Stable cubic metal-semiconductor alloy clusters: X_4Y_4 (X=Cu,Ag,Au,Ti; Y=C,Si)

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Ab initio calculations have been performed on the electronic structures for some semiconductor-metal alloy clusters Au_nSi_m (n,m=1–4), upon which very stable cubiclike clusters X_4Y_4 (X=Cu,Ag,Au,Ti; Y=C,Si) have been found. The calculations show that relativistic effect as well as the ionic bonds may together play the key role in the cubic structures. The large highest occupied lowest unoccupied molecular orbital gaps (0.8–2.24 eV) make them attractive for optoelectronic applications and the perfect cubic structures make some of them desirable for cluster-assembled materials, such as one-dimensional nanotubes.

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I. INTRODUCTION

As silicon is the most important semiconducting element in microelectronics industry, Si clusters have been extensively investigated both experimentally[1] and theoretically[2,3] for their potential applications as building blocks to build up well-controlled nanostructures. Since the discovery of the very stable cagelike C_{60} fullerenes,[4] searching for free standing carbon and carbon-free clusters such as C_n and Si_n with cagelike structures has attracted much attention during the last decade. Unfortunately, the cagelike structures for pure Si clusters have never been found due to their unfavorable sp^2 hybridization. However, by doping transition metal atoms, hexagonal prism $W@Si_{12}$,[5] fullerenelike $M@Si_{16}$, cubiclike $M@Si_{14}$ and Frank-Kasper tetrahedral $Ti@Si_{16}$ and adodecahedral $Zr@Si_{20}$ clusters[6] have been found. All these metal-encapsulated silicon clusters are stabilized by the interaction of the center doped metal atoms with the silicon cages. However, at present, the $M@Si_n$ assembled nanomaterials are rarely constructed.[7]

Gold is a well known typical metal and shows novel properties in atomic scale. Though the d electrons may take part in the bonding and dominate the physical and chemical properties for Au_n clusters, the jellium model still successfully predicated that Au_n (n=2,8,18,20,34) may be magic clusters, which has been confirmed experimentally by mass spectrometry analysis.[8,9] Studies show that due to relativistic effect,[10] which enhanced stronger sd hybridization and dd interaction in gold, up to 13 atoms, small anionic Au_n clusters favor planar structures.[11] And recent research predicates that the relativistic effect continues to play a role in the structures and bonding of large Au clusters. The configuration of Au_{20} (Ref. 12) was found to be a tetrahedral structure with all of the atoms located on the surfaces, which can be considered four triangle Au_{10} planes merged together making a quasi-two-dimensional structure. The latest studies show that Au_n (n=32,33,34,35) clusters can unexpectedly have cagelike structures.[13] The above results proposed a great challenge for the studies of silicon structures. Can we stabilize one class of silicon cage, such as cube, by appealing to gold?

As cubic structures are easily found in human life we expect that cubic structures may exist and even be universal in the microscope world. As the smallest special cage, cubic units may be even more suitable to build up cluster-assembled materials. In this paper, we report that Si_4 and C_4 clusters indeed can be stabilized to almost perfect cubic structure by alloying with four Au atoms. Other stable cubic metal-semiconductor alloy clusters X_4Y_4 (X=Cu,Ag,Au,Ti; Y=C,Si) with large highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps are also studied.

II. CALCULATION DETAILS

The calculations are based on the density functional theory (DFT) with spin-polarized generalized gradient approximation (GGA)[14] implemented in the VASP code.[15] The interactions of the valence electrons with the ionic cores are described by projected augmented wave (PAW)[16] method, with a scalar relativistic effect included. The wave functions are expanded in plane waves with an energy cutoff of ~400 eV. We use a simple cubic cell of 15 Å edge length with a periodic boundary condition, and the Γ point approximation for Brillouin zone sampling. The ground states of clusters are obtained by comparing the energies of many random configurations followed with optimizations by conjugated gradient (CG)[17] and simulated annealing methods. In order to explicitly consider the relativistic effect for Au atoms, we have also used the ADF code[18] to do ZORA (zero order regular approximation) scalar relativistic calculations for solid support.

III. RESULTS AND DISCUSSION

First of all, we have studied the geometrical and electronic structures for Au_nSi_m (n,m=1–4) clusters. The ground state structures, the binding energies defined with the form of E_b=−[$E(X_nY_m)$−$nE(X)$−$mE(Y)$], the HOMO-LUMO gaps (E_{gap}) and the bond lengths have been presented in Fig. 1. The calculated average Au-Si bond lengths in-
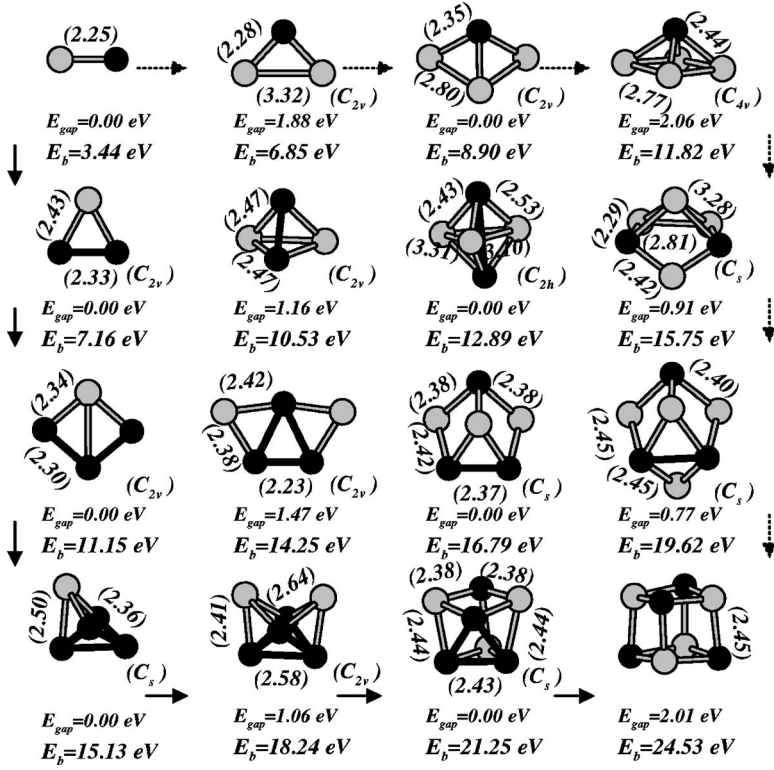
FIG. 1. The geometrical structures for Au_nSi_m $(n,m=1-4)$ clusters. The HOMO-LUMO gaps (E_{gap}) and the main bond lengths are marked for all clusters. Two possible growth modes along the solid line and the dotted line are also shown, respectively. Black spheres: Si atoms, gray spheres: Au atoms.

crease from 2.25 Å for AuSi dimer to 2.45 Å for Au_4Si_4 cluster. For every cluster comprising an odd number of gold atoms, we find 1 μ_B magnetic moment. For those clusters with an even number of gold atoms, large HOMO-LUMO gaps ranging from 0.77 to 2.06 eV have been obtained. These results indicate that the electronic structures of silicon clusters may be tunable by doping gold atoms with different stoichiometries. As shown in Fig. 1, Au_4Si, Au_2Si_4, and Au_4Si_4 clusters have 2.06, 1.06 and 2.01 eV HOMO-LUMO gaps, respectively, indicating their high stabilities, which has been confirmed, in the case of Au_4Si, by experimental work.[19] For the noble metal Au(Ag, Cu), electronic configuration s^1d^{10} for the PAW potential has been used in VASP calculation. If we regard that per gold (silicon) contributes one (four) valent electron(s), Au_4Si, Au_2Si_4, and Au_4Si_4 clusters have 8, 18, and 20 electrons, respectively, which happens to coincide with the magic numbers predicated by the jellium model for gold clusters. However, it seems that Au_2Si, Au_2Si_2, and Au_2Si_3 clusters with large HOMO-LUMO gaps carrying 6, 10, and 14 valence electrons, respectively, failed to be predicated as stable clusters by the jellium model.

It is interesting to find that the Au_4Si_4 cluster prefers cubic structure with about 24.53 eV binding energy and a 2.01 eV HOMO-LUMO gap, indicating its high inertness. As presented in Fig. 1 and Table I, the bond length of Si-Au is 2.45 Å. The four Au atoms and the four Si atoms are just alternatively located on the eight apexes of one cube with little distortion. From Fig. 1, one can notice that there may be many growth paths from the reactive linear AuSi dimer to the high stable Au_4Si_4 cluster, however, we assume that the two most possible growth paths may be along the dotted-line

path and the solid-line path, respectively. In fact, along the dotted-line path, the four Au atoms will first be grown up one by one and then the four Si atoms have been grown step by step on the Au_4 core. On the contrary, for the solid-line path the four Si atoms will be first grown up. It is also worth mentioning that the geometrical structures for both Si_3Au_4 and Au_3Si_4 clusters are just like one cubic removed one apex. If one Si(Au) atom is added to the removed apex of $Si_3Au_4(Au_3Si_4)$ followed with one simple optimization, then

TABLE I. Calculated properties of X_4Y_4 (X=Cu,Ag,Au,Ti; Y=C,Si) clusters. In the brackets, C and T_d represent cubic and tetrahedral configurations, respectively. $\bar{R}$(Å) includes average bond lengths of X-X, X-Y and Y-Y, respectively; E_{gap}(eV) is a HOMO-LUMO gap; E_b(eV) is the binding energy defined with $E_b=-[E(X_4Y_4)-4E(X)-4E(Y)]$; X-C indicates the average charge flow from per X atom to per Y atom in X_4Y_4 clusters, obtained from Voronoi deformation density (VDD)[20] analysis.

Clusters	$\bar{R}$(Å)			E_b(eV)	E_{gap}(eV)	X-C(e)
	X-X	X-Y	Y-Y			
Cu_4C_4 (C)	2.69	1.91	2.71	26.74	2.10	0.35
Ag_4C_4 (C)	3.03	2.14	3.03	19.07	1.67	0.34
Au_4C_4 (C)	2.96	2.15	3.10	22.81	1.83	0.30
Cu_4Si_4 (T_d)	3.62	2.30	2.77	24.31	1.93	0.12
Ag_4Si_4 (T_d)	4.18	2.55	2.70	20.27	1.42	0.17
Au_4Si_4 (C)	3.30	2.45	3.61	24.53	2.01	0.07
Ti_4C_4 (C)	2.77	1.97	2.78	45.73	2.24	0.55
Ti_4Si_4 (C)	3.02	2.43	3.77	30.54	0.84	0.33

$$E_{gap}=0.00\ eV$$
$$E_b=26.52\ eV$$

$$E_{gap}=0.52\ eV$$
$$E_b=27.52\ eV$$
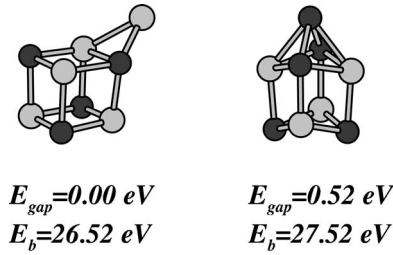
FIG. 2. The geometrical structures for Au_5Si_4 and Au_4Si_5 clusters. Black spheres: Si atoms, gray spheres: Au atoms.

the cubic Si_4Au_4 cluster has been obtained. Recent study results declare that both Si_4 and Au_4 show much higher stability relative to their neighbors,[21] which supports our idea that Si_4 and Au_4 cores could be first grown and there may be competition between these two different growth paths. As presented in Fig. 2, the geometrical structure of $Au_5Si_4(Au_4Si_5)$ can be obtained by growing one Au(Si) atom on the edge (face) of the cubic Au_4Si_4, with a small distortion of the cube, which again predicates the stability of Au_4Si_4 cluster.

In Fig. 3, we present the dissociation energy for one Au(Si) atom from $Au_nSi_4(Au_4Si_m)$ clusters ($n,m=1-5$). Much higher stability for Au_4Si_4 relative to its neighbors can be seen clearly. We have also further studied the interaction between two cubic Au_4Si_4 clusters. The reacted product keeps these two cubic units almost intact with about 2.56 Å distance and about 1.66 eV reaction energy E_R [for two Au_4Si_4 clusters, $E_R=-[E((Au_4Si_4)_2)-2E(Au_4Si_4)]$, as shown in the inserted panel in Fig. 3. The HOMO-LUMO gap still reaches about 1.0 eV, which suggests that stable self-organized assemblies of the cubic Au_4Si_4 unit may be very possible.

The relativistic effect may indeed play an important role in the structure for the X_4Si_4 cluster. As has been mentioned, Au clusters favor planar or cagelike structures due to the relativistic effect, then one may ask a question—does the relativistic effect still work in the binary alloy cubic Au_4Si_4 cluster? In order to make this question clear, we have also studied the electronic structures for Cu_4Si_4 and Ag_4Si_4 clusters. The calculated results show that both Cu_4Si_4 and Ag_4Si_4 clusters prefer cubiclike structures with relatively large distortion. In fact, the most stable structures for both Cu_4Si_4 and Ag_4Si_4 are inlaid tetrahedronlike, which can also be regarded as four metal atoms which adsorb on the four surfaces of the inner Si_4 tetrahedron, constituting the outer tetrahedron. And the ratio of Cu-Cu(Ag-Ag) distance to that of the Si-Si is
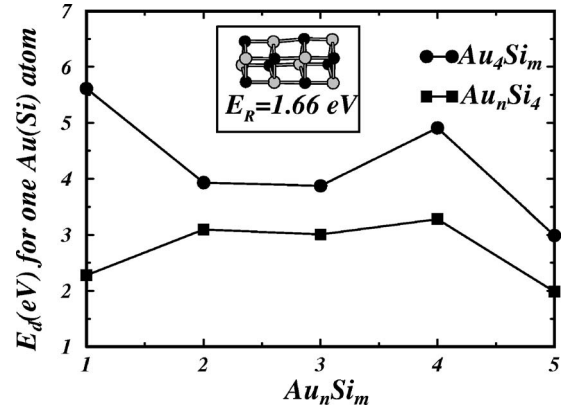

FIG. 3. The dissociation energy (E_d), $E_d(n)$ $=\{E[Au(Si)_nSi(Au)_4]-E[Au(Si)]-E[Au(Si)_{(n-1)}Si(Au)_4]\}$ for one Au(Si) atom from $Au_nSi_4(Au_4Si_m)$ cluster ($n,m=1-5$). Much higher stability for Au_4Si_4 relative to its neighbors can be seen clearly. In the inserted figure, the configuration for two reacted Au_4Si_4 clusters is presented, which also indicates the extraordinary stability of the Au_4Si_4 cluster.

about 1.31 Å (1.55 Å), which can be seen from Table I and Fig. 4. These results indicate that the relativistic effect does work in the cubic Au_4Si_4 cluster. We have also made the comparison between relativistic and nonrelativistic calculations performed by both VASP and ADF codes for Au_4Si_4. The calculations performed by both these two codes show that, in a nonrelativistic level, the cubic structure is not stable for Au_4Si_4, which will distort to the inlaid-tetrahedronlike structure, however, in a relativistic calculation level, the inlaid-tetrahedronlike configuration will relax again to cubic structure. Our calculations also show that in the cubic structure (owing to the stabilization of s electrons of Au), the charge flow from per Au atom to per Si atom is only about 0.07 e (see Table I). While in the inlaid-tetrahedronlike structure obtained with nonrelativistic calculations, the charge flow reaches to about 0.2 e, however, the Au-Si bonding lengths have been lengthened to about 2.68 Å, making the total binding energy decrease. The relativistic effect may be very weak in Cu_4Si_4 and Ag_4Si_4 clusters, and these two clusters prefer inlaid-tetrahedronlike structures. These results indicate that the relativistic effect may really play a key role in the cubic structure, though we also guess that the size effect for Cu, Ag, and Au atoms may be important in the structural differences.

As the same important semiconducting element silicon, carbon has also attracted much attention for applications in
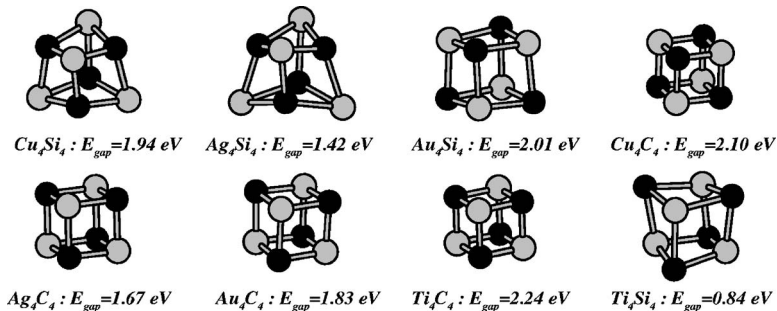

$Cu_4Si_4 : E_{gap}=1.94\ eV$ $Ag_4Si_4 : E_{gap}=1.42\ eV$ $Au_4Si_4 : E_{gap}=2.01\ eV$ $Cu_4C_4 : E_{gap}=2.10\ eV$

$Ag_4C_4 : E_{gap}=1.67\ eV$ $Au_4C_4 : E_{gap}=1.83\ eV$ $Ti_4C_4 : E_{gap}=2.24\ eV$ $Ti_4Si_4 : E_{gap}=0.84\ eV$

FIG. 4. The geometrical configurations for X_4Y_4 ($X=Cu, Ag, Au, Ti; Y=C, Si$) clusters. The HOMO-LUMO gaps are also marked for each cluster. The black spheres and the gray spheres correspond to the semiconductor atoms and the metal atoms, respectively.

nanoscience. Can a C_4 cluster also be stabilized to cubic structures by alloying with noble metal atoms? We are surprised to find that the most stable structures for all the X_4C_4 (X=Cu,Ag,Au) clusters are almost perfect cubic configurations (see Table I and Fig. 4). The bond length of Cu-C in Cu_4C_4 cluster is 1.91 Å, which is about 10% smaller than the Ag-C and Au-C bond lengths (2.14 Å, 2.15 Å) in Ag_4C_4 and Au_4C_4 clusters, respectively. There are 2.10, 1.67, and 1.83 eV HOMO-LUMO gaps for X_4C_4 (X=Cu,Ag,Au) clusters respectively, indicating their high inertness and stability. As discussed above, due to the relativistic effect, the Au_4Si_4 cluster can be stabilized to cubic structure. So it is reasonable for Au_4C_4 to favor cubic configuration. However, it seems difficult to understand the almost perfect cubic structures for X_4C_4 (X=Cu,Ag) clusters. In fact, the cubic structures for X_4C_4 (X=Cu,Ag) clusters may be understood from the point of view of X-C ionic bonds. As shown in Table I, the charge flow from X (X=Cu,Ag,Au) to C atom is about 0.30–0.35 e, which is obviously larger than that in X_4Si_4 (X=Cu,Ag) clusters with inlaid-tetrahedronlike structures. In the mean time, as all the X_4C_4 (X=Cu,Ag,Au) clusters are almost perfect cubic configurations, so we regard that the size effect does not work in a cubic-noncubic alternative in X_4Si_4 (X=Cu,Ag,Au) clusters. The results above encourage us to make one conclusion that both the relativistic effect and the ionic bonding may dominate the cubic structures.

In order to know whether the semiconductor Y_4 (Y=C,Si) clusters can be stabilized to cubic structures by alloying with other transitional metal elements, we have also studied the electronic structures of Ti_4Y_4 (Y=C,Si) clusters. (It is well known that Ti can easily alloy with carbon and silicon.) As presented in Fig. 4, the Ti_4C_4 cluster also prefers perfect cubic structure with about 1.97 Å Ti-C bond length. The 2.24 eV (see Table I) large HOMO-LUMO gap and the 45.73 eV large binding energy indicate its extraordinary stability. In fact, intensive work has been done for Ti_xC_y clusters in both theoretical and experimental fields[22] following the original discovery of the metallocarbohedrenes (MetCars) Ti_8C_{12} by Castleman and co-workers.[23] Wang *et al.*[22] found that $Ti_3C_8^-$, $Ti_4C_8^-$, $Ti_6C_{13}^-$, $Ti_7C_{13}^-$, $Ti_9C_{15}^-$, and $Ti_{13}C_{22}^-$ clusters show abundant (magic) negative ion peaks in mass spectra, and from Ti_4C_8 these clusters prefer cubiclike growth pathways. It is interesting that the structure for the Ti_4C_8 cluster can just be regarded as putting an additional four C atoms on the apexes of the cubic Ti_4C_4 cluster forming four C-C dimers. The results above strongly imply that the Ti_4C_4 cluster may be the smallest cubic unit in Ti_xC_y growths. Ti_4Si_4 cluster is found to favor cubiclike structure with about 0.8 ratio of Ti-Ti distance to Si-Si distance. Despite the large binding energies, Ti_4Si_4 has a relatively smaller HOMO-LUMO gap of 0.84 eV, which could be partially attributed to the distortions from perfect cubic structures. The electronic analysis shows that the average charge flow from per Ti atom to per Y (Y=C,Si) atom is 0.55 e and 0.33 e, respectively, indicating again that the strength of the ionic bonds of Ti-Y (Y=C,Si) may indeed play an important role in a cubic-noncubic alternative. Here, we simply state that in our calculations Mulliken analysis predicates obvi-
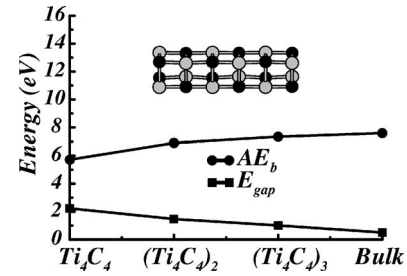

FIG. 5. The average binding energies per atom (AE_b) and the HOMO-LUMO gaps (E_{gap}) in eV for finite nanotubes of $(Ti_4C_4)_n$ (n=1,2,3) and for the infinite Ti_4C_4 nanotube. The structure for the infinite nanotube has also been shown.

ously larger charge flow for Au_4Si_4, Ti_4C_4, and Ti_4Si_4 clusters than VDD does, for example, about one electron charge flow from per Ti atom to per C atom has been obtained with Mulliken analysis for Ti_4C_4, whereas for other clusters with the Au and Si components, both methods lead to similar results.

Recent studies show that both finite and infinite hexagonal silicon nanotubes can be stabilized by the interactions of transition metal atom with hexagonal $M@Si_{12}$ cluster units,[7] and by using high-resolution transmission electron microscopy, a stable 3 Å in diameter armchair carbon nanotube can be grown inside a multiwalled carbon-carbon nanotube.[24] However, here we simply report that Ti_4C_4 units can be self-organized to stable finite and infinite quadrate nanotubes with only about 1.99 Å diameter by the strong Ti-C ionic bonding. (For the infinite nanotube, $7 \times 1 \times 1$ k points have been used.) As presented in Fig. 5, in the nanotubes, the Ti_4C_4 units still keep almost perfect cubic symmetry with about 5% bonding lengths increasing along the tube axis. The average binding energy (AE_b) increases from about 5.7 eV for the Ti_4C_4 cluster to about 7.3 eV for the infinite Ti_4C_4 nanotube. For the infinite nanotube, the HOMO-LUMO gap has been decreased to about 0.5 eV, indicating its semiconducting character. Constant-temperature (600 K) molecular dynamic simulations performed by VASP show that the infinite (finite) nanotubes still keep almost perfect quadrate symmetry in a time duration of 1 ps with the time step of 1 fs, showing that the Ti_4C_4-organized nanotubes are indeed very stable. (The details for the cubic nanotubes will be published separately.)

IV. SUMMARY

In summary, we have shown that, due to the relativistic effect and the ionic bonding, semiconducting Y_4 (Y=C,Si) clusters can be stabilized to cubic structures by alloying with transition metal elements X (X=Cu,Ag,Au,Ti). The metal-semiconductor alloy cubic clusters Au_4Si_4, X_4C_4 (X=Cu,Ag,Au) and Ti_4C_4 clusters have large binding energies and large HOMO-LUMO gaps, making them desirable for self-organized microelectronic devices and other nanoscale device applications. And we also hope such cubic clusters deserve further experimental investigations.

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