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SPRING COLLEGE IN CONDENSED MATTER
ON
"THE INTERACTION OF ATOMS & MOLECULES WITH SOLID SURFACES"
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# BASIC STRUCTURAL AND ELECTRONIC PROPERTIES OF SEMICONDUCTOR SURFACES (Part III)

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## The Si cleavage Surface

The surface (111) of Si is created by cleaving the crystal with a cutting plane normal to the (111) direction. The surface obtained in this way can be maintained clean (without contamination) only in an ultra-high vacuum ($\sim 10^{-10}$ Torr). The periodicity of the ideal bulk plane would be the one of an exagonal network of Si atom belonging to the same sublattice. So each silicon atom would be surrounded in the plane by 6 second neighbours. Assuming that the cut brokes one bond per atom, each surface atom is linked to three nearest neighbors on the second plane.

The simple unreconstructed ideal surface has never been observed. The LEED pattern shows a (2×1) reconstruction. Extra-spots appears as indicated in Fig. 1. This corresponds to a doubling of periodicity along $\vec{a}_1 = a/2(0,1,\bar{1})$ or, equivalently, to choose a new double surface cell with rectangular unit cell with $\vec{A}_1 = a/2(11\bar{2})$ and $\vec{A}_2 = a/2(\bar{1},1,0)$. The SDBZ is then obtained by folding the ideal one into a rectangular shape.

A detailed description of the properties of the (111) surfaces of diamond structure is given in Ref 26. We will summarize the main points. (2×1) structure is metastable and, by heating the sample in U.V. conditions at 500°–700°K, one obtaines a 7×7 pattern[24], with a unit cell 49 time larger than the ideal one, which is the stable structure. The (2×1) structure cannot be restored again. At 1150°K the 7×7 structure reversibly tranforms into a (1×1) structure[28]. The (1×1) pattern does not imply that the surface is ordered. A (1×1) stable structure can be obtained and stabilized by deposition of different atomic species and gas adsorption, also at submonolayer coverage.

It is interesting to follow the hystory of the interpretation of the surface structure of Si(111) and of their electronic properties. All method of determining surface structure (LEED ion and atomic scattering and tunnel microscopy) are indirect, because they require a comparison between experimental ouputs (angle- and energy-resolved intensity curves or current maps)

with complicated calculations which simulate with a model structure the physical system. Different models of the surface structure appeared in 25 years of investigation on this system. In the same years the spectroscopical studies of electronic properties of the surface has been interpreted on the basis of calculations based on these models.

Assuming an ideal termination of the crystal, one has one dangling bond per unit cell - As it can be expected, a band on surface states arises, widely located in the gap. This band should be half-filled and a large density of surface states would be present in the gap, strongly pinning the Fermi level at the surface. In absence of reconstruction the distribution of electron states at the surface would have been of metallic type. The first electronic structure calculations obtained such a picture. The very experiments based on electrical measurements observed states in the gaps, but they were of extrinsic nature (due to absorption or to cleavage defects).

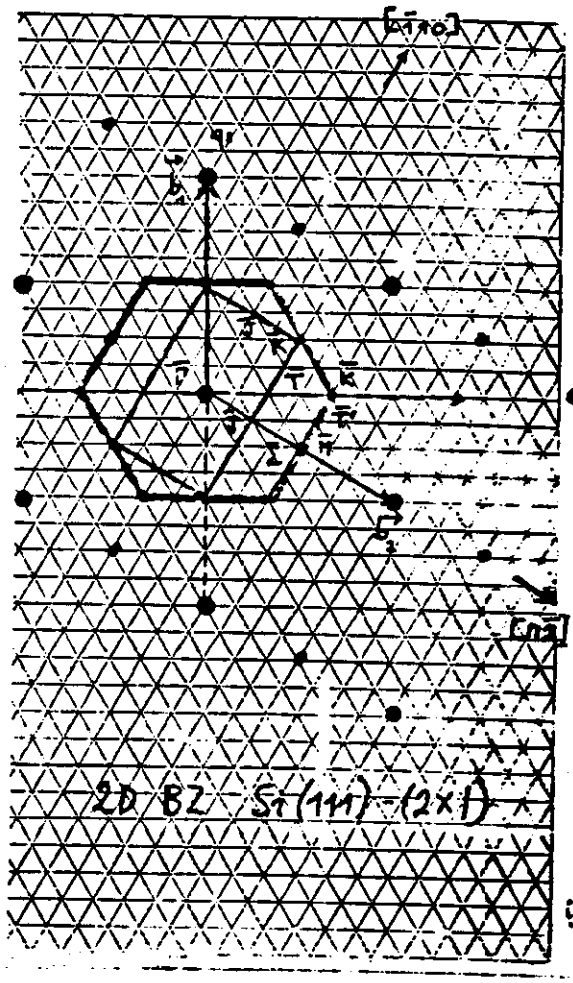



Fig 1- 2DBZ of the Si(111) (2×1) reconstructed surface.

The reconstruction of the surface, with the displacement of the atoms at the surface from their bulk positions, fold the single dangling-bond band obtained in the ideal case in two bands and open a gap along the border of the 2DBZ between these two bands. If this gap is sufficiently wide and bands do not present too large dispersion along the border of 2DBZ they do not overlap and the lower can be completely filled, while the upper is empty. A gap between surface states can exist and the opening of this gap, with the lowering in energy of the filled states is (partially) responsible of the energy gain of the reconstructed phase. This gap (0.45 eV) has been observed many years ago with different techniques. Among them we consider an optical technique, based on the change of surface reflectivity on passing from the clean to the oxidized surface. Multiple internal reflections on freshly cleaved surfaces were used in the early experiments to enhance surface sensitivity[29]. We present in fig 1 the results of a new recent version of this experiment where the dependence of the differential reflectivity on polarization of light is also shown[30].

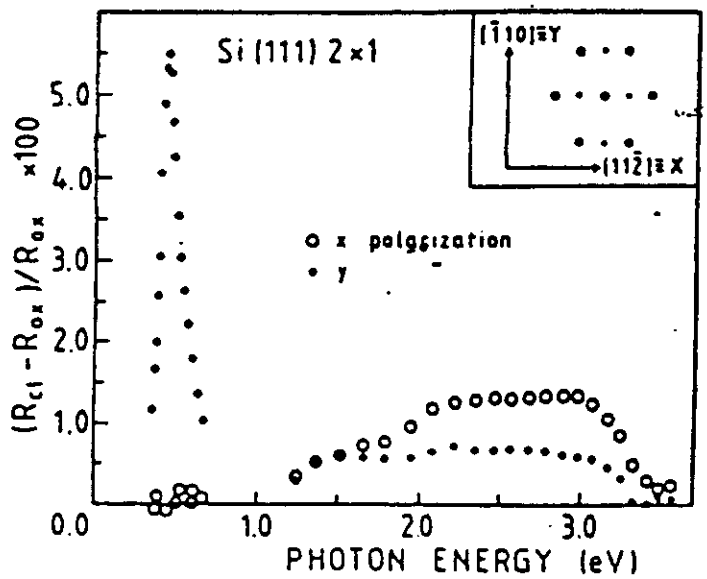
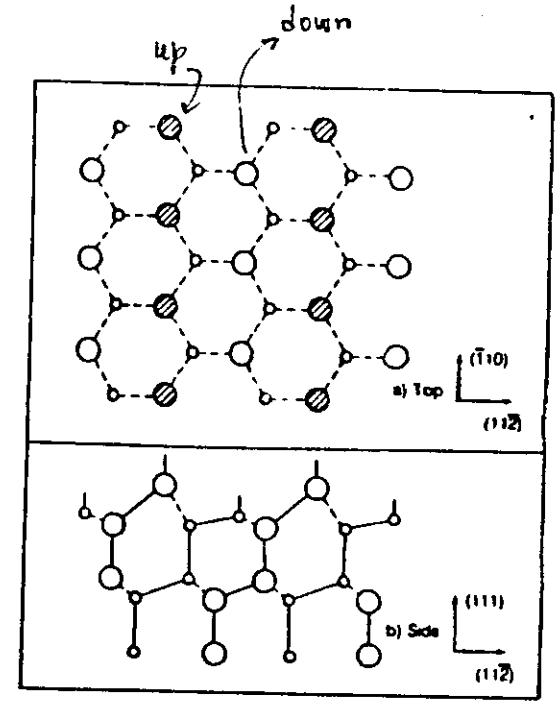
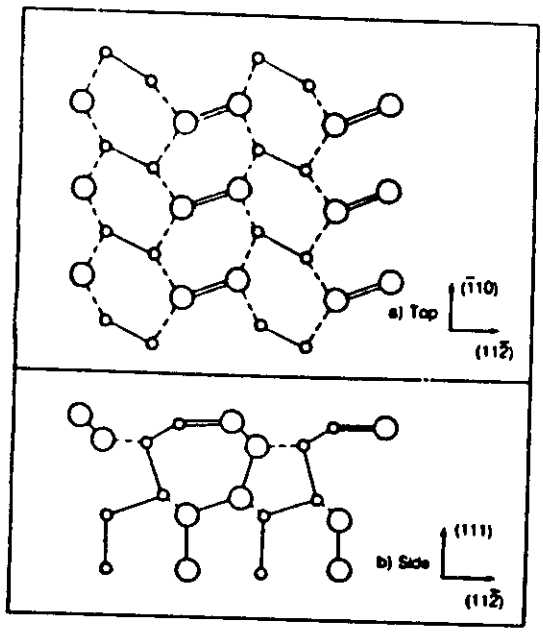


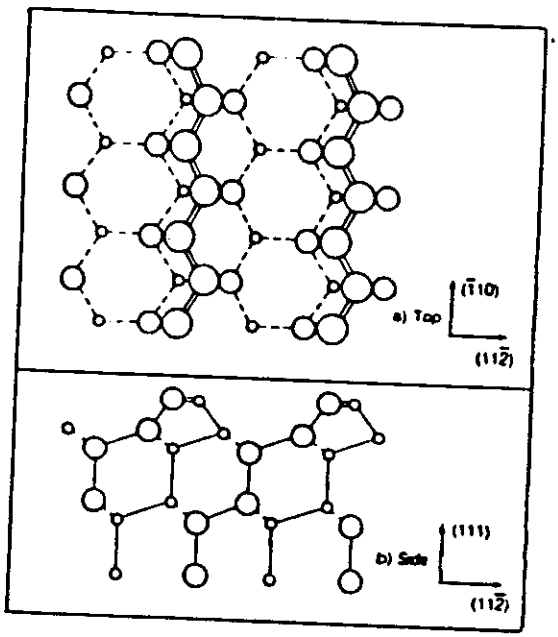

Fig 2. - Differential reflectance surface spectrum of Si (111) × (2×1) with polarization along different axis of reconstructed structure.



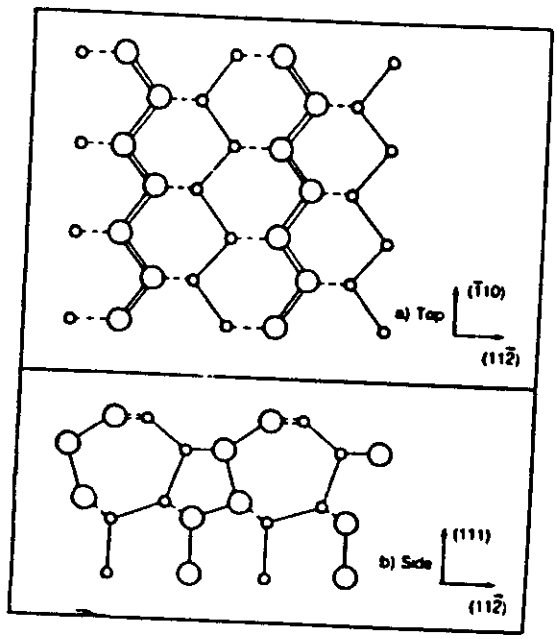

- Buckling model [31]




- Molecular dimer model [33]




- Adatom chain model -




$\pi$ bonded chain model, Pandey [34]

Fig 3. Top and side views of model reconstructions for Si(111) (2×1) - The size of the circle indicate, in both view, in decreasing size order, increasing distance of atomic plane. From Ref. 26

For many years the buckling model[31] was considered a realistic explanation of the existence of the surface gaps. Other models pairing atoms through displacements in the plane were proposed (see Ref. 32-33), with less and more drastic atomic rearrangement at the surface. Pandey pointed out that a gap with non overlapping band cannot be obtained in buckling model and proposed in 1981 (ref. 34) a model with a deep changes of bonds and atomic positions at the two outer atomic plains ($\pi$-bonded chain). Two zig-zag chains are obtained at the surface at the two outer planes, directed along [$\bar{1}10$] direction. This configuration may be reached by a displacement of the atoms at the outer two planes in [$\bar{1}\bar{1}2$] direction, followed by appropriate upward or downword shifts. This direction corresponds to the cleave direction to obtain a good (2×1) single domain LEED pattern.

This model of reconstruction looks consistent with many experimental results. If we consider the methods which directly inquire the geometrical structure of the surface, we note that angular resolved scattering of ions[35,36] are clearly in favour of Pandey's model, with an additional tilt of the chains as indicated in Fig 4. The scanning tunneling microscopy confirms the chain model[37], while questions remain in the interpretation of the LEED data.

The spectroscopical results, which were comparable with the outcomes of the buckling models only with different values of the buckling, compare more favourably with the electronic structure obtained in the Pandey model.

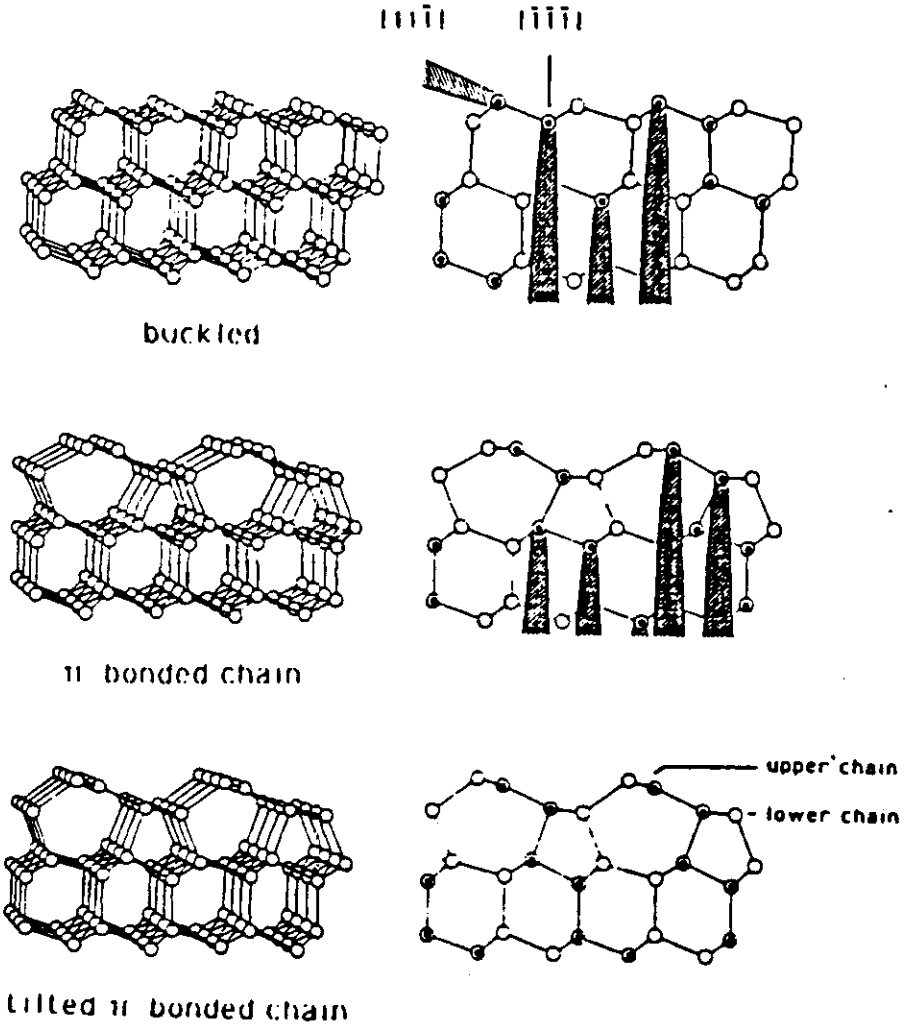



Fig 4 - Models used to interpret (Ref 36) ion scattering data -

In particular the bands at the surface show a gap along the border $\bar{J}$-$\bar{K}$ of the 2DBZ (see Fig 5)- The filled band has a dispersion which favourably compares with the photoemission results. The value of the gap is lower than one seen in the optical experiment - It can be increased assuming a tilt of the chain. However we must also consider the problem of the evaluation of the gap in LDA approximation, which reduces the possibilities of a careful comparison between the experiments and theory on this point.

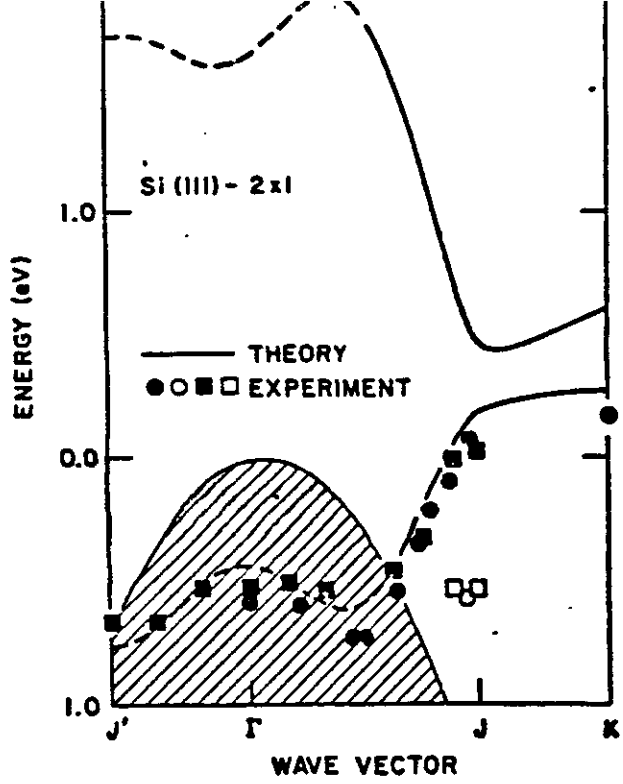



Fig 5 - Surface energy band calculated with the Pandey model by Northrup and Cohen (38)

The inverse photoemission technique, which samples the empty states and can show the dispersion of the bands higher than the Fermi energy, gives also (Hanson et al) results in agreement with this model.

A stronger confirm of the models comes from the results of differential reflectance with different polarization of the lights, shown in Fig 2 - The symmetry and the localization of the states involved in the transition give vanishing matrix element of the optical transition when the $\vec{A}$ vector of the e.m. field is directed in the direction normal to the chain so that the peak at 0.45 eV has a maximum intensity if $\vec{A}$ is directed along the chain direction $[\bar{1}10]$ and is disappearing when $\vec{A}$ is along $[11\bar{2}]$ - A similar effect is shown also in Electron energy loss spectra where the contribution of this interband surface excitation is observed, for low energy electrons, when the scattering plane is parallel to the chain and reduces almost completely

when the plane is normal to the chain.

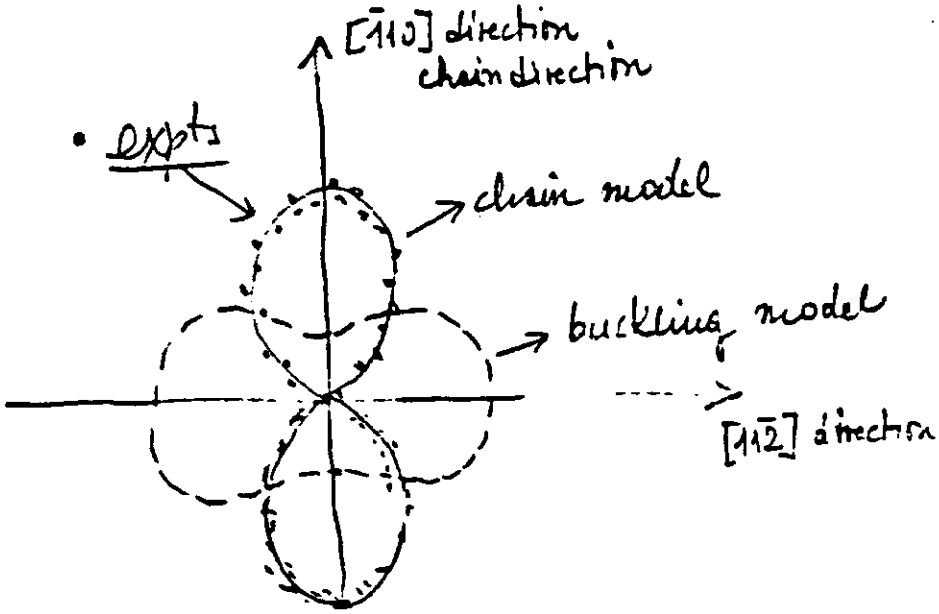
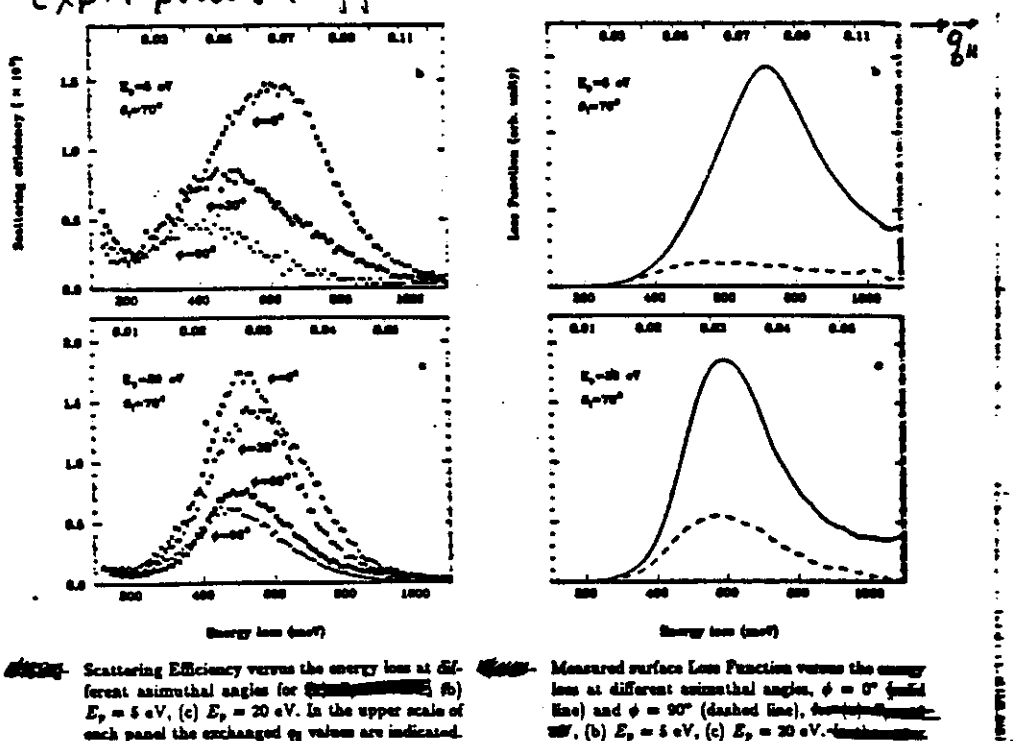



Fig 6 – Optical absorption dependence as a function of the polarization of light predicted by the two models. Expt. points support chain model.[39]



Scattering Efficiency versus the energy loss at different azimuthal angles (for [illegible] b) $E_p$ = 5 eV, (c) $E_p$ = 20 eV. In the upper scale of each panel the exchanged $q_{\parallel}$ values are indicated.

Measured surface Loss Function versus the energy loss at different azimuthal angles, $\phi$ = 0° (solid line) and $\phi$ = 90° (dashed line), [illegible] (b) $E_p$ = 5 eV, (c) $E_p$ = 20 eV. [illegible]

Fig 7 – Energy loss spectra observed for two different directions, $\phi = 0°$ (chain directions) and $\phi = 90°$ and the obtained loss function.[40]

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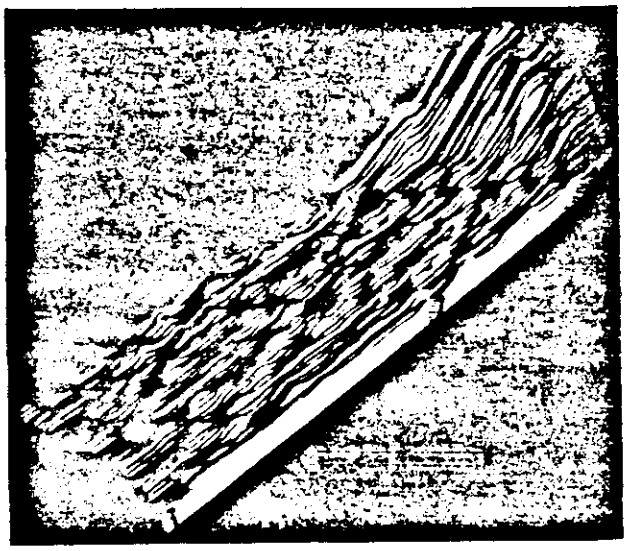
Note: A total energy calculation for a slab terminated by a (2x1) reconstructed chain model surface gives a lowering of the total energy respect to the ideal case; the gain in energy per atom is 1.27 eV.

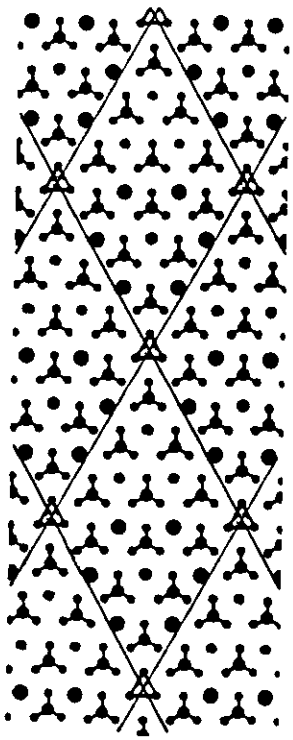
## Si (111) (7×7) structure

The stable structure of the Si (111) after the annealing at high temperature is the (7×7) structure. Many models were developed up to the direct observation of the 7×7 unit cell by Scanning tunneling Microscopy (STM) in 1983 by Binning and coworkers [41]. The model proposed in that paper where the image (at right) was presented, was a modification of a model proposed by Harrison (adatom model; [42] in 1976. This one was a modification of the Lander model based on vacancies (1963).

In this model (shown in the figure) the 12 adatoms saturate 36 dangling bonds of the surface plane and with their dangling bonds, reduces by 24 the number of these at the termination of the crystal. At the corner of the cell a deep minimum is found, surrounded by a pattern of relative maxima with sixfold symmetry.



Relief of two complete 7×7 unit cells, with nine minima and twelve maxima each, taken at 300 °C. Heights are enhanced by 55%; the hill at the right grows to a maximal height of 15 Å. The [211] direction points from right to left, along the long diagonal.



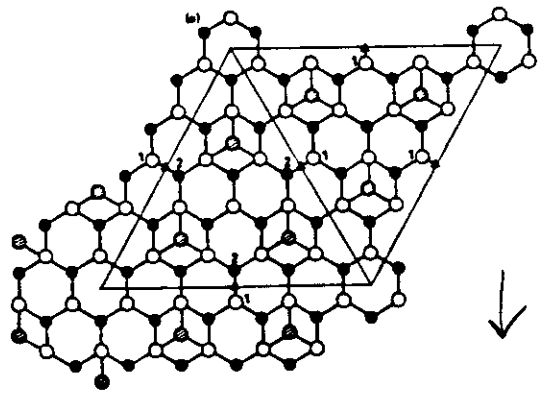
Modified adatom model. The underlying top-layer atom positions are shown by dots, and the rest atoms with unsatisfied dangling bonds carry circles, whose thickness indicates the depth measured as discussed in the text. The adatoms are represented by large dots with corresponding bonding arms. The empty potential adatom position is indicated by an empty circle in the triangle of adjacent rest atoms. The grid indicates the 7×7 unit cells.

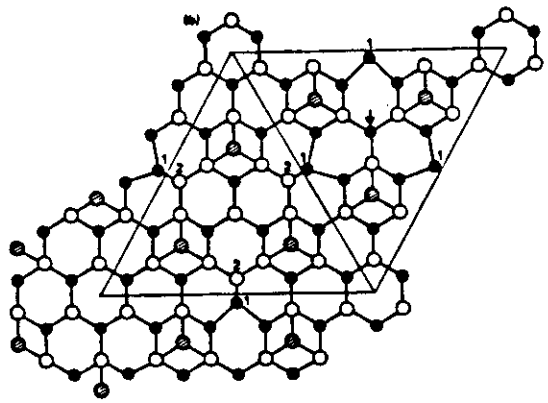
Chadi in 1984 presented a model of the surface based on adatom and simplified total energy calculation in T.B. scheme.[43]

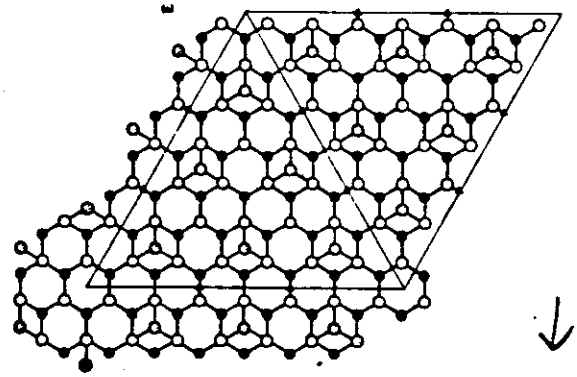
Here we present his model for (5×5) structure (found for Si on Ge(111) after annealing) and (7×7) structures.

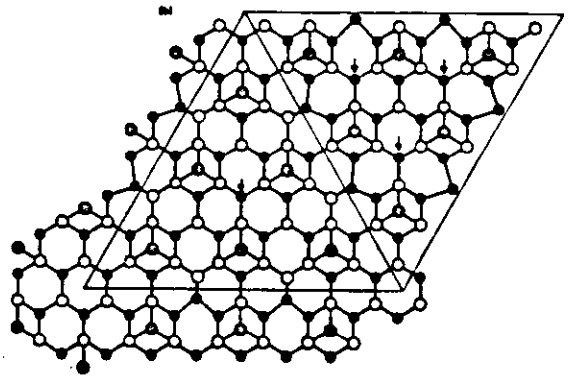
They are based on adatoms - (dashed circles bound to three atoms of the first layer). the first layer atoms are white circle, the secon layer atoms are black.

Shifting and exchanging the position of couples of atoms on passing from a to b, one obtains local configuration with small segments of π-chains.









Many other models were presented and their are compared in the work of Tromp, Hamers and Demuth with the results of Scanning Tunneling Spectroscopy. They compare the maps of electronic charge distribution with applied voltage of −2 and +2 eV with superposition atomic charges evaluated for different models. The choice of applied voltage is done in order to avoid

masking effect arising from surface states located near $E_f$. The model which accounts for of the charge profile observed experimentally is the one by Takayanagi et al.[45] described in the following page, in a paper by the same authors [46].

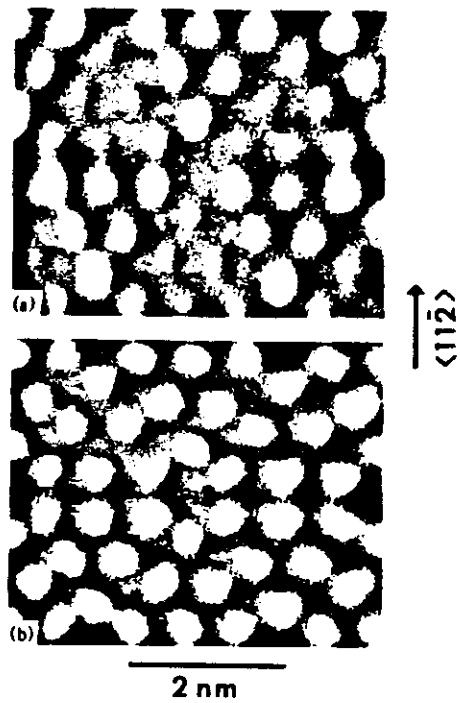
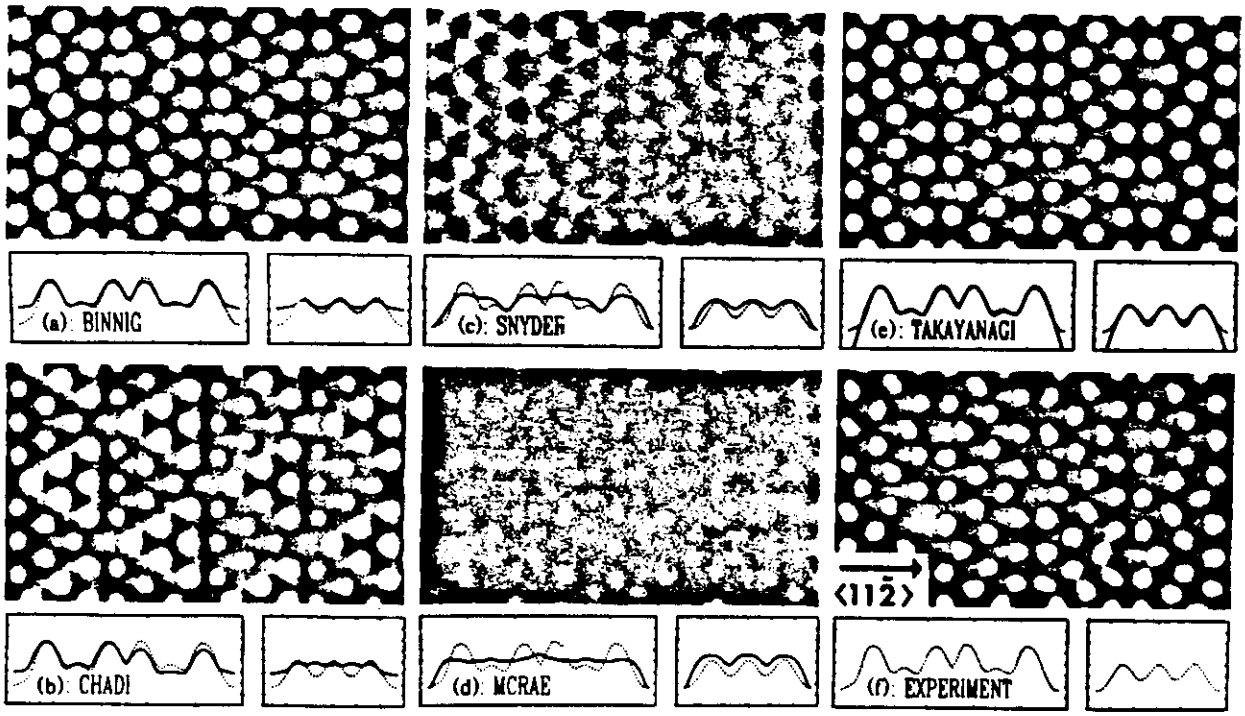
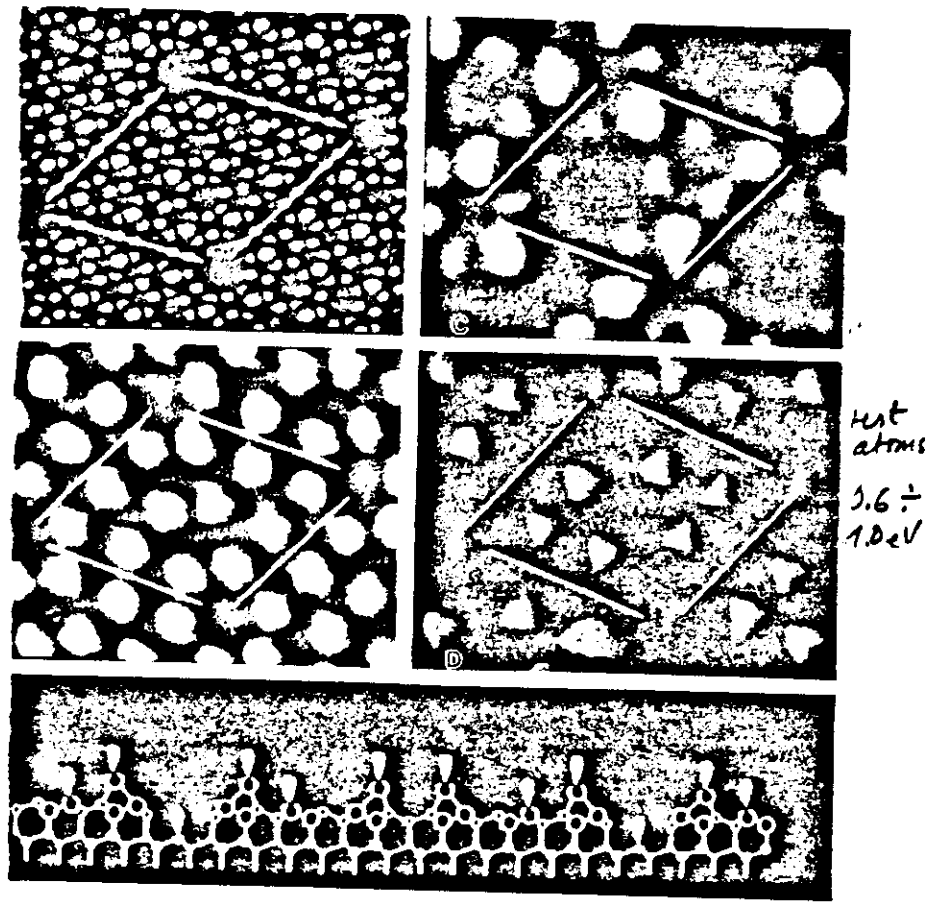



FIG. 1. STM images measured with (a) −2 V and (b) +2 V applied to the sample.




(a)–(e) STM images calculated for (a) Binnig's model, (b) Chadi's model, (c) Snyder's model, (d) McRae's model, and (e) Takayanagi's model. (f) Measured STM image. The line scans run from corner hole to corner hole along the long (left) and short (right) diagonal of the (7×7) unit cell. The vertical range in these line scans is 4 Å. Solid lines are calculations, dashed lines represent the experimental results.

adatoms states $0 \div -0.4$ eV from $E_F$



rest atoms $0.6 \div 1.0$ eV

.1: a. Computer generated ball model of the Si(111)-(7x7) structure. toms are yellow, restatoms blue. b.+2 V CCT;c. Adatom surface states veen $E_F$ and -0.4 eV.; d. Restatom surface states between -0.6 and -1.0 e. Sideview indicating location of adatom and restatom states.

The moodel consists of:

12 adatoms, with their dangling bonds (the 0th plane)

7+1 rest atoms, with dangling bonds - the rest atom ad the corner of the unit cell is located in the 3rd plane.

6 dimers are present.

The short diagonal divides the cell into two parts - the surface states located on the adatoms and the ones on rest atoms have mirror symmetry respect to it - So one assume a <u>stacking fault</u> at the left half of the unit cell between the planes 1-2 and the planes 3-4 - In this region the stacking is the one of hexagonal - diamond structure, instead of the diamond structure - It does not cost large energy to create such fault, and it is compensated by

the overall gain of the structure. With miller subunit models Northrup evaluated the total energy of the structure and found a value of surface energy gain respect to the ideal surface ranging from 1.20 to 1.40 eV/atom. It so justified the feasibility of lower energy per atom than (2x1) structure.

As far as the electronic structure is concerned the (7x7) structures presents a metallic edge due to dangling bond-type surface bonds and a band of states which is localized on rest atoms. This band is located between −0.6 and −1.0 eV and correspond to dangling bonds on rest atoms with double occupation.

Other reconstructed surfaces are found for (111) face of Ge. Si(100)(2x1) surface can be explained in terms of dimer model. A variety of surface reconstruction is found for polar (111) and ($\bar{1}\bar{1}\bar{1}$) surface of III-V's

Ref.s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- Overlayers, chemisorption and interfaces.

The last part of these lectures will consider very shortly some points related to

- disappearance of surface reconstruction due to absorption at low coverages (example H or Cl on Si)
- ordered deposition of metals and new reconstructions (i.e. Ag on Si(111) with $\sqrt{3} \times \sqrt{3}$ reconstruction)
- ordered overlayers on III-V (i.e. Sb on GaAs)
- metal overlayers and metal / semiconductor junctions
- the formation of Schottky barriers
- semiconductor - semiconductor junction and the evaluation of band discontinuities in well-matched structures
- the growth of metallic compounds on Si (i.e. epitaxial silicides - $NiSi_2$) and reactive interfaces -