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# Effect of passivants in energy gap of $Si_{47}X_{24}Y_{36}$ nano-clusters: A theoretical investigation

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ABSTRACT

Passivation on the surface of the nano-cluster $Si_{47}$ core cluster can lead to the formation of $Si_{47}X_{24}Y_{36}$, where X and Y represent the inner and outer layer passivated positions, respectively. Accordingly, X and Y positions can accommodate one and three passivants, respectively. Herein, the density functional theory (DFT) and B3LYP method with the 6-31G(d) basis set were used to generate the electronic structures (HOMO, LUMO and energy gap between HOMO and LUMO) for two different fully passivated Si nano-clusters of $Si_{47}X_{60}$ and $Si_{47}X_{24}Y_{36}$, both with a $T_d$ symmetry. The optimized structures were obtained with the local density approximation (LDA) implemented in SIESTA package. For fully passivated $Si_{47}X_{60}$ nano-clusters (X = –H, $–CH_3$, –OH, $–NH_2$, –F, $–SiH_3$, –SH, –Cl, $–C_2H_5$ and $–OCH_3$) alkyl passivants ($–CH_3$ and $–C_2H_5$) affect insignificantly the calculated energy gaps while electron-withdrawing passivants give red-shifted electronic spectra. Same investigations were also conducted for the partially hydrogenated Si nano-clusters, inner layer passivated $Si_{47}X_{24}H_{36}$ and outer layer passivated $Si_{47}H_{24}Y_{36}$. The calculated energy gaps of Si nano-clusters with inner layer passivation ($Si_{47}X_{24}H_{36}$) are close to that of $Si_{47}X_{60}$, both inner and outer layers passivated. Hence, the outer layer passivant effect is insignificant, which is also demonstrated by insignificant changes in energy gaps ($\leq 0.5$ eV) for the Si nano-clusters with outer layer passivation since the difference of the Mülliken charge is $\leq 0.1$ eV.



## 1. Introduction

Recently, Si nano-clusters have attracted much experimental and theoretical interests since their photophysical properties are similar to those of nanowires and quantum dots [1–8]. The particle sizes of Si nano-clusters in the range of 1 and 5 nm in diameter can exhibit luminescence at visible wavelengths that are enhanced by quantum confinement effects [9]. Clusters of uniform size can be fabricated in a reproducible way that is useful for applications as required in superlattices, high-quality films, and single nanoparticle-based devices. In addition, the distinctive emissions in blue, green, and red were found to be valuable in biomedical tagging and the display applications [10,11]. The photophysical properties of the passivated Si nano-cluster with various passivants could be investigated via quantum chemistry calculation and the results can be made available for the experimental design.

Several calculations, including the semi-empirical modified neglect of diatomic differential overlap (MNDO), the tight-binding, time-dependent density functional theory (TD-DFT), local density approximation (LDA) methods [12–14] and quantum Monte Carlo simulation [15], have been reported to investigate the photophysical properties of hydrogenated Si nano-clusters. Reboredo et al. compared several calculated results with experimental data [16]; Vasiliev et al. proposed the excitation energy for the hydrogenated Si nano-clusters ($Si_nH_m$) by using TD-DFT method [17]. The gradient-corrected Perdew–Burke–Ernzerhof (GGA-PBE) exchange-correlation functional method was used for both structural and electronic state calculations of hydrogenated Si nano-clusters in the ground and excited states [18]. Most of these calculations were focused on the dependence of energy gap (the energy difference between HOMO and LUMO) on the sizes and shapes of the Si nano-clusters.

However, the passivation effects including various passivants and passivated positions, may play an important role on the energy gaps of surface-modified Si nano-cluster. Both experimental and theoretical works indicated that the photophysical properties of Si clusters were affected by surface passivation, chemistry, reconstruction, and the way these clusters are produced [19–22]. It has been shown that surface passivation can affect the energy gaps and photophysical properties of Si nano-clusters. The different chemistry

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of the clusters has also shown to give significant effects on the absorption as demonstrated in cases where oxygen, halogen, or alkyl group was used to substitute some of the hydrogens in the hydrogenated Si clusters [20–22]. Also the surface reconstruction of the nano-cluster was also found to affect the photophysical properties. From a theoretical point of view, replacing some H atoms at the surface of Si nano-cluster might also influence their photophysical properties [23]. Recently, Zhou used the static and TD-DFT calculations to determine the optical property of the core/shell nano-clusters with –F and –OH passivations [24,25]. Fernando et al. discussed the energy gap of Si nano-cluster with the reconstructed surfaces, having a complete alkyl passivation [26].

Although a few papers have been published for the studies of optical and electronic structures of the fully hydrogenated Si nano-clusters with different symmetry and cluster size, there are no systematic studies for these clusters with different passivants and passivated position on the surface of the Si nano-cluster. In 2008, Wang et al. presented a systematic study on generating photophysical properties of a series of Si nano-clusters from $Si_5H_{12}$ to $Si_{281}H_{172}$ [27]. However, the passivating effects, layer by layer, in these Si nano-clusters were not investigated. Theoretically, the passivation on the surface of $Si_{47}$ nano-cluster could be labeled as the inner and outer passivating layers ($Si_{47}X_{24}Y_{36}$, where X and Y are inner and outer passivations, respectively). For the fully passivated Si nano-cluster ($Si_{47}X_{60}$), the effect should depend on the passivated positions. Herein, we study passivants including $–CH_3$, $–C_2H_3$, $–C_2H_5$, $–C_3H_7$, $–CH_2NH_2$, $–OCH_3$, –CN, –OH, $–NH_2$, $–SiH_3$, –SH, –F and –Cl as $T_d$ symmetry with a fully passivated $Si_{47}X_{60}$. Moreover, the $Si_{47}X_{24}Y_{36}$ nano-clusters with various passivants in the inner and outer layers of nano-cluster were used to investigate the passivation effect. The local density approximation (LDA) in the SIESTA package was used to generate the optimized structures of the passivated Si nano-clusters [28–30]. The density functional theory (DFT) and B3LYP method with the 6-31G(d) basis set were applied to determine the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) and the energy gap between LUMO and HOMO. On the basis of the results calculated, we then discuss the photophysical properties and electronic structures of Si nano-clusters with different passivations. The discussions were also extended to the calculated total density of states (TDOS), partial density of states (PDOS) and Mülliken charge distribution of these passivated Si nano-clusters.

## 2. Calculations

According to the geometrical analysis, the hydrogenated Si nano-clusters could be $T_d$ or $I_h$ symmetry. The fully hydrogenated Si nano-cluster contains the diamond-like tetravalent $sp^3$ bonding with a spherical shape and $T_d$ symmetry, where the surface-dangling bonds are terminated by H atoms. We choose the $Si_{47}X_{24}Y_{36}$ nano-clusters with a $T_d$ symmetry, Fig. 1 shows two different passivated types (inner and outer layers). The DFT-based calculation method was employed in this study that was implemented in the SIESTA package, providing a very useful calculation technique for theoretical studies of periodical systems with a large number of atoms [28,30,31]. It used the standard Kohn–Sham self-consistent density functional method in the local density approximations (LDA) and generalized gradient approximation (GGA) with parameterization of Perdew and co-workers [32,33]. The basis set is a linear combination of numerical atomic orbitals (LCAO), which includes double-ξ polarized orbitals, where (2s3p) for the H valence electron and (2s6p5d) for the Si valence electrons were used, and the energy cutoff is 100 Rydberg to define the finite real-space grid. On the basis of the optimized structure of LDA/SIESTA,

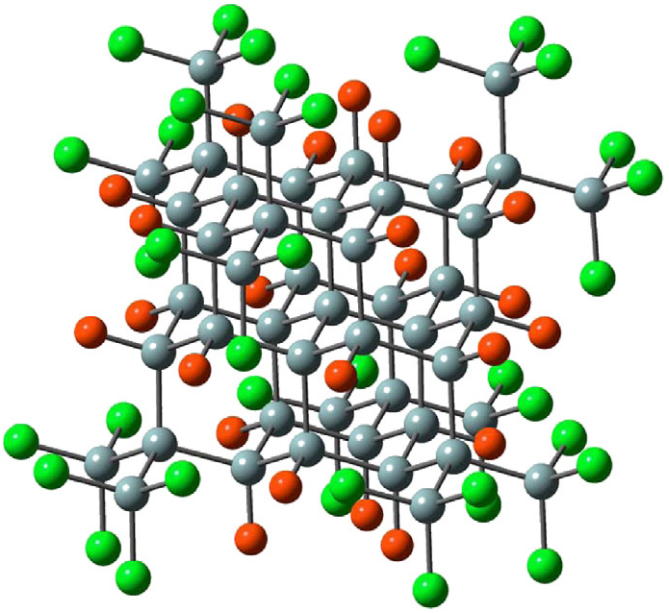

**Fig. 1.** Optimized structure of $Si_{47}X_{24}Y_{36}$ nano-clusters; green spheres indicated the outer layer passivant positions (Y), red spheres indicated the inner layer passivant positions (X) and dark green spheres are silicon atoms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

we used B3LYP hybrid functional with the 6-31G(d) basis set to generate the electronic structure of $Si_{47}X_{24}Y_{36}$ nano-clusters, and calculations were carried out by using the Gaussian 03 package [34]. The calculated HOMO, LUMO, and energy gap were generated by the B3LYP/6-31G(d)//LDA/SIESTA method.

## 3. Results and discussion

The present study is focused on two different fully passivated nano-clusters ($Si_{47}X_{60}$ and $Si_{47}X_{24}Y_{36}$) and used various passivants, which are on two different specified positions with various morphologies and electronic structures. Early research showed that the number of passivants had a great influence on the energy gap. In this study, we discuss the specified passivation with different passivants and generate the relationship between the passivation and the energy gap of Si nano-clusters. Based on the passivation of the $Si_{47}$ core nano-cluster, it is divided into three different passivations: the fully passivated $Si_{47}X_{24}Y_{36}$ (including the inner and outer layer passivations), the inner layer passivation $Si_{47}X_{24}H_{36}$ (24 inner layer with one passivant, indicated as the red sphere in Fig. 1), and the outer layer passivation $Si_{47}H_{24}Y_{36}$ (12 outer layer Si with three passivants, indicated as the green spheres in Fig. 1). The inner and outer layer passivations are 5.5 and 7.5 Å from the center of $Si_{47}$ core nano-cluster, respectively.

Table 1 shows the calculated HOMO, LUMO and energy gap for the fully passivated $Si_{47}X_{60}$ nano-cluster with various passivants. In order to determine the passivation effect on the surface of $Si_{47}X_{60}$ nano-clusters, the alkyl ($–CH_3$, and $–C_2H_5$) oxide (–OH, and $–OCH_3$), nitride ($–NH_2$), sulfide (–SH), halogenated (–F and Cl) and $–SiH_3$ passivants were used for comparison. According to our previous study, the calculated HOMO energy was found to relate to the formation of a dipole on the surface of silicon nano-cluster. The tendency of forming a polar bond is characterized by the electronegativity. Si atom (1.9) has lower electronegativity than those of H (2.1), C (2.5), N (3.0), O (3.5), F (4.0) and Cl (3.2) atoms, thus, all of passivants used in this paper are electron-withdrawing groups with respect to the Si atom, but the dipole forming passivants are