Abstract. Two-, three- and five-dimer cluster models were used to elucidate the structures of small models of the Si(100) surface. Because surface dimers have been shown to have significant singlet diradical character, multi-reference wave functions were used in order to obtain a reliable description of such species. CASSCF (complete active space SCF) geometry optimizations find symmetric structures to be the global minima, with no local minima at buckled structures. This result for the three- and five-dimer clusters implies that dimer–dimer repulsions are not sufficient to cause buckling of these species. These results are in contrast with most previous calculations that predict buckling of surface dimers. The effect of the dynamic part of the electron correlation on surface structure was assessed by performing single point multi-reference perturbation theory (MRMP) calculations along the three buckling normal modes of the three-dimer cluster. Although dynamic correlation effects are found to “soften” motion along the buckling coordinates, the surface remains unbuckled when such correlation effects are included. The MRMP results are in qualitative agreement with the CASSCF predictions. The implications of these results with regard to the structure of the Si(100) surface are discussed.

Keywords: MCSCF – Si (100) – Clusters

Introduction

The Si(100) surface has been the subject of many experimental and theoretical studies [1, 2, 3, 4, 5, 6, 7] due to its importance in the semiconductor industry. These studies have revealed many aspects of the silicon surface including the fact that the Si(100) surface reconstructs, after being cleaved, to form dimers. The experimental bond length of the dimer suggests that the Si-Si bonding in this species is intermediate between those that are typical of a single and double bond. Several computational studies have demonstrated that these dimers have significant diradical character with ~1/3 of an electron occupying the lowest unoccupied molecular orbital (LUMO) in each dimer. This suggests that single-determinant wave functions (e.g. Hartree–Fock and most of the popular implementations of density functional theory (DFT)) are unlikely to provide a reliable description of the structure and bonding of such species, since they cannot account for the significant electron density in the dimer antibonding orbitals. It is therefore essential, when using clusters to describe the Si(100) surface, to use a proper wave function as a starting point.

There are several intriguing questions regarding the Si(100) surface:

i. Are the Si(100) surface dimers buckled or symmetric?
ii. Does dynamic correlation play an important qualitative role in determining the structure of the surface?
iii. Do dimer-dimer interactions affect the structure of the surface?

The physical nature of the Si(100) surface has important implications with regard the underlying origins of reaction mechanisms on the surface, since a physically buckled surface could result in different chemical environments for the two Si atoms in a dimer.

Even those theoretical studies that predict surface buckling give a relatively small stabilization (~0.1 eV per dimer) due to the buckling. Thus, it is clear from the outset that a carefully balanced treatment of electron correlation effects is necessary to definitively resolve the question of whether the surface is buckled.

Electron correlation energy is typically defined as the difference between the “exact” non-relativistic energy and the energy at the Hartree–Fock limit, achieved by using an infinite basis set. Non-dynamic (or internal) electron correlation refers to the electron correlation
that can be recovered by adding flexibility to the wave function, when there are near degeneracies or when the gap between HOMO and LUMO is small enough to permit configurational mixing. The MCSCF (multi-configurational SCF) [8] method is typically used for recovering the non-dynamic electron correlation. The remaining electron correlation is called dynamic correlation, even though there is no rigorous way to separate these two effects. Many body perturbation theory and configuration interaction (CI) are the most common methods to account for dynamic correlation. It can be argued that density functional theory also accounts for some dynamic correlation, since most modern functionals include a correlation component. It is difficult, however, to assess this effect quantitatively, particularly for functionals that contain parameters that are fitted to experimental results. Multi-reference perturbation theory (MRMP) is a commonly used method for including both dynamic and non-dynamic correlation effects.

Redondo and Goddard[9] were the first to show that, because surface dimers exhibit partial di-radical character (significant population of the LUMO), a single reference wave function is not sufficient for an adequate description of the Si(100) dimerized surface, and a multi-reference (e.g. MCSCF) wave function is necessary. A simple way to determine whether or not a system needs a multi-reference wave function is to examine the restricted Hartree-Fock (RHF) orbital energies. When the LUMO orbital energy is negative, the system is frequently multi-configurational and needs a non-dynamic electron correlation correction. Indeed, this is the case for the clusters that are typically used to represent the reconstructed Si(100) surface. Recent studies [9, 10, 11, 12] using cluster models and MCSCF-based methods have predicted that the Si(100) surface dimers are symmetric (or ‘unbuckled’), while single reference methods such as Hartree–Fock or density functional theory (DFT) [13, 14, 15, 16, 17] have generally predicted the only potential energy minimum to be a buckled structure.

Recently, Hess and Doren [13] argued that dynamic correlation plays a significant role in determining the structure of small clusters used to represent the surface and even alters the relative stabilities of buckled and symmetric structures to favor a buckled structure. They optimized a Si$_6$H$_{12}$ single dimer cluster with both DFT and complete active space (CAS) SCF including four electrons in four orbitals, CASSCF(4,4), methods. They found that DFT optimization gives a buckled structure, while CASSCF(4,4) optimization predicts a symmetric (C$_{2v}$) structure as a minimum. Single point MRMP calculations at both the DFT-optimized buckled structure and the CASSCF-optimized symmetric structure predicted the buckled structure to be slightly lower (0.9 kcal/mol) in energy than the symmetric one. Based on these single point MRMP calculations, they concluded that the structure of Si$_6$H$_{12}$ is buckled and dynamic correlation plays an important role in determining the structure. Of course, a comparison of energies of two different geometries that were obtained from different levels of theory may not be reliable, especially where the energy difference is quite small.

Ideally, one should optimize the structure of the clusters at the MRMP level of theory in order to include the effects of both dynamic and non-dynamic correlation on the predicted structure. Unfortunately, MRMP analytic gradients are not yet available, and numerical geometry optimizations of clusters of the size of interest here would be computationally too demanding. One alternative is to distort the cluster along the CASSCF buckling mode(s) and to perform MRMP calculations along the resulting potential energy curve. Following the procedure for the single dimer Si$_6$H$_{12}$ cluster, Gordon, Shoemaker, and Burggraf found that the MRMP energy increases monotonically along the buckling mode, qualitatively in agreement with CASSCF results. They also performed a single reference MP2 geometry optimization starting from both symmetric and buckled structures, and found only a symmetric dimer structure. They therefore concluded that the Si(100) surface is symmetric within a Si$_6$H$_{12}$ cluster model at 0 K, and that dynamic correlation does not have a qualitatively important effect on the predicted geometry. Although this cluster model is clearly too small to provide a realistic description of the Si(100) surface, these results clearly demonstrate that density functional methods are biased toward buckled structures.

It has also been suggested [14, 15, 16] that interactions between adjacent dimers in the same row may have a stabilizing effect on the buckled structure. These DFT calculations indicate that a buckled structure gains extra stability due to dimer–dimer interactions (one Si atom of a dimer is pointing up and the other pointing down in one dimer, with adjacent dimers buckled in the opposite direction). This stabilization has been estimated to be 1.5–3 kcal/mol per dimer in a two-dimer model and 3.5–4.5 kcal/mol in a three-dimer cluster model. On the contrary, recent multi-reference CI calculations using a two-dimer cluster model [10] still predict a symmetric structure as a minimum, implying that dimer-dimer interactions may be over-estimated in DFT calculations.

One may also question whether a cluster of any computationally tractable size can adequately model the Si(100) surface and if so, what an appropriate cluster size might be? An alternative approach, using slab models and periodic boundary conditions, is often considered to be more representative of the surface site interactions than cluster models, as long as the supercells of the slab models maintain a reasonable periodicity. A recent DFT study on H$_2$ desorption from the Si(100) surface using both slab and cluster models [18] has found that the reaction and activation energy for H$_2$ desorption for the monohydride of the Si(100) surface calculated using a three-dimer cluster are close to the results predicted by the slab model.

To the best of our knowledge, clusters containing more than two dimers have not yet been studied using the combined MCSCF and MRMP methods. The present work examines the structure of the surface