Comment on "Observation and Structural Determination of $(\sqrt{3}\times\sqrt{3})R30°$ Reconstruction of the Si(111) Surface"

In a recent Letter,[1] Fan, Ignatiev, Huang, and Tong (FIHT) reported a new metastable structure with $\sqrt{3}\times\sqrt{3}$ periodicity for the Si(111) surface. Their LEED-*IV* analysis suggested a vacancy model with one Si vacancy per $\sqrt{3}\times\sqrt{3}$ unit cell. There is a large compression of the top double-layer spacing (from an ideal value of 0.78 to 0.28 Å) and the atoms in the second layer have lateral displacements of 0.65 Å towards the position of the vacancy. The *IV* spectra of the clean and Ag-deposited $\sqrt{3}\times\sqrt{3}$ surfaces are very similar, which lead FIHT to conclude that the observed structure of Ag/Si(111) is actually due to that of the Si-vacancy structure stabilized by adsorbed Ag adatoms with no long-range order.

We have performed first-principles total-energy calculations to study the structural and electronic properties of the $\sqrt{3}\times\sqrt{3}$ Si-vacancy model. The calculations are done within the local-density-functional formalism[2] (with Wigner local exchange and correlation) using the pseudopotential-plane-wave method.[3] A plane-wave cutoff of 10.5 Ry is used. The Si surface is modeled by an eight-layer slab in a supercell geometry. By fully relaxing the system to equilibrium within the constraints of the Si-vacancy model, we found two zero-force configurations for the Si-vacancy model. One has an expanded top double-layer spacing (1.32 Å) and the Si atoms in the second layer are displaced laterally by 0.72 Å away from the vacancy. Another equilibrium position has a substantially compressed top double-layer spacing (0.05 Å) and the Si atoms in the second layer are displaced by 0.33 Å laterally towards the vacancy. The "compressed bilayer" geometry has lower surface energy [0.27 $J\,m^{-2}$ or 0.22 eV/(surface site)[4]] than the "expanded bilayer" geometry. The lower-energy compressed configuration has structural parameters essentially in agreement with the those deduced from LEED-*IV* analysis, although the theoretical results have a larger compression and smaller lateral displacement. The theoretical nearest-neighbor Si-Si bond length between top- and second-layer atoms is 2.4 Å while that deduced from *IV* analysis[1] is 2.62 Å. As the top layer virtually collapses onto the second layer, the bonding configuration should be largely sp^2 (as pointed out in Ref. 1), which has an ideal bond length of 2.25 Å in a perfect graphitic structure.[5] The vacancies on the surface allow lateral displacements of second-layer Si atoms and hence longer bond lengths, but the 2.62-Å bond length deduced from experiment seems to be a bit too long. We have also carried out extensive calculations[6] on the structural properties of $\sqrt{3}\times\sqrt{3}$ Ag/Si(111). For almost all the models considered, the nearest-neighbor Ag-Si bond length falls between 2.6 and 2.7 Å.

To assess the relative stability of the Si-vacancy model, we have calculated the surface energy for both the $\sqrt{3}\times\sqrt{3}$ Si-vacancy surface and an ideal unrelaxed (1×1) surface. The fully relaxed $\sqrt{3}\times\sqrt{3}$ model has 0.18 $J\,m^{-2}$ or 0.14 eV/(surface site) higher surface energy (less stable) than the unrelaxed (1×1) surface. In view of its high surface energy, we should also consider the possibility of the existence of adatoms of other species which may serve to stabilize the $\sqrt{3}\times\sqrt{3}$ surface.

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[2]See, e.g., *Theory of the Inhomogeneous Electron Gas*, edited by N. H. March and S. Lundqvist (Plenum, New York, 1983).

[3]See, e.g., M. L. Cohen and S. G. Louie, Annu. Rev. Phys. Chem. **35**, 537 (1984).

[4]The conversion here assumes that each surface site, including the vacancy site, occupies an area of 12.767 34 $Å^2$.

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