Si(100) surface states: A success for the (2 × 1) asymmetric dimer model

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Chadi's asymmetric dimer model of the Si(100)-(2 × 1) surface reconstruction has been reported to yield surface-state dispersion curves in serious disagreement with angle-resolved photoemission measurements. We find that this disagreement is removed when the calculations are performed with an improved sp^3s^* model of the electronic structure. The asymmetric dimer model thus appears to be quite compatible with experiment.

Although Si(100)-(2 × 1) is one of the best studied surfaces in semiconductor physics, there is still disagreement concerning its geometrical structure. Over the years, numerous models have been proposed.[1–6] The most appealing of these, in several respects, is the asymmetric dimer model,[6] in which adjacent rows of Si atoms relax toward each other in pairs. Recently, several arguments against this model have been presented,[7,8] the most serious being the disagreement between angle-resolved photoemission measurements of surface-state dispersion curves[9,10] and theoretical calculations of these curves based upon conventional models of the electronic structure as applied to the asymmetric dimer geometry.[6,11] Here we report calculations of surface-state dispersion curves with the improved sp^3s^* model of the electronic structure[12,13]; we find that our results for the (2 × 1) asymmetric dimer model of the Si(100) surface are in good agreement with the measurements.

The sp^3s^* empirical nearest-neighbor tight-binding model of Vogl *et al.*[12] has an extra excited s^* basis orbital in addition to the usual sp^3 basis at each atomic site; this orbital permits a better treatment of the bulk Si conduction bands which, without it, would not exhibit an indirect fundamental gap. Principally, s^* represents the effect of higher-lying atomic states that tend to push some of the states in the solid down to lower energy. The bulk bands, especially those near the fundamental gap, are thus made more realistic,[12] and one might expect the same to be true of the surface levels.

Our results are shown in Fig. 1, together with the measured dispersion curves of Himpsel and Eastman[9] and of Uhrberg *et al.*[10] In previous calculations for another surface, Si(111)-(2 × 1), Buisson *et al.*[14] found that the sp^3s^* model yielded a gap between occupied and unoccupied surface states in good agreement with experiment, but that the absolute surface-state energies appeared to be too high by about 0.5 eV. [It is interesting that the self-consistent pseudopotential calculations for both the (111) (Ref. 15) and (100) (Ref. 11) surfaces also yielded higher energies than the measurements.] For this reason, we have adjusted our calculated surface-state energies for the (100)-(2 × 1) surface downward by 0.5 eV in displaying them to enhance the comparison between theory and experiment with regard to bandwidths and details of the dispersion curves. It can be seen that the agreement is remarkably good.

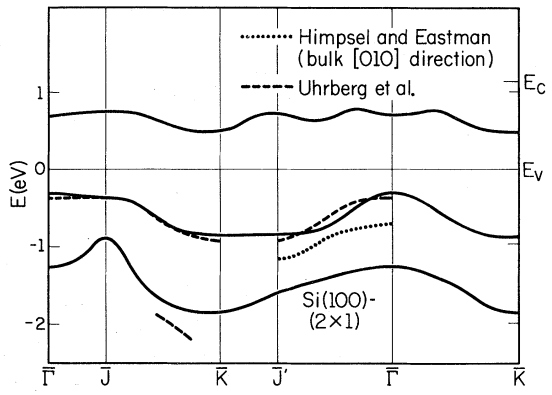

FIG. 1. Dispersion curves for surface states and surface resonances at the (100)-(2 × 1) surface of Si. The energy E is shown as a function of the planar wave vector $\bar{k}$ around the symmetry lines of the surface Brillouin zone (see Fig. 2). Solid lines represent results of the present calculations, shifted by 0.5 eV, dashed lines the measurements of Ref. 10; and the dotted line the measurements of Ref. 9, which were taken from $\bar{\Gamma}$ to $\bar{J}'$ along the [010] direction, rather than along the segment $\bar{\Gamma}$ to $\bar{J}'$ shown in Fig. 2. (The second curve displayed near $\bar{J}'$ in Ref. 9 is not shown here, since it may be due to umklapp processes.[7,10] The [010] data of Ref. 10 are consistent with those of Ref. 9.) E_v and E_c are the Si valence- and conduction-band edges.

Mönch *et al.*[16] have observed transitions from the valence band into a band of empty surface states at the Si(100)-(2 × 1) surface. Their measured gap (between the bulk valence-band maximum and the surface-band minimum) is about 0.6 eV. Our calculated gap for the (2 × 1) asymmetric dimer model is about 1.0 eV (or 0.5 eV after the downward shift used to display the results in Fig. 1), in quite satisfactory agreement with the measurement.

Chadi has given four arguments against the (2 × 1) asymmetric dimer model: The first is that calculations yield lower total energies for more complicated reconstructions; but the energy differences are less than 0.1 eV per atom, and there are considerable uncertainties in current total energy calculations. (Also, the lowest-energy structure is often not the only one observed.) Second, low-energy electron and He-atom diffraction experiments provide evidence for more complicated reconstructions; such experiments appear to imply that the (2 × 1) structure coexists with other structures.[2,17–19] Third, calculations for the (2 × 1) asymmetric dimer model yield only one surface-state band near the valence-band edge, and two appeared to have been observed experimentally.[9] In more recent experiments,[10] however, only one band is observed along the actual symmetry lines of the surface Brillouin zone; the apparent observation of two bands along the [010] diagonal in Refs. 9 and 10 may be attributable to umklapp processes stimulated by other, coexisting, structures.[10]

The one remaining argument (and the strongest one) was the substantial disagreement between the calculated and measured surface-state dispersion curves: The measurements yield a surface-state bandwidth of 0.5 to 0.65 eV,[9,10] and each of the previous theoretical calculations for the asymmetric dimer model had yielded a value about twice this large.

The present calculation, which employs the original (2 × 1) asymmetric dimer model together with the improved sp^3s^* model of the bulk electronic structure, gives dispersion curves that are considerably more satisfactory. As can be seen in Fig. 1, both the 0.65-eV theoretical bandwidth and the detailed variation with planar wave vector $\bar{k}$ are in very good agreement with the measurements. We conclude that the photoemission results support, rather than contradict, the hypothesis of an asymmetric dimer relaxation.

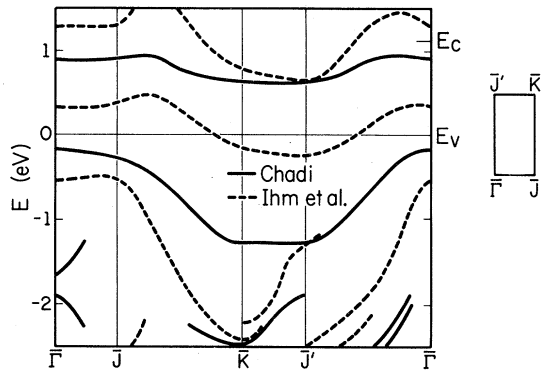

FIG. 2. Calculated dispersion curves of Refs. 6 and 11. Note the relatively large dispersion of the surface band near the valence-band edge.

When the present results are added to the experimental observations, it appears likely that there is a primary (2 × 1) reconstruction of the Si(100) surface which is well described by Chadi's asymmetric dimer geometry, but that some variations of this reconstruction may occur as well.

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