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# RECONSTRUCTION AT SEMICONDUCTOR SURFACES

D. J. Chadi

Xerox Palo Alto Research Center
3333 Coyote Hill Road
Palo Alto, California 94304, U.S.A.

A review of recent work on the atomic geometry at relaxed or reconstructed semiconductor surfaces is presented. The strong effect of atomic displacements on the surface electronic structure is emphasized.

## I. Introduction

In nearly all common semiconductors the surface atomic positions differ considerably from those expected from a consideration of bulk structure alone [1]. LEED studies show that the atomic displacements are generally quite large, but the precise nature of the surface geometry has not been determined except for some simple cases. Theoretical calculations show that the surface structure strongly influences the metallic or non-metallic nature of the surface, the position of surface states relative to bulk states, their dispersion, and their symmetries. A knowledge of the correct surface geometry is, therefore essential for an understanding of surface properties. An acceptable model of the surface geometry should account not only for the LEED spectra but should also lead to a proper description of the electronic properties of the surface.

Completely satisfactory descriptions of the surface geometry have been achieved only in a few cases. For the most part, the surface atomic configurations and the mechanisms leading to surface relaxation or reconstruction are only partially known. But, overall, during the past several years there has been significant progress in the determination of surface atomic and electronic structure. A theoretical method which appears very promising and which in combination with experimental data on surface properties should lead to more accurate predictions of surface geometry is total-energy-minimization. The results of some applications of this method and a review of recent work on the surface atomic structure of several semiconductors is given below. The correlation between atomic and electronic structure is also emphasized.

## II. (110) Surfaces of III-V and II-VI Semiconductors

The most thoroughly studied (110) surface of any zincblende crystal is that of GaAs [2-7]. The 1x1 unit cell contains one Ga and one As atom which are not in their bulk terminated positions but are displaced in an approximately rotational type of motion with As moving out of the surface plane and with Ga moving closer towards bulk atoms. There is now generally very good agreement among several groups on the details of the surface relaxation. Dynamical LEED [2-4], as well as energy-minimization studies [5-7] on surfaces and clusters, predict a tilting of the Ga-As surface bonds of about 27°. Surface relaxation reduces the total energy by over 1 eV per unit cell, with about 90% of the reduction coming from the surface layer alone. Both energy-minimization and dynamical LEED calculations predict a large value of 0.65 A for the relative vertical displacements of the Ga and As surface atoms.

The (110) surface relaxation has a significant effect on the electronic properties. The As and Ga dangling bonds at the surface give rise to an occupied band near the valence-band-maximum and an empty band near the conduction-band-minimum, respectively. In the unrelaxed configuration a part of each band lies within the fundamental band gap. This would lead to Fermi-level pinning near the extrema of the two surface states for n- or p-doped samples. Experimentally, no intrinsic surface states and subsequently no Fermi level pinning are found for a "sufficiently perfect" surface [8-10]. Calculations show [11] that for the 27° relaxation model both the filled and empty dangling-bond surface states are moved out of the band gap. It is remarkable, however, that if the relaxation is carried out too far beyond the optimal 27° bond rotation angle (e.g., to 35° as suggested by initial LEED studies), new types of surface states not related to the Ga dangling bond state appear below the conduction-band-minimum [12] in disagreement with experiment. Thus, at the present time the 27° relaxation model for GaAs is: consistent with LEED data, is the most energetically favorable, and explains the absence of Fermi level pinning in the gap. The calculated positions of the filled and empty surface states are also in generally good agreement with the results of photoemission [13-16], reflectivity [17] and electron-loss-spectroscopy [18,19] measurements. The predicted ordering of surface states with odd or even mirror reflection symmetries is also found to be sensitive to the surface structure. For the 27° (but not the 35°) model, the calculated symmetries are in agreement with those determined via angle-resolved photoemission measurements [20].

In addition to GaAs the (110) surface atomic geometries of InSb, InP and ZnTe have been studied through dynamical LEED [21] and total energy calculations [5]. The results of these studies indicate that the (110) surface relaxations of the III-V semiconductors are quite similar. Both energy-minimization and LEED calculations indicate that the surface anions are displaced significantly less in the more ionic II-VI semiconductors than in the more covalently bonded materials. Overall, the bond-rotation angle at the surface, which gives a partial description of the surface relaxation, appears to lie between 26° to 30° for all the zincblendes.

Even though there are no intrinsic (110) surface states in the band gap of GaAs, extrinsic states due to defects or impurities can occur in the gap. Surface steps resulting from cleavage are one type of defect which affect the surface state distribution [22]. The creation of a step with a height of one interlayer spacing, as suggested by LEED [23], gives rise to a row of either (three-fold coordinated) Ga or As atoms. Recent energy-minimization calculations [24] show that these edge atoms, unlike the atoms at terrace sites, do not move appreciably from their ideal positions. If all the edge atoms are As, a $\simeq$0.5 eV wide partially filled band extending up to 0.4 eV above the valence-band-maximum is expected. Similarly, if all the atoms are Ga, a very narrow partially filled band extending 0.2 eV below the conduction-band-minimum is expected. The addition of very small amounts of hydrogen, or oxygen to the surface, which is found experimentally [10] to improve the properties of the surface, could be related to a large extent to the removal of these extrinsic step-dependent states from the band gap.

## III. Si(111) Surface

### A. Relaxed 1x1

A Si surface with a 1x1 LEED pattern can be stabilized through the addition of small amounts of impurity atoms. A 1x1 pattern does not necessarily suggest that the surface is ordered. Diffuse scattering from a disordered surface combined with coherent scattering from substrate atoms can result in a 1x1 LEED pattern. For an ordered surface, atomic relaxation can only involve an expansion or contraction of the interlayer spacing at the surface. Several LEED calculations [25-26] have indicated an ordered surface with an interlayer contraction of between 0.12 to 0.16 A. A recent study [27] of the relative magnitudes of diffuse and coherent scattering suggests, however, that the surface is most probably disordered. It is not yet clear whether the different conclusions reached by the separate LEED analyses result from differences in sample preparation (e.g., type of impurity atom used to stabilize the surface) or whether they result from the analyses of the LEED data itself. The relaxation of the 1x1 surface has also been examined by energy-minimization [28,29]. Calculations on surfaces and clusters predict a contraction in interlayer spacing of 0.15 and 0.08 A, respectively, in fairly good agreement with LEED results. It should be noted that these results are obtained with the assumption that the 1x1 surface is stable. It is possible to test the accuracy of this assumption by calculating the change in the total-energy for small arbitrary displacements of the surface atoms. It would be interesting, for example, to test the stability of the 1x1 surface against a 2x1 type of buckling distortion in this way.

Experimental studies of the electronic structure of the 1x1 surface also give a clue to the surface periodicity. For an ordered 1x1 surface, a half-filled band of surface states lying above the bulk valence-band-maximum is expected. These states, if present, can be detected by photoemission measurements. The electronic structure of the 1x1 surface as determined from recent photoemission measurements [30] is inconsistent with that for an ordered surface. The photoemission measurements fail to show the existence of a partially filled surface band above the valence-band-maximum. Instead, they show similarities between the spectra of the 1x1 and 7x7 surfaces in the energy position of surface related structure. This would suggest that the 1x1 surface is disordered and that the 1x1 LEED pattern results from scattering from subsurface atoms.

## B. 2x1 Reconstruction

This is one of the most extensively studied surface reconstructions. Experimental and theoretical studies point to a reconstruction which results from a buckling of the surface as was proposed initially by Haneman [31]. The magnitude of the buckling is, however, still a matter of dispute with different estimates [5,31,32] varying by a factor of 2 or more. The 2x1 reconstruction splits the half-filled dangling-bond band of the 1x1 surface into two bands separated by a small gap. Transitions between these bands have been measured in reflectivity [33] and electron-loss experiments [34]. The threshold for excitation between the two sets of states, as obtained from recent reflectivity measurements, is near 0.4 eV. Surface photovoltage measurements [35] which measure valence-to-empty surface state transitions also indicate a threshold of about 0.4 eV. These experiments can be used to gain information on the magnitude of the surface buckling. Calculations [36] show that the threshold and the energy of the peak in the joint-density-of-states between the dangling-bond bands increases linearly with the buckling. A comparison between the calculated [37] joint-density-of-states for the Haneman model and the experimental spectra [33] suggests that the Haneman model and some of the models from LEED could be appreciably underestimating the magnitude of the buckling [38]. If surface excitonic effects are large, the underestimation of the buckling would be even greater.

The 2x1 surface is thought to be stabilized by steps [39]. There have been several experimental [39-41] but very few theoretical studies [42-43] of steps on this surface. A (111) step involves one double layer of atoms. Two step configurations with edge atoms in the $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$ directions are possible. The $[11\bar{2}]$ edge atoms have one dangling bond while the $[\bar{1}\bar{1}2]$ ones have two broken bonds. LEED studies surprisingly show [40] that the steps are of the $[\bar{1}\bar{1}2]$ type. We have recently used energy-minimization calculations [44] to study reconstruction and domain orientation at steps. The results are very interesting in that they show that the 2x1 domain orientation at a $[\bar{1}\bar{1}2]$ step is determined by the bonding geometry of edge atoms. The rows of up-down atoms are found to propagate at a 60° or a 120° angle with respect to these atoms. This configuration is found to have an appreciably lower energy than the one in which the rows are oriented parallel to the edge atoms. We are now investigating the energy differences between the fully reconstructed $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$ steps to determine the lowest energy geometry. The electronic structure of the relaxed and reconstructed steps will be determined simultaneously with the structural determination.

## C. 7x7 Reconstruction

This is the thermodynamically stable surface of Si(111) and is the largest superlattice to occur on a clean semiconductor surface. A 7x7 reconstruction has also been induced on the Ge(111) surface by adding small amounts of Sn to the surface [45]. Several models for the atomic geometry of the 7x7 surface have been suggested but there is as yet no definitive structure which can satisfactorily explain all the experimental observations.

Lander [46] proposed a vacancy model with "warped benzene rings" at the surface. Other models are: adatoms instead of vacancies [47], buckled 2x1-like surface [48,49], "milk-stool" model [50], and epitaxial microdomain model [51]. A charge-density-wave buckling distortion resulting from the nesting of the Fermi surface has also been suggested [52] as the mechanism leading to surface reconstruction. Evidence for a "rough" surface (e.g., vacancies, adatoms, microdomains, etc.) comes primarily from chemisorption studies [53]. The 7x7 structure appears to be more stable against chlorination and hydrogenation than the 2x1 surface. Contrary evidence for a "smooth" (i.e., non-vacancy) surface comes from photoemission measurements [49,54]. The normal emission spectra of the 7x7 surface and the photon energy and polarization dependence of the dangling-bond band emission are found to be very similar to those for the 2x1 surface [54]. The emission from the dangling-bond states of both surfaces is a maximum at a 50 eV photon energy for p-polarized light and for normal emission. The back-bond surface states are also found to be at nearly the same energy with respect to the valence band maximum for both surfaces. For the 7x7 surface, a very low density of surface states at the Fermi energy is found [54]. Depite the similarities in the normal emission spectra, reflectivity [55] and energy-loss measurements [34] show a significant difference between the 2x1 and 7x7 surfaces. For subgap excitation energies, no transitions that can be identified with the filled and empty dangling bonds of the 7x7 surface have been observed. This result is difficult to explain by any of the structural models which have been suggested so far.

## IV. Ge(111) c-2x8

The smallest unit cell for the thermodynamically stable surface of Ge(111) has been assumed to be 2x8 for several years [56]. The reciprocal unit mesh of the 2x8 lattice has, however, many extra spots which are not seen in LEED. The absence of these spots in the LEED spectra has been attributed to the vanishing of the surface structure factor. We have recently shown [24] that the smallest unit cell for the stable Ge(111) surface is c-2x8 and not 2x8. The absence of many 1/8 order spots in LEED occurs naturally for the c-2x8 cell. The reciprocal mesh of the c-2x8 cell matches perfectly the diffraction spots seen in recent reflection-high-energy-electron-diffraction experiments [57]. These measurements show the presence of 1/4 order and related spots which are apparently too weak to be seen in LEED measurements.

Photoemission studies show [58] that the Ge(111) 2x1 and c-2x8 surfaces are very similar with maxima in the surface band density at 0.7 and 0.6 eV below the top of the valence band, respectively, and with practically the same density of states. Chemisorption studies [59] which indicate that the c-2x8 reconstruction is easily removed by $\simeq 0.1$ monolayer coverage of impurity atoms also suggest that the surface is smooth with no vacancies or other sharp structure. A buckled model consistent with the c-2x8 periodicity and the weak 1/4 order beams in LEED has been constructed [24]. Reflectivity measurements similar to those on the 2x1 surface would be very helpful in giving more information on the surface atomic and electronic structures.

## V. Si(100) 2x1 and c-4x2

Many distinct surface reconstruction models have been suggested for the Si(100) surface. Dynamical LEED analyses [60-62] have not led to any definitive conclusions on the nature of the surface reconstruction. They indicate, however, that the reconstruction extends at least several layers into the bulk. The pairing (or dimer) model [63] gives [64] the best agreement between theory and photoemission experiments [65]. A five-layer relaxed model [67] gives better overall LEED results [60-61] than other models but is not completely satisfactory. The originally suggested symmetric pairing model in which the surface atoms are all equivalent is not the most energetically favorable geometry [68,69]. Buckling of the dimer which produces an asymmetry in the displacements of the atom lowers the total energy by about 0.16 eV/dimer. The asymmetric dimers configuration as shown in Fig. 1 leads to some charge transfer and to a partially ionic bond between the atoms of the dimer making the (100) surface somewhat similar to the (111) surface. The stacking of asymmetric dimers of "up-down" and "down-up" orientation can be used to make unit cells with 2x1, c-4x2, p-2x2, c-2x2 periodicities as shown in Fig. 2. The dipole-

dipole type of interactions between dimers at the surface are nearly the same and most favorable for the latter three structures. The 2x1 and c-4x2 structures are the ones that have been seen most clearly in LEED and He diffraction experiments [70]. Evidence for the possible presence of regions on the surface with 2x2 periodicity comes form the same measurements [70] which show scattering into forbidden (1/2, 1/2) spots. Since the total energies of the c-4x2 and the 2x2 structures are quite similar, all three structures are quite likely to occur at the surface.

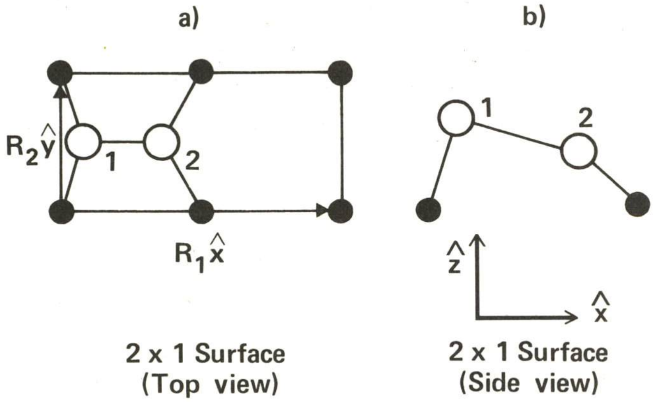

Figure 1. Top and side views of the asymmetric dimer geometry on the Si(100) surface

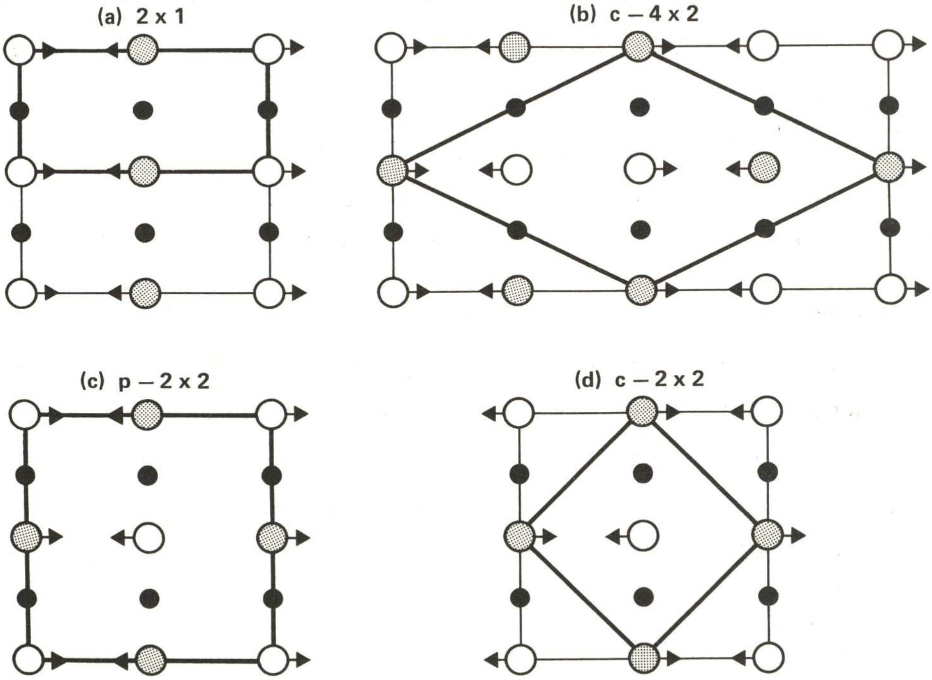

Figure 2. The surface unit cells for the 2x1, c-4x2, p-2x2 and c-2x2 surfaces are shown in (a)-(d), respectively. The large open and dotted circles form the "up" and "down" atoms of the asymmetric dimers. The second layer atoms are shown as dark circles. Only directions and not magnitudes of displacements from ideal and unrelaxed positions are shown

The asymmetric dimer geometry unlike all previously tested structures [64,71] has a semiconducting band structure in agreement with experiment [68-69]. The calculated $\simeq 1$ eV dispersion of the dangling-bond band for the 2x1 surface is, however, about a factor of 2 larger than the experimental band width obtained from angle-resolved photoemission measurements. For 2x2 and c-4x2 surfaces the calculated band widths are in much better agreement with experiment [66]. The photoemission measurements also give some indication for the presence of 2x2 domains at the surface: Two surface states, one at the Brillouin zone center and one at the 2x1 zone boundary, having the same energy but differing by a (1/2, 1/2) wavevector are observed [66]. The assumption that the two states are related by an Umklapp process would require the presence of either c-2x2 or p-2x2 domains at the surface. The observation of other states related by the same Umklapp process would be needed to strengthen the case for 2x2 domains.

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