Kink mechanism for formation of the Si(111)-(2×1) reconstructed surface

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An atomic mechanism is proposed to account for the generation of the (2×1) reconstruction of the (111) surface of silicon on cleavage at low temperature. The π-bonded chain model is assumed for the reconstruction. By reducing the dimensionality of the phase transformation, the proposed kink mechanism provides a low-energy pathway for the reconstruction. The energy gain due to surface reconstruction must be considered in theories of lattice trapping during fracture.

The (2×1) reconstruction of the Si(111) surface can only be generated by cleavage. Since it is now generally accepted that crack propagation in brittle materials is controlled by the motion of kinks at the crack tip,[1] an intimate relationship between the atomic structure of the kink and that of the (2×1) silicon reconstruction is suggested. In this Brief Report, an atomic model for such a kink is suggested which provides a low-energy path for creation of the π-bonded chain (2×1) reconstruction. This metastable surface is readily transformed (irreversibly) to the stable (7×7) surface by annealing at 600 °C.

The energy balance, which controls crack growth, between strain-energy release and the work required to generate fresh internal surfaces must take account of any energy gain due to surface reconstruction. The energy barrier to kink motion determines the range of applied stresses over which a crack neither grows nor heals, and this in turn depends on the atomic structure of the kink. In the study of crack creep at higher temperature, kink velocity (and hence crack velocity) depends on the kink migration and nucleation energy (and applied stress), and so on the details of the kink's atomic structure. For all these reasons, and in view of the large amount of experimental and theoretical work which has been done on this system, the atomic structure of kinks at crack tips in silicon is a matter of some importance in both surface science and fracture mechanics. The observation of the (2×1) reconstruction after cleavage at 4 K (Ref. 2) allows thermal effects to be neglected, greatly simplifying calculations. The generation of dislocations, which becomes important above the brittle-ductile transition in silicon[3] at about 550 °C, is not considered in the following model.

Research in several fields, including fracture mechanics, surface physics, and dislocation kink theory is relevant. Thomson, Hsieh, and Rana[4] were the first to consider atomistic energy barriers to two-dimensional crack propagation, which they termed "lattice trapping." The effect is similar to the Peierls barrier to dislocation motion.[1] A general review of the physics of fracture has recently been given by Thomson.[5] For three-dimensional cracks containing kinks, Kanninen and Gehlen have shown that a kink increases the mobility of cracks in iron.[6] By representing a double kink at a crack tip by a set of double jogs on dislocations (used to simulate a mode-1 crack), Lin and Hirth[7] have estimated the activation energy at low loads for double-kink formation using the methods of continuum elasticity. In a series of papers, atomistic calculations for cracks in silicon have been used by Sinclair[8] to investigate the dependence of kink migration energy on the form of the interatomic force law used, and to discuss the implications of thermally activated kink pair nucleation at high temperatures. A considerable body of literature exists on the temperature- and stress-dependent motion of kinks on dislocations in semiconductors (see Jones[9] for a recent review). Atomic models have been proposed for kinks on the commonly observed partial dislocations in silicon.[10] Here a fair body of evidence (including theoretical[11] and experimental[12] work) suggests that the additional half-plane which constitutes the 30° partial dislocation in silicon terminates between the narrowly spaced (111) "glide" planes, rather than the more widely spaced "shuffle" planes. Reconstructions along the cores have also been considered.[12] The direct observation of kinks on dislocations by atomic resolution electron microscopy (using a projection normal to the dislocation line) has been attempted.[13] In surface science, two reviews have recently appeared which discuss the Si(111)-(2×1) surface extensively.[14,15] Recent experimental work by a variety of techniques (angle-resolved photoemission spectroscopy,[16] ion scattering,[17] scanning tunneling microscopy[18,19]) appears to support a model similar to that proposed by Pandey,[20] containing π-bonded chains along [110] and forming the shorter axis of the (2×1) cell. It has been found that the direction of cleavage (mode 1) is strongly correlated with the orientation of the domains formed.[21] These results are consistent with the idea that the π-bonded chains run parallel to the crack line.

Figure 1 shows a projection of the silicon structure down [111]. The internal (111) surfaces of the crack lie in the plane of the page, above the kinked crack line *YUX*. Double kinks are supposed to nucleate at *O* and propagate outward as shown by the arrows, leaving (2×1) reconstructed material behind on both internal surfaces, as the crack line advances down the page. Rebonding of atoms *B* and *D* (see below) advances the kink from 1 to 2. By reducing the dimensionality of the phase transforma-

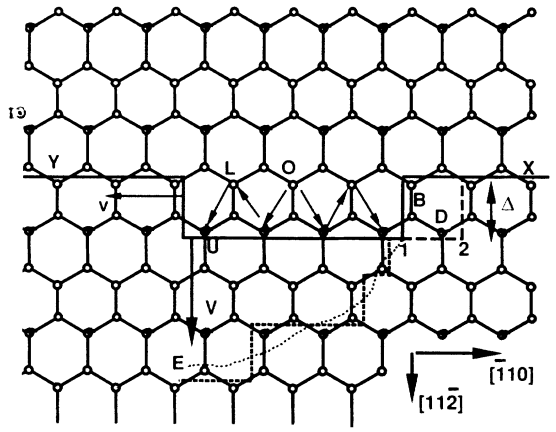

FIG. 1. [111] projection of the silicon crystal structure, showing a crack line *YUX* and kinks moving outward with velocity v imparting a forward velocity V to the crack line. The internal (111) surfaces of the crack lie in the plane of the page above the crack line. Bond D is normal to the page (see Fig. 2).

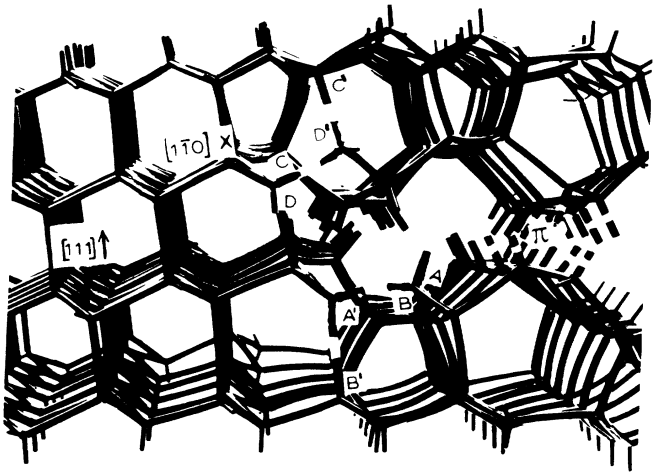

FIG. 2. Three-dimensional model, viewed along [1$\bar{1}$0] of Fig. 1, showing π-bonded chains and kinks on the upper (C,D) and lower (A,B) internal (111) surfaces of a crack in silicon. Five- and seven member rings can be seen in the planes behind the kinks on both internal surfaces.

tion from that of a line (the crack line) to a "point" (the kink), this process requires less energy than the coherent advance of the entire crack line and will therefore be preferred. Ahead of the crack a region of strained "shuffle" bonds will occur, approaching the Si(111)-(1×1) structure. A wide kink (width measured along [1$\bar{1}$0]) may occur, corresponding to a gradual twist or rotation of the bonds labeled in Fig. 2 about [1$\bar{1}$0], however calculations[8] suggest that kinks are rather compact at room temperature in silicon. The crack velocity V depends on the kink velocity v (both shown in Fig. 1) and on the nucleation rate.[1] If the crack is assumed to lie between the widely spaced shuffle planes (as shown in Fig. 2), the breakage of a single bond at L (Fig. 1) reconstructs the lower surface, while breaking bond U reconstructs the upper surface. A continuously curved crack (shown dotted at E) may be approximated at the atomic level by a number of kinked segments (shown dashed).

Figure 2 shows a three-dimensional model, viewed along the crack line [1$\bar{1}$0], while Fig. 3 shows a simplified [1$\bar{1}$0] projection for the lower internal surface. The same bond B can be identified in all three figures. In Fig. 2, the banded bonds labeled π represent the π-bonded chains. Alternating five- and seven-member rings are seen at the termination of the (111) internal surfaces. A kink is shown in the foremost plane of atoms in Fig. 2 parallel to the page. The kink is advancing out of the page. This occurs by the rebonding of bond A to A' and B to B' for the lower surface (and D to D' and C to C' for the upper). In detail, in Figs. 2 and 3, we imagine the bonds B—A' and B'—A' to be broken. Then A rebounds with A' and B with B'. Bond P (in Fig. 3) contributes to the π-bonded chain. This process generates the alternating five- and seven-member rings, as shown. A similar process occurs for the upper surface. This is similar to the mechanism described in the pseudopotential total-energy calculations of Northrup and Cohen[22] for the buckled to chain-model reconstruction. The second-nearest-neighbor environment is, however, different for the kink. (Northrup and Cohen's calculations refer to the coherent phase transformation of an infinite periodic surface, without the mediation of defects.) We note the misregistry of the fivefold and sevenfold rings across the crack.

In considering the energetics of a pathway from the buckling model[14] to the π-bonded chain model, an energy barrier of 0.03 eV per surface atom was calculated,[22] which is available thermally at room temperature. For the kink described here, additional energy (supplied by external stresses) is required to break bonds such as A (Fig. 2) across the crack. The observed cleavage energy is about 1 eV per surface atom, much less than 2.3 eV, the calculated bond strength of bulk silicon. A total reduction in energy of about 0.2 eV is found in going from the (1×1) to (2×1) chain-model reconstruction.[22] An accurate calculation of the kink mobility and nucleation energies by pseudopotential methods would appear to require prohibitively large amounts of computing space and time. In addition, the periodic boundary conditions (requiring two cracks and four kinks) used for defects[11] must be combined with the flexible boundary conditions required to represent the externally applied stress,[8] and this requires a very large supercell. The recent potential due to

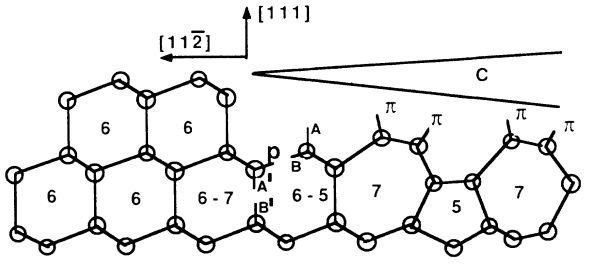

FIG. 3. Schematic representation of Fig. 2, showing a [1$\bar{1}$0] projection of a crack C and kink B generating (2×1) reconstruction of the lower internal surface. Bond B can be identified in all three figures.

Tersoff[23] may, however, be useful for investigating the important questions of the kink width and the dependence of kink energy on applied stress.

In Fig. 2, atom A may, as an alternative (depending on applied stresses), rebond with either of its other two nearest neighbors instead of A'. The result, if propagated, will produce a new domain of the (2×1) surface structure, rotated by 60°. This is consistent with the observation of multiple domains on single-crystal cleaved silicon, which may be nucleated independently as a result of crack branching[5] or by multiple cracks originating at different surface flaws. In addition, the pinning of cracks at defects (such as emerging bulk dislocations), cleavage steps, and Wallner lines[24] (due to the interaction of the stress wave reflected from boundaries and defects with the crack) may all be important in deflecting the kink's direction.

The emission of dislocation loops from crack tips in silicon has been observed at high temperatures by electron microscopy,[25] and is also facilitated by kinks. Thus calculations of the relative magnitude of the dislocation and crack-tip kink energies are important for our understanding of the ductile-brittle transition[26,3] in this material. We note that, if the Pandey model is accepted, the crack kink is of the shuffle type, while the dislocation kink (which is thermally activated at high temperatures) is believed to be of the glide type. By analogy with the theory of charged kink motion on dislocations in silicon,[27] effects due to doping and optical illumination on the ductile-brittle transition temperature might be expected.

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