

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

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 tetraordinated 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's contribution¹ to this discussion provides an interesting and well-motivated model for Si₃₃ and Si₄₅ clusters with a tetraordinated 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 Si₄₅ 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's, we have found two similar structures, denoted as *T1* and *T2*, which possess full *T_d* symmetry of lower energy than Kaxiras's.

We have used a variation of Tománek and Schlüter's tight-binding model² to check several possible isomers of Si₄₅. This was chosen because it has previously been carefully calibrated against the Si₁₀ 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's. 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 Si₄₅ 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 I.

The *T1* and *T2* structures are closely related. Like the Kaxiras structure, both consist of a tetrahedrally coordinated central atom, which is in a bulklike environment. However, the outer atoms of the cluster are not similar to a reconstructed surface. The outermost atom is hexacoordinated, 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.

TABLE I. Cohesion energy per atom (in eV) for Si₄₅ isomers: "Kax" is from Ref. 1, "Benz" corresponds to seven stacked benzenelike rings with a three-atom cap (Ref. 2), "Naph" corresponds to four stacked naphthalenelike rings and a five-atom cap (Ref. 2), and *T1* and *T2* are the two new tetrahedral structures described in the text.

Isomer	Method/Potential		
	Kaxiras and Pandey ^a	Tersoff ^b	Tight binding ^c
Kax	3.9	4.0	3.4
Benz	3.8	4.0	3.6
Naph	4.0	4.3	3.6
<i>T1</i>	4.1	Unstable	3.9
<i>T2</i>	Unstable	4.5	4.0

^aKaxiras and Pandey (Ref. 5).

^bTersoff (Ref. 5).

^cReference 2.

D.A.J. acknowledges support from the American Chemical Society-Petroleum Research Fund, Research Corporation, and the State University of New York Research Foundation, and T.F.G. acknowledges support from the Office of Naval Research and the National Science Foundation under Grant No. CHE-9016789.

Brian L. Swift,^(a) Daniel A. Jelski,^(b)
and Donald E. Higgs

Department of Chemistry
State University of New York
College at Fredonia
Fredonia, New York 14063

Tapio T. Rantala^(c) and Thomas F. George

Center for Electronic and Electro-optic Materials
Departments of Chemistry and Physics and Astronomy
239 Fronczak Hall, State University of New York at Buffalo
Buffalo, New York 14260

Received 10 September 1990

PACS numbers: 61.50.Lt, 36.40.+d

^(a)Present address: Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY 14456.

^(b)Author to whom correspondence should be addressed.

^(c)Present address: Department of Physics, University of Oulu, SF-90570 Oulu, Finland.

¹E. Kaxiras, Phys. Rev. Lett. **64**, 551 (1990); Chem. Phys. Lett. **163**, 323 (1989).

²T. T. Rantala, D. A. Jelski, and T. F. George, J. Cluster Sci. **1**, 189 (1990), and references therein; D. Tománek and M. A. Schlüter, Phys. Rev. B **36**, 1208 (1987).

³M. F. Jarrold, U. Ray, and K. M. Creegan, J. Chem. Phys. **93**, 224 (1990); S. Maruyama, L. R. Andersson, and R. E. Smalley, J. Chem. Phys. (to be published), and references therein.

⁴J. R. Chelikowski and J. C. Phillips, Phys. Rev. Lett. **63**, 1653 (1989), and references therein.

⁵The classical potentials are from E. Kaxiras and K. C. Pandey, Phys. Rev. B **38**, 12736 (1988); J. Tersoff, Phys. Rev. B **37**, 6991 (1988).