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Novel metal-encapsulated caged clusters of silicon and germanium

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Abstract. We report the recent findings of metal (M) encapsulated clusters of silicon from computer experiments based on *ab initio* total energy calculations and a cage shrinkage and atom removal approach. Our results show that using a guest atom, it is possible to wrap silicon in fullerenelike (f) structures, as sp^2 bonding is not favorable to produce empty cages unlike for carbon. Transition M atoms have a strong bonding with the silicon cage that are responsible for the compact structures. The size and structure of the cage change from 14 to 20 Si atoms depending upon the size and valence of the M atom. Fewer Si atoms lead to relatively open structures. We find cubic, f, Frank-Kasper (FK) polyheral type, decahedral, icosahedral and hexagonal structures for M@Si$_n$ with $n = 12-16$ and several different M atoms. The magic behavior of 15 and 16 atom Si cages is in agreement with experiments. The FK polyhedral cluster, M@Si$_{16}$ has an exceptionally large density functional gap of about 2.35 eV calculated within the generalized gradient approximation. It is likely to give rise to visible luminescence in these clusters. The cluster-cluster interaction is weak that makes such clusters attractive for cluster assembled materials. Further studies to stabilize Si$_{20}$ cage with M = Zr, Ba, Sr, and Pb show that in all cases there is a distortion of the f cage. Similar studies on M encapsulated germanium clusters show FK polyhedral and decahedral isomers to be more favorable. Also perfect icosahedral M@Ge$_{12}$ and M@Sn$_{12}$ clusters have been obtained with large gaps by doping with divalent M atoms. Recent results of the H interaction with these clusters, hydrogenated silicon fullerenes as well as assemblies of clusters such as nanowires and nanotubes are briefly presented.

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1 Introduction

In recent years great experimental and theoretical efforts [1,2] have been made to understand the properties of clusters as well as other nanostructures of silicon in order to find suitable components for future miniature devices. The finding of visible luminescence in porous silicon [3] added further interest in using silicon for optoelectronic devices, tunable lasers, tagging and displays. Bulk silicon is a poor emitter of light due to the indirect band gap. Therefore, new structures of silicon particularly in nanoforms are interesting as their properties could be very different from bulk and it could be possible to integrate photonics with electronics in future miniature devices [4]. Recently a metal (M) doped silicon cluster, Si$_{12}$M (M = W, Mo, and Cr) was reported [5] in which the M atom lies at the center of a hexagonal prism. Extensive computer experiments on M encapsulated silicon [6–13] and germanium [11,12,14] clusters led to the findings of novel fullerenelike (f), cubic (c), Frank-Kasper (FK) polyhedral, icosahedral (i) as well as other forms of clusters. These have higher symmetries as well as higher stabilities as compared to elemental Si, Ge, and Sn clusters [1,15]. There is a preference for a certain number of Si, Ge or Sn atoms around a particular M atom. This makes us believe that such clusters can be produced almost exclusively in large quantities by appropriately choosing the M atom. An evidence for this was also found in the experiments of Beck [16] more than a decade ago who obtained large abundances of Si$_{15}$M and Si$_{16}$M, M = Cr, Mo, and W clusters and little abundance of other M doped clusters. These results are markedly different from those on elemental Si and Ge clusters as in the range of 12−16 atoms, there is no particular large abundance of these clusters [2] as well as the results of reference [5]. Earlier Jackson and Nellermoe [17] attempted to stabilize a dodecahedral Si$_{20}$ cage with a Zr atom at the center and obtained a large gain in energy. However, studies by Kumar and Kawazoe [6] showed that 20 atoms around a single Zr atom were too many and that

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there were distortions in the cage such that some atoms came out leading to the shrinkage of the cage. This led to the finding [6] of the Zr@Si_{16} fullerene using an atom removal and cage shrinkage approach as well as the FK polyhedral isomer of Ti@Si_{16}. Some of these M encapsulated clusters have even larger highest occupied-lowest unoccupied molecular orbital (HOMO-LUMO) gaps than known for any of the elemental silicon or Ge clusters. Icosahedral Ge and Sn clusters [11,12] as well as hydrogenated silicon fullerenes [13] have also been predicted with large gaps. These results are interesting for optoelectronic devices and there is potential for self-assembly of such clusters that is expected to be important for the miniature devices. Here we briefly review these developments.

2 Computational approach

The calculations were done using an *ab initio* ultrasoft pseudopotential plane wave method [18] and spin polarized generalized gradient approximation (GGA) [19] for the exchange-correlation energy. The clusters were placed in a simple cubic supercell with periodic boundary conditions. The Brillouin zone integrations were performed using the Γ point. Besides the cage shrinkage method, a few selected structures were also optimized for each cluster using the conjugate gradient method. The relaxed structures were found to have zero spin in most cases. Studies of the dynamic stability, ionization potentials (IPs) and electron affinities (EAs) have also been performed using the Gaussian method [20] and hybrid functionals.

3 The cage shrinkage approach

This approach was discussed in reference [6]. It was an effort to stabilize the Si_{20} fullerene cage with encapsulation of M atom and to find the optimal number of atoms around an M atom. Zr atom has large radius among the transition M atoms. However, optimization of this structure led to the shrinkage of the cage such that one Si atom sticks out. This atom was removed and the remaining structure, reoptimized. This procedure was repeated until the structure became closed packed so that no more atom could be removed. This led to the finding of the Zr@Si_{16} fullerene. Similar structures were also obtained for Ti and Hf. However, encapsulation of smaller atoms such as Cr, Mo, and W led to 15 Si atom cages while for Fe, Ru and Os, 14 Si atom cages were found to be optimal. Besides these clusters, a large number of calculations were performed with various M atoms on other possible cages such as 15 Si atom cages with Ti, Hf and Zr and 16 Si atoms around Cr, Mo, and W to obtain other structures with high stability.

4 Results

The close packed symmetric f cage of 16 Si atoms (Fig. 1a) has eight pentagonal (not regular) and two square faces as compared to 12 regular pentagonal faces in the dodecahedral C_{20} fullerene. Each Si atom on the cage is tricoordinated similar to the carbon fullerenes. Also there are double bonds between the square and the ring atoms so that each Si atom has two single bonds and a double bond [9]. The Si–Si bond lengths (2.257 Å for the double bonds and 2.283 and 2.34 Å for the single bonds in f-Ti@Si_{16}, obtained by using all electron 6-311+g* basis and B3PW91 hybrid functional in the Gaussian method)

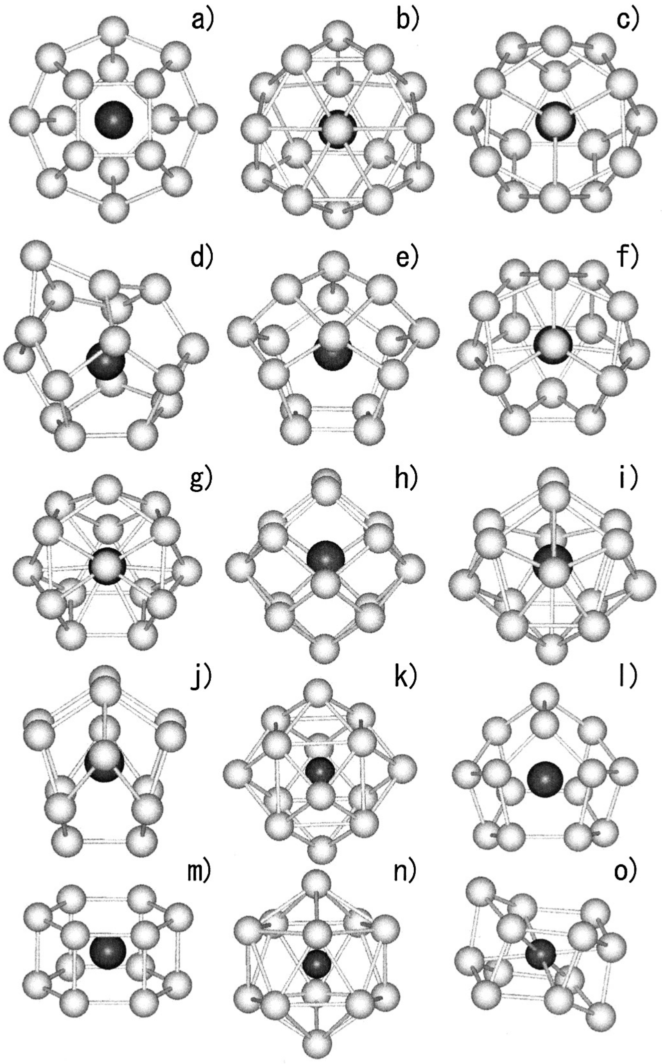

Fig. 1. M encapsulated clusters of silicon. (a) M@Si_{16} fullerene (M = Ti, Zr, Hf), (b) FK–M@Si_{16} (M = Ti, Hf), (c) another FK like isomer of M@Si_{16} that is a tetracapped hexagonal antiprism, (d) lowest energy structure of M@Si_{16}, M = Cr, Mo, and W, (e) f isomer of M@Si_{15}, M = Cr, Mo, and W, (f) an FK like isomer of M@Si_{15} obtained from a cubic structure, (g) another FK type isomer of M@Si_{15} in which position of one Si atom is different, (h) a c isomer of M@Si_{15}, M = Ti, Zr, Hf, Ru, and Os, (i) a decahedral isomer of M@Si_{15}, (j) f-M@Si_{14} for Fe, Ru, and Os, (k) bcc isomer of M@Si_{14}, (l) f-Os@Si_{14}, (m) h-M@Si_{12}, (n) i-M@Si_{12} and (o) Be@Si_{12}. M (dark atom) is inside the cage. (b), (c), (g–k), (m), and (n) are also the structures for some of the M encapsulated Ge clusters.

Table 1. BEs (eV/atom), EEs (eV), and HOMO-LUMO gaps (eV) of the f and FK isomers of M@Si_{16} clusters with selected M atoms. FK1 represents the isomer shown in Figure 1c.

Cluster	BE	EE	Gap
FK–Ti@Si_{16}	4.135	11.269	2.358
FK1–Ti@Si_{16}	4.134	11.509	2.247
f-Ti@Si_{16}	4.089	12.733	1.495
f-Zr@Si_{16}	4.162	13.965	1.580
FK1–Zr@Si_{16}	4.145	12.057	2.331
FK–Zr@Si_{16}	4.141	11.814	2.348
f-Hf@Si_{16}	4.175	14.176	1.576
FK1–Hf@Si_{16}	4.171	12.399	2.352
FK–Hf@Si_{16}	4.167	12.160	2.488

are slightly smaller than the value in bulk Si and the bonding is covalent. Similar behavior is expected for Zr and Hf as the size of the cage is nearly the same. Also the size of f-M@Si_{16} is close to that of C_{60}, but the former is lighter. Thus, *one M atom changes the structure and properties of silicon clusters all together. It is due to the large gain in energy by M doping so that silicon atoms transform themselves in a way that optimizes the M–Si interactions, making these M doped clusters to be the most stable in the family of Si clusters known so far.* The HOMO-LUMO gaps are also large (Tab. 1) and this should make such clusters very abundant and possibly useful for optoelectronic and other applications. The energy gain in adding one Si atom on f-Zr@Si_{16} cage is only 3.211 eV within GGA and the binding energy (BE) of the $Si_{17}Zr$ structure (one Si atom capping Zr@Si_{16} on a bridge site) is 4.109 eV/atom. This is lower than the value of 4.162 eV/atom for the f-Zr@Si_{16} cage in GGA. Therefore, f-Zr@Si_{16} shows magic behavior. Similar results were obtained for the isoelectronic Hf@Si_{16}. However, encapsulation of Ti in the f cage is not the closest packed due to its smaller size. The Si cage is also not able to compress further enough to bind optimally. Therefore, an FK polyhedron (Fig. 1b) was found to be 0.781 eV lower in energy. It has tetrahedral symmetry. There are four interconnected capped hexagons of Si. The Ti–Si bond lengths in this structure are slightly reduced as compared to the f structure and it enhances the interaction of Ti with the Si cage. The higher coordination of Si, however, leads to an elongation of the Si-Si bonds (2.37−2.66 Å in GGA). There is a large charge transfer of about 3 electrons from Ti to the Si cage [9] in contrast to a very small charge transfer in the case of the f isomer. Also this isomer has an *exceptionally* large GGA gap of 2.358 eV that lies in the visible range. Calculations [9] using the B3PW91 hybrid functional gave the gap to be 3.12 eV and therefore, there could be luminescence in the blue region. Another FK like isomer (Fig. 1c) is nearly degenerate but has 2.151 eV GGA HOMO-LUMO gap. This isomer was also found [14] for M@Ge_{16} cluster. Similar calculations for the isoelectronic M = Hf and Zr showed FK–Hf@Si_{16} to be nearly degenerate with the f isomer, but its HOMO-LUMO gap was slightly larger (2.488 eV) than for M = Ti. Another isomer of this structure shown in Figure 1c lies about 0.1 eV lower in energy and has 2.352 eV HOMO-LUMO gap. However, FK–Zr@Si_{16} lies 0.355 eV higher in energy than the f isomer and has the HOMO-LUMO GGA gap of 2.448 eV. The other FK like isomer lies 0.283 eV higher in energy than the f isomer and the gap is 2.331 eV. These results suggested that both Ti and Hf encapsulated Si clusters with FK polyhedron structure should be strongly abundant and that *Hf doping is unique to produce two different stable degenerate isomers with different bonding natures and significantly different band gaps.* In this conference, large abundances of $Si_{16}Ti$ and $Si_{15}Ti$ have been reported [21] while the intensities of other Ti doped clusters were found to be significantly lower. $Si_{15}Ti$ cluster is discussed below. These experimental results support our theoretical predictions, though the structure still needs to be verified by experiments. Interaction between two f clusters has been found [6] to be relatively weak with 1.345 eV BE in GGA and a significant reduction in the band gap. However, for FK isomers, this interaction is very weak (0.048 eV) and the gap remains large, making these species attractive for self-assembly. Studies with several other M atoms showed the FK structure to be stable but generally there were other structures that had lower energies.

Efforts were also made [10] to stabilize Si_{20} in the C_{20} fullerene structure with bigger M atoms such as Ba, Pb, Sr, and Ca. However, in all cases there were distortions in the cage. The distortions were minimum for Ba. It is to be noted that Ba doped clathrate compounds of silicon have 20 and 24 atom silicon cages. However, these cages are interlinked. The embedding energies (EEs), defined as the difference in the energy of the Si_n cage with the respective atomic positions of M@Si_n plus the isolated M atom and the M@Si_n cluster, of these M atoms in the cage of silicon atoms are much smaller (less than 2.5 eV) than the BE of elemental silicon clusters. However, the EEs of transition metals are very large (see Tabs. 1 and 2). Therefore, transition M atoms are important for the stability of M encapsulated clusters.

Encapsulation of smaller M atoms such as Cr, Mo, and W was found [7] to lead to the further shrinkage of the f-M@Si_{16} structure such that a Si atom caps M@Si_{15} cluster as shown in Figure 1d. Several other structures such as the one shown in Figure 1c, slightly distorted FK and capped structure of the M@Si_{15} isomer shown in Figure 1g lie about 1 eV higher in energy. Removal of the capping atom in Figure 1d and subsequent reoptimization led to a stable f-M@Si_{15} cage (Fig. 1e). For Cr, the HOMO-LUMO gap is relatively small (0.808 eV) and the BE is 3.883 eV/atom. The EE (8.936 eV) of Cr in the cage is significantly lower than ≈14 eV obtained for Zr and Hf (see Tab. 1) due to the complete quenching of the magnetic moment of the Cr atom. Another 15-atom Si cage was obtained from a body centered c structure by placing one more Si atom on a face of the cube with M at the center. Optimization with Cr led to the structure shown in Figure 1f. It lies 1.071 eV lower in energy than the f isomer and has a large (1.537 eV) HOMO-LUMO gap suggesting its strong stability. This structure is completely different from the

Table 2. BEs (eV/atom), EEs (eV), HOMO-LUMO gaps (eV) of low lying isomers of selected M@Si$_n$ (n = 14–16) clusters. d is the decahedral isomer; the c-M@Si$_{15}$ structure for M = Cr, Mo, and W are similar to the FK1 structure.

Cluster	BE	EE	Gap
f-Si$_{16}$Cr	3.934	8.817	1.244
f-Si$_{16}$Mo	4.132	12.091	1.195
f-Si$_{16}$W	4.246	14.053	1.208
f-si$_{16}$Fe	4.010	9.426	1.294
f-Si$_{16}$Ru	4.188	12.445	1.230
f-Si$_{16}$Os	4.252	13.551	1.246
c-Ti@Si$_{15}$	4.076	10.454	1.237
d-Ti@Si$_{15}$	4.077	11.102	1.577
c-Zr@Si$_{15}$	4.087	12.998	1.287
d-Zr@Si$_{15}$	4.083	13.491	1.551
c-Hf@Si$_{15}$	4.116	14.507	1.262
d-Hf@Si$_{15}$	4.113	15.002	1.572
c-Cr@Si$_{15}$	3.950	8.936	1.537
FK1–Cr@Si$_{15}$	3.950	8.937	1.329
c-Mo@Si$_{15}$	4.125	11.726	1.659
FK1–Mo@Si$_{15}$	4.127	11.867	1.488
c-W@Si$_{15}$	4.250	13.700	1.747
FK1–W@Si$_{15}$	4.252	13.702	1.561
FK1–Ru@Si$_{15}$	4.195	12.841	1.459
FK1–Os@Si$_{15}$	4.261	13.831	1.567
c-Fe@Si$_{14}$	4.018	8.404	1.162
c-Ru@Si$_{14}$	4.194	11.136	1.409
f-Ru@Si$_{14}$	4.184	12.939	1.488
c-Os@Si$_{14}$	4.259	12.111	1.453
f-Os@Si$_{14}$	4.258	14.024	1.576

f isomer. The mean coordination of Si atoms on this cage is 4. The higher coordination of Si atoms in this structure leads to slightly elongated Si-Si bonds (2.36–2.57 Å). The M–Si bond is, however, slightly shorter (2.54–2.83 Å) than in the f isomer with the majority of bonds having the lower value that leads to a better M–Si interactions in this structure. There is another isomer, FK1, shown in Figure 1g which is similar to Figure 1f but one Si atom is placed differently. It is nearly degenerate with the isomer in Figure 1f and has a slightly smaller gap. Similar calculations on M@Si$_{16}$ with M = Mo and W showed the capped caged structure of Figure 1d to be the lowest in energy as for Cr. Also optimizations of M@Si$_{15}$ with M = Mo and W showed an increase in the gap to 1.659 and 1.747 eV in the c derived structure, respectively. The bonding properties of these isoelectronic clusters are similar. The isomer (Fig. 1g) is also nearly degenerate (0.028 eV lower in energy for Mo with 1.488 eV gap). The magic nature of this FK type isomer is clearly seen from the fact that capping of one Si atom on this leads to an energy gain of only about 2.72 eV. Further support was obtained from the second order difference in energy [7]. The different growth modes of 15 and 16 Si atom clusters were proposed to lead to their simultaneous large abundances as observed [16]. Magic nature of 15 and 16 silicon atom clusters with Cr has also been reported in this conference by Bergeron and Castleman Jr [22] and is in agreement with our calculations. Further calculations [7] on M = Ti, Zr, Hf, Ru, and Os for the 15-atom silicon cage gave a different c-M@Si$_{15}$ structure (Fig. 1h) with large BEs and about 1.2 eV HOMO-LUMO gaps. There is also a tricapped decahedral isomer (Fig. 1i) of Ti@Si$_{15}$ which is obtained from the optimization of the FK like isomer and is only 0.019 eV lower in energy (nearly degenerate) and has 1.578 eV gap. In fact this isomer can be obtained from the c isomer by a slight change of the atoms. Both of these isomers could be abundant in experiments. The stability of the c as well as decahedral type structures of Ti@Si$_{15}$ with large HOMO-LUMO gaps is in agreement with the large abundance of the 15 Si atom cluster reported in this conference [21].

Optimizations of the f-M@Si$_{16}$ cage with still smaller M atoms, Fe, Ru, and Os led to the further shrinkage of the cage such that two Si atoms capped a M@Si$_{14}$ cage [6]. Removal of the two capping atoms and subsequent optimizations led to a f-M@Si$_{14}$ cage (Fig. 1j) which can also be called a capped decahedron. However, a body centered c structure (Fig. 1k) is lower in energy and has larger HOMO-LUMO gap. For Ru and Os, both the f and the c isomers are nearly degenerate. The magnetic moment of the M atom is again quenched completely. Another f structure with Os (Fig. 1l) has all the silicon atoms tricoordinated with other Si atoms. It is slightly higher in energy than the structures shown in Figure 1j as well as Figure 1k. FK and c structures of M@Si$_{15}$ have also been obtained for M = Ru and Os with large gaps. For Fe the gap is significantly smaller. These calculations suggested that 14- and 15-atom Si cages are optimal for M = Fe, Ru, and Os. Capped decahedral 14 Si atom cages have also been obtained for Cr, Mo, and W with large gaps. Calculations with M = Ni, Pd, and Pt gave c structure to be of lowest energy, but there is a magnetic moment of 2 μ_B and the HOMO-LUMO gap is small (<0.5 eV). Therefore, these clusters are unlikely to be abundant.

The valence states of the M atom lie near the HOMO of the Si cage and interact covalently with the latter and the nearby states. This leads to the lowering of the energy of the Si cage states in a range of about 2 eV below the HOMO but the deeper states are only weakly perturbed. In Figure 2 we show the electronic states of the f-Zr@Si$_{16}$ and FK-Ti@Si$_{16}$ clusters. The higher symmetry of the FK cluster makes the states more degenerate. The peak positions in a photoemission experiment may look similar but the FK isomer will have more sharp features as compared to the f isomer. A detailed report of the atomic and electronic structures will be presented elsewhere [23].

Similar studies [14] were carried out on M encapsulated germanium clusters. In this case the f-M@Ge$_{16}$ structure transforms into the FK polyhedron which again has a large HOMO-LUMO gap of about 2 eV similar to the Si based clusters. The 14- and 15-atom clusters have a tendency to prefer capped decahedral structures. It is due to the weaker covalent character of Ge. The lowest energy

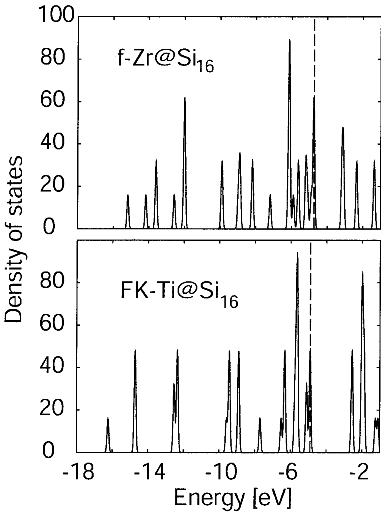

Fig. 2. The Gaussian broadened (half width 0.05 eV) Kohn-Sham energy spectra of f-Zr@Si_{16} and FK-Ti@Si_{16} clusters. Broken line shows the Fermi energy.

structures of M = Zr, Hf and Ti with 16 Ge atoms is the same as shown in Figures 1b and 1c. A low lying isomer with 15 Ge atoms is shown in Figure 1f (also Fig. 1g). The 14 Ge atom c cluster is similar to that of silicon. A few more decahedral isomers with 14 and 15 Ge atoms were obtained [14] by different cappings. Again there is a large gain in the BE as compared to the elemental Ge clusters.

Further studies have been carried out [13] on 12 atom cages with M encapsulation. For $Si_{12}M$, M = Cr, Mo, and W, a hexagonal prism (Fig. 1m) has the lowest energy as also obtained earlier [5]. The BE and gaps are 3.84, 4.02, and 4.18 eV and 0.85, 0.90, and 1.34 eV, respectively. These gaps are lower than the values obtained for the 15- and 16-atom Si cages except for $Si_{12}W$. Also the BE of the 15- and 16-atom cages are higher than the corresponding values for the $Si_{12}M$ clusters. Therefore, 15- and 16-atom cages are more stable than $Si_{12}M$ in agreement with the finding of the laser evaporation experiments [16]. Similar results have been obtained for Ge. As the sizes of these M atoms are significantly larger than that of a Si atom, these can not form close packed structures with 12 Si atoms. This is, however, possible with smaller M atoms as it has been shown [11,12] with divalent M atom doping of Ge and Sn icosahedral cages (Fig. 1n) that are lowest in energy. Doping of Be in silicon, however, leads to a chair shape structure (Fig. 1o) to be lower in energy as compared to the icosahedral structure. Also interestingly Mn doping leads to magnetic isomers [12]. For Ge and Sn these have 5 μ_B magnetic moment and icosahedral structure while for Si, a hexagonal prism has the lowest energy with 1 μ_B magnetic moment and 1.6 eV HOMO-LUMO gap. This magnetic cluster is, therefore, interesting for cluster assembly. Further studies [13] with two W, Mo or Cr atoms have been shown to give rise to a double hexagonal prism structure of $Si_{18}M_2$. These are found to be inert in experiments [5] similar to $Si_{12}M$. The stability of these clusters is due to strong dimer formation tendency of these M atoms. Interaction of H with these clusters shows weak bonding [13] in agreement with the absence of hydrogenated species of $Si_{12}M$ and $Si_{18}M_2$. However, there is a weakening of the M–Si interactions with H adsorption as some charge is removed from the region of the M–Si bonds to the H–Si bonds. The cage size also becomes slightly bigger and the M atom tend to move towards the wall of the cage to optimize interaction with the Si atoms. This also leads to some distortions in the cage. Removal of the M atom further led to the findings of empty center symmetric hydrogenated fullerenes [13] of $Si_{12}H_{12}$, $Si_{16}H_{16}$, and $Si_{20}H_{20}$. These have large gaps and could exhibit photo-luminescence. An independent experimental study [24] on silicon clusters with 10−20 atoms showed preference for equiatomic concentration of hydrogen at around 400 C. These were speculated to be caged clusters and a cage structure of $Si_{14}H_{14}$ with f structure of Si_{14} as shown in Figure 1l was found to be lower in energy than a heptamer prism isomer, supporting our predictions. As the size of these cages is large enough, we inserted a Si atom in the empty space. However, interaction of these hydrogenated fullerenes with a Si atom is weak and this supports the magic nature as well as the stability of these empty cages.

Assemblies of clusters have also been studied. It is found [25] that a nanowire of Zr@Si_{16} fullerenes is semiconducting while a nanotube of silicon has been stabilized [26] by assembling $Si_{12}Be$ clusters which transform from chair structure to hexagonal form when assembled. These nanotubes are metallic. It is important to note that elemental silicon wires of such a size tend to distort and agglomerate. These studies have, therefore, opened up new possibilities of developing novel structures of silicon and germanium that could have important implications for the future nanodevices.

5 Summary

In summary, we have presented a brief review of the recent developments of M atom encapsulated silicon and germanium caged clusters from computer experiments based on an *ab initio* method. These form 12-, 14-, 15-, and 16-atom cages with M at the center, depending upon the size of the M atom. The shape and the HOMO-LUMO gap depend upon M. Most notable among these are the fullerenelike, cubic, Frank-Kasper polyhedral, hexagonal and icosahedral structures. Interaction between the fullerenelike cages is relatively weak while interaction between the Frank-Kasper polyhedral clusters is van der Waals type. These results show that one M atom changes the properties of elemental Si and Ge clusters drastically. It has opened up new avenues for the development of elements of future nanodevices. The strong stability of these clusters results from the strong M–Si interactions that also fix the size of the cage. The size of the M atom plays an important role as we showed for Ti and Zr doping. The electronic structure of the cage is also important as two M atoms with nearly the same size but different valency will in general have different structures, or have magnetic solution.

In the latter case, such structures would act as superatoms whose valence can be changed by changing the M atom such as in $Si_{12}M$ with M = Cr and Mn. The electron and hole doping in these clusters can be either by changing the M atom or a silicon atom. Some of the predictions have been supported by recent experiments that were presented in this conference. We hope that these clusters could be produced in large quantities by tuning the experimental conditions as the size selectivity in these clusters is rather strong. The HOMO-LUMO gaps in these clusters are large and this is attractive for opto-electronic applications. It is likely that similar novel structures could occur in other clusters using guest atom(s) and it would be interesting to explore these. This is currently under investigation.

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