Using the small Si cluster as a building block

A. J. Lu

Physics department of Donghua University, Shanghai, 201620, P. R. China
ajlu@dhu.edu.cn

Abstract. Assembly between Si₄ clusters is calculated to search for the Si₈ cluster with the lowest energy. Tetrahedral Si₄ cluster leads to a larger binding energy of the assembled Si₈, compared with the rhombus Si₄ cluster, although the latter is confirmed as the configuration with the lowest energy among the isomers of Si₄. So the prediction of larger silicon clusters should involve the building blocks with the lowest energy as well as those are meta-stable. The binding energy of silicon clusters versus the number of building blocks shows a unique curve. Thus, using the binding energy of the building blocks to predict the energy evolution of larger silicon clusters is suggested as a new feasible scheme for the medium-sized silicon clusters.

1. Introduction

Silicon clusters have been studied for decades as they are hopeful candidates in the application of electric and opto-electric fields [1-6]. It was demonstrated as the switch in the current circuit and reported as the possible blue-light emitter due to the large energy bands in the quasi-0D structure [7].

Unique properties are tightly related with the structure of the cluster, so the prediction of the atomic structure of the silicon clusters is hot topic in physics and material science [8]. Several attempts were made to seek for the most efficient method of finding the configuration of the cluster with the lowest energy. For example, generic scheme is one of the most popular methods in the work of searching for the medium-sized silicon clusters [9-12]. It is successful and has been used to predict many important structures of silicon clusters in theory.

The biggest problem occurred in the structure searching is the determination on the found structure whether it is stable. That was usually treated as the differentiation of the total energy of obtained structure whether the lowest one. Only when the cases with the lower total energies were found, the comparison ruled out the ones with larger energy and the others were reserved. It is natural to suspect the dependence of the searching scheme whether efficient and complete. We used our theoretical calculation to show a new way to determine the energy evolution of the silicon cluster, based on the smaller cluster regarded as the building block.

Based on the previous work, we calculate the energy of silicon clusters Siₙ (n<12) coupled with the smaller silicon clusters used as the building blocks. These small clusters used as building blocks are so-called seeds in our work, and we find a unique curve between the number of seeds and the binding energy of the assembled result. Furthermore, the result indicates that, the larger silicon clusters showing larger binding energy which is calculated from the building blocks should be the structure with lower energy more possibly. In another word, the curve of binding energy of the building blocks could be a criterion to differentiate the clusters from the unstable candidates. Thus a new method to determine the configuration of the silicon cluster at medium-size is suggested.
2. Methods
Density functional theory has been confirmed one of the most efficient methods to calculate the energy evolution of the nano-sized materials. It is our choice to deal with the silicon clusters. A well-developed SIESTA package [13-15] was used and the exchange-correlation functional was selected as General Gradient Approximation (GGA) proposed by Perdew, Burke and Ernzerhof (PBE). Double-zeta basis with polarization was employed and the potential of silicon was checked in the calculation of the bulk silicon crystal. The cubic supercell was considered as $15 \times 15 \times 15 \text{ Å}$ so that the distance between neighboring clusters is large enough to ensure the interaction between them negligible.

During the full-relaxation, the Si$_4$ cluster in different configuration was optimized. The one with rhombus structure was found the most stable as the total energy of it is lower than the tetrahedral one by 0.54 eV/atom. Such a result is consistent with the early report submitted by Khakomov et al [16].

3. Results and discussions
It has been predicted that the small silicon clusters would assemble when they are close to each other, due to the activity of the cluster related with the large ratio between surface area and the volume. Such a phenomenon was confirmed in our calculation. When the distance between two Si$_4$ clusters was fixed manually, we calculated the total energy of the Si$_4$-Si$_4$ system. Fig. 1 shows the energy evolution of the assembly, starting from (a) two rhombus Si$_4$ clusters and (b) two tetrahedral Si$_4$ clusters. Both of the procedures were found exothermal, which indicates the assembling taking place automatically.

![Fig. 1 Energy evolution of two Si$_4$ cluster assembling. X-Y plane shows the distance and orientation between the bottom centers of the two clusters. The variance of the total energy shows the energy lowering is much sharper in (b) between two tetrahedral Si$_4$ clusters than that in (a) between a pair of rhombus Si$_4$ clusters.](image)

In Fig. 1(a), the distance between the clusters is measured between the centers of two rhombus configurations when they are approaching parallel. In Fig. 1(b), the distance is measured between the bottom centers of two neighboring tetrahedral Si$_4$ clusters. In fact, we found the energy evolution different when the two tetrahedral Si$_4$ clusters approaching in different ways. Here is the typical case that leads to the lowest energy. The orientation of the distance was indicated in Fig. 1, and such a mapping of total energy revealed energy variation during the assembling in the real space totally.

As the definition of the distance varies in the figures, the quantity at each point is not of importance. It is emphasized the slope of the energy surface which shows the stabilization of the assembled structures. The slope of the energy surface is much larger in Fig. 1(b) than that in Fig. 1(a), indicating the tetrahedral Si$_4$ clusters are more favorable candidates in the assembling. As it has been confirmed that the tetrahedron is a meta-stable structure of Si$_4$ cluster, such a result shows that the assembling
happens on meta-stable structures more possibly. It means that during the searching of the medium-sized silicon clusters, the seed clusters at meta-stable states must be included. The total energy is not always the best proof in the cluster searching.

In the analysis of the binding energy, defined as $E_b = E_{\text{seed}} \times n - E_{\text{product}}$, such a finding is even more remarkable. Although the total energy of the Si$_4$-Si$_4$ assembled structures varies slightly, indicated in the inset of Fig. 2, the binding energy shows a large difference between the main products. It is shown in Fig. 2 that the binding energy of the tetrahedral Si$_4$ clusters induced structure is larger than that coming from rhombus Si$_4$ clusters of 5 eV or so. Such a large difference would be hidden if we are only concerned of the total energy of the structures. A further detailed observation revealed that the final structures in these two assembles are different, as they are in C$_{2h}$ symmetry and D$_{3d}$ symmetry respectively. These two configurations were discussed in ref [17], where they concluded the former one as the isomer with lower energy, which coincides with our work perfectly.

Such a result notified us again that the Si$_4$ structure at meta-stable is important in assemble process. If only the rhombus Si$_4$ clusters were considered in assemble, the Si$_8$ in C$_{2h}$ would be missed in the searching procedure. We could only obtain the Si$_8$ in D$_{3d}$ symmetry starting from rhombus Si$_4$ clusters. Moreover, we were enlightened by the amplification of the binding energy difference in Fig. 2. It is hopeful using binding energy to assist the seeking of the larger sized silicon clusters as it is sensitive to the atomic structure among the isomers.

Based on our definition of the binding energy per seed, $E_{b's} = (E_{\text{seed}} \times n - E_{\text{product}})/n$, we calculated the binding energy of a series of silicon clusters. The data points of the binding energy of the clusters versus the number of seeds are displayed in Fig. 3. It is interesting that all of them obey the same rule as they fall in a common line no matter which seed we used. The filled squares show the binding energy of the clusters using the atomic silicon as seed; the filled circles indicate the binding energy of the cluster using the Si-Si dimer as seed; the filled triangles show the binding energy of the cluster using the Si$_4$ as the building blocks. Red line is guidance to our eyes. It is clear that the binding energy increases as the number of seeds increases and saturates. That is a reasonable result because the binding energy should converge to the binding energy of silicon bulk crystal gradually.

In fact, in Fig. 3 we do not show results of the structure with the lowest energy only. That is, the data point showing two dimers assembling is related with the rhombus Si$_4$ cluster, the data point showing two Si$_4$ coupling results in the Si$_8$ cluster in D$_{3d}$ symmetry. Both of them are accepted as the structure with the lowest energy. The points according to them are higher than the red line in position.
showing the stable building blocks leading to the stable assembled result. The point displaying three Si4 clusters is just one case we test on, and its binding energy is some smaller than the comparative dot in the red line. In the further confirmation calculation we found that, such a structure is not the configuration with the lowest energy. Such a result demonstrates that, it is hopeful to judge the configuration whether the one with the lowest energy through taking the curve as a reference. If the found structure showing a binding energy smaller than the corresponding point in the line shown in Fig. 3, the structure should not be the structure with the lowest energy. It means that, we could use the binding energy of the cluster to search for the new configurations, and even estimate the minimum of the binding energy of medium-sized silicon clusters based on the energy of the building blocks. For example, the binding energy of Si12 cluster (made up of three Si4 clusters) should be not smaller than 4.14 eV, so that e may filter the structures in the geometry searching of the silicon clusters firstly.

4. Conclusion

Based on DFT calculation we study the assembling of smallest silicon clusters. We confirmed the assembling an exothermal process and this assembling tightly related with the searching of larger silicon clusters in theoretical study. It is found that the binding energy of the cluster could be estimated from the energy of the smaller clusters which could be regarded as building blocks. The reference line comes from the binding energy of silicon clusters versus the number of building blocks—silicon atoms. Only the structure shows the binding energy larger than the corresponding point indicated by the curve could be the structure with the lowest energy. It is a new suggestion to filter the structure in the work of structure searching of silicon clusters.

Acknowledgement

This project was supported by the Fundamental Research Fund for the Central Universities (No.2009C03-1-01) and the Starting Funding for Youth Teacher in Donghua University.

[1] L. Mitas, J. C. Grossman, I. Stich, and J. Tobik, Phys. Rev. Lett. (2000)84, 1479.
[2] F. Baletto and R. Ferrando, Rev. Mod. Phys. (2005)77, 371.
[3] U. Landman, R. N. Barnett, A. G. Scherbakov, and P. Avouris, Phys. Rev. Lett. (2000)85,1958.
[4] K. D. Hirchman et al, Nature (London) (1996)384, 338.
[5] S. Y. Lin et al, Nature (London) (1998)394, 251.
[6] S. Yoo et al, J. Am. Chem. Soc. (2003)125, 13318.
[7] Robert Dalpé, Elaine Gauthier and Marie-Pierre Ippersiel. The State of Nanotechnology Research: Report to the National Research Council of Canada[P]. May, 1997.
[8] L. S. Pedroza and A. J. R. da Silva, Phys. Rev B (2007)75, 245331.
[9] S. Yoo and X. C. Zeng, Ang. Chem. Int. Ed. (2005)44, 1491.
[10] K. –M. Ho, A. A. Shvartsburg, B. Pan, Z. –Y. Lu, C. –Z. Wang, J. G. Wacker, J. L. Fey, M. F. Jarrold, Nature.(1998)392, 582.
[11] B. Liu, Z. –Y. Lu, B. Pan, C. –Z. Wang, K. –M. Ho, A. A. Shvartsburg, M. F. Jarrold, J. Chem. Phys. (1998)109, 9401.
[12] I. Rata, A. A. Shvartsbrug, M. Horoi, T. Frauenheim, K. W. M. Siu, K. A. Jackson, Phys. Rev. Lett. (2000)85, 546.
[13] P. Ordejón, E. Artacho and J. M. Soler, Phys. Rev. B (1996)53, 10441.
[14] E. Anglada, J. M. Soler, J. Junquera and E. Artacho, Phys. Rev. B (2002)66, 205101.
[15] E. Artacho, E. Anglada, O. Dieguez, J. D. Gale, A. Garcia, J. Junquera, R. M. Martin, P. Ordejón, J. M. Pruneda, D. Sánchez-Portal and J. M. Soler, J. Phys.: Condens. Matter (2008)20, 06420.
[16] Z. M. Khakomov, P. L. Tereshchuk, N. T. Sulaymanov, F. T. Umarova and M. T. Swihart, Phys. Rev B (2005)72, 115335.
[17] K. Raghavachari and C. Mc. Rohlffing, J. Chem. Phys (1988)89, 2219.