High reactivity of silicon suboxide clusters

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The recent silicon-oxide-assisted formation of Si nanostructures has been studied based on quantum-mechanical calculations of Si_nO_m ($n,m = 1-8$) clusters. We found that (1) energetically the most favorable small silicon-oxide clusters have O atomic ratios at around 0.6, and (2) remarkably high reactivity at the Si atoms exists in silicon suboxide Si_nO_m clusters with $2n > m$. The results show that the formation of Si-Si bonds is preferred and thus facilitates the nucleation of Si nanostructures when silicon suboxide clusters come together or stack to a substrate.

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Silicon oxide has found important applications in wide fields such as microelectronics, optical communications, and thin-film technology.[1–3] Recent work[4] further showed that silicon oxide could also play an important role in the fabrication of an important nanometer material, the Si nanowire,[5,6] which has attracted much attention for its interesting quantum confinement effect as well as useful electrical, optical, mechanical, and chemical properties. The formation of Si nanowires was achieved by using Si powder sources mixed with SiO_2.[4] A high yield of nanowires has been obtained when the chemical compositions of Si and O in the source are approximately equal.[7] On the contrary, the important role of oxide is not needed in the conventional growth mechanisms of nanowires.[8,9] To understand the oxide-assisted formation mechanism, the exploration of silicon oxide clusters about their geometric, electronic, and chemical properties would provide useful information.

To promote various technological applications based on silicon oxide, theoretical investigations have been performed on small silicon oxide clusters. Systems, such as isolated SiO_2, gas-phase oligomers $(SiO_2)_n$ ($n \leq 8$, $n = 18$),[10] $Si(SiO_2)_n$ ($n = 2,3$), $(SiO_2)_n$ ($n = 1-4$), $(SiO_2)_n$ ($n = 3-5$),[11] Si_3O_m ($m = 1-6$),[12] $Si_2O_4^{2-}$, $Si_2O_5^{2-}$,[13] charged and neutral Si_nO_m ($n \leq 6$, $m \leq 12$),[14] and $(SiO)_n$ ($n \leq 5$),[15] have been studied using *ab initio* theories. Information achieved includes geometric structures, energetics, bonding,

energy gaps, and valence electronic structures of these species. However, understanding of the oxide-assisted formation of Si nanowires in which silicon oxide acts as a special "catalyst" would require a systematic study of Si_nO_m. In this work, we have made such a systematic study of Si_nO_m ($n,m = 1-8$) at the quantum-mechanical level, aiming at elucidating the oxide-assisted formation mechanism of silicon nanowires.

Energetically, the more favorable structure has been searched for each composition of Si_nO_m ($n,m = 1-8$) by means of calculations with density functional theory (DFT). The DFT calculations in this work used the popular B3LYP method, which is based on the Becke-type three-parameter density functional theory.[16] An economic basis set, where 3-21G and 6-31G* were selected to describe Si and O, respectively, according to their electronegativities and charge transfers,[17] was used in B3LYP calculations for most of the atomic clusters considered. The standard 6-31G* was also used in B3LYP calculations for small clusters ($m + n < 12$). Table I lists the geometric parameters and cohesion energies of SiO and SiO_2 species calculated with different levels of theories. Spin polarization energies have been included in the calculations for free Si and O atoms when obtaining the cohesion energies. It is shown that B3LYP of DFT calculations predict quite accurate geometric parameters while they un-

TABLE I. Geometric parameters and cohesion energies per atom (eV) of SiO and SiO_2 calculated with different theoretical methods.

	Method			
	B3LYP/3-21G:Si; 6-31G*:O	B3LYP/6-31G*	G2MP2	Other calculations (Ref. 14)
	Bond length (Å)			
SiO	1.54	1.52	1.54	1.54
SiO_2 ($D2h$)	1.54	1.52	1.53	
	Cohesion energies per atom (eV)			
SiO	−3.66	−3.91	−4.16	−4.03
SiO_2 ($D2h$)	−3.56	−3.95	−4.27	−4.18
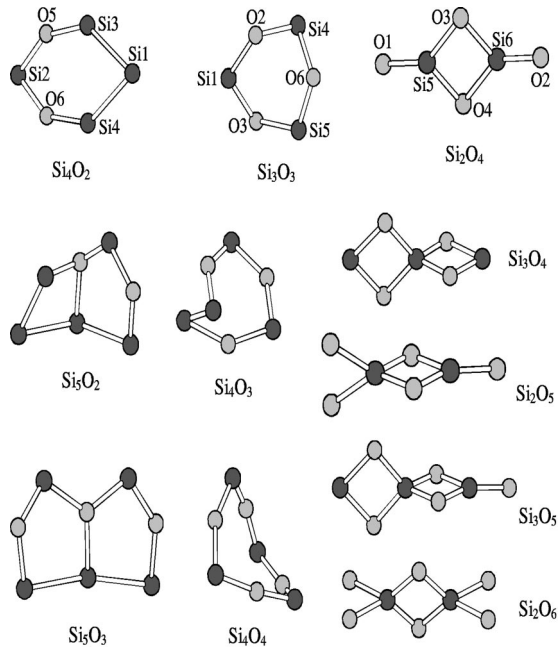
FIG. 1. Geometric structures of representative Si_nO_m clusters for $n+m=6$, 7, and 8.

FIG. 2. Cohesion energy per atom of Si_nO_m ($n,m=1-8$) clusters as a function of O ratio based on total energy calculations with B3LYP/3-21G:Si; 6-31G*:O. The decreasing size of the symbol $\times$ is related to increasing cluster size ($n+m$).

derestimate the cohesion energy in comparison with the more accurate values predicted by the G2.

In the search for possible structures of Si_nO_m ($n,m=1-8$) clusters, initial structures were constructed based on the geometries of smaller clusters for which optimizations had been done. An inverse routine was used for constructing some alternative initial structures, in which the smaller structure was deduced from a larger cluster with a certain amount of atoms removed. The details of the calculation and the geometric results are reported elsewhere.[18] The optimized structures deduced for some representative clusters are shown in Fig. 1. The structures of silicon-rich clusters mainly consist of planar or buckled rings that favor the constituent Si and O atoms to be alternately arranged. However, Si atoms bonded to up to four O atoms were found in oxygen-rich clusters. Large silicon-rich oxide clusters may have more than two pendant Si atoms. The structures obtained in this work are consistent with those found in previous studies.[11,12,14,15,19] The cohesion energies per atom of the deduced configurations of Si_nO_m clusters as functions of the O atom ratio based on total energy calculations with B3LYP are shown in Fig. 2. As shown in Fig. 2, the calculated cohesion energies with the economic basis set show minima at about 0.6 of the O atom ratio. The DFT calculations using the standard basis set of 6-31G* for smaller clusters also show the same trend. The minimum of a larger-size cluster tends to shift to higher atom ratio of O. It is expected that the minima would be stabilized at an atom ratio of O of about 0.67 (silicon dioxide) if the cluster size were sufficiently large. The results indicate that the energetically most favorable small clusters are silicon monoxide like. It is noted that the experimentally deposited silicon oxide material has an atom ratio of O of about 0.49 when the highest yield of Si nanowires is achieved.[7]
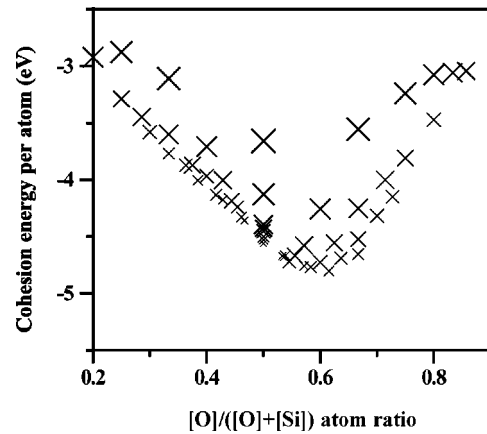
Density-of-states (DOS) calculations[20] were further done for every energetically most favorable structure described above, based on the coefficient matrix of eigenfunctions obtained from the B3LYP (with the economic basis set) calculations. The total DOS (TDOS) is projected onto the constituent atoms to deduce the contribution of the individual atoms to the total electronic structures. The projection allows the elucidation of the properties of electronic states in the bands and in the gap as well as their relationship with the atoms involved.[20] Such a treatment was used in this work to find the atoms in which the frontier orbitals [the highest occupied molecular orbital (HOMO) and the lowest unoccupied MO (LUMO)] reside. Early studies[21] have established that the overlap between the HOMO of one molecule and the LUMO of another would determine the nature of the chemical reaction. A smaller energy difference between the HOMO of one molecule (electron donor) and the LUMO of the other (electron acceptor) would indicate a more favorable reaction to take place. Following that, DOS analysis can show the reactive sites [where the partial DOS (PDOS) of the frontier orbitals shows larger intensities] and reactivity (by the closeness of the HOMO to the LUMO in the reaction systems) in the silicon oxide clusters.

We denote the closest MO's to the gap, which contain a significant contribution from the Si and O atoms, as $HOMO_{Si}$, $HOMO_O$, $LUMO_{Si}$, and $LUMO_O$, respectively. The calculation of TDOS and PDOS shows that there is no significant mixing between the atomic orbitals of Si and O atoms in the first few HOMO's and in the LUMO for most silicon-rich or oxygen-rich clusters because their frontier orbitals are mainly contributed from the unsaturated atoms. The atoms more saturated in the cluster would contribute to the MO at a higher binding energy.

Figure 3 shows the $LUMO_{Si}$, $LUMO_O$, $HOMO_{Si}$, and $HOMO_O$ of silicon oxide clusters as functions of the O atom ratio obtained from B3LYP calculations. Their fittings using fourth-order polynomials are shown as solid curves for the frontier orbitals of Si and as dashed curves for the frontier orbitals of O. Significant differences in the distribution of frontier orbitals are revealed for the systems with O ratio
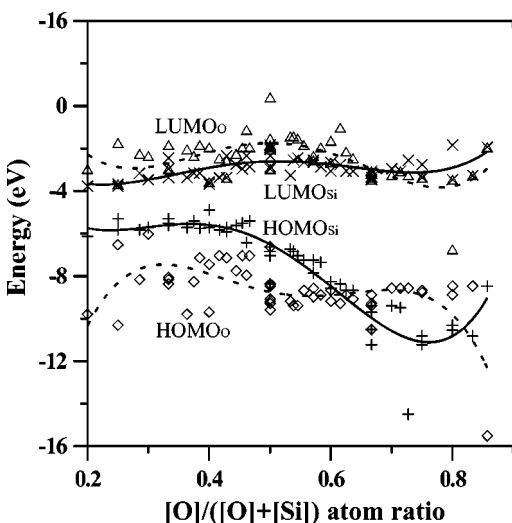
FIG. 3. $LUMO_{Si}$ ($\times$), $LUMO_O$ ($\triangle$), $HOMO_{Si}$ (+), and $HOMO_O$ ($\diamond$) of Si_nO_m clusters determined based on the calculations using B3LYP/3-21G:Si; 6-31G*:O. Their fittings using fourth-order polynomials are shown with solid curves for $LUMO_{Si}$ (upper) and $HOMO_{Si}$ (lower), while dashed curves represent $LUMO_O$ (upper) and $HOMO_O$ (lower).
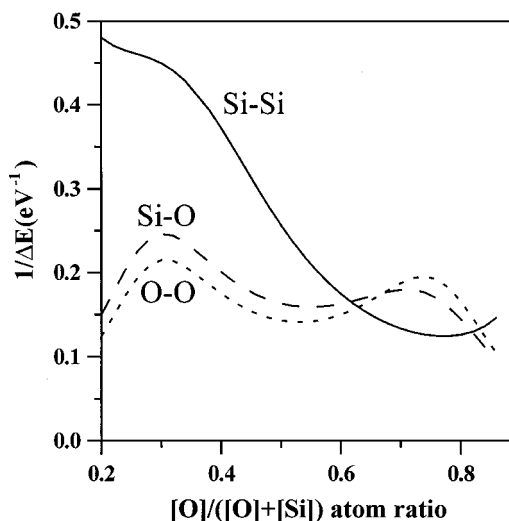

FIG. 4. The inverse of the energy difference [ΔE = LUMO (electron acceptor) $-$ HOMO (electron donor)] and thus the reactivity (proportional to the inverse of the energy difference) for the formation of a Si-Si bond, a Si-O bond, or an O-O bond between two silicon oxide clusters as a function of the Si:O ratio, calculated using the $LUMO_{Si}$, $LUMO_O$, $HOMO_{Si}$, and $HOMO_O$ fitted by fourth-order polynomials as described in Fig. 3.

greater than 0.62 (close to the 0.67 of silicon dioxide) and that smaller than 0.62. With a smaller O ratio, $LUMO_O$ is higher than $LUMO_{Si}$, while $HOMO_O$ is lower than $HOMO_{Si}$. But the difference between them decreases as the O atom ratio increases. When the silicon-oxygen ratio approaches 1:2 or even large, $HOMO_{Si}$ becomes lower than $HOMO_O$. In addition, the $LUMO_{Si}$ and $LUMO_O$ are comparable and mixed together in general at and after such a point. The HOMO and LUMO variations coincide with a previous finding that the HOMO-LUMO gap decreases as the O content of a Si_nO_m cluster is lowered.[14]

The interesting findings obtained above show that (1) the HOMO mainly locates at the Si atoms for silicon suboxide clusters ($m<2n$), but at the O atoms for oxygen-rich silicon oxide clusters; (2) the LUMO for most clusters locates at the Si atoms, particularly for the silicon suboxide clusters; and (3) the energy difference between $HOMO_{Si}$ and $LUMO_{Si}$ decreases significantly once the atom ratio of O is less than 0.62. From the viewpoint of orbital interaction, the results indicate that, when $m<2n$, the Si atom has a higher reactivity than the O atom and the extent of this reactivity depends on the atom ratio of the O atom. The smaller the O atom ratio, the higher is the reactivity. Once the number of O atoms approaches $2n$ or larger, the reactivity becomes very poor. Therefore, the reaction between silicon suboxide cluster with any type of silicon oxide cluster would result in a bond formation between Si and Si of both clusters, whereas the reaction between oxygen-rich silicon oxide clusters would most likely lead to bonding between O and Si atoms in both clusters with a low reactivity. The trends of bond formations can be clearly seen from Fig. 4, which depicts the inverse of the energy difference and thus the reactivity for the formation of a Si-Si bond, a Si-O bond, or an O-O bond between two silicon oxide clusters as a function of the Si:O ratio, calculated using the $LUMO_{Si}$, $LUMO_O$, $HOMO_{Si}$, and

$HOMO_O$ fitted by fourth-order polynomials as described in Fig. 3. Thus the reactivity to form a Si-Si bond of two silicon oxide clusters is significantly larger than that to form a Si-O or O-O bond, once the atom ratio of O is less than about 0.62.

To lend support to the idea that the trend of reactivity can be reliably deduced from the analysis of frontier orbitals, we calculate the reaction energy barrier height and reaction heat between two Si_4O_2, Si_3O_3, and Si_2O_4 clusters, respectively. The reactions were assumed to occur at the following reactive sites (see Fig. 1): Si1 for Si_4O_2, Si1 for Si_3O_3, and O1 for Si_2O_4, according to our DOS decompositions. The energy barrier and reaction heat at the B3LYP and 6-31G* level of calculation is 0.244 eV and -1.07 eV for the reaction between two Si_4O_2 clusters and 2.63 eV and 0.75 eV for the reaction between two Si_3O_3 clusters. The smaller energy barrier and the exothermic reaction heat in the former reaction indicate a higher reactivity between two Si_4O_2 clusters than between two Si_3O_3 clusters.[22] The significant difference in reaction energetics would ensure that the relative reactivity of Si_4O_2 clusters would remain higher than the Si_3O_3 clusters even at higher temperatures. On the other hand, there is no binding found between Si_2O_4 clusters, indicating an unfavorable bond formation. In addition, the reaction of two Si_4O_2 clusters occurring at Si2, the less reactive site, shows a much higher reaction barrier and endothermic heat (2.22 eV and 1.24 eV), indicating poorer reactivity. For Si_3O_3 clusters, no binding was found for the reaction occurring at the O2 site. All these results are consistent with the conclusion from the analysis of frontier orbitals.

The richer the Si atoms in the cluster, the higher will be the chance for them to form a Si-Si bond. However, the cohesion energy per atom of the silicon-rich clusters is much higher as shown in Fig. 2, indicating a smaller chance of

their presence in the gas phase. The optimum ratio of Si atom to O atom in the silicon suboxide clusters to achieve the highest yield and formation of Si nanowire should be close to 1, as also observed experimentally (about 49 at. % of O).[7] Our recent experiment using silicon monoxide has given the largest yield of Si nanowires.[23] It is worthwhile noting that a recent experimental report on the formation of the crystalline phase of Si nanoclusters from the deposition of silicon-rich oxide[24] can also be understood in the context of our present study.

From the above observations, the following mechanism of oxide-assisted Si nanowire nucleation is supported. In this mechanism, part of the highly reactive Si atoms in the silicon suboxide clusters deposited on the substrate (possibly covered by silicon oxide) would form bonds with the substrate atoms, anchoring the cluster to the substrate so that the motion of the clusters is limited. The remaining reactive Si atoms facing outwards from the substrate are exposed to the vapor, favoring further stacking of silicon oxide clusters. They act as nuclei to absorb reactive silicon oxide clusters and facilitate the formation of Si nanowires with a certain crystalline orientation. The oxide-assisted growth of silicon nanowires is being accepted widely.[25,26] We expect that the present oxide-assisted formation mechanism of nanostructures may be applicable to a wide range of materials synthesis or design.

In conclusion, silicon suboxide clusters Si_nO_m ($m < 2n$) possess high reactivity at the Si atoms, while small silicon-monoxide-like clusters are energetically more favorable in the gas phase. Therefore, the oxide-assisted nucleation of Si nanostructures is due to the formation of Si-Si bonds when the highly reactive silicon oxide clusters meet.

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[1] C. R. Helms and B. E. Deal, *The Physics and Chemistry of SiO$_2$ and the Si-SiO$_2$ Interface* (Plenum, New York, 1988).

[2] E. Desurvire, Phys. Today **47(X)**, 20 (1994).

[3] D. A. Muller, T. Sorsch, S. Moccio, F. H. Baumann, K. Evans-Lutterodt, and G. Timp, Nature (London) **399**, 758 (1999).

[4] Y. F. Zhang, Y. H. Tang, N. Wang, D. P. Yu, C. S. Lee, I. Bello, and S. T. Lee, Appl. Phys. Lett. **72**, 1835 (1998).

[5] T. Ono, H. Saitoh, and M. Esashi, Appl. Phys. Lett. **70**, 1852 (1997).

[6] A. M. Morales and C. M. Lieber, Science **279**, 208 (1998).

[7] N. Wang, Y. H. Tang, Y. F. Zhang, C. S. Lee, and S. T. Lee, Phys. Rev. B **58**, R16 024 (1998).

[8] R. S. Wagner and W. C. Ellis, Appl. Phys. Lett. **4**, 89 (1964).

[9] F. C. Frank, Discuss. Faraday Soc. **5**, 48 (1949).

[10] J. A. W. Harkless, D. K. Stillinger, and F. H. Stillinger, J. Phys. Chem. **100**, 1098 (1996).

[11] L. S. Wang, S. R. Desai, H. Wu, and J. B. Nichloas, Z. Phys. D: At., Mol. Clusters **40**, 36 (1997).

[12] L. S. Wang, J. B. Nicholas, M. Dupuis, H. Wu, and S. D. Colson, Phys. Rev. Lett. **78**, 4450 (1997).

[13] T. Sommerfeld, M. K. Scheller, and L. S. Cederbaum, J. Chem. Phys. **103**, 1057 (1995).

[14] S. K. Nayak, B. K. Rao, S. N. Khanna, and P. Jena, J. Chem. Phys. **109**, 1245 (1998).

[15] J. R. Chelikowsky, Phys. Rev. B **57**, 3333 (1998).

[16] A. D. Becke, J. Chem. Phys. **98**, 5648 (1993).

[17] R. Q. Zhang, T. S. Chu, and S. T. Lee, J. Chem. Phys. **114**, 5531 (2001).

[18] T. S. Chu, R. Q. Zhang, and H. F. Cheung, J. Phys. Chem. B **105**, 1705 (2001).

[19] L. S. Wang, H. Wu, S. R. Desai, J. Fan, and S. D. Colson, J. Phys. Chem. **100**, 8697 (1996).

[20] R. Q. Zhang, C. S. Lee, and S. T. Lee, J. Chem. Phys. **112**, 8614 (2000).

[21] R. Hoffmann, Rev. Mod. Phys. **60**, 601 (1988), and references therein.

[22] T. Naito, S. Nagase, and H. Yamataka, J. Am. Chem. Soc. **116**, 10 080 (1994).

[23] Y. F. Zhang, Y. H. Tang, C. Lam, N. Wang, C. S. Lee, I. Bello, and S. T. Lee, J. Cryst. Growth **212**, 115 (2000).

[24] K. Kim, M. S. Suh, T. S. Kim, C. J. Youn, E. K. Suh, Y. J. Shin, K. B. Lee, H. J. Lee, M. H. An, H. J. Lee, and H. Ryu, Appl. Phys. Lett. **69**, 3908 (1996).

[25] J. L. Gole, J. D. Stout, W. L. Rauch, and Z. L. Wang, Appl. Phys. Lett. **76**, 2346 (2000).

[26] Y. Q. Zhu, W. K. Hsu, N. Grobert, M. Terrones, H. Terrones, H. W. Kroto, D. R. M. Walton, and B. Q. Wei, Chem. Phys. Lett. **322**, 312 (2000).