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Comment on "Effect on Surface Reconstruction on Stability and Reactivity of Si Clusters"

by

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For Si_{45} we find two similar structures which possess full T_d symmetry of lower energy than Kaxiras'.

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Comment on "Effect on surface reconstruction on stability and reactivity of Si clusters" by Efthimios Kaxiras, Phys. Rev. Lett. 64, 551 (1990).

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The structure and properties of medium-size clusters, few tens of atoms, has been a subject of several recent theoretical and experimental studies.[1-3] In particular, the question of the transition from highly-coordinated structures, typical for small clusters, to tetra-coordinated diamond structures, which is the bulk limit, has attracted much interest and created discussions in the literature,[4] although mainly based on theoretical arguments.

Kaxiras' contribution[1] to this discussion provides an interesting and well-motivated model for Si_{33} and Si_{45} clusters with a tetra-coordinated core and a bulk silicon-like reconstructed surface structure, thus suggesting that the transition region might start already at a cluster size of about 40 atoms. While this may be the case, we want to draw attention to our recent results for Si_{45} clusters, which suggest that the most stable isomers have still higher coordination numbers (from 4.0 to 4.2) than suggested by Kaxiras (about 3.1). Indeed, using classical potentials including Kaxiras', we have found two similar structures, denoted as T1 and T2, which possess full T_d symmetry of lower energy than Kaxiras'.

We have used a variation of Tomanek and Schlüter's tight-binding model[2] to check several possible isomers of Si_{45}. This was chosen because it has previously been carefully calibrated against the Si_{10} cluster, with results matching both *ab initio* and experimental data. We have correlated the tight-binding data with results from two classical potentials, including Kaxiras'. We find that the stability of a given isomer depends on which classical model we use, but that in general all methods qualitatively agree. In the absence of more definitive experimental data concerning Si_{45} against which the classical potentials can be calibrated, we believe that the tight-binding method is the most accurate available. The different structures are motivated by various experimental data,[2] and the results from these calculations are shown in Table 1.

Table 1. Cohesion energy per atom (in eV) for Si_{45} isomers: "Kax" is from Ref. 1, "Benz" corresponds to seven stacked benzene-like rings with a three-atom cap,[2] "Naph" to four stacked naphthalene-like rings and a five-atom cap,[2] and T1 and T2 are the two new tetrahedral structures described in the text.

Isomer: Method/Potential	Kax	Benz	Naph	T1	T2
Kaxiras[5]	3.9	3.8	4.0	4.1	unstable
Tersoff[5]	4.0	4.0	4.3	unstable	4.5
Tight-Binding[2]	3.4	3.6	3.6	3.9	4.0

The T1 and T2 structures are closely related. Like the Kaxiras structure, both consist of a tetrahedrally-coordinated central atom, which is in a bulk-like environment. However, the outer atoms of the cluster are not similar to a reconstructed surface. The outermost atom is hexa-coordinated, and further, the clusters consist in part of six-membered rings arranged in a tetrahedral pattern around the center. One can think of the isomers as being a bulk atom surrounded by reconstructed clusters rather than a reconstructed surface.

We suggest that these structures can account for at least some of the complicated experimental data, i.e., the relative stability of the cluster compared with the bulk surface.[3] Further, all computational methods are consistent in that the T_d structures are of lowest energy.

Full results of our investigation and a discussion will be published elsewhere. DAJ acknowledges support from the American Chemical Society-Petroleum Research Fund, Research Corporation and SUNY Research Foundation, and TFG acknowledges support by the Office of Naval Research and the National Science Foundation under Grant CHE-9016789.

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