$J'$ and downwards by 0.2 eV from $\Gamma$ to $J$.

In conclusion, these calculations imply that the buckling lattice distortion would not drive a $2 \times 1$ reconstruction on a perfect Si(111) surface. Instead, they show that a $2 \times 1$ spin-density wave is energetically favorable and induces the insulating behavior observed on both cleaved and laser-annealed Si(111). The nonbuckled antiferromagnetic surface is shown to be stable against buckling type distortions.

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# New π-Bonded Chain Model for Si(111)-(2×1) Surface

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Several qualitatively different structural models have been examined in a critical evaluation of spectroscopic and other data for the Si(111)-(2×1) surface. Within the one-electron theory, only a novel π-bonded chain model with a covalent surface, and not the generally accepted buckled model with an ionic surface, is consistent with the data.

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In spite of extensive and concerted experimental and theoretical effort, the determination of surface atomic structures of covalent semiconductors has remained one of the most outstanding problems in surface physics.[1] Of the proposed models[2-5] for the cleaved (111) surface of Si, which shows a (2×1) reconstruction, the buckling model[2] with alternate rows of surface atoms moving in and out of the surface [Fig. 1(a)] has been the most widely accepted model. Such a conclusion is based primarily on model-dependent calculations[6,7] of surface energy bands and their comparison with spectroscopic data, especially ultraviolet photoemission spectra (UPS)[7-9] and
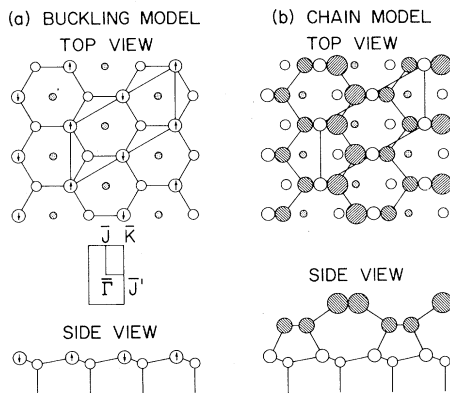
FIG. 1. Surface geometry of Si(111)-(2×1). (a) The buckling model: Alternate rows of surface atoms (largest circles) are displaced in and out as shown schematically by arrows. (b) The chain model: The topology of the zig-zag chain structure of the top two layers (shaded circles) is similar to that of the ideal (110) surface. Deeper layers are in their ideal positions. All bond lengths have their ideal values (2.35 Å) except for bonds along the chains in the top layer which are contracted by 0.1 Å. Both models have a reflection symmetry about the (1$\bar{1}$0) plane. The surface unit cell (a parallelogram) and the surface Brillouin zone (a rectangle) are also shown.

surface reflectance spectra.[10] Surface energy calculations[11] and low-energy electron-diffraction (LEED) studies[12] also agree on the buckled nature of the surface. However, none of the studies agree on the degree of buckling.

Two recent developments lead me to reexamine this surface. First, an unambiguous determination[13] of the symmetry and energy-band dispersions of surface states has been achieved through polarization-dependent angle-resolved photoemission spectroscopic (ARUPS) measurements along symmetry directions on a cleaved surface with a single (2 × 1) domain. Second, core-level shifts of surface atoms relative to atoms in the bulk have been measured.[14] From extensive studies of the buckling model, with buckling parameters varying over a wide range, I have not been able to find any buckling model which leads to a semiconducting surface with an observed[10] band gap of at least 0.25 eV and which is still consistent with any of the observed features of surface-state energy bands[7,9,13] (signs of dispersions, the large bandwidth, absence of states with odd parity with respect to the reflection plane) as well as small surface core-level shifts.[14] It is the purpose of this Letter to discuss some of the difficulties buckling models have in explaining data on Si(111)-
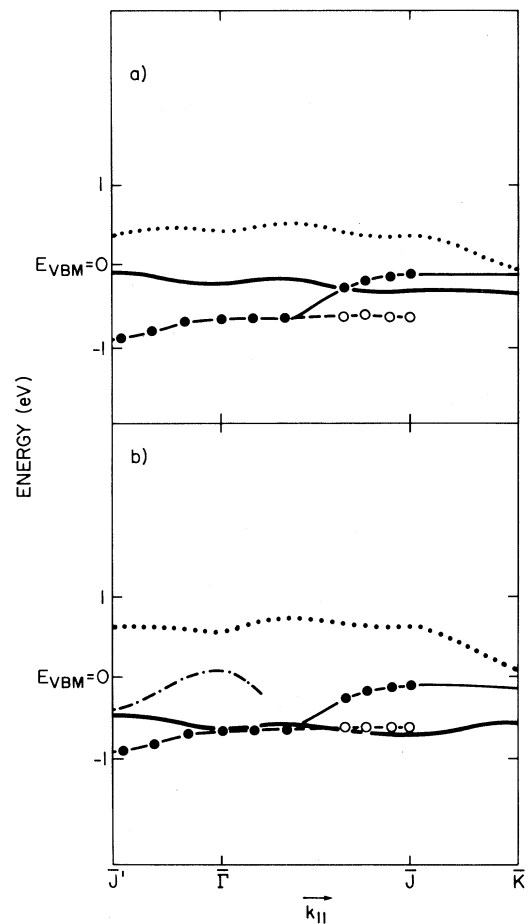


FIG. 2. Surface-state energy bands for Si(111)-(2×1) along principal directions in the surface Brillouin zone. The heavy solid lines and dotted lines show the occupied and the empty dangling-bond bands, respectively. The dashed line in (b) shows a back-bonding surface resonance. The UPS bands are shown by circles and light lines. The filled (open) circles correspond to strong (weak) features in the measured spectra. Calculations for two buckling models are presented. (a) Buckling model 1: derived from LEED (Ref. 12); (b) buckling model 2: derived from surface-energy minimization (Ref. 11).

(2 × 1) and to propose a new π-bonded chain model whose surface electronic structure is consistent with all the data mentioned above. Buckling and chain models lead to Si(111)-(2 × 1) surfaces that differ, in addition to the geometry, in the fundamental physical and chemical nature of the surface. This has important consequences, some of which are discussed briefly.

The π-bonded chain model, shown schematically in Fig. 1(b), was arrived at after consideration of several variations of each of the following classes of models: the buckling model[2]; the double-bond

model[3]; the conjugated chain model[4]; the pairing model[5]; models with adatoms in threefold sites[15]; and models based on high-density $\beta$-tin, hexagonal, and body-centered-cubic (bcc) phases of Si.[16] The present model belongs to the last class; its local bonding is a simple variation of the bcc phase. The two important features of the model are the nearly parallel dangling bonds on nearest-neighbor atoms and the chain structure.

To illustrate problems associated with buckling models, in Fig. 2 surface-state energy bands are shown for two buckling models which are representatives of models with large and moderate bucklings.[11,12] Calculations are based on a realistic tight-binding scheme[17] which gives results in good agreement with self-consistent calculations. Also shown are UPS bands—i.e., surface-state bands derived from ARUPS.[13] Only states near the valence-band maximum (VBM) are shown. While the two models give qualitatively similar dispersions, they differ from UPS bands even qualitatively. The UPS band disperses up in going from $\bar{\Gamma}$ to $\bar{J}$ and down from $\bar{\Gamma}$ to $\bar{J}'$. Theoretical bands show the opposite dispersion in both directions. The UPS band is ~0.6 eV wide as compared to the calculated bandwidth of ~0.3 eV. Models with moderate buckling, similar to model 1,[12] lead to either a metallic surface or a small band gap, which is inconsistent with optical data. Also, for such models, the average position of the calculated bands is higher by ~0.5 eV relative to the UPS band [Fig. 2(a)]. Model 2,[11] like other models with large buckling, gives a strong back-bonding surface-state–resonance band of odd parity with respect to reflection in the plane through $\bar{\Gamma}\bar{J}'$. Though the energy position of this band varies with buckling, in careful polarization-dependent ARUPS measurements[9,13] such states have not been observed in the energy interval 0 to $-1.5$ eV.

Surface-state energy bands for the chain model are shown in Fig. 3. In order to determine the tight-binding parameters[17,18] for Si atoms in the chain, a scaling of C parameters for going from diamond to graphite was determined (from band calculations of diamond and graphite), and Si parameters were scaled accordingly for a bond-length contraction of 0.1 Å (Fig. 1). Surface energy bands based on the scaling of Ref. 17 and the scaling described above are shown in Figs. 3(a) and 3(b), respectively. Self-consistent pseudopotential results[18] are also very similar to Fig. 3(b). The two calculations differ basically in the position of surface bands but not in dispersion or
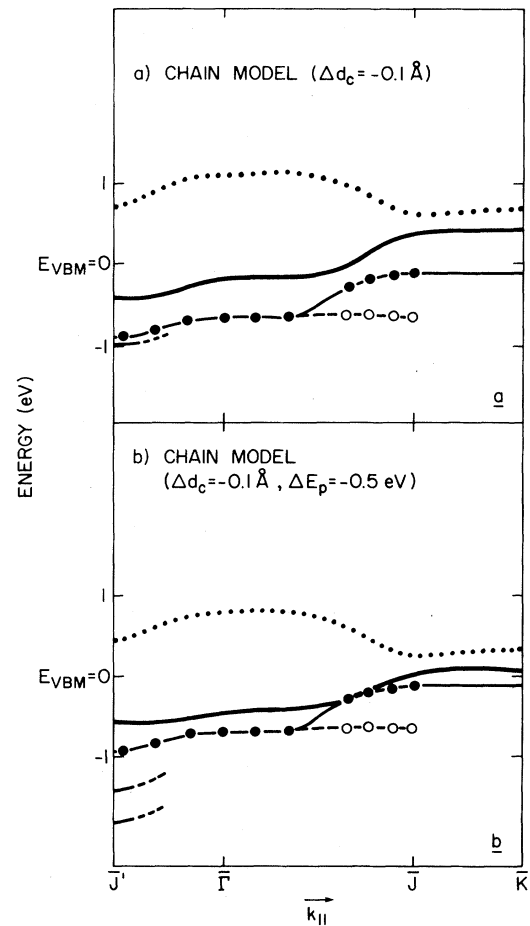


FIG. 3. Surface-state energy bands for the chain model of Si(111)-(2×1) compared with the UPS bands. Symbols are defined in Fig. 2. Results for two different calculations are shown.

band gaps. Clearly, the surface energy bands agree remarkably well with UPS bands in dispersion and bandwidth as well as position [especially in Fig. 3(b)]. Experimentally, the connectivity of bands cannot be determined and, in fact, it was proposed[13] that there are two bands: one at ~ $-0.7$ eV which is nearly flat and extends throughout the Brillouin zone, and the other near VBM which exists only in the vicinity of the $\bar{J}$ point. However, ARUPS spectra[13] for directions corresponding to the $\bar{J}$ point (and its vicinity) show a single strong peak centered around the VBM (filled circles in Fig. 3) with only a weak shoulder at ~ $-0.7$ eV (open circles in Fig. 3). Within the chain model all the strong features (filled circles) find a natural explanation; they correspond to a single $\pi$ band. The weak features in ARUPS[13] might be due to bulk states, surface resonances, or umklapp processes not considered here. In agree-

ment with polarization-dependent ARUPS measurements,[9,13] all surface states are derived from $p_z$ ($z$ along surface normal) orbitals. Because of differences in the bands in Figs. 3(a) and 3(b), which give a measure of the uncertainty in the present calculations, no attempt has been made at the optimization of the geometry. However, several variations of the chain model have been considered[18] and found to give similar surface bands, the most geometry-dependent quantity being the magnitude of the band gap.

The chemical nature of the surface in the buckling model and in the chain model is quite different. The buckled surface is ionic, the amount of charge transfer depending somewhat on the degree of reconstruction. In the present calculation for the buckling models, the "up" atom gains ~0.8 electrons and the "down" atom loses ~0.4 electrons. This charge redistribution gives rise to large Coulomb potentials which result in correspondingly large shifts of binding energies of core electrons of surface atoms relative to bulk atoms. Within a simplified model calculation,[18,19] I find that core levels for "up" atoms are shifted up (less tightly bound) by ~3 eV. This is in serious disagreement with recent measurements[14] of surface core-level binding energies which show shifts of only 0.6 eV or less. In the chain model, the surface is covlaent and no charge transfer between surface atoms in expected. However, there is a gain of ~0.25 electrons by one of the atoms in the top-layer chain while one of the atoms in the underlying chain loses ~0.15 electrons (nonequivalence of atoms along the chain is caused by underlying layers). Such small electron transfers are consistent with measured small surface core-level shifts.

Surface reflectivity[10] of Si(111)-(2 × 1) shows a strong peak associated with transitions between occupied and empty surface-state bands. Oscillator strengths for these transitions are similar to optical transitions in the bulk. In the buckling model, however, because of very small overlap between occupied and empty states (localized on "up" and "down" atoms which are second nearest neighbors), the oscillator strength for transitions between them is an order of magnitude smaller.[6,18] In the chain model, occupied and empty states are not spatially separated; they are the bonding and antibonding $\pi$ states with large oscillator strengths as observed.[10]

Important experimental evidence in favor of the buckling model comes from chemisorption of atomic hydrogen which is known[20] to destroy half-

order diffraction peaks of Si(111)-(2 × 1). Within the buckling model, removal of half-order peaks follows naturally: both "up" and "down" atoms make identical bonds with H, leading to an ordered (1 × 1) H structure with only a single binding site for H, and a saturation coverage of one monolayer. However, recent high-resolution LEED studies[21] show that the (1 × 1) structure is not a true (1 × 1) H structure; it results from surface disordering (etching, steps) caused by H chemisorption. Further, two distinct binding sites for H were observed, and the saturation coverage was significantly larger (~1.5) than a monolayer. While these more accurate measurements are in serious contradiction with the buckling model, precisely this type of behavior is expected from the chain model: with increasing H coverages, the saturation of dangling bonds (i.e., weakening of $\pi$ bonding) causes the chains to be broken up, leading to disorder and new sites for H chemisorption. Additional evidence in favor of the buckling model has been found via LEED[12] and surface-energy minimization.[11] However, these studies did not consider any of the other models for Si(111)-(2 × 1). Thus the selection of the buckling model over others, based on such studies, is not justified.

In summary, I have shown that recent photoemission, surface core-level, optical, and H chemisorption data cannot be understood on the basis of a buckling model for Si(111)-(2 × 1). I have also proposed a new $\pi$-bonded chain model for this surface and have shown that it explains all the data mentioned above. Similar studies[18] of diamond (111) and other surfaces[22] of Si suggest that $\pi$ bonding should be considered as a viable alternative to buckling for other covalent semiconductor surfaces as well.

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# Nature of a Nematic–Smectic-$A$–Smectic-$C$ Multicritical Point

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Recent x-ray data on the angles and 2-theta shifts in the smectic-$C$ phase of a binary liquid-crystal mixture were analyzed via a mean-field theory. We demonstrated that the smectic-$A$–smectic-$C$ transitions ($AC$) are mean-field-like. This conclusion is consistent with recent heat-capacity data along the $AC$ transition line. Furthermore, the nematic–smectic-$A$–smectic-$C$ point in this binary mixture is found to be in the vicinity of the tricritical point along the $AC$ and nematic–smectic-$C$ transition line.

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The smectic-$A$ ($A$) and the smectic-$C$ ($C$) phases in liquid crystals can be characterized by a one-dimensional density wave whose wave vector is along ($A$) or at an angle ($C$) to the nematic ($N$) director. Recently it has been shown that in appropriate binary liquid-crystal mixtures it is possible to have lines of second-order $NA$ and $AC$ transitions crossing over to a line of first-order $NC$ transitions.[1] The triple point where these three transition lines intersect in the temperature-composition phase diagram is the $NAC$ multicritical point (see Fig. 1). Many theoretical models[2-4] have been proposed to describe this system. Among these theories, the most appealing model, proposed by Chen and Lubensky, predicts that the $NAC$ point is a Lifshitz point.[2] However, we will demonstrate that a simple theory based on a free-energy expansion of coupled order parameters by Benguigui[4] is consistent with recent x-ray and heat-capacity measurements[5-7] on the $AC$ transition of mixtures of

octyloxy- and heptyloxy-$p$-pentyl-phenyl thiolbenzoate ($\overline{8}$S5-$\overline{7}$S5). This theory predicts a correct $NAC$ phase diagram obtained by thermodynamic studies.[8] In addition, a tricritical point on the $AC$ line near the $NAC$ point was predicted by the theory but the existing data analysis failed to prove it.[5-7]

Both the tilt angles and the 2-theta shifts in the smectic-$C$ phase were measured by an x-ray scattering study in mixtures of $\overline{8}$S5 and $\overline{7}$S5.[5,6] In contrast to the usual fitting procedure with a simple power law for the order parameter ($\Psi$, the tilt angle in the $C$ phase) of each mixture, the data were analyzed by employing an analytic expression obtained from a mean-field free energy including a $\Psi^6$ term. In doing so we were able to fit all of the experimental data points. Moreover, the salient features of this fitting result are the following: (i) The AC transitions are mean-field like; (ii) the tricritical region increases as the concentration of $\overline{7}$S5 increases