result should be brought into better agreement with experiment.

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[16] B. Vinter, to be published.

Photoemission Measurements of Step-Dependent Surface States on Cleaved Silicon (111)

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Ultraviolet photoemission spectroscopy has been used to measure surface states on cleaved silicon with varying step-atom densities determined by low-energy-electron diffraction. For high step densities (~ 10%) a new surface-state peak is found at an energy 0.4 eV higher than the main surface-state peak. These measurements are the first demonstration that surface-state photoemission spectra depend strongly on cleavage steps.

Intrinsic surface states have been observed in several laboratories by ultraviolet photoelectron spectroscopy (UPS) for cleaved silicon, germanium, and gallium arsenide as well as for annealed silicon and germanium surfaces.[1-5] It is somewhat surprising that most results on the same surface obtained by different workers tend to agree since the surface morphology may not be reproduced.[4-7] An exception to this rule are UPS experiments[2] on cleaved gallium arsenide (110) where it has been suggested that surface steps on poor-quality cleavages may play an important role in determining the surface-state distribution.[4,5] We report in this paper the first experimental correlation of surface steps observed by low-energy-electron diffraction (LEED) and UPS measurements of surface-state energy distributions. The present measurements are restricted to the (111) cleavage faces of silicon but qualitatively similar results should be obtained on other cleaved semiconductor surfaces.[6-8]

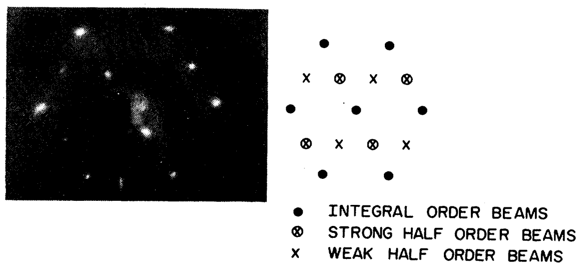
The importance of surface steps on semiconductor surfaces has been recognized by a number of authors. Henzler has discussed LEED techniques for determining step heights and terrace widths.[6-8] Ibach and co-workers have determined the step dependence of oxygen chemisorption on cleaved silicon surfaces.[9] Since detailed studies of surface states[1-3] have been made on both annealed and cleaved silicon surfaces, this material seems to be most appropriate for studying the correlation of surface states and surface steps. We find that both dangling-bond surface states and back-bond surface states depend on the step density. Some additional features of dangling-bond states near the band gap of high-step-density cleaved surfaces are found to be similar to previous results on annealed (111) surfaces.[3]

Single crystals of boron-doped Si were used with carrier concentrations in the range 10^{14}–10^{15} cm^{-3}. The samples were oriented with (111) surfaces parallel to notches cut in a bar of $5 \times 15 \times 70$ mm^3 dimensions which allowed multiple cleavages. Experiments were performed in a stainless-steel ultrahigh-vacuum chamber with a base pressure of $\sim 5\times10^{-11}$ Torr. Hydrogen could be introduced from a high-purity flask by a standard leak valve. A polycrystalline tungsten ribbon of dimensions $6\times20\times0.2$ mm^3 was heated to ~2000°K to dissociate the H_2 gas into H atoms. This proved to be a factor of $\sim 10^2$ more efficient than the shielded filament of an ion gun used in previous UPS studies of hydrogen adsorption on silicon surfaces.[10] A PHI 15-250 double-pass cylindrical-mirror electron-energy analyzer[11] was used with a He resonance lamp for UPS measurements. Other details of the multiple-technique apparatus have been previously described.[12]

Typical experimental LEED observations are shown in Fig. 1 for (a) low-step-density and (b) high-step-density surfaces at 40-eV primary energy. Using the methods discussed by Henzler[6,8] we verified that the average step height is one double layer (3.14 Å) and that the fractional density of step-edge atoms is $(3\pm2)\%$ for the low-step-density surface [Fig. 1(a)] and $(10\pm2)\%$ for the high-step-density surface [Fig. 1(b)]. The low-step-density surface has two domain

CLEAVED SILICON 2 X 1

(a) LOW STEP DENSITY



(b) HIGH STEP DENSITY

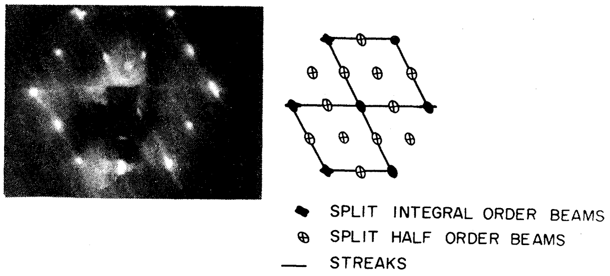


FIG. 1. LEED patterns (40 eV) for cleaved silicon surfaces with (a) low step density (~ 3%) and (b) high step density (~10%). Even the low–step-density pattern exhibits some elongation of the diffraction beams and has two domain orientations of unequal intensity. The high–step-density pattern exhibits split diffraction beams and streaks indicating a considerable distribution of step dimensions.

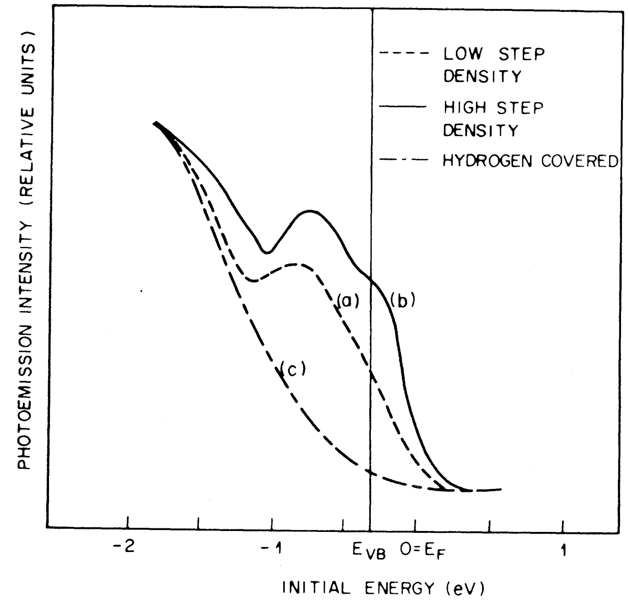


FIG. 2. UPS for the "dangling-bond" surface states near the valence-band maximum E_{VB}. The initial energy scale corresponds to curve *b* for the high–step-density surface. Curves *a* and *c* have been shifted by +0.25 and +0.35 eV to align E_{VB} (see text).

orientations of unequal intensity within the ~ 0.5 mm diam of the LEED beam. The high–step-density surface exhibits a splitting of the integral, order and one-half–order LEED beams as well as streaks which appear along two of the three possible domain orientations of steps. The streaks indicate a type of one-dimensional order which is probably caused by a considerable distribution of step dimensions over some parts of the cleaved surface.

The one-half–order LEED features were not present on the highest step-density surfaces [~ (16 ± 3)%] we observed and were found only on surfaces with step density less than (12 ± 2)%. This suggests that strain fields (or other local forces) inhibit reconstruction for terrace widths less than 40–50 Å on cleaved silicon. Similar quenching of 2× 1 reconstruction on cleaved germanium (111) surfaces has been reported by Henzler[6] for terrace widths less than 60–75 Å.

The average distribution of steps was found to be strongly dependent on the orientation of cleavage notches with respect to the (111) plane. In most cases, consecutive cleavages from the same sample bar produced step densities within a ± 3% range.

Photoemission results for these two clean surfaces (see Fig. 1) are shown in Fig. 2 for a photon energy $\hbar\omega = 21.2$ eV. After UPS measurements on each clean surface, data were obtained for the hydrogen-covered surface with the light intensity held constant. The Fermi energy reference, E_F, was determined from UPS data on clean Cd films evaporated *in situ* over the cleaved Si(111). The position of the bulk valence band E_V was determined from direct-transition peaks present in UPS data at $\hbar\omega \leq 11.7$ eV.[1-3] For the low–step-density surface we find $E_F - E_V = 0.55 \pm 0.15$ eV (curve *a* in Fig. 2) but for the high–step-density surface $E_F - E_V = 0.30 \pm 0.15$ eV. For ~ 1 monolayer coverage of atomic hydrogen on both surfaces we find $E_F - E_V = 0.65 \pm 0.15$ eV. The low–step-density clean surface has a broad Gaussian-like band of surface states with a single peak at 0.9 ± 0.1 eV below E_F in good agreement with previous results from several laboratories.[1-3] However, the high–step-density surface has a double-peaked structure with an addi-

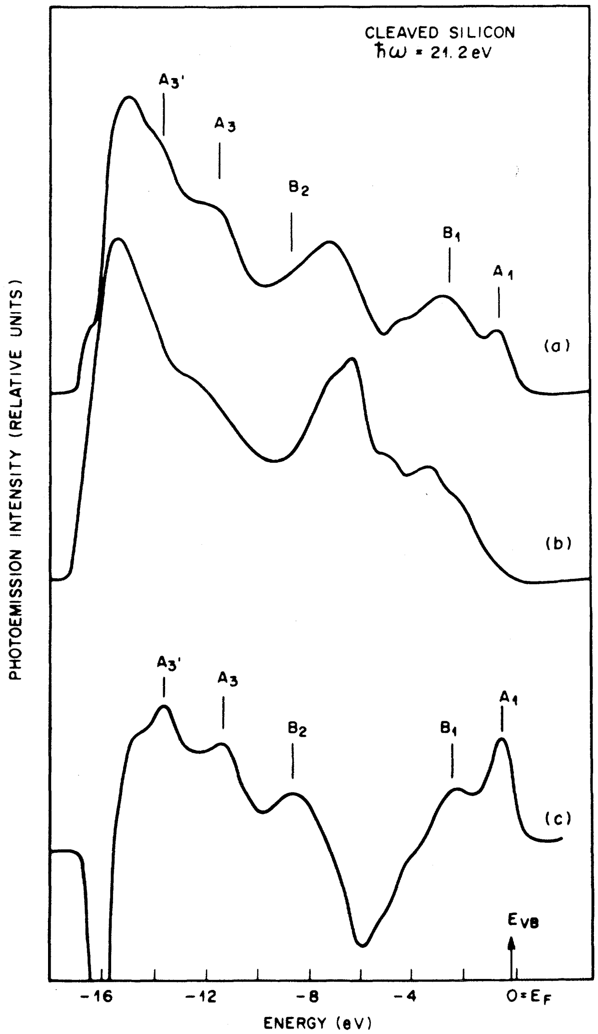


FIG. 3. UPS for clean low-step-density surface (curve *a*), after adsorption of ~1 monolayer of atomic H (curve *b*), and the difference curve (curves *a*−*b*) with the vertical scale times 1.5 (curve *c*). The features B_1, B_2, A_3, and $A_{3'}$ are due to back-bonding surface states below the valence-band maximum.

tional peak which occurs 0.4 eV higher than the previous peak and thus has a large overlap into the band-gap region *above* the bulk-valence-band maximum. The sharp increase in photoemission near E_F (see Fig. 2, curve b) suggests that these additional step-dependent surface states may be nearly metallic similar to a previous interpretation of results for the annealed Si(111) 7× 7 surface.[12]

These results are qualitatively similar to a recent reinterpretation[4,5] of Eastman and Grobman's UPS data on cleaved GaAs(110). They found surface states which are ~0.5–1 eV higher in energy than surface states on low-step-density surfaces and extend into the forbidden gap. Although no detailed information on the density of cleavage steps is available it has been suggested that a high step density is responsible for the "extra" surface states.[4,5]

TABLE I. Surface states on cleaved silicon with steps.

Transition	Energy[a] (eV)	Step dependence
A_1	0.5 ± 0.2	Strong
B_1	2.4 ± 0.2	Strong
B_2	8.6 ± 0.2	Weak
A_3	11.3 ± 0.4	Weak
$A_{3'}$	13.5 ± 0.4	Strong

[a] Measured relative to E_V. The position of $E_F - E_V$ varied with step density from 0.30 eV for high step density to 0.55 eV for low step density.

In Fig. 3 we show UPS data over a wider energy range for the low-step-density surface, curve *a*; the hydrogen covered surface, curve *b*; and their difference, curve *c*. Back-bond surface states are labeled B_1, B_2, A_3, and $A_{3'}$ along with the dangling-bond states A_1 of Fig. 2 using the previous notation.[3,12] Numerical values for peak energies are given in Table I. The high-step-density surface gave similar results for B_2 and A_3 peaks but showed an increase in peaks B_1 and $A_{3'}$ as well as the results discussed above (see Fig. 2) for A_1. Because of the overlap of bulk states below E_V we cannot resolve any splitting of back-bond peaks B_1 and $A_{3'}$ on the high-step-density surface as found for the A_1 dangling-bond peak.

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[12] J. E. Rowe, H. Ibach, and H. Froitzheim, to be published.

Thermal Charge-Transfer Transitions in Organic Donor-Acceptor Solids

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A simple model for the temperature dependence of charge transfer in organic donor-acceptor solids is presented. It is shown that under certain conditions a transition can occur from a state of smaller charge transfer below the transition temperature to one of larger charge transfer above. The possible relevance of these results to observed metal-insulator transitions in organic solids is discussed.

It is the purpose of this note to point out the possible occurrence of an electronic instability in certain organic charge-transfer solids, exemplified by tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ),[1] in which states of zero and unit charge transfer lie very close in energy. In such a solid the equilibrium amount of charge transfer will be determined by an interplay between the orbital energy required to transfer an electron from donor to acceptor and the resulting change in Madelung energy. On the basis of a simple model of this situation, it will be shown that under certain conditions an electronic phase transition can occur from a state of small charge transfer below the transition temperature to one of substantial charge transfer above. The model employed here is similar in spirit to that introduced by Falicov and Kimball[2] to describe temperature-dependent charge transfer between localized and Bloch states in inorganic semiconductors.

The model system consists of an array of N donor molecules (D) and N acceptors (A) considered in the atomic limit, i.e., all intermolecular transfer interactions are ignored. The Hamiltonian for the system is

$$\mathcal{H}=\sum_i[\epsilon_A q_i^A+\epsilon_D(2-q_i^D)]+\tfrac{1}{2}\sum_{ij}[V_{ij}^{AA}q_i^A q_j^A+V_{ij}^{DD}q_i^D q_j^D+V_{ij}^{AD}(q_i^A q_j^D+q_i^D q_j^A)], \tag{1}$$

where ϵ_A is the energy of the lowest, normally empty acceptor orbital, ϵ_D is the energy of the highest, normally filled donor orbital, $q_i^A(q_i^D)$ is the net charge on the ith acceptor (donor), and the V_{ij}'s represent the Coulomb interactions between ith and jth unit cells. In the approximation in which the q_i's are replaced by their average values (1) becomes, apart from an additive constant,

$$\mathcal{H}=N(aq+bq^2), \tag{2}$$

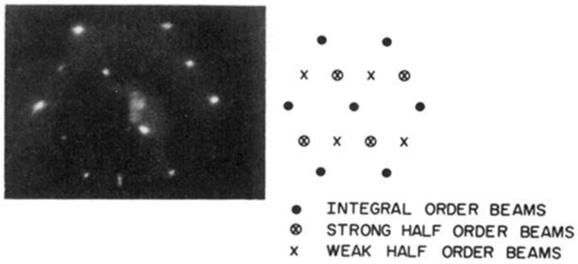
where

$$q=\langle q_i^D\rangle=-\langle q_i^A\rangle, \quad a=\epsilon_A-\epsilon_D, \quad b=\tfrac{1}{2}\sum_j(V_{ij}^{AA}+V_{ij}^{DD}-2V_{ij}^{AD}). \tag{3}$$

(Note that, in principle, a and b can be of either sign, depending on the details of the particular system.)

The entropy of the system follows from the observation that in the charge state of the system represented by $D^{+q}A^{-q}$ there are Nq holes (of spin degeneracy 2) to be distributed among N donors and Nq electrons among N acceptors. States with two holes (electrons) on the same donor (acceptor) will be

(a) LOW STEP DENSITY



(b) HIGH STEP DENSITY

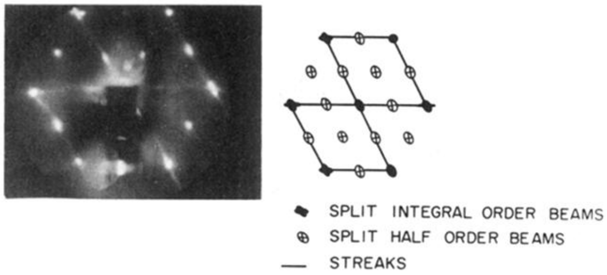


FIG. 1. LEED patterns (40 eV) for cleaved silicon surfaces with (a) low step density (~ 3%) and (b) high step density (~10%). Even the low–step–density pattern exhibits some elongation of the diffraction beams and has two domain orientations of unequal intensity. The high–step–density pattern exhibits split diffraction beams and streaks indicating a considerable distribution of step dimensions.