

## THE ENERGETICALLY FAVORABLE CONFIGURATIONS FOR FORMING SILICON NANOSTRUCTURES

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### ABSTRACT

Using density functional calculations, we show that the energetically favourable configurations of silicon monoxide clusters  $(\text{SiO})_n$  for  $n \geq 5$  facilitate the nucleation and growth of silicon nanostructures as the clusters contain  $sp^3$  silicon cores surrounded by silicon oxide sheaths. The frontier orbitals of  $(\text{SiO})_n$  clusters are localized to a significant degree on the silicon atoms on the surface, providing high reactivity for further stacking with other clusters. The oxygen atoms in the formed larger clusters prefer to migrate from the centers to the exterior surfaces, leading to the growth of  $sp^3$  silicon cores.

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## Introduction

Silicon (Si) suboxide clusters have drawn much attention since they play a crucial role in the oxide assisted growth of silicon nanowires (SiNWs) [1-3]. Their predominant role in the synthesis of SiNWs has been revealed in many experiments in which high yields of nanowires surrounded by SiO<sub>2</sub> sheaths were obtained by either thermal evaporation or laser ablation of Si powder mixed with SiO<sub>2</sub> or simply SiO [1-3]. Interestingly, the maximum yield of SiNWs compared to that from a metal containing target was achieved when the chemical compositions of silicon and oxygen in the source are equal, whereas hardly any or no SiNWs can be obtained with pure SiO<sub>2</sub> materials [2]. This indicates clearly that gasphase Si suboxide clusters, especially silicon monoxide clusters, generated by evaporation of sources containing Si and SiO<sub>2</sub> or SiO, play an important role in the nucleation and growth of SiNWs. Obviously, the mechanism of oxide assisted growth is quite different from the classical vapor liquid solid mechanism involved in metal catalyzed growth [1,4,5]. To understand the oxide assisted formation process, the exploration of silicon oxide clusters with wider ranges of sizes and oxygen ratios is highly desirable.

Small silicon oxide clusters Si<sub>n</sub>O<sub>m</sub> (n,m = 1-8) have been studied both experimentally and theoretically [6-10]. Planar and buckled ring configurations have been oxygen rich clusters were predicted to be rhombuses arranged in a chain with adjacent ones perpendicular to each other. Although Si suboxide clusters are shown to be highly reactive to bond with other clusters and prefer to form Si-Si bonds based on the analysis of their frontier orbitals [11], no direct theoretical evidence on the formation of sp<sup>3</sup> Si cores inside Si oxide clusters has been presented so far due to insufficient knowledge of Si suboxide clusters with a wider range of sizes. However, such clusters are expected to lead to nucleation of Si nanocrystals via the combination of small Si suboxide clusters. We study the energetically most favourable configurations of Si monoxide clusters (SiO)<sub>n</sub> for n ranging from 3 to 21 and their corresponding electronic properties calculated using density functional theory (DFT), with the aim to elucidate the oxide assisted growth process of SiNWs.

Calculations

Our calculations were conducted at DFT level using the GAUSSIAN 98 package [12] and a SIESTA code [13]. B3LYP/6-31G\* of DFT have accurately reproduced the properties of  $\text{Si}_n\text{O}_m$  obtained from both experiments and other high level calculations [6,9,10,14]. SIESTA adopts a localized linear combination of numerical atomic orbital basis sets for the description of valance electrons and norm conserving nonlocal pseudopotentials[15] for the atomic core to improve its computational efficiency. The generalized gradient approximation corrections in the form of Perdew, Burke, and Ernzerhof[16] and the double- $\zeta$  plus polarization orbital basis sets were employed throughout the SIESTA calculations. The energetically more favourable structures of  $(\text{SiO})_n$  clusters were searched with various designed initial configurations which were first annealed at 500 K for 2 ps with a Verlet algorithm using SIESTA with a force tolerance less than  $0.01 \text{ eV/\AA}$ . For small  $(\text{SiO})_n$  ( $n < 11$ ), the relaxed structures using SIESTA were further optimized using B3LYP/6-31G\* calculations were performed with the structures optimized by SIESTA based on the finding that the optimized configurations obtained using B3LYP/6-31G\* and SIESTA were very close, with the difference in bond lengths and bond angles being less than 1.7% and 3.6%, respectively, for small clusters, Binding energies were calculated from the difference between the total energy of a cluster and the energies of the corresponding isolated spin polarized Si and O atoms.

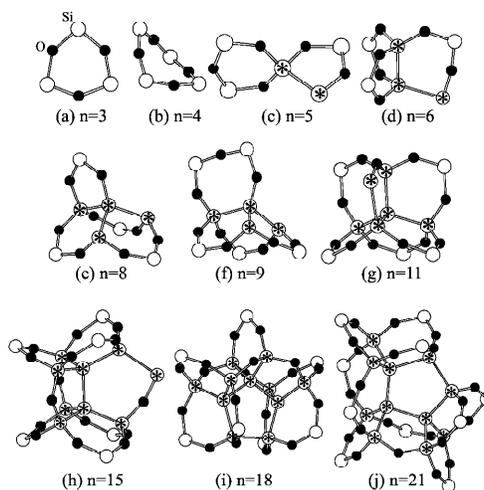


FIG.1. The structures of silicon monoxide clusters  $(\text{SiO})_n$ , The open circles containing stars represent Si atoms in Si cores, the open circles containing stars

represent Si atoms in Si cores, the open circle the unsaturated Si atoms, and the filled smaller circles O atoms.

The energetically most favorable configurations of the  $(\text{SiO})_3$  and  $(\text{SiO})_4$  clusters are the planar and buckled-ring configurations [6,17], respectively, as shown in Fig. 1. For the  $(\text{SiO})_5$  cluster, the one involving a Si-Si bond (Si cored), as shown in Fig. 1, is energetically more favorable than the buckled structure. The total binding energies of buckled and Si-cored isomers at different levels of calculations are given in Table I. The data clearly show that the Si-cored structure is more stable than the buckled configuration by about 0.3 to 0.4 eV due to the formation of a four-coordinated Si atom in the center of the cluster. The energetically most favorable configurations of larger representative clusters  $(\text{SiO})_n$  for  $n$  ranging from 6 to 21 are presented in Fig. 1 as well. The following characteristics are observed: (1) a Si core (represented by the open circles containing stars in Fig. 1 surrounded by a silicon oxide sheath is involved; (2) the Si-Si bonds prefer to form in the center rather than at the cluster surface so as to reduce the strain caused; (3) most of the Si atoms in the Si core have three or four coordinates with Si-Si-Si bond angles close to  $109^\circ$  (the value found in silicon crystal), which is quite different from that of pure Si clusters of the same size [18]; (4) with increasing cluster size, the size of the Si core increases and the fraction of Si atoms with three and four coordinates increases correspondingly, making the cluster more stable; and (5) starting at  $n = 18$  all of the Si atoms in Si cores are four-coordinated, indicating the formation of  $sp^3$  Si cores similar to the configuration in the Si crystal. Figure 2 depicts the binding energies of  $(\text{SiO})_n$  clusters containing Si cores as a function of  $n$ , together with those containing buckled structures. It is clear that: (1) the configurations containing Si cores become energetically more favorable than the buckled structures for  $n=5$  and larger; and (2) the cluster becomes increasingly more stable with increasing Si core size. As the two structures from  $n = 5$  to  $n = 8$  in Fig. 2 are close in energy, we further estimate their relative population at  $900^\circ\text{C}$  (the growth temperature of SiNWs [3] by assuming the process is at equilibrium and described by the Boltzmann factor  $\exp[-E/kT]$ , where  $k$  is Boltzmann's constant,  $E$  is the energy difference, and  $T$  is temperature in Kelvin. The results shown in the inset in Fig. 2 confirm that the structures containing Si cores still play the major role at such a high temperature starting at a size as small as  $n = 8$ . To understand the formation of Si cores, we

calculated the binding energies of some  $(\text{SiO})_n$  clusters with the configurations in which an O atom resides in the Si cores. We found that all of these configurations are energetically less favorable than those with the O atom located at the cluster surface, due to the higher strain caused, indicating that they are metastable. Moreover, the difference in binding energy between the metastable structure and the most stable configuration becomes increasingly larger with increasing cluster size. For example, for the  $(\text{SiO})_5$  cluster the energy difference is 0.37 eV [Fig. 3(a)], whereas for the  $(\text{SiO})_9$  cluster the energy difference increases to 0.90 eV. We considered three different isomers of the  $(\text{SiO})_{21}$  cluster with an O atom residing in different sites from the center to the surface of the cluster, as shown in Fig. 3(b). The most stable configuration is the one with O located on its surface with a total binding energy of 211.74 eV, while the binding energy decreases as the O atom moves from the surface into the cluster (from 209.43 to 208.42 eV). Based on these results, we conjecture that the O atom can migrate from the center of the silicon monoxide cluster to its surface via bond switching, resulting in the formation of  $sp^3$  Si core.

TABLE I. Total binding energy (eV) of the isomers of  $_{\text{SiO}_5}$  cluster. ‘‘Buckled’’ was presented in Ref. [17], and ‘‘Si-cored’’ is shown in Fig. 1(c). MP2 refers to MP2/6-31G\*; MP2/SIESTA represents MP2/6-31G\*\*/SIESTA; DFT is B3LYP/6-31G\*; and DFT/SIESTA stands for B3LYP/6-31G\*\*/SIESTA.

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	MP2	MP2/SIESTA	DFT	DFT/SIESTA	SIESTA
Buckled	-46.9740	-46.8134	-47.0920	-46.8827	-52.1547
Si-cored	-47.4175	-47.2597	-47.3970	-27.2419	-52.9616

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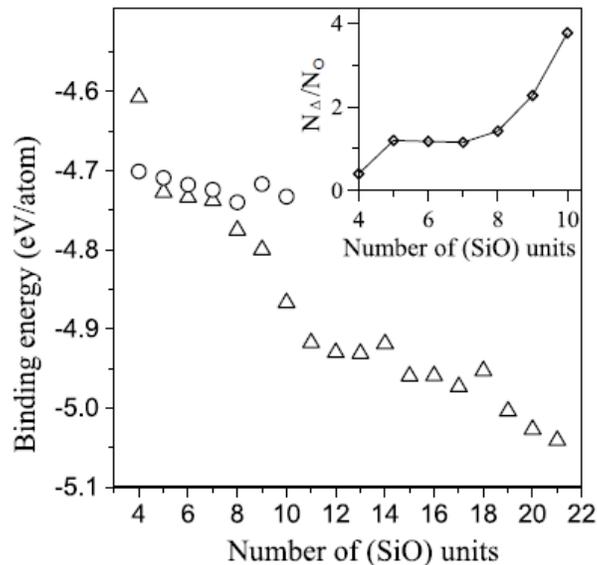


FIG. 2. Binding energy (eV/atom) of  $(\text{SiO})_n$  clusters versus  $n$ . The up triangles are  $(\text{SiO})_n$  with the Si-cored structure surrounded by a silicon oxide sheath, and open circles are those with buckled-ring structure. The inset shows the relative population of the former ( $N_{\Delta}$ ) and the latter ( $N_0$ ) structures at  $900^{\circ}\text{C}$ .

The estimated migration barrier is about 1.79 eV for the  $(\text{SiO})_5$  cluster [see Fig. 3(a)], which is close to the energy barrier ( $\sim 1.3$  eV) of the O atom diffusing in Si crystal in the oxidation process [19]. It is expected that the high strain involved in the  $(\text{SiO})_n$  cluster may cause the O atom to migrate to the surface. Similarly, the study of  $\text{SiO}_2=\text{Si}(100)$  interfaces showed that stress release via excess atom (Si) emission is essential and universal [20]. The electronic structures of  $(\text{SiO})_n$  clusters have been analyzed to reveal their chemical reactivity. The energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital are found to be 2.0–4.5 eV, which is much lower than that for silicon dioxide clusters of the same size [9,14], indicating that  $(\text{SiO})_n$  clusters have higher chemical reactivity [11]. More importantly, the HOMO is localized to a significant extent on the Si atoms at the cluster surface, as revealed by density-of-state decomposition [11], making these regions the likely reactive sites. The combination of these clusters may easily occur through the Si-Si bonding between them, forming larger clusters. Subsequently, the reconstruction and O migration will give rise to the formation of a  $(\text{SiO})_n$  cluster containing a large  $sp^3$  Si core. However, this process cannot be

revealed with molecular dynamics simulations due to insufficient simulation time (computations using currently available facilities could be performed at most for a few picoseconds) and the high energy barrier of O migration in  $(\text{SiO})_n$  clusters. Nonetheless, the migration of O atoms in  $(\text{SiO})_n$  clusters could be driven by the heat released in the reconstruction process and/or by the strain involved in the large clusters formed by the combination of small clusters.

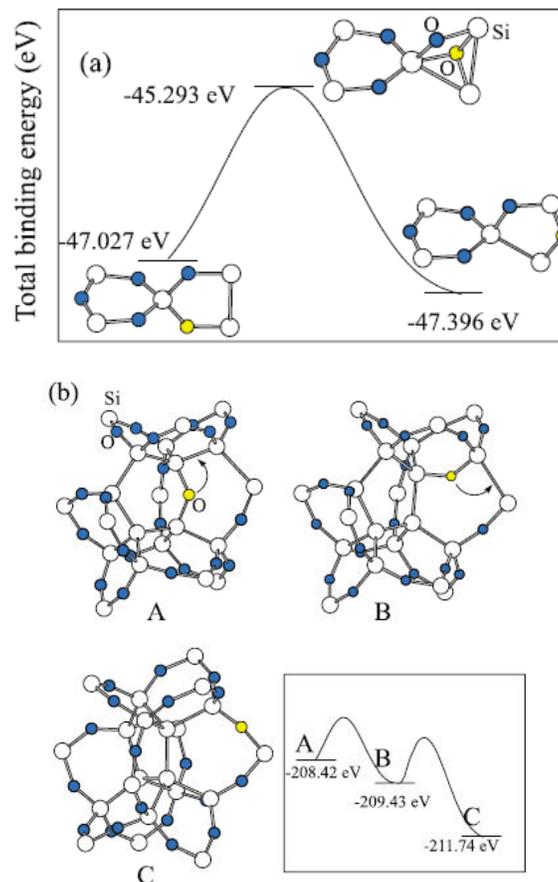


FIG.3. (color). Possible path of O atom migration from the center of a  $(\text{SiO})_n$  cluster to its surface; (a)  $(\text{SiO})_5$  and (b)  $(\text{SiO})_{21}$ .

The structural transition to the diamond structure in Si clusters as the cluster size exceeds a critical value (300– 500 atoms) has been revealed both experimentally and theoretically [18,21,22]. Similarly, the possible structural transitions are deduced here for  $(\text{SiO})_n$  clusters, making these clusters act as nuclei or precursors for the subsequent growth of Si nanostructures.

Considering that the Si atoms in the Si core have the character of  $sp^3$  hybridization similar to that in Si crystal, the critical size [ $n = 18$ ; see Fig. 1(i)] for the structural transition is seen to be much smaller than that of pure Si clusters (400–500 atoms) [18]. It is also noteworthy that the structure of the  $sp^3$  Si core surrounded by the silicon oxide sheath in our calculation is still slightly different from the tetrahedral structure in a Si crystal but is more like the hexagonal structure that has been studied theoretically [23] and experimentally [24]. A transition from the hexagonal to the tetrahedral structure may be expected at a certain size so that the  $(SiO)_n$  clusters are suitable to act as the nucleus and precursor for the subsequent growth of Si nanostructures such as SiNWs. We now discuss the nucleation and growth of Si nanostructures, in particular, SiNWs [2,3], from these clusters. In an experiment using SiO powder or a mixture of Si and SiO<sub>2</sub> powder as the source, the evaporated  $(SiO)_n$  clusters deposited on a substrate would be anchored due to their high reactivity at Si sites. The deposited clusters would act as the nuclei to absorb  $(SiO)_n$  clusters from the vapor because of their remaining reactive Si atoms facing outwards from the substrate. A Si core would start to form at a size of  $n=5$ . The nuclei containing a Si core would grow larger with the assistance of O diffusion from the core to the surface layer during deposition. The O diffusion length depends on the temperature and the crystallographic orientation of the crystalline core formed, leading to the formation of SiNWs with different crystalline orientations such as  $\langle 110 \rangle$  and  $\langle 112 \rangle$ , as observed in our experiments [3]. It is worth noting that the above process may be similarly responsible for the ready formation of Si nanocrystals in the  $sp^3$  configuration from amorphous SiO [25,26]. To conclude, using DFT calculations we show that the energetically most favorable structures of silicon monoxide clusters  $(SiO)_n$  for  $n \geq 5$  contain a  $sp^3$  Si core surrounded by a silicon oxide sheath. Because of their high chemical reactivity, a combination of these clusters may easily take place, forming clusters with a large  $sp^3$  Si core via subsequent reconstruction and O migration from the center to the surface of the clusters. The crystalline Si cores thus formed can act as nuclei and precursors for subsequent growth of Si nanostructures.

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