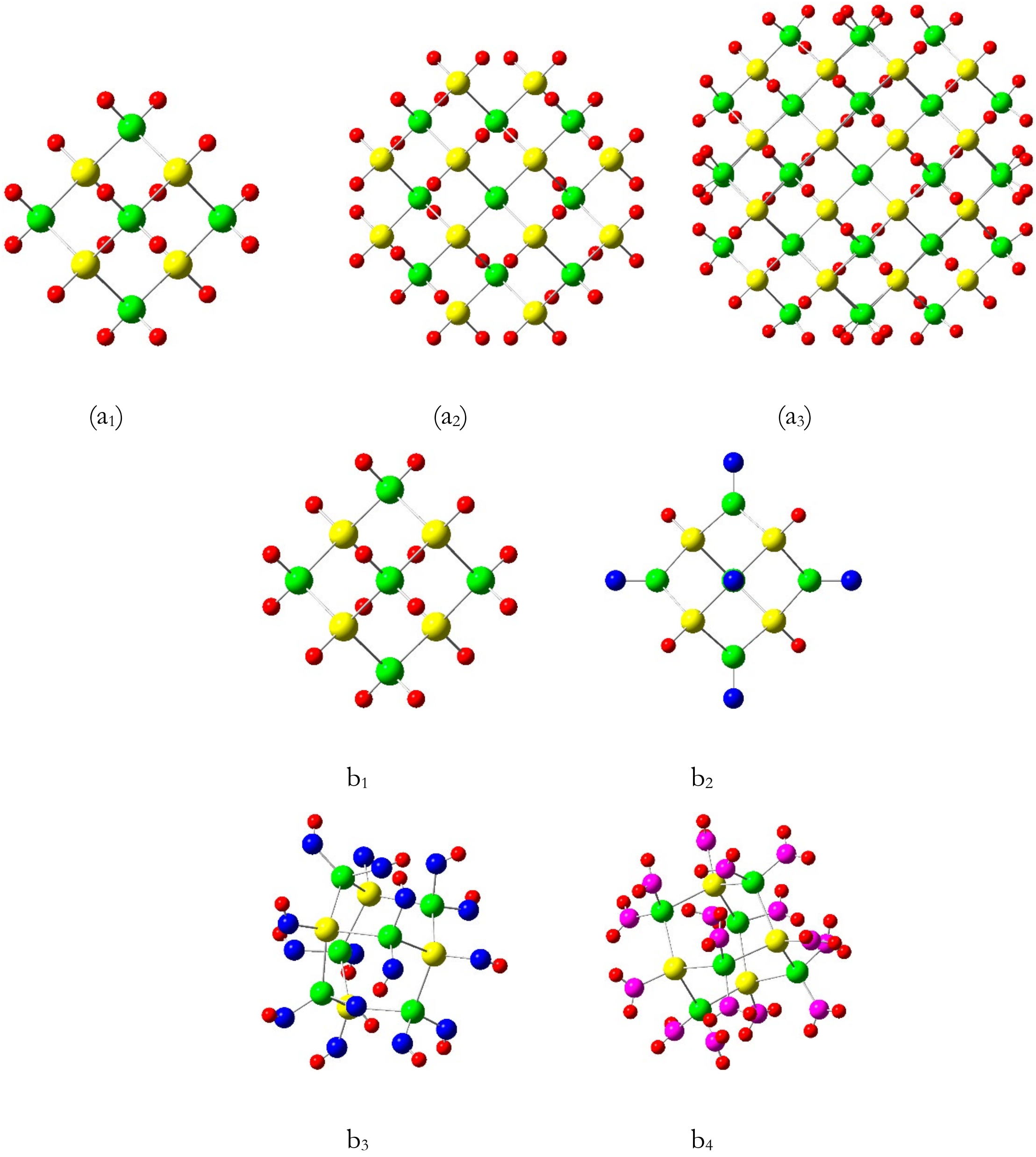
The optimized structure for various dot sizes, and different surface functionals for the smallest size dot, are shown in Figure 2. The number of atoms used to compose the GeSn nanocrystal, and the average diameter in each case, are given in Table3. The average bond lengths have also been calculated after the optimization of the structure. The average Ge-Sn, Ge-H, Sn-H, Ge-O, Sn-O, Ge-N, Sn-N, O-H and N-H bond lengths are given in Table 4, and amount to 2.664-2.708Å, 1.553-1.539 Å, 1.707-1.721 Å, 1.679-1.849 Å, 1.016 Å, 2.004 Å, 0.979 and 1.016 Å, respectively. The Ge-Sn bond length was reported by R. Beeler et al. as 2.628Å [18]. The value for Ge-Sn obtained in this work is in good agreement with it. The Ge-H, Ge-O, O-H, N-H, Sn-H and Sn-O bond lengths are also quite close to the values from the literature [11](1.548Å), [13](1.810Å), [15](0.960Å), [16](1.008Å) [19](1.700Å) and [20](1.913Å) There is no bond between Ge and H atom in the dot5 GeSn nanocrystal.

3.1.3 SiSn nanocrystals

The optimized structure for various dot sizes and surface functional of the smallest size dot are shown in Figure 3. The number of atoms used to compose the SiSn nanocrystal, and the average diameter in each case, are given in Table 5. The average bond lengths have been calculated after optimization of the structure, and for Si-Sn, Si-H, Sn-H, Si-O, Sn-O, Si-N, Sn-N, O-H and N-H they amount to 2.601-2.650Å, 1.490 Å, 1.704-1.723 Å, 1.597Å, 1.645 Å, 1.763 Å, 0.978 and 1.015 Å, respectively (Table 6). The bond lengths calculated here are similar to, or just slightly larger than values from the literature. There is no bond between Si and H atom in the dot5 SiSn nanocrystal.

3.2 Electronic Properties

The ground-state properties of SiGe, GeSn, and SiSn nanostructures are calculated using the density functional theory (DFT). All dot structures are initially designed as a big box zincblende structure, and then some atoms are cut out if they are beyond the dot radius. In this situation, there are many Si, Ge and Sn atoms at the surface of the dots without 4 bonds with the neighboring atoms. These atoms require some more surface atoms, and then H, O, OH and NH_2 are added to complete 4 bonds. In this work, the electronic properties are investigated, as well as the effect of variable dot diameter when it is covered only by H atoms, and also the effects of the surface functional in the smallest nanocrystals only. Furthermore, the most important orbital in a molecule is the frontier molecular orbital, called the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other molecules. At the ground state, the HOMO, LUMO are generally considered first because they are also relevant for the optical energy gap. Figure 4 shows the HOMO, LUMO, and the HOMO-LUMO gap of the SiGe, GeSn, and SiSn. The HOMO-LUMO gap is defined as the difference between the HOMO and LUMO energy levels. The gap will decrease when the diameter increases. The value of the gap in a structure depends on its diameter, because of the quantum confinement effects. When the diameter increases, the HOMO-LUMO gap will decrease. In the special case of dot3 of SiGe, GeSn and SiSn nanocrystals the effect of the surface functional on the optical properties is also studied. The H, O+H, OH, and NH_2 that are used for covering the dot all around, are the surface functional. From Figure 4, the HOMO-LUMO gap of the dot with hydrogen atoms on the surface is largest then for dots with another surface functional. In the case of NH_2 covered dots, the HOMO energy level is shifted up, when compared to the H covered dot. On the other hand, the LUMO energy level of the dot covered by O+H shifts down. In the case of the OH group that terminates bonds around the dots, the oxygen atom and hydrogen atom influence both HOMO to move up and LUMO to move



(a$_1$) (a$_2$) (a$_3$)

b$_1$ b$_2$

b$_3$ b$_4$

Figure 2. The Optimized structure of GeSn nanocrystals. The green, yellow, red, blue and pink represents the Ge, Sn, H, O and N atoms, respectively. The a$_1$, a$_2$ and a$_3$ show GeSn structures with different diameters: dot3, dot5, and dot7. The b$_1$, b$_2$, b$_3$, and b$_4$ show the GeSn structures that vary the surface functional such as H, O+H, OH, and NH$_2$.

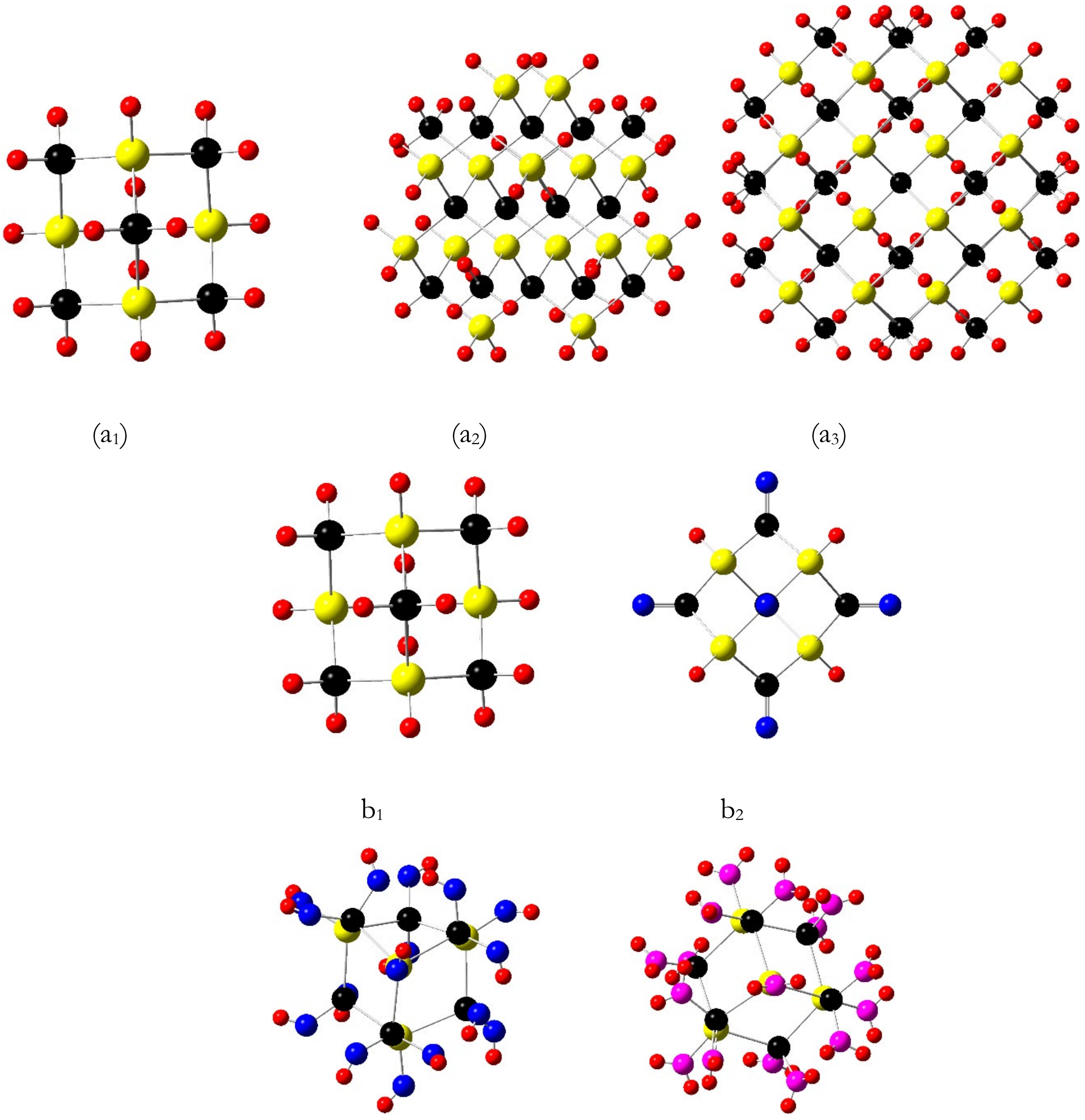
Table 3. The number of different atoms in each of the GeSn structures considered, and the average diameter after optimization.

GeSn

	Surface functional	**Number of atoms**					**Diameter**
		Ge	**Sn**	**H**	**O, N**	**All**	**Å**
dot3	**H**	6	4	16	-	26	8.172
	O	6	4	4	6	20	9.505
	OH	6	4	10	10	30	10.282
	NH	6	4	32	16	58	10.334
dot5	**H**	14	16	34	-	64	12.409
dot7	**H**	38	28	64	-	130	16.261

Table 4. The average bond length of Ge-Sn, Ge-H, Sn-H, Ge-O, Sn-O, Ge-N, Sn-N, O-H and N-H in each of GeSn nanocrystals considered.

Bond length of GeSn (Å)									
Surface functional		**Ge-Sn**	**exp**	**Ge-H**	**exp**	**Sn-H**	**Exp**		**exp**
H	**dot3**	2.667		1.553		1.721			
	dot5	2.681		1.551	1.548[11]	1.720			
	dot7	2.684		1.554		1.725	1.700[19]		
		Ge-Sn		**Ge-O**		**Sn-H**			
O+H	**dot3**	2.724	2.628[18]	1.679	1.810[13]	1.707			
		Ge-Sn		**Ge-O**		**Sn-O**		**O-H**	
OH	**dot3**	2.703		1.849		1.937	1.913[20]	0.979	0.960[15]
		Ge-Sn		**Ge-N**		**Sn-N**		**N-H**	
NH	**dot3**	2.708		1.849	1.850[17]	2.002		1.015	1.008[16]



(a1) (a2) (a3)

b1 b2

b3 b4

Figure 3. The Optimized structure of SiSn nanocrystals. The black, yellow, red, blue and pink represent the Si, Sn, H, O and N atoms, respectively. The a_1, a_2 and a_3 show SiSn structures with different diameters: dot3, dot5, and dot7. The $b_{1,}$ $b_{2,}$ $b_{3,}$ and b_4 show the SiSn structures with different surface functional: H, O+H, OH, and NH_2.

Table 5. The number of different atoms in each of SiSn structures considered, and the average diameter after optimization.

SiSn

	Surface functional	**Number of atoms**					**Diameter**
		Ge	**Sn**	**H**	**O, N**	**All**	**Å**
dot3	**H**	6	4	16	-	26	8.056
	O	6	4	4	6	20	9.147
	OH	6	4	16	16	42	9.701
	NH	6	4	32	16	58	9.874
dot5	**H**	14	16	40	-	70	11.963
dot7	**H**	38	28	64	-	130	15.493

Table 6. The average bond length of Si-Sn, Si-H, Sn-H, Si-O, Sn-O, Si-N, Sn-N, O-H and N-H in each of SiSn nanocrystals considered.

Surface functional		**The bond length of SiSn (Å)**							
		Si-Sn	**exp**	**Si-H**	**exp**	**Sn-H**	**exp**		**exp**
H	**dot3**	2.601		1.490		1.720			
	dot5	2.624		1.488		1.714			
	dot7	2.614		1.490	1.481[10]	1.723	1.700[19]		
		Si-Sn		**Si-O**		**Sn-H**			
O+H	**dot3**	2.650	2.602[21]	1.597		1.704			
		Si-Sn		**Si-O**		**Sn-O**		**O-H**	
OH	**dot3**	2.641		1.714	1.655[12]	1.945	1.913[20]	0.978	0.960[15]
		Si-Sn		**Si-N**		**Sn-N**		**N-H**	
NH_2	**dot3**	2.643		1.766	1.763[14]	2.007		1.015	1.008[16]

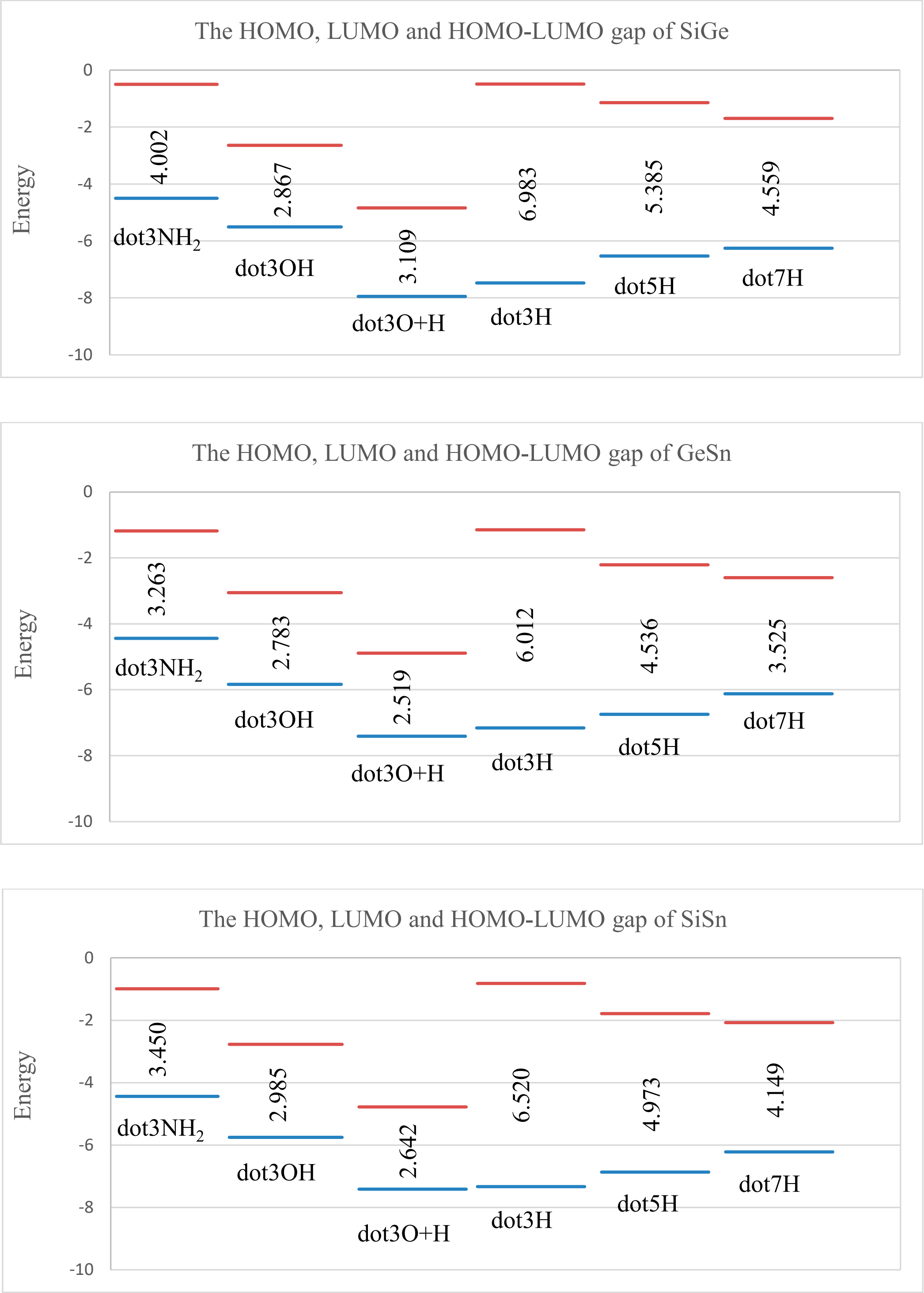


Figure 4. The HOMO (blue), LUMO (orange) and HOMO-LUMO gap of SiGe, GeSn and SiSn nanostructures.

down in energy. It is shown that the optical gap of the SiGe, GeSn and SiSn nanocrystals can be tuned by varying the surface functional. Another method of gap tuning is to vary the diameter of the structure, coming directly from the quantum confinement effect. All this enables the engineering of the electronic and optical properties of the quantum dots.

3.3 The Electronic Absorption Spectra

An important property in optoelectronic, medical and biosensing applications is the optical absorption spectrum of the dots. The simulation of the absorption spectra of dots also shows their light-harvesting capability. The oscillator strength of transitions in the quantum dots is calculated by the time-dependent density functional theory (TD-DFT), which is generally used to study the peak absorption energies in the structure. The results of absorption spectra calculations for these nanocrystals are shown in Figures 5 and 6 for various diameters, and also for different surface functional of smallest nanocrystals. The peak absorption for various diameters and termination by H atoms are in agreement with the values of the HOMO-LUMO gap in all SiGe, GeSn and SiSn nanocrystals. The UV-visible absorption peaks for the dot3, dot5, dot7 of SiGe nanocrystals

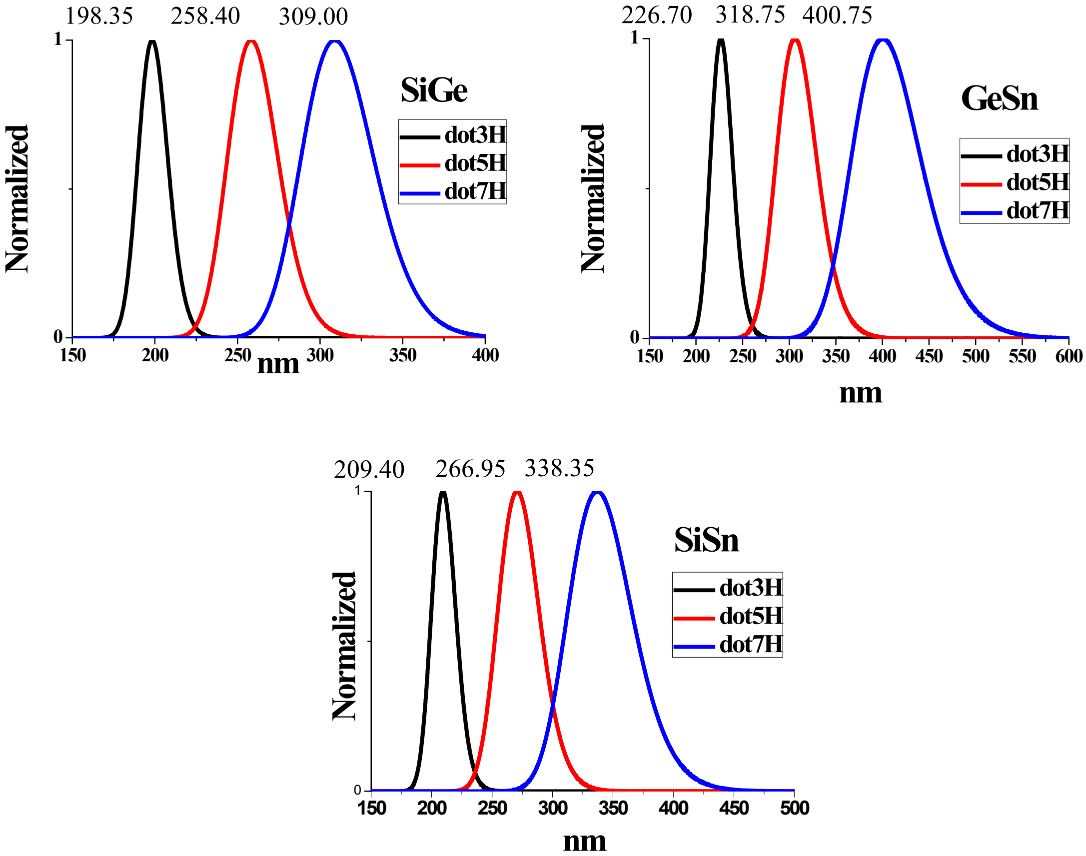


Figure 5. The absorption spectra of SiGe, GeSn and SiSn nanostructures with different diameters.

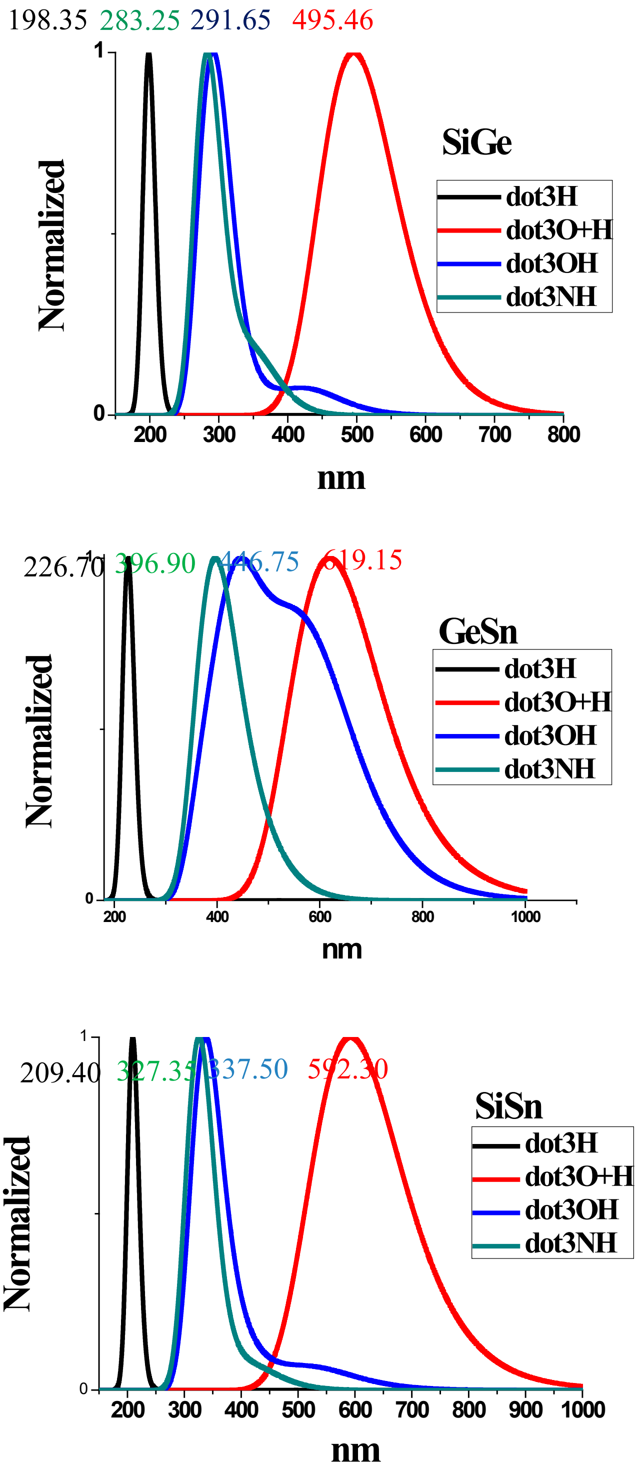


Figure 6. The absorption spectra of dot3 based on SiGe, GeSn and SiSn nanostructures, with different surface functionals.

are calculated to be 198.35 nm, 258.40 nm, and 309.00 nm, respectively, while the peak absorption of GeSn nanocrystals of dot3, dot5 and dot7 are found at 226.70 nm, 318.75 nm and 400.75 nm. The dot3, dot5, and dot7 of SiSn nanocrystals show the peak absorption at 209.40 nm, 266.95 nm, and 338.35 nm. The effect of surface functional on absorption energy is studied because it also enables tuning the optical properties. In this work, the H, O+H, OH, and NH_2 are used to cover the overall SiGe, GeSn and SiSn dots. The peak absorption of the SiGe dots appears at 198.35nm, 495.46nm, 291.65 nm and 283.25 nm for H, O+H, OH, and NH_2 respectively. The peaks of GeSn dot are at 226.70 nm, 619.15 nm, 446.75 nm and 396.90 nm, and for SiSn dot they are found at 209.40 nm, 592.30 nm, 337.50 nm and 327.35 nm, for H, O+H, OH and NH_2 surface functional respectively. From the above discussion, the optical properties of SiGe, GeSn and SiSn dots can be significantly tuned both by their diameter (due to the quantum confinement effect) and by the choice of the surface functional, i.e. by terminating the dot with H, O, OH group and NH_2.

3.4 HOMO LUMO Orbital

The HOMO–LUMO energy gaps of SiGe, GeSn and SiSn dots are shown in Figures 7 and 8 for various dot diameters and surface functional, respectively. According to Figure 7, the HOMO is

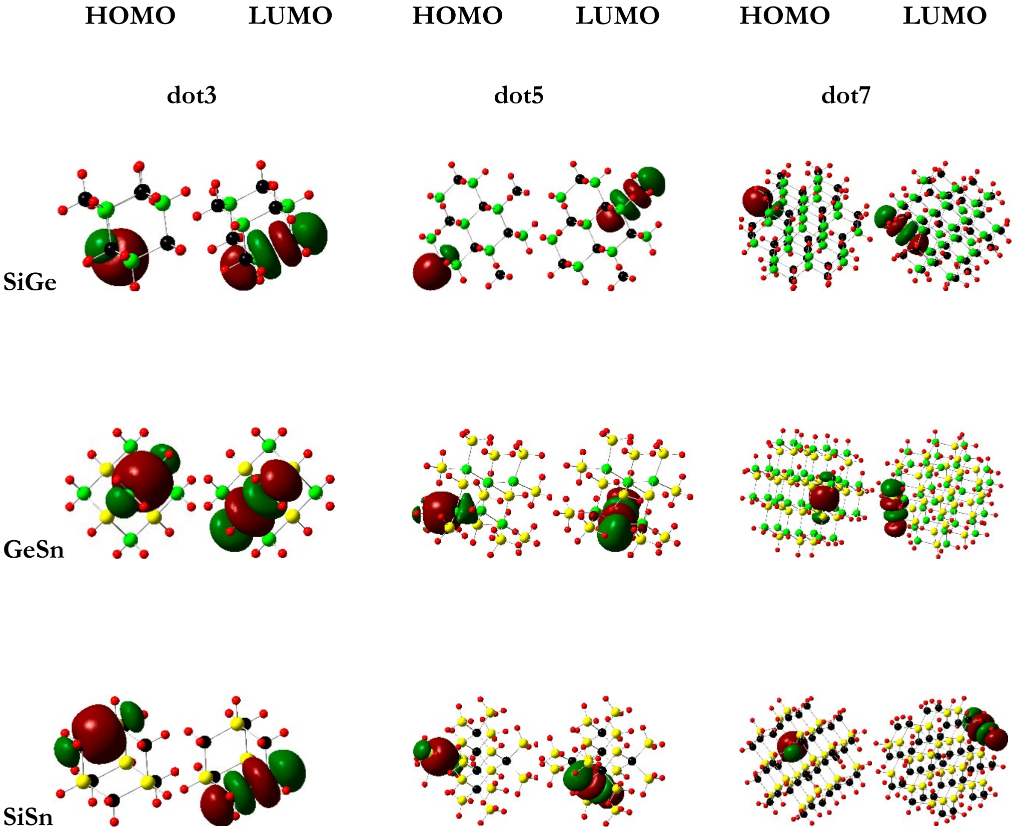


Figure 7. The charge distribution of HOMO and LUMO states of SiGe, GeSn and SiSn nanocrystal with various diameters where the black, green, yellow and red balls represent the Si, Ge, Sn and H atoms, respectively.

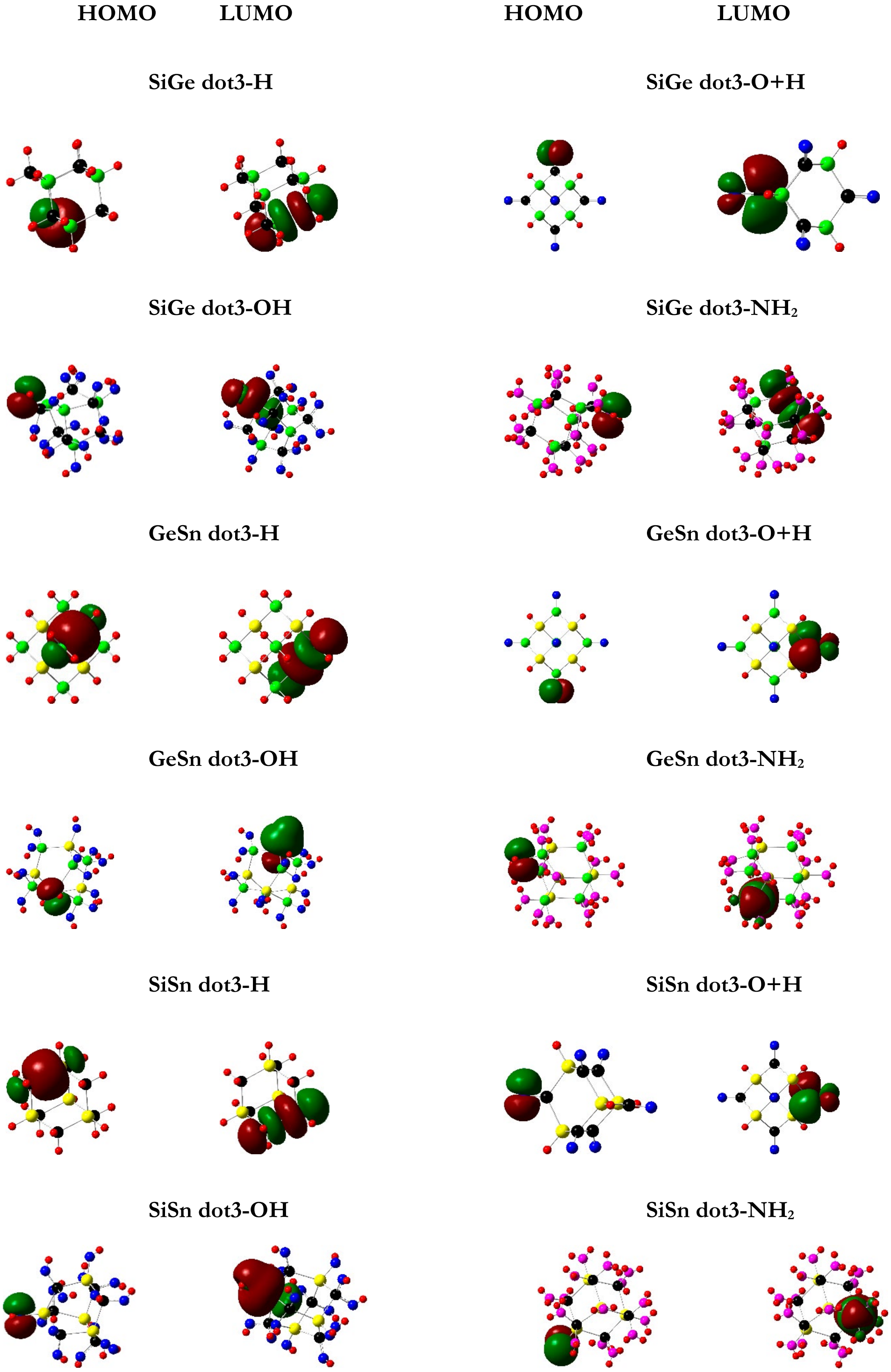
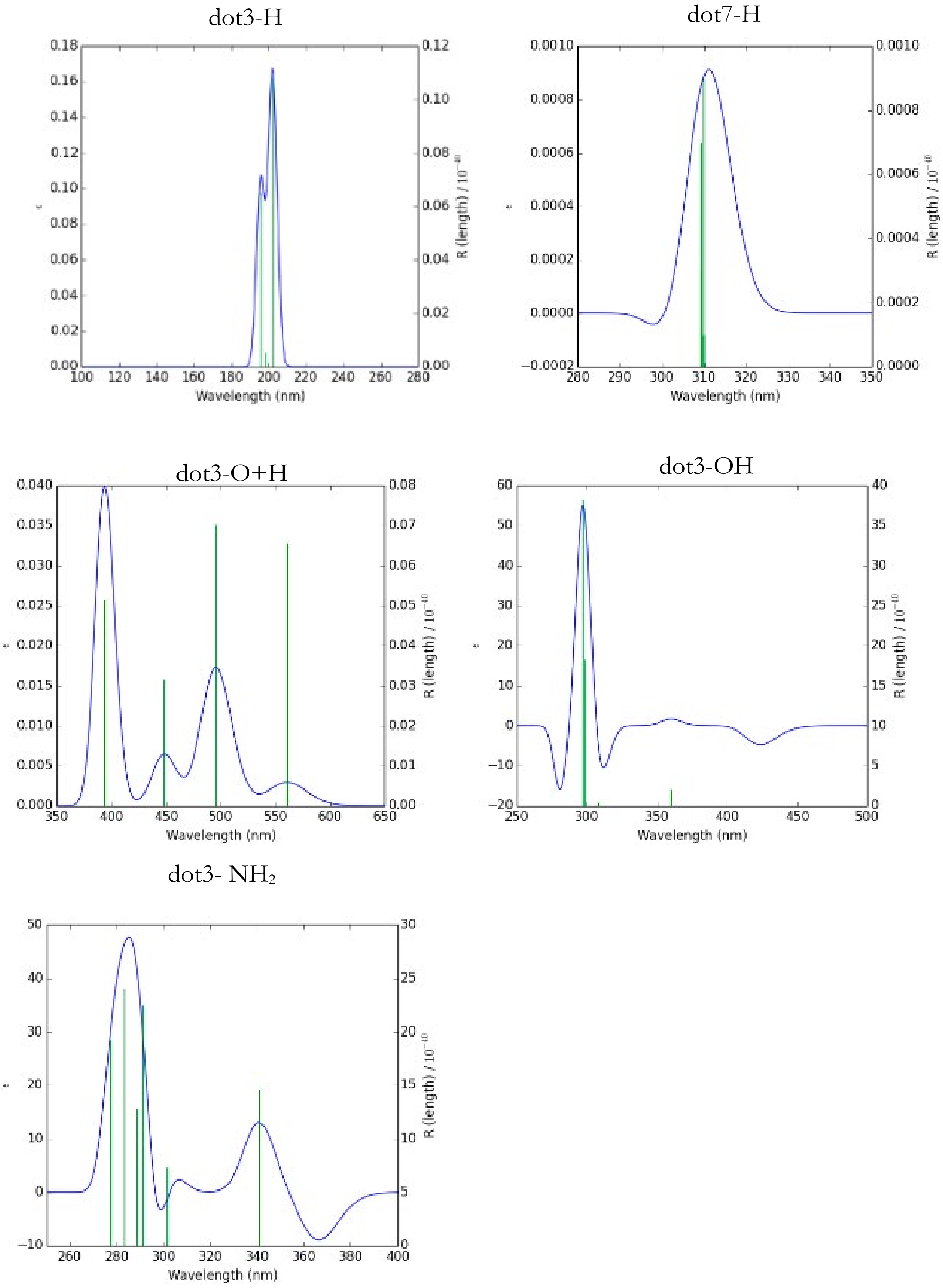


Figure 8. The charge distribution of HOMO and LUMO states of SiGe, GeSn and SiSn nanocrystals with various surface functional where the black, green, yellow, blue, pink and red balls represent the Si, Ge, Sn, O, N and H atoms, respectively.


dot3-H

dot7-H

dot3-O+H

dot3-OH

dot3- NH_2

Figure 9. The ECD spectra of the SiGe, GeSn and SiSn nanocrystals.

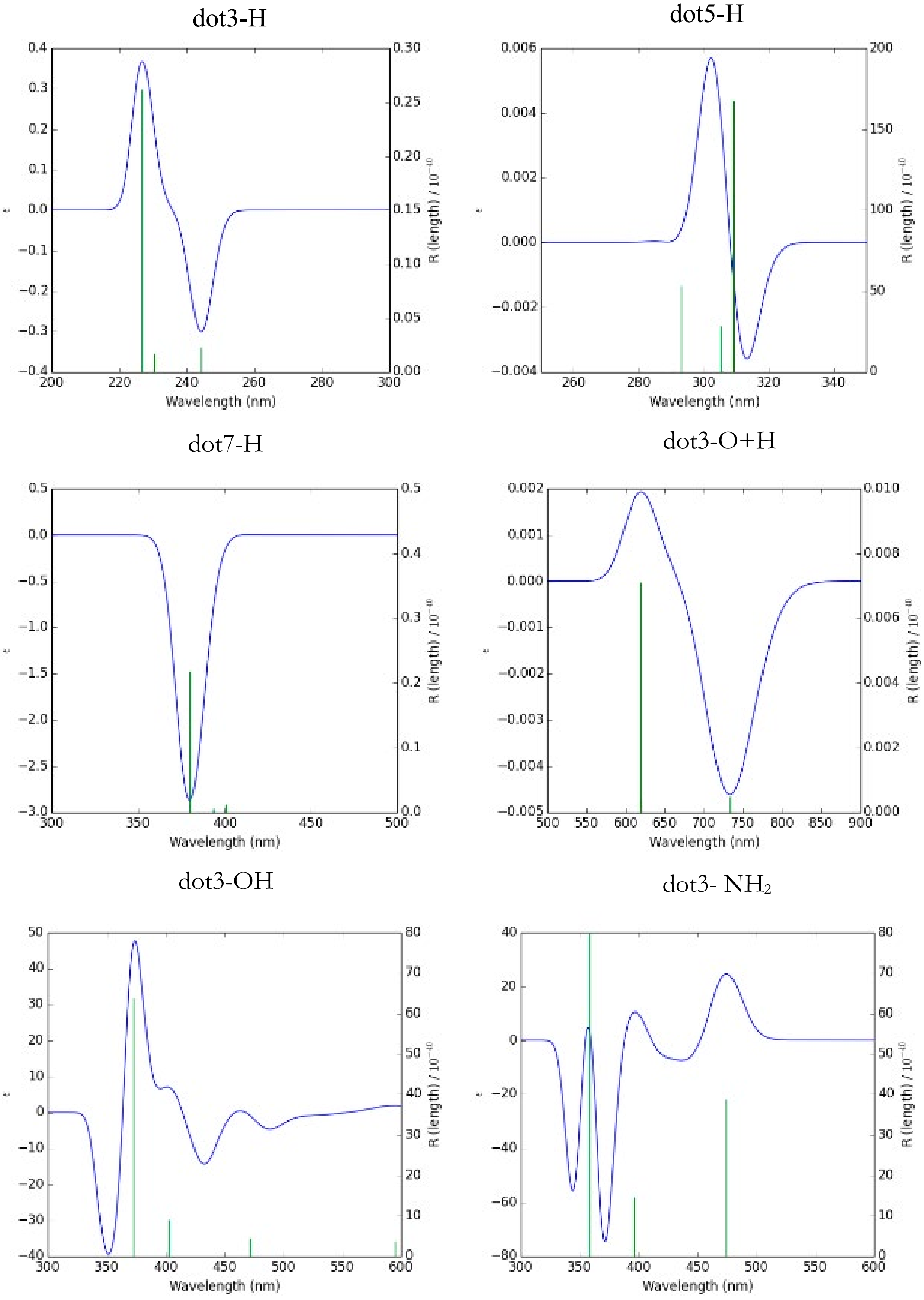


Figure 10. The ECD spectra of the GeSn nanocrystals.

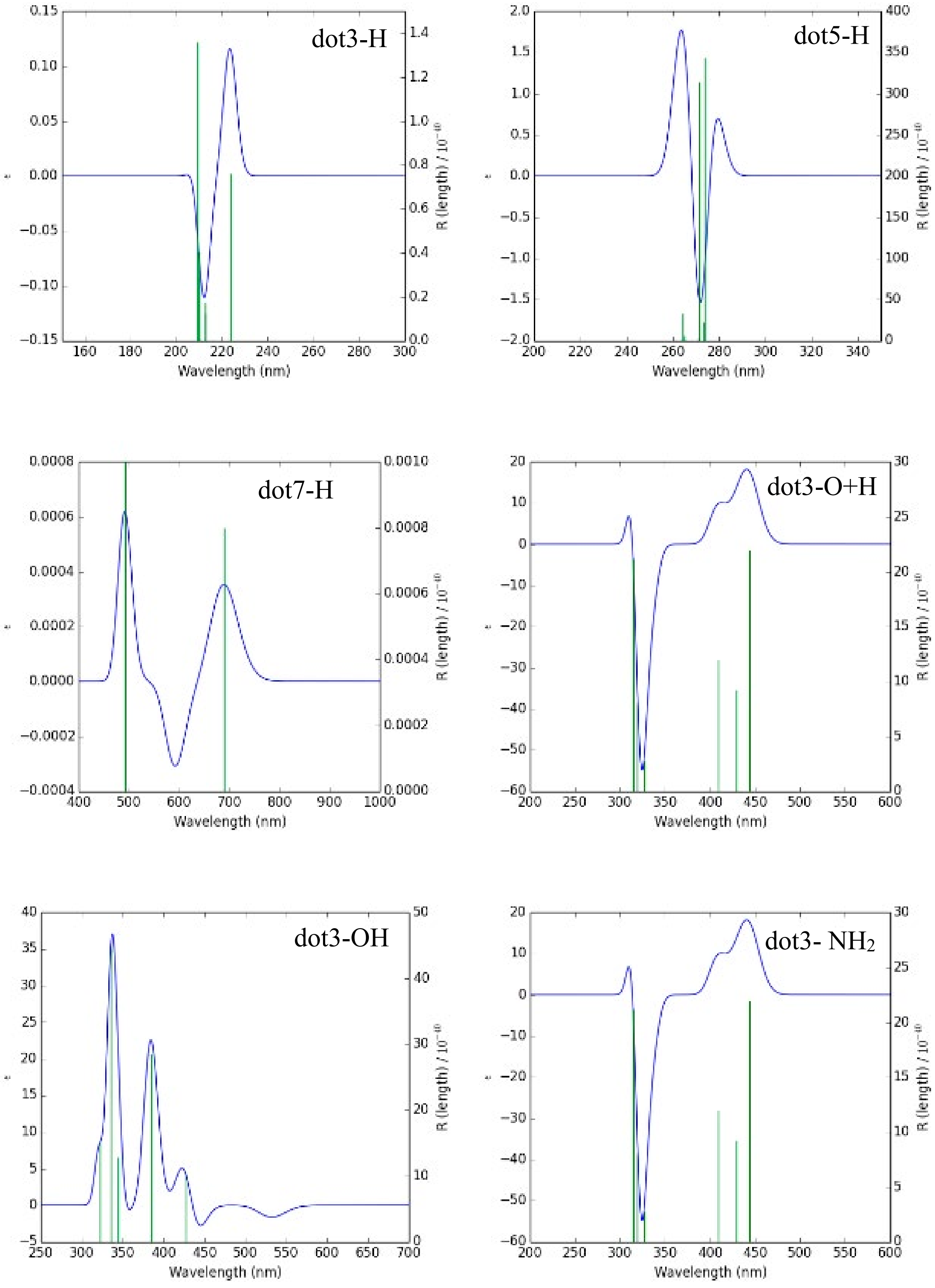


Figure 11. The ECD spectra of the SiSn nanocrystals.

located below the dot surface and LOMO near the surface of the dot. In the case of GeSn and SiSn for dot7, the HOMO electron cloud is located inside the dots, but the charge distribution in SiGe shows that it is at the surface. The HOMO and LUMO charge distributions, for various surface functionals, are shown in Figure 8. The HOMO and LUMO electron charge are found at the surface of the dot. In the special case of termination by O+H, these structures have the double bond only between the oxygen atom and Si, Ge or Sn atom. The HOMO electron cloud is then located mostly near the oxygen atom.

3.5 Electronic Circular Dichroism (ECD) Spectra

The calculation of ECD spectra is used for the characterization of structures that absorb energy. The results from the ECD calculations are usually compared with the results from experiments. It may enable classifying the structure according to the type of chirality, like R or L type. From Figure 9, 10, and 11, the ECD spectra also show all possible patterns for SiGe, GeSn and SiSn nanocrystals, corresponding to the structures represented in Figures 1, 2 and 3. In the case of SiGe dot5-H, it is surprising that there is no peak in the ECD spectrum. This is different for other structures. There are different patterns in the ECD spectra, although it is the same surface functional and type, but different diameters of the dots. This is also the case for different surface functionals.

4. CONCLUSIONS

In this work, the geometry and electronic structure of SiGe, GeSn and GeSn dots are studied by the DFT method, and the UV-Visible absorption spectra are investigated by the TD-DFT method. The dot (nanocrystal) parameters are varied by either (1) changing the dot diameter, or (2) using various surface functionals, such as H, O+H, OH, and NH_2. The average bond lengths found in this work are typically slightly larger than the lengths reported in the literature. The quantum confinement effect is important for the HOMO-LUMO gap and visible photoluminescence and enables their tuning. The surface functional that covers the nanocrystals also affects the HOMO-LUMO energy levels and absorption energy, enabling the electronic and optical gap engineering.

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