Structural, electronic and optical properties of tetrahedral \( Si_x Ge_{47-x} : H_{60} \) nanocrystals: A Density Functional study

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The structural, cohesive, electronic and optical properties of mixed SiGe:H quantum dots are studied by Density Functional Theory (DFT) calculations on a representative ensemble of medium size nanoparticles of the form \( Si_x Ge_{47-x} : H_{60} \). The calculations have been performed in the framework of the hybrid non-local exchange-correlation functional of Becke, Lee, Parr and Yang (B3LYP). Besides the ground state DFT/B3LYP values we provide reliable results for the lowest spin and symmetry allowed electronic transition based on Time Dependent DFT (TDDFT/B3LYP) calculations. Our results show that the optical gap depends not only on the relative concentrations of silicon, germanium and hydrogen, but also on the relative position of the silicon and germanium shells relative to the surface of the nanocrystal. This is also true for the structural, cohesive and electronic properties allowing for possible electronic and optical gap engineering. Moreover, it is found that for the cases of nanoparticles with pure Ge or Si core, the optical properties are mainly determined by the Ge part of the nanoparticle, while silicon seem to act as a passivant.

1 Introduction

The possibility of tunable photoluminescence (PL) from silicon and silicon-like (e.g. germanium) quantum dots (and nanowires), has stimulated intensive research on this type of materials over the last decade [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]. Until recently, silicon nanocrystals have practically “monopolized” the interest of the researchers. A large portion of this type of work has been devoted to understanding the visible photoluminescence of these materials and its dependence on the diameter of the nanoparticles. It is widely accepted and well established by now (see for instancerefs. 12-15) that the luminescence of oxygen-free Si nanocrystals
(of well defined diameter) is mainly due to quantum confinement (QC) of the corresponding nanoparticles. This is also true for Ge nanoparticles\cite{7,8}. It is known that the effect of quantum confinement is even more pronounced for the case of Ge nanoparticles. This can be easily understood by comparing the electron and hole effective masses and dielectric constants of Si and Ge. In particular, the smaller electron and hole effective masses of Ge along with the larger dielectric constant (compared to Si) result in a larger exciton Bohr radius for Ge. Consequently, it might be expected that the effect of QC on the optical properties of Ge nanoparticles will be more pronounced. The PL properties of such nanocrystals (Si or Ge) are mainly controlled by suitably regulating the size of the nanocrystals and in many cases, their surface passivation. The possibility of combining the advantages of Si (in the electronic properties) with those of Ge (especially structural and mechanical properties) appears to be a natural extension of scientific interest and an intriguing and potentially promising field for the development of optoelectronic nanodevices. It has been demonstrated by both experimental observation\cite{13} and theoretical calculations\cite{13,14} that the lattice mismatch of Si and Ge has a significant effect on the electronic properties of $Si_{1-x}Ge_x$ alloys. The induced strain affects mainly the tail of the conduction band which results in an almost linear decrease of the indirect band gap. In this sense, it may be expected that a similar behavior may introduce interesting optical features in $Si_xGe_y : H_z$ nanocrystals. Several of these issues have been recently addressed by Ming Yu et. al.\cite{20} in the framework of Density Functional Theory. In particular, they have performed DFT/LDA molecular dynamics calculations on medium size $Si_xGe_y$ and $Si_xGe_y : H (x + y = 71)$ mixed nanoparticles. Especially for the case of hydrogenated nanocrystals they found that the dependence of the single particle HOMO-LUMO gap on the relative composition of the clusters exhibits many similarities with the corresponding one of the bulk $Si_{1-x}Ge_x$ alloys. At this point it should be noted that the structure of the specific nanocrystals has been fully relaxed through a molecular dynamics procedure with an initial temperature of 1000 K. As a result a large portion of the strain induced by the Si/Ge mismatch (in the initial geometric configurations) has been largely relieved. However, it would be interesting to expand the investigation for the case of mixed Si/Ge nanocrystal which have not undergone such an annealing procedure. In this case, the aforementioned strain can not be fully relieved since the individual atoms are only allowed to a local relaxation around their original position (i.e. they are not allowed to diffuse through the shells). With this in mind, we have examined the optical and electronic properties of mixed nanocrystals of the form $Si_xGe_{47-x} : H_{60}$. We have studied in detail the variation of the cohesive, electronic and optical properties as a function of $x$. Moreover, we have examined the dependence of these properties on the position of each atomic species relative to the nanocrystal’s surface.
2 Technical details of the calculations

All ground state calculations in this work are based on Density Functional Theory (DFT), while all excited state calculations are based on TDDFT. In both cases we employed the nonlocal exchange-correlation functional of Becke, Lee, Yang and Parr (B3LYP) \[18\]. The accuracy of these calculations (TDDFT/B3LYP) for the optical gap has been tested before by by comparison with high level multireference second-order perturbation theory (MR-MP2) calculations for the case of Si nanocrystals\[5\]. The size of the $\text{Si}_x\text{Ge}_{47-x}:\text{H}_{60}$ nanocrystals considered here is approximately 10-12 Å. The symmetry of the nanocrystals is $T_d$ and their geometries have been fully optimized within this symmetry constraint using the hybrid B3LYP functional. To preserve the $T_d$ symmetry, we substituted shells of silicon (rather than isolated atoms) by equivalent germanium shells. This choice introduces an additional restriction on the variation of Si concentration. This procedure imposes some constraints in the relaxation of the interatomic forces. In particular, although bond lengths and angles are allowed to relax, the atoms are not allowed to change their relative position in the nanoparticle. As a result, migration from the inner core to the surface (or vice versa) is not possible (such migrations were both allowed and observed in the MD calculations of Ming Yu et al\[20\]). We have examined in detail most of the structural (bond length distribution), cohesive (binding energies), electronic (DOS, electronic gaps) and optical properties as a function of the concentration $x$. The optical gap is defined as the energy of the lowest spin and symmetry allowed excitation calculated by the TDDFT/B3LYP method. Moreover, for the same concentration $x$ we have considered alternative ways of substitution of the shells of silicon atoms by germanium. The bulk of our calculations were performed with the TURBOMOLE \[15\] suite of programs using Gaussian atomic orbital basis sets of split valence [SV(P)]: [4s3p1d]/[2s] quality \[16\]. Test calculations with the larger TZVP basis set revealed only marginal deviations from the corresponding SV(P) results.

3 Results and discussion

3.1 Structural and cohesive properties

Representative geometries of $\text{Si}_x\text{Ge}_{47-x}:\text{H}_{60}$ nanoclusters are shown in figure 1 for various concentrations and substitutions. The bonding characteristics of the various structures can be easily visualized and described graphically in a synoptic way, through the bond-length distributions, which is presented if figure 2. All graphs in figure 2 correspond to nanocrystals with the silicon atoms concentrated in the inner core of the nanoparticle. As we can see the Si-Si distribution has a peak around 2.48 Å for the first shell of neighbors (connected to the central atom) and a second peak around the 2.37 Å for the rest of the silicon atoms. This second peak, corresponding to shorter bond-lengths by 0.1 Å, is more or less constant, with a tendency
to approach the bulk value of 2.36 Å for larger nanocrystals. This is also true for Ge-Ge bonds. Comparing figures 2(a) and 2(b) we can see that in both cases the bonds of the central atom with the first shell of neighbors are longer by 0.1 Å. We also observe in figs. 2(e) and 2(f) that there are no Ge-Ge bonds, although there is a significant amount of germanium atoms. Such bonding characteristics are found to be directly related to both the electronic and optical properties of the nanoparticles. As was explained earlier, with the same concentrations ($x$) more than one nanocrystals can be constructed. Moreover, since the Ge substitutions in the present work deal with spherical shells of neighbors rather than with individual atoms, we can distinguish two classes of nanocrystals with similar concentrations; Those with the Ge atoms in the inner core, and those with the Ge atoms in the outer shells ("surface"). The structural and cohesive characteristics are different in the two cases. As we can see in figure 3, we have two distinct curves depending on the exact location of the Ge layer relatively to the surface of the nanocrystals. It is clear from this plot that it is preferable to have the Ge atoms in the "inner" part of the nanocrystal. This tendency is directly related to the effect of surface hydrogen atoms and it can be quantified by considering the binding energy of the independent $Si-H (BE_{Si-H})$ and $Ge-H (BE_{Ge-H})$ bonds. This can be approximated by the formulae

$$BE_{Si-H} = \frac{BE_{SiH_4}}{4}, \quad BE_{Ge-H} = \frac{BE_{GeH_4}}{4}$$

($BE_{SiH_4}$ and $BE_{GeH_4}$ are the corresponding binding energies of the $SiH_4$ and $GeH_4$ molecules). In this way we can define the surface energy of the nanoparticle as

$$SE = N_{Si-H} \cdot BE_{Si-H} + N_{Ge-H} \cdot BE_{Ge-H}$$

(where $N_{Si-H}$ and $N_{Ge-H}$ are the number of Si-H and Ge-H bonds respectively). The dependence of surface energy on the composition of the nanocrystals and the position of Si and Ge atoms relative to the surface is shown in figure 3b. It becomes evident from this figure that the stability of the hydrogenated clusters is largely determined by their surface. Almost 63% of the total binding energy of the nanocrystals is attributed to the surface Si-H/Ge-H bonds. As a result, the large differences is surface energy between Ge(core) and Si(core) nanoparticles (fig.3b) is responsible for the shape and energetic ordering of the total binding energies shown in fig. 3a. However, it should be noted that without the hydrogen passivation of the dangling bonds, it would be natural (energetically favored) for the Ge atoms to segregate onto the surface in order to minimize the cost of the dangling bonds. Indeed, as was stated by Taran et al [19], for hydrogen-free SiGe nanoclusters, germanium tends to segregate onto the surface. The above conclusions, are in agreement with recent theoretical calculation (LDA) of Ramos et. al [21]. Moreover, the observed trends, are consistent with a series of experimental data (see ref.21-26 of Ramos et. al [21]).
3.2 Electronic and optical properties

In figure 4 we have plotted the total and the projected density of states (DOS and PDOS) for four typical nanocrystals. The DOS curves were generated from the eigenstates of the ground state calculations with a suitable gaussian broadening\cite{22}. The largest variation with the Ge concentration occurs in the valence band edges, while the conduction band edge is relatively less sensitive. From these diagrams it can be seen that the hydrogen contribution lies deep in the valence band (in the energy region between -10.5 eV to 9.0 eV) leaving Si and/or Ge to dominate the character of the band edges. For The cases of $Si_5Ge_{42} : H_{60}$ and $Si_{17}Ge_{30} : H_{60}$ nanoparticles (Si in the core and Ge in the surface) this hydrogen related peak appears to be slightly broadened. This is probably due to the looser binding of the hydrogen atoms with the surface Ge atoms (looser as compared with the corresponding Si-H binding). An interesting conclusion which can be drawn from the DOS diagrams is related to the character of the conduction band edges. It appears that when the core (Si or Ge) is adequately large (i.e. $\sim 30\%$ of the nanoparticle) then the conduction band edge exhibits a Si or Ge character respectively. This indicates that excitations of valence electrons to the Lowest Unoccupied Molecular Orbital (LUMO) or even LUMO+1, tend to partially confine the excited electron to the nanoparticle core. Calculations of the HOMO-LUMO gap of mixed $Si_xGe_y : H_z$ nanocrystals have also been recently performed by Yu et al. \cite{20}, specifically for nanocrystals with a total number of Si and Ge atoms of 71 ($x+y=71$). These calculations were based on density-functional theory (DFT) in the local-density approximation (LDA). The resulting HOMO-LUMO gaps range from 3.3 - 4.1 eV corresponding to the pure Ge and pure Si nanocrystals. In order to compare our calculation with the results of Yu et al.\cite{20} we performed similar DFT/B3LYP calculations for the pure $Si_{71}H_{84} Ge_{71}H_{84}$ nanoparticles. Our values of 4.0 eV for the pure Ge nanocrystal and 4.6 eV for the pure Si nanocrystal are in very good agreement with the values of Yu et al. if one considers the inherent tendency of LDA\cite{5} to underestimate the single particle HOMO-LUMO gap by approximately 0.6-0.7 eV. A striking difference in the work of Yu et al.\cite{20} is that instead of shells of atomic neighbors, used in the present work (strained nanocrystals), the Ge atoms in ref \cite{20} are distributed more homogeneously, and they are allowed to diffuse through the shells (complete relaxation of strain). As a result the gap dependence on Ge concentration appears to be practically linear. As a means to provide a more accurate and detailed account of the optical properties of these nanocrystals we employed the TDDFT/B3LYP combination in order to calculated their optical gap (i.e. lowest symmetry and spin allowed electronic excitation). The results are shown in table 1. The first comment that can be made by inspecting these values concerns the nature of the transitions. It is evident that for the nanoparticles in which the Ge atoms reside in the inner core, the lowest allowed transition is always between the HOMO- and LUMO orbitals. Moreover these transition appear to have relatively larger oscillator strengths. On the contrary, when there is a silicon inner core, the oscillator strengths are smaller, while the nature of the transitions becomes more complex.
For example, we can see a non negligible degeneracy concerning the fundamental optical gap together with an increase on the multireference character of the transitions. In figure 5 we show a graphic representation of the variation of the optical gap as a function of the number of Si atoms \( x \) contained in the nanocrystal. Both types of nanoparticles (Si(core) and Ge(core)) are included. We can clearly distinguish two sets of points (disjoint curves) which correspond to the two different types of clusters (Si(core) and Ge(core)). An analogous variation is also observed for the HOMO-LUMO gap (i.e. we have an upper and a lower curve). Surprisingly enough, the larger optical (and HOMO-LUMO) gaps correspond to germanium atoms lying in the surface region, which as we have seen in figure 3 is not energetically as stable as the opposite case. Usually, the most stable structures are the ones which exhibit the largest gap. However, this rule of thumb seems not to be applicable in this case. It is interesting to point out that for the case Ge(core) nanoparticles the gap decreases as the size of the core increases. This is a common quantum confinement behavior (see for example ref [1, 5, 7]).

Comparing the optical gap of Ge(core) \( Si_x Ge_y : H_z \) with the corresponding one of \( Ge_5 : H_{12} \) cluster we find that it is smaller by 2.47 eV (the optical gaps are 3.73 eV for \( Si_{42} Ge_5 : H_{60} \) and 6.2 eV for \( Si_5 : H_{12} \)). This large difference may originate from a less effective passivation of the Ge core by the Si passivants (less effective compared to Ge passivation by H atoms). To check this hypothesis we performed a simple line of argument which goes as follows. By simple calculations on \( SiH_4 \), \( GeH_4 \), and \( H_3 Si - GeH_3 \) molecules we can find the binding energies for the \( Ge - H \), and \( Si - Ge \) bonds. In particular, we find (as expected) that \( BE_{Ge-H} > BE_{Si-Ge} \). Next, we modify the \( Ge - H \) bond length in \( GeH_4 \) molecule in order to equate the resulting \( BE_{Ge-H}^* \) to \( BE_{Ge-Si} \). This is achieved when the \( Ge - H \) bond in \( GeH_4 \) molecule is elongated to \( \sim 2.1 \) Å. We used this new \( Ge^* - H \) bond distance for the passivation of the \( Ge_5 H_{12} \) cluster and calculated again its optical gap. The new value is now 3.7 eV and practically coincides with the 3.73 eV of the Ge(core) \( Si_{42} Ge_5 : H_{60} \) nanoparticle. This result, although it does not prove the aforementioned hypothesis, is highly suggestive of its validity.

The only other \( Si_x Ge_{47-x} : H_{60} \) nanoparticle with a Ge core fully capped (passivated) by Si atoms, suitable for extending the test of our hypothesis, is \( Si_{30} Ge_{17} : H_{60} \) (which should be compared to \( Ge_{17} H_{36} \)). However, the \( Ge - H \) bond elongation to \( \sim 2.1 \) Å for the \( Ge_{17} H_{36} \) cluster appears problematic since it brings the hydrogen passivants too close to each other inducing significant \( H - H \) interactions.

On the other hand the variation of the optical gap for the case of Si(core) \( Si_x Ge_{47-x} : H_{60} \) nanoparticles as a function of the Si core size (upper curve in fig.5) appears to be unexpected (as the Si core increases the gap also increases). This behavior suggest that the hypothesis of quantum confinement is not applicable here. In other words, the specific behavior can not be explained by considering that the Germanium atoms passivate the inner Si core. Surprisingly, an explanation can be obtained again by considering the Si atoms of the inner core to passivate “internally” the outer shell of Ge atoms (see fig.6). In order to test this we performed additional
calculation on modified versions of the $Si_1Ge_{46} : H_{60}$ and $Si_5Ge_{42} : H_{60}$ nanoparticles. In particular, we removed the inner Si atoms and we passivated the created internal Ge dangling bonds with hydrogen. The results indeed show an increase of the optical gap as we go from $H_1Ge_{46} : H_{60}$ to $H_5Ge_{42} : H_{60}$. At this point it should be noted that the “internal” hydrogen passivation is (again) more effective than the passivation by Si ($BE_{Ge-H} > BE_{Si-Ge}$). As a result these calculation could only reproduce the trend of gap increase and not the actual values. Unfortunately, the $Ge-H$ bond elongation to $\sim 2.1\text\AA$ which was shown to reproduce the results of fig. 5 (lower curve) in a quantitative manner can not be used since it leads to close proximity of adjacent hydrogens in the interior of the nanoparticle. The conclusions of the last two paragraphs are summarized in a synoptic way in figure 6. In both cases (fig6a and fig6b), the optical properties are mainly determined by Ge part of the nanoparticle while silicon seem to act mainly as a passivant.

4 Conclusions

We have shown that, indeed, the mixed SiGe nanocrystals have optical and electronic properties intermediate between those of pure Si and Ge nanocrystals. The large variety of optical and band gaps depends, not only on the size of the nanocrystals and the relative concentrations of Si and Ge, but also on the relative spatial distribution of the Ge atoms with respect to the surface of the nanocrystals. The stability of the structures is largely define by the hydrogen surface passivation. As a result, the most stable nanoparticle are those with the silicon atoms on the surface (mostly due to the larger binding energy of the Si-H bonds). The optical properties of Si(core) and Ge(core) nanoparticles are found to exhibit significant differences. For the Ge(core) nanocrystals the lowest spin and symmetry transition are always between the HOMO and LUMO orbitals, while for the Si(core) ones both HOMO-1 and LUMO+1 contributions are important (in this case the transitions exhibit a more pronounced multireference character). The variation of the optical gap as a function of the core size (Si or Ge) depends drastically on the nature of the core (Si or Ge). However, for both cases the optical gap variation can be rationalized by considering that the silicon atoms behave as simple passivants of the Ge cluster. These additional degrees of freedom with regard to the properties of mixed SiGe:H nanoparticles may be important in the future design of such (and similar) systems, allowing for possible electronic and optical gap engineering.

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References

[1] L. T. Canham, Appl. Phys. Lett., 1990, 57, 1046

[2] Wilcoxon J P, Provencio P P and Samara G A, Phys. Rev. B, 2001, 64 035417

[3] M. V. Wolkin, J. Jorne and P. M. Fauchet G, Allan and C. Delerue, Phys. Rev. Lett., 1999, 82, 197

[4] I. Vasiliev, J. R. Chelikowsky and R. M. Martin Phys. Rev. B, 2002, 65, 121302-1

[5] Garoufalis C S, Zdetsis A D and Grimme S, Phys. Rev. Lett., 2001, 87, 276402

[6] C. S. Garoufalis and A. D. Zdetsis, Phys. Chem. Chem. Phys., 2006, 8, 808813

[7] Weissker H Ch, Furthmuller J and Bechstedt F, Phys. Rev. B, 2002, 65 155328

[8] C S Garoufalis, M S Skaperda and A D Zdetsis, Journal of Physics: Conference Series, 2005, 10, 97

[9] Sundholm, D. Nano Letters, 2003, 36, 847-849

[10] Lehtonen O, Sundholm D., Phys. Rev. B, 2005, 72, 085424

[11] Moskalenko, A.S., Yassievich, I.N., Physics of the Solid State, 2004, 46, 1508-1519

[12] Chan T. L.; Ciobanu C. V.; Chuang F. C., Lu N.; Wang C. Z.; Ho K. M. Nano Lett., 2006, 6, 277

[13] Rubin Braunsten, Arnold R. Moore, and Frank Herman, Phys. Rev., 1958, 109, 695

[14] Robert W. Jansen and Otto F. Sankey, Phys. Rev., 1987, B 36, 6520 (1987)

[15] TURBOMOLE (Version 5.6), Universitat Karlsruhe, 2002

[16] Schafer A, Horn H and Ahlrichs R, J. Chem. Phys., 1992, 97, 2571

[17] M.E.Casida, in : Recent Advances in density function

[18] P. J. Stephens and F. J. Devlin and C. F. Chabalowski and M. J. Frisch, J. Phys. Chem., 1994, 98, 11623

[19] J. Tarus, M. Tantarimaki, K. Nordlund, Nucl. Instr. Meth. B, 2005, 228, 51-56

[20] Ming Yu, Jayanthi C S, Drabold D A and Wu S Y, Phys. Rev. B, 2003, 68 035404
[21] L. E. Ramos, J. Furthmüller, and F. Bechstedt Phys. Rev. B, 2005, 72, 045351

[22] N. M. O’Boyle, GaussSum 2.0, 2006. Available at [http://gaussum.sf.net](http://gaussum.sf.net)
Table 1: Lowest Spin and symmetry allowed electronic transitions

| nanoparticle | core excitation energy (eV) | Oscillator Strength | Dominant Contributions |
|--------------|------------------------------|--------------------|------------------------|
| Si$_{46}$Ge$_1$ : $H_{60}$ | Ge 3.80 | 0.086 | H→L (98%) |
| Si$_{42}$Ge$_5$ : $H_{60}$ | Ge 3.73 | 0.155 | H→L (98%) |
| Si$_{36}$Ge$_{17}$ : $H_{60}$ | Ge 3.69 | 0.261 | H→L (97%) |
| Si$_{18}$Ge$_{29}$ : $H_{60}$ | Ge 3.54 | 0.201 | H→L (98%) |
| Si$_{12}$Ge$_{35}$ : $H_{60}$ | Ge 3.52 | 0.177 | H→L (98%) |
| Si$_0$Ge$_{47}$ : $H_{60}$ | Ge 3.46 | 0.254 | H→L (98%) |
| Si$_1$Ge$_{46}$ : $H_{60}$ | Si 3.74 | 0.205 | H→L (97%) |
| Si$_5$Ge$_{42}$ : $H_{60}$ | Si 3.88 | 0.017 | H→L+1 (57%), H-1→ L (35%) |
| | | 3.92 | 0.110 | H-1→L (60%), H→L+1 (38%) |
| Si$_{17}$Ge$_{30}$ : $H_{60}$ | Si 3.91 | 0.067 | H-1→L (93%) |
| | | 4.0 | 0.036 | H→L+1 (81%), H-1→L+1 (17%) |
| | | 4.0 | 0.030 | H-1→L+1 (15%), H→L+1 (79%) |
| Si$_{29}$Ge$_{18}$ : $H_{60}$ | Si 3.97 | 0.079 | H→L (96%) |
| | | 4.03 | 0.083 | H→L+1 (97%) |
| Si$_{35}$Ge$_{12}$ : $H_{60}$ | Si 3.99 | 0.121 | H→L (88%), H→L+1 (8%) |
| Si$_{45}$Ge$_0$ : $H_{60}$ | Si 4.02 | 0.116 | H→L (71%), H→L+1 (26%) |
Fig. 1 Typical $Si_xGe_{47-x} : H_{60}$ nanocrystal (a) $Si_{42}Ge_5 : H_{60}$ (b)$Si_{30}Ge_{17} : H_{60}$, (c) $Si_{5}Ge_{42} : H_{60}$ (d) $Si_{17}Ge_{30} : H_{60}$). The Ge atoms are shown with green color, while Si atoms are blue.

Fig. 2 Bond distribution in $Si_xGe_{47-x} : H_{60}$ for x=0, 1, 5, 17, 29, 35, 47. The Ge-Ge, Si-Ge and Si-Si bond distributions are shown separately. The constant number of the hydrogen atoms (60) is not shown in the graphs.

Fig. 3 (a) Total binding energy as a function of the number of silicon atoms (b) Surface energy

Fig. 4 Projected and total Density density of states (PDOS and DOS) of 4 representative nanocrystals.

Fig. 5 The variation of the optical gap as a function of the number of silicon atoms, for the two categories (Ge(core) and Si(core)) of $Si_xGe_{47-x} ; H_{60}$ nanocrystals

Fig. 6 Schematic representation of (a) Ge)core nanoparticle, which behaves as a Ge nanoparticle passivated by silicon, and (b) Si(core) nanoparticle which behaves as a hollow Ge nanoparticle with surface hydrogen passivation and internal Si passivation.
Figure 1: Typical $Si_xGe_{47-x} : H_{60}$ nanocrystal (a) $Si_{42}Ge_5 : H_{60}$ (b)$Si_{30}Ge_{17} : H_{60}$, (c) $Si_5Ge_{42} : H_{60}$ (d) $Si_{17}Ge_{30} : H_{60}$). The Ge atoms are shown with green color, while Si atoms are blue.
Figure 2: Bond distribution in $Si_{x}Ge_{47-x}:H_{60}$ for $x=0, 1, 5, 17, 29, 35, 47$. The Ge-Ge, Si-Ge and Si-Si bond distributions are shown separately. The constant number of the hydrogen atoms (60) is not shown in the graphs.
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